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June 10 - 13, 2003

SYMPOSIUM I

Functional metal oxides-semiconductor structures

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E-MRS 2003 SPRING MEETING

SYMPOSIUM I

Tuesday, June 10, 2003 — Morning
Mardi 10 juin 2003 — Matin

08:20 **OPENING**

Session I Metal oxides for advanced Si technology –Growth
Session chair: P. Bloechl

I-I.1 8:30 -Invited-

MOS CAPACITOR PHYSICS FOR CRYSTALLINE OXIDES ON SEMICONDUCTORS

R. McKee, Oak Ridge National Laboratory, USA

The barrier height or band offset problem is central to understanding MOS capacitor physics at semiconductor junctions and it is a critical issue for alternative gate oxide development that must be addressed if we are to make any real inroads to the daunting problem of replacing SiO_2 on Si.

The Schottky-Mott formulation of the barrier height theory for a metal/semiconductor junction and Anderson's early band-edge offset study of semiconductor/semiconductor junctions form the basis on which this problem has traditionally been considered; namely a bulk termination treatment of the junction electrostatics. While these theories have certainly been insightful, they consistently misrepresent the barrier height or band-edge offsets because real interfaces, apparently from interfacial structure variations, modify the intrinsic band alignment.

The bulk-termination view of the problem has been enhanced over the years with an ever-increasing formalization of theoretical techniques, but Tung has recently argued, from the perspective of molecular systems in chemical physics, that these techniques and their refinements are not adequately accounting for bond polarization and chemical bonding-induced charge transfer. While this issue can be debated, what is certain is that whether first principles theory is used or whether the molecular systems approach is applied, a lack of detailed knowledge about the interface structure often leaves us in a quandary. The quandary is that we do not know how to predict, apriori, the evolution of the physical and electrical structure of the interface when two materials are joined. This is clearly apparent for even the simplest of systems, and we have no guidance on this issue for the important problem of barrier height adjustment for alternative gate oxides on silicon.

Here we will present a generalization of Tung's view by expanding it to show that the interface, even at monolayer thicknesses, should be identified as a distinct phase both in a thermodynamic and electrodynamic sense. First principles theory then shows us that the interface phase does two things: it constrains the physical structure of the junction, and it sets the electrical boundary conditions that establish the junction electrostatics.

In this talk we will introduce and analyze energy band diagrams that are part of the barrier height problem for crystalline oxides on semiconductors (COS). We will use these data to draw a clear distinction between a bulk termination view of the problem and our interface phase thesis. An immediate outcome of this distinction is functionalization of the barrier height concept itself. This functionalization (Figure 1) is via a "Coulomb Buffer" that is identified with charge transfer and ionic bonding between alkaline earth metal atoms in an interfacial silicide and oxygen in the oxide dielectric. This buffer is apparent here from the structure specifics of heteroepitaxy, but it is an electrodynamic concept with far-reaching implications.

I-I.2 9:10

MBE GROWTH OF EPITAXIAL GATE OXIDES ON SILICON: ISSUES FOR CMOS INTEGRATION

G.J. Norga(a), J. Fompeyrine(a), A. Guiller(a), J.P. Locquet(a), H. Siegwart(a), C. Marchiori(a,b), D. Halley(a) and C. Rossel(a), (a)IBM Research Division, Zurich Research Laboratory, Sauemerstrasse 4, 8803 Rueschlikon, Switzerland, (b)Laboratorio MDM - INFM, Via C. Olivetti 2, 20041 Agrate Brianza (MI), Italy

The interest in crystalline oxides on silicon (COS) grown by MBE has increased dramatically in recent years because of their potential, among others, as "ultimately scaled" gate dielectrics for silicon CMOS. Notwithstanding the unique advantages of COS over both amorphous and polycrystalline high-k systems, the long cycle times inherent to MBE represent a serious challenge for their successful integration with silicon CMOS. In this paper we present a reduced cycle time COS process, consisting of 4 steps: (1)the preparation of a clean, 2x1 reconstructed Si (100) surface; (2)the deposition of a monolayer of alkaline earth metal (3)oxygen introduction and growth of several monolayers of an epitaxial alkaline earth oxide at low temperature (200C); (4)growth of a SrZrO3 perovskite layer. Traditionally, step 1 is achieved by UHV "flashing" of a thin native or chemical silicon oxide at ~ 800C in the MBE. Next, step 2 is performed at the same elevated temperature to obtain the formation of an alkaline earth disilicide diffusion barrier. The long times needed for heating to and cooling from 800 C reduce the throughput of the MBE significantly. We demonstrate that the oxide flashing can be avoided, and instead a lower temperature (Tmax =500C) HF-last-based surface preparation route can be used, resulting in clean, 2x1 reconstructed Si (100) surfaces prior to growth. By depositing the full alkaline earth metal monolayer at low temperature (T = 200C), high-quality epitaxial SrZrO3 layers could be grown within considerably shorter cycle times. In conclusion, we present a blueprint for future MBE tool and process development in view of meeting throughput requirements for integration in a high-volume, advanced CMOS manufacturing environment.

I-I.3 9:30

LANTHANUM ALUMINATE ON SILICON FOR ALTERNATIVE GATE DIELECTRIC APPLICATIONS

L.F. Edge, V. Vaithyanathan, J. Lettieri and D.G. Schlom, Department of Materials Science and Engineering, Pennsylvania State University, USA, S.A. Chambers, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, USA, Y. Yang and S. Stemmer, Materials Department, University of California, Santa Barbara, USA, H. Li, Y. Wei and K. Eisenbeiser Physical Science Research Laboratory, Motorola Labs, USA

LaAlO$_3$ is one of the most promising alternative gate dielectrics for the replacement of SiO$_2$ in silicon MOSFETs. Single crystalline LaAlO$_3$ is known to have a dielectric constant of 24 and an optical bandgap of 5.6 eV. The band offsets between LaAlO$_3$ and Si have been predicted to be in the range 2.1 to 3.5 eV for electrons and 1.0 to 1.9 eV for holes.^{1,2} It will be shown that LaAlO$_3$ is stable in contact with silicon under standard MOSFET processing conditions. Epitaxial Si has been grown by MBE on single crystals of LaAlO$_3$ and annealed at 1026 °C, which is a standard implant activation anneal for MOSFETs, and the interface remained stable and free of SiO$_2$. A major challenge in the growth of alternative gate dielectrics on Si is the formation of unwanted SiO$_2$ at the interface. One technique to prevent the formation of SiO$_2$ is to grow in a low temperature / excess oxidant regime. We have investigated the oxidation kinetics of Al and La, both individually and together (codeposition), to determine the minimum oxygen partial pressure required to achieve fully oxidized LaAlO$_3$. Using these optimized conditions, amorphous LaAlO$_3$ films as thin as 10 Å have been grown on silicon by MBE. XPS analyses indicate that the films are fully oxidized and show no SiO$_2$ at the interface, even after prolonged exposure of the films to air.

[1]J. Robertson, MRS Bull. 27(3) (2002) p. 220. ^{2}P. W. Peacook and J. Robertson, J. Appl. Phys. 92 (2002) p. 4713.

I-I.4 9:50

PULSED LASER DEPOSITION OF THIN PRxOy FILMS ON SI(100)

D. Wolfframm(a), M. Ratzke(a), M. Kappa(a), M.J. Montenegro(b), M. Döbeli(b), Th. Lippert(b) and J. Reif(a), (a)IHP/BTU JointLab, and BTU Cottbus, LS Experimentalphysik II, Universitaetsplatz 3-4, 03044 Cottbus, Germany, (b)Paul Scherrer Institut, 5232 Villigen, Switzerland

PrxOy thin films have been grown by Pulsed Laser Deposition (PLD) on Si(100) surfaces. The chemical composition of PrxOy layers with different thickness was investigated using core level (Si 2p, Pr 3d, O 1s) x-ray photoelectron emission spectroscopy (XPS). The line shape analysis of emission spectra does not indicate any interfacial mixing but suggests the formation of a silicate (Si-O-Pr) at the PrxOy/Si interface accompanied by the appearance of a silicon sub-oxide state. Although Pr6O11 was used as target material, XPS spectra have shown that the PrxOy films consist of two Pr-O sub-oxides (Pr2O3, Pr6O11). The intensity ratio of the two sub-oxides did not change with increasing PrxOy layer thickness but the Pr and O core levels are slightly shifted to lower binding energy. Using Rutherford Backscattering (RBS) spectroscopy for the Pr6O11 target material we already found a much too high oxygen to praseodymium intensity ratio than expected. Not only the chemical instability of the Pr6O11 target material could be the reason for the decomposition but also the strong hygroscopic behaviour of this material. C-V measurements for PrxOy-layers of different thickness yield an average dielectric constant of k=33 for the amorphous PrxOy layers on Si(100). That corresponds to an EOT of about 1.05 nm for a 9.7 nm PrxOy layer.

10:10 **BREAK**

I-I.5 10:30 -Invited-

DEVELOPMENT OF EPITAXIAL OXIDES ON SEMICONDUCTORS BY MOLECULAR BEAM EPITAXY

Ravi Droopad, Zhiyi Yu, Jay Curless, Mike Hu, Karen Moore, Dan Marshall, Brad Craigo, Dirk Jordan, Corey Overgaard, Hao Li, Yong Liang, Motorola Labs, Physical Sciences Research Laboratories, 7700 S. River Parkway, Tempe AZ 85226, USA

The semiconductor industry is facing the major problem of replacing the gate dielectric as the reduction of the dimensions of Si CMOS devices continues. Presently SiO2 is being used but at thickness below 20 Å, it suffers from high tunneling leakage current and reliability problems. Alternative high-k materials to replace SiO2 need to be developed as soon as possible. The alkaline earth oxides such as epitaxial barium strontium titanate (BaxSr1-xTiO3) and lanthanum aluminate (LaAlO3) have a substantially higher dielectric constant than SiO2 and are ideal candidates for gate dielectrics. These oxides by virtue of their epitaxial nature can be also be used to enable other functional oxides on semiconductors for the realization of novel integrated devices incorporating oxides and semiconductors. Examples include ferroelectric memory elements, surface acoustic wave devices and magnetic devices for spintronic applications. In this presentation we will present our approach in depositing high quality epitaxial oxide layers on silicon. Growth is initiated in an MBE system on a (2x1) reconstructed Si(100) surface with elemental sources and oxygen, and proceeds with a (1x1) reconstruction. The interface evolution is studied by in-situ XPS and SPM measurements. Ex-situ analysis of the oxide layer suggests that growth proceeds with a 45° rotation of the lattice with respect to the silicon lattice to accommodate the large lattice mismatch between the oxide layer and silicon.

I-I.6 11:10

GATE OXIDE ATOMIC LAYER DEPOSITION STUDIED BY IN SITU INFRARED SPECTROSCOPY

M.M. Frank(a), S. Dörmann(b), Y.J. Chabal(a,b,c), S. Sayan(a), E. Garfunkel(a), G.D. Wilk(d), M.L. Green(c,e), M.-Y. Ho(c), A. Delabie(e), B. Brijs(e), (a)Department of Chemistry and Laboratory for Surface Modification, and (b)Department of Physics, Rutgers University, Piscataway NJ 08854, USA, (c)Agere Systems, Allentown PA 18109, USA, (d)ASM America, Phoenix AZ 85034, USA, (e)IMEC, Kapeldreef 75, 3001 Leuven, Belgium

An in situ spectroscopic approach will be presented that opens the way to improving interface engineering during atomic layer deposition (ALD) and chemical vapor deposition (CVD) of high-permittivity (high-k) dielectrics on silicon. Specifically, we compare Al2O3 and HfO2 deposition on hydrogen-passivated, oxidized, and chemically functionalized Si substrates. With infrared spectroscopy, we can identify the relevant surface species (e.g. -OH, -H, organic groups, oxides) in situ with submonolayer sensitivity. Furthermore, the growth and structure of thin oxide films can be investigated through detection of their characteristic phonon modes. For growth on H-passivated Si, where an incubation period and unwanted interfacial SiO2 formation adversely affect control over device properties, we find that the metal precursor (e.g. trimethylaluminum, TMA), can initiate nucleation on this surface, instead of the oxidizing agent (e.g. water) as previously believed. These results suggest a novel method to activate hydrogen-terminated silicon for Al2O3 and HfO2 deposition, namely using extended metal precursor pre-exposure, and to minimize the formation of interfacial SiO2, namely by initiating Al2O3 growth at room temperature. Enhanced HfO2 growth is indeed demonstrated by Rutherford backscattering (RBS). We have also followed thermal processing in situ, complementing our earlier ex situ X-ray diffraction, medium energy ion scattering, and photoemission studies and have thus been able to quantify high-k phase behavior and interfacial SiO2 regrowth.

I-I.7 11:30

ATOMIC LAYER DEPOSITION OF DIELECTRIC SILICATE FILMS

Kaupo Kukli(a)*, Mikko Ritala(a), Markku Leskelä(b), Timo Sajavaara(b), Juhani Keinonen(b), Rama I. Hegde(c), David C. Gilmer(c), Philip J. Tobin(c), (a)University of Helsinki, Department of Chemistry, P.O.Box 55, 00014 Helsinki, Finland, (b)University of Helsinki, Accelerator Laboratory, P.O.Box 43, 00014 Helsinki, Finland, (c)Motorola, Advanced Products Research and Development Laboratory, 3501 Ed Bluestein Blvd., Austin TX 78721, USA, *Also at: University of Tartu, Institute of Experimental Physics and Technology, Tähe 4, 51010 Tartu, Estonia

SiO2 has been the basic dielectric material in field-effect transistors and memory devices. Upon shrinking device dimensions, HfO2 is considered as one of the most promising candidates to replace SiO2 and atomic layer deposition (ALD) as a prospective growth technique. However, epitaxy of pure HfO2 on Si(100) is not realized and the Si surface remains defective and unstable. The formation of interfacial SiO2 or Si-Hf-O occurs. Since the interfacial layers can not be avoided, one should consider controlled growth of Hf-Si-O. The silicate/silicon interface may not be as defective as the HfO2/Si interface. Herewith the carrier mobility in the case of Hf-Si-O can exceed that in HfO2 based transistors. The permittivity of the amorphous silicate remain between the values characterizing SiO2 and HfO2.

In this work, amorphous 2-200 nm thick Hf-Si-O and Zr-Si-O thin films were grown by ALD at 300-500 ºC. The films were grown via alternating exposure of the substrate surface to gaseous Si(OC2H4)4 and metal halide (HfI4 or HfCl4) flows. Water was used as an additional oxygen precursor in hydrolysis reactions. The silicate films were also grown without H2O. The composition of the films was fairly insensitive to the growth temperature, pulsing sequence and metal precursor, and was uniform throughout the film thickness, approaching the stoichiometry of HfSiO4. The relative content of Hf (Zr) could be increased by introducing separate intermittent metal oxide growth cycles. The effective permittivity of silicates varied between 6 and 10. The films contained some residual carbon, chlorine and iodine in the amounts less than 0.5 at. %.

I-I.8 11:50 YTTRIUM OXIDE, Y2O3, THIN FILMS: MICROSTRUCTURE-INTERFACIAL REACTIONS-INTERNAL STRESS AND DIELECTRIC PROPERTIES

R.J. Gaboriaud, F. Paumier, F. Pailloux and P. Guerin., Laboratoire de Métallurgie Physique, Université de Poitiers, CNRS-SP2MI, BP 301792, 86962 Chasseneuil-Futuroscope cedex, France

Y2O3 has recently attracted much attention because of the large variety of its technical applications in optoelectronic wave guide and metal oxide-semiconductor devices. Owing to its high thermodynamic stability and its rather high dielectric constant (12-18) in comparison with the SiO2 value (3.9) Y2O3 is under consideration as potential replacements for SiO2. Thin films of Y2O3 have been deposited by laser ablation and ion beam sputtering (IBS) with and without secondary ion beam assistance (IBAD) on different substrates, MgO, SrTiO3 and Si. Internal strain(stress) measurements were performed by means of X-ray diffraction experiments on as-deposited films and films annealed either in a quartz tube furnace or in-situ in the X-ray goniometer. Strong compressive stresses are observed whatever the substrate is. Epitaxy relationships (Y2O3/MgO or SrTiO3), interfacial reactions (Y2O3/Si), kinetic of the stess relaxation phenomena (Y2O3/Si) and microstructure on cross section samples studied by HRTEM are presented and discussed in terms of oxygen network behavior and the related crystallographic phase shift possibility. Electrical properties of the MOS heterostructure Al- Y2O3-Si are studied through the C-V and leakage current measurement as a function of the stress observed in the thin oxide film. A 10+6 factor is obtained between the leakage current in the IBS as-deposited and stress free samples respectively.

12:10 **LUNCH**

Session II: Metal oxides on silicon: modeling and experimental studies of interfaces and defects

Session chair: A. Stesmans

I-II.1 13:30 -Invited-

AB-INITIO SIMULATIONS ON INITIAL GROWTH STEPS OF HIGH-K OXIDES ON SILICON

Peter E. Bloechl(a), Clemens J. Foerst(a,b), Christopher Ashman(a), (a)Clausthal University of Technology, Germany, (b)Vienna University of Technology, Austria

One of the most acute challenges of semiconductor industry is the introduction of new so-called high-K gate oxides. Conventional SiO2 based gate oxides need to be replaced in order to avoid quantum mechanical leakage currents through ultrathin oxide layers. High-K oxides provide the characteristics of an ultrathin gate oxide at a larger thickness and thus avoid tunneling currents. The integration of High-K oxides in silicon technology poses the challenge of forming atomically well-defined interfaces. State of the art electronic structure calculations and ab-initio molecular dynamics simulations of the deposition of metals onto silicon and the formation of oxides have been performed. Atomic structure, chemical binding and electronic structure have been analyzed for a wide range of different adsorption structures of Zr, Hf, and Sr on silicon. Our simulations shed light on silicide formation with early transition metals and the step-wise formation of High-K oxide on silicon (001).

I-II.2 14:10 -Invited-

INTERFACE AND DEFECT STRUCTURES IN EPITAXIAL OXIDE THIN FILMS

J.W. Seo, Institute of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Perovskite-type compounds ABO3 represent one of the most actively studied materials classes. The transition element B can take a mixed valence depending upon oxygen or A-site doping, and many interesting properties can be obtained, such as high-TC superconductivity, colossal magnetoresistance, ferroelectricity or high dielectric constants.

Nowadays, epitaxial thin films of complex oxides can be produced with structural perfection by molecular beam epitaxy. In particular, the recent achievement to grow complex oxides epitaxially on Si opens the door for their implementation in current devices. Nevertheless, their integration is hindered by aspects such as i) thermodynamic instability against Si, ii) large oxygen diffusion coefficients favoring an amorphous SiO2 interfacial layer and iii) a mixed valence induced tendency towards a high "intrinsic" defect density. These critical aspects can lead to poorly defined interfaces and charge traps which affect the electrical properties in a high K stack. In this contribution, we review representative defect structures, interface effects and oxidation channels in perovskite materials; examples are given in the systems such as LaFeO3, LaTiOx and La2CuO4. Then, we turn to the structure and stability of the complex oxide/Si interface taking thermodynamic and kinetic considerations into account. We show that the formation of SiO2 interfacial layer is not only determined by the oxygen pressure during growth but also by the oxygen diffusion channels, which can be correlated to the presence of planar defects. As examples, the results on epitaxial growth of LaZrOx and SrTiOx layers on Si are presented.

I-II.3 14:50

INTERFACE ATOMIC STRUCTURE AND BAND OFFSETS AT HIGH K OXIDE:Si INTERFACES

P.W. Peacock, J. Robertson, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, U.K.

High dielectric constant oxides are needed to replace silicon dioxide as the gate oxide in future CMOS devices. The band offsets should exceed 1V to inhibit leakage currents. The atomic structure and bonding across the interface between representative high K oxides, ZrO2 and SrTiO3, and Si have been modeled, and their electronic structure and band offsets have been calculated. Atomic models of the epitaxial interfaces Si:ZrO2(100), Si:ZrO2(111), Si:SrO(100), Si:SrTiO3(100) are used as examples. Because the bonding in the oxides is ionic, the bonds across the interface must satisfy more conditions to give charge neutrality and an absence of interface states, than for the simpler case of the SiO2:Si interface. Models of Si:ZrO2(100) and Si:ZrO2(111)are made with both Zr-Si and Zr-O bonded interfaces. The total energy of the interfaces is found to compare their stabilities. It is found that changing the oxide termination can vary the band offset by 0.5 eV, compared to those values previously determined by matching bulk charge neutrality levels [1].

[1] J Robertson, J Vac Sci Technol B 18 1785 (2000)

I-II.4 15:10

STRUCTURAL CHARACTERIZATION OF EPITAXIAL Y2O3 ON Si(100) AND OF THE Y2O3/Si INTERFACE

S. Spiga, C. Wiemer, M. Fanciulli, Laboratorio MDM-INFM, 20041 Agrate Brianza, Italy, F. D'Acapito, INFM-OGG c/o ESRF,GILDA CRG, 38043 Grenoble, France, F. Boscherini, INFM and Department of Physics, University of Bologna, 40127 Bologna, Italy, A. Dimoulas, G. Vellianitis, G. Mavrou, MBE Laboratory, Institute of Materials Science, National Center for Scientific Research DEMOKRITOS, 15310 Athens, Greece

The search for high dielectric constant (k) oxides to replace SiO2 in the development of the next generation ULSI devices is a formidable task. Stringent requirement related to electrical and structural properties, interface engineering and thermal stability must be fulfilled. Several oxides, such as Ta2O5, ZrO2, HfO2, Y2O3, as well as silicates are currently considered. Epitaxial crystalline oxides on silicon could offer advantages such a higher dielectric constant and better control of the interfaces with respect to other growth techniques. Y2O3 grows hetero-epitaxially on Si(100) and it is a good candidate for SiO2 replacement due to its predicted thermodynamic stability in contact with silicon and its relatively high k (14-18). In this contribution we report on a structural study of Y2O3 films, 1.5 to 20 nm thick, grown on Si(100) by electron beam evaporation in a MBE system at 450 °C. X-Ray absorption spectroscopy (XAS) measurements at the Y K-edge (17038 eV) were performed at the GILDA beam line of the European Synchrotron Radiation Facility in Grenoble (France). In particular, XAS in grazing incidence geometry (Refl-EXAFS) was used to study the interface atomic environment and the evolution of the epilayer structure with thickness. Preliminary XAS measruments at the O k-edge (performed at the BEAR beamline of ELETTRA, Trieste, Italy) will also be discussed. Complementary information on the epitaxial quality, the film thickness and the roughness of the surface and of the interface were obtained by x-ray diffraction (XRD) and x-ray reflectivity (XRR).

I-II.5 15:30

AB INITIO INVESTIGATION OF REACTION PATHWAYS DURING HIGH-K GATE OXIDES ATOMIC LAYER DEPOSITION

L. Jeloaica(a), A. Estève(a), M. Djafari Rouhani(a,b), D. Estève(a), G. Mazaleyrat(a), (a)Laboratoire d'Analyse et d'Architecture des Systèmes, LAAS-CNRS, 7 Ave. Colonel Roche, 31077 Toulouse, France, (b)Laboratoire de Physique des Solides, Univ. Paul Sabatier, 31062 Toulouse Cedex, France

We present an ab initio investigation of the initial stage of atomic layer deposition of HfO2, ZrO2 and Al2O3 high-k films, by studying the decomposition of HfCl4, ZrCl4 and Al(CH3)3 precursor molecules on OH-terminated SiO2 surface. For each precursor, possible reaction pathways and associated activation barriers are determined, compared and discussed. For all precursors, the reaction proceeds through the formation of intermediate complexes having equivalent formation energies and resulting in HCl and CH4 formation with activation energies of 0.88, 0.91 and 1.04 eV for Hf, Zr and Al based precursor, respectively. The reaction product of Al(CH3)3 decomposition is found to be more stable than its chemisorbed intermediate complex as compared to the endothermic decomposition of HfCl4 and ZrCl4 chemisorbed precursors. The hydrolysis of the end chemisorbed products of both ZrCl4 and HfCl4 reactions decomposition is also investigated. Here, activation barriers around 1 eV are determined.

I-II.6 15:50

AB-INITIO STUDY ON THE SURFACE STRUCTURES OF GAMMA-AL2O3

Henry Pinto and Simon Elliott, NMRC, UCC, Lee Maltings, Prospect Row, Cork, Ireland

The controlled growth of alumina films by atomic layer deposition (ALD) is of great interest to the electronics industry, as high-k dielectrics are being sought for the next-generation MOSFETS [1]. Many aspects of the surface structure and reactivity of alumina are still unknown, but are amenable to computation. We present a theoretical study of the alumina polymorph gamma-Al2O3. The calculations are based on density functional theory (DFT). In order to predict the bulk crystal structure of g-Al2O3, we have compared the total energies of 17 non-equivalent possible structures of a 40 atom cell, derived from the perfect spinel by replacing the Mg by Al and removing Al. The lowest energy structure has widely separated Al-vacancy sites, in agreement with previous works [2]. The second part of this work deals with alumina surfaces. For gamma-Al2O3, we estimated the energy of several relaxed surfaces, namely (001), (111) and (110). The atomic and electronic structure of the most stable (001) surface is discussed. Finally, we studied the interaction of alumina surfaces [both (001) gamma-Al2O3 and (0001) alpha-Al2O3] with ALD precursors H2O and Al(CH)3 and these results are discussed in light of available experimental data. References

[1]G.D. Wilk, R. M. Wallace, J. M. Anthony, J. Appl. Phys. 89, 5243 (2001).
[2]C. Wolverton, K. C. Hass, Phys. Rev. B 63, 024102 (2001).

16:00 **Event of general interest organized by Symposium A**

Session III: Magnetic oxides
Session chair: J.P.-Locquet and J.W. Seo

I-III.1 14:00 -Invited-

ROLE OF THE INTERFACE IN OXIDE-BASED MAGNETORESISTIVE SYSTEMS

J.M. de Teresa, D. Serrate, P.A. Algarabel, L. Morellon, M.R. Ibarra, Instituto de Ciencia de los Materiales de Aragón, Universidad de Zaragoza-CSIC, Facultad de Ciencias, Zaragoza 50009, Spain

In this contribution I will focus on two types of magnetoresistive systems where the interface (oxide-oxide or metal-oxide) is known to play a crucial role. The first type is artificial magnetic tunnel junctions, which consist of two ferromagnetic electrode layers separated by an insulating barrier layer (normally an oxide). These systems show tunnel magnetoresistance (TMR) and have potential applications in non-volatile memories (MRAM). In the beginning it was thought that the TMR was only controlled by the spin polarisation of the ferromagnetic electrodes. However, some results appeared in the last 4 years suggest that the TMR can be tailored by interface effects between the electrode and the barrier. I will discuss some results on tunnel junctions with magnetic oxide electrodes as well as with metal electrodes. The second type of systems to discuss is polycrystalline magnetic oxides, which can show intergrain magnetoresistance (IMR) when intergrain tunnelling is the main conduction mechanism. These systems have potential applications as low-field magnetoresistive sensors. I will discuss some results obtained with magnetic oxides like manganites, double perovskites and magnetite. The MR response seems to be controlled not only by bulk properties (spin polarization, saturation field and TC) but also by the magnetic state of the grain surface. Experiments up to 60 T indicate that the grain surface magnetization is difficult to saturate.

I-III.2 14:40

HALL EFFECT STUDY OF MAGNETORESISTIVE PEROVSKITE LaNi0.5Co0.5O3 THIN FILMS

J. Androulakis(a,b) and J. Giapintzakis(a,c), (a)Institute of Electronic Structure and Laser, Foundation for Research and Technology–Hellas, P.O. Box 1527, Vasilika Vouton, 71110 Heraklion, Crete, Greece, (b)Department of Chemistry, University of Crete, Leoforos Knossou, 71409 Heraklion, Crete, Greece, (c)Department of Materials Science and Technology, University of Crete, P.O. Box 2208, 71003 Heraklion, Crete, Greece

We study the Hall effect of LaNi0.5Co0.5O3 magnetoresistive oxide thin films grown on Si (100) substrates by pulsed laser deposition. The conduction mechanism is found to depend on both types of carriers, namely electrons and holes. Analysis of the Hall data in the framework of Chamber's two-band conduction model suggests that the observed magnetoresistance at low temperatures arises from an electron-mobility enhancement effect. On the other hand, ligand-holes seem to be responsible for the stabilization of the strong ferromagnetic interactions present in the compound. To our knowledge, this is the only other experimental observation, besides X-ray absorption experiments, consistent with ligand-hole ferromagnetism in cobaltites in agreement with theoretical predictions.

I-III.3 15:00

ORIGIN OF THE INCREASED RESISTIVITY IN EPITAXIAL FE3O4 FILMS

W. Eerenstein, T.T.M. Palstra and T. Hibma, University of Groningen, Nijenborg 4, 9717 CR Groningen, The Netherlands, S. Celotto, University of Liverpool, Brownlow Hill, Liverpool L69 3BX, U.K.

Magnetite, Fe3O4, has received a lot of interest due to the combination of several intersting properties. It is ferrimagnetic with a high Curie temperature (858 K) and it is conducting with a large degree of spin-polarisation. Furthermore, epitaxial thin films exhibit magneto-resistance. This has been related to the presence of anti-phase domain boundaries. An anti-ferromagnetic coupling is present at a large fraction of these boundaries, blocking the spin-polarized conduction electrons. The resistivity of these films is enhanced with respect to the bulk and increases with decreasing film thickness. We will show that this can be related to a significant decrease in the domain size with decreasing film thickness. The total conductivity of the Fe3O4 films has been modelled as a function of the bulk- and boundary conductivities using the effective medium approximation.

I-III.4 15:20

STRUCTURAL AND MAGNETIC PROPERTIES OF Sr2FeMoO6-X DOUBLE PEROVSKITE

S. Colis(a,b), G. Pourroy(a,b), F. Bailly(b), M. Lacroix(b), A. Dinia(a,b), (a)IPCMS-GMI, 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France, (b)ECPM, 25 rue Bequerel, 67087 Strasbourg Cedex 2, France

Ferromagnetic oxides like Sr2FeMoO6-X double perovskite are very attractive since they presents ferromagnetic order above room temperature. Moreover, such system presents a band structure which leads to a large magnetoresistance, being very interesting for spin electronics applications. Bulk Sr2FeMoO6-X double perovskite have been prepared from appropriate mixtures of SrCO3, MoO3, and Fe(C2O4)·2H2O using the ceramic method. The structure of the final double perovskite has been analyzed by x-ray diffraction. In addition to the perovskite phase, other phases like SrMoO4 and Fe have been observed for different preparation conditions. The magnetic properties are found to vary strongly with the sintering temperature and with the redox N2/H2 flow. This flow is established to eliminate the oxygen excess. The highest magnetization value is found for the sintering temperature of 1000°C and for a low flow of N2/H2. This magnetization reaches 27 emu/g and 47 emu/g at 18 kOe respectively at room temperature and at 5K. These low values indicate a non-negligible amount of antisite defects and/or an incomplete reaction leading to the final perovskite compound.

15:40 **BREAK**

I-III.5 16:00 LASER ABLATION OF FERROMAGNETIC Co:ZnO FILMS DEPOSITED FROM Zn AND Co METAL TARGETS ON (0001) Al2O3 SUBSTRATES

W. Prellier, A. Fauchet, B. Mercey, Ch. Simon and B. Raveau}, Laboratoire CRISMAT, CNRS UMR 6508, 6 Bd Marechal Juin, 14050 Caen Cedex, France

Diluted Magnetic Semiconductors of III-V types have been obtained by doping semiconductors with magnetic impurities. These materials are very interesting due to their potential applications for spintronics. However, the low Curie temperature (TC) has limited their interest. Based on the theoretical works, several groups have studied the growth of Co-doped ZnO films which is a good candiate having a high TC. Different Curie temperature have been obtained. This controversy between research teams may result from the growth method used and/or from the growth conditions.
Therefore, the objective of this investigation is two fold : first to develop an accurate method to grow the Co:ZnO films with a precise doping and second to understand their properties. To achieve such a goal, Co-doped ZnO films were deposited from two pure metal targets of Zn and Co. High quality Co-doped ZnO thin films have been grown utilizing the pulsed laser deposition technique on (0001) Al2O3 substrates performed in an oxidizing atmosphere, using Zn and Co metallic targets. We firstly optimized the growth of ZnO in order to obtain the less strained film. Highly crystallized Co:ZnO thin films are obtained by an alternative deposition from Zn and Co metal targets. This procedure allows an homogenous repartition of the Co in the ZnO wurzite structure which is confirmed by the linear dependance of the out-of-plane lattice parameter as a function of the Co dopant and the transmission electron microscopy study. In the case of 20% Co doped, the film exhibits ferromagnetism with a Curie temperature close to the room temperature. Correlations between the preparation, the microstructure, the structure and the physical properties of the films will be presented.

I-III.6 16:20 MAGNETIC PROPERTIES OF Co/Al2O3/Co JUNCTIONS DEPOSITED BY ULTRA HIGH VACUUM ION BEAM SPUTTERING

C. Maunoury(a), N. Marsot(a) and C. Schwebel(a), C. Clerc(b), (a)Institut d'Electronique Fondamentale, Université Paris-Sud, Bât. 220, 91405 Orsay Cedex, France, (b)Centre de Spectroscopie Nucléaire et de Spectrométrie de Masse, Université Paris-Sud, Bât. 108, 91405 Orsay Cedex, France

We are currently studying Co/Al2O3/Co magnetic tunnel junction deposited on a (111) silicon substrate by Ar+ ion beam sputtering using two different targets (Co, Al) under ultra high vacuum (UHV). To form the Al2O3 insulator barrier, oxygen is introduced into the chamber during the aluminum target sputtering. The oxidation process of aluminum oxide barrier is optimized by Auger Electron Spectroscopy (AES) and Rutherford Backscattering Spectroscopy (RBS). Conditions of ultra low deposition rate of Co and Al2O3 are defined using lithography process.
We use Magneto-Optical Kerr Effect (MOKE) to investigate the magnetic anisotropy of the thin films. Magnetic properties are determined for different Co layer thicknesses (from 20 Å to 80 Å).

I-III.7 16:40 ZnO - BASED SEMIMAGNETIC SEMICONDUCTORS: GROWTH AND MAGNETISM ASPECTS

A.I. Savchuk, P.N. Gorley, V.V. Khomyak, S.K. Ulyanytsky, S.V. Bilichuk, Dept. of Phys. Electronics and Non-Traditional Energy Sources, Chernivtsi National University, 58012 Chernivtsi, Ukraine, A. Perrone, University of Lecce and National Nanotechnology Laboratory of Institute of Matter Physics, 73100 Lecce, Italy, P.I. Nikitin, General Physics Institute, 117942 Moscow, Russia

Zinc oxide - based semimagnetic semiconductors belong to perspective spintronic materials because of recent prediction of ferromagnetism at room temperature [1]. We report here on growth and magneto-optical characterization of single crystals and thin films of Zn1-xMnxO solid solutions. The samples of the single crystals with $0 < x < 0.1$ have been grown by the technique of sublimation. To obtain thin films we used rf magnetron sputtering and pulsed laser ablation techniques. Magneto-optical experiments (magnetoabsorption and Faraday rotation spectra) were carried out at temperature range of (4.2-300) K in magnetic fields up to 5 T. The observed features in magneto-optical properties of Zn1-xMnxO crystals and thin films can be explained in framework of paramagnetic state which is typical for II1-xMnxVI semimagnetic semiconductors. On the other hand, the revealed ferromagnetic behavior for several samples perhaps is associated with some kind of precipitations in these samples.
Research is supported by INTAS grant No.2001-0354.
[1] T.Dietl, H.Ohno, F.Matsukura, J.Cibert, D.Ferrand, Science,287,1019 (2000).

I-III.8 17:00 EPITAXIAL STRAIN IN FUNCTIONAL CERAMIC THIN FILMS - A CASE STUDY FOR La-Sr-Mn-O

Hanns-Ulrich Habermeier, MPI-FKF, Heisenbergstr. 1, 70569 Stuttgart, Germany

In ceramic materials their functionalities such as ferromagnetism, superconductivity or ferroelectricity strongly depend on the localarrangement of the anion-cation building blocks within the crystallographic unit cell. Using the chemical route by substituting cations of different Ionic radii structural changes of the crystal lattice and thus their physical properties can be tailored at an atomic scale. An alternative to the chemical route makes use of the epitaxial strain in thin films with a controllable lattice misfit of substrate and film. Pseudomorphically grown thin films exhibit an adjustable lattice strain which in turn affects the physical properties by a local distortion of the anion-cation building blocks. This principle is explored experimentally using doped rare earth manganites.
In addition to the CMR effect, they can exhibit a metal-insulator transition at a temperature, TMI, close to Tc where localised electrons become itinerant. Both, double exchange and Jahn-Teller [JT] lattice distortions, play an important role in determining their electronic and magnetic properties. In this contribution the magnetotransport properties of ultrathin La-Sr-Mn-O films are explored are analysed and discussed within the frame of magnon-phonon scattering and and the percolative nature of the metal-insulator transition.

I-III.9 17:20 RELEVANCE OF THE 3D TO 2D GROWTH TRANSITION IN SrRuO3 NANOMETRIC FILMS ON THE TRANSPORT PROPERTIES

G. Herranz, B. Martínez and J. Fontcuberta, Institut de Ciència de Materials de Barcelona Campus U.A.B., Bellaterra 08193 Catalunya, Spain, F. Sánchez, M.V. García-Cuenca, C. Ferrater and M. Varela, Departament de Física Aplicada i Òptica, Universitat de Barcelona, Diagonal 647, Barcelona 08028 Catalunya, Spain

Epitaxial SrRuO3 nanometric films were grown on SrTiO3(0 0 1) substrates by pulsed laser deposition. At first stages the growth develops by the formation of elongated 3D islands following the substrate steps along [1 0 0] directions. At a thickness of about 10 nm, these islands merge together, and thereafter the growth proceeds essentially by 2D step-flow and the films become progressively smoother. This unusual 3D to 2D transition film growth has a strong impact on the electronic transport properties of the films. At the regions where the elongated islands merge together, structural disorder develops leading to a well oriented pattern of defective regions. On one hand, this results in the emergence of an in-plane resistivity anisotropy due to the differential electronic properties of the island-merging boundaries. On the other hand, the microstructural disorder provokes a shortening of the electronic mean free path. As a result of this, the conductivity at low temperature becomes somewhat suppressed. These findings could be of relevance for technological applications of SrRuO3, and specifically for the electronic transport properties across magnetic tunnel junctions. Finally, we report on the growth and characterization of SrRuO3/SrTiO3/SrRuO3 heterostructures grown on SrTiO3(100) substrates. The hysteresis loops of these heterostructures reveal uncoupled magnetic switching of the electrodes.

17:40-19:30 POSTER SESSION I

I/PI.01 ELECTRICAL AND STRUCTURAL PROPERTIES OF SrRuO3 AND La0.5Sr0.5CoO3 UNDER HDROGEN ANNEALING

D. Halley, D. Widmer and C. Rossel, IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland and S. Cariglio, University of Geneva, DPMC, 24 Quai Ernest-Ansermet, 1211 Genève 4, Switzerland

The metal gate eliminates the depletion problem experienced with conventional polysilicon gates in CMOS technology. The search for suitable work function fM, combined with low reactivity toward the gate dielectric has lead toward pure metals and metallic compounds such as nitrides, silicides and oxides. Among metallic oxides with good electrical conductivity (r < 500 mWcm) and adequate work function two candidates are SrRuO3 (fM = 5.2 eV) and La0.5Sr0.5CoO3 (fM = 4.3 eV). One particular requirement in CMOS technology is the stability of the whole stack under annealing in forming gas (FG, 95% Ar, 5%H2) at about 500 oC. We have investigated the thermal stability of epitaxial films of both oxides grown by pulsed laser deposition on SrTiO3 substrates. In situ resistivity r and X-ray diffraction measurements performed on SrRuO3 under 100 mbar of FG show a sharp increase of r around 450 oC but no decomposition (in contrast to powder). Annealing under vacuum shows a similar behavior that suggests that the loss of oxygen is the dominant mechanism. Indeed a subsequent treatment under O2 at 550 oC of the high resistive films allows to recover the low resistance state. Our main observation is that the addition of 1-2 % oxygen to the FG during annealing hinders the resistive transition below 630 oC. This is one important result towards the possible integration of this material into MOSFET fabrication. Similar behavior was observed for La0.5Sr0.5CoO3 .

I/PI.02 BEHAVIOUR OF HYDROGEN IN HIGH K OXIDE GATE OXIDES ON SILICON

P.W. Peacock, J. Robertson, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, U.K.

High dielectric constant (K) oxides are needed as replacement gate oxides. However, they appear to suffer from a large fixed charge. This is presently a critical factor which could limit their performance [1]. This could arise from native defects such as vacancies or from hydrogen, which is ubiquitous in the processing and is used in the post-deposition annealing step. The fixed charge is generally positive in most candidate oxides, except in Al2O3 in which it is negative [2]. The charge states of hydrogen in the perfect lattices of many oxides has been calculated. We find that the oxides fall into two classes. In most oxides such as ZrO2, TiO2, or SrTiO3, the hydrogen is only stable as the positive charged state (proton), as in ZnO [3], whereas in the wide gap oxides SiO2, Al2O3 and ZrSiO4 the negative and neutral state is also possible for higher Fermi level positions. This suggests that hydrogen is a possible cause of the fixed charge in the high K oxides, as it naturally accounts for the sign change. The bonding of hydrogen was studied in the two cases. In all cases, the proton bonds to an oxygen ion to give the OH- ion. When the H0 and H- are stable, the H tends to be in a more interstitial position, not as close to an oxygen.

[1] eg, S Guha et al, in MRS Bulletin special issue on high K oxides (March 2002)
[2] E Gusev, et al, Tech Digest IEDM (2001)
[3] C G van de Walle, Phys Rev Lett 85 1012 (2000)

I/PI.03 SILICON OVERGROWTH ON (LaxY1-x)2O3 / Si (001) BY MBE

G. Vellianitis, G. Mavrou, G. Apostolopoulos, A. Dimoulas, MBE Laboratory, Institute of Materials Science, NCSR "DEMOKRITOS", Athens, Greece, R. Scholz, Max Planck Institute for Microstructure Physics, Halle, Germany

Silicon overgrowth on epitaxial metal oxides on silicon is attractive for the realization of fully epitaxial silicon-on-insulator or novel 3D device architectures. So far, Si (Ge) /metal oxide alternate layers have been grown only along the <111> crystallographic direction using Si (111) substrates and Pr2O3 [1] or (LaxY1-x)2O3 [2] insulators. In the present work, we show that silicon overgrowth by MBE is also possible on Si (001) substrates with the following epitaxial orientation relationship: top Si(110) // (LaxY1-x)2O3 (110) // Si (001) substrate (x=0-24%), which is confirmed by RHEED, XRD and HRTEM. This may have important implications concerning potential applications since higher carrier mobilities are expected along Si <110>, while Si(001) is the standard type of substrates used by the industry. However, due to surface thermodynamics, the top Si layer grows in Volmer-Weber mode forming 3D islands (as indicated by RHEED and HRTEM) with a relatively high density of defects. Some of these defects are twin boundaries, which are, formed in the insulator replicated in the top Si layer. In this work we show (i.e. by RHEED) that, by using 40 miscut Si (001) substrates, the amount of twinning in the Si top layer is reduced mainly due to the corresponding reduction of twinning in the insulator [3]. Although a step forward has been made, exploitation of these semiconductor/metal oxide structures is not possible unless device quality Si overlayers with smooth morphology and very low defect density are obtained.

1. H.J. Osten et al., Mater. Sci. Eng. B 87, 297 (2001)
2. V. Narayanan et al., J. Appl. Phys. 93, 251 (2003)
3. G. Apostolopoulos et al., Appl. Phys. Lett. 81, 3549 (2002)

I/PI.04 PHYSICAL CHARACTERIZATION OF MIXED HfAlOx LAYERS BY COMPLEMENTARY ANALYSIS TECHNIQUES

H. Bender, Th. Conard, O. Richard, B. Brijs, J. Pétry, W. Vandervorst, IMEC, Kapeldreef 75, 3001 Leuven, Belgium, C. Defranoux, P. Boher, SOPRA, 26 rue Pierre-Joigneaux, 92270 Bois-Colombes, France, N. Rochat, C. Wyon, CEA-LETI, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France, P. Mack, J. Wolstenholme, Thermo VG Scientific, Imberhorne Lane, RH19 1UB East Grinstead, West Sussex, U.K., R. Vitchev, L. Houssiau, J-J. Pireaux, FUNDP, rue de Bruxelles 61, 5000 Namur, Belgium, A. Bergmaier, G. Dollinger, TU München, James Franck Strasse, 85748 Garching, Germany

Mixed Hf-Al-oxides are considered as possible gate dielectrics for future advanced devices. The full development of the material deposition processes also requires the optimization of the physical analysis procedures for these materials. No single technique will be able to determine all the important material properties of these layers and therefore the combined effort by complementary techniques is necessary as discussed in this paper.

HfAlOx layers are deposited by Atomic Layer Deposition with different cycle ratios on a 1 nm oxide grown in-situ by rapid thermal oxidation on 200 mm silicon wafers. The samples are analyzed by spectroscopic ellipsometry, X-ray reflectometry, angular resolved and single angle X-ray photo-electron spectroscopy, attenuated total reflection infrared spectroscopy, time-of-flight secondary ion mass spectroscopy, high resolution elastic recoil detection, Rutherford backscattering spectrometry and transmission electron microscopy. It will be shown that by the combination of the information deduced from the different analysis techniques for the thickness, chemical and structural characterization of the layers, the measurement methodologies for the different techniques can be optimized and good agreement can be obtained for important material parameters as e.g. the layer thickness, density, composition and interlayer thickness and nature.

I/PI.05 HIGH RESOLUTION DEPTH PROFILING OF FUTURE GATE DIELECTRIC MATERIALS

A. Bergmaier, G. Dollinger, L. Görgens, P. Neumaier, TU München, Physik Department E12, 85747 Garching, Germany, H. Bender, B. Brijs, Th. Conard, IMEC, Kapeldreef 75, 3001 Leuven, Belgium, L. Houssiau FUNDP, rue de Bruxelles 61, 5000 Namur, Belgium

Al2O3, HfO2 and mixed Al-Hf-oxides are considered as possible gate dielectrics for future devices. The development and optimization of the material deposition processes require the optimization of physical analysis techniques for these materials. High resolution elastic recoil detection (ERD) with swift heavy ions is a very suitable technique to measure quantitative depth profiles of the main contributing elements and also impurities with a depth resolution better than 1nm. The oxide layers are deposited by metal organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD), respectively, on a 1nm oxide grown in-situ by rapid thermal oxidation on 200 mm silicon wafers. The samples were investigated for their elemental composition at the Q3D magnetic spectrograph at the Munich tandem accelerator. The H, C and O profiles were obtained using a 40 MeV 197Au beam, Al profiles were analyzed with 170 MeV 127I and the Hf profiles were measured in a forward RBS geometry using a 40 MeV 63Cu beam. A detection limit of about 1% of a monolayer could be achieved while the depth resolution was better than 0.5 nm. The measurements revealed hydrogen an carbon contaminations at the interfaces. The mixed oxides showed an increase of the Hf-concentration and a decrease of the Al-concentration with depth. The results will be compared with standard RBS and SIMS measurements.

I/PI.06 Pr2O3/Si(001) INTERFACE REACTIONS AND STABILITY

Hans-Joachim Müssig, Jarek Dabrowski, IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany, Dieter Schmeisser, BTU Cottbus, Angewandte Physik-Sensorik, Postfach 10 13 44, 03013 Cottbus, Germany

Pr2O3 is currently under consideration as a potential alternative gate dielectric candidate for sub-0.1 micron CMOS technology. For all thin gate dielectrics, the interface with Si plays a key role. In order to maintain a high-quality interface and channel mobility, it will be important to have no metal oxide or silicide phases present at or near the channel interface. We studied the Pr2O3/Si(001) interface by using synchrotron radiation photo-electron spectroscopy and ab initio calculations. Our results provide evidence that a chemical reactive interface exists consisting of a mixed Si-Pr oxide such as (Pr2O3)x(SiO2)1-x. There is no formation of neither an interfacial SiO2 nor interfacial silicide: all Si-Pr bonds are oxidized and all SiO4 units dissolve in the Pr oxide. Interfacial silicates like (Pr2O3)x(SiO2)1-x are promising high-k dielectric materials because they represent incremental modification of SiO2 films by Pr ions so that the interface characteristics can be similar to Si-SiO2 interface properties. The ternary phase diagram indicates that this pseudobinary alloy remains amorphous and stable on Si up to high temperatures, without phase separating into crystalline Pr2O3 and SiO2. Under ultrahigh vacuum conditions, silicide formation is observed when a silicate film is heated above 800 °C. The praseodymium silicate system observed at the Pr2O3/Si(001) interface offers greater flexibility towards integration of Pr2O3 into future CMOS technologies.

I/PI.07 VUV SPECTROSCOPIC ELLIPSOMETRY APPLIED TO THE CHARACTERIZATION OF HIGH K DIELECTRICS

P. Boher, C. Defranoux, SOPRA, 26 rue Pierre-Joigneaux, 92270 Bois-Colombes, France, H. Bender IMEC, Kapeldreef 75, 3001 Leuven, Belgium

New high k dielectric materials are intensively investigated to replace the silicon dioxide as gate dielectric in the next generations of electronic devices. Their layer thickness of the order of some nanometers will be a critical stage of the process. Spectroscopic ellipsometry has long been recognized as a powerful technique for thin film characterization and is now used routinely to control thin films and multilayers at different stages of the device fabrication process. For very thin layers like high k dielectrics, the interface properties play a key role in the device. A precise physical model is then needed to extract accurate information from ellipsometry. In addition, since these layers are completely transparent in the visible and UV range, the correlation between thickness and refractive index is very high and so, structural and thickness information cannot be extracted independently.

In the proposed paper, we use vacuum ultraviolet spectroscopic ellipsometry (VUVSE) to characterize such layers. The advantage is that all the candidates for high k dielectrics become absorbent when the wavelength is reduced down to 190nm. So, the correlation between thickness and refractive index is reduced and more precise structural information can be deduced. Atomic Layer Deposited HfO2, Al2O3 and mixed HfAlOx layers will be studied in the proposed paper. We will show that VUVSE can provide not only the thickness of the layers but also valuable information on the composition and crystalline character of the layers. In particular, the effect of post growth thermal annealing can be understood and controlled. X-ray reflectometry (XRR) and transmission electron microscopy (TEM) will be used as comparative techniques to check the VUVSE results.

I/PI.08 Ru AND RuO2 GATE ELECTRODES FOR ADVANCED CMOS TECHNOLOGY

K. Frohlich, K. Husekova, D. Machajdik, Institute of Eelectrical Engineering, SAS, Dubravska 9, 84104 Bratislava, Slovakia, J.C. Hooker, Philips Research Leuven, Kapeldreef 75, 3000 Leuven, Belgium, M. Fanciulli, S. Ferrari, C. Wiemer, MDM – INFM, Via C. Olivetti 2, 20041 Agrate Brianza, Italy, A. Dimoulas, G. Vellianitis, Institute of Materials Science, NCSR "Demokritos", Patriarchou Grigoriou & Neapoleos, 15310, Athens, Greece, Philips Research Eindhoven, WA 14, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Due to the downscaling of device dimensions in CMOS technology, the introduction of metal gate electrodes and high-k dielectrics will be necessary in order to meet future performance requirements. In particular, deposition techniques such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) have been identified as promising methods for growth of these materials. In light of this, we have analyzed properties of Ru and RuO2 gate electrodes prepared on SiO2, atomic-layer CVD (ALCVD) Al2O3 and MBE Y2O3 dielectric films. The Ru and RuO2 were grown by metal-organic chemical vapor deposition at the temperature 250 °C. The dielectric and metal gate electrode films were analysed by X-ray diffraction, X-ray reflectivity and time of flight secondary ion mass spectroscopy (ToF SIMS).

Resistivity of the films at room temperature was in the range 100 - 200 mWcm. Thermal stability of the Ru and RuO2 films in forming gas (10% H2 + 90% N2), nitrogen and oxygen environments was investigated by applying low temperature (420 °C, 30 min) and rapid thermal (800 - 1000 °C, 30 s) annealings. The results indicate good thermal behavior of the Ru films but limited thermal stability of the RuO2 films. Ru and RuO2 gate electrode workfunctions were extracted from high-frequency capacitance-voltage measurements on metal-oxide-semiconductor (MOS) capacitors. The obtained results are discussed in connection with applications of Ru and RuO2 films as gate electrodes in CMOS technology.

I/PI.09 Withdraw

I/PI.10 GROWTH TEMPERATURE RELATED TRENDS OF ELECTRICAL PROPERTIES IN ATOMIC LAYER DEPOSITED HfO2 FILMS

G. Scarel, S. Spiga, C. Wiemer, S. Ferrari, G. Tallarida, E. Bonera, and M. Fanciulli, Laboratorio MDM-INFM, Via C. Olivetti 2, 20041 Agrate Brianza (MI), Italy

Understanding electrical properties and optimization of electrical performance in high-k oxides is one of the key steps leading to their application as SiO2 substitutes in CMOS devices. To begin this task, 10 nm thick HfO2 films were grown at three different temperatures (Tg = 150 ºC, 250 ºC, and 350 ºC) on p-type Si(100). The substrates were HF-last treated, covered with a thin layer of chemical oxide and heated in low vacuum (~ 1 mbar) before film deposition. This preparation was chosen to improve the electrical properties and eliminate carbon contaminations. Longer precursor pulses (HfCl4 and H2O) were applied during the first stage of the deposition to improve stoichiometry and density of the first film layers. Since the ALD growth rate was proven to be dependent upon Tg, the number of cycles was adapted to reach the target thickness (10 nm) at each value of substrate temperature. Post-deposition rapid thermal annealing was applied for 60 s in N2 at 900 ºC. Structural and chemical film properties were studied with far infrared spectroscopy and x-ray reflectivity, x-ray diffraction, time of flight - secondary ion mass spectrometry and atomic force microscopy. Electrical properties were derived from CV and IV characteristics. The differences detected in the three as grown and annealed films were correlated with Tg, given that all other growth parameters were kept constant (except the number of cycles, to ensure constant film thickness).

I/PI.11 SmxNd1-xNiO3 THIN-FILM SOLID SOLUTIONS WITH TUNABLE METAL-INSULATOR TRANSITION SYNTHESIZED BY ALTERNATE-TARGET PULSED-LASER DEPOSITION

Andrea Ambrosini, Bernard Mercey, and Jean-Francois Hamet, Laboratoire CRISMAT-ISMRA,6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

The materials of the family LnNiO3 (Ln= Pr, Nd, Sm, Gd) are of interest for their sharp metal-insulator (MI) transitions, which makes them interesting candidates for technical applications such as thermochromic coatings or sensors. However, none of the above compositions display a transition at room temperature. Thin-film solid solutions of SmxNd1-xNiO3 were synthesized on NdGaO3 substrates by pulsed-laser deposition using alternating NdNiO3 and SmNiO3 targets. The films were characterized by x-ray diffraction and variable-temperature four-probe conductivity measurements. The films grow in the {100}pseudocubic direction. There is a nearly linear increase of the metal-insulator transition from 199 K for x = 0 to 378 K for x = 1, with the composition corresponding to x = 0.6 displaying a transition near room temperature.

I/PI.12 MODELING THE DIFFRACTION PROFILES OF CVD-GROWN PEROVSKITE OXIDE MULTILAYERS

M. Nemoz(a), E. Dooryhée(a), J.L. Hodeau(a), J.A. Rodriguez(a), C. Dubourdieu(b), R. Pantou(b), M. Rosina(b),H. Roussel(b), J. Lindner(b)*, I. Maurin(b), F. Weiss(b), J.P. Sénateur(b), N. Lemée(c), F. Le Marrec(c), (a)CNRS, Laboratoire de Cristallographie, BP166X, 38042 Grenoble, France, (b)Laboratoire des Matériaux et du Génie Physique, INPG/CNRS, ENSPG BP46, 38402 St Martin d'Hères, France, (c)Laboratoire de Physique de la Matière Condensée, 33 rue St Leu, 80039 Amiens, France. (*)Present address: Aixtron AG, Kackerstr. 15-17, 52072 Aachen, Germany

The present general interest for nanostructured material is related to the possibility of achieving new physical properties, opening the way to a large number of applications (in optics, electronics...). The understanding of the physical phenomena requires a deep knowledge of the structure (morphology, strain, chemical composition, interface state).

We have studied (BaTiO3/SrTiO3)n, (BaTiO3/PbTiO3)n and (La0.7Sr0.3MnO3/SrTiO3)n epitaxial multilayer synthesized by the chemical vapor deposition of the organo-metallic precursors (MOCVD) and pulsed laser deposition (PLD). These multilayers have been examinated by laboratory and synchrotron X-ray techniques (reflectivity and high angle diffraction) and by HRTEM. A key issue in the structural characterization of such systems is the description of the lattice deviations and defects. We have extended a diffraction model(1), previously applied on metallic multilayers, to the more complex case of perovskite structures.We evaluate the presence and the magnitude of the coherence length, the interface roughness, the discrete thickness fluctuations, and the intra-layer gradients of strain and atomic diffusion. We describe the high sensitivity of the diffraction profiles to the interface state, in particular the macro-strain profile (lattice parameter gradient) as well as the atomic composition profile.

1 Fullerton et al. Phys. Rev. B45 (1992) 9292.

I/PI.13 DIELECTRIC PROPERTIES AND ELECTRONIC TRANSITIONS OF POROUS AND NANOSTRUCTURED CERIUM OXIDE FILMS

S. Logothetidis(a), P. Patsalas(a), E.K. Evangelou(b), J. Tsiaousis(a) and N. Frangis(a), (a)Aristotle University of Thessaloniki, Department of Physics, Solid State Physics Section, 54124 Thessaloniki, Greece, (b)University of Ioannina, Department of Physics, P.O. Box 1186, 45110, Ioannina, Greece

Cerium Dioxide (CeO2) exhibits exceptional electronic properties such as optical transparency and high refractive index (n) and high dielectric constant (k). Therefore it is suitable for ultra-thin gate oxide in CMOS technology and for high-n components in optical devices. We study the electronic properties of nanostructured and porous Cerium Oxide (CeOx) films, 110-500 nm thick, grown on Si by electron beam evaporation (EBE) and ion beam assisted deposition (IBAD). The film microstructure and morphology (grain size, orientation, porosity, defect concentration, surface and interface roughness) are controlled by varying appropriately the process parameters and have been studied by X-Ray Reflectivity, Atomic Force Microscopy (AFM) and high-resolution TEM. The optical properties have been studied by Spectroscopic Ellipsometry (SE) and k was determined by capacitance measurements on Al/CeOx/Si devices. The calculated values of k (ranging from 20 to 30) are affected by the electronic transitions and by the polar lattice vibrations occurring at 275 cm-1, which are strongly correlated with the microstructure and morphology of the films. We investigate how the microstructure and morphology variations affect the absolute values of the dc dielectric constant and of the dielectric function at the UV-Vis (electronic transitions) and IR (bond vibrations) spectral regions. In addition, we investigate the very important role of the defects, which have the form of grain boundaries, trivalent Ce3+ and O vacancies. As a result we were able to tailor n and k of CeOx films controlling their porosity and defect density.

I/PI.14 GROWTH AND RELAXATION OF (Zr,Y)O2 EPITAXIAL LAYERS ANALYZED BY XRD RECIPROCAL SPACE MAPPING

A. Boulle, O. Masson, R. Guinebretière, A. Dauger, Science des Procédés Céramiques et de Traitements de Surface UMR 6638, ENSCI, 47-73 avenue Albert Thomas 87065 Limoges Cedex, France

Zirconium oxide is a key material in number of optic, optoelectronic and microelectronic potential applications. Despite of this great interest, very few is known about strain and strain relaxation in ZrO2 epitaxial layers. One reason for this lack of knowledge may be that oxides generally exhibit high defect densities as compared to semiconductor materials.

In this work we use a high-resolution X-ray diffraction (XRD) set-up dedicated to the study of nanostructured oxide materials. Several reciprocal space maps have been recorded as a function of the growing conditions of sol-gel derived yttria stabilized zirconia (YSZ) epitaxial layers deposited onto (11-20)-cut sapphire substrates. Microstructural parameters of crucial importance such as the film thickness, thickness fluctuation, lateral crystallite size, amount of strain and strain relaxation, defect densities, mosaicity,... could be recovered by analysing selected sections of the reciprocal space maps. Using the XRD results, it is shown that two mechanisms take place simultaneously upon epitaxial growth of the layers: islanding occurs in order to minimize the interfacial energy, whereas 1/2 [110] dislocations are introduced to relieve the strain energy. Moreover because of the symmetry of the substrate, the dislocation density is anisotropic in the film plane.

I/PI.15 PERFORMANCES OF HAFNIUM OXIDE PRODUCED BY RADIO FREQUENCY SPUTTERING FOR GATE DIELECTRIC APPLICATION

L. Pereira, A. Marques, H. Águas, N. Nedev, S Georgiev, R. Igreja, E. Fortunato, R. Martins, Departamento de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP, Campus da Caparica, 2829-516 Caparica, Portugal

The search for new dielectric materials to be used on metal-oxide-semiconductors (MOS) or metal-insulator-semiconductor (MIS) structures to replace the silicon oxide (SiO2) has been growing up. The aim is to have materials with high dielectric constants that could allow the use of thicker films and so, to reduce the role of leakage currents that happens in devices using very thin SiO2 layers. Apart from that, if a dielectric layer with a very low defect density at the interface can be produced with a high dielectric constant, we can have MOS or MIS devices able to support high currents.

In this work we present data concerning the production of hafnium oxide (HfO2) thin films by rf sputtering that present suitable characteristics to be used as a gate dielectric, taking advantage of its high dielectric constant and stoichiometry reached under certain deposition conditions (Argon + Oxygen gas flows, substrate temperature and rf power). Data concerning the role of the deposition parameters on the electrical properties of the films produced using capacitance-voltage (C-V) and current-voltage (I-V) measurements will be shown, together with data concerning the optical properties and degree of films’ compactness measured by spectroscopic ellipsometry (SE). Apart from that, the role of the deposition parameters on the films morphology and structure will be also presented, together with an electrical model of the structure behaviour, determined from spectroscopic impedance data.

I/PI.16 ZT AND ZTS THIN FILMS PRODUCED BY MOCVD TO BE USED AS HIGH-K DIELECTRICS

G. Padeletti, A. Cusmà, M. Viticoli, G.M. Ingo and S.Viticoli, Istituto per lo Studio dei Materiali Nanostrutturati-CNR, Area della Ricerca di Roma, Via Salaria Km. 29.300, 00016 Monterotondo St., Roma, Italy

The growing diffusion of personal computers and satellite communications systems turned out into an intensive research activity focused on the synthesis and on the study of new materials for the realization of next generation micro-devices.
In recent years the need for miniaturisation has had a dramatic impact on the field of microelectronics: the evolution of the industrial interest from discrete components into multifunctional electroceramic systems became so significant that led the R&D work to a relevant effort in such direction. With this trend, integration technology and surface and interface phenomena gain a major importance. In this work we describe the synthesis and characterization of both ZrxTi1-xO4 (ZT) and tin doped ZT thin films grown via a non conventional MOCVD apparatus, on different kinds of substrates: SiO2, SiO2/Ti/TiN/Pt and TiN/Ir/IrO2/Pt. The samples have been chemically, morphologically and structurally characterised by AFM, XRD, FEG, SEM+EDS and XPS. Also high and low frequencies electrical characterisation has been performed. The influence of the substrate on the morphological features of the films will be discussed. Electrical measurements have also been performed with the aim to find out the dielectric properties of the films and to point out both the influence of the process parameters on the electrical properties of the films and the relationship between the electrical properties of the materials and their structural and chemical characteristics.

I/PI.17 NEGATIVE-BIAS-TEMPERATURE-INSTABILITY (NBTI) IN METAL-INSULATOR-SEMICONDUCTOR (MIS) STRUCTURES

S.N. Volkos, A.R. Peaker, I.D. Hawkins and E. Efthimiou, Centre for Electronic Materials and Department of Electrical Engineering and Electronics, UMIST, Manchester M60 1QD, U.K.

Despite the fact that the NBTI in p-channel MISFETs has been extensively studied during the last 40 years, the exact mechanism that generates interface traps and positive oxide charge in such devices, after low field (< -6 MV/cm) operation at elevated temperatures (> 100 0C), is still unknown. It has been suggested that the NBTI mechanism can be modelled by electrochemical reactions that involve hydrogenated Pb centres, water/hydrogen-related species and holes at the interface. Meeting the ITRS scaling requirements, calls for, amongst other challenges, shrinking down device dimensions into the submicron regime as well as introducing high-k metal oxides into the device manufacturing process. Taking into account that a number of key issues regarding next generation devices, such as interface quality and thermodynamic stability, are yet to be resolved, it is expected that the NBTI will continue to have an impact on the operating performance of future submicron device architectures.
[...] Our work provides only a partial picture within the framework of understanding the principles underlying the NBTI in MIS-based devices. Further work is required over a larger range of aging conditions (i.e. aging field, time and temperature) to allow a better approach of the NBTI-induced device degradation. This will ensure that future submicron device architectures, comprising high-k materials, will demonstrate the projected performance reliability and lifetime.

I/PI.18 TITANIUM SALICIDE PHASE POLYMORPHIC TRANSITION STUDY VERSUS THE BIAS POLARIZATION CHANGE APPLIED TO THE SUBSTRATE DURING THE TI STARTING FILMS DEPOSITION

D. Mello(a), D. Trapani(b), G. Franco(a), M.G. Grimaldi(b), (a)ST Microelectronics, Stradale Primosole 50, 95100 Catania, Italy, (b)Università degli Studi di Catania, Facoltà di Scienze Mat. Fis. e Nat., dip. di Fisica e Astronomia, via S. Sofia, 95100 Catania Italy

Following the scaling down of Non Volatile Memories increased the difficulties to the interconnection fulfilling and to perform metallic strip. PVD technique was used in microelectronics manufacturing for Contact and Via fulfilling.
In order to overcome such difficulties Ionized Metal Plasma (IMP) has been used. Using IMP deposition method substrate is polarized, ions directionality has given, properties improves and an enhance uniformity deposition is possible. In this work we have investigated change in TiSi2 formation starting from Ti IMP film deposited on <100> Silicon substrate when the bias polarization have been varied. IMP Titanium films have been deposited, without substrate polarization, with 100W ÷ 400W of bias polarizations. A different grain size in mixed phase TiSi2 films (correlated with starting films) has been observed. The smaller grain sizes increase the probability to have triple points (which are C54 phase nucleation points). The aim of this work is the employ of this grain size reduction to improve the TiSi2 film nucleation in order to have TiSi2 formation in narrow lines.
To check chemical and physical differences in TiSi2 films TEM and SIMS characterizations have been performed and transition phase curves have been realized.

I/PI.19 FREQUENCY EFFECT ON THE METAL/POLISILICON/OXIDE/SILICON CAPACITANCE

H. Dib(a), Z. Benamara(a), B. Zebentout(a), F. Raoult(b), (a)Laboratoire de microélectronique appliquée, Université Djillali Liabes, Sidi Bel Abbès 22000, Algérie, (b)Groupe de Microélectronique et Visualisation, CCMO - URA CNRS 1648, Université de Rennes I, Campus de Beaulieu, 35042, Rennes cedex, France

In this work, we study the frequency dependence of metal/polisilicon/oxide/silicon (MSPOS) structure. We present the capacitance-voltage (C-V) characteristics at four frequencies (10KHz, 100KHz, 400KHz, 1MHz). In order to study the behavior of MSPOS capacitance in frequency, the polysilicon/oxide/silicon structure is realised. It is elaborated on the monocrystalline silicon with "N" type doped (r= 0.008Wcm, NDm = 2´1018cm-3). The thickness is of 381µm. The draw oxide of 100nm is realised on the silicon surface. The growth of polysilicon is realised by low pressure chemical vapor deposition (LPCVD) method in the following conditions : temperature = 620°C, pressure = 0.1Torr. The thickness is analysed by scanning electronic microscopy and is evaluated at 300nm. The metallisation of the front and backside contacts is obtained by evaporating a aluminium layer with square gate = 384´10-5cm-2. The sample is electrically characterized by C(V) measurements for different frequencies. For these measurements, the "capacitance meter" is connected to the front gate. The results show that the C-V curves present a dispersion when the frequency decreases. The increase of the frequencies translate the CT(V) curve about negative voltage and cause the decrease of the minimum value of capacitance. The variation of the capacitance for low frequencies is less important than the one of the high frequencies. For the 10KHz, the capacitance increases from 105 to 118 pF, when the gate voltage varying from -20V to 20V. The characteristics for 1MHz, 400KHz and 100KHz have the same value of the maximal capacitance, CMAX= 115pF. The minimal capacitance is equals to 73, 75,and 83pF when the frequency is equals to 1Mhz, 400KHz and 100KHz respectively.

I/PI.20 CHORINE EFFECT ON FLASH MEMORIES RELIABILITY AND CONTAMINATION REDUCTION

F. Cordiano(a), G. Franco(a), G. Mondio(b) (a)STMicroelectronics S.r.l. Stradale Primosole 50, Catania Italy, (b)INFM-Dipartimento di Fisica della Materia e Tecnologie Fisiche Avanzate, Universita' degli studi di Messina, Salita Sperone 31, Messina, Italy

The shrinking of semiconductor devices dimension has led to focus the attention on contamination control in critical processes such as thin oxide growth, where neutral particles or ion could reduce the reliability of the oxide. The introduction of TLC in diffusion processes allowed a considerable reduction of contamination and, at the same time, good results in wafer reliability tests. This being due to the “catching” property of chlorine in forming molecules with transition and alkali metals that can be easily expelled from the wafer surface. This is the result of a study of Dr. Mehrad M. Moslehi who showed that, for thick gate oxide more than a few hundred angstroms and in a processing environment where contaminants are not under control, addiction of chlorine species (in concentration of 3.5%) to the oxidation ambient could improve the MOS threshold voltage stability. The aim of this work is to understand, in ULSI era, what is the best chlorine species concentration among 0.5%, 1.0% and 1.5% in a furnace ambient that assures low concentration of contaminants and higher values of the parameters of ultra-thin oxide strength, such as Qbd and Ebd (breakdown charge and field). The correlation of these last results with chemical data, obtained by spectroscopic techniques such as Auger, TXRF and SIMS will show that 1.0 % of HCl helps to improve oxide strength and reduces contaminants concentration.

I/PI.21 MIXED LANTHANUM-ZIRCONIUM EPITAXIAL PYROCHLORES AS GATE DIELECTRICS

A. Guiller(a), C. Marchiori(a,b), G. Norga(a), D. Halley(a), J.W. Seo(v), H. Siegwart(a), C. Rossel(a), J.-P. Locquet(a) and J. Fompeyrine(a), (a)IBM Research, Zuerich Laboratory, Rueschlikon, Switzerland, (b)Laboratorio MDM-INFM, Milano, Italy, (c)IPMC, EPFL, Lausanne, Switzerland

In the coming years, aggressive scaling in CMOS technology may trigger the transition from silicon dioxide to alternate gate dielectric oxides. If chemical and structural integration issues can be solved, epitaxial dielectrics will be a first step towards many novel device structures and functions. The solid-solution system between lanthanum sesquioxide and zirconium dioxide do in principle allow a combination of optimum structural, chemical and dielectric properties. We have already reported that epitaxial growth could be obtained directly on silicon substrate and that the films do exhibit good structural properties. Despite this, in-situ RHEED characterization clearly show that an amorphous interlayer may be present from the very beginning of the growth process. A first structural analysis allows us to estimate the thickness of this layer, although it may be inhomogeneously distributed across the interface. Once a homoepitaxial growth regime is reached, oxygen diffusion processes and a limited thermodynamical stability of the interface can lead to a further amorphous interlayer regrowth. Based on post-anneals and capacitance-voltage measurements on MOS structures, we extract both interlayer regrowth and dielectric constant. A kinetically controlled regrowth will be discussed and first results presented, where the ambiant pressure during growth is varied towards very low oxygen activity values.

I/PI.22 ELECTRICAL CHARACTERIZATION OF MOCVD SrTiO3 THIN FILMS ON Si SUBSTRATE

F. Ducroquet (a), J. Legrand(a), Y. Chang(a), C. Lamard(a), A. Sibaï(a), L.Auvray(b), S. Lhostis(b,c) C. Dubourdieu(b), J.P. Sénateur(b), (a)LPM (UMR CNRS 5511), INSA-Lyon, Bât B. Pascal, B.P. 69, 69621 Villeurbanne cedex, France (b)LMGP (UMR CNRS 5628), INPG, ENSPG, B.P.46, 38402 St Martin d'Hères, France, (c)STMicroelectronics, 850 rue Jean Monnet, 38926 Crolles cedex, France

Alternative high k dielectric materials have received more attention as CMOS technology integrating SiO2 gate oxide approaches its fundamental limits. Promising results of crystalline oxides (SrTiO3 and BaTiO3) on Silicon or Germanium grown by MBE have already been reported.

In this work, electrical properties of SrTiO3 thin films have been investigated. The SrTiO3 layers were grown by pulsed liquid-injection metal organic chemical vapor deposition (MOCVD) on n- and p-type Si substrate. MOS capacitors were fabricated by evaporation of Au electrodes. For as-deposited 15nm thick SrTiO3 film, the equivalent oxide thickness (EOT) and gate current density was 1.5nm and 10-2A/cm2 (@-1V) respectively. This result is achieved when the interface region (which has a lower dielectric constant) and the composition stoichiometry of the SrTiO3 film are optimized. The dielectric constant of the SrTiO3 layer (excluding the interface region) is larger than 50 for a wide range of thickness. Low-temperature hydrogen annealing improves the EOT, leakage current and interface state density (Dit). After annealing, Dit decreases down to 2´1011cm-2eV-1.

I/PI.23 ELECTRICAL PROPERTIES OF METAL-OXIDE-SILICON STRUCTURES WITH LaAlO3 AS GATE OXIDE

B. Mereu(a,b), G. Sarau(a), A. Dimoulas(c), G. Apostolopoulos(c), J.C. Hooker(d), I. Pintilie(a), T. Botila(a), M. Alexe(b), (a)National Institute for Material Physics, Bucharest-Magurele, Romania, (b)Max Planck Institute of Microstructure Physics, Halle, Germany, (c)Institute of Materials Science, National Center for Scientific Research "Demokritos", Athens, Greece, (d)Philips Research Leuven, Belgium

High-k dielectric materials are presently investigated for alternative gate dielectrics in MOSFET devices. In order to meet future requirements of the CMOS technology, the new gate materials have to satisfy requirements such as low leakage currents and low density of interface traps. LaAlO3 (LAO) is one of the most promising alternative gate dielectrics due to its high dielectric permittivity of about 25 and wide energy band gap of about 5 eV.

In this paper electrical investigations performed on complex MOS structures with amorphous LaAlO3 as gate oxide deposited on rapid thermal processed SiO2 buffer layer are presented. The substrate is p-type Si with Al as backside contact and Mo gate electrode. The temperature dependence of the leakage current in the range 26 K-300 K shows that direct tunneling of holes occurs for negative bias. The band diagram of this structure will be presented along with estimations of band offsets. Interface trap density (Dit) at the Si/oxide interface and bulk trap density are evaluated using the conductance method and Optical Charging Spectroscopy (OCS) method, respectively.

I/PI.25 THE IMPROVED THERMAL STABILITY OF HfO2 AND (HfO2)X(Al2O3)1-X FILMS BY REACTIVE SPUTTERING

Dongwon Lee(a), Y.S. Kim(a),Y.E. Hong(a), Dae-Hong Ko(a), Ja-Hum Ku(b), Cheol-Woong Yang(c), (a) Yonsei Univ., Dept. of Ceramic Engineering, Seoul, Korea, (b)Process Development Team, Semiconductor R&D Division, Samsung Electronics Ltd. Korea, (c)Sungkyunkwan Univ. School of Metallurgical and Materials Engineering, Suwon, Korea

As the gate oxide thickness of MOSFET semiconductor devices are scaled down to sub-micron range, approaching the quantum tunneling limits, the leakage current and the reliability. A physically thick film of a high dielectric constant is a possible solution which allows to achieve a large capacitance and to reduce the leakage current. High-k oxides such as Ta2O3, Al2O3, TiO2, ZrO2, and HfO2 have received considerable attention. Among these oxides, HfO2 is one of the most promising material because of its large dielectric constant (k>25) and large band gap (Eg>5.5eV). However, pure as-deposited amorphous HfO2 crystallizes during post-deposition annealing at above 400℃ which may induce grain boundary leakage current and non-uniformity of the film thickness. Also, annealing in an oxygen rich ambient will lead to fast diffusion of oxygen through the HfO2 film, causing the growth of uncontrolled low-k interfacial layer.

In this study, we investigated that a comparative study of the thermal stability and the microstructure of HfO2 and (HfO2)x(Al2O3)1-x films deposited on the single (100) substrate upon annealing temperature. The composition of (HfO2)x(Al2O3)1-x films were confirmed by RBS. Upon annealing temperature, phases were identified by XRD. As annealing temperature increased, HR-TEM analyses show the thickness of the interlayer between HfO2 or (HfO2)0.84(Al2O3)0.16 film and Si substrate became thicker. Corresponding to the results of HR-TEM, the Capacitance Equivalent Thickness(CET) of HfO2 system increased from ~25Å of as-deposited to ~34Å at 800℃. In case of (HfO2)0.84(Al2O3)0.16 system, the CET value increase to ~34Å at 800℃. These results show the improvement of the thermal stability of (HfO2)x(Al2O3)1-x system than HfO2.

I/PI.24 OPTIMIZATION OF R.F. MAGNETRON SPUTTERED ALUMINA FILMS FOR GATE INSULATORS IN ORGANIC FIELD EFFECT TRANSISTORS

Michael Voigt , Moritz Sokolowski, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstraße 12, 53115 Bonn, Germany

Thin films of alumina (thickness = 160 nm) were prepared by r.f. magnetron sputtering from an Al2O3 ceramic target in pure Ar or in Ar and O2 mixtures. The aim was to achieve good dielectric films for gate insulators in organic field effect transistors.

The breakdown fields (Eb) depend remarkably on the partial pressure of O2 in the sputter plasma and on the history of the Al2O3 target. When O2 was added to the Ar sputter gas we observed a remarkable decrease in deposition rate up to about a factor of three. By varying the partial pressure of O2, we found the highest Eb values at a partial pressure of 1% O2 (Eb = 0.7 MV/cm). Even higher Eb of 1.2 MV/cm were observed, if the Al2O3 target was first conditioned by sputtering 30 min in a mixture of Ar + O2 (1:1) and subsequent sputtering of the film in pure Ar. Hereby we define Eb as the field strength for which a current density higher than 10-7 A*cm-2 is observed for the first time. We speculate that this increase in the Eb is due to OH- ions, generated in the sputter plasma from residual water and O2 and incorporated into the sputtered films. AFM studies show that all the films are relatively porous with grain sizes of 0.3-0.5 mm and a surface roughness of about 1.5 nm. For the investigated sputter gas compositions no observe differences in the film morphology were observed.

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I/PI.26 ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION OF TITANIUM OXIDE FILMS FROM TICL4 PRECURSOR

A. Khakifirooz *, M. Arvand, M. S. Tarighat, S.S. Mohajerzadeh, Thin Film Lab., Electrical and Computer Eng. Dept., University of Tehran, Iran, * Microsystems Technology Labs., Massachusetts Institute of Technology, USA

Titanium oxide films are deposited on p-type (100) silicon wafers via APCVD using TiCl4 precursor and oxygen, hydrogen peroxide, or water as the oxidant. Nitrogen is used as the carrier gas and bubblers are kept at room temperature. Deposition is carried out at temperatures in the range of 150-400ºC and the effect of temperature and gas flow on the deposition rate and film roughness is studied. Films deposited at 200ºC show a dielectric constant of about 10 with less than 10 mV hysteresis in CV curve. SEM, XRD, and FTIR are used to study the film morphology and composition. The effect of post-deposition annealing in oxygen ambient is also studied. Low-temperature nature of the process is employed in fabricating thin film transistors on flexible PET substrates.

I/PI.27 STRUCTURAL AND OPTICAL PROPERTIES OF SPUTTERED TITANIUM OXIDE THIN FILMS MODIFIED BY Hf DOPING

J. Domaradzki, E.L. Prociow, D. Kaczmarek, Faculty of Microsystem Electronics and Photonics, ul. Janiszewskiego 11/17, 50-372 Wroclaw, Poland, A. Podhorodecki, R. Kudrawiec, J. Misiewicz, Institute of Physics, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland, W. Mielcarek, Electrotechnical Institute, ul. M. Sklodowskiej Curie 55-61, 50-369 Wroclaw, Poland

Structural and optical properties of Ti Hf-doped oxide films have been investigated. Layers were deposited on heated silica and sapphire substrates from metallic Ti target with different Hf content in reactive atmosphere of oxygen by magnetron sputtering process. The low pressure of reactive gas and appropriate ratio of effective to collective power during deposition process has been chosen to assume dielectric nature of obtained films.

Using X-ray diffraction (XRD) examinations, both: in as-deposited and in annealed samples crystalline phases of anatase and rutile have been found. Manufactured layers were transparent in a wide range of visible light what makes them suitable for many applications such for example optical coatings and UV filters. On the basis of optical measurements the optical band-gap versus Hf content in obtained layers has been also estimated. It has been shown that manufacturing wide band-gap oxide composites by introducing atoms of transition metals such Hf ones into Ti oxide lattice modify its optical and electrical properties.

I/PI.28 METHODS TO REDUCE THE LOADING EFFECT IN SELECTIVE AND NON-SELECTIVE EPITAXIAL GROWTH OF SIGEC LAYERS

J. Hållstedt, E. Suvar, C. Menon and H.H. Radamson, Royal Institute of Technology (KTH), Department of Microelectronics and Information Technology (IMIT), Electrum 229, Kista-Stockholm 164 40, Sweden

Various methods to reduce both global and local loading effects during non-selective and selective epitaxial growth of Si1-x-yGexCy ($0<x<0.20$ and $0<y<0.01$) layers have been proposed. Evaluation of the proposed solutions for issues such as defect generation and the possibility for integration in device structures have been performed. The key point in these methods is based on reduction of surface diffusion of the adsorbed species on the oxide. In non-selective epitaxy, this may be achieved by introducing a thin silicon polycrystalline seed layer on the oxide. The impact of the thickness of this layer on both the global and local loading effect, and also on the epitaxial quality have been studied. In selective epitaxy, increasing the HCl partial pressure reduces the local loading effect however this is not an appropriate solution since the defect density in the layer is increased. Other alternatives such as introducing square nitride or polycrystalline stripes around the oxide openings acting as diffusion barriers to reduce the loading effect have also been studied. These results are important for down-scaling the device sizes which otherwise may suffer from variations in composition and growth rate. In this study, high-resolution x-ray reciprocal lattice mapping (HRRLM), atomic force microscopy (AFM), and secondary ion mass spectroscopy (SIMS) have been used as the main characterization tools.

I/PI.29 INVESTIGATION OF THE STRAIN RELAXATION MECHANISM IN THE Si-SiO2 SYSTEM DURING THE PROCESS OF ITS FORMATION

D. Kropman(a), V. Poll(a), T. Kärner(b), Ü. Ugaste(c), E. Mellikov(c), U.Abru(d), V.Paomets(d), (a)Estonian Maritime Academy, (b)Institute of Physics, Tartu University, (c)Tallinn Pedagogical University, (d)Tondi Electronics, Tallinn, Estonia

The results of the studies of the influence of generation and annihilation of point defects on the stresses evolution in the Si-SiO2 system during the process of SiO2 formation by means of electron paramagnetic resonance (EPR), infrared absorption spectroscopy, deflection measurements and transmission electron microscopy (TEM) are presented. The obtained results confirm the interdependence between the stresses relaxation in the Si-SiO2 system and point defects in Si and SiO2. It has been established that the dependence of the EPR signal intensity from vacancy type defects on the oxidation time (oxide thickness) is non-monotonous and is accompanied by a non-monotonous change of the stresses in the Si-SiO2 system. The stresses can be reduced by an appropriate choice of the oxidation conditions (oxidation time, cooling rate).

I/PI.30 IMPROVEMENT OF SIO2 ETCH CHARACTERISTICS USING MAGNETIC ENHANCED STRAIGHT ANTENNA PLASMA FOR LARGE AREA PROCESSING

Y.J. Lee, K.N. Kim, B.K. Song, and G.Y. Yeom, Dept. of Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea

The development of large-area plasma source with high density is desired for a variety of plasma processes from microelectronics fabrication processes in semiconductor industry to flat panel display device fabrication processes. The plasma sources developed to date for the production of high-density and large-area plasmas mainly are focused on the externally planar ICP. However, due to its large inductance with the scale-up to larger areas and the cost and the thickness of its dielectric material, the conventional ICP device using an external spiral antenna has reached its limit in extending the process area. By inserting a straight antenna into plasma with external magnetic fields, the induction of a strong electric field in the plasma and the efficient transmissions of power to plasma are possible and it can be used as large area plasma processing for future application in large-scale production.

In this study, to improve both the plasma density and the uniformity of the internal ICP source, several internal-type straight antenna designs working with permanent magnets were used in a square shaped (1020mm´830mm) plasma. Under optimized arrangement of the permanent magnets, the uniformity of the Ar+ ion density less than 10% could be obtained while maintaining high plasma densities on the order of 1´1011cm-3. In the application to SiO2 etching processes, SiO2 etch rates about two times higher than those etched using the without the magnetic fields could be obtained in our experimental conditions. To understand the effects of various magnets and process conditions on the plasma characteristics, a quadrupole masss spectrometer (QMS) and a Langmuir probe located on the sidewall chamber were used.

Session IV : Metal oxides for advanced Si technology –Characterization and device testing

Session chair: R. Droopad and R. McKee

I-IV.1 8:30 -Invited- ADVANCED GATE STACK FOR MIXED-SIGNAL CMOS APPLICATIONS

Y. Ponomarev, Philips Research Leuven, Belgium

The necessity to aggressively scale CMOS to sustain the historical trend of performance improvement with every generation calls for inevitable introduction of new materials (high-k gate dielectrics, metal gate electrodes, mobility-enhancing materials in the channel). However, this will have significant consequences to the operation of non-digital parts of the IC, which might be either beneficial or detrimental, depending on the application block. In this paper we will review the effects caused by the introduction of new gate stack materials, with special emphasis on devices in the analogue/RF parts of the circuitry. We will show that early feedback loop between new materials and transistor architectures on one side and application domains on the other is of vital importance to ensure future SOC success.

I-IV.2 9:10 CHARGING EFFECTS ON THE CARRIER MOBILITY IN SOI WAFERS COVERED WITH HIGH-K THIN FILMS

D. Halley, J. Fompeyrine, J.P. Locquet, G. Norga, A. Guiller, U. Drechsler, H. Siegwart, C. Marchiori,* and C. Rossel, IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland *also at Laboratorio MDM - INFM, Milano, Italy

Considerable efforts are ongoing to implement high-k oxides as a replacement for the SiO2 gate dielectric in MOSFET’s. Besides material quality issues, the origin of charge trapping and the reduction of channel mobility at the high-k/Si interface need to be understood. A simple alternative for measuring carrier mobility is the pseudo-MOSFET technique on SOI wafers with gate voltage applied to the backside. We investigated the influence of SrZrO3 and ZrO2 films (5-10 nm) deposited by MBE on low-doped SOI wafers. As compared to virgin SOI the electron and hole mobilities at the Si/SiO2 interface are strongly reduced, whereas the threshold (VT) and flatband (VFB) voltages are shifted to large negative values. We find a “universal” correlation between the electron mobility me and the interface trap density Dit, derived from VFB- VT. This me(Dit) curve is valid for all deposited films and annealing conditions and can be related to the degradation of the bottom interface with the buried oxide. By playing with different annealing treatments in forming gas (FG) one can reduce Dit and enhance the contribution of the top high-k/Si interface to the total drain current. By combining Hall effect (van der Pauw) with Y-MOSFET measurements the effective mobility at the top interface can then be extracted. The present approach is well suited to investigate relative changes of mobility during in-situ anneal.

I-IV.3 9:30 MBE LANTHANUM-BASED HIGH-k GATE DIELECTRICS AS CANDIDATES FOR SiO2 GATE OXIDE REPLACEMENT

G. Vellianitis, G. Apostolopoulos, G. Mavrou, A. Dimoulas, MBE laboratory, Institute of Materials Science, NCSR “DEMOKRITOS”, Athens, Greece, J.C. Hooker, Philips Research Leuven, Belgium, T. Conard, IMEC, Leuven, Belgium, M. Butcher, Oxford Applied Research Ltd., U.K.

Gate dielectrics with permittivity k higher than 20 have drawn attention for the replacement of SiO2 gate in transistors. The most studied compounds are based on Hf, but metal oxides containing lanthanum may also give high k values due to the large polarizability (a~6.07 Å^3) of the La+3 ion. As La-based oxides are not easily accessible by chemical vapor deposition methods at the present time, we investigated perovskite-like LaAlO3 (LAO) and pyrochlore La2Hf2O7 (LHO) materials by MBE using RF plasma source of atomic oxygen. The latter oxide is commensurate with the Si lattice so that direct epitaxy could be possible. Only limited work has been reported on LaAlO3 [1,2]. The oxides were deposited either on bare Si substrates or on 1.5 nm RTO/Si and 1 nm Al2O3/Si to obtain more stable interfaces. The CV curves measured in MIS capacitors were analyzed solving self-consistently the Poisson and Schrodinger equations to take fully into account quantum mechanical effects. From the dependence of the equivalent oxide thickness (EOT) as a function of physical thickness tph, the dielectric permittivity was estimated to be around 14 and 20 for the LAO and LHO, respectively, which are lower than expected probably due to slight deviations from the stoichiometric compositions. For all dielectrics with the smallest tph ~3 - 4 nm, the EOT was found to be less than 1.5 nm and the gate current Jg less than 10-2 Acm-2. Record values of EOT~1.15 nm, Jg~1.6x10-3 Acm-2 @ 1V for the LAO and 1.3 nm, 1x10-4 Acm-2 @ 1V for the LHO were obtained in as-grown samples, which represent results beyond the state-of-the-art for this class of materials.

1. B.E. Park and H. Ishiwara, Appl. Phys. Lett. 79, 806 (2001)
2. W. Xiang et al., J. Appl. Phys. 93, 533 (2003).

I-IV.4 9:50

THERMAL OXIDATION OF STRAINED SI/SIGE: IMPACT OF SURFACE MORPHOLOGY AND EFFECT ON MOS DEVICES

S.H. Olsen(a), A.G. O'Neill(a), D.J. Norris(b), A.G. Cullis(b), S.J. Bull(a), S.C. Chattopadhyay(a), K.S.K. Kwa(a), L.S. Driscoll(a), A.M. Waite(c), Y.T. Tang(c), A.G.R. Evans(c), (a)University of Newcastle, (b)University of Sheffield, (c)University of Southampton, U.K.

The performance of surface channel MOS devices depends on gate oxide interface quality. Carrier transport is enhanced in strained Si, thus its use for MOSFET channels can increase device performance. Thermal oxidation produces the highest quality SiO2. This paper compares thermal oxidation of strained Si with unstrained Si. Strained Si is achieved by epitaxial growth on relaxed SiGe. The impact of large-scale cross-hatching roughness inherent in relaxed SiGe alloys on strained Si oxidation is investigated. The nanoscale oxide interface roughness and oxidation rate of strained Si are found to correlate with the undulating cross-hatch period, increasing and decreasing, respectively, with the degree of surface vicinality. Further, analysis suggests strained Si oxidation kinetics arise primarily from local variations in the SiGe substrate orientation due to cross-hatching, rather than strain. Devices fabricated on relatively smooth SiGe material exhibit electrical performance enhancements exceeding 75% compared with devices fabricated on material with severe cross-hatching. Likely causes for the dependence of strained Si oxidation kinetics on surface morphology and the impact on MOS devices are discussed. The enhanced performance of strained Si/SiGe MOSFETs over Si control devices with equivalent oxide interface roughness is also presented. Strained Si devices exhibit mobility gains greater than 100% and significant increases in transconductance compared with control devices.

10:10 **BREAK**

I-IV.5 10:30 -Invited-

DEFECTS IN STACKS OF Si WITH NM-THIN HIGH-K DIELECTRIC LAYERS: CHARACTERIZATION BY ELECTRON SPIN RESONANCE

A. Stesmans and V. Afanas'ev, Department of Physics, University of Leuven, 3001 Leuven, Belgium

The work addresses the application of the electron spin resonance technique (ESR) to the investigation of Si/insulator structures with ultrathin high-k dielectric layers. Studied entities include stacks of (100)Si with nm-thin layers of SiOx, ZrO2, Al2O3, and HfO2, grown by various chemical vapor deposition methods. Generally, after hydrogen photodesorption, prominent trivalent-Si interface defects (Pbo, Pb1 Si dangling bond type centers) are observed at the (100)Si/dielectric interfaces. While likely expected in cases such as Si/SiOx/ZrO2 with deposited SiOx interlayer, this Pbo, Pb1 fingerprint, generally unique for the thermal (100)Si/SiO2 interface, indicates that the as-deposited (100)Si/metaloxide interfaces are basically Si/SiO2-like. Comparison of three different preparation methods of the (100)Si/HfO2 structure shows the Pb-type defect signature, and hence the interface, to be sensitive to the kind of deposition process. The Pb-type defects may serve as atomic probes utmost sensitive to the strain state of the interface, which will be discussed. Also is addressed the influence of post-deposition thermal treatment. This will include, among others, the effect of annealing in H2 on the interface defects (passivation efficiency) and on the multilayer structure in general. Data will also be presented of parallel electrical analysis with respect to the correlation of Pb-type defects and fast interface traps. A general conclusion is that ESR may provide detailed information with respect to the established interface quality.

I-IV.6 11:10

INJECTION INDUCED CHARGING OF HfO2 INSULATORS ON Si

V.V. Afanas'ev and A. Stesmans, Laboratory of Semiconductor Physics, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

Hafnium oxide represents an attractive material for gate insulation in metal-oxide-semiconductor devices because of its high dielectric constant (k~20-25), thermal stability, and good insulating properties. However, still little is known regarding the charge trapping in the HfO2-based insulators on Si, which can lead to threshold voltage drift impairing the long-term device reliability. Here we report on charge trapping in HfO2 films (5-120 nm thick) grown on (100)Si from different metal precursors (HfCl4, metallo-organic source, hafnium nitrate). The experiments were performed by using optical generation of electron-hole pairs in the oxide by 10-eV photons with monitoring the trapped charge by the capacitance- voltage technique. The deposition chemistry appears to have strong impact on the density and sign of the trapped charge: Positive charge was observe in films obtained from HfCl4 and metallo-organics, while negative charge is dominant in the films grown from the nitrato precursor. The observed weak dependence of the saturated trapped charge density on the HfO2 thickness suggests that it is primarily associated with a silicon oxide interlayer grown between the substrate and HfO2 during deposition. The latter conclusion is further affirmed by the observed enhancement of the positive charging after mild oxidation of the samples at 650 °C. This result indicates the properties of the interfacial silicon oxide like layer as the key factor in affecting electrical stability of the HfO2- based insulating stacks.

I-IV.7 11:30

BAND GAP OF ALCVD MIXED OXIDE AlZrO AND HfAlO MEASURED BY XPS

J. Pétry*, W. Vandervorst*, T. Conard, IMEC, Kapeldreef 75, 3001 Leuven, Belgium, *also: INSYS, KULeuven, Belgium

In view of understanding the electrical characteristics of gate stacks based on high k dielectrica, it is essential to know their precise band structure as the leakage current strongly depends on the band gap and band offset. Whereas pure ZrO and HfO-oxides suffer from rapid crystallization during subsequent thermal processing, adding Al to the film delays this crystallization. Hence mixed oxides might form an attractive material.

This paper investigates the effect of thickness, composition and anneal temperature in N2 on the band gap of the mixed oxide layer and the band offset with the Si substrate for layers grown by Atomic Layer Deposition. For 1:1 (Al/Zr or Al/Hf) mixed oxides, once the bulk value is reached, that is for thickness larger than 2 nm, the bandgap does not depend any longer on the thickness of the mixed oxide. Moreover, in both cases (AlZrO and AlHfO) the bulk values of the bandgap shows a linear dependence on the Al2O3 molar percentage, going from 5.6 (5) eV for pure ZrO2 (HfO2) to 6.7 eV for pure Al2O3. Since normally the films are subjected to various anneals to improve the electrical quality as well as during the poly-silicon activation step, the effect of anneal temperature on the band gap and valence band alignment is also studied. Here AlHfO and AlZrO seem to act differently: while the annealing temperature does not have any influence on the band gap of AlZrO mixed oxide, the annealing in N2 at temperature from 900ºC generates an increase in the band gap value measured by XPS for AlHfO.

I-IV.8 11:50

EELS STUDY OF OXYGEN SUPERSTRUCTURE IN EPITAXIAL Y2O3 LAYERS

A. Travlos, N. Boukos, G. Apostolopoulos, A. Dimoulas, K. Giannakopoulos, Institute of Materials Science, National Center for Scientific Research “Demokritos”, 15310 Ag. Paraskevi, Athens, Greece

The superstructure observed in epitaxial Y2O3 layers grown on (001)Si in ultra high vacuum (UHV), is studied by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). The fine structure of the oxygen K-edge is examined in the superstructure domains and defect free regions of the epitaxial layers in comparison to that obtained from reduced and stoichiometric bulk Y2O3. It is shown that the superstructure domains are oxygen deficient. It is deduced that during the epitaxial growth of Y2O3 layers on (001)Si in UHV, oxygen vacancies are introduced and order into a superstructure creating non-stoichiometric regions in an otherwise stoichiometric Y2O3 layer. This ordering is attributed to the minimization of the mismatch stress of the epitaxial Y2O3 layers. Furthermore it is shown that oxygen deficiency introduces a change of the density of states of the lower conduction band of Y2O3 and a decrease of its electronic gap by 0.8 eV.

12:10 **LUNCH**

Session V: Multicomponent oxides I
Session chair: Y. Ponomarev, H. Kohlstedt

I-V.1 14:00 -Invited-

NEW MATERIALS, GROWTH PROCESSES & CHARACTERIZATION METHODS FOR ADVANCED GATE STACKS

J.-P. Locquet(a), G. Norga(a), A. Guiller(a), C. Marchiori(a), J.W. Seo(b), H. Siegwart(a), J. Fompeyrine(a), D. Halley(a) and C. Rossel(a), (a)IBM Research Zurich, 8803 Rueschlikon, Switzerland, (b)EPF Lausanne, 1015 Ecublens, Switzerland

In the coming years, the current Si CMOS gate stack material set will be replaced (high mobility channel / SOI, high K dielectric, metal gate). The main challenge is to find a materials set leading to a high channel mobility while minimizing the trapped charge density. Since, the poor thermodynamic stability between Si /complex oxides prevents a clean interface, our emphasis is on kinetic process innovations.

First, a new MBE tool with an optimized process window is proposed. Next, we focus on the epitaxy of gate oxides (LaZrO3.5 & SrTiO3 on plain Si & SOI wafers) and oxide metal gates (SrRuO3 and La0.5Sr0.5CoO3) on SrTiO3. RHEED, AFM, XRD and TEM studies confirm the structural quality. To control the defects, the transport properties (IV, CV, Hall mobility) are measured before, during and after process gas anneals (forming gas FG, O2, Ar) in variable temperature & magnetic field setups. The use of SOI wafers permits a simple mobility estimate using the pseudo-MOSFET technique. Annealing the high K/SOI in FG reduces the charge density at both interfaces while improving the mobility. For the oxide metal gates, adding 1-2 % O2 to the FG anneal, maintains the required low resistive state.

I-V.2 14:40

MORPHOLOGY AND MICROSTRUCTURE OF FERROELECTRIC Bi3.25La0.75Ti3O12 FILMS GROWN ON Si(100)

M.-W. Chu, S.K. Lee, N.D. Zakharov, H.N. Lee and D. Hesse, Max-Planck-Institut fur Mikrostrukturphysik, Weinberg 2, 06120 Halle (Saale), Germany

Ferroelectric Bi3.25La0.75Ti3O12 (BLT) films, up to 2 £gm thick, were grown by pulsed laser (PLD) and chemical solution (CSD) deposition on SrRuO3(110)/YSZ(100)/Si(100) and Pt(111)/Ti/SiO2/Si(100) substrates, resp. Crystallographic orientation, morphology and microstructure of the films were analyzed by TEM. CSD-grown films are polycrystalline, whereas epitaxial films of (118), (100), and mixed (118)/(100) orientations were grown by PLD. (100)-oriented and mixed (118)/(100)-oriented films are obtained on 10 nm thin SrRuO3(110) bottom electrodes that are stretched by the underlying YSZ buffer layer. A cross-sectional TEM study indicates that the orientation of mixed (100)/(118)-oriented films is a function of film thickness: (118)-oriented grains appear exclusively in a ~0.25 £gm thin film region near the BLT/SrRuO3 interface. It turned out that both (118)- and (100)-oriented nuclei form on the stretched SrRuO3(110) bottom electrode, and that due to the specific PLD growth conditions the growth of the (100) nuclei is favoured over that of the (118) nuclei. Thus after a transition period only (100)-oriented grains develop. The polycrystalline films exhibit values of the remanent polarization Pr around 10 £gC/cm2, whereas predominantly (100)-oriented films show very high Pr values in excess of 30 £gC/cm2. Fatigue studies and high-resolution TEM investigations are under way in order to study the role of lattice defects (intergrowth defects, stacking faults, out-of-phase boundaries) in both PLD- and CSD-grown films.

I-V.3 15:00

IMPROVEMENT OF FERROELECTRIC AND PYROELECTRIC PROPERTIES OF PZT THIN FILMS BY DOPING MN

Qi Zhang and Roger W. Whatmore, Cranfield University, School of Industrial and Manufacturing Science, Cranfield, MK43 0AL Bedford, U.K.

Pb(Zr0.3Ti0.7)O3 (PZT 30/70) and Mn-doped Pb(Zr0.3Ti0.7)O3 (PMZT 30/70) thin films have been fabricated on Pt/Ti/SiO2/Si substrates by a chemical solution deposition technique. It was found that the addition of Mn to the PZT thin films greatly improves their ferroelectric and pyroelectric properties. It is demonstrated that the Mn-doped (1 mol%) PZT showed very low hysteretic fatigue up to 1010 switching bipolar pulse cycles under 10V, combined with excellent retention properties. The Mn-doped PZT thin films also exhibited well-defined hysteresis loops with a remnant polarization (2Pr) of 65-70 C/cm2 and a coercive field (2Ec) of 220 kV/cm for a film thickness of 300nm. Dielectric constant and loss (tan) at 33 Hz for Mn-doped PZT thin films are 252 and 0.008, respectively while they are 315 and 0.02, respectively, for the undoped PZT thin films. The relevant pyroelectric coefficients (p) of a 650-700nm thick film are 3.52x10-4 Cm-2K-1 and detectivity figures of merit FD= 3.85x10-5 Pa-0.5 for Mn-doped PZT, compared with p= 2.11 x10-4 Cm-2K-1 and FD=1.07x10-5Pa-0.5 for the undoped PZT films. This means that the Mn-doped PZT thin films are excellent candidates as device materials for both memory and pyroelectric applications. The possible mechanisms by which Mn influences the ferroelectric properties of PZT thin films are analyzed and discussed.

I-V.4 15:20

LOW TEMPERATURE GROWTH OF EPITAXIAL COMPLEX OXIDES FILMS BY AN EXCIMER LASER MOD

Tetsuo Tsuchiya, Iwao Yamaguchi, Takaaki Manabe, Toshiya Kumagai and Susumu Mizuta, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan

Epitaxial complex oxides films such as Pb(ZrTi)O3(PZT) films on SrTiO3(STO) and La-doped on SrTiO3(LSTO) substrates and La0.7Sr0.3MnO3(LSMO) films on LaAlO3 (LAO) substrate were prepared by an excimer laser MOD(ELMOD) at a temperature range from 25℃ to 500℃. The effects of starting materials, substrate, laser fluence, and temperature on the formation of their films were investigated by IR, UV and XRD(theta-2theta scans, rocking curve analysis, pole-figure analysis). In the case of PZT films, epitaxial grown PZT films on STO and LSTO substrates were obtained by ArF laser irradiation without heat treatment. In the case of LSMO film, epitaxial grown LSMO films on LAO substrate were obtained by ArF laser irradiation above 350℃. P-E hysteresis measurement for PZT films and resistivity measurement for LSMO films were performed as a function of preparation condition such as laser fluence and shot number and so on, respectively. The detailed experimental results will be described in presented paper.

This study was supported by Industrial Technology Research Grant Program in 2002 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

15:40 **BREAK**

I-V.5 16:00 -Invited-

OXIDE-SEMICONDUCTOR MATERIALS FOR QUANTUM COMPUTATION

Jeremy Levy, Center for Oxide-Semiconductor Materials for Quantum Computation, and Department of Physics and Astronomy, University of Pittsburgh, USA

Oxide-semiconductor heterostructures have many applications in computer technology, from alternative gate dielectrics to ferroelectric memories. This talk will focus on an application to a much more speculative technology, namely, quantum computers. As yet undeveloped, quantum computers can solve certain problems exponentially faster than ordinary computers. One of these problems, number factorization, can be used to crack public key encryption schemes like RSA, which is widely used in the internet.

The state of experimental quantum computation is primitive--neither quantum bits (qubits) nor quantum gates (qugates) have been demonstrated in a scalable form. I will describe a proposal to create a quantum processor using ferroelectrically coupled electron spins in Silicon. Quantum information is stored in the spin of electrons, which form a conveninent two-level system. The electrons are confined in the semiconductor (Si) using the static polarization from an epitaxial ferroelectric. Fast optical gating occurs using the nonlinear process of optical rectification. Ge quantum dots are used as "windows" that allow light to initialize or "boot" the quantum computer. Initial steps toward the development of quantum information technology using ferroelectric/semiconductor heterostructures will be presented.

This work is supported by DARPA QuIST through ARO contract number DAAD-19-01-1-0650.

I-V.6 16:40

OXIDES FERROELECTRIC (Ba,Sr)TiO3 FOR MICROWAVE DEVICES

H.V. Alexandru, C. Berbecaru, Faculty of Physics, University of Bucharest, A. Ioachim, M.I. Toacsen, G.M. Banciu, L. Nedelcu, National Institute for Materials Physics, Bucharest-Magurele, Romania

Ferroelectric materials have important applications in microwave domain (dielectric resonators, substrates for microwave hybrid integrated circuits, steerable antenna etc). BaO-SrO-TiO2 ternary compounds (BST), in paraelectric phase, have considerably high dielectric constant, which can be modified with a bias field. Applications of electrically controlled devices using this material are possible for varactors, phase shifters, tunable filters etc. (Ba,Sr)TiO3 compounds were prepared by solid-state reaction. Additives MgO (1 mol %) and MnO2 (0.5 mol %) were used to improve the crystalline structure and porosity. 1 mol % TiO2 rich phase composition improve the sintering and thermal treatment, making high dielectric constant and low losses materials. The milling acetone versus distilled water media results is compared after sinterization at 1260 oC.

X-ray structural data, collected with a Seifert diffractometer, mean size of the crystallites, samples density and porosity were measured. Permitivity and losses were measured versus temperature at 1 kHz and also in high frequency domain (around 1 GHz). The Curie point of the transition has a linear dependence on X strontium fraction TC(oC) = 120 - 360 X. A distribution of the Curie points, typical for ceramic materials, was measured. Dielectric losses of 0.001 at 1 GHz shows Ba0.5Sr0.5TiO3 ceramic is suitable for high frequency applications.

I-V.7 17:00 PYROELECTRIC ULTRA-NANOCRYSTALLINE BATIO3 THIN FILMS ON SI

Vera Lyahovitskaya, Yishay Feldman, Ilya Zon and Igor Lubomirsky, Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

The issue of a minimal grain size, at which nanocrystalline ceramics or thin films still exhibit properties of a crystalline body, for instance pyroelectricity or ferroelectricity, is becoming increasingly important because effort to incorporate ferroelectric and pyroelectric oxides, mainly Pb(Zr,Ti)O3 and (Ba,Sr)TiO3, into microfabrication processes has grown tremendously. Up till now the smallest grains, demonstrating pyroelectric or ferroelectric behavior, are of the order of a few nm, which is equivalent to a few tens unit cells.

We have developed a technique to prepare ultra-nanocrystalline films of BaTiO3 on bare Si. The size of the grains in these films is below the limit detectable by electron diffraction (ED) or X-ray diffraction (XRD) ("5 unit cells). Despite that, the films demonstrate a pyroelectric and piezoelectric response comparable with those of BaTiO3 single crystals (5-15%). Moreover, the films do not form detectable crystallites even upon heating to 800 oC. This clearly implies the presence of a stable local order, whose nature is yet to be understood. Thus the films represent an intermediate state between totally disordered materials and crystalline materials. Thus the crystal-like properties like pyroelectricity and piezoelectricity may originate from the local ordering alone. The dielectric constant of the ultra-nanocrystalline BaTiO3 films is below 30, which makes them very attractive for pyroelectric sensor applications.

I-V.8 17:20 HYDROGEN POST-ANNEALING EFFECT OF THE FERROELECTRIC PROPERTIES OF (Pb0.72,La0.28)Ti0.93O3 FILMS FABRICATED BY PULSED LASER DEPOSITION

Kyoung Bo Han, Chang Hoon Jeon, Hee Sauk Jhon, Sang Yeol Lee, Department of Electrical and Electronic Engineering, Yonsei University, 134 Shinchondong, Seodaemunku, Seoul 120-749, Korea

Dielectric thin films of (Pb0.72La0.28)Ti0.93O3(PLT(28)) have been deposited on Pt(111)/Ti/SiO2/Si(100) substrates in-situ by pulsed laser deposition using different annealing and deposition parameters. The effect of hydrogen annealing on the ferroelectric properties of PLT thin films has been investigated. The diffusion of hydrogen into the ferroelectric film was caused by annealing process and resulted in the destruction of polarization.

The film was grown by a two-step deposition process in order to improve electrical property. Two-step process to grow PLT films was verified to be useful to enlarge the grain size of the film and to reduce the leakage current characteristics. Structural properties and electrical properties including dielectric constant, ferroelectric characteristics, and leakage current characteristics of PLT thin films were shown to be strongly influenced by the grain size. The film deposited by using two-step process including pre-annealing treatment shows a strong (111) orientation. However, the small grain size was observed in the films deposited by using single-step process with hydrogen annealing process. The film deposited by using two-step process including pre-annealing treatment shows the leakage current density of below 10-7 A/cm2 for the field of smaller than 100 kV/cm.

17:45-19:30 POSTER SESSION II

I/PII.01 OPTICAL CONDUCTIVITY OF SOL-GEL DERIVED PbZr0.52Ti0.48O3 THIN FILMS ON Pt-COATED SUBSTRATES

N.R. Aghamalyan, G.R. Badalyan, A.G. Hayrapetyan, Y.A. Kafadaryan, A.L. Manukyan, M.V. Simonyan, N.J. Wu*, Institute for Physical Research, National Sciences Academy, 378410 Ashtarak-2, Armenia, *Texas Center Superconductivity and Advanced Materials, University of Houston, Houston TX 77204-5004, USA

Polycrystalline tetragonal thin films of PbZr0.52Ti0.48O3 (PZT) have been deposited on the nickel, (001) ZnO and (111) platinum coated (110) sapphire substrates by sol-gel technique.

Optical properties of the PZT thin films have been studied by far-infrared reflectivity spectroscopy in the 200-10000 cm-1 frequency range at 300 K. The frequency dependence of the optical characteristics of the films is calculated by Kramers-Kronig transformation of the reflectivity spectra and analyzed by a Drude-Lorentz model. Sapphire/Pt/PZT structures reveal semiconducting properties (effective carrier concentration, N/m*, is up to 10^20 cm-3, plasma edge is located near 3000 cm-1) and their optical conductivity is well described by the free-carrier term and an overdamped midinfrared component. This effect can be related to the charge carrier transfer at Pt/PZT contact and formation of the conductive interfacial layer.

I/PII.02 PROPERTIES OF BaTiO3 THIN FILMS DEPOSITED BY RADIOFREQUENCY DISCHARGE ASSISTED PULSED LASER DEPOSITION

S. Canulescu(a), G. Dinescu(a), G. Epurescu(a), F. Craciun(b), P. Verardi(b), C. Grigoriu(a), M. Dinescu(a), (a)National Institute for Lasers, Plasma and Radiation Physics, PO Box MG–16, 76900, Bucharest, Romania, (b)CNR-IDAC, Area di Ricerca Tor Vergata, Via del Fosso del Cavaliere 100, 00133 Roma, Italy

BaTiO3 (BTO)ferroelectric thin films were grown on different substrates as MgO, (Pt coated) Si, sapphire, quartz by radiofrequency discharge assisted Pulsed Laser Deposition (PLD).

A standard experimental set-up consisting in a pulsed YAG-Nd laser working at different wavelengths (266nm, 355nm, 532nm, 1064nm) and at an incident fluence in a range of about 2-20 J/cm2 and assisted by a radio frequency plasma discharge (power RF of about 50-500mW in a gas flow ranged from 1-100 sccm) was used to produce films starting from a BTO ceramic target. Using radio frequency plasma in PLD process, the oxygen atoms are excited and/or ionized, plasma reactivity increases and oxygen vacancies in deposited thin films are effectively reduced, so dielectric and ferroelectric properties of the thin films are improved. The deposited thin films have been characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscope (AFM), dielectric and ferroelectric measurements: a comparison with films obtained without RF discharge has been carried out.

I/PII.03 PREPARATION AND FUNCTIONAL PROPERTIES OF FERRO-ELECTRIC FILMS BASED ON LEAD TITANATE

A.M. Khoviv, V.A. Logacheva, Yu.Yu. Yakimova, A.M. Samoylov, Voronezh State University, Universitetskaya Sq. 1, 394006 Voronezh, Russia

In this work the two-stage technique has been used to fabricate lead titanate films on Si (100) substrates. Firstly, the polycrystalline Pb and Ti layers (thickness of metal films was approximately 500 nm) have been deposited on Si wafers by DC magnetron sputtering. On the second stage the Pb/Ti/Si or Ti/Pb/Si heterostructures have been annealed in the dry O2 atmosphere under ambient pressure.

By XRD measurements it has been found, that after annealing at T = 973 K during 10 minutes the Pb/Ti/Si heterostructures with the external Pb layer have consisted of PbTiO3 and PbO phases mixtures. The thickness of these heterogeneous films was about 3000 nm with the average size of the grains ~ 580 nm. The C - V characteristics of these films show the normal ferroelectrics behaviour. The residual polarization and coercive field for these films were 16.8 mC/cm2 and E=4.8 kV/cm, respectively. The results of X-ray measurements show that after annealing at T=973 K the Ti/Pb/Si heterostructures with the Ti external layer have contained the different titanium oxides and PbO. The increase in the temperature of annealing up to T=1173 K results in the formation of lead titanate PbTiO3 with little excess of TiO2 (rutile). The investigations of the electrical properties show that after annealing these Ti/Pb/Si heterostructures with the external Ti layer have no the ferroelectric properties and demonstrate the properties of the linear insulator only.

I/PII.04 FERROELECTRIC PROPERTIES OF LEAD ZIROCONATE TITANATE THIN FILMS DEPOSITE ON RUTHENIUM/RUTHENIUM OXIDE BOTTOM ELECTRODES

Young Park and Joon Tae Song, School of Information and Communication Engineering, Sungkyunkwan University 300 Chunchun-dong, Jangan-gu, Kyunggi-do, 440-746 Suwon, Korea

It has become clear over the past few years during development of thin film ferroelectric devices that the electrodes play an important role in determining the device properties and performance. Oxide electrodes of Pb(Zr,Ti)O3 thin films inhibit fatigue primarily by acting as s sink for oxygen vacancies. These oxide electrodes, however, are known to cause higher leakage current density compared with Pt electrodes. In this paper, in situ deposited Ru/RuO2 bottom electrodes have been investigated as new bottom electrodes for PZT thin film capacitor application. As a comparison, leakage current and fatigue properties of PZT thin films on RuO2 bottom electrodes are also presented. This new Ru/RuO2 bottom electrodes are expected to reduce the degradation ferroelectric fatigue and excellent ferroelectric properties. Leakage current density of PZT films deposited on Ru/RuO2 electrodes are about two orders of magnitude lower than those of PZT films deposited on RuO2 electrode. An improvement of ferroelectric properties and excellent fatigue-resisting properties were also observed. This new Ru/RuO2 bottom electrodes enable us to fabricate highly reliable capacitor for memory device.

I/PII.05 THE EFFECT OF CERIUM DOPING IN BARIUM ZIRCONATE TITANATE THIN FILMS DEPOSITED BY RF MAGNETRON SPUTTERING SYSTEM

Won Seok Choi(a), Junsin Yi(a), and Byungyou Hong(a,b), (a)School of Information and Communication Engineering, Sungkyunkwan University, Suwon 440-746, Korea, (b)Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon 440-746, Korea

Structure and electrical properties of Ba(Zrx Ti1-x)O3(BZT) and Ce-doped Ba(Zrx Ti1-x)O3(BCZT) thin films with the mole fraction of x=0.2 had been investigated. BZT and BCZT films were prepared on Pt/Ti/SiO2/Si substrate by a RF magnetron sputtering system. We have investigated the effect of Ce doping in BZT thin film. The argon to oxygen gas ratio is 4:1 and the deposition temperature is 500 oC. X-ray diffraction patterns were investigated for the two different samples. No critical difference for the surface roughness was investigated between BZT and BCZT thin films. The dielectric constant(εr) was lower in BCZT thin films compared to BZT films(εr(BZT)=145, εr(BCZT)=121). And, the dissipation factor(tanδ) was reduced in BCZT thin film. The leakage current was also reduced in Ce-doped BZT.

I/PII.06 ENHANCEMENT OF THE FERROELECTRIC PROPERTIES OF Pb(Zr,Ti))O3 THIN FILMS FABRICATED BY LASER ABLATION

Chang Hoon Jeon, Kyoung Bo Han, Hee Sauk Jhon, Sang Yeol Lee, Department of Electrical and Electronic Engineering, Yonsei University, 134 Shinchondong, Seodaemunku, Seoul, 120-749, Korea

Thin films of phase-pure perovskite Pb(Zr0.43Ti0.47)O3 (PZT) were deposited in-situ onto Pt/Ti/SiO2/Si substrates by pulsed laser deposition. We have systematically investigated the effect of the various parameters on PZT film by PLD. PZT thin films on p-type(100) Si substrate was fabricated by pulsed laser deposition technique using a Nd:YAG laser with different energy density of 1.5 to 4 J/cm2 and deposited on various substrate temperature(450℃ to 650℃) and annealing time(5 to 30 min.). By way of the result of microstructural and electrical properties of the film, the favorite condition of the PZT film deposited by PLD was 2.5 J/cm2, 550℃of substrate temperature and 20 minutes of annealing time. X-ray diffraction(XRD), scanning electron microscope(SEM), I-V, C-V measurement and hysteresis was used to investigate the electrical, microstructural properties of the thin films.

I/PII.07 STRUCTURAL AND ELECTRICAL PROPERTIES OF SOL-GEL DEPOSITED Pb(Zr0.92Ti0.08)O3 THIN FILMS DOPED WITH Nb

I. Boerasu, M.J.M. Gomes, M. Perreira, University do Minho, Campus de Gualtar, 4710-057 Braga, Portugal and L. Pintilie, National Institute of Materials Physics, PO Box MG-7, 76900 Bucharest, Romania

PZT thin films with Zr/Ti ratio of 92/8 and doped with various content of Nb were deposited by sol-gel on Pt coated Si substrates. This Zr/Ti ratio was chosen in order to speculate for pyroelectric applications the transition between the rhomohedral phases of low and high temperature. The influence of Nb content on structural and physical properties of the PZT film was studied. Pyrochlor phase is present in the film after annealing in air. This secondary phase seems to be metastable for films with 0 % and 2 % Nb doping and can be suppressed by further annealing in oxygen enriched atmosphere, with a considerable enhancement of the rhombohedral perovskite phase. In case of 4 % Nb doping the pyrochlor phase still exists after annealing in oxygen atmosphere, suggesting that excess Nb stabilise this phase. The annealed films exhibit (111) or (110) preferred orientation but no relation with the Nb content can be made. Standard current-voltage measurements were performed in order to establish the Nb influence on the leakage current. The pyroelectric effect was evidenced in these films.

I/PII.08 SPUTTER DEPOSITED Pt-Ir OXIDES THIN FILMS and THEIR CHARACTERIZATION

Kiyoshi Kuribayashi, Yoshito Fujita, Hideyuki Ishige and Takaya Iwanuma, Department of Environmental and Material Engineering, Teikyo University of Science & Technology, Uenohara, Yamanashi 409-0193 Japan

Pt-Ir and their oxides thin films were prepared on Si(100) substrates at temperatures from 400℃ to 600℃ by reactive rf magnetron sputtering with Pt-20 mass% Ir target and Ir chips set on the target. X-ray fluorescence analysis revealed that deposited films had a composition from Pt-0 mass% Ir to Pt-60 mass% Ir. Further increase in Ir content in the films resulted in a delamination from a substrate. Deposition atmosphere was varied with O2 / Ar flow ratio from 0 to 20%. Deposited films consisted of Pt-Ir alloy and their oxides such as PtO, PtO2 and IrO2, which were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. Resistivity of the films were measured by d.c. four probe method to be from a order of 10-4 Ω・cm to 10-3 Ω・cm. In order to study performance of the films as electrode, SrTiO3 as dielectric and Pt as upper electrode were sputter deposited on Pt-Ir-oxide / Si substrate in order. And current / Voltage characteristics of SrTiO3 was measured in comparison with that of Pt/ SrTiO3/ Pt /Si structure.

I/PII.09 SYNTHESIS OF LEAD TITANATE THIN FILMS BY SOLID STATE REACTIONS

Vytautas Stankus, Julius Dudonis, Kaunas University of Technology, Physics, Studentu 50, Kaunas, Lithuania

The performed scientific research work is devoted to a metal oxide lead titanate (PbTiO3) thin films. This work was focussed mainly on preparation and investigation of thin PbTiO3 films microstructure formation ex-situ, using solid state reactions by annealing Pb/Ti and X(Pb/Ti) multilayer structures in oxygen atmosphere. The primal structures were formed by reactive magnetron sputtering deposition method. Structure changes, phase composition transition of as deposited and post-annealed thin films were measured and analyzed using X-ray diffraction method. The kinetic reactions and crystallites growth's regularities in annealed thin films were investigated too. The surface morphology were investigated by SEM microscopy.

It was concluded that there is a possibility to get perovskite PbTiO3 thin films through oxidation and solid state reactions by annealing the Pb/Ti or X(Pb/Ti) structures in atmosphere. Pure nanocrystalline PbTiO3 forms at 650oC temperature and in 60 minutes as the minimal time. The quality and surface roughness of formed thin films heavily depends on substrate type, annealing temperature, multilayer structure and cooling rate. There was shown and researched PbTiO3 formation from the two-layer (Ti/Pb) and multilayer metallic systems. Regardless of similarity of the methods, results show entirely different formation mechanisms. This indicates that solid-state reaction mechanism may be changed artificially, forming corresponding heterostructures.

Research of complex combinations, which are forming in thin layers by solid-state reactions, could help better understand what mechanisms are taking place inside them. This would allow better control of the structure and its corresponding properties.

I/PII.10 BNT CERAMICS SYNTHESIS AND CHARACTERIZATION

A. Ioachim, G. Stoica, M.I. Toacsen, G.M. Banciu, L. Nedelcu, National Institute for Materials Physics, Bucharest-Magurele, H.V. Alexandru, C. Berbecaru, F. Stanculescu, Faculty of Physics, University of Bucharest, Romania

BaO-Nd2O3-TiO2 ternary compounds (BNT) are very attractive for applications in the microwave range. The Curie constant decreases rapidly with Nd concentration. Around room temperature, in paraelectric phase, the dielectric constant is high, can be monitored with a bias field, is quite stable with temperature and the losses are remarkable low (<10-3).

Several sets of samples, produced by ceramic technology, were analyzed. Dielectric measurements were performed on the temperature range -100 / +100 oC and down the pyroelectric technique was used to find the Curie points. X-ray spectra revealed the orthorhombic structure of BaNd2Ti5O14 (1/1/5 ternary compound) as dominant phase. Three type of dopants were used to improve high frequency characteristic of materials: 0.3-0.5 mol % PbO for Ba substitution and NiO and/or ZnO (less than o.2 wt %), in order to obtain higher densities and lower sintering temperature. These additives act as inhibitors of the grain growth and improve Q quality factor at high frequencies. Joint methods of characterization SEM, EDX, WDX, (A.Ioachim et al, J.Electr.Eng.-in press) were used to investigate the microstructure of materials. High Nd concentration ceramics ~20 wt %, sintered 2 hours at 1250 oC appears to be suitable for dielectric resonators (permitivity ~ 80-90 and Q ~ 2000) up to frequencies of 3 GHz.

I/PII.11 INTRINSIC CONDUCIVE OXIDE - p-InSe SOLAR CELLS

Z.D. Kovalyuk(a), V.M. Katerynchuk(a), A.I. Savchuk(b) and O.M. Sydor(a), (a)Chernivtsi Department of the Institute of Materials Science Problems, The National Academy of Sciences of Ukraine, 5 Iryna Vilde St., 58001 Chernivtsi, Ukraine, (b)Dept. of Phys. Electronics and Nontraditional Energetics, Chernivtsi National University, 58012 Chernivtsi, Ukraine

Some properties of InSe single crystals make them attractive for applications in solar energy conversion devices. InSe has an energy gap at room temperature of about 1.2 eV, which is very close to maximum efficiency in solar cells. The layered crystalline structure allows preparing thin films with perfect mirror-like surfaces without dangling bonds that is the ground of creating the p-n-junctions of high quality. The thermal oxidation of such p-InSe substrates leads to the creation of the surface oxide layer with a metallic conduction and high transparency. Such an obtained intrinsic oxide - p-InSe junction is the active element of the corresponding photosensitive heterostructure.

The properties of the conductive oxide on the InSe surface and the photoelectrical characteristics of the intrinsic oxide - p-InSe structures in dependence on time - temperature oxidation conditions are analyzed. The current-voltage and capacitance - voltage characteristics are an evidence for the creation of high quality p-n-junction on the conductive oxide - layered crystal interface. It is found that for the best samples at a power illumination 100 mW/cm^2 the open circuit voltage ranges from 0.60 to 0.62 V and the short circuit current is 36 to 40 mА/сm^2 (Т=300 К). Loading characteristics of the intrinsic oxide - p-InSe solar cells were investigated at different illumination levels. It is found that the series resistance affects the photoelectrical properties of the heterojunctions.

I/PII.12 DESCRIPTION OF Ga2O3 FILM CREATION ON THE GaSe SURFACE WITHIN THE FRAME OF LATTICE GAS MODEL

Y.M. Stakhira, N.K. Tovstyuk, Ivan Franko Lviv National University, Phys. Dept., 50 Dragomanov St., Lviv 79005, Ukraine

It is well known, the combination of metal oxide and layer semiconductor significantly widen the photoconductivity spectrum of received heterostructure. The observed GaSe thermooxidation is slightly unexpected from the point of thermodynamic view [1], because at small T<450C creation of Ga2Se3 is observed, at T>650C Ga2O3 phase is created, while Gibbs potential of gallium oxide is smaller then Ga2Se3 one. Thermodynamics of GaSe oxidation in the gas lattice model for two atoms type (oxygen and selenium) and in the condition of in turn different energy states occupation (a state is in sites, b state is in interstitial) are carried out. Sharp redistribution of selenium and oxygen atoms depending on: і) their chemical potentials, іі) oxygen chemical potential and average occupation number of selenium are obtained. The correlation between oxygen, selenium chemical potentials and energy parameters of a,b sites filling by Se and O is found. It is shown, that at low temperatures selenium dominates, at higher temperatures it is replaced by oxygen. Interaction between Se and O, considered within the average field approximation showed that the region of sharp redistribution is the I-st type phase transition.

1. Berchenko N.N. et al. Characteristics of phase formation during GaSe oxidation. // Materials chemistry and physics.- 1997.- v.51.-p.125.

I/PII.13 STUDY OF DENSITY OF TRAPS IN HIGH PERFORMANCING TFTS MADE UP IN UNHYDROGENATED IN SITU DOPED FILMS

H. Boudiaf(a), F. Le Bihan(a), Z. Benamara(b), L. Pichon(c), F. Raoult(a), (a)Groupe Microelectronique, UMR CNRS 6164, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France, (b)Laboratoire de Microelectronique Appliquée, Université Djillali liabès, Sidi bel abbès 22000, Algérie, (c)GREYC-ISMRA, 6 Bd du Maréchal Joffre, 14050 Caen, France

Low temperature unhydrogenated in situ doped polysilicon thin film transistors with an APCVD SiO2 deposited gate insulator were fabricated. The polysilicon layers which make up the active layer and the in situ doped source and drain region were deposited, after an optimization of the deposition pressure step, in the amorphous state and crystallized by thermal annealing.

To obtain a good APCVD SiO2 gate insulator / active layer interface quality, an oxygen Plasma + RCA-type wet cleaning were used: These TFTs exhibit good electrical properties : a low threshold voltage (2V), a high field effect mobility (>60 cm2.V.S-1) and a high On/Off state current ratio (> 107) in the linear mode.

It is worth noting that the hydrogen passivation was not performed, and the above electrical performances are similar to those obtained on the hydrogenated TFTs. These high performances could be correlated to the low states density of traps at intergranular boundaries and /or at SiO2 gate insulator / active layer interface.

I/PII.14 PHOTOCONDUCTIVITY AND PHOTOINJECTION OF Li DOPED ZnO FILMS FOR PHOTODETECTOR APPLICATIONS

N.R. Aghamalyan, R.K. Hovsepyan, E.S. Vardanyan, Institute for Physical Research of National Academy of Sciences of Armenia, 378410 Ashtarak-2, Armenia

The nominally pure ZnO is n-type semiconductor. The n-type conductivity is suppressed at doping of ZnO film by Li ions in small quantities. Creating sandwiches from ZnO layers with the different content of Li impurity it is possible to obtain Schottky barriers on a basis semiconductor- semiconductor. We used sandwich consisting from three ZnO layers doped accordingly 1, 5 and 10 at. % of Li ions to obtain the Schottky contacts of a semiconductor- semiconductor type. The spectral dependence of photoconductivity current has two peaks: 3.33 and 3.23 eV. The first peak is caused by excitation of electrons from a valence band to conductivity band. The second peak situated in the optical transparence region a ZnO film coincides with a spectral maximum of a photoinjection current in the single-layer ZnO film with 0.8 at. % Li. This peak is apparently stipulated by photoinjection of charge carriers on semiconductor-semiconductor boundary in a sandwich consisting from layers with the different Li content. Thus, the spectral region of a photosensitivity of a sandwich reaches from ~3 eV up to ~3.8 eV, i.e. enhanced in comparison with a single-layer ZnO film.

I/PII.15 INTRINSIC CONDUCIVE OXIDE - p-InSe SOLAR CELLS

Z.D. Kovalyuk(a), V.M. Katerynchuk(a), A.I. Savchuk(b) and O.M. Sydor(a), (a)Chernivtsi Department of the Institute of Materials Science Problems, The National Academy of Sciences of Ukraine, 5, Iryna Vilde St., 58001 Chernivtsi, Ukraine, (b)Dept. of Phys. Electronics and Nontraditional Energetics, Chernivtsi National University, 58012 Chernivtsi, Ukraine

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I/PII.16 STRUCTURE OF ZNO DIELECTRIC THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING

V.A. Karpina(a), V.I. Lazorenko(a), C.V. Lashkarev(a), V.D. Dobrowolski(a), L.I. Kopylova(a), V.A. Baturin(b), S.A. Pustovoytov(b), A.Ju. Karpenko(b), S.A. Eremin(b), P.M. Lytvyn(c), (a)Institute for Problems of Material Sciences, National Academy of Sciences of Ukraine, 3 Krzhyzhanovsky str., Kyiv 03142, Ukraine, (b)Institute of Applied Physics, National Academy of Sciences of Ukraine, 40032 Sumy, Ukraine, (b)Institute for Semiconductor Physics, National Academy of Sciences of Ukraine, 45 Nauka Ave., Kyiv 03028, Ukraine

Thin films of zinc oxide were deposited by RF magnetron sputtering using zinc target and Ar+O2 as working gas. The thickness of films was in interval 0.2-0.4 mm. All films were dielectrics. We investigated the structure of ZnO thin films in dependence on substrate temperature and composition of working gas. The best results were obtained at 20-30% of O2 and a temperature of a glass substrate about 300oC. Films have only one strong peak (002) in XRD spectra and transparency 85%. The surface morphology was studied by AFM. The AFM images shows that the films have granular surface with grain size about 60 nm. The films are characterized by smooth surfaces with average roughness 5 nm. Optical absorbtion and luminescence as well as photoconductivity were measured and discussed. Having an excelent UV shielding these films can be used as protective ones.

I/PII.17 STUDY OF ELECTRICAL AND OPTICAL PROPERTIES OF ZINC OXIDE THIN FILMS GROWN BY REACTIVE MAGNETRON SPUTTERING METHOD

Kh.A. Abdullin, A.B. Aimagambetov, A.T. Issova, B.N. Mukashev, S.Zh. Tokmoldin, Institute of Physics and Technology, Ibragimov Street 11, Almaty 480082, Kazakstan

Zinc oxide (ZnO) is very perspective material for practical applications, because thin films of ZnO have high electrical conductance and high optical transparency. Main purpose of this report was ZnO films grown process study. The ZnO films were fabricated by dc reactive magnetron deposition on glass and silicon substrates using a metallic zinc target. The relationship between preparation conditions and thin film parameters was investigated. The discharge power dependence as well as total pressure and oxygen partial pressure dependence of deposition speed was defined. The optimal regimes for obtaining of minimum resistivity were determined. p-n-junctions were formed by reactive magnetron deposition of ZnO films on р-type silicon substrates; their volt-ampere characteristics were measured. The value of forbidden gap was obtained from optical transmission measurements.

I/PII.18 X-RAY, OPTICAL AND ELECTRICAL CHARACTERISATION OF DOPED NANOCRYSTALLINE TITANIUM OXIDE THIN FILMS

J. Domaradzki, E.L. Prociow, D. Kaczmarek, Faculty of Microsystem Electronics and Photonics, ul. Janiszewskiego 11/17, 50-372 Wroclaw, Poland, A. Podhorodecki, R. Kudrawiec, J. Misiewicz, Institute of Physics, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland, W. Mielcarek, Electrotechnical Institute, ul. M. Sklodowskiej Curie 55-61, 50-369 Wroclaw, Poland

It is well known that in the case of a wide range materials used in opto- and microelectronics it is possible to modify its structural, optical and electronic properties by introducing additional atoms into master-lattice matrix (i.e. doping). This law has been also proven in the case of insulators and conducting oxides and in the past few years has been extensively developed.
In the present work we have reported results of basic optical and X-ray diffraction examinations of modified titanium oxide thin film layers. Samples were obtained by deposition in low pressure hot target magnetron sputtering process. Besides structural and optical, features special interest has been put onto electrical properties of obtained layers. It has been shown that manufactured layers were sensitive upon light illumination. On the basis of measured photocurrent basic studies on electrical-charge transport and its behavior has been also discussed. It has been shown that atoms of transition or noble metals, such in this case V, Co and Pd ones modify the electronic state structure of oxide by introducing additional close situated energy levels which may be activated by light or thermal excitation.

I/PII.19 STRAIN EFFECTS IN MANGANITE THIN FILMS: A REVIEW OF THE EXPERIMENTAL RESULTS

W. Prellier and B. Mercey, Laboratoire CRISMAT, CNRS UMR 6508, Bd Marechal Juin, 14050 Caen, France

Perovskite type manganites such as RE1-xAxMnO3 (R=rare earth ion and A=alkaline earth ion) have been extensively investigated due their properties of colossal magnetoresistance. The CMR effect originates from a competition between a ferromagnetic metallic state and an antiferromagnetic insulating state. The efforts to understand the magnetotransport properties of manganite thin films have shown that the physical properties are often different from their bulk compounds. The main cause involves strains, including the substrate-induced strains which modify the lattice parameters of the film and after their properties. In manganite thin films, the strain may modify the Mn-O-Mn angles and Mn-O distances. Consequently, this affects the bandwidth and also the JT distortions, so that the DE and CO/OO phenomena are drastically influenced.
Based on this idea, we have grown various charge-ordered thin films having the composition A0.5Ca0.5MnO3 (A=Pr,Ca), using the pulsed laser deposition technique. Through these compositions, we will show how the choice of the substrate can affect the structural and the physical properties of the film as compared to the bulk material. The thickness dependence will also be presented. This will be compared to the state of art after a review of the different results obtained on these compounds in the past years.

I/PII.20 EPITAXIAL GROWTH OF FERROMAGNETIC INSULATING LA1-XBIXMNO3 PEROVSKITE THIN FILMS

M. Gajek(a), C. Ferrater(b), F. Sanchez(b), M. Varela(b), J. Fontcuberta(a), (a)Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigación Científica, 08193 Bellaterra, Catalunya, Spain, (b)Department de Física Aplicada i Òptica, Universitat de Barcelona, Avinguda Diagonal 647, 08028 Barcelona, Spain

La1-xBixMnO3 perovskites show particular behaviour among the manganite materials family. It is known that it is simultaneously ferromagnetic and insulating over a large range of La concentrations [1] which makes it a very promising material for novel spin electronics devices. The pristine BiMnO3 compound can only be prepared (in bulk form) under high pressures. In this paper we shall report on the growth of La1-xBixMnO3 epitaxial films. Low La doping (≥10%) allows lower pressure synthesis. In addition, the use of substrates with smaller lattice parameter is essential to provide an artificial pressure during the deposition process. In the present work, we report the growth of this phase by the mean of epitaxial stabilization at low pressure on SrTiO3 and LaAlO3 substrates [2]. The effect of La substitution of Bi sites and thickness influence on magnetic and structural properties are investigated. The influence of growth parameters on the evolution of the surface morphology is also described.

[1] Troyanchuk JETP 78 (2), 214, February (1994)
[2] E. Ohshima & al. Solid State Communications 116 (2000) 73-76

I/PII.21 ELECTRONIC STRUCTURE OF EPITAXIAL Fe3O4 LAYERS ON MgO AND MgAl2O4 SUBSTRATES STUDIED BY X-RAY ABSORPTION, PHOTOEMISSION AND FLUORESCENCE

S.A. Krasnikov(a), R. Höhne(b), T. Chassé(a), R. Szargan(a), (a)Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig, Germany, (b)Department of Superconductivity and Magnetism, Institut für Experimentelle Physik II, Universität Leipzig, Linnéstr. 5, 04103 Leipzig, Germany

Investigation of Fe3O4 films (protected and unprotected by thin BaTiO3 layer) with different thicknesses on single crystal MgO and MgAl2O4 substrates were carried out by x-ray absorption (XAS) and photoemission spectroscopy (XPS) and x-ray fluorescence (XF). All samples were prepared by pulsed laser deposition (PLD). The photoemission (VG ESCALAB 220i-XL) and absorption (total electron yield mode) measurements on epitaxial Fe3O4 films demonstrate the important role of the protecting layer to prevent the further oxidation of Fe3O4 to Fe2O3 stage in the case of thin films (2.5 nm range). The XF (X-ray monochromator XES 300 using synchrotron radiation at the U41-PGM beam-line at BESSY II) measurements across the Fe L2,3 thresholds demonstrate resonant effects which provide information about the d-d transitions and charge-transfer excitations. Information about local partial densities of states was obtained from a comparative analysis of Fe L and O K x-ray fluorescence and VB photoemission spectra.

I/PII.22 MAGNETOELECTRONIC PROPERTIES OF SEMICONDUCTOR/SPIN-VALVE STRUCTURES

V. Sohatsky, V. Kovalenko, Department of Radiophysics, Taras Shevchenko Kiev University, Ukraine, C. Schneider, J. Schumann, Leibniz Institute of Solid State & Material Research, Dresden, Germany

Thin film structures with ferromagnetic (FM) and semiconducting (SC) layers that are promising for spintronic applications still have a lot of fundamental problems to be solved. A few methods as MOKE magnetometer, optical spectroscopy, conductivity measurements and tunnelling microscopy were used to study the effects of electron transport and irradiation on remagnetization of spin-valves of based compositions Co/Cu/Co, Co/Cu/NiFe, Co/Al2O3/Co with the thicknesses from monolayer up to 10 nanometers (the latter were determined by Auger or LEED spectroscopy) deposited on Si substrates. A difference in the direct and opposite perpendicular to plane conductivity due to FM-SC Schottky barrier were changing with applying magnetic field as well as under irradiation. MOKE hysteresis loops were recorded with 0.63 and 0.488 microns laser beam both in local (up to 1 micron) and total film areas at temperatures 290-350K. A distortion (displacement) of the hysteresis loops measured with longitudinal Kerr effect were in a principal agreement with the theoretical evaluations of the spin-valves in-plane anisotropy. At the same time the electric transport measurements showed that influence of electric currents on remagnetization in case of the additional irradiation by low-intensity (<5 mW) polarized laser light can surpass the value obtained earlier. Changes of the hysteresis loops shape under external bias are especially manifested in the vicinity of the domain wall instability points.

I/PII.23 THE GROWTH AND MAGNETIC PROPERTIES OF CoCr2O4 EPITAXIAL FILMS

U. Lüders(a,b), J.F. Bobo(b) and J. Fontcuberta(a), (a)Institut de Ciència de Materials de Barcelona – CSIC, Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalunya, Spain, (b)Laboratoire de Physique de la Matière Condensée INSA, 135, Avenue de Rangueil, Toulouse, France

Epitaxial growth of oxides is rather well known for simple systems like the perovskites, while the growth of more complex oxides is still under investigation. The latter, like the spinel oxides, show a rich diversity of electrical, magnetic and optical properties, the application and performance of which would be improved by the use of epitaxial thin films.

CoCr2O4 (CCO) is a ferromagnetic cubic spinel with a TC of about 100K. The lattice parameter is 8.33Å. In this paper we shall report on the growth of CCO epitaxial films on single crystalline (001) oriented substrates, either isostructural (MgAl2O4) or rocksalt (MgO) structure, with the aim of determining the role of lattice/structure mismatch (3% or -1.2% respectively) on the structural and magnetic properties of the films. The films were grown by RF magnetron sputtering; irrespectively on the substrate we achieved either in plane and perpendicular to plane epitaxial films with a crystal structure similar to bulk. The magnetization measurements show a TC of around 100K. The dependence of the magnetic properties on the substrate will be reported. It will be shown, that for some range of growth parameters it is not possible to achieve a continuous film, but well-separated oriented islands are formed.

I/PII.24 MAGNETORESISTIVE PROPERTIES OF LaMnO(3+Х) WITH DIFFERENT OXYGEN CONTENT

V.I. Lazorenko, G.V. Lashkarev, K.D. Skurtul*, A.N. Shmyreva*, M.V. Radchenko, M.E. Bugayova, L.I. Petrosyan, Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzhizhanovsky st, 03680 Kiev-142, Ukraine, *National TechnicalUniversity of Ukraine

Till now an examination of manganites with different content of oxygen practically was not carried out. At the same time the oxygen in this compound plays a decisive role for the determination the ratio of concentrations Mn4+/Mn3+. The research of effect of this ratio on physical properties of manganite attracts great interest because of the attempts to reach high values of MR at low magnetic fields.

Electroresistance, magnetoresistance, thermoelectric power and magnetic susceptibility for three groups of ceramic samples of lanthanum manganite LaMnO(3+Х) with different oxygen content were investigated in the temperature range 77-300К. For all groups of samples the presence of ferromagnetic ordering at Curie temperature 220-245К was accompanied by the appearance of negative magnetoresistance and temperature interval of semiconductor conductivity. The maximum value of negative magnetoresistance 13 % at magnetic field 0,5T and 77К was observed for two-phase samples with the least oxygen content. In the temperature region higher than Curie point all sample groups are characterized by semiconductor conductivity with an activation energy 0,12eV, peculiar to the basic phase LaMnO3,15. It was assumed that hole transport occurs through d - states of manganese, which form the valence band of LaMnO3,15.

I/PII.25 SYNTHESIS AND CHARACTERISATION OF La1-xNaxMnO3+d THIN FILMS MANGANITES

I. Alessandri(a), E. Bontempi(a), L. Malavasi(b), G. Flor(b), M.C. Mozzati(c), C.B. Azzoni(c) and L.E. Depero(a), (a)INSTM and Laboratorio di Strutturistica Chimica - Università di Brescia, via Branze 38, 25123 Brescia, Italy, (b)INSTM, Unità di Pavia, Dipartimento di Chimica Fisica "M.Rolla", Università di Pavia, V.le Taramelli 16, 27100 Pavia, Italy, (c)INFM, Unità di Pavia, Dipartimento di Fisica "A.Volta", Università di Pavia, via Bassi 6, 27100 Pavia, Italy

Since the discovery of the colossal magnetoresistence (CMR) in manganese perovskites, these materials have attracted a renewed interest because of their potential applications in magnetoelectronics and spintronics. Development of low field magnetoresistence (LFMR) devices can be obtained from manganites thin films deposited onto lattice mismatched substrates.

Sodium-doped manganites thin films were grown by Rf-magnetron sputtering on various single-crystalline substrates, such as SrTiO3, NdGaO3 and Si, with different orientation. We investigated the influence of various parameters (microstructure, thickness, synthesis conditions, oxygen stoichiometry etc..) on transport and magnetoresistive properties. An exhaustive structural characterisation was performed by means of several techniques: X-ray microbeam diffraction, X-ray reflectivity (XRR), glancing angle X-ray diffraction (GIXRD), micro-Raman spectroscopy, scanning electron microprobe and atomic force microscopy (AFM).

I/PII.26 MECHANOCHEMICAL SYNTHESIS, STRUCTURE AND PHYSICAL PROPERTIES OF NANOCRYSTALLINE CERAMICS BASED ON Bi2O3 METASTABLE SOLID SOLUTIONS

V. Zyryanov, N. Uvarov, V. Kostrovskii, Institute of solid state chemistry, Novosibirsk, Russia M. Ivanovskaya, SRIPCP BSU, Minsk, Belarus

New orthorhombic metastable phase d`-Bi2O3 and severe new Bi2O3-based solid solutions with fluorite (Bi2-xSbxO3, Bi2-xCaxO3-0.5x, Sb2-x-yBixCayO3-0.5y) and perovskite (Bi2BaO4, BiCaxSbyOz) related structures were obtained by mechanochemical synthesis at room T. The characterization of powders and dense samples after hot pressing was made by XRD, XPS, Raman and IR, ESR spectroscopy, DTA/DTG, conductivity measurements. Anti-Vegard's dependence was observed for solid solutions Bi2-xSbxO3 of black color. The model of "antiglass" structure for mechanochemical origin powders will be discussed. Structural transformations of metastable oxides take place simultaneously with oxidation/reduction during heating in the air beginning from 300C. Metastable d`-Bi2O3 and other Bi-rich compounds reduce under heating in the air with formation Bi2+. This unusual phenomenon is related to radical formation like BiO+ during mechanical treatment. Bi2-xCaxO3-0.5x demonstrates superionic conductivity (10-3 S/cm at 500C) up to decomposition.

Sb2-x-yBixCayO3-0.5y is a precursor for materials with promising properties of sensor, proton conductor, and absorbent. This work was partly supported by RFBR (grant 02-03-33330) and INTAS (grant 01-2162).

I/PII.27 INVESTIGATION OF STRUCTURAL PROPERTEIES NANOCRYSTALLINE WO3 FILMS FORMED BY EVAPAORATION AND ANNALING

A.H. Jayatissa and S.T. Cheng, Materials Science and Engineering Program, CMD Department, Western Michigan University, Kalamazoo MI 49008, USA

The effect of thermal annealing on tungsten oxide (WO3) thin films deposited by vacuum evaporation was investigated. The properties of films were studied in terms of annealing temperature and annealing time. It was found that the crystallinity and physical properties of WO3 films were changed by annealing temperature as low as 100 oC. The X-ray diffraction and Raman spectroscopy indicated that the as-deposited films were composed of nanometer size grains. While the crystal structure remained monoclinic, the size of crystals changed from nanometers to hundreds of nanometers by annealing in 100-600 oC range. It was also found that the films annealed at 500 oC for 5 hours had low surface roughness, good adhesion and high optical transmittance whereas films annealed at 600 oC were delaminated. Surface topography was also investigated with atomic force microscopy. The optical gaps calculated from the transmission spectra were in good agreement with those reported for crystalline WO3 films.

Session VI Multicomponent oxides II
Session chair: J. Levy and J. Robertson

I-VI.1 8:30 -Invited- CRYSTALLINE OXIDES ON SEMICONDUCTORS : ENABLERS OF NEXT-GENERATION FUNCTIONAL ELECTRONICS

R. Ramesh, University of Maryland, College Park, USA, D.G. Schlom, Penn. State University, USA, C.B. Eom, University of Wisconsin, Madison, USA, R. Droopad and K. Eisenbeiser, Motorola, PSRL, Tempe, USA

Complex multicomponent oxides continue to be prominently featured at various levels of science and technology evolution, from the most basic science to advanced product development. In some cases(e.g., memories), the complexity of the integration with Si-CMOS is quite high. The common theme to all of this is the ability to create Epitaxial Oxides on Semiconductors(COS) without compromising the structure, chemistry and intrinsic properties of either one of them. In some of the early work, epitaxial perovskites on silicon was accomplished through complex buffer layers and templates. Recent developments in this field have dramatically simplified this template approach and the field is poised to create NEW devices which take advantage of the existence of structural, chemical and electronic interfaces between the semiconductor and the functional oxides. It is our belief that this field is now at another very exciting stage of evolution with the potential to impact several technology areas. In this presentation, we illustrate the potential of COS through some examples involving ferroelectric, piezoelectric and magnetic oxides on silicon, enabled through the use of novel, perovskite templates on silicon.

I-VI.2 9:10 EFFECT OF THE TUNNELLING OXIDE THICKNESS AND DENSITY ON THE PERFORMANCE OF MIS PHOTODIODES

H. Águas(a), A.Goullet(b), L. Pereira(a), E. Fortunato(a), R. Martins(a), (a)Departamento de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP, Campus da Caparica, 2829-516 Caparica, Portugal (b)Laboratoire des plasmas et Couches Minces, Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, 44322 Nantes cedex 3, France

In this work metal-insulator-semiconductor (MIS) photodiodes with a structure: Cr/a-Si:H(n+)/a-Si:H(i)/oxide/Au was studied, where the main objective was to determine the influence of the oxide layer grown by different techniques on the performance of the devices. The results achieved show that the photodiodes performances are a function of both oxide thickness and oxide density and that similar results are achieved when thin < 20Å dense oxides or thicker > 20Å porous oxides are used. Anodic oxidation, H2O2 oxidation, evaporation of SiO2 by electron gun, and chemical deposition of SiO2 by plasma of HMDSO were investigated.

The experimental data show that the thickness of the oxide is easily controlled with the hydrogen peroxide oxidation technique, which is also the easiest and cheapest known technique. By proper control of the oxide thickness it was possible to achieve photodiodes exhibiting an open circuit voltage of 0.7V and short circuit current density under AM1.5 illumination above 11 mA/cm2, with a response times less than 1 ms, a diode quality factor of about 1 and a ratio of 107 between forward and reverse currents. The ideal oxide thickness, determined by spectroscopic ellipsometry was estimated to be in the range of 5 to 30 Å, depending on the oxidation technique used, which determines the degree of the oxide density. In this work it is also presented a method for reducing the saturation current of the diodes by burning small short-circuits by applying to the devices a controlled reverse voltage.

I-VI.3 9:30 FIELD-EFFECT TRANSISTOR BASED ON NANOMETRIC THIN CdS FILMS

G. Sarau, E. Pentia, B. Mereu, V. Draghici, M. Lisca, T. Botila, National Institute of Materials Physics, PO Box MG-7, Bucharest-Magurele 76900, Romania

CdS thin films were deposited by CBD (Chemical Bath Deposition) method on SiO2/Si (n-type) substrates. Approximately 70-nm thick nano-crystalline CdS layers were obtained. The SiO2 film was obtained by standard thermal oxidation and has a thickness of about 250 nm. Pseudo-MOS structures were realized by deposition of two coplanar electrodes of Au (drain and source) on CdS surface. The gate contact is aluminum deposited on the backside of the Si substrate. The as-deposited films were then annealed at 300 °C for about 1 h in air. The drain current-voltage characteristics were performed in dark and under illumination with white and monochromatic light. Normal field effect transistor characteristics are obtained in case of positive gate voltage, the device acting as an n-channel transistor in the accumulation mode. An on/off - current ratio of 102 is reported, this being limited in our case by geometry. Under illumination the drain current-voltage characteristics tend to become linear as the intensity of light increases.

I-VI.4 9:50

STUDIES ON THE CRYSTAL GROWTH ASPECTS OF EFFICIENT OPTICAL DATA STORAGE MATERIAL: Mn DOPED NEAR-STOICHIOMETRIC LITHIUM NIOBATE (Mn:SLN)

G. Ravi(a), K. Kitamura(a), S. Takekawa(a), M. Nakamura(a), Y.Liu(a) and H.Hatano(b), (a)Advanced Materials Laboratory, National Institute for Materials Science (AML/NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, (b)Corporate Research and Development Laboratories, Pioneer, 6-1-1 Fujimi, Tsurugashima, Saitama 350-2288, Japan

Among all other photo refractive crystals, lithium niobate is believed to be the most promising material for digital data storage applications. These crystals need to be grown with high optical perfection that can provide good photo refractive properties, such as high capacity recording, reversibility, ability to record efficient volume holograms with modest laser power and availability in large size and good quality. However, one serious problem in the implementation of holographic data storage is the gradual erasure of the stored information during readout, i.e., volatile or destructive readout. Recently we have demonstrated nonvolatile two-color holographic recording with high sensitivity in as-grown SLN crystal doped with 8 ppm of Mn [1]. In the present investigation, growth aspects of optical quality Mn doped near stoichiometric lithium niobate (SLN) crystals studied for different doping concentrations and good quality crystals have been grown with optimized growth parameters. For Mn doped SLN crystals, the absorption edge is shifted to longer wavelength side with the doping level. A change in Curie temperatures with respect to doping concentration of Mn has been observed. The effect of Mn doping on the optical properties has been analyzed by measuring the two-color holographic recording, refractive indices and optical damage threshold of the grown crystals. The results will be presented in detail.

[1] Y. Liu, K. Kitamura, S. Takekawa, G. Ravi, M. Nakamura, H. Hatano and T. Yamaji, Appl. Phys. Lett. 81(2002)2686-2688.

10:10 **BREAK**

I-VI.5 10:30

INFRARED SPECTROSCOPY STUDY OF LI-DOPED AND GA-DOPED THIN ZNO FilMS

Y.A. Kafadaryan, S.I. Petrosyan, A.L. Manukyan, A.G. Hayrapetyan, R.K. Hovsepyan, E.S. Vardanyan, Institute for Physical Research, National Academy of Sciences, Ashtarak-2, 378410, Armenia

Li-doped (0-10 at. %) and Ga-doped (0-2.0 at.%) ZnO films were grown in the wurtzite structure on a (0001) sapphire substrates and their electronic and phonon properties characterized by the polarized oblique (45^o) and near-normal incidence reflectivity spectroscopy in the frequency range of 30000-200 cm^-1. Modeling of optical reflectivity spectra using Drude-Lorentz model enabled us to determine : i) LO phonon-plasmon coupling in the Li-ZnO films with free carrier density n<10^18 cm^-3); ii) conductivity, scattering mechanism and surface plasmon effect in the high-conductivity (n~10^21 cm^-3) Ga-ZnO films. These results are discussed in connection with structural and dc-electrical measurements.

I-VI.6 10:50

ITO FILMS DEPOSITED BY RF-PERTE ON UNHEATED POLYMER SUBSTRATES – PROPERTIES DEPENDENCE ON ALLOY COMPOSITION

C. Nunes de Carvalho(b), G. Lavareda(a), A. Amaral(c), (a)Departamento de Ciência dos Materiais, FCT-UNL, Quinta da Torre, 2825-114 CAPARICA, Portugal; ·(b)Centro de Física Molecular, Complexo I and (c)Departamento de Física, IST-UTL, Av. Rovisco Pais, 1049-001 LISBOA, Portugal

In reactive thermal evaporation, ITO films are usually obtained through the evaporation of a 90%In:10%Sn alloy on heated substrates. Since the appearance of devices mounted on flexible substrates, new vacuum techniques have been reported in order to obtain good transparent and conductive ITO films at low temperature as a key towards cheap, mass production, flexible displays. In this work we continue the study of one of these deposition techniques - radio frequency plasma enhanced reactive thermal evaporation (rf-PERTE) - with the influence of the In:Sn alloy composition on the main properties of ITO films. We varied the Sn contain in the alloy in the range 5-20%. The other deposition parameters were kept constants: rf power: 50 W; oxygen pressure: 7´10-4 mbar; rf electrode distance from substrates: 10 cm and deposition rate: 0.1-0.2 nm/s. The substrates are of polyethylene terephthalate (PET); area 10´10 cm2. ITO films thickness is around 60 nm. First results show ITO films deposited from a 90%In:10%Sn alloy with a visible transparency of about 80% and a sheet resistance of about 2.4´102 W/sq. with the opportunity for further improvement. The appearance of cracks or fractures in the ITO films due to substrate deformation in tension was also investigated.

I-VI.7 11:10

SILICON BASED MOS UV AND IR PHOTODETECTOR USING ULTRA THIN Ta2O5 FILM OPERATING IN BOTH BIAS POLARITIES

V. Mikhelashvili and G. Eisenstein, Department of Electrical Engineering, Technion-Israel Institute of Technology, Haifa 3200, Israel

A metal-oxide-semiconductor (MOS) structure with an ultra thin (effective oxide thickness equal to 2 nm) Ta2O5 film on a P-type Silicon substrate is proposed and demonstrated as a photodetector in the UV and IR spectral ranges. Room temperature electron beam gun evaporation is used for the dielectric deposition while the metal gate contact is Pt. The structure is photosensitive for either bias polarity of the applied voltage. For a negative electrode voltage, the largest observed responsivities are 0.4-0.5 and 0.8-0.9 A/W for wavelength ranges of 300-500 and 850-950 nm, respectively. At zero gate bias, positive charges accumulate near the Si interface due to high work function of Pt. Dark current rectification is transformed into the weak injection regime with an increase of the negative applied voltage. For positive gate bias, the dark current is limited by thermal generation of the minority carriers at the Si-Ta2O5 interface and tunneling through the thin oxide film. Under illumination at negative gate bias, the generated non-equilibrium electrons move without limitation to the back electrode (the conduction band offset between Ta2O5 and Si is 0.36 eV), while the generated holes accumulate at the Ta2O5-Si boundary since their penetration to the gate is limited by a high barrier ~ 3 eV (the valence band offset for Ta2O5 and Si). [...]The observed behavior of the photo current under positive gate bias is analogues to conventional MOS structures with ultra thin oxides.

I-VI.8 11:30

a-Si TFT ENHANCEMENT BY PLASMA PROCESSING OF THE INSULATING/SEMICONDUCTOR INTERFACE

G. Lavareda, E. Fortunato, Dep. Ciência dos Materiais, FCT/UNL, 2825 Monte de Caparica, Portugal, C. Nunes de Carvalho, A. Amaral, Centro de Física Molecular, IST/UTL, 1049-001 Lisboa, Portugal

Functional Metal Oxides - Semiconductor Structures Thin Film Transistors made with silicon nitride and silicon carbide as dielectric were submitted to N2, H2 and O2 plasma treatment of the insulator/semiconductor interface. Silicon nitride is widely used as gate dielectric with very good bulk properties but with network matching problems at the interface with amorphous silicon. Carbon-rich silicon carbide can be an alternative as dielectric material, presenting better SiC/a-Si interface properties, but having lower bulk performance. A stack SiN/SiC layer was already proposed and studied in a previous work, presenting the advantages of both materials. In this study, surface treatments of O2, N2 and H2 plasmas were applied to SiN and to SiC layers before a-Si deposition in order to make the passivation, oxidation or nitridation of the last insulating layers deposited. Results show an improvement of the field effect mobility from 0.35 to 0.52 cm2/V.s in the passivated (hydrogenated) SiN TFTs. An improvement is also observed in SiC TFTs, but less evident. Another effect observed is that TFTs with H2 plasma treated interfaces don't require any further annealing and present much smaller degradation with voltage stress. Preliminary results of N2 and O2 plasmas over the SiN layer show also an improvement in the TFT characteristics, namely in the stability of the threshold voltage

I-VI.9 11:50

EFFECT OF THE SUBSTRATE TEMMPERATURE ON THE PROPERTIES OF ZNO FILMS GROWN BY RF MAGNETRON SPUTTERING

Fatma Chaabouni, Mohamed Abaab, Bahri Rezig, BP 37, Le Belvedere, Tunis 1002, Tunisie

ZnO is a wide band gap semiconductor that has attracted tremendous interest for its potential applications in optoelectronics, solar cell, gas detection... In the present work, thin ZnO films were deposited by RF magnetron sputtering usig ZnO target on glass subtrate with different substrate temperatures (25 to 400°C), with the aim of establishing suitable deposition conditions for obtaining good quality films. Using this technique, transparent(T>80%) and high resistive films (resistivity of the order of 104 to 108 W cm) were obtained. For these films, it was was found that by increasing the substrate temperaure, the cristallinity was inhanced and the grain size was increased. Furthermore, the electrical resistivity and the band gap (3.3eV) were decreased. The electrical properties of ZnO films were investigated using the impedance spectroscopy technique with the frequency ranging from 5 Hz to 13 MHz. The impedance data, represented by means of Nyquist diagrams, showed distinct arcs from lowest (Hz) frequency to highest (MHz) frequency due to the contribution of the grain and grain boundaries to the mechanism of the charge transfer in the material. The conduction is dominated by the grain boundary effect at low substrate temperature (with a frequency of relaxation of 20 kHz) while at high temperatures, the contribution of the grains is predominant(the frequency of relaxation is of 300 kHz). The result of this study suggests that the variation of the deposition temperatures allowed the control of the grain size and that impdance spectroscopy may be a practical method for the correlation between microstructure evolution and the electical properties.

12:10 **LUNCH**

Session VII : Nanostructured oxides
Session chair: J.-M. DeTeresa

I-VII.1 13:30 -Invited-

CURRENT TRANSPORT AND SIZE-EFFETCS IN ULTRA-THIN FERRROELECTRIIC BARRIER

H. Kohlstedt(a),I. Rodriguez Contreras(a), N.A. Pertsev(b), A. Gerber(a), I. Schubert(c), C.L. Jia(a), K. Szot(a) and R. Waser(a), (a)Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, (b)Institut fur Schichten- und Grenzflächen, 52425 Jülich, Germany, (c)A.F. Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia

Recent theoretical work, either with ab-initio techniques or by using the mean-field approach predict ferroelectricity in filims down to a few number of unit cells (1 - 5 nm), if the ferroelectric film are under compressive strain. We will present our development of so-called ferroelectric tunnel junctions with the following layer sequence: SrTiO3(substrate)/SrRuO3(electrode)/BaTiO3 or PbZrxTi1-xO3 (as ferroelectric)/SrRuO3 or Pt as top electrode. These heterostructures have been investigated by XRD, RBS, AFM and HRTEM. The aim of our work is to study fundamental aspects of electron tunnelling and electron transport through a ferroelectric material and the influence of the transport current on the ferroelectric polarization state of the barrier material. For thicknesses ranging between 240 nm and 8 nm common ferroelectric hysteresis loops were observed. For thinner barriers tunnel junctions with areas down to 4 µm2 were fabricated. The I-V characteristics voltages showed switching events with two resistive states. The origin of the switching will be discussed in the framework of direct electron tunnelling, resonant tunnelling, and electron transport via defects.

I-VII.2 14:10

NANOSTRUCTURED LaCoO3 THIN FILMS BY SOLUTION AND VAPOR-PHASE ROUTES

Lidia Armelao, Davide Barreca, ISTM-CNR and INSTM, Padova University, Padova, Italy, Gregorio Bottaro, Alberto Gasparotto, Eugenio Tondello, INSTM and Department of Chemistry, Padova University, Padova, Italy

Rare metal complex oxide thin films have been widely studied for their appealing applications in ferroelectrics, magnetic devices, catalysts, fuel cells and chemical sensors. In this widespread scenario, lanthanum cobaltite (LaCoO3) has been the subject of thorough investigations mainly in the form of powder materials.[1] More recently, an increasing attention is being addressed to nanostructured LaCoO3 thin films, whose preparation procedure has a great influence on their crystallization, chemical structure and performances.

The present work is focused on nanostructured LaCoO3-based layers obtained by CVD and Sol-Gel routes. The combined use of such synthetic approaches offers important advantages for the preparation of nanosystems with tailored features, provided that a proper choice of synthesis and processing conditions is performed. In particular, the films were obtained by sequential deposition of single phase oxide layers and ex-situ thermal treatments. The effects of the preparation routes on the single and multi-layers properties is investigated by means of X-ray Photoelectron Spectroscopy (XPS), X-ray Excited-Auger Electron Spectroscopy (XE-AES), Grazing Incidence X-ray Diffraction (GIXRD) and Transmission Electron Microscopy (TEM). The results are compared with those obtained for lanthanum cobaltite thin films prepared by the sol-gel route.[2]

[1] L. Armelao, G. Bandoli, D. Barreca, M. Bettinelli, G. Bottaro and A. Caneschi, Surface and Interface Analysis 2002, 34, 112

[2] E. Bontempi, L. Armelao, D. Barreca, L. Bertolo, G. Bottaro, E. Pierangelo and L. E. Depero, Crystal Engineering, in press

I-VII.3 14:30

SYNTHESIS OF NONOCRYSTALLINE CERAMCIS USING A NOVE ELECTROSTATIC SPRAY ASSISTED VAPOUR DEPOSTITON METHOD

K.L. Choy, School of Mechanical, Materials, Manufacturing Engineering and Management, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

This contribution presents an overview of the emerging cost-effective Electrostatic Spray Assisted Vapour Deposition (ESAVD) process for the synthesis of nanocrystalline ceramics. ESAVD is a variant of the CVD process. It involves spraying atomised charged precursor droplets across an electric field. Nanocrystalline ceramic powders or films can be deposited by tailoring homogeneous or heterogeneous chemical reactions in an open heated atmosphere. ESAVD is an atomistic deposition method and can produce highly pure materials with structural control at nanometer scale level and at low processing temperatures. The versatility of ESAVD has led to the deposition of films and powders for a wide range of applications, including electrical, optoelectronics, catalytic, structural and functional applications. The fundamental aspects of ESAVD including process principle and deposition mechanism will be presented. The microstructure of the nanostructured materials produced by ESAVD method will be discussed. The scientific and technological significant of the ESAVD methods will be discussed and compared with other vapour processing techniques such as conventional Chemical Vapour Deposition (CVD) and Physical Vapour Deposition (PVD).

I-VII.4 14:50

SYNTHESIS OF IRON OXIDE NANOCOMPOSITES USING LAYERED DOUBLE HYDROXIDES

A.V. Lukashin, M.P. Nikiforov, M.V. Chernysheva, A.A. Eliseev, Yu. D. Tretyakov, Dept. of Materials Science, Moscow State University, 119992 Moscow, Russia, Yu.V. Maximov, I.P. Suzdalev, Semenov Institute of Chemical Physics, Kosygina str. 4, 117977 Moscow, Russia, P. Gornert, D. Berkov, INNOVENT e.V., Prussingstr 27B, 07745 Jena, Germany

In the present work, a novel method for the preparation of oxide nanostructured materials is discussed. The method is based on chemical modification of anion-substituted layered double hydroxides (LDH). It combines the simplicity of chemical methods and the possibility to prepare two-, one-, or zero-dimensional nanoparticles in oxide/hydroxide matrices. Chemical modification of LDHs intercalated with FeEDTA complex is a promising way for synthesis of iron oxide nanoparticles fixated in the matrix. During chemical reactions of anions in the interlayer space of LDHs, reaction zone is spatially constrained by the hydroxide layers, giving rise to the conditions similar to those in 2D nanoreactors, such as Langmuir-Blodgett films and self-assembling monolayers. The simplicity of chemical synthetic methods as well as ability of the formation of nanostructures directly in matrix governed the use of this method. It was found that chemical modification of intercalated LDHs results in the formation of iron oxide nanoparticles with different morphology and composition (FeO, Fe3O4, alpha-Fe2O3, gamma-Fe2O3), depending on the composition of initial precursors and conditions of chemical modifications. The formation of nanostructures incorporated into LDH matrix was investigated by TEM, SQUID, and by other methods. Obtained samples characterized by several types of magnetic ordering of iron oxides nanostructures. This work is supported by INTAS (01-204).