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E-MRS Spring Meeting 2002
June 18 - 21, 2002

SYMPOSIUM D

Physics & Chemistry of Advanced Laser Materials Processing

Symposium Organizers:

Valentin Craciun, National Institute for Laser, Bucharest, Romania

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Wolfgang Kautek, Berlin, Germany

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E-MRS 2002 SPRING MEETING

SYMPOSIUM D

Tuesday, June 18, 2002
Mardi 18 juin 2002

Morning
Matin

Session I: Fundamentals of ns- and fs-laser interactions with solids and laser plasma dynamics

Nanosecond regime interactions

- D-I.1** 9:00 **FUNDAMENTAL STUDIES OF LASER INTERACTIONS WITH IONIC CRYSTALS**
T. Dickinson, Washington State University, Department of Physics, Pullman, USA
Insulating inorganic materials with wide bandgaps have a number of applications due to their unique electrical and optical properties. Processing such materials with lasers is challenging because of their lack of absorption and often unforgiving mechanical properties. We present our current research on the mechanisms involved in causing modification of surfaces of ionic crystals. We first examine the wavelength dependence of photodesorption and photodecomposition of a oxyanion containing inorganic, NaNO_3 at wavelengths that span the uv absorption of the nitrate anion. Secondly we examine the consequences of simultaneous exposure of single crystals of NaCl and NaNO_3 to both radiation (laser and electron beam) and water. A dramatic synergism is presented and explained in terms of bond weakening due to localized chemisorption.
- D-I.2** 9:30 **THEORETICAL DESCRIPTION OF DRY LASER CLEANING**
N. Arnold, Angewandte Physik, J. Kepler University, Altenbergerstraße 69, 4040 Linz, Austria
We present a theoretical analysis of dry laser cleaning with ns pulses. Approximate adhesion potential is introduced. The laser cleaning process is formulated as an escape problem from this potential under the action of cleaning force produced by thermal expansion. Adhesion potential is characterized by the typical temporal and spatial scales: period of small oscillations t_0 , and equilibrium deformation h_0 . Their dependence on particle size r and material parameters is given. Laser pulse duration t should be compared with t_0 and overall substrate and particle thermal expansion $l+Dr$ with h_0 . With $t < t_0$ (large particles) cleaning proceeds in the "elastic energy regime" which reduces to the condition $l+Dr > h_0$. As a result, cleaning fluence $f_{cl} \sim r^{1/3}$. With $t > t_0$ (small particles) cleaning proceeds in the inefficient "force regime" and $f_{cl} \sim t^2/r^2$, which favors shorter laser pulses. With $t > t_0$, if the fronts of the laser pulse are steep enough, $tf \ll t_0$, cleaning occurs when particle kinetic energy exceeds that of adhesion. This leads to $f_{cl} \sim t/r^{5/6}$ for the "kinetic energy" regime. Utilization of resonance effects either by modulation of ns laser pulse or employing the train of pulses with delay equal to $t_0(r)$ is analyzed. Effects of the near field focussing by dielectric spheres and ensuing decrease in cleaning threshold are discussed. Theoretical results are compared with experimental $f_{cl}(r)$ dependence for SiO_2 particles on Si surface.
- D-I.3** 10:00 **PHOTO INDUCED PROCESSES ON GRAPHITE/ICE INTERFACE**
D. Chakaroy, Department of Applied Physics, Chalmers University of Technology and Göteborg University, 412 96 Göteborg, Sweden
The structure of ice and its chemical properties are strongly influenced and altered by incoming photons. Our model system consists of thin films with submonolayer to several monolayers thickness deposited at ultrahigh vacuum and liquid nitrogen temperatures on atomically clean graphite (0001) surface. The films are characterized before, during, and after cw or pulsed (ns) irradiation with 220 - 700 nm photons using temperature programmed desorption - isothermal desorption spectroscopy (TPD - ITD) and high-resolution electron energy loss spectroscopy (HREELS). We will discuss the phenomena of "photon annealing" of pure amorphous films and their structure-selective laser ablation: A new non-thermal mechanism by which submonolayer and multilayer pure amorphous ice films, deposited at $T < 100$ K on graphite surface, crystallize due to UV radiation [1]. In the case of ice doped with alkali metals, we will report on the observations of photoreactions induced on graphite (0001) surface covered with thin ice film at 90 K. Introduction of submonolayer amounts of alkali atoms to the system leads to photodesorption of H_2 , CH_4 , CO , and CO_2 [2, 3]. In both cases the operating mechanism is associated with photo excited charge carriers in the graphite substrate.
[1]. Phys. Rev. Lett., 81 (1998) 5181
[2]. Surface Sci., 420 (1999) 174
[3]. J. Chem. Phys. 115 (2001)

Symposium D

- D-I.4** 10:15 CARRIER DE-TRAPPING INDUCED BY THE STRONG ELECTROMAGNETIC FIELD OF A FREE ELECTRON LASER
M.A.J. Klik, T. Gregorkiewicz, Van der Waals Zeeman Institute, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands, I.V. Bradley, J.-P.R. Wells, FOM Institute for Plasma Physics Rijnhuizen, P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands
The effects of intense mid-infrared (MIR) radiation on the photoluminescence (PL) of Yb³⁺ in p-type InP have been investigated in the wavelength range of 7-17 μ m. It was found that effective quenching of the Yb³⁺ intra-4f-shell luminescence intensity, resulting from a primary excitation with a short pulse from a Nd:YAG laser (532 nm), can be observed during the 4 ns length of the MIR pulse. The wavelength dependence of this effect reveals two regimes of quenching. For MIR photon energy above the energy required for reversing the Yb³⁺ excitation process (the backtransfer process), direct absorption of a single photon by the excited Yb³⁺ ion facilitates the creation of an electron-hole pair, thereby losing the excitation of the RE-ion. The quenching process with low energy MIR photons (smaller than the energy needed for the backtransfer) can be explained as a bending of the conduction band of InP, due to the highly intense MIR field. A quenching process becomes possible in such a system, by tunneling of the electron (hole) from a virtual electron-hole pair that can be generated, towards the conduction (valence) band. Theoretical predictions from these models are compared with the measured data.
- 10:30 **BREAK**
- D-I.5** 11:00 COMBINED CONTINUOUS-MICROSCOPIC MODELING OF LASER PLUME EXPANSION
T.E. Itina, J. Hermann, Ph. Delaporte and M. Sentis, LP3 FRE 2165, Faculté des Sciences de Luminy, Case 917, 13288, Marseille, France
A novel hybrid model is developed to study the dynamics of the laser plume expansion in vacuum or into a background gas. The method takes advantages of both continuous and microscopic simulation approach. As a result of the combination of two different numerical methods, such as, large particles and direct Monte Carlo simulation, the model describes high-rate laser ablation for a wide range of the background pressure (from 0 to hundreds of Pa).
The proposed model is used to investigate the different regimes of the laser plume interaction with background gases. Particularly, the plume-gas mixing and energy exchange are taken into account. The dynamics of the laser plume expansion is investigated under different experimental conditions, such as, background pressure, atomic weight, and laser parameters. The conditions for snowplough effect and for shock wave formation are discussed.
- D-I.6** 11:15 ION DYNAMICS IN THE LASER PLUME FROM ABLATED METALS AND HIGH TEMPERATURE SUPERCONDUCTORS
B. Thestrup, B. Toftmann, J. Schou, Department of Optics and Fluid Dynamics, Riso National Laboratory, 4000 Roskilde, Denmark, and B. Doggett, J. G. Lunney, Department of Physics, Trinity College, Dublin 2, Ireland
The plume from a solid target irradiated by a laser operating at 355 nm at fluences around and above 1 J/cm² consists typically of ions as well as neutrals. The ion fraction varies from one material to another. The expansion of the plasma plume produced by the laser ablation of copper in vacuum and oxygen was studied using an array of Langmuir probes, with which one can measure the angular distribution of ion time-of-flight signals. The probes are located in a semicircular array in a distance of 80 mm from the target. The results were compared with the ablation of a YBaCuO target at the same laser conditions. The dynamics of the plasma expansion in oxygen can be described using a semi-analytic blast wave model.
- D-I.7** 11:30 EXPERIMENTAL AND THEORETICAL INVESTIGATION OF LASER INDUCED PLASMA OF TITANIUM BASED TARGET
A. Casavola, G. Colonna, A. De Giacomo, O. De Pascale, Dipartimento di Chimica, Università di Bari, Italy, IMIP-CNR, sect. Bari, Italy, Centro Laser, Valenzano, Bari, Italy
The plasma produced by the interaction of laser with solid matter concerns an important aspect of many technological applications as material processing, pulsed laser deposition and chemical trace analysis.
In the last decade a large effort has been devoted to the comprehension of the basic question of the laser induced plasma in order to improve the in situ diagnostic of solid matter. Anyway some discrepancy between theoretical approach and experimental data are still caused by the assumptions, generally used, for the interpretation of experimental data based on the LTE (local thermodynamic equilibrium) condition. Here we present a theoretical approach for the interpretation of optical emission spectroscopy measurement that can be used also in non-equilibrium condition. In this approach we couple a fluid dynamic model with a complete collisional-radiative model coupled self-consistently with Boltzmann equation to investigate the existence of non-equilibrium during the expansion of the plume.
So, the theoretical model can be a very powerful tool to extract quantitative information from emission spectra of the plasma induced by the interaction between a KrF laser and a Ti target, even if the local thermodynamic conditions cannot be considered.
- D-I.8** 11:45 PRESSURE EFFECTS DURING EXCIMER LASER ABLATION OF MAGNESIUM DIBORIDE TARGETS
S. Amoruso, M. Armenante, R. Bruzzese, N. Spinelli, R. Velotta, X. Wang, Istituto Nazionale per la Fisica della Materia, Unita di Napoli, Via Cintia Complesso Universitario di Monte S. Angelo, 80126 Napoli, Italy
The recent discovery of superconductivity in MgB₂ with a transition temperature of 39 K has attracted much interest for its rather simple binary intermetallic character and its promise for future electronics. MgB₂ thin films have been recently produced through laser ablation into an Ar atmosphere, observing a strong dependence of the deposited films on the background gas pressure. The study of the influence of the gas pressure on the plasma expansion dynamics is an important issue to elucidate the conditions for optimum growth for the MgB₂ films.
In the present communication we report, for the first time, a time- and space-resolved investigation on the emission spectrum of the plume produced by a pulsed laser on a MgB₂ target irradiated at different Ar ambient pressures. Our investigation is focused on the identification of the strongest emission lines from excited species in MgB₂ laser ablated plasmas over a broad range of wavelengths 200-800 nm. Then, time resolved optical spectroscopy was used to map the evolution

Symposium D

of selected chemical species. Based on these distributions, information on MgB2 laser produced plasma chemistry and dynamics were determined as a function of the ambient Ar gas pressure. In particular, our results show that Ar gas influence the plasma kinetics and dynamics by promoting excitation and ionisation of the plume species, especially for the most volatile Mg atoms.

Symposium D

- D-I.9** 12:00 ANALYSIS OF THE PLASMA PRODUCED BY PULSED REACTIVE CROSSED-BEAM LASER ABLATION OF $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$
M.J. Montenegro(a), T. Lippert(b), S. Müller(a), A. Weidenkaff(b), P. Willmott(c), A. Wokaun(a), (a)Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, (b)University Augsburg, Universitätstr. 1, 86159 Augsburg, Germany, (c)University of Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland
The development of oxygen bifunctional electrodes will play an important role in the realization of electrically rechargeable air based batteries. Perovskites, e.g. ($\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$), are promising candidates for catalysing oxygen reduction/generation reactions. To study and compare the activity of different electrodes it is necessary to prepare crystalline, adhesive thin films of the catalyst on a stable and inactive substrate. Then the catalytic activity can be determined without problems such as reactions of the substrate and uncertainties about the number of active catalytic sites. The $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ films were deposited on MgO (001) and stainless steel substrates using pulsed reactive crossed-beam laser ablation (PRCLA).
With the reactive gas pulse, e.g. N_2O , a plasma is observed which is much brighter and that extends further from the point of ablation. The application of an oxidating gas results in the formation of films without pronounced oxygen deficiencies, making additional oxidizing steps unnecessary. The film stoichiometry ($\text{La}_{0.64\text{Å}}\text{Ca}_{0.35\text{Å}}\text{Co}_{0.95\text{Å}}\text{O}_{3.21\text{Å}}$) was calculated from RBS spectra, confirming that the films produced by PRCLA have the same stoichiometry as the target. The plasma was analysed in detail by time and space resolved emission spectroscopy to study the interaction and reactions of the gas pulse with the ablation plume. The emission spectra reveal mainly an overall increase of all bands without pronounced diatomic species.
- D-I.10** 12:15 PLUME DYNAMICS OF IRON DISILICIDE STUDIED BY LASER IONIZATION TIME-OF-FLIGHT MASS AND OPTICAL EMISSION SPECTROSCOPIES
A. Narazaki, T. Sato, Y. Kawaguchi, H. Niino and A. Yabe, National Institute of Advanced Science and Technology (AIST), Japan
Laser ionization time-of-flight (TOF) mass spectrometry and optical emission studies have been performed on the excimer laser ablation plume from an iron disilicide target in order to optimize the conditions for pulsed laser deposition of the beta phase of iron disilicide films. Neutral fragments generated from the laser ablation of iron disilicide in vacuum were studied as a function of ablation fluences in the range of $0.5\text{--}4\text{ J/cm}^2$ by laser ionization TOF mass spectroscopy. With an increase in the ablation fluence, the fragments with larger mass appeared and the translational velocity of the species increased drastically; for instance, the velocity of Fe at 65 mm changed from $1.6 \times 10^3\text{ m/s}$ at the ablation fluence of 0.5 J/cm^2 to $6.5 \times 10^4\text{ m/s}$ at 2.5 J/cm^2 . The appearance of the fragments with large mass at higher ablation fluences indicates the ejection of silicon, iron and silicon-iron clusters and the formation of such clusters in the plume. On the other hand, the plume dynamics of iron disilicide in helium background gas as well as in vacuum was explored by plume emission analysis in the wavelength range of $200\text{--}950\text{ nm}$. As a result, some luminescent lines were observed over $350\text{--}400\text{ nm}$ only in 1 Torr helium, in addition to bright emission lines from Si and Fe observable in both vacuum and helium.
- D-I.11** 12:30 LASER ABLATION RATE OF HYDROXYLAPATITE IN DIFFERENT ATMOSPHERES
J.L. Arias, M.B. Mayor, J. Pou, B. Leon and M. Pérez-Amor, Departamento de Física Aplicada, Universidade de Vigo, Lagoas-Marcosende 9, 36200 Vigo, Spain
Hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a calcium phosphate used as coating for dental and orthopaedic implants, because its composition and structure is similar to the mineral part of bone. Pulsed laser deposition (PLD) has been applied as an alternative to traditional plasma sprayed coating technique.
Hydroxylapatite targets were ablated with 0.9 Jcm^{-2} using an ArF laser (193 nm) at 20 Hz in order to investigate the ablation rate of hydroxylapatite in different atmospheres: water vapour, Ar and O_2 . The ablation rate was measured by profilometry for different pressures in the range $15\text{--}80\text{ Pa}$. The ablation rate depends on the backscattering of the ablated particles by the molecules of the gas, which produces a material redeposition on the target surface, different for each one. The ablation rate in a water vapour atmosphere presents a particular behaviour due to a different phase decomposition of hydroxylapatite under ArF laser irradiation compared to the other gases.

Tuesday, June 18, 2002
Mardi 18 juin 2002

Afternoon
Après-midi

13:00

POSTER SESSION I

Laser and photo-induced surface processing, microfabrication and nanoengineering

- D/PI.01** LASER-INDUCED PHOTOCONDUCTIVITY OF FERROMAGNETIC SEMICONDUCTOR
Q.Y. Semchuk, Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17 General Naumov Street, 03164 Kyiv, Ukraine, M. Willander and M. Karlsteen, Department of Physics, Chalmers University of Technology and Goteborg University, 41296 Goteborg, Sweden
The influence of a strong electromagnetic wave on kinetic phenomena in ferromagnetic semiconductors is considered. For their sequential consideration, quantum kinetic equations for electrons and magnons featuring an electron - magnon interaction at the presence of a high intensity high-frequency electromagnetic field of an electromagnetic wave are obtained.
It is shown, that the change of a ground state of conduction electrons at the presence of a strong electromagnetic wave results in a change of probability of electron - magnon interaction. It in turn results in the change of the electrical conductivity of the ferromagnetic semiconductor. The new mechanism of photoconduction not connected with the change of number of carriers in a conduction band of ferromagnetic semiconductors and with heating of conduction electrons is given.
The density of an electrical current in a ferromagnetic semiconductor a strong variable electromagnetic field and weak constant electric field is calculated. The valuation of the electrical conductivity of the ferromagnetic semiconductor in the infrared area of the spectrum is made. It is shown, that the magnification of amplitude of a variable electromagnetic field results in magnification of the conductivity of the ferromagnetic semiconductor for a fixed temperature.
- D/PI.02** INCREASING THE CONDUCTIVITY OF PHOTOREFRACTIVE BaTiO₃ SINGLE CRYSTALS BY DOPING Ru
C.H. Lin, C.Y. Huang and J.Y. Chang, National Central University, Institute of Optical Sciences, 320 Chung-Li, Taiwan, R.O.C.
BaTiO₃ crystals due to its self-pumped phase-conjugation and large electro-optic coefficient are important photorefractive materials. High gain, fast response time and proper beam fanning BaTiO₃ crystals are desirable. We proposed an alternative solution to increase the speed of photorefractive BaTiO₃ single crystals by doping Ru. We fabricated a series of photorefractive BaTiO₃ single crystals doped with different concentration of Ru, and then investigate their optical and photorefractive properties. The absorption spectra, beam-coupling gain and response time at wavelengths 633nm and 532nm were measured. The results show that there is an absorption peak around 460nm of these red crystals; major carriers are holes for pumping wavelengths at 633nm and 532nm. The electro-optic gain is highly dependent on intensity, and larger than un-doped BaTiO₃ single crystals. The response time is decreased by dark conductivity, and little dependent on intensity and wavelength.
- D/PI.03** CANCELLED
- D/PI.04** INFLUENCE OF THE BULK STATES IN TWO-PHOTON PHOTOEMISSION SPECTRA OF CU(100) AND AG(100) SURFACES
Y.J. Dappe and A.A. Villaeys, I.P.C.M.S.-G.S.I., 23 rue du Loess, 67037 Strasbourg Cedex, France
Two-photon photoemission spectroscopy is now well established as a useful tool to probe the ultrafast dynamics taking place in the surface electron states. In a previous work [A. A. Villaeys, Y. J. Dappe and F. P. Lohner, Phys. Rev. B 63, 155113 (2001)], the autocorrelation function (n=0) and the cross-correlation function (n=1) of the Cu(111) electron surface states, have been analysed. From this analytical evaluation the lifetime of the first image-potential state has been determined and the dynamics of the intrinsic surface state has been elucidated. In the present work, we study the dynamics of the Cu(100) and Ag(100) surface electrons. To this end, we have extended the model to the high-order image-potential states, say n=1, 2, and 3. The physics underlying these processes is quite different since there is no intrinsic surface state for Cu(100) and Ag(100). Here, transitions occur between the occupied bulk band states, located below the bottom of the energy gap, and the image-potential states. We stress the importance of including the complete distribution of the bulk band states, to recover the correct ratio between the magnitude of the different cross-correlation curves. This emphasizes the role played by the bulk band states in the global evolutions.
- D/PI.05** LASER THERMAL PROCESSING (LTP) FOR ULTRA SHALLOW JUNCTION FORMATION: NUMERICAL SIMULATION AND COMPARISON WITH EXPERIMENTS
M. Hernandez(a), D. Zahorski(a), J. Boulmer(b), D. Débarre(b), G. Kerrien(b), T. Noguchi(b), T. Sarnet(b), C. Laviro(c), M.N. Semeria(c), D. Camel(d), J.L. Sautillier(d), (a)SOPRA, 26, rue Pierre Joigneaux, 92270 Bois Colombes, France, (b)Institut d'Electronique Fondamentale, CNRS UMR 8622, Université Paris-Sud, 91405 Orsay, France, (c)CEA/DRT-LETI/DTS, 17 avenue des Martyrs, 38054 Grenoble Cedex 9, France, (d)CEA/DRT-DTEN/LESA, 17 avenue des Martyrs, 38054 Grenoble Cedex 9, France
Laser Thermal Processing (LTP) is a promising technique for the ultra shallow junction (USJ) formation. In the last few years LTP has become a potential solution for sub-0.1 micron technology requirements, as focused by the International Technology Roadmap for Semiconductors (ITRS).
This paper presents a numerical simulation of the propagation of the melting front and re-growth of Si-based structures during excimer (XeCl-308 nm) laser irradiation. The influence of the pulse duration has been highlighted in the simulation and compared with experiments. Therefore, two different types of XeCl lasers with different pulse durations have been used for the experiments in order to validate the model (SOPRA-VEL 15, 200 ns-15 J and Compex Lambda Physics, 20 ns-200 mJ). The comparison between the simulation and the experimental results has been carried out using results from in-situ reflectance measurements (transient reflectivity), SIMS, SRP and four-point probes. The different implantation conditions used for this study were B⁺ or BF₂⁺ implanted Si wafers, with or without Ge⁺ pre-amorphization.
The numerical simulation was performed using an industrial flow modeling tool based on the finite element method. It allows to simulate the melt front propagation of real 2D and 3D CMOS devices. Preliminary simulation results have also been obtained for real CMOS-like structures, where the gate behavior under laser irradiation and the lateral diffusion of dopant is of great interest.

- D/PL.06** THERMAL MODELLING OF SURFACE PULSED LASER ANNEALING
N. Semmar, C. Boulmer-Leborgne GREMI, UMR 6606 CNRS, Université d'Orléans, BP 6744, 45067 Orléans Cedex 2, France
This modelling is especially applied to the annealing of a film deposited on a substrate taking into account the interface roughness. Study of the thermal field over a surface, is usually performed by considering the assumption of 'semi-infinite medium'. However, the melting of a thin film deposited on a roughly substrate surface induces bad thermal contacts commonly known as 'thermal contact resistance'. In this work the heat conduction problem is resolved by using the implicit finite differences method. The heat source (i.e. the laser intensity) is treated as a surface boundary layer, when the photon surface absorptivity is thermally dependent. The thermal contact resistance is introduced in the computation procedure when the heat wave propagation reaches the thin film/substrate interface. It is then possible to calculate the critical temperatures and the melting threshold fluence for high and low contact resistance values (i.e. high and low substrate roughness). Under these conditions, the temperature and heat flux profiles are plotted for both conductive and non-conductive thin film materials heated by pulsed lasers. Finally, from experimental data on sample cross sections it is possible to estimate the heat penetration and the melting pool depth in correlation with the observed roughness.
- D/PL.07** UV PICOSECOND LASER-INDUCED EFFECTS ON CVD DIAMOND SURFACE INVESTIGATED BY PHOTOELECTRIC WORK FUNCTION MEASUREMENTS AND SURFACE ANALYSIS
D. Vouagner(a), B. Champagnon(b), J. Lebruscq(c), Y. Show(d), J.P. Girardeau-Montaut(a), (a)Laboratoire de Sciences et Ingénierie des Surfaces, Université Claude Bernard, Lyon I, 43 bd du 11/11/1918, 69622 Villeurbanne Cedex, France, (b)Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Claude Bernard, Lyon I, 43 bd du 11/11/1918, 69622 Villeurbanne Cedex, France, (c)Département de Physique des Matériaux, Université Claude Bernard, Lyon I, 43 bd du 11/11/1918, 69622 Villeurbanne Cedex, France, (d)Department of Electronics, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, Japan
Due to its superior electrical, optical, chemical and mechanical properties, CVD diamond is a promising material for a wide range of applications. It is a particularly attractive material for the elaboration of new devices in the field of electronic, optoelectronic and new photocathodes for ultrafast electron and x-ray sources which interest is considerably increasing since the recent development of ultrafast laser sources. In this paper, we investigate picosecond laser-induced effects on undoped CVD diamond surfaces as a function of irradiation time. In-situ photoelectric work function variations are reported. Diamond films are characterized by x-ray electron spectroscopy and microRaman analysis, before and after laser irradiation, in order to observe surface structural transformations.
- D/PL.08** MICROSTRUCTURAL TRANSFORMATIONS IN THIN a-Si FILMS INDUCED BY SUCCESSIVE EXCIMER LASER SHOTS
K. Mirouh, A. Bouabellou, A. Karaali, Laboratoire des Couches Minces et Interfaces, Université de Constantine, Campus Chaab Errassas, Constantine 25000, Algérie and A. Mosser, 23 rue du Loess, 67037 Strasbourg, France
Excimer laser annealing of thin amorphous silicon layers (a-Si) is used to produce polysilicon films. It has been shown that the increase in the laser energy could induce microstructural transformations, passage from large grains microstructure to another characterised by fine grains. The present work reports that these microstructural transformations can be obtained by successive excimer laser shots. The a-Si layers are deposited on quartz substrate by LPCVD and annealed using KrF excimer laser (1,2 and 2,9 J/cm²) for several pulses. TEM investigations show that the microstructural transformations, for the same number of shots, are more important in the lower laser energy case.
- D/PL.09** INTERFERENCE MICROSCOPY FOR NANOMETRIC SURFACE MICROSTRUCTURE ANALYSIS IN EXCIMER LASER PROCESSING OF SILICON FOR FLAT PANEL DISPLAYS
A. Benatmane(a), P.C. Montgomery(a), E. Fogarassy(a) and D. Zahorski(b), (a)Laboratoire PHASE, CNRS, 23 rue du Loess, BP 20 CR, 67037 Strasbourg Cedex 2, France, (b)SOPRA-SA, 23 rue Pierre Joigneaux, 92270 Bois-Colombes, France
Thin film semiconductor materials have received much attention recently, especially in the field of large area electronics due to a strong market growth of flat panel displays addressed by active matrices of polysilicon thin film transistors (TFT's). One of the most promising ways for obtaining high quality polysilicon TFT's on cheap glass substrates consists of crystallizing amorphous silicon (a-Si) by pulsed excimer laser annealing. However, this step needs to be carefully controlled during the in-line panel manufacturing process in the easiest and fastest way.
In this work, the phase transformation mechanisms and the microstructures resulting from the laser crystallization of amorphous silicon were investigated by phase stepping microscopy (PSM). This automated mode of interference microscopy allows the rapid, non-destructive and quantitative measurement of nanometric surface morphology. PSM was used to investigate the crystallization process in Si thin films on glass irradiated using a large area (~40cm²) and long pulse duration (200ns) excimer (XeCl) laser, which was especially designed for the manufacturing of flat panel displays. From the comparison of the results obtained by interference microscopy and Atomic Force Microscopy (AFM), the PSM technique has been shown to be one of the most interesting alternative ways that could be used for controlling the laser annealing process in an industrial environment.
- D/PL.10** INFLUENCE OF LASER FLUENCE IN ARF-EXCIMER LASER ASSISTED CRYSTALLISATION OF A-SiGe:H FILMS
S. Chiussi, E. Lopez, J. Serra, P. Gonzalez, C. Serra*, B. Leon, Dpto. Fisica Aplicada, E.T.S.I.I. University of Vigo, Lagoas Marcosende 9, 36200 Vigo, Spain; *C.A.C.T.I., University of Vigo, 36200 Vigo, Spain, F. Fabbri, L. Fornarini, ENEA Frascati, Via Enrico Fermi 27, 00044 Frascati (Roma), Italy, S. Martelli, Centro Sviluppo Materiali, Via di Castel Romano 100, 00128 Roma, Italy
Polycrystalline silicon germanium (poly-SiGe) based devices are attracting a peculiar attention in micro- and optoelectronics provoking an increasing interest in exploiting Excimer laser crystallisation for producing polycrystalline SiGe alloys with uniform and controlled grain size. This technique, already assessed in TFT production, has proved as a valuable low thermal budget technique for the crystallisation of amorphous silicon. Main advantages are the high process quality and reproducibility as well as the possibility of tailoring the grain size in both, small selected regions and large areas. In order to explore the feasibility of Excimer laser crystallisation for producing poly-SiGe films, hydrogenated a-SiGe:H coatings have been crystallised at room temperature with spatially uniform ArF-Laser pulses. The fluence of the laser pulses has been tailored in order to dehydrogenate the films prior to the crystallisation process, thus avoiding explosive evaporation of hydrogen and damage of the films.
The influence of the laser fluence on the structure and chemical composition has been determined by extensive characterisation through XRD, AFM, SEM, TEM, and depth profiling XPS. A comparison of the experimental results with a theoretical model predicting the dependence of temperature gradient in the film from the experimental parameters such as laser fluence, film composition and thickness has also been performed and used for refining the process parameters.

- D/PL.11** **VISIBLE PHOTOLUMINESCENCE FROM NANOCRYSTALLINE Ge GROWN AT ROOM TEMPERATURE BY PHOTO-OXIDATION OF SiGe USING A 126 NM LAMP**
J.-Y. Zhang, A.J. Kenyon and I.W. Boyd, Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K.
Heterostructures of SiGe/Si display several attractive electronic and optical properties. Many optical studies have been made on various types of nanocrystalline Ge to understand the quantum effects on the photogenerated carriers and to explore novel optical device possibilities involving these quantum size effects. These investigations have demonstrated that nanocrystalline Ge embedded in a SiO₂ matrix is responsible for visible photoluminescence (PL). In this paper, for the first time, we report rapid photo-oxidation of SiGe at room temperature using a 126 nm excimer lamp. The structure and composition of the oxidised layers were investigated by FTIR, Raman spectroscopy, ellipsometry, and XPS, while their electrical properties were determined by I-V and C-V measurements. The PL spectra of the Ge nanocrystals were measured by using 454.5-514.5 nm excitation light from an Ar ion laser. FTIR spectra of the oxidised SiGe samples exhibited the Si-O stretching absorption band of SiO₂ around 1070 cm⁻¹ for different exposure times (30, 60, 120, 240 s). It was found that UV annealing at 400°C in oxygen could significantly increase the intensity and stabilise the visible PL. The intensity ratio of the 590nm/655nm ratio in the PL spectra decreased with annealing time, indicating an increase in the size of the nanoparticles.
- D/PL.12** **IMPACT OF EXCIMER ULTRAVIOLET RADIATION DURING POST DEPOSITION ANNEALING OF HAFNIA THIN FILMS**
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Hafnia thin films on silicon have been exposed to ultraviolet (UV) radiation during conventional post deposition oxygen annealing. The UV radiation was generated via a high intensity excimer lamp located near the sample surface. The proximity of the lamp to the sample during annealing allowed oxygen, which has been broken down into reactive atomic oxygen and ozone, to directly interact with the sample while it was being annealed. This resulted in enhanced oxygen incorporation into annealed sample. Additionally, it has been found that the application of UV radiation allows the hafnia films to be annealed at lower temperatures while maintaining properties exhibited by conventionally annealed samples at higher temperatures. By carefully controlling the temperature and oxygen pressure, better control of unwanted interfacial layers that may grow during conventional oxygen anneals can be achieved. The characteristics of the oxygen incorporation in the bulk and interfacial regions have been studied by x-ray reflectivity and diffraction, x-ray photoelectron spectroscopy, capacitance-voltage and current voltage measurements.
- D/PL.13** **RAPID OXIDATION OF SILICON USING 126 NM EXCIMER RADIATION AT LOW PRESSURE**
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In previous work, we have reported that photo-oxidation of silicon has been found to proceed fastest by employing the shortest wavelength VUV lamp radiation from an Ar excimer lamp source. Oxidation rates as high as 5 nm/min were readily achievable at room temperature, which is more than two orders of magnitude higher than that for UV-induced oxidation of silicon using a typical low pressure mercury lamp at a temperature of 350°C, and immeasurably higher than for thermal oxidation. Here we report the results of our extended investigation of rapid VUV oxidation of silicon using 126 nm excimer lamp at low pressures. Oxidation rates as high as 8 nm/min have been achieved. Unlike thermal and higher pressure oxidation process, no saturated growth rate was observed. Furthermore, film thickness up to 24 nm have been obtained, which are not possible with conventional thermal oxidation processes at temperature below 500°C. The films are found by FTIR and XPS to be stoichiometric in nature. I-V measurements from metal oxide semiconductor (MOS) devices fabricated using a 17 nm SiO₂ layer showed that leakage current densities as low as 4×10^{-8} A/cm² at an electric field of 1 MV/cm can be obtained in the as-grown films. Further electrical and optical properties of these films will be discussed.
- D/PL.14** **ULTRASHORT PULSE LASER INTERACTION WITH ANODIC METAL OXIDE LAYERS IN ELECTROLYTE CONTACT**
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The removal and accelerated corrosion monitoring of metal coating systems is of general interest in materials science and engineering technology. The femtosecond and nanosecond laser ablation and delamination at 800 nm and 532 nm, respectively, of anodic oxide layers on aluminium alloys in electrolyte contact were investigated. Laser-induced modifications of the oxide layer resulted in an ionic contact between electrolyte and metal, which produced a current transient and thus allowed the in-situ electrochemical monitoring of the modification. Oxide coatings with different optical properties, almost transparent and opaque, were examined. The transparent anodic oxides showed contrasting ablation mechanisms in the nanosecond and femtosecond pulse duration regime: nanosecond pulses caused spallation, whereas femtosecond treatment led to ablation. Current signals measured in the transparent film were consistent with light absorption below the metal-oxide interface and with film spallation. Irradiation of the opaque coating yielded ionic current transients within the so-called shock-affected-zone of the oxide layer. This investigation provided insight into the role of the penetration depth of light and the heat-affected zone, the extent of the shock-affected zone, and the defect formation in the coating and at the solid-solid interface between metal and oxide.
- D/PL.15** **X-RAY AND ELECTRICAL CHARACTERIZATION OF PHOTO-CVD ZIRCONIUM OXIDE LAYERS**
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Zirconium oxide (ZrO₂) has many promising properties required by alternative gate dielectric oxides such as relatively high dielectric constant (high-k) value, relatively wide band gap and thermal stability in direct contact with Si while it tends to crystallise at low temperatures leading to undesired polycrystalline films. Low-temperature deposition and processing is thus required to prevent crystallisation. Photo-assisted processing provides a promising approach to low temperature processes for gate dielectrics while also being capable of large area processing. In this paper, photo-CVD involving the recently developed high-intensity excimer UV lamps has been used successfully in preparing ZrO₂ layers with high quality. ZrO₂ growth at different temperatures ranging from 50-350°C has been investigated in terms of its refractive index determined by ellipsometry while its growth has been observed at temperatures as low as 100°C. The possible structure and composition of the layers formed has been estimated by X-ray analysis. Electrical measurements have also been reported for these oxide layers.

- D/PI.16** LASER-INDUCED HETEROGENEOUS PROCESSES AT DEPOSITION OF ELEMENTS FROM IRON CARBONYL VAPORS
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Laser-induced processes of element deposition from iron carbonyl ($\text{Fe}(\text{CO})_5$) vapors are quite effective for formation of narrow-band semiconductor films and layers. These processes are heterogeneous. The rate constant of heterogeneous reaction of Fe atom deposition was about 3.4×10^6 cm/s while irradiating SiO_2 substrate surface with KrF-laser radiation and was about 1.2×10^{-3} cm/s and 2.8×10^{-3} cm/s at the same vapor pressure and while irradiating Si and SiO_2 substrate surface with Ar^+ -laser radiation accordingly. From the comparison of deposition rates of photofragments and deposition rates of Fe atoms on the substrate surface it was found out that atomic iron could form as the result of secondary processes of the interaction of photofragments with precursor molecules on the substrate surface. The role of thermochemical processes of $\text{Fe}(\text{CO})_5$ dissociation was found out too when the substrate surface temperature was about 900 K while absorption of KrF-laser radiation of the deposited film. Content analysis made by EDXS and AES of deposited films gave kinetic data about deposition of Fe, C, O atoms.
- D/PI.17** GIANT LASER-INDUCED OPTICAL ABSORPTION IN TITANIA-BASED GELS
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Sol-gel materials are promising from the point of view of nano-technologies. Laser processing of these materials reveals their unusual optical properties. In this communication we report on the observation and elucidation of giant laser-induced optical absorption in initially transparent titania-based gel. This induced absorption appeared as material darkening at the place of irradiation; the gel recovered its transparency after the end of irradiation.
In our experiments we have used a full solid-state laser operating at different wavelengths from IR to deep UV. We present data on kinetics of the optical density transformation of irradiated samples. Samples of different aging time and thickness were irradiated with different laser fluences and wavelengths. Luminescent and absorption spectra of irradiated spots have been measured.
A phenomenological model describing the experimental results has been developed. It allows a deeper insight into the involved microscopic mechanisms of the observed phenomena.
- D/PI.18** CO₂-LASER INDUCED STRUCTURE CHANGES IN PZT SOL-GEL FILMS
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Ferroelectric lead zirconite-titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films are still of interest as promising materials for miniature pyroelectric detectors or piezoelectric sensors. Traditional thermal treatment (electric furnace or powerful source UV irradiation) of PZT sol-gel films has problems in case of micro-composites. It does not allow local treatment of selected layers of the composites. Localised and non-destructive treatment of the surface is possible by focused laser beam or electron beam of sufficient energy. The main advantage of laser processing is selection of separate layers of a multi-layered micro-composite for treatment by choosing a suitable . Recently pulsed excimer lasers ArF (wavelength: $\lambda = 193$ nm), XeF ($\lambda = 351$ nm) and XeCl ($\lambda = 308$ nm) have been used to crystallise PZT sol-gel thin films. Because the fundamental ion absorption edge of PZT layer starts at $\lambda > 6000$ nm the CO₂ laser ($\lambda = 10400$ nm) can also be used for thermal treatment of PZT films. Since materials used in microelectronics, such as Si, Ge, GaAs, are relatively transparent at $\lambda = 10400$ nm, the CO₂ laser may be preferable. It means that it would be possible to heat the PZT film without heating the Si substrate. X-ray studies showed that the perovskite structure of PZT sol-gel layer grows at the expense of pyrochlore as number of CO₂ laser pulses or intensity of radiation is increased.
- D/PI.19** CHEMISTRY AND PHYSICS OF SOLID STATE SOL-GEL LASER MATERIALS
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The sol-gel process is a chemical synthesis technique for preparing oxide gels, glasses and ceramics at far lower temperatures than is possible by conventional methods. This technique enables for the first time the introduction of organic molecules into glass having characteristic spectral features. The approach is based on the hydrolysis and condensation of molecular precursors such as metal alkoxides, and by controlling the chemistry of the process one can prepare oxide powders, thin films, fibers and bulk materials at ambient temperatures. The resulting properties of the laser material are determined by the nature of the interaction and compatibility between the dopant molecule and the matrix. The nature of the local environment around the dopant molecule is frequently a critical consideration in achieving the desired property. To design and optimize a material whose optical behaviour is based on properties induced by molecules, it is necessary to understand the local environment of the molecule. The emphasis of this paper is to review our present understanding of two aspects of the prepared laser material molecular environment: the chemistry of solvent filled pores and the properties of molecule-matrix interactions. Further, besides the chemistry of the matrices, we have attempted to investigate the laser material using FTIR, Raman, fluorescence and UV visible techniques.
- D/PI.20** DENSIFICATION AND CRYSTALLISATION OF SnO₂:Sb SOL-GEL FILMS USING EXCIMER LASER ANNEALING
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Classical annealing in order to obtain crystallized conducting oxide films elaborated by the sol-gel route does hold only for thermally resistant substrates. In the case of polymer substrates, the thermal treatment must be confined in the film region to prevent substrate damaging. For this aim, pulsed laser irradiation can be used to heat the surface of the film. The present paper reports our successful results to achieve crystallization of SnO₂:Sb sol-gel films by excimer laser processing. Single layers of SnO₂:16 at% Sb were deposited by dip-coating on Pyrex glass and dried at 150°C or 200°C. After this treatment, the films are quasi amorphous, with some crystal nuclei in the range of 2-3 nm, and non conductive. Excimer lasers were used for thermal processing. The electrical resistivity of the laser annealed regions was determined by four-probe measurements. The chemical composition, structure and morphology of the films before and after laser irradiation were studied by Rutherford Backscattering Spectrometry (RBS) and Transmission Electron Microscopy (TEM). These studies confirm that the films are crystallized whereas the substrate is not affected. Our results show that laser irradiation can be successfully used to crystallize sol-gel thin films and suggest new developments in the field of organic electroluminescent diode devices.

D/PI.21 WITHDRAW

D/PI.22 CHARACTERISATION OF THE LASER SURFACE NITRIDED LAYER OF NiTi SHAPE MEMORY ALLOY
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Over the last two decades, NiTi shape memory alloys have been increasingly considered for use in external and internal biomedical devices. However, there is concern regarding the corrosion property of NiTi alloys in in-vivo condition. Corrosion products of the alloys, especially the release of nickel ions, have deleterious effect to the body. In this study, laser surface nitriding (LSN) was carried out on Ti-50.8 at% Ni shape memory alloy so as to modify the surface properties of this alloy. The characteristics of the LSN surface layer were analysed by XRD, SEM, TEM and XPS. The results show that a continuous thin titanium nitride (TiN) surface layer, with good interfacial adhesion with the modified surface layer, was formed on the outmost surface of the NiTi alloy after the LSN treatment. Titanium and small amount of TiO were identified in the LSN layer. Carbon and oxygen were also found in this layer, probably due to contamination by the atmosphere during the laser melting process. Only minimal amount of nickel was detected in the surface TiN layer. TiN also exists in dendritic form distributed evenly within the modified layer. Nickel release rate out of the LSN NiTi alloy immersed in Hank's solution at 37°C, examined by atomic absorption spectrometry, decreased obviously during the test period.

D/PI.23 INCIPIENT SURFACE PROCESSES IN LASER PULSE-MOLTEN 'REAL' METALS
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Laser-induced cleaning was studied in real time by mirror electron microscopy. Polycrystalline Cr, Ni, and Bi films, evaporated on quartz glass substrates, were treated by 25 ns single and double laser pulses (pulse spacing 1 µs). Images of the transient surface stages caused thereby were visualized with a mirror electron microscope with a time resolution of nanoseconds [1]. The contrast in the short-exposure images is mainly determined by changes of the local work function. Removal of adsorbates and oxides as well as formation of a new surface layer during cool-down were tracked. Melting of the metal film and partial evaporation lead to an initial purification of the laser-treated area. Regrowth of surface layers can start in an early stage during cooling, only few 10 ns after the laser pulse in a metal with a high solubility of oxygen in the liquid. Furthermore, exfoliation due to excessive stresses produces an additional image contrast, revealing that the typical cracking of heated Cr films starts about 200 ns after the laser pulse. Processes accompanying laser pulse-cleaning (diffusion to the surface, mechanical break-down) are uncovered by mirror electron microscopy. This work was in part supported by the Deutsche Forschungsgemeinschaft.
[1] H. Kleinschmidt, O. Bostanjoglo, Rev. Sci. Instrum. 72, 3898 (2001).

D/PI.24 LASER PROCESSING OF TITANIUM IN AIR: INFLUENCE OF TRACES OVERLAPPING
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Titanium oxide coatings on titanium, due to their mechanical and chemical behavior, present interesting properties for applications like bone implants, thermal barriers, photocatalysis, gas sensors and optical coatings. Laser surface oxidation of titanium allows obtaining oxide coatings with very good adhesion maintaining the excellent mechanical properties of bulk titanium. The combination of the high processing velocity, high spatial resolution and versatility of this technique makes it specially useful for industrial production. Laser treatments are accomplished by scanning the laser beam on the substrates surface line by line with parallel traces at constant speed. The laser beam scanning speed and the overlapping between adjacent traces decisively affect the morphology, the composition and, hence, the functional properties of the resulting coatings.
In this work surface treatments of titanium have been achieved in air with a Nd:YAG ($\lambda = 1064$ nm) laser. The effect of the laser beam scanning velocity and the overlapping of the parallel traces have been systematically studied through several characterization techniques in order to point out the different physical mechanisms involved during processing and their influence on the properties of the obtained coatings, specially, surface morphology and crack formation.

D/PI.25 SELECTIVE MELTING OF A MULTILAYER COMPONENT
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The laser surface treatment is applied to a multilayers component (copper alloy covered with two slender coatings, nickel and gold). The aim of the study is to melt the whole gold layer (thick < 1 µm) without damage the underlying layers. The gold melting must be homogeneous and the process must be fast to avoid heat diffusion in the depth. For these reasons, the laser has been chosen for surface treatment.
A thorough study has been realised on the laser parameters (wavelength, pulse duration, fluence, homogeneity of the laser beam...) to find the best conditions to melt the whole gold layer.
TEM and SEM observations of transversal cross have been achieved to estimate the gold melting depth and to observe the modifications of gold structure led by the laser treatment.
The application of this laser surface treatment is to improve the corrosion resistance of electrical contacts due to columnar microstructure of gold deposited by electrolytic process.
The roughness of the substrate is a limiting parameter on the efficiency of laser treatment. To improve the corrosion resistance of rough samples, a laser treatment of substrate has been performed to smooth the substrate and enhance the quality of the gold and nickel deposits which probably depend on the roughness of substrate.

D/PI.26 INTERMIXING AT INTERFACES OF KrF LASER IRRADIATED Co/W MULTILAYERS
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The mixing at interfaces, formation of magnetically dead interlayers and increase of interface roughness could significantly lower the giant magnetoresistance ratio (GMR) in multilayers (MLs). From this point of view the MLs from ferromagnetic Co and refractory W spacer with low level of mutual miscibility present an interesting possibility. In this paper the interface reactions were studied in MLs with 5 and 10 periods and Co layers 1 or 2nm thick in as deposited state and after KrF laser irradiation (fluences 0.05 and 0.2 Jcm⁻²; 0.2 Jcm⁻², 1 or 10 pulses). Samples were studied by X-ray diffraction (XRD), X-ray reflectivity and diffuse scattering at grazing incidence completed by simulations of the spectra and by resistometry. All MLs showed regular periodic structure with layer thickness close to the nominal values. The interfacial roughness was 0.4-0.6 nm. The XRD patterns revealed strongly textured structure of the Co and W layers with structural coherency between fcc Co(111) and bcc W(110) lattice planes across the ML stack. For some layer thickness combinations the presence of hexagonal Co₃W was detected by grazing incidence XRD. The stability of layering was preserved up to laser fluence 0.150 Jcm⁻².

- D/PI.27** **STUDY THE CORROSION BEHAVIOUR OF LASER SURFACE MELTING OF ALUMINIUM ALLOY BY USING SMALL BEAM AND LINE BEAM LASER**
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Laser surface melting offers significant potential in the improvement of corrosion performance of aluminium alloys. The beneficial effect of LSM mainly arises from the grain refinement, and the removal of inclusions and other detrimental phases by dissolving them in the matrix. In order to treat a surface for industrial application, overlapping of tracks, corresponding to the width of the laser beam, is necessary especially for large area coverage. The overlapping results in re-heating of a portion of the adjacent, previous track with consequent microstructural change that can influence the corrosion behaviour. This paper examines the use of a line beam laser for improving the corrosion resistance of Al alloy 2014-T6. The solidification patterns and alloy microstructure are determined for various treatment parameters and related to the resultant corrosion resistance of the alloy. The microstructures and chemical compositions of the as-received and laser-melted specimens are analysed by using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffractometry (XRD).
- D/PI.28** **FATIGUE BEHAVIOUR OF LASER MACHINED 2024 T3 AERONAUTIC ALUMINIUM ALLOY**
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High power laser applications as welding, machining, marking are in the phase of implementation in several industrial sector to take advantage of it high processing velocity, clean processing conditions, and a high versatility. However, the HAZ zone is expected to affect the fatigue resistance.
In this communication, fatigue behaviour of laser machined 2024 aluminium alloy has been studied to evaluate a possible certification of laser-based machining in the aeronautic industry. Laser machining of the samples was carried out using a CO₂ laser in 1.6 mm thick test samples. The used test design agrees with the requirements of Airbus AITM 1-0011 standards in order to obtain the future certification of the process. Experimental fatigue results were statistically processed. Application of linear and non linear models to the obtained curves was necessary to estimate the fatigue life curve parameters. Results can be separated into two parts: low cycle fatigue (LCF) and high cycle fatigue (HCF). For the first, the experimental curve lies just below the aeronautic requirements AITM 1-0011 for its use in drilling. This means that for this range of application both laser milling and drilling can technically be applied. For the HCF regime the latter conclusion is also valid as the experimental curve is above the requirements. Relations between the fatigue behaviour and the microstructure are in progress to improve the understanding of the laser related change induced in such material.
- D/PI.29** **AN INVESTIGATION OF THE EFFECT OF PULSE FREQUENCY IN LASER MULTIPLE-LAYER CLADDING OF STAINLESS STEEL**
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The consolidation of metal powder onto a solid substrate using a laser beam allows a fusion bond to be formed and layers clad in this way can form a wall or surface suitable for rapid prototyping applications. The final wall geometry and microstructure of metals deposited in this way are determined in part by the pulse frequency of the laser beam used. A 1200 W CO₂ laser, operating over a range of different pulse frequencies, has been used to investigate this effect. Microstructural characterisation of multiple layers of consolidated 316L steel was carried out and the surface profiles of the different samples were assessed. The hardness and surface roughness of the samples produced at different pulse frequencies were compared both with each other and with the wrought material.
- D/PI.30** **THE EFFECT OF LASER PULSE WIDTH ON MULTIPLE-LAYER 316L STEEL CLAD MICROSTRUCTURE AND SURFACE FINISH**
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Multiple layer cladding by laser allows a fully dense wall or surface to be built-up from the consolidation of a metal or alloy powder on a solid substrate or previously consolidated layers. The microstructure and surface finish of the part are determined by process parameters, one of which is the pulse width of the laser used. In this work a CO₂ laser, operating over a range of pulse widths and at different levels of mean power output, was used to assess this effect. Microstructural characterisation of multiple layers of 316L steel in a 'as consolidated' state was carried out. The surface roughness and hardness of the samples were compared with pulse widths in order to further quantify the effect.
- D/PI.31** **CHARACTERISATION OF A STEEL SURFACE AFTER XeCl LASER IRRADIATION**
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In recent years, the laser treatment of metals and alloys has emerged as novel surface modification technique specially in many fields related to surface preparation like cleaning, dust or paint removal.
In this paper, we report the surface modification of steel with an excimer laser under room atmosphere. The morphology, phase and compositional changes after laser treatment were characterised by means of XRD, GIXRD, XPS, AES and SEM. The results show that excimer laser treatment favour the formation of Fe³⁺ oxides (mainly Fe₂O₃), and that this effect is more pronounced at higher fluence. In the same time, the formation of a FeO_{1-x} layer adjacent with the bulk and a low transformation of the γ -Fe into δ -Fe have been observed. Auger depth profile realised in solidified steel melt area and the surrounding area have shown that oxide is formed during plasma expansion and then deposits on the steel surface. These results suggest that Fe₂O₃ is generated by the condensation of the ablated species such as iron and oxygen atoms. SEM investigations exhibit the creation of spherical structures of few ten of nanometers diameter on the whole treated surface: the surface nanostructuration strongly depends on the laser fluence used.
Complementary studies to understand the formation of the Fe₂O₃ nanoparticles and to determine the effects of this oxide layer for protection against corrosion will be presented.

- D/PI.32** COMPARISON OF REPAIR OF TOOLS BY CO₂ LASER SURFACING AND BY ARC SURFACING
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Die casting tools for aluminium and magnesium alloys are subjected to cyclic thermo-mechanical loads. The tools are, therefore, usually made of special hot-working tool steels (H11, H13). Lately precipitation-hardened maraging steels have been quite successfully introduced for this application. It has turned out that die casting tools made of maraging steel have a longer operation life than those made of common hot-working tool steels.
The operation life of usually very costly die casting tools can be efficiently extended by a timely repair of the surface of a tool engraving.
The aim of the investigation was to find a fast and cost-effective repair procedure for damaged tools made of maraging steel. In the paper, results of CO₂ laser surfacing and arc surfacing of damaged areas at the surface of the tool engraving are described. The results include microstructural and micro-chemical analyses of the surfaced layer supported by analyses of micro-hardness, toughness, and residual stresses in samples obtained with different surfacing processes.
Taking into account the advantages of laser surfacing over the other surfacing processes found in the investigation, fast and efficient maintenance of damaged tools can be expected.
- D/PI.33** PARAMETER RELATIONSHIP AND OPTIMISATION IN LASER METAL TUBE BENDING
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In laser bending of metal tubes, the process parameters, such as laser power, beam diameter, scanning speed and scanning angle, have great influences on the final bending result. The influences of these parameters on the bending process and final bending result has been investigated experimentally using a high power diode laser. The variations of wall thickness and ovalization of cross section of laser bending were measured. As the bending is obtained mainly by the upsetting of tube intrados, the wall thinning at the extrados has been greatly reduced compared to mechanical bending. In addition, the ovalization of cross section has been decreased owing to the local continue deformation. Based on the experimental results, the optimal parameters for laser tube bending is proposed and methods for improving the process have been discussed.
- D/PI.34** FINITE ELEMENT ANALYSIS OF LASER TUBE BENDING PROCESS
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Laser bending of tubes is a process in which laser-induced thermal distortion is used to bend tubes without hard tooling or external forces. For understanding the mechanism of laser bending, the finite element analysis was conducted to investigate the development of stress and strain during bending process. When the laser irradiates to tube surface, the heat-affected region intends to expand due to temperature rise. Being restricted by surrounding rigid material, this expansion induces plastic deformation in the heated region. When the laser beam passes by, the temperature decreases and the material shrinks. The shrinkage of heated region exerts a tension stress to its surrounding material. As the laser beam scans the tube surface continuously, the cumulative tension stress induce the tube bent towards the laser beam direction. The FE modelling was used to assess the effect of laser and material conditions on the stress development and bending performance. The validation of FE modelling is measured.
- D/PI.35** LASER TRANSFORMATION OF OXOALUMINUM HYDRIDE (HAIO) THIN FILMS
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In this communication, we present the application of Chemical Vapor Deposition (CVD) for the elaboration of oxoaluminum hydride (HAIO) thin films. MetalOrganic CVD (MOCVD) is a thermochemical process that have the advantage to use low temperature and only one precursor. More specifically, an organometallic precursor, bis (ter-butyl dihydroaluminum) [H₂AlO'Bu]₂ was used for generate the HAIO layers on a copper substrate heated at 280°C.
The synthesized films were treated by different laser treatments (355nm, 4.3 ns and 266nm, 4.3 ns) These irradiation were achieved by a FTICRMS (Fourier Transform Ion Cyclotron Resonance Mass Spectrometer) laser microprobe allowing the observation of mass fingerprint for these thin films.
Laser parameters such as photonic wavelength, laser power density, and the laser pulse number were determined in order to obtain the most important transformation of thin film. The transformation process either photochemical or thermal are then investigated.
For the laser ablation at two ultraviolet wavelength, 266 and 355nm, a dehydrogenation of HAIO is observed via the infrared peak assigned to Al-H bond decreasing. It seems, according to the mass spectrometry results that the laser ablation transform the oxoaluminum hydride on aluminum oxide.
- D/PI.36** DIFFERENCES IN THE BEAM INTERACTION CHARACTERISTICS OF A CO₂, A Nd:YAG AND A HIGH POWER DIODE LASER WITH AN ALUMINA BIOCERAMIC
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Fundamental differences in the beam absorption characteristics experienced by materials when interacting with different lasers is an aspect of great significance, since the outcome of many lasers processing procedures are governed by this parameter. To this end a variety of techniques and approaches have been employed to examine the differences between the beam interaction characteristics of a CO₂ laser, a Nd:YAG laser and a high power diode laser with an alumina bioceramic. By employing a derivative of Beer- Lambert's law, the laser beam absorption lengths of the three lasers can be calculated. Similarly it is possible to calculate the thermal loading value of the material. Also, the fluence threshold values at which significant material removal occurs could be found graphically. Absorptivity measurements will be made to ascertain whether or not there is any correlation between the actual absorptivity of the alumina bioceramic and the absorption lengths of each of the three lasers. An examination of the propagation of the melt pools induced by the three lasers in the alumina bioceramic will be conducted and compared with the Stefan solution to the heat diffusion equation. Further, the findings will be related back to the melt depths observed in the alumina bioceramic after interaction with the three lasers.

Symposium D

- D/PI.37** ANOMALOUS MELTING AND EVAPORATION OF LASER-PULSED CHROMIUM FILMS
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Melting and evaporation of chromium and nickel films, which have very similar caloric parameters, by 6 ns laser pulses, are tracked by nanosecond multi-frame transmission electron microscopy. Contrary to nickel, melting and evaporation of chromium films proceed in a domain-patterned manner. This ablation is preceded by a shock-like lattice deformation of 3-4% within much less than 10 ns during heat-up which is probably the fastest step of an incomplete body-centered cubic to face-centered cubic phase transition 17 K below the melting point at 2110 K. This lattice deformation causes extremely high short-lived local pressures of more than 10 GPa. Such excessive pressures lead both to an increase of the melting point, and to an unfamiliar decrease of the enthalpy of evaporation. Therefore stressed and relaxed crystal regions melt at different temperatures and evaporate with different rates. These results show that simulations of melting and evaporation processes, which are based on the tabulated thermal parameters (e. g. melting temperature and latent heats), are misleading, if very high stresses are present.
- D/PI.38** POROSITY/BUBBLE FORMATION MECHANISM IN LASER SURFACE ENAMELLING
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The grouts between commercial tiles applied to walls and floors can be contaminated over time and normally have to be removed by manual or mechanical processes. To overcome the contamination problem, a specially developed tile grout was used to fill the voids between the tiles. The base filler was overlaid with an enamel surface that glazes after laser irradiation. One problem discovered in this work is that bubbles and porosities were formed after laser treatment. The use of water glass (sodium silicate) as a binder has been under taken in this study. This paper investigates the mechanism of bubble formation and its effects on the enamel surface. The results and the technique for the removal of bubble/porosities are presented in the paper.
- D/PI.39** RAPID LASER SURFACE ENAMELLING BY POWDER FEEDING TECHNIQUE
R. Akhter and L. Li, Laser Processing Research Centre, Department of Mechanical, Aerospace & Manufacturing Engineering, University of Manchester Institute of Science and Technology (UMIST), Manchester M60 1QD, U.K., R.E. Edwards and A.W. Gale, Department of Civil and Construction Engineering, University of Manchester Institute of Science and Technology (UMIST), Manchester M60 1QD, U.K.
Enamelling process normally requires very long curing/setting time. This paper reports a new rapid laser enamelling process by powder feeding technique. A special application of the technique has been developed for tile grout sealing. The laser parameters, powder feeding parameters and their effects on the enamelling process are presented. Rapid solidification in the laser enamelling process is studied and compared with conventional enamelling process. The interface between the enamel and the substrate are investigated.
- D/PI.40** ORIENTATION CONTROL OF INDIUM OXIDE FILMS BY A COATING PHOTOLYSIS PROCESS
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Epitaxial grown In₂O₃ films were prepared on single crystalline yttria stabilized zirconia (YSZ) substrates by a metalorganic compound (MO) coating photolysis process with excimer laser. The effects of substrate, laser fluence, repetition rate or other factors on the orientation of the films were investigated by IR, UV and XRD(theta-2theta scans, rocking curve analysis, pole-figure analysis). When a MO spin-coated films on SiO₂, single crystalline MgO(100) and single crystalline STO(100) substrates were irradiated by ArF excimer laser at a fluence of 50mJ/cm² and at a repetition rate of 5Hz for 5min, polycrystalline In₂O₃ films were obtained. On the other hand, in the case of using YSZ(001) substrate, In₂O₃ films on YSZ(001) substrate were (00C) axis oriented and were highly in plane aligned. The crystallinity of the In₂O₃ films was found to depend on laser fluence, repetition rate, shot number and concentration of starting materials. Crystallization or orientation mechanisms of In₂O₃ films by coating photolysis process are also discussed. The detailed experimental results will be described in presented paper.
- D/PI.41** HAFNIUM OXIDE LAYERS DERIVED BY PHOTO-ASSISTED SOL-GEL PROCESSING
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Unlike most of the high dielectric constant (high-k) layers grown on Si, the pure metal-oxide hafnium oxide (HfO₂) has been found to be thermodynamically stable in contact with Si. It also has many desirable properties such as high dielectric constant (~ 30) and relatively wide band gap (~5.68 eV) while being compatible with n+ polysilicon without the need for any barrier layer, and thus is a promising alternative gate dielectric for deep submicron CMOS technology. Sol-gel processing has been widely used to fabricate high-quality ceramics and glasses with advantages of low cost, relative simplicity, and easier control of the composition of the layers formed. Sol-gel processing in combination with the use of recently developed high-intensity excimer UV lamps provides the possible basis for the preparation of high quality dielectric layers. This paper reports the formation of HfO₂ thin films by photo-assisted sol-gel processing involving such excimer lamps. Properties of the films derived by sol-gel processing without and with the UV irradiation steps will be investigated using ellipsometry, IR analysis and UV spectrophotometry. The effects of UV irradiation in O₂ and N₂O gases will be compared. Preliminary electrical measurements of these layers will also be reported.
- D/PI.42** ARF-EXCIMER LASER INDUCED CHEMICAL VAPOUR DEPOSITION OF SIGEC FILMS
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The growing interest in the development of silicon germanium carbon (SiGeC) based devices for micro- and optoelectronics provoked an increasing attention in valuable low thermal budget techniques capable to produce such alloys on large areas as well as on small selected regions. Excimer laser induced chemical vapour deposition (LCVD) in parallel configuration is a soft alternative deposition technique that has already proved to be a feasible method for the production of various thin film semiconductors. This contribution will investigate the possibility of exploiting this technique for the production of ternary SiGeC alloys and demonstrate that coatings with uniform composition, structure and thickness can be deposited on different substrates such as polymers, glass, and Si-wafer.
The samples have been extensively analysed by profilometry, FTIR, Raman spectroscopy, XPS-depth profiling, AFM, SEM and H-effusion for identifying the most important experimental parameters determining the growth rate as well as the homogeneity in stoichiometry and structure. The results of this study have been used for refining the experimental parameters in order to produce coatings with well-tailored composition and thickness as well as for estimating the possibility of depositing on very large areas.

- D/PI.43** THE FORMATION OF BOUNDARY POROSITY IN LASER SURFACE TREATMENT OF CERAMICS
D. Triantafyllidis, L. Li, F.H. Stott, UMIST, Manchester, U.K.
Laser melting and re-solidification is one of the techniques used to densify and homogenise ceramic surfaces. Even though complete sealing of pores is achieved on the surface, pores have been observed in the treated zone/untreated bulk boundary. It is believed that these pores are formed from trapped gases from the sintering stage. These pores may lead to reduced spalling resistance and fracture strength of the ceramics.
This paper describes qualitatively the formation of the pores in the treated zone/untreated bulk boundary. Theoretical models describing the final boundary porosity and pore size distribution, including pore coalescence, are presented. The models show that pore formation is independent of laser processing parameters, whereas a dependence of pore coalescence on processing speed and power density is shown. Porosity in the treated zone/untreated bulk boundary is also dependent on the porosity and pore size distribution prior to laser treatment. The theoretical models are compared with experimental results based on the laser surface treatment of three types of refractory ceramics. A good agreement between the model predictions and experimental results is shown.
- D/PI.44** MESOSCOPIC MODELLING OF DENTAL LASER ABLATION
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A great deal of experimental research regarding laser ablation of dental tissue, using CO₂ and excimer lasers, has been conducted recently. However, the mechanisms by which light interacts with dental tissue and dental material is removed are not fully understood.
A great deal of experimental research regarding laser ablation of dental tissue, using CO₂ and excimer lasers, has been conducted recently. However, the mechanisms by which light interacts with dental tissue and dental material is removed are not fully understood.
We are currently developing a mesoscopic simulation of the process of dental laser ablation, taking into account the structure and chemical composition of dental materials: enamel and dentine.
To simulate the CO₂ laser ablation process, a finite elements code is being used. We are studying the effects of heat diffusion through the sample, temperature dependence of material parameters, and different laser parameters.
In our model of the excimer laser ablation process, we are establishing the importance of several different mechanisms, such as single photon absorption, energy transfer by recombination of electrons, energy transport by electrons, thermal evaporation of particles and others. The change in material properties during the ablation process is also considered. Temperature and stress maps of the simulated structure will be presented as well as charts illustrating the sensitivity of the models to the various laser parameters.
- D/PI.45** LASER INTERACTION WITH PARCHMENT IN THE NEAR-ULTRAVIOLET AND NEAR-INFRARED WAVELENGTH RANGE
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A detailed diagnostic study of the interaction of nanosecond laser pulses from the near-ultraviolet into the near-infrared wavelength range with various types of contemporary and ancient parchments is presented. The advantages of laser cleaning due to the absence of chemical agents, spectroscopic selectivity, micro-precision, computer-aided handling can only be verified when physico-chemical diagnostics guarantee destructionless processing. Scanning Electron Microscopy (SEM) data are correlated with morphological changes in dependence on the laser fluence and wavelength. The question, to what extent the chemical degradation of collagen is affected by various laser treatment parameters, could be resolved by Transmission Electron Microscopy (TEM) of collagen fibres collected from the outermost laser-exposed surface layer. It is also shown how Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT), and Pyrolysis Capillary Gaschromatography (PY-CGC) can be employed in the chemical diagnostics of laser cleaning of parchment. This study suggests that the ageing status of parchment artefacts plays a major role in assessing the laser cleaning limits.
- D/PI.46** EFFECT OF LASER RADIATION ON COMPOSITION AND GROWTH RATE OF AEROSOL PARTICLES
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The formation of small (nano) particles by gas-to-particle conversion is strongly affected by processes that take place on the particle surface. The composition of the particle and its growth rate depend on the incorporation of vapor and impurity molecules into the particle and on the evaporation of these molecules from the particle.
The resonance laser radiation can excite the internal degrees of freedom of molecules both of the vapor and the impurity components. The difference in the interaction of excited and non-excited molecules with the particle surface leads to change in the deposition process.
The problem of the selective influence of the laser radiation on the deposition processes in aerosol systems is studied in the paper on the basis of molecular-kinetic approach. It is shown that the laser radiation can affect both the concentration of impurity molecules in the growing aerosol particles and the particle growth rate.
This work was supported by grant No A4072205 GA AS CR.
- D/PI.47** LASER CLEANING OF PRINTED CIRCUIT BOARDS
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Resin contaminants around holes are produced in manufacturing of printed circuit board (PCB). Many drawbacks were found for conventional cleaning method. In this paper, we demonstrate that laser cleaning is a powerful cleaning tool to remove resin contaminants from PCB surface without damage. An Nd:YAG laser is used as a light source for laser cleaning. The beam profile of YAG laser can be reshaped and homogenized into a square beam with uniform energy distribution in the focal plane of the focusing lens using an optical system. The PCB surfaces before and after laser cleaning were observed by an optical microscope, analysed by X-ray Photoelectron Spectroscopy (XPS) and monitored by acoustic wave detection. The cleaning threshold is about 75 mJ/cm² and no damage is observed at below 400 mJ/cm². The cleaning efficiency, cleaning threshold, damage threshold and real-time monitoring will be discussed in detail.

- D/PI.48** 'RECTO' AND 'VERSO' LASER CLEANING OF FILMS
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Pulsed laser can provide high intensity short duration light pulses. Their interaction with a surface can produce several effects, depending on the beam intensity and pulse duration, and therefore on the peak temperature reached by the sample, ranging from simple heating to surface ablation. For intermediate values, we have the so-called "laser cleaning": the laser generated acoustic shock wave is able to remove extraneous particles from sample. In recent years, laser-cleaning technique has emerged as an attractive method for removing contaminants from critical surfaces. It has been found especially effective in removing sub micron particles or organic films and has found applications in several fields from hi-tech manufacturing to conservation and restoration. Laser cleaning has been successfully used to remove fungi from paper, however laser radiation interacts with ink and can easily induce discoloration, so that applications to paper restoration and conservation are very limited. Here we examine, by means of photo thermal deflection technique performed on both film surfaces, the thermo-mechanical behaviour of an opaque film under laser irradiation, showing that it is possible to use laser pulses to efficiently remove small particles from rear film surface. The proposed "verso laser cleaning" technique can be useful in situations in which laser light interaction with front surface has undesirable side effects, for example avoids problems due to ink damage or discoloration
- D/PI.49** INFLUENCE OF FABRICATION PROCEDURE ON BASIC CHARACTERISTICS OF SEMICONDUCTOR LASERS
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Broad-area contact ridge waveguide technology has been used for manufacturing lasers from AlGaAs/InGaAs or AlGaAs/GaAs SCH- or GRIN-SCH-SQW laser diode structures grown by MBE. The stripe-geometry ohmic contacts were made by sputtering of Cr/Pt and were defined by the conventional photolithography. The ridge was formed utilising Ar-ion etching by removing the highly p-doped GaAs cap layer besides the stripe. The P-I, I-V curves, and light field intensity distributions were measured and images from SEM were analysed for evaluation of the manufactured lasers. We report on the anomalies of the basic laser characteristics if the metal alloy covered the entire ridge as usually in the lasers fabricated by this technique. This was quite different if the metallic layer was confined to the stripe width. The results presented are surprising in the context of the broad-area contacts and are discussed in categories of effects those influence the electrical characteristics of a (Cr/Pt)- p-AlGaAs Schottky diode formed outside the stripe. Poor rectifying behaviour of the diode, responsible for a lack of the current spreading confinement, is attributed to the presence of defects in the vicinity of the metal-semiconductor interface which are introduced during the processing steps.
- D/PI.50** ETCHING OF FUSED SILICA AND GLASS WITH EXCIMER LASER AT 351 NM
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The etching of solid surfaces at the interface to liquids is a new promising method for micro-machining. In comparison to previous experiments by KrF-excimer laser (applicable only to deep UV-transparent materials like fused silica or CaF₂) this work concentrates on XeF-excimer laser etching of two technical glasses (corning: Pyrex, Schott: D263) and fused silica. The applied liquid for the etching experiments consist of a solvent (acetone, cyclo-hexane, tetrachloroethylene) and an dissolved absorber like pyrene with different concentrations (0 to 0.4 mol/l). The etch rate and the threshold fluency depend on the material properties. For example D263 glass shows a linear increase of the etch rate up to 12 nm/pulse at 1.3 J/cm² and reveals an etch threshold fluency of 800 mJ/cm². The surface topography of the etched areas depends very strong on the used glass. The surface roughness of etched Pyrex increases with etch depth and shows typical etch pits in the micron range. Compared to Pyrex the etched surface of D263 glass is smooth. First results of micro-structuring of glass will be presented and discussed.
- D/PI.51** LASER INDUCED ETCHING OF TUNGSTEN AND FUSED SILICA IN WF₆
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Etching of tungsten and fused silica induced by a focused argon-ion laser beam at $\lambda = 514$ nm has been investigated on a composite consisting of a thin W-layer sputtered onto a SiO₂ substrate. Pure WF₆ gas serves as the reactant for both W and SiO₂ etching. The process starts with pure chemical etching of tungsten. As the thin W layer is etched through, it continues as a combination of etching of both tungsten and silica. The latter is most probably caused by the formation of fluorine radicals at high temperatures. The analysis of the process is supported by accurate theoretical simulations on the profile evolution of the etched holes.
- D/PI.52** ATTENUATED TOTAL REFLECTION MEASUREMENTS ON POLY-CARBONATE SURFACES STRUCTURED BY LASER ILLUMINATION
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Periodic structures were studied on spin-coated Poly-Carbonate films: (a) sub-micrometer Laser Induced Periodic Surface Structures were generated by polarized ArF excimer laser beam; (b) micrometer periodic lines were ablated by imaging a mask onto the samples. The change in the thickness and the surface roughness was determined by an attenuated total reflection setup. The difference between the resonance places measured on the structured and untreated surface parts was very small in the case (a), proving that there is no significant material removal during LIPSS formation. The plasmon scattering caused by the sub-micrometer roughness weekly depends on the direction of the plasmon propagation. The broadening of the resonance curve started after 400 laser pulses, the roughness increased up to 800 laser pulses and after 1000 pulses the curve became narrower corresponding to the changes in the topography detected by atomic force microscopy. The shift of the resonance peak measured on the ablated samples (b) indicated a change in thickness corresponding to the rate of ablation. The effect of the micrometer structures on the broadening of resonance curves depends on the direction of plasmon propagation.

- D/PI.53** BLEACHING WAVE REGIME OF LASER POLYMERIZATION WITHOUT INITIATORS FOR CREATION OF 3D STRUCTURES IN ACRYLATES
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 We studied the process of formation of 3D polymer structures by initiating polymerization with laser radiation. Polymers based on such monomers as methyl methacrylate (MMA) and ethyleneglycolmonomethacrylate (EGM) were investigated. Polymerization was initiated by the fourth harmonic radiation of a Q-switched Nd:YAP laser (270nm) without any specially introduced initiator. Initiation is provided by the direct photolysis of monomers. At this wavelength the absorption of monomers is significantly higher than the absorption of corresponding polymer. It results in bleaching of the media during polymerization. This allows polymerization of layers whose thickness is much more than the penetration depth of initiating radiation. Using the suggested technique a cylindrical structure 400 nm in diameter and 400 nm in length was synthesized. With appropriate focusing it is possible to obtain structures with diameter less than 100 nm.
 Theoretical model is developed, which considers three stages of the process i.e., the induction period, fast polymerization period (in the gel-effect regime), and polymerization wave.
 The suggested technique is promising for fabrication of 3D photonic structures.
- D/PI.54** MICROSTRUCTURAL STUDY OF CO₂ LASER MACHINED HAZ IN 2024 ALUMINIUM ALLOY
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 Laser machining is an attractive alternative to traditional machining because critical operation parameters in aeronautic industry like processing time, versatility, contamination and finished can be improved. The main disadvantage of laser machining is high temperature reached by material during the processing. This heating promotes the appearance of a heat affected zone (HAZ), in which material microstructural properties can be highly modified. Indeed, fatigue cycle number for crack generation can be reduced inducing a reduction of the fatigue life.
 HAZ thickness depends on machining parameters such as laser used (CO₂, YAG, semiconductor diodes), laser power, laser cutting mode (pulse, continuous), assisted gas (H₂, N₂, inert gas) and material properties. Microstructural changes have an important effect on macroscopic properties like fatigue crack generation, elastic yield and tensile strength.
 In this work the HAZ thickness appeared in a 2024 aluminium alloy is reported using scanning electron microscopy and optical microscopy, after Keller wet etching. The results using different models of the literature are compared to simulated values. The purpose is to understand the phenomenon generating the HAZ in the considered alloy and to determine parameters that minimize this effect in the considered material.
- D/PI.55** EXCIMER LASER INDUCED PATTERNING OF POLYMER SURFACES
Y. Martel(a), K. Callewaer(a), K. Naessen(b), P. Van Dael(b), R. Baet(b) and E. Schacht(a), (a)Department of Organic Chemistry-Polymer Material Research Group, Ghent University, Krijgslaan 281-54, 9000 Ghent, Belgium and (b)Department of Information Technology, Ghent University, Sint-Pietersnieuwstraat 41, 9000 Ghent, Belgium
 Patterning and/or inducing a chemical change of a polymer surface with a geometrical accuracy and high spatial resolution impacts a number of applications¹. A number of technologies can be applied for the fabrication of microstructures. Laser ablation is a powerful flexible technique for rapid patterning of very small features, which can be applied for a number of different polymer materials. This study discusses the irradiation of a series of segmented polyurethanes with excimer lasers. By varying the different building blocks, a polymer is obtained with good ablation properties in terms of no debris formation and cavities with sharp edges. Furthermore, this polymer is used as a photoresist on a gold substrate. We are able to ablate the polymer layer until the gold surface is reached in patterned way (width: 10 μm). Different biomolecules can be attached on the bare gold by self-assembled monolayers (SAMs). The segmented polyurethanes (SPU) are based on a commercially available polycarbonate (PC), chain-extender and diisocyanate. The SPU are irradiated with a KrF₂ (λ = 248 nm) and an ArF₃ (λ = 193 nm) excimer laser. Segmented polyurethanes based on an aromatic diisocyanate (MDI) can be classified as high absorbing polymers for both lasers, resulting in cavities with sharp edges and high surface quality. By varying
 The energy density of the laser, the absorption coefficient of the polymers can be calculated. The absorption coefficient of the polymer at 193 nm is higher than at 248 nm.
 The segmented polyurethane with MDI as diisocyanate is used as polymer coating on gold and irradiated with an ArF excimer laser. We have ablated lines (width: 10 μm) in the polymer coating until the gold surface is reached. It is known from literature² that alkanethiols (HS-(CH₂)_n-X) form self-assembled monolayers (SAM) on gold surfaces. In a first step a alkanethiol with a carboxyl acid-endgroup is attached at the patterned gold surface. After removal of the remaining polymer coating, a second alkanethiol with a methyl-endgroup is attached. Due to reactive endgroups of SAMs, it is possible to covalently bound biomolecules (e.g. glucose oxidase) to the surface.
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- D/PI.56** LASER-INDUCED PERIODIC SURFACE STRUCTURE FORMATION PROCESS ON POLY-CARBONATE FILMS
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 Laser Induced Periodic Surface Structures were generated on different poly-carbonate films by polarized ArF excimer laser beam. The structure formation process and the role of the initial surface structures – like grains on oriented and amorphous thick films, and holes on thin spin-coated films – was studied by Atomic Force Microscopy at different angles of incidence. In the case of “s” polarized incident beams symmetry breaking and competition of structures of different periods was shown around the scattering objects. The LIPSS generating feedback mechanism was described as the interference of the incoming beam and the beams scattered on the previously existing structures, for both type of polarization. Droplet formation was detected on thick films at low fluences; and on spin-coated films having very small thickness at high number of laser pulses. The phase- and chemical changes during the LIPSS formation were identified.

- D/PI.57** **DIFFRACTIVE OPTICAL ELEMENTS WRITTEN BY PHOTODEPOSITION**
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Photo-excited processes have been used in this investigation to create planar elements for miniaturized optical and optoelectronic applications. We have investigated processes for laser writing Diffractive Optical Elements(DOE) elements directly by photodepositing a-Se from aqueous Se colloid solutions. The setup employs a computer based highly linear laser scanner which allows to deposit the designed optical diffractive profile of the elements by direct beam writing in a photodeposition cell. The basic characteristics of the written patterns were limited in this investigation to typical linewidths of about 25 micrometers, 0.2 micrometers thick and length of about 1 cm. The laser employed was an Argon ion laser with a typical maximum power of about 75 mW at a wavelength of 390 nm allowing a writing speed of about 20 micrometers per second. Various elements were produced such as linear gratings, and cylindrical and circular profiled DOE.
- D/PI.58** **DESCRETE MODEL FOR DESCRIPTION OF INCUBATION EFFECTS OF MULTIPULSE FEMTOSECOND LASER ACTION**
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There is presented a phenomenological model for description of incubation effects in multi-shot femtosecond laser action on wide bandgap dielectrics. Presented model is aimed at clarifying of physical processes and correct description of nonlinear decreasing of ablation and damage threshold of transparent dielectrics resulting from multi-shot laser action. The model is based on taking into account 1) formation of colour centers through laser-induced ionization, 2) variations of initial and defect- induced absorption with increasing of temperature, 3) incubation of heat in focal area of laser beam. Key points for developing of the model are 1) small duration of laser pulse that is much smaller than time separation between two consequent pulses, 2) temperature dependence of absorption. One of intentions is to study and describe feedbacks appearing during considered type of laser action. Heating is described by a numerical consequence rather than by an equation but each term of the consequence is a solution to heat-conduction equation. Obtained results include 1) estimation of the lowest value of ablation and damage threshold corresponding to the limiting case of unlimited number of pulses, 2) connection between characteristics describing decreasing of ablation thresholds for multi-shot action and characteristics of laser-matter interaction (e.g., rate of defect generation per pulse). Obtained results are compared with experimental data.
- D/PI.59** **INSTABILITY OF CRISTAL LATTICE OF WIDE BAND-GAP DIELECTRIC UNDER ACTION OF HIGH-INTENSITY FEMTOSECOND LASER PULSE**
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The paper is devoted to theoretical consideration of one of possible mechanisms of femtosecond laser-induced breakdown and damage of dielectrics with band gap 3 or more times larger than photon energy. It is well known from high-frequency electronics that action of high-amplitude electric field on semiconductors can result in decreasing of band gap and its collapse. The collapse can also result from strong excitation of electronic subsystem and ionization. Those effects have been observed in experiments on femtosecond laser action on semiconductors. We present generalization and extension of those ideas to the case of femtosecond laser interaction with wide band-gap dielectrics. In the framework of presented model there are estimated 1) time delay between pulse action and lattice destruction, 2) threshold laser intensity, 3) critical density of ionized electrons.
- D/PI.60** **SINGLE- AND MULTI-PULSE FEMTOSECOND LASER ABLATION OF OPTICAL FILTER MATERIALS**
J. Krueger(a), M. Lenzner(a,d), S. Martin(a), M. Lenner(b), C. Spielmann(b,e), A. Fiedler(c), W. Kautek(a), (a)Laboratory for Thin Film Technology, Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany, (b)Photonics Institute, Vienna University of Technology, Gusshausstr. 27-29/387, 1040 Vienna, Austria, (c)Rupp + Hubrach Inferoptics / Laserschutz GmbH, Laubanger 18, 96052 Bamberg, Germany, (d)Present address: Katana Technologies GmbH, Albert-Einstein-Ring 7, 14532 Kleinmachnow, Germany, (e)Present address: Department of Physics, University of Wuerzburg, Am Hubland, 97074 Wuerzburg, Germany
Commercially available absorption filters (Schott BG18 and BG36) were investigated with respect to their single- and multi-pulse ablation threshold using laser pulses from a Ti:Sapphire laser in the range between 30 and 340 fs. It could be observed, that the threshold fluence decreases for shorter pulse durations. The similarity of the measured multi-pulse threshold fluences with those of undoped glass material (around 1 J/cm² for a pulse duration of 30 fs) suggests that, for very short pulses, the threshold is independent on the doping level and therefore, linear absorption does not significantly contribute to laser-induced damage. For >100 pulses per spot and all pulse durations applied, the threshold fluences saturate. This independence on the number of applied pulses leads to technically relevant damage threshold values.
- D/PI.61** **MICROPROCESSING OF SUBSTRATES AND COATINGS OF TRIBOLOGICAL INTEREST USING ULTRASHORT LASER PULSES**
G. Dumitru, V. Romano, H.P. Weber, Institute of Applied Physics, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland, M. Sentis, J. Hermann, S. Bruneau, W. Marine, Groupement Interdisciplinaire Ablation Laser et Applications, LP3 FRE2165 CNRS - Université de la Méditerranée, GPEC UMR 6631 CNRS, Faculté des Sciences de Luminy, Case 917, 13288 Marseille, France
This work presents investigations on the femtosecond laser ablation behaviour of some hard substrates and coatings that are extensively used in tribological applications. Diamond and hard metal (bulk materials), as well as diamond-like carbon and titanium carbonitride were the studied materials. The correlation between the hardness and geometry of the gliding surfaces, different wear mechanisms and the size of the wear particles is briefly described. The positive role of surface microstructuring in delaying the breakdown of tribological systems and also the problems encountered when nanosecond laser pulses are used for the microstructuring of thin films are mentioned. The experimental investigations were performed in air at low fluences (0.5 – 6 J/cm²), using a Ti:sapphire laser. Different analysis methods (AFM, SEM, optical microscopy) were used to observe the surface morphology changes that were induced by the laser radiation. From these examinations and from the incident fluence profiles, the threshold values for surface damaging and for material ablation were determined. From the above mentioned materials, diamond showed the highest threshold values and the ablation rates determined at fluence values of about 6 J/cm² were in the range 100 – 200 nm per pulse for all the investigated materials.

D/PI.62

SELF-ORGANIZED SURFACE STRUCTURES ON INSULATORS UPON FEMTOSECOND LASER ABLATION

F. Costache, M. Henyk, J. Reif, LS Experimentalphysik II, BTU-Cottbus, Universitätsplatz 3-4, 03044 Cottbus, Germany
After laser ablation from ionic crystals with ultra-short pulses (120 fs, 800 nm), the crater morphology was examined ex-situ by optical, scanning electron and atomic force microscopes.

In BaF₂ and CaF₂, at relatively low ablation rate and up to several thousands laser shots, several periodic structures (ripples) occurred at the crater bottom. A fine pattern was found perpendicular to the laser beam polarization with a period of about 200-300 nm. After a higher number of laser shots, a second ripple pattern was observed running perpendicular on the first one with a period of 600-1100 nm. In any case, the structure period was insensitive to the angle of incidence variation. The development of the crater morphology was investigated by increasing the number of laser shots.

ToF mass spectrometer measurements performed during the structure creation showed in all cases a strong emission of fast ions with kinetic energy of about 100 eV. The fact that the surface is electrostatically decomposed by Coulomb explosion calls into question thermal effects as the origin of the ripples.

Furthermore, the influence of interference patterns on the ablated spot was investigated by a two-beam experiment. The laser pulses from both beams were subsequently delayed in a range of 0 - 200 ps with respect to each other, in order to follow the dynamics of the surface relaxation.

We conclude that the crater morphology suggests self-organization mechanisms for the surface relaxation upon ablation.

D/PI.63

EXCIMER LASER ABLATION LITHOGRAPHY APPLIED TO REFLECTIVE DIFFRACTIVE OPTICS FABRICATION

M. Flury(a), A. Benatmane(b), P. Gérard(a), P. Montgomery(b), J. Fontaine(a), J.P. Schunck(b), E. Fogarassy(b), (a)Laboratoire des Systèmes Photoniques, ENSAIS, Bld de la Victoire, Strasbourg, France, (b)Laboratoire des Systèmes Photoniques, Pôle API, Illkirch, France, Laboratoire PHASE, CNRS, Strasbourg, France

We present a study on the design, fabrication and tests of Diffractive Optical Elements (DOEs) used with high power laser beams. Two types of DOEs are considered: the Fourier and Fresnel elements. The design is established with the help of the iterative Fourier transform algorithm and the algorithm of Yang and Gu. We discuss the influence of the diameter of the incident beam, the phase profile, the M² factor, the electromagnetic modes and the spatial coherence on the performance in the wavefront reconstruction. We show how the performances in the reconstruction process are related to the properties of the incident beam. We propose two alternative techniques for the fabrication step: the Laser Ablation Lithography (LAL) and the contact photolithography with flexible masks. The first technique requires the use of a dedicated micromachining station with a pulsed KrF laser emitting at 248 nm. LAL technique, as opposed to direct etching with laser ablation, allows to produce binary DOEs with different substrates. The multilevels approach is demonstrated with a calibration of the ablation process. We show also that the second solution is limited today to the case of binary DOEs for laser sources emitting in the infrared domain (wavelengths above 2 microns). We propose different configurations for currently used high power laser sources. These propositions are validated by optical and thermal simulations based on Turunen rigorous electromagnetic method. New applications of DOEs are finally introduced, like laser marking or multi-points brazing.

D/PI.64

MICROFABRICATION OF BIOPOLYMER PATTERNS BY THE SUB-PS LASER INDUCED FORWARD TRANSFER PROCESS

A. Karaiskou(a), I. Zergioti(a), D. Kafetzopoulos(b), C. Fotakis(a), (a)Foundation for Research & Technology – Hellas, Institute of Electronic Structure and Laser, P. O. Box 1527, Heraklion 71110, Greece, (b)Foundation for Research & Technology – Hellas, Institute of Molecular Biology and Biotechnology, P. O. Box 1527, Heraklion 71110, Greece

A process for fabricating precision patterns of biopolymer materials onto solid substrates is presented in this paper. The Laser Induced Forward Transfer method was used to produce patterns of DNA spots (1 - 200 μm) by means of 0.5 ps KrF laser. This method utilizes pulsed lasers to remove selectively material, which has been previously deposited on a laser-transparent substrate, by means of laser transfer and deposition it onto a substrate. The dynamics of the sub-picosecond LIFT process of DNA molecule was investigated for time delays between 0.01-4 ns following laser irradiation pulse. The material ejected by the sub-picosecond LIFT process was measured to be highly directional with narrow angular divergence (2°). The laser transfer of molecules such as DNA opens up new applications possibilities for the fabrication of biosensors and arrays for multi-analyte assays.

D/PI.65

LASER FORWARD TRANSFER OF SOFT MATERIALS

D. Young, B. Ringeisen, H. Kim, R.C.Y. Auyeung, and D.B. Chrisey, Naval Research Laboratory, Washington DC, USA, D.D. Dlott, School of Chemical Sciences, University of Illinois at Champaign-Urbana, USA

Matrix-assisted laser forward transfer has been found to be a versatile method for producing mesoscopic patterns of rheological fluids and soft materials. Time-resolved microscopy studies on the laser forward transfer of colloidal inks and protein solutions provide an explanation for this versatility. Depending on the characteristics of the incident laser pulse and its interaction with the fluid layer, soft materials can be ejected at velocities ranging from subsonic (<50 m/s) to supersonic (>1000 m/s). The ejected material can take the form of a thin columnar jet, a plume of dispersed aerosolized particles, or a discrete disk of largely undisturbed material (when the transferred material has significant degree of elasticity). Many of these observed phenomena are unique to soft matter, and have not been observed in laser induced forward transfer (LIFT) of solid-state materials.

This level of control over transfer conditions allows tailoring of the transfer process to many different classes of materials, and three recent applications of soft laser forward transfer will be discussed. First, rapid prototyping of mesoscopic electronics devices can be accomplished by patterning with microelectronic inks. Second, efficient patterning of protein solutions has been demonstrated using 355 nm laser pulses and a metallic absorbing layer. This has application to the fabrication of high-density, high-throughput microarrays used in proteomics. Finally, matrix-assisted laser forward transfer can be used to produce patterns of living mammalian cells, with near-100% viability, and is a potential method for CAD/CAM three-dimensional tissue engineering.

15:45

BREAK

Symposium D

Femtosecond regime interactions

- D-I.12** 16:00 SUB-100-FEMTOSECOND LASER INTERACTION WITH SOLIDS
Ch. Spielmann, Photonics Institute, Vienna University of Technology, Gusshausstr. 27, 1040 Vienna, Austria and Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
In the last few years we have witnessed a tremendous progress in ultrafast optics. Nowadays laser systems delivering pulses as short as 12fs are commercially available. Not only the pulse duration has been substantially reduced, but also the lasers have become more reliable and stable. These systems are now suitable for laser based material processing in industrial applications. In this talk the progress in the development of laser sources will be briefly reviewed. These novel laser source have been extensively used to study laser material ablation in a wide pulse duration range spanning from a few picoseconds down to 5fs. These studies revealed different mechanisms causing laser induced damage. The physical processes relevant in the different time domains will be described. Examples for material processing of transparent and absorbing dielectrics, and semiconductors will be presented and compared. Further, implications of these short pulses for laser safety issues will be briefly addressed.
- D-I.13** 16:30 THEORETICAL APPROACH TO LASER INDUCED FEMTOSECOND STRUCTURAL CHANGES AND THEIR ANALYSIS BY ULTRASHORT X-RAY PULSES
M.E. Garcia, Institute for Theoretical Physics, Freie Universität at Berlin, Arnimallee 14, 14195 Berlin, Germany
Femtosecond laser pulses produce bond breaking processes which lead to ultrafast material modifications, which involve phase transitions and ablation. In the last years different types of laser induced structural changes were observed, which can be described by our microscopic theoretical approach [1-5]. It consists in molecular dynamics simulations performed on potential energy surfaces which change in time due to the laser excitation, electron thermalization processes and diffusion.
In this talk I will discuss different ultrafast structural changes taking place in carbon and silicon. In particular, the time scales and the mechanisms for nonequilibrium melting and ablation will be analysed.
Finally, and regarding the possibility of a 'direct' observation of these phenomena by using ultrashort x-ray pulses, preliminary calculations of EXAFS- and diffraction spectra during time-dependent structural changes will be presented.
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[2] H. O. Jeschke, M. E. Garcia and K. H. Bennemann, Phys. Rev. B 60, R3701 (1999).
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[5] H. O. Jeschke, M. E. Garcia and K. H. Bennemann, J. Appl. Phys. 91, 18 (2002).
- D-I.14** 17:00 ELECTRON DISTRIBUTION RELAXATION IN SOLID HITTED BY FEMTOSECOND LASER PULSE
L.D. Pietanza, G. Colonna, S. Longo and M. Capitelli, Centro di Studio per la Chimica dei Plasmi del CNR and Department of Chemistry, University of Bari, via Orabona 4, 70126 Bari, Italy
Advance of femtosecond laser technology makes possible to create and investigate transient non-equilibrium electron distribution functions in semiconductors and metals. These experimental investigations have shown that, after the femtosecond laser pulse excitation, the electron distribution is far from equilibrium. In the theoretical study of the electron relaxation, however, an instantaneous electron thermalization is generally supposed and the relaxation of the electron distribution is described by a two temperature model.
The aim of this work is to study the temporal evolution of the electron distribution even before the thermalization. For such purpose, we have performed a kinetic study of the electron dynamic relaxation inside a Au film subjected to a femtosecond laser pulse developing a time dependent numerical solution of the Boltzmann equation for the electrons inside the film. In the Boltzmann equation, we have considered the collision integrals due to electron-electron and electron-phonon collisions and a perturbation term due to the laser pulse. Our results show that, after the pulse excitation, electron distributions are very far from equilibrium as expected by experimental results and therefore the two-temperature model is inadequate for the theoretical description of the phenomenon.
- D-I.15** 17:15 CONTROL OF LASER DESORPTION USING FEMTOSECOND AND NANOSECOND PULSES
W.P. Hess, A.G. Joly, K.M. Beck, Pacific Northwest National Laboratory, P.O. Box 999, Richland WA 99352, USA, D.P. Gerrity, Department of Chemistry, Reed College, Portland OR 97202, USA, P.V. Sushko and A.L. Shluger, Condensed Matter and Materials Physics, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
Laser control is currently a topic of intense research. Experiment and theory show how specific product pathways can be selected by irradiation with one or more laser beams. Laser control schemes typically involve small gas-phase molecules to reduce the number of reactive pathways and decrease energy redistribution rates from laser-prepared states. Sophisticated quantum and optimal control schemes have been developed to overcome these and other difficulties. Due to the complexity of condensed phase chemistry, control of laser induced solid-state reactions has received much less attention. Nonetheless, laser control of desorbed products and states is possible by judicious choice of laser wavelength, pulse duration, or delay between pulse pairs. Theory indicates that it is possible to excite the surface over the bulk using tunable laser sources in ionic crystals. We recently demonstrated nearly exclusive emission of hyperthermal Br (2P_{3/2}) from laser excited KBr and control of ion emission from MgO surfaces using femtosecond pulse pairs. We explore the mechanism of laser desorption in experiments using a sequence of multiple laser pulses. The first laser pulse induces formation of transient species and the second pulse then excites the intermediate state to induce desorption of selected species or quantum states. Selective desorption raises the intriguing prospect of selective surface modification. The principles described here should be extendable to other alkali halides.

- D-I.16** 17:30 **MICROSCOPIC SIMULATION OF SHORT PULSE LASER ABLATION OF SILICON**
Patrick Lorazo(a,b), Laurent J. Lewis(b) and Michel Meunier(a), (a)Département de Génie Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Ecole Polytechnique de Montréal, Case Postale 6079, Succursale Centre-Ville, Montréal, Québec, Canada, H3C 3A7, (b)Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, Canada, H3C 3J7, Canada
 A novel model, combining both Monte Carlo and molecular-dynamics techniques, has been developed to address the mechanisms underlying picosecond laser ablation of silicon. This unique approach allows us to identify the sequence of events leading to matter removal from a silicon substrate irradiated with a single 266 nm, 15 ps, laser pulse. In brief, the laser energy is directly coupled to the electronic degrees of freedom through electron-hole pair creation and free-carrier absorption. Carrier dynamics are subsequently described within a Monte-Carlo scheme by a complex interplay between numerous processes, namely carrier-phonon and carrier-carrier scattering, Auger recombination, and impact ionization. Atom dynamics are treated following a standard molecular-dynamics procedure using the Stillinger-Weber potential. Above the characteristic threshold energy for ablation, it is observed that matter removal is brought about by the rapid relaxation of the hot (> 10000 K) and dense ($\sim 10^{23}$ cm⁻³) electronic gas in the *molten*, metallic-like, silicon material. On a mesoscopic scale, a precise assessment of the mechanisms leading to ablation is achieved by following the thermodynamic trajectory of the system in real time. On a microscopic scale, our results indicate that the melting and ablation threshold energies are independent of Auger recombination and impact ionization.
- D-I.17** 17:45 **LASER ABLATION OF POLYMERS BY RESONANT INFRARED VIBRATIONAL EXCITATION: MECHANISM AND APPLICATIONS**
R.F. Haglund, Jr., Vanderbilt University, Nashville TN, USA, D.M. Bubb, Seton Hall University, East Orange NJ, USA, M.R. Papantonakis, Vanderbilt University, Nashville TN USA, J.S. Horwitz, Naval Research Laboratory, Washington D.C., USA
 A year ago, we reported unusually efficient, non-destructive ablation and deposition of poly(ethylene glycol) by resonant infrared (RIR) excitation using a tunable, picosecond-pulse free-electron laser. Since then, we have applied this technique to polymers that in various ways have defied attempts at conventional ultraviolet pulsed laser deposition (PLD) and that have applications potential in photonics, electronics and medicine; these have included poly(styrene), poly(tetrafluorethylene), and fluoropolyol. We have also deposited the films at elevated temperatures in contrast to the earlier studies of room-temperature RIR-PLD. To verify the applications potential of the films, we analyzed the composition, morphology, physical and chemical structure, and optical properties of the films by various microscopic and spectroscopic techniques. Measurements of the wavelength, intensity and fluence dependence show that the ablation mechanism depends not only on the optical absorption coefficient, but on the specific character of the polymer bonds. For example, in poly(styrene) and poly(ethylene glycol), excitation of the intermolecular bonds produces efficient, non-destructive ablation, whereas excitation of intramolecular bonds leads to photofragmentation. The strong nonlinear dependence on density of vibrational excitation shows that the untangling of the polymer chains may occur in a regime of moderate thermal confinement due to nonlinear absorption.
- D-I.18** 18:00 **NEGATIVE ION EMISSION FROM DIELECTRIC CRYSTALS UPON ULTRA SHORT LASER PULSE IRRADIATION**
M. Henyk, J. Reif, LS Experimentalphysik II, Brandenburgische Technische Universität Cottbus, Universitätsplatz 3-4, 03044 Cottbus, Germany
 The mechanism of particle emission upon sub-band gap laser light excitation has been the subject of various studies up to present. Most of them deal with the detection of positive ions and by excited particle luminescence or with topographic surface inspection. To our knowledge, however, only little is known about laser induced negative ion emission. In this contribution, we report on such experiments on nominally transparent dielectrics (Al₂O₃, BaF₂, NaCl), irradiated by an 800 nm – 100fs laser in the multiple pulse regime (N-on-one). A state-of-the-art time-of-flight mass spectrometer was used for detection, in combination with ion trajectory simulations.
 In a widely accepted model, the energy of near infrared laser pulses is absorbed at defect states, followed by photoemission, leading to positive charging of the surface and subsequent explosion under the mutual Coulomb repulsion of positive ions. Consequently, the contributions of negative ions to the total sputter yield should be of minor importance. Our measurements confirm indeed the preferred emission of electrons and positive ions. In order to detect negative ions a significant higher laser intensity must be applied. Even under the condition of strong excitation, the incubation phase is significantly longer than for positive ion emission, appearing to be less dependent on the laser intensity. Therefore, it is obvious that negative ions are generated through a secondary ablation process, characterised by the following features: (1) the appearance of incubation does not represent a change in the absorption cross section by the accumulation of surface defects, (2) the obtained kinetic energy distributions can be fitted with shifted Maxwell-Boltzmann functions, (3) the center-of-mass velocity from negative ions is two orders of magnitude lower as for positive ones, but for all ionic species independent of the mass.
 We conclude that after repeated surface Coulomb explosion with increasing laser shot number the surface roughness is increased, leading to the expulsion of neutrals. These, in turn, may capture electrons in the gas phase. Consistent with this assumption is the observation that, in contrast to a strongly forward directed positive ion emission, the angular distribution of negative ions is broad. A further indication for neutral precursors is given by the exclusive presence of singly negative charged species, the dominance of simple atomic fragments (O⁻, F⁻, Cl⁻), the similar width of positive and negative energy distribution and the existence of Al₂O₃⁻ in the mass spectrum from Sapphire.

D-I.19

18:15

GAS PHASE PARTICLES FORMATION DURING FEMTOSECOND LASER ABLATION

O. Albert and, J. Etchepare, LOA, CNRS, ENSTA, Ecole Polytechnique, 91761 Palaiseau Cedex, France, C. Boulmer-Leborgne, GREMI, Université d'Orléans, 45067 Orléans, France, E. Millon and J. Perrière, GPS, Univ. Paris VII, 2 Place Jussieu, 75251 Paris Cedex 05, France

Time resolved imaging and spectroscopic measurements have been used to study the plasma induced at the surface of metallic, semiconducting or insulating targets by irradiation with femtosecond (fs) and nanosecond (ns) laser pulses. Large differences were observed in the plasma expansion dynamics as a function of pulse duration. We focus in this presentation on nano-sized aggregates that appear as an important feature encountered in fs interaction. These aggregates, which present a size in the 10 to a few hundred nanometer range and lead to films formed by their random stacking, are different from the spherical micrometer size droplets which are frequently observed in ns laser ablation. These aggregates are the result of a gas phase condensation effect during the plasma expansion, and are characterised by a specific spectral response that corresponds to a black body like emission, which is mainly observed during fs laser ablation. These findings will be presented in the case of Ti, Si and TiO₂, and their correlation with film growth, structure, composition and morphology will be analysed and discussed. The non existence of these aggregates for other materials will also be discussed.

Symposium D

Wednesday, June 19, 2002
Mercredi 18 juin 2002

Afternoon
Après-midi

Session II: Laser and photo-induced surface processing, microfabrication and nanoengineering

Physical and chemical surface modifications

- D-II.1** 14:00 INDUSTRIAL APPLICATIONS OF HIGH POWER DIODE LASERS IN MATERIALS PROCESSING
F. Bachmann, Rofin-Sinar Laser GmbH, Germany
In recent years, (Ga, In)(As, N) alloys, with low N contents, have attracted increasing attention. In particular, GaInAsN has appeared to be a very interesting candidate for 1.3 μ m emitting devices; thus standard laser diodes and VCSELs have been fabricated. However, growth of these alloys remains problematic in terms of N incorporation control and material quality.
We have studied plasma-assisted molecular beam epitaxy growth of GaAsN and GaInAsN using a RF plasma cell to provide reactive nitrogen from ultrapure N₂. Plasma emission spectroscopy has been performed in order to identify its different species (N, N₂, N₂⁺, …) and their concentration evolution as a function of N₂ flow rate and RF power. These results have been related to N concentration in GaAsN bulk material and Ga_xIn_{1-x}As_{1-y}N_y/GaAs quantum wells (QW). N₂⁺ ions emission has been investigated in order to minimize their concentration and consequently to limit the deterioration of the growing surface.
On the other hand, we have studied the incorporation of impurities due to the RF plasma cell. Oxygen, generally responsible for low photoluminescence performance, has been observed and its incorporation reduced, allowing growth of 1.3 μ m emitting QWs at room temperature. Other impurities, less affecting optical properties, have been detected and related to growth conditions. These studies allowed us to define optimal conditions for RF plasma cell utilization, leading to the growth of 1.3 μ m laser diodes.
- D-II.2** 14:30 LASER-ASSISTED SYNTHESIS OF ULTRA SMALL METAL NANOPARTICLES
A. Naryan(a), L. Landström(b) and M. Boman(b), (a)Louisiana Tech University, Institute for Micromanufacturing, Ruston LA 71272, USA, (b)Uppsala University, the Angstromlaboratory, Institute of Materials Chemistry, 751 21 Uppsala, Sweden
Palladium and silver particles have (to our knowledge) for the first time been synthesized in the liquid phase by photolytic decomposition from their ammine complexes. Short pulses (fwhm 15 ns) of 193 nm excimer light were used in the experiments. The particles were probably formed by a photolytic decomposition of excess ammonia yielding atomic hydrogen, which in turn reduces the metal ions to metal. The particles were characterized by transmission electron microscopy (TEM), high resolution scanning electron microscopy, Raman spectroscopy, nuclear reaction analysis, X-ray fluorescence spectroscopy and X-ray diffraction. The size of the metal particles, as measured by TEM, could be varied in the range 0.5 to 2.5 nm by varying the experimental parameters such as laser fluence and reactant concentrations. X-ray and electron diffraction revealed that the particles consisted of the pure metals. Preliminary results indicated a deviation from a log-normal size distribution which may be attributed to the occurrence of so called 'magic numbers'.
- D-II.3** 14:45 LASER INDUCED GRADED DOPING IN TITANIUM DIOXIDE THIN FILMS
G. Benvenuti, E-Halary-Wagner, A. Brioude, P. Hoffmann, EPFL Lausanne, Switzerland
Thermal Chemical vapour Deposition of titanium dioxide from Titanium tetraisopropoxide (TTIP) is achieved either with chemical beams, in the pressure transition regime, or in the viscous flow regime. The high index of refraction of the deposits > 2.6 is characterized by spectral ellipsometry and spectral reflectance measurements. Laser induced deposition at room temperature is compared with the thermal deposits concerning deposition rate and chemical composition, in all three regimes with and without oxygen as reaction partner. Deposition is carried out on different substrates like glass, stainless steel, copper, and silicon wafers. Furthermore, by addition of a different oxide precursor (e.g. for SiO₂ deposition) preferential laser decomposition of one of the precursors allows 3D graded depositions of oxide mixtures for micro-optical applications.
- D-II.4** 15:00 LASER INDUCED MODIFICATION OF THE LUMINESCENT PROPERTIES OF NANOCRYSTALLINE ZnO
C. Radoj, S.M. Wiggins, J. Solis Instituto de Optica, CSIC, Serrano 121, 28006 Madrid, Spain, P. Fernandez, J. Piqueras, Departamento de Fisica de Materiales, Fac. Ciencias Fisicas, Univ. Complutense, 28040 Madrid, Spain
The effect of nano- and pico-second pulsed laser irradiation on the structure and luminescent properties of ZnO nano-crystalline samples has been studied by means of X-ray diffraction measurements, scanning electron microscopy (SEM) and cathodoluminescence spectroscopy (CL). The samples consisted of pressed pellets of commercially available ZnO powder which was ball grinded over time periods of 20, 40 and 60 hours in order to generate nanocrystalline ZnO. The samples were then analysed by X-ray diffraction and their topographies and CL spectra studied in a Hitachi S2500 SEM microscope using either emissive or cathodoluminescence modes. Measurements were performed at liquid nitrogen temperature. The irradiation experiments were carried out using laser pulses at 583 nm with a duration of either 6 ns or 30 ps (FWHM) performing both single and multiple laser exposures over regions of "300 mm in size, leading to fluences typically in the 10 to 100 mJ/cm² range. After irradiation, the CL spectra of regions irradiated at different fluences and with different number of pulses were recorded. Changes observed in the relative intensities of the characteristic violet and green luminescent bands of ZnO are discussed in terms of the effect of irradiation on the grain size and defect structure of the material, affecting its luminescent properties.

Symposium D

- D-II.5** 15:15 **LIGHT INDUCED CHANGES OF TRANSPORT PHENOMENA IN LaSrMnO THIN FILMS**
H.-U. Habermeier(a), H. Zhang(a), F.R. Razavi(a), D. Casa(c), M. von Zimmermann(b), B. Keimer (a,c), J.P. Hill(b), (a)Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany, (b)Dpt. of Physics, Brookhaven National Laboratory, Upton NY, USA, (c)Dpt. of Physics, Princeton University, Princeton NJ, USA
Manganese oxides show a rich variety of ground states whose interplay gives rise to a variety of transport anomalies. External fields such as a magnetic field epitaxial strain and photons in the wavelength range from x-rays to visible light are the most prominent examples. We have studied the temperature dependent transport properties such as resistivity, carrier concentration and Hall mobility of slightly doped LaSrMnO thin films exposed to near UV light and observe drastic changes in the metal-insulator transition temperature and the charge carrier mobility. Furthermore, x-ray irradiation causes an interesting memory effect when the films are repeatedly exposed to x-rays at low temperatures. We provide a qualitative explanation of this unusual effect based on different orbital correlations in these films.
- D-II.6** 15:30 **HYDRODYNAMIC EFFECTS ON THE MOLTEN SURFACE OF A LASER-IRRADIATED ALUMINUM SAMPLE**
P. Mosaner, Marco Bonelli and A. Miotello, INFN and Dipartimento di Fisica, Università di Trento, 38050 Povo (Trento), Italy
We studied the morphological effects following the hydrodynamic processes occurring at the surface of a melted aluminium sample during pulsed laser irradiation. We used a KrF excimer laser, 248 nm wavelength and 20 ns pulse duration. Among the different effects produced by a nanosecond laser pulse on a metal surface (heating, melting, ablation, reaction with the external atmosphere, etc.) the phenomena following the hydrodynamic processes can be detected by Scanning Electron Microscopy analysis of the surface morphology which exhibits evidence of frozen convective motion in the molten phase. We performed systematic analysis of the influence of the laser pulse energy density on the turbulence of the molten bath; moreover, we analysed the effect of external pressure and number of pulses on the frozen surface structure. Liquid wave motion, which results in typical wavelike frozen structure, can be induced in a reproducible way thus permitting a controlled tailoring of the surface morphology.
- D-II.7** 15:45 **PREDICTION OF MELT GEOMETRY IN LASER CUTTING**
L. Tomesani, University of Bologna, Italy, G. Tani, University of Florence, Italy, G. Campana, University of Bologna, Italy
Laser cutting processes are probably the most common industrial applications in the manufacturing of metal and non-metal parts among the laser technologies. With the aim of minimizing setup and keeping machining costs as low as possible, many analytical models are available for process planning activity, in order to manage the high number of process variables involved. One of the most important features of a process planning tool is to predict the melt geometry during the cut. In this paper a theoretical model for melt prediction is implemented as a function of material thickness. In fact, the depth of the melt layer is ever increasing from the top of the sheet toward the bottom, and this leads to the difficulting of ejection of the liquid phase for increasing cutting speed. Thus, much earlier the maximum speed is reached, the formation of drosses at the bottom of the sheet is observed. The model exploits an evaluation of the melting zone geometry basing on mass and force balance, distributed along the cutting depth. The proposed model, allows the evaluation of critical conditions of liquid expulsion from the cut, thus allowing the prediction of dross formation under different operating conditions. The geometry of the kerf is based on a model already developed by the authors
- 16:00 **BREAK**
- D-II.8** 16:30 **A NEW ERA OF CRYSTALLIZATION : ADVANCES IN LATERAL CRYSTALLIZATION AND CRYSTAL ENGINEERING**
T. Voutsas, Display Group, Sharp Labs of America, Inc., 5700 NW Pacific Rim Blvd., Camas WA 98607, USA
Low temperature poly-Si technology has entered the LCD market. New products and applications are expected and the way to materialize such expectations is by the introduction of innovative technologies that can substantially improve the characteristics of poly-Si TFT devices. One such key technology is crystallization. This paper will review the progress in poly-Si crystallization technologies over the past several years, culminating to the development of advanced processes that aim to produce large-grained poly-Si films with a controlled, engineered microstructure. Emphasis will be placed in the presentation of laser annealing and its implications in the present and future of poly-Si TFT technology. Data and theoretical predictions will be presented supporting the notion that laser annealing by itself and/or in combination with other techniques can provide a multitude of poly-Si microstructures suitable to meet the demands of current, or future, polysilicon-based display products.
- D-II.9** 17:00 **USJ FORMED BY SINGLE SHOT LASER DOPING FOR Si TRANSISTORS**
T. Noguchi, Institut d'Electronique Fondamentale, UMR8622, Université Paris-Sud, Bat. 220, 91405 Orsay Cedex, France
Intensive study on the device and the process is being done for Si ULSIs as well as for poly-Si TFTs (Thin Film Transistors) in FPD (Flat panel Display) by performing an efficient activation process such as RTA (Rapid Thermal Annealing) or ELA (Excimer Laser Annealing). After ELA using only single shot of UV pulsed beam, an ideal impurity doping with higher activation of carriers can be attained by melting the silicon surface instantaneously without modifying the carrier profile. The technique also makes possible the higher incorporation of dopant concentration above its equilibrium solubility.
Precise control of USJ for S/D (Source and Drain) is an important issue to suppress the SCE (Short Channel Effect) for sub-0.1 μ m Si CMOSFETs with keeping the high on-current in low driving voltage. An ELA using a uniform beam of lumped shot has been studied in order to form S/D with shallow junction in MOS transistors comparing with a conventional thermal annealing in solid phase. A promising result and its possibility of ELA after I^2 (Ion Implantation) for the USJ in sub-0.1 μ m MOSFETs, for an application to TFTs and SOI gates are described.
The single shot ELA using a lump beam with high absorption for silicon layers in the UV region is an effective and a promising doping process and should be developed for Si micro-electronics in next generation.
The author thanks co-researchers and his friends for encouragement.

Symposium D

- D-II.10** 17:30 A SIMPLE ANALYTICAL METHOD FOR CHARACTERIZING THE MELT REGION OF A SEMI CONDUCTOR UNDER PULSED LASER IRRADIATION
J.Y. Degorce and M. Meunier, Département de Génie Physique, Ecole Polytechnique de Montréal, P.O. Box 6079, Station Downtown, Montréal, H3C 3A7, Canada
Focusing a pulsed laser with sufficient fluence on a semiconductor surface results in a local melting of the material. Determination of the melted region dimensions requires solving the three dimensional heat transfer equation; this is cumbersome due to the temperature dependence of various parameters involved such as the thermal conductivity, the specific heat and the thermal diffusivity. To overcome these limitations, we have derived a simple analytical solution based on the energy balance evaluated at the interface between the liquid and solid phases. Simple expressions are given for the minimum fluence for melting, melt lifetime as well as the radius and depth of the molten pool as a function of laser power and pulse duration. We will present two limiting cases corresponding to a small and broad laser beam compared with the thickness of the melted region i.e. a 'three-dimensional' and 'one-dimensional' problem, respectively. We have applied our approach to silicon and have found very good agreement between calculations and measurements, as well as with experimental results from the literature. Due to its simplicity and flexibility, the method provides a convenient tool for rapid analysis of experimental data.
- D-II.11** 17:45 LOWERING OF THE LASER CRYSTALLIZATION THRESHOLD OF a-Si:H BY THE PRESENCE OF Si CLUSTERS AT THE SURFACE
A. Hadjadj and A. Beorchia, Dynamique des Transferts aux Interfaces, DTI, Université de Reims, BP 1039, 51687 Reims Cedex 2, France, J.L. Bubendorff, LMET, Université de Reims, 51685 Reims Cedex 2, France, and L. Boufendi, GREMI Université d'Orléans, BP 6759, 45067 Orléans Cedex 2, France
In the presence of Si particles at their surface, we observed that the crystallization of hydrogenated amorphous silicon (a-Si:H) films can occur, even at laser power density well below that needed in the case of a "flat" surface. This effect is interpreted by the local electromagnetic field enhancement produced by a sphere-plan system. This system, which was proved to give rise to an enhancement factor up to 10^6 in the case of free electron metal like system, can easily provide the factor of about 20-30 necessary to achieve the crystallization of the material at the laser power density used in this experiment. The heating by the laser beam is expected to modify the dielectric function of Si and to shift the resonance of the sphere-plan system such as its matches that of the incident laser beam.
- D-II.12** 18:00 OPTICAL CHARACTERIZATION OF EXCIMER LASER PROCESSING OF ULTRA SHALLOW JUNCTIONS
G. Kerrien(a), T. Sarnet(a), D. Débarre(a), T. Noguchi(a), J. Boulmer(a), M. Hernandez(b), D. Zahorski(b), C. Laviro(c), M.N. Semeria(c), (a)Institut d'Electronique Fondamentale, CNRS UMR 8622, Université Paris-Sud, 91405 Orsay, France, (b)SOPRA, 26, rue Pierre Joigneaux, 92270 Bois Colombes, France, (c)CEA-DRT - LETI/DTS, 17, avenue des Martyrs, 38054 Grenoble Cedex 9, France
Excimer laser annealing (ELA) of ion-implanted silicon is studied experimentally as a potential solution to process ultra-shallow junctions of the future CMOS generations. Junctions with depths ranging from 20 to 80 nm are realized at 308 nm on B+ or BF₂+ implanted Si wafers, with or without Ge+ pre-amorphization. A special attention has been paid to in-situ and ex-situ optical diagnostics in order to follow the laser induced phenomena. The melting / crystallization process, which highly depends on the implanted ion and dose, and the dopant activation are real time monitored by transient reflectometry at 670 nm. The activated dopant dose evolution as a function of the laser fluence and shot number is deduced from IR spectroscopy of the processed samples. Comparison with sheet resistance measurements and SIMS depth profiles shows that optical diagnostics are very helpful tools to control the laser annealing process.
- D-II.13** 18:15 PHYSICAL CHEMISTRY OF THE FEMTOSECOND AND NANOSECOND LASER-MATERIAL-INTERACTION WITH SiC AND A SiC-TiC-TiB₂ COMPOSITE CERAMIC COMPOUND
P. Rudolph, K.-W. Brzezinka, R. Wäsche, W. Kautek, Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
The interaction of nanosecond laser pulses in the ultraviolet wavelength range and femtosecond laser pulses in the near-infrared region with the direct semiconductor SiC and the composite compound SiC-TiC-TiB₂ was investigated in respect to resulting physicochemical processes. Surface analytical techniques, such as XPS, μ -Raman, and EDX were used to identify the chemical changes between untreated and laser-treated areas. Single-pulse irradiation led to material modifications in the condensed state in most instances. Multi-pulse results differed depending on the pulse duration. In the nanosecond case, melting of the surface and redeposited material (debris) were observed. With femtosecond pulses instead, only negligible melting and few debris could be detected. Additionally, periodic structures (ripples) appeared, with parallel orientation and in most cases two different periodicities for a particular material. Laser ablation of all the studied compound materials exhibited preferential ablation of the lighter component elements. Crystal structure changes of the irradiated surface were observed as a consequence of laser-induced melting and resolidification. An oxidation process interfered with all this processes so that unstoichiometric oxides were formed.

D-II.14

18:30

LONG PULSE DURATION EXCIMER LASER ANNEALING OF Al ION IMPLANTED 4H-SiC
C. Dutto, E. Fogarassy, D. Muller, D. Mathiot, Laboratoire CNRS-PHASE (UPR 292), 23 Rue du
Loess, BP 20, 67037 Strasbourg Cedex 2, France

Silicon carbide (SiC) is a wide-gap semiconductor which presents unique material properties especially suitable for high temperature, high power and high frequency applications. However, SiC device fabrication has to face to various technological difficulties. Among them, one of the more crucial appears to be the doping step. The high melting point and limited diffusion of impurities into SiC have greatly restricted the use of ion implantation and furnace annealing commonly employed in the silicon microelectronics industry to incorporate and activate the dopants. As an alternative to classical thermal heating, laser processing was recently demonstrated to be suitable for the doping of SiC. The use of high powerful pulsed laser beams in the nanosecond duration regime allows to deposit a large amount of energy in short time into the near-surface region, while maintaining the substrate essentially at room temperature. Under suitable conditions, the irradiation leads to the surface heating to a depth not exceeding a few hundred of nanometers, at a maximum temperature above the melting point of SiC ($T \sim 3100$ K). However, when working in the liquid phase, it appears very difficult to avoid surface degradation and change in the material stoichiometry.

For these reasons, we investigated in this work the possibility to anneal the Al ion implantation induced damage into 4H-SiC by laser processing in solid phase using a long pulse duration (200 nsec) XeCl excimer source. In order to obtain a square-like Al atom distribution over approximately $0.15\mu\text{m}$, multiple-implantation technique carried out at room temperature was used up to a maximum energy of 120keV. The thermal numerical simulation and SIMS profil confirm that the laser annealing process at such an energy occurred in the solid phase regime. XPS and AFM studies revealed that this ultra-rapid thermal process allow one to keep a surface stoichiometry ($[\text{Si}]/[\text{C}]$) near unity and prevent any significant sublimation of the Si species, even at temperature above 2000K. The recovery quality of the lattice disorder was followed by using Rutherford backscattering spectrometry of 2MeV He^+ ions in channeled geometry (RBS/C). Finally, the specific advantages of using a long pulse duration excimer source in laser processing of 4H-SiC in the solid phase regime are discussed.

Thursday, June 20, 2002
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Session II: Laser and photo-induced surface processing, microfabrication and nanoengineering

Surface cleaning, microfabrication and nanoengineering

- D-II.15** 8:30 **DRY EXCIMER LASER CLEANING APPLIED TO NUCLEAR DECONTAMINATION**
Ph. Delaporte, M. Gastaud, M. Sentis, O. Uteza, Lasers, Plasmas and Photonic Processes Laboratory (LP3), FRE 2165 CNRS - Université de la Méditerranée, W. Marine, Groupe de Physique des États Condensés (GPEC), UMR 6631 CNRS - Université de la Méditerranée, P. Thouvenot, J.L. Alcaraz, J.M. Le Samedy, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Cadarache, DEN/DED/SEP, D. Blin ONECTRA, France
 Excimer laser ablation is a very powerful process for dry cleaning. Under some conditions, it is possible to remove a layer (oxide, painting, ...) deposited on a material without any modifications of the chemical and physical properties of the surface. In laboratories, the efficiency of this technique has been clearly demonstrated for a lot of kind of applications. In nuclear energy production field, there is a great interest in developing an efficient dry decontamination process. We realized a nuclear decontamination prototype based on excimer laser ablation process, and we tested it in nuclear facilities.
 A review of the laser decontamination experiments performed in the world will be done. Our laser cleaning prototype will be described. It is mainly composed of a XeCl laser, a bundle of fibers for beam transmission, optical systems, collection cell with filter for ablated particle recovery, computer control of cleaning efficiency and beam displacement.
 Different kinds of materials, representative of contamination usually founded in nuclear field, have been irradiated. Decontamination factors (initial activity/residual activity) higher than 15 for fixed contamination and up to 100 for unfixed contamination have been obtained. With these performances, the laser technique is the most efficient technique of dry and fast decontamination.
- D-II.16** 9:00 **REAL-TIME MONITORING OF LASER CLEANING BY AN AIRBORNE PARTICLE COUNTER**
W.D. Song, M.H. Hong, S.H. Lee, Y.F. Lu and T.C. Chong, Laser Microprocessing Laboratory, Data Storage Institute, DSI Building 5, Engineering Drive 1 (off Kent Ridge Crescent, NUS), Singapore 117608, Singapore
 An airborne particle counter was used to real-time monitor laser cleaning. During laser cleaning of film-type contamination or particles on substrate surfaces, particles are generated by laser irradiation of film-type contamination or ejected from substrate surfaces by laser irradiation of particles on substrate surfaces, which are detected by the particle counter. It was found that no particles are detected at below cleaning threshold and total number of particles detected increases with laser fluence above cleaning threshold. The total number of particles detected decreases with increasing pulse number and cleanliness of substrate surfaces can be observed after total number of particles detected close to zero. We also observed that total number of particles detected depends on laser wavelength. Short wavelength results in large number of particles detected at the same laser fluence. Real-time monitoring of laser cleaning, in areas such as cleaning threshold, cleanliness of substrate and cleaning efficiency is discussed in detail in this paper.
- D-II.17** 9:15 **INTERACTION OF ns-LASER PULSES WITH PAPER**
J. Kolar(a), S. Pentzien(b), M. Strlic(c), D. Müller-Hess(d), K. Troschke(d), E. Pilch(e), W. Kautek(b), (a)Preservation Department, National and University Library, Turjaska 1, 1000 Ljubljana, Slovenia, (b)Laboratory for Thin Film Technology, Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany; (c)Faculty of Chemistry and Chemical Technology, University of Ljubljana, Askerceva 5, 1000 Ljubljana, Slovenia, (d)Institut für Papierrestaurierung, Finsterer Gang 71, Schloss Schoenbrunn - Orangerie, 1030 Wien, Austria, (e)Austrian State Archives, Nottendorfer Gasse 2, 1030 Wien, Austria
 The paper reports on immediate effects of pulsed laser operating at 532 nm and fluences below 2.5 J/cm² on cellulose and paper containing carbon particles and fungal stains caused by various fungal cultures. Colour differences were determined spectrophotometrically, the degree of polymerisation viscosimetrically and chromatographically, while diffuse reflectance FTIR was used to gain insight into the changes in the chemical composition. It was demonstrated that the treatment successfully removed most of the carbon particles while only partial removal of fungal stains was accomplished. Although no detectable immediate changes were observed after treatment of paper with a laser beam at 532 nm, the irradiation of paper containing carbonaceous contaminants resulted in significant discoloration of the treated substrate. The possible reasons for the extensive formation of yellow chromophores are discussed.
- D-II.18** 9:30 **LASER TREATMENT OF FOXING AT 157nm**
E. Sarantopoulou(a), **Z. Samardzija**(b), **S. Kobe**(b), **M. Besenicar**(b), **Z. Kollia**(a), **P. Argitis**(c), **A.C. Cefalas**(a), (a)NHRF, TPCI, Athens, Greece, (b)Jozef Stefan Institute, Ljubljana, Slovenia
 Laser treatment [1] of old paper at 157nm [2] is an effective method of removing foxing and organic stains from old paper because: a) at 157nm photo-dissociation of organic matter is taking place b) absorption at this wavelength is at least one order of magnitude higher in comparison to 193 and 248nm, allowing therefore high resolution depth control, and c) the limit of the spatial resolution control over exposed areas could be extended down to 100 nm. In this communication results are evaluated by mass spectroscopy and X-ray microanalysis of laser treated and non-treated surfaces. Contrary to mass spectroscopic results, X-ray microanalysis indicates the presence of iron in foxing areas. Additionally SEM imaging of foxing areas indicate the presence of spores in the non treated areas by laser.
 [1] J. Kolar, M. Strlic, S. Pentzien, W. Kautek, Appl. Phys. A71, 87 (2000).
 [2] A. C. Cefalas, E. Sarantopoulou, Z. Kollia, Appl. Phys. A 73, 571 (2001).

Symposium D

- D-II.19** 9:45 SURFACE FUNCTIONALIZATION WITH PERIODIC MICRO-NANO STRUCTURES BY INTERFERING LASER BEAMS
F. Mücklich, Z. Liu, T. Recktenwald and C. Daniel Functional Materials, Dep. Materials Science, Saarland University, Saarbrücken, Germany
By the interference of 2, 3 or 4 coherent laser beams of sufficient power (e.g. from a pulsed Nd:YAG-laser) it is possible to transform periodic light patterns on the surface directly into various kinds of periodic microstructure modifications on the surface. Depending on the interference conditions the feature size and periodicity can be varied between 200nm and 20µm for millimeter sized arrays of lines or dots.
Different examples will be shown for the formation of periodic intermetallic surface composites such as NiAl and others. Periodic arrays of nanoclusters of Al can also be formed within a matrix of Alumina. Beside the local phase formation also the local crystallization as well as topography effects can be achieved. With topography effects in the micrometer scale the wetting behaviour can be significantly modified. The theoretical simulation and the experimental tuning of the 3D temperature distribution regarding the time domain is the precondition for such microstructure functionalization.
- D-II.20** 10:00 SELF-ORGANIZATION OF SILICON NANOCONE ARRAY INDUCED BY PULSED CO₂ LASER IRRADIATION
W.J. Wang, Y.F. Lu, C.W. An, M.H. Hong, T.C. Chong, Data Storage Institute, DSI Building 5, Engineering Drive 1, Singapore 117608, Singapore
The self-organized structures consisting of nanocones and microgratings were induced on the front silicon surface by the cumulative pulsed CO₂ laser irradiation when the silicon substrate backside surface coated with a thin material layer. The streams of nanocone were found after several laser pulse irradiation and located along the plateaus of the micrograting structures, which were caused by the LIPSS effect under single pulse irradiation at low laser intensity. The silicon surface was patterned with a nanocone array of two different average sizes at higher laser intensity. The larger cones were of 200 nm in diameter and 10 nm in height, and distributed in rows. The smaller cones with diameter and height of 70 nm and 2 nm respectively, and scattered between the two adjacent rows of the larger cones. The absorption of silicon to CO₂ laser beam is considered to be promoted by the increase of free carrier concentration and thermal energy resulting from the laser interaction with the coating materials on the substrate backside surface.
- D-II.21** 10:15 STRUCTURING OF SAPPHIRE BY LASER-ASSISTED METHODS, ION-BEAM IMPLANTATION, AND CHEMICAL WET ETCHING
A. Crunteanu, P. Hoffmann and M. Pollnau, Institute of Applied Optics, Department of Microtechnique, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland, Ch. Buchal, Institut für Schicht- und Ionentechnik (ISI), Forschungszentrum Jülich, 52425 Jülich, Germany
Sapphire is an attractive material for micro- and opto-electronic systems applications because of its excellent mechanical and chemical properties. However, because of its hardness, sapphire is difficult to machine. Titanium-doped sapphire is a well-known broadly tunable and short-pulse laser material and a promising broadband light source for applications in low-coherence interferometry. We investigated several methods to fabricate rib structures in sapphire that can induce channel waveguiding in Ti:sapphire planar waveguides. These methods include direct laser ablation, laser-micromachined polyimide stripes, selective reactive ion etching, and ion-beam implantation followed by chemical wet etching. Depending on the method, we fabricated channels with depths of up to 1.5 µm. We will discuss and compare these methods. Reactive ion etching through laser-structured polyimide contact-masks has so far provided the best results in terms of etching speed and roughness of the etched structures.
- 10:30 **BREAK**
- D-II.22** 11:00 TWO-PHOTON PHOTOPOLYMERIZATION AS A TOOL FOR MAKING MICRODEVICES
S. Kawata, Department of Applied Physics, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan
The classical diffraction limit in light technology has been broken with use of nonlinear response of optical process as well as chemical process. We have applied such effects to the fabrication of three-dimensional (3D) subwavelength structures in photopolymerizable resin[1,2]. In this talk, I will report our recent research progress, including a systematic investigation on the achievement of sub-diffraction limit spatial resolution[3], fluorescent dye-doping photopolymerization[4], micronano device functionalization and analysis of their mechanical properties[5], 3D imaging to two-photon excitation related focal spots[6], and so forth. As a comparison, I will also introduce our work in single photon photopolymerizations.
[1] S. Maruo, O. Nakamura and S. Kawata, Opt. Lett. 22, 132 (1997)
[2] S. Kawata, H.-B. Sun, T. Tanaka and K. Takada, Nature, 412, 697 (2001)
[3] T. Tanaka, H.-B. Sun, S. Kawata, 80, 312 (2002)
[4] H.-B. Sun, T. Tanaka, K. Takada and S. Kawata, Appl. Phys. Lett. 79, 1411 (2001)
[5] H.-B. Sun, K. Takada and S. Kawata, Appl. Phys. Lett. 79, 3173 (2001)
[6] H.-B. Sun, T. Tanaka and S. Kawata, Appl. Phys. Lett. to be published (2002)

Symposium D

- D-II.23** 11:30 FLEXIBLE FABRICATION OF MICROLENSSES IN POLYMER LAYERS WITH EXCIMER LASER ABLATION
K. Naessens, P. Van Daele, R. Baets, Ghent University/IMEC Dept. of Information Technology, Sint-Pietersnieuwstraat 41, 9000 Gent, Belgium
Excimer laser ablation is a flexible microfabrication technique suitable for surface structuring of polymers because of their high UV absorption and non-thermal ablation behavior. Due to the non-contact and direct-write nature of the process, laser ablation is a very attractive technology allowing realization of micro-optical functionality on top of opto-electronic components in a late phase of a heterogeneous assembly.
In this paper we propose a flexible fabrication technique for microlenses and arrays of microlenses with excimer laser ablation and report on the present status of experimental results. Based on scanning a polymer surface with an excimer beam along well-chosen multiple concentric contours, microlenses of arbitrary shape can be realized. The choice of ablation parameters and the selection of scanning paths are discussed. Optical performance and lens surface quality are evaluated by imaging experiments, scanning electron microscopy and profilometer measurements. Wavefront analysis of the ablated lenses using a Mach-Zehnder interferometer with a HeNe-laser source, shows rms aberration values lower than 0.2 for spherical microlenses.
- D-II.24** 11:45 ULTRAVIOLET LASER STRUCTURING OF POLY (ETHER ETHER KETONE)
Y. Feng, J. Gottmann, E.W. Kreuzt, Lehrstuhl für Lasertechnik, RWTH Aachen, Steinbachstr. 15, 52074 Aachen, Germany
Structuring of poly (ether ether ketone) (PEEK) by ultraviolet ArF excimer laser in different atmosphere (air, vacuum, O₂, Ar) has been investigated. The fluences used are in the range of 0.08 - 1.5 J/cm². The experimental data of PEEK structured in air can be well represented by the idealized model derived from the photochemical approach.
The phenomenon of melting observed in the cases of PEEK structured in air at higher fluences is assumed to be contributed to thermal effect caused by the interaction between the plume and the surface, since it is absent in the other atmosphere. It is suggested that the mechanism of ablation at the fluences investigated by ArF excimer laser is mainly photochemical in nature.
The roughness at the bottom of the structure varies vigorously when PEEK is structured in air while much smoother in the other atmosphere. The roughness gets to the lowest point at 0.6 J/cm². Scanning electron microscopy photographs show that at 0.6 J/cm² the debris redeposited on the bottom are at least.
Black debris on the surface around the structure is always visible regardless of the nature of the added gas, a clear pattern can be seen on the PEEK structured in air. On the contrary, its shape is irregular and sometimes erratic in Ar and O₂. In general, the debris scatters to much larger area and covers the surface as a thin film. It almost vanishes when ablation is done in vacuum.
- D-II.25** 12:00 PERIODIC MICROSTRUCTURING IN DOPED POLYCARBONATE FILM BY LASER INTERFERENCE
F. Yu and F. Mücklich, Institute of Materials Science, University of Saarland, PO Box 151150, 66041 Saarbrücken, Germany
Microstructures are widely used in microelectronics, optics and optoelectronics. The application of high power lasers enables direct microstructuring in polymers without further photolithographic processing steps. Unfortunately, the properties of normal polymers don't well satisfy the requirements due to low light absorption coefficient and high photochemical stability. These properties can be modified by means of adding a second UV-sensitive component or incorporating photoactive units in the macromolecules. In this study Polycarbonate thin films doped with UV-sensitive materials were prepared on the glass substrate with spin-coating. The ablation threshold was determined using only one pulse at each point, rather than usually with a few tens of pulses. Periodic one-dimensional linear patterns and two-dimensional dot arrays with high aspect ratio were produced with Nd:YAG high power interference laser beams. The structures obtained were characterized with atomic force microscope and white light interferometer. The structural parameters (depth/spacing) depend on the laser fluence, the angle between the beams and pulse number of the laser. On the base of these results, the structuring process was optimized, and the ablation mechanism, by which photothermal effect predominates, was discussed. This modified polymer is suitable for laser processing in production of microelectronic and optical components.
- D-II.26** 12:15 APPLICATIONS OF LASER LITHOGRAPHY ON OXIDE FILM TO TITANIUM MICRO-MACHINING
P.-F. Chauvy(a), P. Hoffmann(b), D. Landolt(a), (a)Laboratoire de Métallurgie Chimique, Département des Matériaux, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne EPFL, Switzerland, (b)Institut d'Optique Appliquée, Département de Microtechnique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne EPFL, Switzerland
Due to its good mechanical properties and chemical inertness, titanium is the material of choice for implantable devices in medicine and dentistry. For many of those applications the surface topography must be carefully controlled to achieve optimum cell adhesion and differentiation [1]. Fabrication of micro-systems relevant for bio-medical application also implies that suitable micromachining methods are developed toward 3D processing capability. Electrochemical micromachining is a useful method for the fabrication of well-defined surface structures in the micrometer range [2]. Normally, anodic dissolution is carried out through a suitably patterned photoresist, but the use of this technique is usually limited to planar surfaces. Recently, it has been shown that a laser patterned anodic oxide film could assume the function of the photoresist [3]. The key feature of this method is the combination of the flexibility of sequential laser writing with the 3D and parallel processing capacity of electrochemical anodisation and dissolution.
Surface microstructuring of a cylinder and complex multilevel microstructures will be presented to illustrate the interest of the method.
[1] B. D. Boyan, T. W. Hummert, D. D. Dean and Z. Schwartz, *Biomaterials*, 17, 137 (1996).
[2] C. Madore and D. Landolt, *J. Micromech. Microeng.*, 7, 270 (1997).
[3] P.-F. Chauvy, P Hoffmann, D. Landolt, *Electrochem. Solid-State Lett.*, 4 (5), C31 (2001).

D-II.27

12:30

EXCIMER LASER MICROVIA TECHNOLOGY IN MCMs

B. Manirambona, J. De Baets, A. Vervaeet, University of Gent, ELIS-TFCG/IMEC, 9000 Gent, Belgium

Microelectronics is moving towards smaller and lighter devices with high I/O counts. This involves the development of small via generation processes. Laser ablation technology is compatible with conventional PCBs. It allows to bring more functionality in the PCB or to utilize components like chip scale packages (CSP) in order to obtain multi chip module laminates (MCM-L)

In the current work, we use a UV laser in order to generate high density arrays of microvias (well < 100 micron in diameter). Blind vias and patterns are generated by controlled pulsed excimer laser. This kind of laser is much more powerful and efficient than the non-excimer lasers. Microvias are opened in the dielectric of the resin coated copper (RCC) down to the underlying copper. We show that the depth ablation is controlled and that the copper surface is not damaged.

This paper will briefly describe the physico-chemical properties of the excimer laser and the interactions with the material under study. We will report on our first experimental results of microvia making and pattern formation by laser scanning. Holes and pattern plating that result from both electroless and electrodeposition of copper will be discussed. Special attention will be paid to the shape aspect and the shape ratio of the formed vias by means of profile measurements, optical inspection and SEM investigation.

Thursday, June 20, 2002
Jeudi 20 juin 2002Afternoon
Après-Midi

13:00

POSTER SESSION II

Pulsed laser deposition of nanostructured materials and thin films

- D/PIL.01** **FRactal Description of Clusters Formed in the Thin Films Growth Simulations**
K. Zembrowska, L. Pyziak, M. Kuzma, I. Stefaniuk, Institute of Physics, University of Rzeszow, Rejtana 16A, 35-959 Rzeszow, Poland
The first Si monolayer growing on Si (001) substrate by pulsed laser deposition method (PLD) was simulated using Monte Carlo procedure. A various growing conditions like, temperature of substrate, energy of adatoms, etc. were introduced into simulation. The shape of clusters formed depends on these conditions clearly. The best method for description of cluster shape is their fractal characterization. Box fractal dimension of these planar objects was studied. This parameter selects very well the shape of such clusters, which are most favorable for the epitaxial layer-growing mode. The relation between the fractal dimension of clusters and PLD parameters was established.
- D/PIL.02** **Visualization Modeling of Laser Assisted Thin Film Growth**
A. Peled, N. Mirchin, M.Sidi, Y. Muchnick, Electrical and Electronics Department, Holon Academic Institute of Technology, 52 Golomb St., Holon 58102, Israel
For analyzing laser assisted processes we have developed a computerized visualization technique which relies on sampled or computer generated micrographs of particles for simulating deposition, aggregation and coagulation of particles during thin film growth, using 2D Fourier transforms techniques. We use a many body particle diffusion simulator on surfaces to predict particle structure evolution in time 'snapshots' and time movies. The simulation program in this work is used to investigate deposition and diffusive fronts in a-Se photodeposition experiments, starting from initial SEM micrographs. Our surface microstructure time 'tracking' scheme relies on transforming the original image of the deposited particles into a synthetic image in the Fourier spatial frequency domain. Then we perform the modeling of the physical material deposition and subsequent surface redistribution such as diffusion and other flow driving mechanisms. The 2D-Inverse Fourier Transform (IFT) is then used to obtain the real - space, time dependent 'snapshots'. In particular, using a-Se initial photodeposited particle configurations we realized by simulation that the trend for finger type growth is due to surface diffusion rather than growth by coarsening of individual particles.
- D/PIL.03** **Laser Production of Metal Clusters in a Supersonic Beam and Studies of Their Reactivity Towards Biological and Inorganic Systems**
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The study of neutral and ionized clusters has developed rapidly due to the unique capability of this state of matter to bridge the gap between isolated gas and condensed phase. Recently a considerable interest has been developed in production of metal atoms pure and complexed with different systems in order to study the formation of nanostructures. For this purpose we have developed in our laboratory an experimental apparatus, consisting of two vacuum chambers separated by a 1 mm diameter conical skimmer. In a small ablation chamber a reacting gas is introduced through a pulsed nozzle of 0.4 mm diameter. In the same ablation chamber a metal rotating target is vaporized by 248 nm, 0.5 J/pulse KrF excimer laser. The formed plasma is entrained in the reacting gas and expanded into vacuum forming a supersonic jet. After being skimmed the beam enters in a second differentially pumped chamber, equipped with a time of flight mass spectrometer. The clusters in the beam are collected on a suitable substrate or ionized by a tunable dye laser (5 ns time duration), detected by a channeltron, digitalized and stored on a PC. The experiments have been performed on clusters of transition metals with ammonia or molecules of biological interest. In the first case, production of nitriles, suitable for electronic applications, is observed and cluster ionization potential is measured. In the second case information on the affinity of biomolecules towards transition metals in gaseous phase.
- D/PIL.04** **Nanoparticles and Nanoballoons of Amorphous Boron Coated with Crystalline Boron Nitride**
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Solid- and hollow-cored nanoparticles of amorphous boron coated with crystalline boron nitride (BN) have been synthesized by pulsed-laser-vaporization of BN, where the laser plume was controlled with modulated plasma jet. The hollow particles (nanoballoons) were coated with BN both on the interior and exterior surfaces. Solid particles ranged from a few to 40 nm in their size. Typical diameter of the hollow particles and their wall thickness were about 200 and 30 nm, respectively. The nanoballoons were obtained only when the plasma-modulation was synchronized with the ArF excimer-laser pulses.
- D/PIL.05** **Highly Crystalline sp³-Bonded BN Prepared by a Novel Plasma-Assisted Laser Ablation Method**
S. Komatsu, K. Kurashima, Y. Moriyoshi, K. Okada, and M. Mitomo, National Institute for Materials Science, Advanced Materials Laboratory, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
It is known that sp³-bonded boron nitride has a polytypic form such as 5H-BN in addition to the popular cubic and wurtzite forms. The sp³-bonded 5H-BN was grown by laser-assisted plasma CVD (chemical vapor deposition). Here we found that plasma-assisted laser ablation of BN could produce highly crystalline sp³-bonded BN as well as its nanocrystallites depending the growth conditions.
Laser plumes generated by the ablation of BN with pulsed excimer laser at 193 nm were hit by synchronized plasma packets with the propagation speed of 20-100 m/sec. Gray powder product was trapped with a mesh collector and examined with a high-resolution transmission electron microscope and electron energy loss spectroscopy.
- D/PIL.06** **Scanning Nuclear Microprobe Analysis of Pulsed Laser Deposited Thin Films and Particulates: Experiments and Numerical Modelling**
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The thickness and chemical composition of pulsed laser deposited thin Bi and SiGe alloy films have been measured by Rutherford backscattering spectrometry with lateral resolution of few microns. The experimental results are completed with computer simulation of RBS spectra, elemental maps and tomographic images, which help in the identification of the different kinds of particulates and provide real 3D information. The impact of surface roughness on RBS characterisation of thin films is also discussed.

- D/PIL.07** STRUCTURE AND COMPOSITION OF CARBON NITRIDE FILMS GROWN BY SUB-ps PLD
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 CN_x (0.01 < x < 0.20) films have been deposited by ablating a graphite target in N₂ atmosphere with a hybrid dye/excimer laser system delivering pulses of 500 fs duration at 248 nm. Changes in surface composition and morphology of the as grown films, as a function of N₂ pressure (between 0.3 and 60 Pa), laser pulse energy (max. 10 mJ), and spot area are reported, by means of XPS and SEM analysis, respectively. In the pressure domain investigated, the nitrogen content increases as a power function. More interestingly, while both pulse energy and spot area influence the chemical composition of the films, the same fluence achieved by using different spot sizes results in films of different N content. Deposition of micrometer sized particulates was apparently suppressed, while sub-micron features of typically circular shape were present over the smooth film surface.
- D/PIL.08** PULSED LASER ABLATION DEPOSITION OF NANOPARTICULATE Fe FILMS: MORPHOLOGY AND MAGNETIC PROPERTIES
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 In this work we report on the preparation, morphology and hysteretic properties of nanoparticulate Fe films deposited using the pulsed laser ablation technique. Our ultra high vacuum (UHV) deposition system has a base pressure of 10⁻⁹ mbar, rotatable target holder and, in order to improve the particle size homogeneity, a refrigerated substrate holder with x, y, z and f movements. We used a Nd-YAG laser having an energy per pulse of 180 mJ, a pulse width of 4 ns and, by adequately focusing the beam, we achieved an instantaneous power density of 10¹¹ W/cm². The deposition time varied from 300 to 2700 s and the pressure range from UHV to 2.6 x 10⁻¹ mbar of Ar. The deposition of nanoparticulate films formed by homogeneously sized particles having diameters in the range of the 10-20 nm will allow i) the analysis of the influence of the exchange and dipolar couplings on the hysteretic and relaxational properties of systems having controlled crystallochemical and morphological properties and ii) the evaluation of the use of that type of films as recording media.
- D/PIL.09** STUDY OF PLASMA EXPANSION BY FEMTOSECOND PULSED LASER ABLATION AND DEPOSITION OF DIAMOND-LIKE CARBON FILMS
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 Pulsed laser deposition is a well-known technique used for thin film deposition such as oxides or hard and wear resistant Diamond-Like Carbon (DLC) coatings. Usually the film deposition has been principally performed with laser pulse duration in the nanosecond range. The present study has been realized by ablating graphite targets with femtosecond laser pulses (10⁻¹⁵ s range).
 DLC films have been deposited in high vacuum conditions at room temperature. The 800nm, 150fs laser pulses have been generated by a mode-locked Ti:Sapphire laser, including an amplification stage. The pulse energy was 1.5mJ at a repetition rate of 1kHz and the fluence range was between 1 and 6J/cm². The films deposited onto (100) p-type silicon substrates have been characterized by various techniques. Plasma plume has been imaged by a gated I-CCD camera in the UV-visible range. The behaviour of the plume shape as well as the kinetic energy of the particles have been investigated.
 Compared to conventional nanosecond laser ablation, femtosecond laser allows the production of high energy (up to a few keV) particles in the plasma which may strongly affect the structure and properties of the deposited films. The behaviour of the expansion dynamics and the properties of thin films will be correlated in order to determine the optimal growth conditions for femtosecond pulsed laser deposition of DLC films.
 This work was supported by the Région Rhône-Alpes (Thématiques Prioritaires), the Conseil Régional de la Loire and the European Community (Fonds FEDER).
- D/PIL.10** PULSED LASER DEPOSITION OF DLC AND ta-C FILMS: REDUCING INTERNAL STRESS BY THERMAL ANNEALING
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 In order to obtain DLC and ta-C films of relevant thickness (exceeding 1 micrometer), it is necessary to solve the critical problem related to the internal compressive stress (some GPa) leading to delamination at a threshold thickness value of the films. The Griffith's theory explains the delamination process by looking at the excess of elastic energy inside the film which overcomes the cohesive energy between film and substrate. To increase the above mentioned threshold thickness value there are two possibilities: 1) the improvement of the interface adhesion (for example through surface micro-roughening and/or surface activation), and 2) the reduction of the internal stress. In this work we were able to produce stable DLC and ta-C films, over silicon substrate, having thickness exceeding 1 micrometer, by thermal annealing after the pulsed laser deposition steps. We performed thin film curvature measurement to evaluate the stored elastic energy in the films and proved the agreement between the fracture mechanical theory and experimental results. We also carried out some studies on the influence of time and temperature parameters on thermal annealing effects.
- D/PIL.11** MORPHOLOGICAL STUDY OF PLD GROWN CARBON FILMS
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 Carbon nitride films have been deposited by ArF excimer laser ablation of a graphite target in argon ambient of pressures between 10⁻⁴ and 200 Pa. Besides carbon, ex-situ RBS and ERDA measurements revealed the presence of hydrogen and oxygen in the films. Apparent growth rates at 8 J cm⁻², defined as the measured thickness per number of pulses, indicate three growth regimes. Below 1 Pa the growth rate is almost constant at around 0.30 Å/pulse; between 1 Pa and 100 Pa the rate of thickness increase drops to 0.18 Å/pulse and finally, above 100 Pa the growth rate further decreases below 0.07 Å/pulse. Parallel AFM and SEM measurements revealed characteristic differences in the surface morphology in each domain. Comparative analysis of mass densities, apparent growth rates and microstructure provides information on the growth mechanism in the pressure domain investigated.

Symposium D

- D/PII.12** BORON NITRIDE THIN FILMS DEPOSITED BY RF PLASMA REACTIVE PULSED LASER ABLATION
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Boron nitride is one of the most interesting III-V compounds for its physical properties such as hardness, high melting point, large band gap and low dielectric constant.
The boron nitride forms several different phases that are analogous to those of carbon. BN is thermally stable and its coatings are often utilized for increasing materials hardness as protective coating against corrosive agents. It is also a good insulator for diodes application.
Thin films of boron nitride have been deposited by reactive pulsed laser ablation of boron target in presence of a radio frequency (RF) nitrogen plasma. The gaseous species have been deposited at several temperatures, using the on-axis configuration, on Si (100) substrates.
Thin films have been characterized by Scanning Electron Microscopy and X-Ray Diffraction. A comparison between the thin films deposited by conventional ns laser ablation and reactive RF plasma assisted is also reported. Besides, Optical Emission Spectroscopy of the two experimental procedures, has been performed in order to highlight the role played by the ionized and neutral species speed distributions during both deposition methods.
- D/PII.13** LASER DEPOSITED ALUMINUM-NITRIDE FOR ELECTRON FIELD EMISSION DEVICES
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Diamond, Cubic Boron Nitride (C-BN) and Aluminum-Nitride (AlN) are some of the commonly used wide band semiconductors for cold cathode applications. Due to their fabrication at temperature over 700 °C, these materials often encounter undesirable grain growth, poor uniformity, step coverage and poor emission properties.
In this paper we present a low temperature fabrication method based on the pulsed laser deposition technique. In this method, using pulsed ArF laser ablation technique, Si and Si micro-tips were coated with AlN in a N₂ ambient in the 30-700°C temperature range. The AlN film properties were studied using RHEED, IR, X-ray diffraction, AFM and SEM measuring instrument. Field emission properties such as aging effects and emission current noise of the film were investigated. It was found that the AlN coated Si tips have lower threshold emission voltage, higher current and better stability than bare Si tips.
The result indicated that the method using AlN for cold cathode applications is less dependent on emission characteristics, deposition temperature and surface preparation. It is functional at low threshold of emission voltage, provides high current density, better stability and uniformity.
- D/PII.14** PULSED LASER DEPOSITION OF THIN REFRACTORY METAL NITRIDE FILMS
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Thin films of transition metal (Ti, V, Mo, Ta, W) nitrides films exhibit extreme hardness, high melting point, good chemical inertness and thermodynamic stability. Depending on the nitrogen content their electrical resistivity can be tuned over a wide range. Therefore they are used as diffusion barriers and electrodes in semiconductor devices, stable ohmic contact and as hard wear-resisting materials in coatings. Reactive laser ablation deposition (RPLD) is emerging as a convenient technique for the deposition of nitride films by simply ablating metal targets in low-pressure nitrogen atmosphere. We already reported on the successful laser deposition of Ti and V nitride films. Here we report on RPLD of Mo, Ta and W nitride films. Mo, Ta and W discs were ablated in low-pressure (1, 10 and 100 Pa) nitrogen atmosphere by KrF excimer laser pulses at fluences of 7-8 J/cm² and repetition rate of 20 Hz. Films were deposited on silicon wafers, placed at 40 mm from the target. Substrates were either at room temperature or heated to 250 and 500 °C. RBS spectrometry was used to calculate thickness of the films (30-550 nm, depending on nitrogen pressure, target composition and substrate temperature) and their mean composition. All the films were shown to be polycrystalline by XRD investigations. Composition, structure, surface morphology, microhardness and electrical resistivity of the films will be discussed as a function of both the nitrogen pressure and substrate temperature.
- D/PII.15** MULTILAYERED METAL OXIDE THIN FILM GAS SENSORS OBTAINED BY CONVENTIONAL AND RF PLASMA-ASSISTED LASER ABLATION
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Thin films of indium oxide, tin oxide and copper oxide have been deposited as multilayered systems by conventional and reactive pulsed laser ablation (2nd harmonic Nd-YAG laser) of metallic targets. The interest towards these materials is due to their extremely versatile sensitivity to a wide range of toxic gas agents (SO₂, CO, NO_x).
The employment of reactive pulsed laser ablation and deposition (RPLAD) has been chosen because of its several advantages, such as deposition in high partial pressure, crystallization of films at low temperature and high deposition rate. The comparison between the RPLAD process with the conventional ns laser ablation highlights that the main return is related to the ablated particles high energy.
The gaseous species have been deposited on Si (100) substrates positioned in front of the target by a holder heatable up to 1000 K.
Thin films have been successively characterized by Scanning Electron Microscopy, X-Ray Diffraction, and Electrical Resistivity measurements.
The comparison between the morphological and structural characteristics of thin films deposited by both methods is reported.

- D/PIL.16** STRUCTURE AND DIELECTRIC PROPERTIES OF ULTRA-THIN ZrO₂ FILMS PREPARED BY PULSED LASER DEPOSITION
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ZrO₂ thin films have been prepared on Pt coated silicon substrates and directly on Si substrates by pulsed laser deposition technique using a ZrO₂ ceramic target under different deposition conditions. X-Ray diffraction and atomic force microscopy investigation showed that the films prepared at a substrate temperature of 300 °C in 20Pa oxygen and nitrogen ambient are amorphous. There existed an amorphous interfacial layer between ZrO₂ thin film and Silicon substrate, which was confirmed to be zirconium-silicate by x-ray photoelectron spectroscopy. High Resolution Transition Electron Microscope (HRTEM) investigations also revealed this amorphous interface. The physical thickness of the deposited films ranged about from 4.5nm to 13.3nm evaluated from the growth rate which was determined by optical step technique. The equivalent oxide thickness (EOT) of the films was about 1-3nm, as extracted from the capacitance-voltage (C-V) curves. The EOT and leakage current of the films post-annealed in Nitrogen and Oxygen ambient were different. The EOT increased after annealing in the N₂ gas ambient due to the densification, while it decreased in O₂ gas ambient because of the growth of the interface layer. The leakage current characteristics of as-deposited ZrO₂ films and post-annealed ZrO₂ films have been investigated comparatively. The films post-annealed in O₂ ambient have lower leakage currents with an acceptable value about 16.9mA/cm². Optical transmittance measures would be used to determine the band-gap of the ZrO₂ thin films, and the dielectric constant of ZrO₂ thin films deposited under different conditions would be determined in the Pt/ZrO₂/Pt structures. The results show that the ultra-thin ZrO₂ films prepared by pulsed laser deposition have acceptable structure and dielectric properties required by a candidate of high-K gate dielectrics.
- D/PIL.17** ROLE OF THE SUBSTRATE ON ZnSe FILMS GROWN BY PULSED LASER ABLATION
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ZnSe layers have been grown by pulsed laser ablation technique on different substrates, as GaAs, sapphire and amorphous quartz. The substrate temperature has been optimized at 400 °C. The films have been studied by means of X-ray diffraction, reflectance, absorption and photoluminescence spectroscopy from 10 K to 300 K. The X-ray diffraction spectra have shown that all the layers have a single-crystal structure and their orientation and crystalline quality depend strongly on the substrate type. Reflectance and absorption spectra as a function of the temperature have been analysed by means of classical models in order to obtain the temperature dependence of the band gap energy and to study the role of acoustic and optical phonons in the thermal band gap shrinkage. Experimental results have shown that the contribution of acoustic phonons is larger in ZnSe layers deposited on quartz substrate. A link between the acoustic phonons contribution and structural disorder has been discussed. All the ZnSe layers have shown luminescence emission at room temperature. This fact is particularly interesting for ZnSe films deposited on quartz substrate, in view of applications as ZnSe based devices fabrication on optical windows and inexpensive substrates.
- D/PIL.18** PULSED LASER DEPOSITION OF MN-DOPED ZnO THIN FILMS
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Pulsed laser deposition has been used to prepare thin films of Mn-doped ZnO. An 248 nm excimer laser at a fluence of 1.5 J/cm² was used to irradiate a ZnO target doped with Mn. The Mn fraction was varied up to 0.3. The films were deposited on (0001) sapphire at 500 °C in a 0.4 mbar atmosphere of oxygen. Optical spectroscopy and a Langmuir probe were used to diagnose the plasma conditions and to investigate the interaction of the laser ablation plume with the background gas during the growth. In situ optical reflectometry was used to monitor the growth of the film. The effects of Mn doping were investigated using X-ray diffraction and photoluminescence spectroscopy. SQUID magnetometry was used to characterise the magnetic properties
- D/PIL.19** STRUCTURAL AND OPTICAL PROPERTIES OF Er DOPED ZnO THIN FILMS GROWN BY PULSED LASER DEPOSITION
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The optical properties of ZnO (high refractive index and transparency over a large wavelength range) and emitting properties of Er in the 1.5 µm region make Er-doped ZnO thin films promising materials for planar optical amplifying devices. Pulsed laser deposition (PLD) is an interesting technique to grow complex oxides and it allows the incorporation of high Er concentrations, up to 2%at. The aim of this work is to demonstrate the feasibility of ZnO waveguides by PLD, and to study the relationship between their structural and optical properties.
Er-doped ZnO thin films have been grown by PLD on SiO₂ substrates under various conditions (substrate temperature and O₂ pressure), and showed the classical hexagonal phase. However, the crystalline quality and the surface morphology of the films strongly depend on the conditions as well as on the Er concentration. The optimised growth conditions (700 °C and a pressure of 10⁻⁶ mbar), give highly (001) textured films with a smooth surface. The waveguiding properties of these films were studied using m-lines spectroscopy (at a visible and an IR wavelengths). The results showed a good light confinement and the measured refractive indices were found to be similar to the bulk values. Er-photoluminescence in the visible and Infra-Red ranges and excited level lifetime measurements were also investigated and compared to the bulk ones. The correlation between these optical properties and the structural features will be discussed.

- D/PII.20** Pt/Ni AND Pd/Ni THIN FILMS BASED GAS SENSORS
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A Surface Acoustic Wave (SAW) device containing a delay line consisting of two SAW transducers deposited on a silicon substrate with a piezoelectric overlayer and a top continuous floating electrode was realized. ZnO piezoelectric layers having a thickness of 2.5 μm (for a desired wavelength, $\lambda = 50 \text{ mm}$) have been deposited on Cr-Au interdigital transducers (ID) (1000 \AA thickness) grown by thermal evaporation on (100) silicon substrate. An Al floating (top) electrode was deposited onto the ZnO layer in the zones overlapping the ID regions. The free silicon area in-between the two ID transducers was covered with different sets of membranes of Pt/Ni and Pd/Ni. ZnO films were grown by laser ablation of Zn target in oxygen and metallic membranes by alternative laser ablation of single targets. X-ray diffraction spectra are presented. Scanning electron microscopy shows smooth surface for films prepared using UV laser wavelengths ($\lambda = 265$ and 355 nm , respectively) for laser ablation. Very small traces of nickel oxide have been evidenced by XPS studies on films deposited for pressures superior to 10-4 mbar. Electric responses of the test structures have been tested by network analyzer HP 8753A in amplitude format S11 and S12. The quality of the ZnO film has been controlled by piezoelectric probe.
- D/PII.21** DEFECTS OF CRYSTAL STRUCTURE $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ THIN LAYERS GROWING BY PLD
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 $\text{Hg}_{1-x}\text{Cd}_x$ layers have been obtained by pulsed laser deposition method (PLD) using two types of lasers: YAG: Nd³⁺ ($\tau = 250 \text{ ns} - 40 \text{ ns}$) and excimer one ($\tau = 25 \text{ ns}$). The crystal structures of layers were investigated by the electron-diffraction method. The dependence of the laser beam parameters on the layer structure was determined. Layers obtained were of various crystallography qualities (polycrystalline, monocrystalline). The layers with texture were more representatives. Their diffraction patterns exhibit a rich symmetry witch point on a variety orientation of nucleus of crystallization. The proposed model of twins growing during deposition is under construction. The influence of layer growing conditions on the size of the macroscopic defects was discussed too.
- D/PII.22** ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION OF THIN BARIUM STRONTIUM TITANATE FILMS DIRECTLY ON SI: CHARACTERIZATION OF THE INTERFACIAL LAYER
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Thin barium strontium titanate (BST) films, regardless of the deposition technique, have always exhibited much lower dielectric constant values than those measured for the bulk. The presence of fine grains, mechanical stresses, oxygen vacancies, and the formation of interfacial layers or rough interfaces have been identified or suggested as causes for this situation. The formation of an interfacial layer is of particular concern for the growth of BST films directly on Si substrates because of the high temperatures and oxygen pressures required during deposition. An ultraviolet-assisted pulsed laser deposition (UVPLD) technique was employed to growth high quality-high dielectric constant films on Si at much lower temperatures and oxygen pressures than those usually employed during conventional PLD. To account for the observed improvement of the structural and optical properties of the grown BST films, a detailed investigation using x-ray reflectivity and diffraction, x-ray photoelectron spectroscopy, high-resolution transmission electron microscopy and Rutherford backscattering spectrometry, variable angle spectroscopic ellipsometry, and capacitance-voltage and current-voltage measurements were performed and the results are presented here. One of the most surprising results is that some of the formed SiO_2 is not located at the interface but homogeneously mixed with the first monolayers of the grown BST films.
- D/PII.23** MODIFICATION OF PULSED-LASER-DEPOSITED $\text{SrFe}_{12}\text{O}_{19}$ THIN FILMS BY IR LASER IRRADIATION IN MAGNETIC FIELD
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Strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) belongs to the magnetoplumbite hexagonal oxides of M-type. The strong anisotropy and high coercivity of thin M-type hexaferrite films, along with their chemical and mechanical stability makes them very important class of materials for microwave and high-density magnetic and magneto-optical applications.
Thin $\text{SrFe}_{12}\text{O}_{19}$ films were deposited on sapphire (0001) substrates by XeCl excimer laser at repetition rate of 2 Hz and fluence of 2.5 J/cm^2 . The deposition was carried out in oxygen pressure of 13 Pa and substrate temperature of 800°C. The as-deposited films were irradiated afterwards by free-running Nd:YAG laser at energy density of 110 mJ/cm^2 whose onset was synchronized with that of a magnetic-field pulse having induction of 0.5 T. The temperature reached at the samples surface is lower than the melting point of the film.
The present work is a continuation of our earlier experiments on the effect of simultaneous application of pulsed laser and high-intensity pulsed magnetic field on the properties of magnetic materials. The laser deposited samples were placed in the direction of the magnetic field applied and were irradiated at lower energies (<650 mJ), compared to the previous experiments.
The structural and magnetic properties of the films were investigated using XRD (X-ray diffraction), AFM (atomic force microscope) and VSM (vibrating sample magnetometer).
- D/PII.24** NEAR-FIELD MICROSCOPY INVESTIGATION OF LASER-DEPOSITED COATED CONDUCTORS
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Thanks to its efficiency and flexibility, pulsed laser deposition is an appealing route to the production of coated conductors, at least for samples of a short length. We have applied this technique to fabricate YBCO/YSZ onto biaxially-textured Ni-based substrates. X-ray film diagnostics suggests the achievement of the correct structure in both YSZ and YBCO layers, but electrical measurements demonstrate poor transport properties.
Such a discrepancy in diagnostics results gave us motivations for a detailed near-field scanning optical microscopy (NSOM) analysis of the samples. Since YBCO reflectivity is known to depend on the oxygen content, the ability of NSOM to map the surface-scattered intensity with a sub-wavelength space resolution offers a highly valuable tool for detailed investigations within grain regions or at grain interfaces.
Results demonstrate that, depending on process parameters, oxygen content can be inhomogeneous within a single grain, with a decreasing trend from the center to the border peculiar of growth onto Ni-based substrate. Due to the sensitivity of electrical properties on YBCO oxygen stoichiometry, the finding may explain on a microscopic basis the observed electrical behavior, and set the basis for a novel diagnostics method.
Work supported by CNR through Progetto Applicativo "Applicazioni della superconduttività ad alta Tc".

- D/PIL.25** PROPERTIES OF FERROELECTRIC THIN FILMS BASED ON Nb-MODIFIED PZT PRODUCED BY PULSE LASER ABLATION TECHNIQUE
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 Using the general formula $Pb_{1-x/2}(Zr_{0.65}Ti_{0.35})_1-xNb_xO_3 + 10\%$ mole PbO excess ($x=0.01$ and $x=0.04$) (PZTN) ferroelectric thin films were deposited by ablation technique on Pt (111) coated Si (100) and MgO (100) substrates using either a Nd:YAG(356 and 564nm) either a XeCl excimer (308nm) laser.
 X-ray diffraction and Raman spectroscopy were used to determine the crystallographic structure. According to the substrate, the films exhibit perovskite structure with preferential alignment along (111) or (100) planes, with only small amounts of non-perovskite pyrochlore phase.
 The index of refraction (n) and absorption coefficient (alpha) from PZTN films produced on MgO substrates and the modeling of the optical spectra in the range of 250 to 2500 nm are reported. Also, the effective dielectric function is calculated versus frequency. Then, the band gap energy of the different PZTN films was estimated under the assumption of direct band-to-band transition.
 On the other hand, ferroelectric and dielectric characterization of the as-produced thin films was performed.
 Key words: PZTN thin film, laser ablation, optical properties, effective dielectric function.
- D/PIL.26** SYNTHESIS OF BULK In_2O_3 - Sc_2O_3 AND THEIR TRANSPARENT CONDUCTING OXIDE FILMS
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 Bulk In_2O_3 - Sc_2O_3 alloys were synthesized in a cubic phase (space group Ia3) with Sc_2O_3 content varying between 0 to 30 weight percent. The lattice parameters of these alloys showed a linear dependence on the composition. Films were deposited on glass substrates at a temperature of 250 oC in an oxygen pressure of 10 mTorr using a pulsed laser deposition technique. Films with Sc_2O_3 composition varying between 0 to 10 weight percent show resistivities varying between 1.85×10^{-3} ohm-cm and 2.18×10^{-1} ohm-cm, while their optical transparencies were more than 80 % for wavelengths between 400 and 900 nm.
- D/PIL.27** PULSED LASER DEPOSITION OF A NI-YSZ CERMET USED AS THE ANODE MATERIAL IN SOLID-OXIDE FUEL CELLS (SOFC)
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 In this poster we present the results of the micro-structural, morphological, and electrical characterizations of Ni-YSZ cermet thin-films produced by Pulsed Laser Deposition (PLD) from a composite NiO-YSZ target on cold alumina substrates in a residual oxygen atmosphere. XRD was used to assess the phase-ratio transfer between the targets and the crystallized films by the Averbach-Cohen method and a two-points resistivity measurement was carried out under $H_2:N_2$ as a function of Ni content and temperature. SEM was used to evaluate the morphological changes imparted to the films by an annealing in a non-equilibrium partially reducing $CH_4:O_2$ mixture. We found that the films are composite in nature and that when NiO is mixed with YSZ to form a cermet, it takes the rhombohedral structure rather than the usual cubic, both in the films and in the target. We also found that the former were poor in nickel-containing phase with respect to the latter and that this deficiency increases with increasing Ni content in the targets. The electrical measurements showed that NiO is reduced in Ni by $H_2:N_2$ to form the cermet. It is pointed out that the percolation model, suggesting again the composite nature of the films, can explain the behaviour of conductivity as a function of Ni content. Finally it is showed that a significant amount of surface roughness and specific area can be achieved by annealing as-deposited films in a $CH_4:O_2$ atmosphere, making them suitable for use as anodes in SOFCs.
- D/PIL.28** CARBON/LiBO-GLASS/CoLiBO MULTILAYER FORMATION BY LASER ABLATION
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 The multilayer of carbon, LiBO-glass and CoLiBO with very different melting temperatures and optical properties were prepared by laser ablation. The films were deposited on silicon and silicon oxide substrates, in one vacuum cycle with a laser wavelength of 1064nm. At this wavelength the transmission of the pure LiBO-glass is nearly 100%, while the carbon and the CoLiBO is quite absorptious. Therefore we used a special sintered powder target. 1Hz repetition rate with 2J-pulse laser energy was used. The experiment was carried out at room temperature without any ambient gases. The properties of the laser-ablated films were investigated by several methods, such as TEM, SIMS, EELS, XPS, AFM and RBS. Also the resistivity of the films were measured separately.
 The result shows good quality homogenous films. We succeeded to form amorphous graphite-like carbon layer. The surface is quite homogenous with no clusters larger than 10nm. The adhesion between the substrate and the layer was very good. The Li/B/O ratio is the same in the LiBO target and in the deposited layer. The resistivity of the carbon layer was $10m\&\#8486;cm$, the LiBO-glass layer was $100M\&\#8486;cm$ and the CoLiBO layer was $100m\&\#8486;cm$. In the carbon film spontaneous charge accumulation was observed which might be correlated to a Li transport through the multilayer.
- D/PIL.29** EXCIMER PULSED LASER ABLATION DEPOSITION OF YSZ AND TiN/YSZ THIN FILMS ON Si SUBSTRATES
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 Ytria-stabilized zirconia (YSZ, Y_2O_3 - ZrO_2) is a very interesting material because of its relevant characteristics (high chemical stability, electrical resistivity, high dielectric constant, magnetic permittivity, etc.). It is used as buffer layer for epitaxial growth of superconductor or ferroelectric crystalline films, as insulating layer in semiconductor devices, etc. High substrate temperatures (600-800 oC) are usually necessary to grow good-quality films. In this work, we report on the deposition of thin YSZ films and TiN/YSZ bilayers on Si substrates at room temperature by pulsed laser ablation (PLD) using a KrF excimer laser. PLD emerged in the last years as a very useful technique to deposit thin films of materials with complex stoichiometry on substrates at room temperature. YSZ targets were ablated at the KrF laser fluence of 4 J/cm² in vacuum (~10-5 Pa) and in low-pressure (1, 10 Pa) oxygen atmosphere. TiN/YSZ/Si bilayers were deposited in two steps without exposure to the air: first, YSZ films were deposited onto Si (100) substrates by ablating a YSZ target in oxygen atmosphere (1 Pa), then a Ti target was ablated in nitrogen ambient gas (1 Pa). YSZ and Ti targets were ablated at a laser fluence of 4 and 6 J/cm², respectively. Morphological and structural characteristics were investigated by RBS, SEM and XRD techniques. Optical and electric properties were investigated by Fourier transmission in infrared (FTIR) and C-V techniques, respectively.

- D/PIL.30** STOICHIOMETRIC ANALYSES OF Cd_{1-x}MnxTe FILM DEPOSITION BY PULSED LASER ABLATION
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The present work is a study of the processes that control the stoichiometry of semimagnetic semiconductor films deposited by pulsed laser deposition. In particular the possible causes of the incongruent transfer in deposition of Cd_{1-x}MnxTe films on heated substrates, during the ablation in vacuum by a XeCl pulsed excimer laser, are investigated. Different experiments were carried out in order to identify the contributions of target, substrate or plume effects on the matter transfer in the film deposition. During the laser ablation ($F = 6 \text{ J/cm}^2$) of a Cd_{1-x}MnxTe target ($x = 0.50$) films were deposited onto unheated substrates at different collecting angles with respect to the plume expansion direction and their composition was analysed by energy dispersion X-ray spectroscopy and Rutherford backscattering spectrometry. In addition, the angular distribution of the emitting chemical species in the plume was investigated by a combination of wavelength, temporal and spatial resolved optical emission spectroscopic measurements. The results are used as the basis for a discussion devoted to comprehend the causes of the possible changes in stoichiometry during Cd_{1-x}MnxTe film depositions by considering the possible processes occurring at the target, at the substrate or in the plume during the transit from the target to the collector.
- D/PIL.31** PULSED LASER DEPOSITION OF SUPERCONDUCTING RBCO THIN FILMS
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Superconducting thin films of ReBaCuO (Re= Sm, Eu, Gd) have been deposited by Pulsed Laser Ablation and Deposition on SrTiO₃ substrates at different substrate temperature and reduced oxygen partial pressure. The resistivity vs. temperature measurements show the onset and the offset of the superconducting transition between 95K and 70K. For all the investigated Rare Earths we find a substrate temperature value for which the grown film has the offset of the superconducting transition above 90K. Morphological and structural analyses, performed by Scanning Electron Microscopy and X-Ray Diffraction, are also reported and discussed.
- D/PIL.32** CHALCOGENIDE GLASS THIN FILM WAVEGUIDES DEPOSITED BY EXCIMER LASER ABLATION
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We report on the growth and characterization of thin film optical waveguides of chalcogenide glasses on lithium niobate (LiNbO₃) and glass substrates at room temperature by pulsed laser deposition (PLD). Thin film waveguides made of chalcogenide glasses are highly desirable for novel infrared integrated optical devices. The low characteristics vibrational frequencies of chalcogenide bonds allow light propagation far out into infrared (0.5-10 μm). Furthermore, their low phonon energy implies low non-radiative relaxation rates, which makes them ideal candidate for laser host media. It has been demonstrated that it is possible to deposit planar waveguides of materials with complex composition by using the PLD technique. In the present work Pr³⁺-doped and un-doped chalcogenide glass targets (GeS₂-GaS₂-CsI) were ablated in vacuum ($\sim 10^{-5}$ Pa) by KrF excimer laser at the fluence of 2 J/cm^2 . The ablated material was deposited on LiNbO₃ and glass slide substrates. Morphological and structural characteristics of the films were obtained by RBS, SEM and XRD. Transmittance and reflectance measurements of the films deposited on glass substrates in the range 400-2500 nm, allowed us to calculate the complex optical refractive indexes as a function of wavelength. The waveguiding properties of the films were investigated by the prism coupling technique (m-line spectroscopy). The feasibility of waveguide amplifier and laser made of Pr³⁺-doped chalcogenide was investigated by a computer code.
- D/PIL.33** ENHANCED MAGNETORESISTANCE OF La_{0.7}Sr_{0.3}MnO₃-IRON OXIDE MULTILAYERED THIN FILMS PREPARED BY PULSED LASER DEPOSITION
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La_{0.7}Sr_{0.3}MnO₃/iron oxide multilayered thin films have been successfully prepared alternatively on single crystal silicon substrates by pulsed laser deposition. Both the atmosphere in the chamber and the substrate temperature have been optimized in terms of low-field magnetoresistance enhancement. By using an oxygen pressure of 15-20 Pa, and a substrate temperature of 700°C, a series of multilayered thin films with various thickness combinations of La_{0.7}Sr_{0.3}MnO₃(LSMO) layer and iron oxide layer. It is revealed that the magnetoresistance of the multilayered thin films decreases with increasing thickness of the iron oxide layer. The MR value goes up to 23% under a magnetic field of 3 kOe at 80K.
- D/PIL.34** ELECTRIC PROPERTIES OF PULSE LASER DEPOSITED Ag₃SbS₃ and Tl₃SbS₃ THIN FILMS
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Ag₃SbS₃ and Tl₃SbS₃ are seemed to be very attractive for many technical applications due its high electro-optical effect, significant double-beam refraction and transparency in the wave length 0.6-14 μm . Nevertheless, the electric properties of the compounds (bulk materials and thin films) are poorly investigated. The abstract reports first data of electric characteristics of thin films deposited on KCl wafers by pulse laser evaporation technique under the following conditions: the substrate temperature was 300 K, time of deposition was varied from 5 to 17 minutes, the film thickness had not exceeded 0.8 μm . The current - voltage measurements carried out at the room temperature were shown power-behaved dependence $I = 0.6 \pm 1.3 (V_a)^m$ (V_a stands for applied voltage) similar to that of the current limited by space charge region in typical barrier structures. The so-called electric field-induced aging was also studied. It was found that the current character is sufficiently changed (the power-like mode of charge carriers transport is replaced by the velocity saturation mode of the carriers transfer). The experimental data made us enable to perform numerical simulation of the results obtained and to construct an energy band diagram of the studied structures.

- D/PIL.35** GROWTH OF CALCIUM PHOSPHATE THIN FILMS BY IN SITU ASSISTED ULTRAVIOLET PULSED LASER DEPOSITION
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 Calcium phosphate (CaP) thin films, including hydroxyapatite (HA), are studied to optimize the manufacturing technology of the bone prostheses. A drawback of the CaP thin films is their poor mechanical characteristics, especially hardness, tensile strength and adherence to the metallic substrate. We report a new method for the growth of high quality CaP films with a significant increase of their mechanical properties. The growth was performed by the pulsed laser deposition technique assisted by *in situ* ultraviolet radiation emitted by a low pressure Hg lamp (UVPLD). The depositions were made on Si and Ti alloys in very low oxygen pressure (10^{-2} – 10^{-1} Pa) and a substrate temperature of 500-600°C. The films were analyzed by optical microscopy, white light confocal microscopy, electron microscopy, grazing incidence X-ray diffraction and Berkovich nanoindentation in normal and scratch options. A comparison with the properties of CaP films grown by the conventional pulsed laser deposition technique was also performed. The UVPLD grown films were more crystalline and exhibited better mechanical characteristics with values of hardness and Young modulus of 7-8 GPa and 150-170 GPa, respectively, which are uncommonly high for the CaP ceramics. Since the UV radiation photodissociates molecular oxygen and forms atomic oxygen and ozone, a lower oxygen pressure was used during the growth, allowing an increase bombardment of the film by highly energetic species from the laser plume, with a beneficial effect upon mechanical properties.
- D/PIL.36** PULSED LASER DEPOSITION OF LEAD TITANATE THIN FILMS FOR INTEGRATED OPTICS
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 The explosion of optical communication requires efficient linear and non linear optical integrated devices. Lead titanate (PbTiO₃) has been extensively studied as a ferroelectric material. It has attracted great interest for various applications, such as non-volatile random access memory because of its ferroelectric, electro-optic and piezoelectric properties. Therefore, using this material as waveguiding thin films can advantageously extend the use of its properties in integrated optics. Due to its high refractive indices (2.7) and its ferroelectric properties, PbTiO₃ (PT) is a good candidate for frequency doubling by quasi phase matching (QPM). In our work, the PT thin films are prepared by pulsed-laser deposition (PLD) on various substrates such as MgO, SrTiO₃ and Quartz. The chemical composition, the surface roughness and the crystalline structure of the films are studied by Rutherford backscattering spectroscopy (RBS), atomic force microscopy (AFM) and X-ray diffraction (XRD) respectively. The waveguiding properties are investigated by using the prism coupling technique and the frequency doubling of a Nd:YAG laser is studied by the SHEW method (second harmonic generation by evanescent wave).
- D/PIL.37** HYDROXYAPATITE THIN FILMS GROWN BY PULSED LASER DEPOSITION AND RF MAGNETRON SPUTTERING: COMPARATIVE STUDY
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 Hydroxyapatite (HA), Ca₅(PO₄)₃OH, thin films with applications in the biomedical field were processed by pulsed laser deposition (PLD) and radiofrequency magnetron sputtering (RF-MS) techniques. The depositions were made starting from synthetic HA targets on Si or Ti alloys substrates. The PLD films were grown in vacuum on substrates maintained at room temperature, while the RF-MS films were realized in different environmental conditions including argon or/and oxygen at small temperature (20-300°C) of the substrate. After deposition the samples were annealed at 600°C in ambient air for 1 h in order to restore or improve the crystalline structure of the target. The as-deposited and annealed films were structurally and mechanically characterized by grazing incidence X-ray diffraction (GIXRD), Fourier transformation infrared spectrophotometry (FTIR), optical microscopy (OM), white light confocal microscopy (WLCM) and Berkovich nanoindentation. The annealed films recrystallize in the HA structure and exhibit better mechanical characteristics. However, small peaks of CaO secondary phase were noticed in the GIXRD patterns only for the RF-MS films. In return the sputtered films were very smooth (30-40 nm average roughness) in comparison with those ones deposited by PLD (250-300 nm average roughness). A critical comparison between the two deposition techniques on the versatility in high quality pure HA thin films processing was made.
- D/PIL.38** MECHANICAL BEHAVIOR OF ION-BEAM IMPLANTED HYDROXYAPATITE THIN FILMS GROWN WITH AND WITHOUT BUFFER LAYERS BY PULSED LASER DEPOSITION
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 The main problem of the hydroxyapatite (HA), Ca₅(PO₄)₃OH, thin films processing for bone implants fabrication remain their poor mechanical properties and weak density. In this study crystalline HA films were grown by pulsed laser deposition method (PLD) using an excimer KrF* laser ($\lambda = 248$ nm, $\tau = 20$ ns). The films were deposited directly on Ti-5Al-2.5Fe alloys or on substrates previously coated with a ceramic TiN or ZrO₂ buffer layer. After deposition the films were submitted to an ion-beam implantation treatment. We used an Ar⁺ ion beam with energy in the range of (1.2-1.5) MeV at a constant dose of 10^{16} cm⁻², keeping the current density at $1 \mu\text{Acm}^{-2}$. The films were characterized by optical microscopy, scanning electron microscopy, grazing incidence X-ray diffraction and Berkovich nanoindentation in normal and scratch options. The HA implanted and non-implanted films, deposited with and without buffer layers, are discussed in term of the mechanical behavior. The films are denser and, generally, their mechanical properties enhance after ion implantation, while the crystalline structure of hydroxyapatite phase is preserved. However, despite of the increasing in density, the film grown on ZrO₂ buffer layer are fragile and fractures at moderate loads (for the force regime in nanoindentation), namely 12 mN, in comparison with that one deposited on TiN buffer. We explain this comportment by the expected internal stress appearance during the film processing.
- D/PIL.39** DEPOSITION OF THIN POLYMER FILMS
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 Polyethylene glycol (PEG) is a water soluble polymer with many technological applications. It is a good model system for other polymers as well. For this reason PEG has been used for thin polymer film production. The films have been created using matrix assisted pulsed laser evaporation (MAPLE). By this technique the polymer is dissolved into a liquid matrix, which subsequently has been cooled to below 200 K. During laser irradiation the frozen matrix evaporates, whereas the ejected polymer is collected on a suitable substrate. In the work presented here we have studied the growth rate of PEG's with different masses and as a function of the matrix temperature. Moreover, the polymer decomposition during the evaporation has been investigated by means of a mass spectrometer.

Symposium D

- D/PIL.40** PULSED LASER DEPOSITION OF POLYMER THIN FILMS
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Polymer thin films are of great interest for material patterning, coatings, adhesion, roughening, crystallinity, reactivity, their optical properties, laser lithography and direct writing.
UV PLD of polymers is an intense interaction between the target material and laser resulting in chemical modification of the polymer during ablation. We pursue the optimization of the deposition configuration by a proper choice of the fluence, target-substrate distance and substrate temperature. For deposition, we used a stainless steel chamber. We performed the deposition with a KrF* excimer laser source ($\lambda=248$ nm, $\tau_{FWHM}=20$ ns). The laser was operated at the repetition rate of 1 Hz with the incident fluence varied between 0.65 and 1.18 J/cm², which is slightly larger than the threshold value. We used targets prepared by pressing PMMA pellets from ICI Diakon. The target-substrate distance was varied between 2 and 3 cm. The spot size was between 0.045 and 0.076 cm². Ablated material was collected on Si<100> plates held at both room temperature and in the range of 50 - 200 °C. The residual pressure in the chamber during the deposition was between 10⁻⁵ - 10⁻⁶ torr. The number of laser pulses was varied between 10000 and 25000. The films were further characterized by optical microscopy, SEM, TEM, SAED, XRD and XPS. The thickness of the films was 5 μm, with the roughness of 0.4 μm. We obtained highly adherent films with the stoichiometric structure close to the target.
- D/PIL.41** INITIAL WETTING ANALYSIS OF LASER DEPOSITED TI:SAPPHIRE
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The wetting properties for materials in the optical and microelectronic sector are of prime importance for a variety of process and preparation steps. Etching, and wafer direct bonding are only two of the relevant areas of application. Laser deposited Ti:Sapphire holds strong relevance for potential application on micro electronic and micro optical integration. The analysis of their wettability performance is therefore of relevance for potential engineering and manufacturing processes. In this paper, we evaluate the wettability of the deposited film systems, dependent on deposition parameters, to determine the polar and dispersive intermolecular forces of the material by using a control system of liquids. An interpretation of the results, in view of the deposition parameters and potential manufacturing applications is attempted.
- D/PIL.42** NEW LASER CHARACTERISTICS FOR PLD - UNDERMINING PLASMA SHIELDING
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Pulsed Laser Deposition (PLD) is an extremely versatile technique for depositing a wide range of thin films. PLD-systems have been improved continuously while research on the excimer laser source stagnated.
We want to characterize some parameters of interest of the excimer laser source, its improvements and contribution to PLD to create thin films. Parameters of interest to be discussed are the divergence, initial beam size, pulse duration and rise time of the excimer laser pulse. Changing these parameters lead to higher focusability and higher initial peak intensities resulting in decreased plasma shielding.
It could be shown that the temporal distribution of the emitted energy is more important than the total energy per pulse.
- Plasma dynamics
- D/PIL.43** PARTICLE DYNAMICS IN A LASER PLASMA PLUME STUDIED WITH THE PARTICLE-IN-CELL METHOD
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We have studied the plasma plume expansion from a solid target irradiated by a laser with a short pulse. We have performed a one-dimensional numerical calculation based on the particle in cell (PIC) method of Birdsall et al. This method allows us to study ion as well as electrons ejected from a planar surface as a result of laser pulse and includes Coulomb interaction between electrons and ions. Results for the density profiles, the velocity distributions of the ions and the electrons and the time dependence of the kinetic energy of both types of particles will be presented. A significant enhancement of the ion velocities at the expense of electron energy and potential field energy was found.
- D/PIL.44** LASER ABLATION OF Si BY FEMTOSECOND LASER PULSES: MOLECULAR DYNAMICS SIMULATION
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Laser ablation of silicon has been investigated by the molecular dynamics simulation technique. 100 fs laser pulses at wavelengths 308nm and 800nm were used in the simulations. The two-photon absorption of the material is taken into account. The influence of the laser energy density on the process of ablation was studied. The time evolution of the plasma plume was shown. The threshold was determined and the ablation rate as a function of the laser energy density was obtained. The values are in a good agreement with the experimental data of other authors. The dynamics of the shock wave and the temperature distribution into the solid were studied. The velocity of the ablated atoms is several kilometers per second whereas this of the ions exceeds 20 km.s⁻¹. It increases for both species with the laser fluence rise. The model reveals the basic mechanisms and features of the femtosecond laser ablation of silicon.
- D/PIL.45** MID-INFRARED LASER ABLATION OF A HARD COMPOSITE BIOLOGICAL TISSUE: MECHANISTIC STUDIES OF WAVELENGTH, PULSE DURATION AND INTERFACIAL EFFECTS
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Understanding the mechanisms of laser ablation in medicine is maddeningly complex because of the heterogeneity of biological tissues. Although orthopedic applications of ablation have been relatively limited up to now, there is definite interest; moreover, cortical bone is a tractable model systems for mechanistic studies, consisting of mineral crystal, protein and water, each with distinct mid-infrared (IR) absorption bands. In this paper, we report mechanistic studies on mid-IR laser ablation of bovine cortical bone using a picosecond mid-infrared free-electron laser (FEL) at wavelengths corresponding to these absorption bands, as well as a conventional nanosecond Er:YAG laser that is strongly absorbed by water. Diagnostics include optical spectroscopy of the plasma plume, electron microscopy of the ablated region, and photoacoustic spectroscopy. We compare previous results for ablation in air with new studies in which the bone is immersed in perfluorocarbon fluids to control pressure confinement and temperature dissipation, improve ablation efficiency – possibly through nonlinear effects – and reduce collateral tissue damage. The most critical parameter for these interface effects is the molecular weight and thickness of PFC liquid. Ablation with the FEL and an Er:YAG laser at 2.94  μm are evaluated to characterize the effects of fluence vs intensity and elucidate the potential benefits of nanosecond vs picosecond pulse duration.

Symposium D

- D/PIL.46** ANGULAR DISTRIBUTION OF LASER DEPOSITED TI:SAPPHIRE ON SILICON SUBSTRATES
M.J.J. Schmidt and L. Li, Department of Mechanical, Aerospace and Manufacturing Engineering, Laser Processing Research Centre (LPRC), University of Manchester Institute of Science and Technology (UMIST), PO Box 88, Manchester M60 1QD, U.K.
The angular distribution of laser deposited materials on the substrates is of relevance for their potential performance in manufacturing processes, where an even large area deposition is required. The deposition profile for Ti:Sapphire films has been measured for deposition processes under 193 nm excimer laser ablation. The results have been interpreted using gas dynamic principles, using the formation of a Knudsen Layer and an resulting unsteady adiabatic expansion of the ablation plume. The results from the film distribution correlate well with previous direct measurements and models to the expansion of the plume.
- D/PIL.47** NON EQUILIBRIUM CONDITIONS DURING A LASER INDUCED PLASMA EXPANSION
A. Casavola, G. Colonna, M. Capitelli, Dipartimento di Chimica, Università di Bari, Italy and IMIP-CNR, sect. Bari, Italy
A theoretical model to simulate the laser induced plasma expansion with chemical kinetics has been developed and compared with the free flow model results for a Ti target. A further improvement of the chemical model is to consider a complete collisional-radiative model coupled with the fluid dynamic. In this case non-equilibrium distributions of internal energy levels can be observed. The presence of non-Boltzmann distribution is very important because the Boltzmann plot technique fails in this case. So the coupling between collisional-radiative kinetics and the fluid dynamic equation of the plume expansion can improve the understanding of the physics of the expansion and can be a powerful tool to extract quantitative information from emission spectra even if the local thermodynamic conditions cannot be considered.
Our attention has been also focused on the influence of initial conditions on the plume expansion. In particular, changing the initial speed, temperature, pressure and plume extension, the speed of expansion and the width of the TOF (time of flight) peak change. A systematic study of the effect of all these parameters on the plume expansion can lead to a method that allows the determination of initial conditions of the expansion. These data are not available experimentally because of the delay necessary to trigger the measure apparatus with the laser pulse. So the method here presented can be generalized to calculate initial conditions for the LIP expansion.
- D/PIL.48** SPECTROSCOPIC INVESTIGATION OF THE PLASMA GENERATED BY THE INTERACTION OF KrF LASER AND Ti BASED TARGET AT LOW PRESSURE
A. De Giacomo, Chemistry Department of Bari, Italy O. De Pascale, IMIP-CSCP-CNR, Bari, Italy
The most commonly used technique for the diagnostic of laser induced plasma is the optical emission spectroscopy. This technique has been extensively applied for the in situ diagnostic of Pulsed Laser deposition (PLD) and for chemical traces analysis (LIBS) [1]. It allows the experimental study of atomic and ionic state distribution function, of electron number density and of the plasma expansion [2]. Temporally and spatially resolved emission spectroscopy has been successfully employed to develop theoretical model able to explain some aspects of the kinetic processes in LIP (laser induced plasma) after 100 ns from the laser pulse [3]. An optical delay mounted in the spectroscopic system allows to study the first stage of the LIP formation and expansion so that it is possible to established the validity and the duration of LTE. The validity of this assumption and the plasma composition is very important to connect the target chemical composition to the deposited film stoichiometry. Moreover the detection of whole temporal profile of atomic and ionic lines with spectral resolution gives information about the role of each species in the LIP expansion.
[1] A. De Giacomo, V.A. Shakhmatov, G.S. Senesi, S. Orlando, Spectrochim. Acta Part B, 56 (2001) 1459-1472.
[2] D.B. Chrisey, G.K. Huber, Pulsed Laser Deposition of Thin Films, A. Wiley-Interscience Publication, 1987.
[3] A. De Giacomo, V.A. Shakhmatov, O. De Pascale, Spectrochim. Acta Part B, 56 (2001) 753-776.
- D/PIL.49** DYNAMICS OF DIATOMIC AND TRIATOMIC CARBON MOLECULES FORMATION IN LASER PRODUCED PLUME
V.S. Burakov, M.I. Nedeliko, N.A. Savastenko and N.V. Tarasenko, Institute of Molecular and Atomic Physics National Academy of Sciences of Belarus, 70 Scaryna Ave., 220072 Minsk, Belarus
Laser ablation has gained noticeable acceptance as a technique for carbon nanotube synthesis. During the last decade research involving nanophase materials has shown an unprecedented growth because unique properties of such materials. However, very little is known about where and when the nanotubes are formed. Carbon molecules and small carbon clusters are thought to be intermediates in gas phase chemistry taking place in laser produced plume under nanotube growth conditions. This paper presents diagnostic data obtained from the ablation plume of a graphite target. XeCl (10 Hz, 5 mJ) or two Nd:YAG lasers (10 Hz, up to 100 mJ) are used for ablation process. Nd:YAG lasers are operating at 1064 nm and 532 nm. As buffer gas helium at pressure between 0.1 - 500 Torr under static conditions (without flow) is employed. The formation of C₂ and C₃ molecules in plasmas is investigated by monitoring the time-space distributions of these molecules as well as carbon atoms and ions in plasma. The experimental results show that the recombination processes plays a major role in diatomic molecule formation.
- D/PIL.50** COLLIMINATION OF A LASER ABLATION PLASMA PLUME USING A UNIFORM MAGNETIC FIELD
B. Doggett and J.G. Lunney, Physics Department, Trinity College Dublin, Dublin, Ireland
Experiments have been done to investigate the feasibility of using a uniform magnetic field to collimate the flow in a laser ablation plasma. The magnetic field was orientated perpendicular to the target, and was produced using two Halbach cylinder permanent magnets. The field was varied up to 300 mT by changing the separation of the Halbach cylinders. The silver target was used and it was irradiated using a 6 ns Nd-YAG laser at normal incidence. The angular distribution of the plasma flow was measured using a Langmuir probe and gated photography. With magnetic field the ion flux on the axis normal to the target is increased by a factor of four. There is also an increase in the electron temperature.

- D/PIL.51** EMISSION CHARACTERISTICS OF THE PLASMA PLUME GENERATED DURING KrF LASER ABLATION OF A Cr₂O₃ TARGET
 G. Dinescu(a), M.N. Oliveira(b), O. Conde(b), (a)Low Temperature Plasma Physics Department, National Institute for Lasers, Plasma and Radiation Physics, Magurele MG-16, 76 900 Bucharest, Romania, (b)Department of Physics, Faculty of Sciences, University of Lisbon, Campo Grande Ed. C8, 1749-016 Lisbon, Portugal
 Pulsed laser deposition is one of the techniques largely used in deposition of thin films because it offers many advantages such as low temperature of the substrate, good thickness control, possible control of stoichiometry, versatility in using various starting target materials and reactive gases. It has been used to deposit a wide variety of materials and, in particular, metastable compounds which are difficult to grow by other methods. It has been found that film properties are strongly related to the plasma plume characteristics, which results from the laser-target interaction.
 Aiming to obtain Cr_xO_y thin films, and in particular the metastable CrO₂ compound, by pulsed laser ablation of stable chromium oxides, we performed an optical emission study of the plasma plume generated during KrF laser ablation of Cr₂O₃ targets. Results concerning the nature of plasma species, their energy, their spatial and temporal distributions, which are factors that may have large impact on the deposited film properties, are presented. We show that the emission characteristics can be explained by taking into account the atomic energy level peculiarities of the Cr I, Cr II, O I, O II species along with the Boltzmann thermodynamic equilibrium distribution hypothesis. The results complete the tableau describing the plasma plumes generated by ablation of oxide materials, as there are not many references concerning the pulsed laser ablation of chromium oxides.
- D/PIL.52** PLASMA ASSISTED PULSED LASER DEPOSITION
 J. Perrière, GPS- Université Paris VII et Paris VI, 2 place Jussieu, Tour 23, 75251 Paris cedex 05, France and C. Boulmer-Leborgne, A. Basillais, R. Benzerga and E. LeMenn, GREMI-ESPEO, Université d'Orléans, BP6744, 45067 Orléans cedex2, France
 Pulsed Laser Deposition (PLD) method is particularly well suited for oxide materials but in the case of compounds as nitrides the method is limited due to the low reactivity of nitrogen in comparison with oxygen. The reactivity of the constituent species can be increased by a nitrogen plasma assisting the PLD where a plasma production device is coupled to the deposition chamber. This paper presents results for AlN and GaN films obtained by PLD coupled to a nitrogen RF discharge. The composition and structure of the films are studied as a function of the growth conditions and the positive effect of the additional discharge is evidenced. The presence of droplets at the surface of the films is the main drawback of the PLD process. A crossed laser induced plasma plumes device is used to obtain a plasma expansion free of particulates. The influence of experimental conditions is also studied in relation with droplets deposition.
- D/PIL.53** OPTICAL CHARACTERIZATION OF MAGNESIUM DIBORIDE PLASMA PLUME INDUCED BY PULSED LASER ABLATION
 G. D'Amico, A. Di Trolio, U. Gambardella, A. Morone, S. Orlando and A. Santagata, CNR-IMIP, Sezione di Potenza, Zona Industriale di Tito Scalo, 85050 Tito Scalo (PZ), Italy
 Magnesium diboride (MgB₂) is a conventional superconductor material with the highest (39 K) critical temperature. It has gained a wide interest for potential applications thanks to its peculiar physical and mechanical properties.
 We have investigated the expansion of MgB₂ plasma plume produced by pulsed laser ablation of a target, obtained by pressing stoichiometric commercial powders. In order to evaluate the reactivity of the charged and neutral species, time- and space-resolved emission spectroscopy have been performed by using an optical multichannel analyzer during the plasma plume expansion.
 The gaseous species have been collected in vacuum on MgO (100) substrates which were positioned, by a holder heatable up to 800 K, in front of the target. The deposited thin films have also been structurally characterized.
- D/PIL.54** EMISSION SPECTROSCOPY OF ALUMINIUM NITRIDE PLASMA PLUME INDUCED BY ULTRA-SHORT PULSED LASER ABLATION
 V. Marotta, S. Orlando, A. Santagata and A. Giardini, CNR-IMIP, Sezione di Potenza, Zona Industriale di Tito Scalo, 85050 Tito Scalo (PZ), Italy, R. Teghil, Dipartimento di Chimica, Università della Basilicata, Via Nazario Sauro 85, 85100 Potenza, Italy
 Aluminium nitride (AlN) is an attractive material for high temperature microelectronic and optoelectronic device applications. Laser ablation and deposition of such material has been already performed employing ns laser sources. In this case, AlN film depositions have been achieved simply by reactive gas environments. Thus, in order to overcome ns laser ablation and deposition restrictions, the ultra-short laser ablation process has been investigated.
 The plasma plume expansion process of an AlN target ablated by an ultra-short Nd:Glass pulsed laser (200 fs, 1.2 ps) has been surveyed by emission spectroscopy and fast imaging. The data have been collected with spatial and temporal resolution in order to find out the species speed and their angular distribution. Furthermore, comparing the data so obtained with previous studies performed by employing ns laser sources, it has been possible to distinguish different regimes involved during the plasma expansion. These results could also justify the cluster formation, detected by a quadrupole mass spectrometer, observed during the ultra-short laser ablation regime, but not for the ns one.
- D/PIL.55** LASER ABLATION OF POLYMERS STUDIED BY NS-INTERFERENCE AND NS-SHADOWGRAPHY MEASUREMENTS
 M. Hauer(a), D.J. Funk(b), T. Lippert(a), A. Wokaun(a), (a)Paul Scherrer Institut, General Energy Research, 5232 Villigen PSI, Switzerland, (b)Los Alamos National Laboratory, DX-2, MS C920, Los Alamos NM 87545, USA
 Laser ablation of polymers has been studied over the last two decades. Special designed polymers were developed to improve the ablation process, e.g. low threshold fluence, high etch rates and clean ablation structures. One of these polymers, i.e. a photolabile triazene polymer, was studied in detail with ns-interferometry and ns-shadowgraphy.
 Ns-interferometry allows the observation of the laser induced morphological changes of the polymer in the nano- to microsecond time scale with a nm out of plane spatial resolution. The triazene polymer was irradiated at 308 nm and at 193 nm (similar absorption coefficients at both wavelenghts) to analyze the dynamic behavior of the ablation process. The data show clearly that etching of the polymer starts and ends with the laser pulse, suggesting a photochemical decomposition mechanism. For photothermal ablation mechanisms a pronounced swelling and a time-delayed etching is observed (e.g. polyimide)
 The redeposition of the ablation fragments deteriorates quite often the ablation quality. For a more detailed understanding of the material ejection the ablation plume was imaged perpendicular to the polymer surface. The plumes of a photostable (polyimide) and a photolabile (triazene) polymer were compared after irradiation with a XeCl (308 nm) and an ArF (193 nm) excimer laser. The ablation plume of the triazene polymer does not reveal any particles at both irradiation wavelenghts.

Symposium D

- D/PII.56** DIAGNOSTIC OF THE PLASMA PLUME DURING LASER SURFACE TREATMENT
F. Fariant, C. Boulmer-Leborgne, GREMI, UMR 6606 CNRS, Université d'Orléans, BP 6744, 45067 Orléans Cedex 2, France
The excimer laser process reported here is developed to enhance the mechanical and chemical properties of aluminum alloys by forming a nitride or carbide layer on the surface. The laser beam is focused onto the alloy surface in a cell containing 1 bar propylene or nitrogen gas. The irradiated surface is heated, melted and vaporized. A vapor plasma expands from the surface and shock wave dissociates and excites the ambient gas. It is assumed that carbon from plasma in contact with the surface penetrates in depth. Finally a polycrystalline cemented or nitrided layer is formed.
The key role of the plasma formation for the nitride or carbide formation have been shown by number of studies, but this stage of the process is not yet totally well known. The diagnostic of the plasma plume allows analyze of the plasma parameters and the diffusing species production and finally reveals the role of the plasma. The experimental setup of the plasma diagnostic is composed by a fast time resolved ICCD coupled to a monochromator.
- D/PII.57** PLUME DYNAMICS IN TiC LASER ABLATION
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The deposition of thin films of titanium carbide by pulsed laser ablation has already demonstrated that it is possible to obtain carbide coatings with different characteristics by varying the deposition conditions. The films structure and growth mechanism are strictly related to the conditions of the plasma obtained by the interaction of the TiC target with the ns laser beam, but many aspects of the dynamics of the gaseous plume have been not sufficiently clarified. In this work the analysis of the gaseous phase performed by emission spectroscopy and ICCD imaging is reported. The front of the emitting plume, independently from laser fluence, is identified with the presence of C²⁺ ions, while the presence of a double maximum at a laser fluence higher than 3 J/cm² is due to the of neutral and ionised titanium particles travelling with different velocities. The results, compared with those obtained for other carbides of the 4 group, evidence that only in the plume produced from TiC targets there is the presence of a large amount of ions with high kinetic energy. In particular the highly energetic M²⁺ ions (M = Ti, Zr, Hf) are present only in the TiC plume. The different energy and concentration of ions in the different carbides confirms the importance of the ionised part of the plume in the film growth mechanism. In fact only in the TiC films we find a layered structure in contrast with the columnar structure found in the other carbides of the same group.
- D/PII.58** PULSED LASER ABLATION OF Nd AND Pr CARBIDES
R. Teghil, L. D'Alessio, Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, 85100 Potenza, Italy, A. Santagata, CNR-Istituto Metodologie Inorganiche e Plasmi, Sez. Potenza, via S. Loja, Tito Scalo, Italy, D. Ferro, CNR-Centro Termodinamica Chimica alle Alte Temperature, P.le A. Moro 5, 00185 Roma, Italy, G. De Maria, Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy
Lanthanide carbides are very interesting systems to study the laser-material interaction. In particular these carbides are very difficult to prepare and to deposit as thin films and present different stoichiometry and structure related to the metal valence and so they are ideal candidate to clarify the influence of the gaseous phase on the films characteristics.
We have evaporated neodymium and praseodymium carbides by a doubled Nd:YAG laser and we have studied the ablated plume by Time of Flight Mass Spectrometry, ICCD Imaging and Emission Spectroscopy. The results show that in the gas phase the produced clusters have mainly the (MC₂)_n (where M is the metal) stoichiometry, while the velocities of neutral and ions seem to be quite low with similar values for all considered particles.
Preliminary results on the deposited films indicate that they are amorphous in structure and their stoichiometry is very close to MC₂.
- D/PII.59** PULSED LASER DEPOSITION OF PROTEIN THIN FILMS: BSA
M.A. Hernandez-Perez(a), C. Garapon(a), C. Champeaux(b), P. Shahgaldian(c), A. Coleman(c), J. Mugnier(a), (a)Physico-Chimie des Matériaux Luminescents, CNRS-Université Lyon I, 10 rue Ampère, 69622 Villeurbanne Cedex, France, (b)Science des Procédés Céramiques et Traitement de Surface, CNRS-Université de Limoges, France, (c)Institut de Biologie et Chimie des Protéines, CNRS, Lyon, France
Thin films of the protein bovine serum albumine (BSA) were prepared by pulsed laser deposition. Using a KrF excimer laser focused on a target made of pressed powder with a fluence in the 1 to 2 J/cm² range, films of about 500nm thickness could be obtained on silica substrates or SiO₂/Si wafers at room temperature and under pressure of about 10⁻⁵ mbar. The FTIR spectra of the films, recorded in ATR configuration, are identical to those of the starting powders. For fluences lower than 1 J/cm², however, the conservation of the structure of the molecule is not observed. The surface aspect and roughness were studied by AFM. The AFM images show the protein to be deposited as rounded aggregates joined together by filaments, and show no clear ordering. Refractive index and thickness of the films were measured by m-lines spectroscopy. X ray diffraction indicates no long range molecular arrangement.
- D/PII.60** LICVD PAINTING WITH TiO₂
Estelle Halary-Wagner, Tristan Bret and Patrik Hoffmann, Institute of Imaging and Applied Optics, EPFL, Lausanne, Switzerland
LICVD (Light Induced Chemical Vapour Deposition) offers the advantages of selective area growth and precise control of the deposited thickness. Titanium dioxide films can be deposited by this method at low temperature (below 200°C) and is an interesting material due to a broad range of properties such as high index of refraction, photocatalytic effect, chemical inertness, hardness...
In this work, we use titanium tetraisopropoxide as a precursor in an oxygen and nitrogen atmosphere and perpendicular irradiation with a XeCl (308 nm) long pulse excimer laser. We demonstrate that a precise control of the deposited thickness (in the order of few nm) is achievable due to the linear dependence with light dose. Thanks to the very high index of refraction of the material, very thin films (20-160 nm) exhibit interferential colours in reflexion, which are compared to international colorimetric standards (CIE). Using sequential projection imaging of simple mask shapes, complex multilevel multi-coloured deposits are obtained on several-square-millimeters areas in a single sample load. The smallest demonstrated details are 30 micrometers in size. This could be of great interest for applications such as dye-free, long-term, self-cleaning, personalized decorative patterns.

D/PIL.61**GROWTH OF NiMgSb THIN FILMS BY PULSED LASER DEPOSITION**

A. Klini(a), J. Giapintzakis(a), C. Grigorescu(b), A. Manousaki(a), V. Zorba(a), J. Androulakis(a), Z. Viskadourakis(a), and C. Fotakis(a), (a)Foundation for Research & Technology – Hellas, Institute of Electronic Structure and Laser, P. O. Box 1527, Heraklion 71110, Greece, (b)National Institute for Optoelectronics, INOE 2000, P.O. Box MG5, ATOMISTILOR 1, 76 900 Bucharest, Romania

Thin films of the half-Heusler alloy NiMnSb, which is predicted by band structure calculations to be a half-metallic ferromagnet, were grown on various substrates (Si and InAs) using pulsed-laser deposition. A systematic study was performed using excimer lasers of different wavelength (193- 308 nm) and also pulse duration (fs and ns). The growth process occurred at moderate substrate temperatures (190-210 °C), the lowest ever achieved, which are necessary for making devices. We have identified a set of experimental conditions that allow the growth of highly crystalline thin films with nanoscale smooth surfaces. The morphology of the films was examined by atomic force microscopy and scanning electron microscopy. The structural and magnetic properties of the films are consistent with the bulk NiMnSb used as target, which suggests that thin layers of this material could be used in multilayer structures as effective spin-polarized conducting layers

D/PIL.62**HIGH QUALITY HASTELLOY FILMS DEPOSITED BY XeCl PULSED LASER ABLATION**

A. Zocco and A. Perrone, University of Lecce, Physics Department and Istituto Nazionale Fisica della Materia, C.P. 193, 73100 Lecce, Italy, I. Avram, S. Duhalde, C. Morales, T. Pérez and M. F. Vignolo, Facultad de Ingenieria, Universidad de Buenos Aires, Paseo Colon 850, 1063 Buenos Aires, Argentina

Pulsed laser ablation has been used to deposit films of Hastelloy on carbon steel substrate at room temperature. Depositions have been carried out by XeCl excimer laser ablation ($\lambda=308$ nm, $t=30$ ns) of a bulk Hastelloy target in high vacuum system ($p = 10^{-5}$ Pa). In order to obtain as thick and uniform films as possible, we took in account in our experiments the maximum plume deflection angle, which was almost of 11° , as measured by optical studies of the plume. To minimize the effects of the plume deflection, the substrate was placed along the deflected plume axis instead of the normal to the target surface. No depositions have been ever performed with this new geometrical configuration. The plume deflection angle and the ablation rate of Hastelloy target as a function of number of laser pulses per site have been also measured. Scanning Electron Microscopy (SEM), Energy Dispersion X-ray (EDX) spectroscopy and X-Ray Diffraction (XRD) have been performed to analyse, respectively, the surface morphology, the chemical composition and the crystallographic structure of the deposited films. In order to correlate the microstructure of the film surface with its corrosion properties, potentiodynamic curves and linear polarisation resistance analyses have been performed.

15:45

BREAK

Surface cleaning, microfabrication and nanoengineering

- D-II.28** 16:00 LASER WRITING AND TRIMMING OF PHOTONIC CIRCUITS IN PLANAR AND 3-D GLASSES
P.R. Herman, E.S. Rogers Sr. Department of Electrical and Computer Engineering, University of Toronto, King's College Road, Toronto, Ontario, M5S 3G4, Canada
 The advent of silica-based planar optical circuits in manufacturing, and the possible extensions to three-dimensional photonic systems, present numerous opportunities for applying advanced laser systems to fabricate, trim, inspect, and package optical circuits. Such processing is urgently required to improve production yield, speed fabrication, and lower packaging costs for the photonics industry much in the same way that laser technology had served the microelectronics industry for decades. In this paper, we review our work on deep-ultraviolet laser and ultrafast laser photosensitivity studies in silica-based glasses and the possible new roles for laser technology in photonics manufacturing. At the forefront of short-wavelength sources, the 157-nm F2 lasers drives strong photosensitivity responses in low-concentration germanosilicate fibers and planar waveguides that offer novel opportunities in rapid fabrication of fiber components, in photosensitivity enhancement and locking, and in trimming birefringence in optical circuits. For the first time, we also describe the formation of buried waveguide structures in bulk fused silica without the need for ultrafast-laser interaction physics. These observations are compared with waveguides and photonics structures fabricated by nonlinear interactions in glasses with the use of a 50-fs ultrafast laser. Head-to-head comparisons of the deep ultraviolet and ultrafast interactions are summarized for photonic devices characterized at ~1.55 mm telecommunication wavelengths. Ultrafast lasers and ultraviolet lasers both offer strong photosensitivity responses that address niche applications in fabricating complex three dimensional photonic structures and trimming optical circuits for telecommunication applications.
- D-II.29** 16:30 WITH FEMTOSECOND LASER PULSES: APPLICATIONS IN ENGINEERING, PHYSICS AND BIOMEDICINE
W. Rudolph, Department of Physics, University of New Mexico, Albuquerque, NM 87131, USA
 Progress in microscopic imaging with femtosecond laser pulses is reviewed. Imaging techniques are described that make use of the high intensities and the short coherence lengths available with femtosecond pulses. Examples from engineering, physics, and biomedicine are presented.
- D-II.30** 17:00 NOVEL APPROACHES TO LASER PROCESSING THIN FILMS OF ELECTRONIC AND BIOLOGICAL MATERIALS
D.B. Chrisey, B.R. Ringeisen, R.C.Y. Auyeung, A. Pique, J.S. Horwitz, D.D. Bubb, H.D. Young, E.J. Houser, and R.A. McGill, US Naval Research Laboratory, Washington DC 20375, USA
 The value of using lasers to process thin films has increased dramatically in the last 15 years because of the clear advantages lasers can provide for depositing complex new materials in increasingly difficult configurations. Complex materials include multicomponent ceramics and fragile organics and biomaterials that must be deposited as multilayers having discrete interfaces. We have developed novel approaches to laser processing thin films by making use of new target material configurations through the matrix assisted pulsed laser evaporation (MAPLE) technique and by selectively coupling the laser to the vibrational modes of a polymer target using a Free Electron Laser. We have applied these techniques to biocompatible polymers, chemoselective polymers, and biomaterials. In both these techniques, there are mechanistic issues that are unique to the specific material and must be addressed to achieve the full potential of the thin film. This presentation will summarize the fundamental understanding and the progress made toward specific applications by using lasers to processes thin films of electronic and biological materials.
- D-II.31** 17:15 SHADOWGRAPHIC IMAGING OF THE SUB-PS LASER INDUCED FORWARD TRANSFER PROCESS
I. Zergioti, D.G. Papazoglou, A. Karaiskou, C. Fotakis, Foundation for Research & Technology – Hellas, Institute of Electronic Structure and Laser, P. O. Box 1527, Heraklion 71110, Greece
 The sub-picosecond laser induced forward transfer process (LIFT) was investigated by means of time resolved shadowgraphic imaging. The dynamics of the sub-picosecond LIFT process of InO_x and Cr was investigated for time delays between 0.01-10 ns following laser irradiation pulse. Measured values of the velocities of the ejected material were to 400±10 m/s, depending on the laser fluence. The material ejected by the sub-picosecond LIFT process was measured to be highly directional with narrow angular divergence (3°). Such direct dynamic transfer of the material opens up new application possibilities for the fabrication of high spatial resolution microstructures.
- D-II.32** 17:30 FEMTOSECOND LASER MULTI-PULSE INTERACTION WITH OPTICAL FILTERS AND FABRICS
S. Martin(a), J. Krueger(a), M. Lenzner(a)*, A. Fiedler(b), W. Kautek(a), (a)Laboratory for Thin Film Technology, Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany; (b)Rupp + Hubrach Inferoptics / Laserschutz GmbH, Laubanger 18, 96052 Bamberg, Germany; *Present address: Katana Technologies GmbH, Albert-Einstein-Ring 7, 14532 Kleinmachnow, Germany
 Optical filters and fabrics are important parts of laser safety equipment such as goggles and curtains. A choice of these materials with varying absorption spectra is investigated with respect to their resistance to Ti:sapphire femtosecond laser radiation (800 nm wavelength, 1 kHz repetition rate). Pulse durations down to 30 fs and multiple-pulse irradiation conditions are employed to evaluate technically relevant damage thresholds. The ablation threshold fluences of the absorbing filters are comparable to those observed for transparent materials with 30-fs-pulses. These investigations together with scanning electron microscopy of the surface morphology after laser treatment provide insight into the interaction mechanism of the short pulses with the materials.

Symposium D

- D-II.33** 17:45 DEEP-DRILLING AND METALLOGRAPHICAL ANALYSIS OF STEELS AND HARD METALS USING FEMTOSECOND LASER PULSES
G. Dumitru, V. Romano, H.P. Weber, Institute of Applied Physics, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland, M. Sentis, J. Hermann, S. Bruneau, W. Marine, Groupement Interdisciplinaire Ablation Laser et Applications, LP3 FRE2165 CNRS - Université de la Méditerranée, GPEC UMR 6631 CNRS, Faculté des Sciences de Luminy, Case 917, 13288 Marseille, France, H. Haefke, Y. Gerbig, Centre Suisse d'Electronique et de Microtechnique, Jaquet-Droz 1, 2007 Neuchatel, Switzerland
The main goals of the presented work were to investigate the evolution of the ablation rate over a large number of incident femtosecond laser pulses and to study the occurrence of material changes in the immediate vicinity of the laser induced craters, the latter being done through metallographical cuts. The studies were carried out on two types of cemented tungsten carbide (having 6%, respectively 10% cobalt) and on two sorts of steel (highly alloyed and carbon steel). The experiments using femtosecond pulses were performed in ambient air with a commercially available Ti:sapphire laser, delivering 100 fs pulses. The laser beam was attenuated, down to the regime of low fluences ($< 10 \text{ J/cm}^2$) and directly focused on the target surface. Series of microcraters were induced using increasing numbers of ultrashort laser pulses. For comparison purposes, similar experiments were performed using a commercially available Nd:YAG laser, delivering 100 ns pulses. After the laser irradiation, metallographical cuts were made through the samples in order to determine the depths and the shapes of the microcraters induced with different laser parameters. Through metallographical analysis of the surfaces resulted after the cross-section cuts, it was possible to evidence any changes of the crystalline structure of the target materials.
- D-II.34** 18:00 FEMTOSECOND MICROMACHINING IN PURE DIELECTRICS USING HARMONICS OF AN IR FEMTOSECOND LASER
N. Bityurin, A. Kuznetsov, IAP RAS, 603950 Nizhnii Novgorod, Russia
The present communication concerns the expedience of the use of harmonics, first of all second harmonic (SH), for 3D micro-modification of transparent dielectrics. Using harmonics, one decreases the order of multi-photon transition. However, one loses some significant part of laser energy during conversion. In the present communication we estimate the domain of applicability of this approach for different models of controllable modification of pure dielectric matrices. Together with a relatively simple model of multiphoton photochemical-like transformation, we consider less trivial models where multiphoton absorption serves only as a first step of energy transformation from laser beam to the lattice. This step is followed by other processes such as step-wise electronic transitions including step-wise ionization followed by impact ionization. In the latter cases, an advantage of SH over fundamental frequency (FF) is less trivial. In these cases, a combined effect of the SH and FF radiation has advantages over the separate use of both FF and SH
- D-II.35** 18:15 FEMTOSECOND LASERS: POWERFUL TOOLS FOR CLEAN MICRO-MACHINING
R. LeHarzig, N. Huot, E. Audouard and P. Laporte, Laboratoire Traitement du Signal et Instrumentation, Université Jean Monnet, UMR CNRS 5516, 23 rue du docteur Michelon, 42023 Saint-Etienne cedex 2, France
The advent of table top high repetition rate regeneratively amplified femtosecond lasers has opened the way to many recent and fast developments towards applications of economical interest. The most well known are microprocessing, thin film elaboration, waveguide photoinscription, surface treatment, dentistry, ophthalmology. Recent studies on microprocessing and laser-matter interaction using femtosecond lasers will be reported. This will be done using largely presently performed work in Saint-Etienne including investigations on Heat Affected Zone (HAZ). Indeed specific characters appear as compared to what is obtained using multipicosecond/nanosecond laser pulses: Typical submicronic HAZ lengths have been evidenced. The concept of the often vobabled "athermal" interaction will be discussed. Emphasis on actual microprocessing capability of the existing sources to approach industrial applications will be questioned in terms of energy per pulse, timewidth, repetition rates and the need for further source development and control beam improvement stressed. A bref review of the progresses under way in these fields and their capability to answer to actual large scale commercial applications will also be given.

Friday, June 21, 2002
Vendredi 21 juin 2002

Morning
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Session III: Pulsed laser deposition of nanostructured materials and thin films

Formation of nanostructured materials

- D-III.1** 8:30 NANOSCALE MAGNETIC PROPERTIES OF SELF-ASSEMBLED Ni AND Fe PARTICLES IN AMORPHOUS AND CRYSTALLINE MATRICES
D. Kumar, J. Narayan and J. Sankar, Center For Advanced Materials and Smart Structures, North Carolina A & T State University, Greensboro and North Carolina State University, Raleigh, USA
Presently a wide spread of research activities is pursued in the area of nanostructured materials in order to synthesize materials with improved properties so that the performance of nanostructured components in actual devices could be improved. The key to the successful fabrication of these nanostructured materials with improved properties is the development of smart materials by material-engineering and understanding the fundamentals of materials science. In this context that we have developed a novel smart thin film processing method based upon pulsed laser deposition to process nanocrystalline materials with accurate size and interface control with improved mechanical and magnetic properties. Using this method, single domain nanocrystalline Fe and Ni particles in 5-10 nm size range embedded in amorphous as well as crystalline alumina have been produced. By controlling the size distribution in confined layers, it was possible to tune the magnetic properties from superparamagnetic to ferromagnetic in a controlled way. Magnetic hysteresis characteristics below the blocking temperature are consistent with single-domain behavior.
Understanding the atomic structures and chemistry of nanoparticles and particle-host matrix interfaces is often critical to structure-property relationship in solid state structures of nanoscale dimension. In this paper we will be also be presenting our results from investigations in which scanning transmission electron microscopy with atomic number contrast (STEM-Z) and energy loss spectroscopy (EELS) were used to understand the atomic structure of Ni nanoparticles and interface between the nanoparticles and the surrounding matrices. Since Z-contrast imaging and EELS could be performed simultaneously, we were able to make direct correlations between structure and chemistry of the Ni nanoparticles, which were embedded, in amorphous alumina and crystalline TiN matrices using a pulsed-laser deposition process. It was interesting to learn from EELS measurements at individual grains and interface planes that Ni in alumina matrix does not form an ionic bond at the interface indicating the absence of metal-oxygen bond at interface. The absence of metal-oxygen bond, in turn, suggests the absence of any dead layer on Ni nanoparticles even in an oxide matrix.
- D-III.2** 9:00 SYNTHESIS OF SINGLE WALL CARBON NANOTUBES BY THE DOUBLE PULSE LASER VAPORIZATION TECHNIQUE
N. Braidy and **M.A. El Khakani**, INRS-Énergie et Matériaux, Varennes, PQ, Canada; **M. Tabbal**, **T. Christidis** and **S. Isber**, Dept. of Physics, American University of Beirut, Beirut, Lebanon
In this work, we investigate the properties of single-wall carbon nanotubes (SWNTs) that were synthesized, at a furnace temperature of 1150 °C, by laser vaporization of a metal (Co-Ni catalyst) containing graphite target using a single pulse at 532 nm followed by another pulse at 1064 nm, at laser intensities ranging from $(0.8 \text{ to } 3.5) \times 10^9 \text{ W/cm}^2$. The carbon SWNTs were characterized by means of Raman spectroscopy, high resolution transmission electron microscopy (HRTEM) and electron paramagnetic resonance (EPR). The optimal laser intensity that lead to the highest SWNTs yield and the largest bundles, as detected by HRTEM, was determined to be $2.3 \times 10^9 \text{ W/cm}^2$. In addition, analysis of the Raman spectra of the SWNTs indicates that the lowest level of amorphous and/or disordered sp^2 carbon in the deposits also occurs at this optimal value of the laser intensity. The EPR spectra show a sharp single transition occurring at a g-value of 2.002, which is superimposed on a large background signal that is attributed to the residual catalyst particles. The linewidth of the transition was determined to be 9 Gauss and was found to be nearly constant as the measurement temperature was varied from 10 to 300 K. The intensity of the transition shows a Curie-type temperature dependence. Based on these observations, the nature of the paramagnetic centers in the carbon SWNTs is discussed. The effect of annealing temperature on the EPR signal of the carbon SWNTs is also presented.
- D-III.3** 9:15 PREPARATION OF BORON NITRIDE NANOCAPSULES BY PLASMA-ASSISTED PULSED LASER DEPOSITION
S. Komatsu, **Y. Shimizu**, **K. Kurashima**, **Y. Moriyoshi**, **K. Okada** and **M. Mitomo**, National Institute for Materials Science, Advanced Materials Laboratory, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Nanocapsules of crystalline boron nitride (BN), whose diameters ranged from 50 to 300 nm, have been synthesized by pulsed-laser-vaporization of BN, where the laser plume was controlled by modulated plasma jet flow field. Their shapes varied from polyhedrons to cocoons and the interlayer spacings along the c-axis were enlarged according to their size and shape (curvature). Without the synchronization of the laser pulses with the plasma modulation, soot-like BN was obtained. This soot-like BN represented the trace of the precursor state which should have been molded into the nanocapsules if it had been just hit by the modulated plasma packet at the appropriate speed.

Symposium D

- D-III.4** 9:30 **REDUCED CATHODOLUMINESCENT LOSS USING PULSED LASER ABLATION COATING PROCESS**
M. Ollinger, V. Craciun, and R.K. Singh, Department of Materials Science & Engineering, University of Florida, Gainesville FL 32611, USA
Using the novel atomic flux coating process (AFCP), the functionality of particles can be enhanced to give their surface a different property from the bulk. The AFCP uses a 248 nm wavelength excimer laser which strikes a solid target under a low vacuum (10-3 torr) and creates a plume of atomic species. These species or nanoclusters are then deposited onto the host particles that are being mechanically agitated to form discrete or continuous coatings (on the host particles) depending on the desired application. The AFCP can be used in a wide range of applications such as: phosphors for flat panel displays, synthesis of ceramic tungsten carbide/cobalt cutting tools, metal hydride based rechargeable batteries, high strength ceramics, etc. In this study, one of the major problems in the Field Emission Display industry, which is the formation of a non-luminescent "dead layer" after prolonged exposure to the e-beam which reduces the cathodoluminescent efficiency of the phosphor was addressed. To prevent the formation of this dead layer, zinc oxide doped with aluminum and indium tin oxide were used in the AFCP to coat the phosphor powder and shield the phosphor core from forming the non-luminescent layer. These coated phosphors showed increased cathodoluminescent lifetimes as compared to the commercially received ZnS:Ag phosphors. Using x-ray photoelectron spectroscopy, it was found that the nano-scale coatings reduced the reactions taking place on the surface of the phosphors.
- D-III.5** 9:45 **ON THE GROWTH MECHANISM OF PULSED LASER DEPOSITED CARBON NITRIDE FILMS**
T. Szörényi and E. Fogarassy, CNRS-PHASE, BP 20, 67037 Strasbourg Cedex 2, France
During the last decade carbon nitride emerged as a material of both fundamental and technological interest, and ablation in N₂ matured as a well-established technique for carbon nitride film fabrication. The overwhelming majority of the film-based studies report upon the correlation between process parameters (nitrogen pressure and laser fluence) and film properties (most notably the chemical structure), with considerably less attention to the mechanism of film growth. Carbon nitride films have been deposited by ArF excimer laser ablation of a graphite target in N₂ atmosphere of pressures tuned between 1 and 100 Pa. Arrival rates of the constituting elements, mass densities and apparent growth rates have been derived from areal densities of both carbon and nitrogen atoms, determined by ion beam techniques, and film thicknesses, measured by a mechanical stylus. Comparative analysis of these data yields useful pieces of information on the growth mechanism in general and its peculiarities in the pressure domain investigated in particular. The results suggest that the formation, composition and microstructure of carbon nitride films fabricated in this process window is governed by gas phase processes.
- 10:00 **BREAK**
- Complex oxide and metallic film growth
- D-III.6** 10:30 **OXYGEN TRAPPING DURING PULSED LASER DEPOSITION OF OXIDE FILMS**
V. Craciun(a), J. Perrière(b), D. Craciun(c) and R.K. Singh(a), (a)Department of Materials Science & Engineering, University of Florida, Gainesville FL 32611, USA, (b)Groupe de Physique des Solides, Universites Paris VII et VI, Paris, France, (c)Laser Department, NILPRP, Bucharest, Romania
The pulsed laser deposition (PLD) technique owes much of its acceptance and success to the growth of high quality complex oxide thin films. The optimum oxygen pressure during growth of these films can be as high as 200 mTorr. Such high pressures will result in a complete monolayer coverage of the substrate by adsorbed oxygen molecules in a time duration much shorter than 1 ms. Because the deposited atoms arrive in a high concentration pulse of short time duration, it is very likely that some of the adsorbed oxygen molecules can be buried beneath the newly grown layers, remaining trapped inside the deposited film. The trapped oxygen is a source for in situ formation during growth and any further annealing treatments of an interfacial layer between the deposited oxide film and the substrate. This is especially troublesome for Si or metal substrates where this interfacial oxide layer can influence the adhesion, crystalline structure and properties of the deposited film. We have investigated using x-ray photoelectron spectroscopy, x-ray diffraction and reflectometry, variable angle spectroscopic ellipsometry and Rutherford backscattering spectrometry the amount and chemical status of the trapped oxygen inside oxide films grown by the PLD technique. The ratio between chemically bonded oxygen and total oxygen content of oxide films grown by the PLD technique depends on the partial oxygen pressure, deposition temperature and the crystalline structure of the film.
- D-III.7** 10:45 **GROWTH AND PROPERTIES OF Sr_{1-x}La_xCuO₂ (x = 0.1 - 0.2) THIN FILMS**
V. Leca, G. Rijnders, D.H.A. Blank and H. Rogalla, University of Twente, Faculty of Applied Physics, Low Temperature Division and MESA+ Research Institute, PO Box 217, 7500 AE Enschede, The Netherlands
Epitaxial thin films of the electron doped infinite-layer phase with composition Sr_{1-x}La_xCuO₂ (x = 0.1 - 0.2) have been grown by Pulsed Laser Deposition on single terminated (TiO₂ or SrO) and mixed termination SrTiO₃ (001). The deposition pressure used was 3 - 30 Pa (O₂, N₂ or N₂+O₂) while the substrates temperature was, mainly, of 550oC. Film growth has been monitored in-situ by high pressure Reflection High Energy Electron Diffraction (RHEED). The surface morphology of the deposited thin films was investigated by Atomic Force Microscopy (AFM). X-Ray Diffraction (XRD) and High-Resolution Transmission Electron Microscopy (HREM) were used for structural characterization. The electrical resistance of the films showed semiconductive or metallic behavior, depending on the deposition conditions. The films deposited in N₂+O₂ contained the infinite-layer related compound, as the main phase, with c-axis of 3.55-3.7 Å and metallic behavior. Post-deposition annealing in air or nitrogen at 450oC for 15-60 min helped to improve the films' crystallinity, according to XRD data, leading also to a decrease of the films' electrical resistance. HREM micrographs showed the presence of a superstructure, probably due to the presence of oxygen vacancies in CuO₂-x planes. No superconductivity was observed so far in these films. Experiments are in progress to yield superconductivity in these films by choosing a substrate with in-plane lattice parameters closed to 4 Å.

- D-III.8** 11:00 PULSED LASER DEPOSITION OF SrTiO₃ ON InP AND INTEGRATION OF FERRO-PIEZO-ELECTRIC Pb_{0.775}La_{0.15}TiO₃
 E. Vasco(a), C. Polop(a), C. Coia(b), A. Kling(c) and C. Zaldo(a), (a)Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco 28049 Madrid, Spain, (b)Escuela Superior de Ciencias Experimentales y Tecnología, Universidad Rey Juan Carlos, Móstoles 28933 Madrid, Spain, (c)Instituto Tecnológico e Nuclear, Estrada Nacional No 10, 2685 Sacavém, Portugal
 The scientific interest on the integration of modified-PbTiO₃ piezoelectric films on direct-gap semiconductors has motivated our study about SrTiO₃ as a buffer layer on (100)InP. The pulsed laser (KrF) deposition, PLD, has been performed in a wide range of experimental conditions: oxygen dynamic pressure, PO₂ = 10⁻⁵-1 mbar, and substrate temperature, T_s = 480-730°C. Despite of the significant lattice mismatch between SrTiO₃ and InP, (a_{InP}-a_{STO})/a_{InP} 33%), [100]SrTiO₃ textured films were grown with a laser fluence J = 3 J/cm² at PO₂ = 10⁻⁵ mbar and in the T_s = 580-630 °C range. AFM measurements reveal a low SrTiO₃ surface roughness, 1% of film thickness, due to periodic rounded structures separated by an average distance = 240 nm. Pb_{0.775}La_{0.15}TiO₃ (PLT) films were deposited by PLD. These films have [001/100]PLT texture with prevalence of [001] oriented grains and a tetragonality c/a 1.010. The PLT surface appears composed by clustered grains and with roughness, 3% of the film thickness. The cross-sections observed by SEM reveal SrTiO₃ films with a compact columnar growth habit, serving as templates for PLT films with a similar microstructure. RBS of these multilayers shows a uniform composition inside the layers, similar to those of the used targets. Relevant diffusion or chemical reactions between layers were not evidenced with the exception of a slight oxidation of the InP substrate and a Pb enrichment at the surface that can be removed with a developed method.
- D-III.9** 11:15 PULSE LASER DEPOSITION OF PZT FOR MEMS APPLICATION
S. Tamir, Israel Institute of Metals, Technion, Israel, S. Berger, Faculty of Material Engineering, Technion, Israel and S. Yeshurun, Rafael Ltd. Israel
 Lead Zirconium Titanate (PZT) materials are widely used in piezoelectric applications such as actuators. The miniaturization processes of devices such as MEMS introduce difficulties in obtaining high quality PZT thin films due to high stresses and deviation from a stoichiometric composition. PZT films deposited by conventional vacuum deposition techniques, such as sputtering, have shown high stresses and poor piezoelectric performance. However, the pulsed laser deposition (PLD) technique has many advantages over the conventional vacuum deposition techniques with respect to deposition of a multi-component systems that result from the short time and high energy beam pulses. The advantages of the PLD technique is demonstrated in this paper on a PZT thin film. The film was deposited by using an Excimer laser operated at 193nm and frequency of 5-10 Hz, which is directed to a solid PZT target. The laser beam has enough energy for both the ablation of the target and photodissociation of the oxygen molecules in the gas phase. The PZT film was deposited to a thickness of 1µm on a heated substrate of about 400°C. The microstructure of the as-deposited film was found to be amorphous but after heat treatment at 570°C for 1 hour the perovskite structure appeared. Chemical analysis of the film showed the desired chemical stoichiometry. The laser parameters were optimized to obtain a continuous film with a smooth surface without droplets morphology. The stress of the film was determined by measuring the change of the specimen radius of curvature due to the film deposition. The polarization hysteresis was determined at room temperature by measuring the change of capacitance with applied electric field. The results are discussed and compared to those reported in the literature for thin PZT films deposited by the sputtering technique.
- D-III.10** 11:30 LASER DEPOSITION OF SHAPE-MEMORY ALLOY FOR MEMS APPLICATIONS
 A. Camposeo, N. Puccini, F. Fuso, M. Allegrini, E. Arimondo, INFN, Dipartimento di Fisica, Università di Pisa, 56127 Pisa, Italy and A. Tuissi, TEMPE/CNR, Sezione di Lecco, 22053 Lecco, Italy
 Great interest has recently grown on the application of shape-memory films to micro-electromechanical systems (MEMS). Scalable character, large power density and bio-compatibility make shape-memory alloys excellent candidates for demanding applications in a wide range of fields. We have applied pulsed laser ablation to deposit NiTi films onto ordinary Si substrates and Si₃N₄ micro-cantilevers. The dramatic dependence of the shape-memory effect on film composition makes NiTi deposition highly demanding. A thorough in-situ diagnostics of the process has been carried out by ion-mass spectrometry, in order to find out optimal parameters for the growth of stoichiometric films. Results, analyzed by statistical methods, demonstrate that cluster formation efficiently occurs during in-vacuum expansion of the ablated material. Films exhibit the solid-to-solid phase transformation responsible for shape-memory, the relevant temperatures being in good agreement with those of target material. Cantilevered films demonstrate thermo-mechanical effects related to shape-memory, which can be of great relevance in a variety of micro-devices, as all-optical switches, micro-manipulators and micro-pumps. Work supported by CNR through P.F. MSTA II "Leghe a memoria di forma".

Symposium D

- D-III.11** 11:45 **FABRICATION OF PLANAR STRUCTURES FOR OPTICAL WAVEGUIDE APPLICATIONS BY PULSED LASER DEPOSITION AND LASER MICRO STRUCTURING**
J. Gottmann, T. Berden, G. Schlaghecken, R. Wagner, A. Horn, E.W. Kreutz, Lehrstuhl für Lasertechnik, RWTH Aachen, Steinbachstr. 15, 52074 Aachen, Germany
Pulsed laser deposition with KrF ($\lambda = 248$ nm, $t = 20$ ns) and ArF excimer laser radiation ($\lambda = 193$ nm, $t = 15$ ns) is used to grow transparent amorphous Al₂O₃, ZrO₂, BaTiO₃, SiO₂ and SiO_xNy thin ceramic films and multilayer structures for optical applications.
The refractive index of the pulsed laser deposited ceramic thin films is measured by ellipsometry and related to kinetic energy of the film forming particles as determined by space- and time-resolved optical emission spectroscopy of the laser induced vapour/plasma. For optical applications the substrates are moved during deposition to achieve a homogeneous film thickness. Optical spectroscopy is used to control the film thickness of the growing layers and the reflectance and transmittance of the multilayer system during film deposition.
Thin ceramic and polymer films and multilayers are micro structured to form optical wave guiding structures using KrF and ArF excimer laser radiation, Nd:YAG laser radiation ($\lambda = 1064/266$ nm, $t = 40$ ps) and Ti:sapphire laser radiation ($\lambda = 800/266$ nm, $t = 100$ fs).
The resulting structures are characterised using optical microscopy, white light interferometry and scanning electron microscopy. Optical wave guiding properties like damping and guided modes are studied exemplarily and compared to simulations using the beam propagation method.
- D-III.12** 12:00 **UV PULSED LASER DEPOSITION FROM AL₂O₃-TiC CERAMIC COMPOSITES**
O. Conde(a), C. Champeaux(b), M.L. Paramis(a), A. Catherinot(b), R. Vilar(c) (a)Dep. Física, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal, (b)Lab. de Science des Procédés Céramiques et de Traitements de Surface, SPCTS, UMR n°6638 CNRS, Faculté des Sciences, 123 Ave A. Thomas, 87060 Limoges Cedex, France, (c)Dep. Engenharia de Materiais, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
Ceramic composites, used as bulk materials or thin films, have numerous applications in different industrial fields, ranging from microelectronics to aerospace. In particular, Al₂O₃-TiC ceramics are promising materials for micromechanical components and are normally used for computer hard disk recording heads sliders.
Aiming to obtain thin films of this material, pulsed laser deposition (PLD) was carried out in vacuum, at varying laser fluence and substrate temperature, by irradiating Al₂O₃-TiC targets with KrF excimer laser radiation.
Structural and chemical composition studies of the deposited thin films by depth-profile AES and GIXRD showed that carbon is totally absent after sputtering a few surface layers and that the films consist mainly of amorphous oxides. Furthermore, a periodic distribution of the metallic elements was observed along the film depth. These results, corroborated by previously obtained time-resolved emission spectroscopy data, can be explained by chemical reactions between alumina and TiC, occurring at high temperature. The periodicity in the distribution of metallic elements can be related to the rotation/translation movement of the target during ablation and the progressive modification of the surface chemical composition during the first laser pulses, previously shown by some of the authors.
- D-III.13** 12:15 **PULSED LASER DEPOSITION OF AMORPHOUS MAGNETIC FILMS**
S. Acquaviva, A.P. Caricato, M. Fernandez, A. Luches, INFN and University of Lecce, Department of Physics, 73100 Lecce, Italy; Z. Frait, Institute of Physics AS CR, 18221 Prague, Czech Republic; E. Majkova, S. Luby, Institute of Physics SAS, 84228 Bratislava, Slovak Republic
Amorphous magnetic materials of the type Co-Cr-Fe-Si-B or Fe-Nb-Cu-Si-B present unique magnetic properties like narrow and steep hysteresis loop, very high magnetic permeability, low coercivity, etc. They are commonly available as ribbons produced by the rapid cooling of the molten alloy. Pulsed laser ablation is a well-suited technique for the deposition of thin films of such materials, since it preserves the stoichiometry and amorphousness of the target. Ribbons of amorphous magnetic alloys (Co₆₇Cr₇Fe₄Si₈B₁₄ and Fe_{73.5}Nb₃Cu₁Si_{13.5}B₉) were ablated in vacuum (~10⁻⁵ Pa) by the KrF excimer laser (3.5 and 7 J/cm²). Films were deposited on oxidized silicon wafers, placed at 80 mm from the target. 20000 successive laser pulses, at the repetition rate of 20 Hz were used to deposit a single film. RBS was used to calculate thickness of the films (40-120 nm, depending on laser fluence and target composition). Their composition resulted close to the one of the respective targets. All the films were shown to be amorphous by XRD investigations. Ferromagnetic resonance studies show that the g-factors are close to the respective bulk values of the dominant ferromagnetic (FM) metal ($g=2.165$ for Co based film, $g=2.18$ for bulk hcp Co). Magnetization of films is lower than that of bulk FM elements. The decrease can be explained by low thickness of the film and concentration of FM metal lower than 100 % (e.g. $4\mu\text{M}=6.9$ kG for 50 nm thick Co based film, which is approx. 40% of the bulk value).
- 12:30 **LUNCH**

Symposium D

Friday, June 21, 2002
Vendredi 21 juin 2002

Afternoon
Après-midi

New trends in PLD

- D-III.15** 14:00 COMPARATIVE STUDIES OF PULSED-LASER DEPOSITION WITH FEMTOSECOND AND NANOSECOND PULSE DURATIONS
E. Millon, LSMCL, Université de Metz, 57078 Metz Cedex 03, France Also at GPS, CNRS UMR 7588, Université Paris VI et VII, 2 pl. Jussieu, 75251 Paris Cedex 5, France
The dynamic and the composition of laser-induced plasmas influence strongly the crystalline and morphological properties of thin films obtained by pulsed-laser deposition (PLD). The nature and the energies of the species emitted from the target will be different depending on the pulse duration used. In particular lasers working in the femtosecond (fs) regime are widely used in surface processing and more recently for the growth of thin films. This fact is linked to the main specificity of the ultrashort pulse duration that is shorter than the time required to transfer the electronic energy to the lattice. Therefore at the opposite of classical nanosecond pulsed laser ablation, no thermal effect could occur while multiphoton absorption process should allow the absorption of photon energy. Nevertheless, when using fs pulses, new phenomena appear connected to the high kinetic energy of the faster species reaching the substrate when using a fs pulse. Moreover depending on the laser intensity, high collision processes occurring in the fs laser-induced plasma leads to the production of aggregates in the gaseous phase. This feature leads to specific effects on the chemical, morphological and structural properties of thin films grown by fs PLD. In this work, we discuss about the results concerning the characteristics of metallic, semiconductor and oxide thin films obtained both by fs and ns PLD related to the dynamic of plume expansion.
- D-III.16** 14:30 CRITICAL DENSITY EFFECTS IN FEMTOSECOND ABLATION PLASMAS AND CONSEQUENCES FOR PLD DEPOSITION
P.P. Pronko, Z. Zhang, and P.A. VanRompay, Center for Ultrafast Optical Science (CUOS) and Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor MI 48109, USA
Laser ablation plumes produced by a single pulse from ultrafast lasers (or a single pulse from nanosecond lasers) consist, in the far field where PLD occurs, of mostly neutral atoms and a small percentage of ionized species (~1%). In certain cases the ionized species may be the component of interest for the deposition and methods for increasing the charged fraction need to be considered. This paper examines these issues and demonstrates new methods for overcoming the plasma critical density limitations encountered when attempting to have a larger amount of energy absorbed into the initially formed single pulse plasma. Using ultrafast techniques one is given an opportunity to deliver precisely controlled time delayed secondary pulses for this purpose. We show how this technique can be used to change the average charge state and ion density of the far field ablation plasma and the various implications this has for thin film deposition. This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy and performed in CUOS facilities provided through the National Science Foundation under STC PHY 8920108
- D-III.17** 15:00 TIME RESOLVED SPECTRAL ANALYSIS OF PLASMA INDUCED BY FS AND NS PULSED LASER ABLATION
O. Albert(a), C. Boulmer-Leborgne(b), **J. Etchepare**(a), E. Millon(c), J. Perrière(c), (a)LOA, CNRS, ENSTA, Ecole Polytechnique, 91761 Palaiseau cedex, France, (b)GREMI, Université d'Orléans, (c)GPS, Universités Paris VI & VII, 2 place Jussieu, 75251 Paris cedex, France
We present the characterization of femtosecond and nanosecond laser induced plasmas by time resolved emission spectroscopy experiments. In both temporal regimes we could discriminate between ionic and neutral particles by measuring their kinetics. Differences between femtosecond and nanosecond processes are evidenced by change in the amount of species ratios and velocities. As an example, the ion to neutral velocity ratio is increased in femtosecond induced plasma. Ionization rate has also been investigated in both femtosecond and nanosecond plasmas. Moreover, in the femtosecond regime we have observed a modification in the kinetics as a function of fluence and number of shots accumulated on the target. These features highlight the predominant role encountered in the ablation process by the increase of defects concentration in the target. These measurements will be illustrated in the cases of semiconductors and metals.
- D-III.18** 15:15 INTERACTION OF EXCIMER LASER PULSES WITH CARBON FILMS ON TRANSPARENT WINDOWS DURING PLD
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Diamond like carbon (a-C:H) films prepared onto vacuum chamber windows by pulsed laser deposition (PLD) have been studied as a function of the target-window distance. Pulses of an ArF excimer laser focused on a graphite target and a-C:H films were formed on the fused silica entrance window. The deposited layers were analyzed by optical and atomic force microscopy and micro Raman spectroscopy. It was an interesting discovery, that a layer formed more effectively on that window surface, where the laser beam passed through, than around it. The properties of the films were different in thickness, color and structure on these two regions. The laser light probably interacted with the window material and resulted in a more effective film formation process. As the layer thickness exceeded a threshold, cracking and partial ablation of the layer was observed. At the ablated areas deposition restarts, but films are formed with different new features.