



Strasbourg (France)

## E-MRS Spring Meeting 2003

June 10 - 13, 2003

### SYMPOSIUM P

Current trends in crystalline organic  
semiconductors: growth, growth modelling  
and fundamental properties

Symposium Organizers:

Adele Sassella, INFN - University of Milano Bicocca, Italy

Torsten Fritz, TU Dresden, Germany

Peter Günter, ETH, Zürich, Switzerland

Jürgen P. Rabe, Humboldt University, Berlin, Germany

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# E-MRS 2003 SPRING MEETING

## SYMPOSIUM P

Tuesday, June 10, 2003  
Mardi 10 juin 2003

Morning  
Matin

8:40

WELCOME (A. Sassella, T. Fritz)

Session I: Growth techniques for molecular single crystals

Session Chair: T. Fritz

- P-I.1** 9:00 -Invited- GROWTH AND CHARACTERIZATION OF HIGH PURITY MOLECULAR SINGLE CRYSTALS  
**Jens Pflaum**
- P-I.2** 9:40 -Invited- X-RAY DIFFRACTION TOPOGRAPHY OF ORGANIC CRYSTALS  
**H. Klapper**, Mineralogisch-Petrologisches Institut, University of Bonn, 53113 Bonn, Germany  
X-ray diffraction topography is a powerful non-destructive method for the direct observation of defects in nearly perfect crystals. Since organic crystals usually contain 'light' atoms only, they exhibit low X-ray absorption and low scattering power. Thus crystals plates of several millimetres thickness can be studied by transmission methods. Defects appear on high-resolution X-ray films by broad kinematical contrast. The image widths of dislocation lines are large, usually  $> 20 \mu\text{m}$ , leading to limited spatial resolution. Thus the method is suitable only for relatively perfect crystals with low density of defects. The transmission techniques of projection and section topography are explained and illustrated by selected examples of perfect and imperfect organic crystals. Typical defects observed in nearly perfect organic crystals are inclusions, growth striations, defective growth-sector boundaries, grown-in dislocations and glide dislocations. The determination of Burgers vectors of dislocations and the characterization of planar defects (growth-sector boundaries) are discussed and demonstrated. Topographs recorded from typical organic molecular crystals, such as benzil, benzophenone, salol and 2,3-dimethyl naphthalene grown from solution, from supercooled melt, by the Bridgman method and by the Czochralski technique, are presented.  
H. Klapper, X-ray-Topography of Organic Crystals, in: Crystals: Growth, Properties, and Applications 13, p. 109-162. Ed. N. Karl, Springer: Berlin-Heidelberg, 1991.
- P-I.3** 10:20 EXPLORING THE POLYMORPHISM OF CRYSTALLINE PENTACENE  
A. Brillante, **R.G. Della Valle**, L. Farina and E. Venuti, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy, A. Girlando and M. Masino, Università di Parma, Parco Area delle Scienze, 43100 Parma, Italy  
Starting from each of the five X-ray structures published so far for crystalline pentacene, we have computed the structures of minimum potential energy, and obtained two local minima of the potential energy, i.e., two different "inherent structures" of mechanical equilibrium. This behavior, which has been found to be independent of the details of the potential model, indicates that there are at least two different single crystal polymorphs of pentacene. One of the two polymorphs corresponds to the structure originally determined by Campbell and coworkers in 1961. The other polymorph corresponds to the structure found in all more recent measurements. The calculations predict significant differences between the corresponding Raman spectra, which we have checked experimentally, confirming the existence of two polymorphs. The correct identity of the samples, initially assigned only by matching experimental and calculated spectra, is verified directly with X-ray measurements. Finally, we have obtained theoretical information on the global stability of the minima by systematically sampling the potential surface of crystalline pentacene, and found that the two polymorphs correspond to the two deepest minima. Further deep minima with layered structures, which might correspond to the thin film polymorphs found to grow on substrates, are also predicted.
- 10:40 **BREAK**

**P-I.4** 11:20

**STRUCTURAL AND OPTICAL STUDY OF A NOVEL ORGANIC CRYSTAL OF ANTHRACENE-LIKE MOLECULES**

Luciano Miozzo(a), Antonio Papagni(a), Adele Sassella(a), Massimo Moret(b), Marcello Campione(a), (a)INFM and Dipartimento di Scienza dei Materiali, Università degli studi di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy, (b)Dipartimento di Scienza dei Materiali, Università degli studi di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy

We synthesized a new class of anthracene-like molecules, namely tetrafluoro-acridines and we approached a systematic study of their structural, optical and electrical properties in the solid state. Here the results obtained on single crystals of a prototypical member of this class, tetrafluoro-dimethyl-amino-acridine, are discussed. We grew single crystals by slow sublimation under inert gas flow, starting from a powder of the pure material; the growth crystals are millimeter-sized lamellae, useful for the optical studies. The crystal structure, resolved by X ray diffraction, points out the crystals are monoclinic and showing stack arranged molecules along consecutives planes, similarly to other organic semiconductors; the preferential direction of crystal growth is along the stacks. The results of Atomic Force Microscope analysis at molecular resolution are consistent with the X ray diffraction data. Preliminary results of the optical properties of the single crystal show clearly the effect of anisotropy on the absorption spectra, even if only one configuration is accessible, due to the peculiar shape of the samples. Finally we addressed us to the growth of thin films under controlled conditions and the study of their properties completes and confirms such results.

**P-I.5** 11:40

**GROWTH OF HIGH QUALITY CRYSTALS FOR NONLINEAR OPTICS**

P. Laveant, B. Ruiz, H. Wüest, M. Zgonik and P. Günter, ETH, Nonlinear Optics Laboratory, HPF E 11, 8093 Zurich, Switzerland

Recently many efforts have been focused on synthesizing and growing organic crystals for nonlinear optical applications. If well designed, such molecules offer higher yields than inorganic ones, due to high nonlinearities and the pure electronic origin of the effects. For potential high-speed electro-optical applications such as modulators, high quality crystals are although needed.

We present here recent results on DAST, an organic salt offering high second order nonlinear optical coefficient and electro-optical coefficient being respectively 10 time and twice as large as those of the inorganic standard LiNbO<sub>3</sub>. Using a seeded saturated methanol solution in a controlled temperature lowering approach, we obtained numerous high-quality crystals with typical sizes ranging between 1 and 3 cm. Our method and results for bulk growth are shown in addition to different efforts to obtain DAST thin films.

12:00

**LUNCH**

Tuesday, June 10, 2003  
Mardi 10 juin 2003

Afternoon  
Après-midi

Session II: High quality molecular films by OMBE and related techniques  
Session Chair: A. Kahn

**P-II.01** 14:20 -Invited-

#### EPITAXIAL GROWTH OF ORGANIC MOLECULES ON METAL SURFACES

**Eberhard Umbach**, Experimentelle Physik II, University of Würzburg, 97074 Würzburg, Germany  
The optical and electronic properties of organic thin films strongly depend on the morphology and order of the films as well as on their interfaces to substrate and contacts. The growth mechanism and the result of film growth are also largely determined by the properties of the interface between substrate and molecules and by the growth parameters. They actually depend in a subtle way on the material- and site-specific bonding situation at the interface, on the interplay between the anisotropic intermolecular and molecule-substrate forces, and on the dynamics of adsorption and diffusion. Homogeneous and truly epitaxial growth, i.e. Franck-van der Merwe growth with large domains without pin holes which are in registry with the substrate, can only be achieved in special cases and under certain circumstances. Some aspects of organic growth on inorganic substrates will be discussed.

Experiments that are most useful for studying epitaxial growth of organic layers comprise surface sensitive techniques, such as high-resolution low energy electron diffraction (SPA-LEED), near edge x-ray absorption fine structure (NEXAFS), photoemission (XPS, UPS), and x-ray or UV photoelectron microscopy (PEEM) which all can be utilized in-situ during growth. These methods recently revealed a wealth of unexpected phenomena. The phenomena range from various 2-dimensional phase transitions over "manipulation" of molecular orientation, metastability in organic layers, to the temperature- and deposition rate-dependent transition from Franck-van-der-Merwe to Stranski-Krastanov growth. The bonding of the molecules to the substrate which plays a very important role for the interface structure and hence also for the organic growth can be analyzed in detail with electron spectroscopies revealing unexpected features like the involvement of the deep-lying Ag 4d electrons in the molecular bonding, the existence of partly filled (i.e. metallic) molecular bands, and the formation of a lateral as well as a vertical band structure. Various examples using different molecules and substrates will be discussed on the basis of selected experimental results, and the question will be addressed under which conditions epitaxial growth with large domain sizes can be achieved.

**P-II.02** 15:00 -Invited-

#### ORGANISATION, STRUCTURE AND MORPHOLOGY OF ORGANIC THIN FILMS VIA ELECTRON MICROSCOPY

**A. Thierry**, B. Lotz, ICS-CNRS, 6 rue Boussingault, 67083 Strasbourg, France, V. da Costa, J. Le Moigne, IPCMS-CNRS, 23 rue du Loess, 67037 Strasbourg, France, M. Campione, A. Borghesi and A. Sassella, Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy, H. Plank, R. Resel, Institut fuer Festkoerperphysik, Technische universitat Graz, Petersgasse 16, 8010 Graz, Austria

These last decades have seen the progressive emergence of molecular materials (more specifically organic thin films) as challengers to inorganic materials. Organic crystals are known for their potential application in opto-electronic devices. However, if it is challenging to grow organic single crystals, the molecular design of ordered thin films presents attractive advantages in materials science. Reports of functional systems incorporating molecular films already came out these last ten years in the field of light emitting diodes, non-linear optics, field effect transistors...

Thin organic films are obtained using different approaches: vacuum deposition, Langmuir-Blodgett layers or self-assembling techniques. Control of the structural order of these films is essential to preserve, at the macroscopic level the intrinsic molecular properties.

Vacuum deposited films can be ordered via epitaxial orientation on different substrates like, single crystals, rubbed polymer films, friction-deposited polymer films, LB films. We will report the characterization by bright (or dark)-field electron microscopy and electron diffraction of oligomers and polymers films deposited on single crystalline substrates. We have determined the deposit/substrate relative orientations and proposed some specific selection rules for the described epitaxy. Three specific cases have been studied. First, the oriented overgrowth of symmetrically and non-symmetrically substituted diacetylenes, on potassium acid phthalate reveals the competition between the geometrical well-established matching rules and interactions at the molecular level. Second, we demonstrate that the growth mode of highly ordered nano-needles of para-Sexiphenyl, on freshly cleaved mica corresponds to quasiepitaxy. Finally, we will describe the orientation of Dihexylquaterthiophene deposited on potassium acid phthalate by ultra-high vacuum sublimation.

**P-II.03** 15:40

**CONTROLLING THE STRUCTURES OF ORGANIC SEMICONDUCTOR THIN FILMS**

Q. Chen, A.J. McDowall, T. Rada and N.V. Richardson, School of Chemistry, University of St Andrews, U.K.

The growth of thin films of aromatic molecules, such as PTCDA, tetracene and perylene, on semiconductor and metal surfaces is important for developing organic electronic and optical devices. Device performance is very likely to be strongly influenced by the structure and the quality of crystals or thin films. In this presentation, we show that different molecular orientations can be achieved under different surface conditions. Therefore, different polarisations of the electronic states relative to the solid substrate can be realised. We demonstrate that on clean Si(001) surfaces, depending on the adsorbate species, molecular plane can be either perpendicular or parallel to the surface. Meanwhile, on a metal surface, such as Cu(110), we are able to control and vary the azimuthal orientation of aromatic thin films. Furthermore, by changing the tunnelling condition in STM, we are able to emphasise in the image either the p orbital of the adsorbate or the substrate atoms underneath the molecule, thus, the bonding and interaction between the molecule and substrate can be identified.

**P-II.04** 16:00

**THE VAPOUR PHASE GROWTH OF ORGANIC SEMICONDUCTORS ON INERT SUBSTRATES**

Stijn Verlaak(a), Soeren Steudel(a), Dimitri Janssen(a), Michael Deleuze(b), Paul Heremans(a), (a)Imec, Polymer & Molecular Electronics, Kapeldreef 75, 3001 Leuven, Belgium, (b)LUC, Theoretical Chemistry, Universitaire Campus gebouw D, 3590 Diepenbeek, Belgium

The charge transport properties of polycrystalline small-molecule organic thin-film transistors are not only determined by the intrinsic bulk crystal properties of the organic semiconductors, but are often even more dependent on their thin-film morphology. To gain a better understanding of organic thin-film vapour-phase growth, the nucleation of various organic semiconductors on dielectric substrates has been interpreted in terms of nearest-neighbour interactions, in analogy with atomistic theory. The parameters required for this nucleation theory are obtained from preliminary molecular mechanical calculations using the MM3 force-field, and compared with experiment to validate their order of magnitude. One important outcome of this study is the existence of a transition from two-dimensional to three-dimensional growth, which is determined by the inter-layer interactions of the molecular crystal. Films that grow three-dimensionally have a tendency to form ill-connected or isolated grains, deteriorating charge transport through the film. Second, the critical supersaturation below which no nucleation occurs depends on the vapour pressure of the material, which in turn is to a large extent determined by the intra-layer interactions. Using both criteria, a materials ability to form well-connected films can be assessed based on its molecular structure. Pentacene, tetracene and perylene are discussed as case-studies and show at least qualitative agreement with experimental data.

16:20

**BREAK**

Session Chair: A. Sassella

**P-II.05** 16:40

**GROWTH OF HIGHLY ORDERED FILMS OF ORGANIC MATERIALS BY SUMBE: CHARACTERIZATION AND APPLICATIONS**

T. Toccoli, L. Aversa, A. Pallaoro, A. Boschetti, R. Verucchi and S. Iannotta, IFN-CNR Institute for Photonics and Nanotechnology Sediota I TC, 38050 Povo di Trento, Italy

One of the major problems in growing organic semiconductors is the difficulty in controlling structure and degree of ordering in solid state, resulting in depletion of device characteristics. Our approach to cope with this is to improve control on the initial state of molecular precursors and to grow in non-equilibrium conditions. To this end we have developed a deposition method based on supersonic molecular beams (SUMBE), so that kinetic energy, momentum and, to a certain extent the internal energy, can be controlled varying the supersonic expansion. Results obtained on oligothiophenes show that thin films, several hundred of nm thick grown at room temperature on different inert substrates, have optical, morphological and structural properties similar to the corresponding single crystals. We show that crystalline quality of films can be improved up to the possibility to control type of defects and polymorphism, changing the properties of the supersonic expansion. We will discuss the advantages of the proposed method on the basis of recent experiments using Phtalocyanines and Pentacene on different substrates (including a clean Si(111) surface, CaF<sub>2</sub> and quartz) in UHV environment. The effects of initial kinetic energy of molecules in the beam on the properties of the grown films will be discussed showing the major role played by the control that SUMBE can give on the growth process. The effects of thermal processes will also be discussed together with application to device fabrication

**P-II.06** 17:00

**MORPHOLOGY AND GROWTH KINETICS OF ORGANIC THIN FILMS DEPOSITED BY HOT WALL EPITAXY**

A. Andreev, H. Sitter, Johannes Kepler University Linz, Inst. of Semiconductor- and Solid State Physics, 4040 Linz, Austria, H. Hoppe, N.S. Sariciftci, Johannes Kepler University Linz, Linz Inst. for Organic Solar Cells (LIOS), Physical Chemistry, Austria, R. Resel, University of Technology, Inst. of Solid State Physics, 8010 Graz, Austria; D.-M. Smilgies, CHESS G-line, Cornell University, Ithaca NY 14853, USA

Well ordered layers of organic semiconductor para-sexiphenyl (PSP) are interesting for several optoelectronic applications. Recently, we reported that a self-organization of PSP molecules occurs during Hot Wall Epitaxy on mica resulting in very long crystalline, parallel oriented nano-fibers. In this work we have investigated the growth kinetic and morphology of such fibers, in order to find the process controlling parameters. The results can be summarized as follows: a) PSP grows on mica epitaxially, presumably in the Stranski-Krastanov mode; b) a shape transition from randomly distributed small islands with compact shape to elongated ones occurs during the growth; c) with further increase of the island density they become more elongated, quickly reaching a fixed asymptotic width while their height remains much smaller than their length and width; d) the film morphology strongly depends on the growth temperature.

The results obtained on alternative crystalline substrates (MoSe<sub>2</sub>, MoS<sub>2</sub>, GeS, KCl, NaCl) are also presented and discussed.

**P-II.07** 17:20

**GROWTH OF POLYALKYLTHIOPHENE FILMS BY MATRIX ASSISTED PULSED LASER EVAPORATION**

A. Gutierrez, G. Horowitz\*, R. Perez, J. Perrière, J.L. Fave, and A. Yassar\*, Groupe de Physique des Solides, Université Paris 6 et Paris 7, 2 place Jussieu, 75251 Paris, France, \*ITODYS, Université Paris 7, 1 rue Guy de la Brosse, 75005 Paris, France

Materials used in organic electronic devices can be sorted into polymers and small molecules. The most widely used techniques for processing these materials as thin solid films are casting (e.g., dip- and spin-coating) for polymers and vapor deposition for small molecules. Vacuum evaporation and pulsed laser deposition (PLD) of polymers have been reported in the past. However, such a deposition mode usually proceeds by thermal breaking of the polymer chains and repolymerization on the substrate. An alternative approach is Matrix Assisted Pulsed Laser Evaporation (MAPLE) where the solid target consists of a frozen solution of the polymer. In the ideal case all the laser energy is absorbed by the solvent, which is evaporated and then pumped away, thus letting the solute be deposited without chemical degradation. In this work, we use the MAPLE technique to grow films of stereo-random and stereo-regular poly(hexylthiophene). The films are characterized by various techniques, including UV-vis, photoluminescence, IR and Raman spectroscopy, AFM microscopy and X-ray diffraction. MAPLE films are compared to that obtained by conventional spin-coating. Electroluminescent diodes have also been realized and characterized.

18:00-20:00

**POSTER SESSION**

## POSTER SESSION

- P/P01** TECHNOLOGY OF ORGANIC FILM DEPOSITION FROM A GAS PHASE: WHERE WE ARE AND FUTURE TRENDS  
K.P.Gritsenko, Institute of Semiconductor Physics of NASU, 45 Nauki pr., Kyiv 03028, Ukraine  
Recent years showed the flourishing era of functional organic films for various applications in optoelectronics: OLED, FPD, organic transistors, nonlinear devices etc. But instead of inorganic films, where industry are using mainly electron beam evaporation, magnetron sputtering and PECVD, application of these methods to organic molecules is impossible. Only thermal evaporation is using. Hot wall CVD seems promising alternative, but not completely satisfying all industry needs. Laser evaporation of dye and polymer using various IR, VIS and UV lasers have been studied by several research groups worldwide. Encouraging results were obtained, but in many cases unwanted decomposition of organic molecules is present. Only PTFE seems able to produce good quality films using electron, synchrotron, UV laser beam and ionisation-assisted methods. Report review all methods used for dye and polymer film deposition in vacuum, namely thermal, electron beam, laser, PECVD, pyrolysis. Peculiarities of the processes are discussed. Linear evaporators for organic film deposition are discussed. Trends in technology developments are tried to be predicted.
- P/P02** NEW EVAPORABLE ASYMMETRIC DYES  
A.I. Tolmachev, Yu.L. Slominski, M.A. Kudinova, D.G. Krotko, V.V. Kurdiukov, Institute of Organic Chemistry, 5 Murmanskaya str., Kyiv, Ukraine, D.O. Grinko, K.P. Gritsenko, Institute of Semiconductor Physics of NASU, 45 Nauki pr., Kyiv 03028, Ukraine, S. Schrader, L. Brehmer, Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany  
Several new not salt-forming asymmetric polymethine dyes were developed and synthesised. They are conjugated donor-acceptor systems. Evaporation and deposition kinetics of these dyes, film optical properties were studied. Monomethinecyanine bases, derivatives of some nitrogen-containing heterocycles, squaryliums, merocyanines and pyrane derivatives are evaporating by classic way without decomposition.
- P/P03** ORIENTED GROWTH OF DYE FILM ONTO ALIGNED POLYMER SUBLAYER  
K.P. Gritsenko, D.O. Grinko, O.P. Dimitriev, Institute of Semiconductor Physics, 45 Nauki pr., 03028 Kyiv, Ukraine, Yu.L. Slominski, A.I. Tolmachev, Institute of Organic Chemistry, 5 Murmanskaya str., Kyiv, Ukraine, S. Schrader, L. Brehmer, Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany, A. Thierry J.C. Wittmann, Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France  
Films of various squarylium (Sq) derivatives were deposited using thermal evaporation in vacuum. A row of indolenine derivatives of Sq with various side and end groups was studied. Films had different band positions in absorption spectra that dependent on Sq structure. Dyes were deposited onto oriented polytetrafluoroethylene (PTFE) sublayers. Aligned PTFE sublayers were prepared by friction-transfer method and evaporation with consequent rubbing by a cloth. Two Sq compounds revealed oriented growth on PTFE sublayer. Thickness - dependent change in the relative intensity of shorter and longer wavelength peaks was found. Some other vacuum-deposited polymers revealed the ability to orient Sq dye after rubbing. In order to understand the mechanism of oriented growth, some other substrates were tested for Sq oriented growth, aligned PTFE substrate was used for oriented growth of other organic compounds.
- P/P04** VIDEO-MICROSCOPY OF CRYSTAL GROWTH OF TETRACENE IN THIN LIQUID FILMS  
Sylvia Dorsfeld, Michael Voigt and Moritz Sokolowski, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany  
Tetracene vapour deposited onto a thin liquid film of bis(2-ethylhexyl)sebacate at 300 K forms very large (lateral size of several 100 µm) thin crystals, highly oriented with their (001) planes parallel to the substrate (FWHM of rocking scan = 0.3-0.6°). The details of the growth kinetics were studied by in-situ video polarisation microscopy as a function of the deposition rate (2-60 nm/min) and liquid film thickness (1-6 µm). In agreement with classical nucleation theory, the saturation number density of the nuclei increases with increasing deposition rate, indicating a homogenous nucleation in a highly supersaturated liquid. The growth occurs quasi-2dimensional in the film plane and can be divided into two stages.  
In the first stage, nucleation and diffusion limited dendritic growth occurs. In the second stage, the dendrites ripen into pallet shaped compact crystallites with equilibrium facets. The achieved high structural and optical quality of the crystallites are deduced from x-ray diffraction data and their photoluminescence spectra. The Bragg reflections thus are limited by the instrumental resolution and the value of  $d(001)$  is  $(12.15 \pm 0.02) \text{ \AA}$ , and is comparable with the value of vapour grown tetracene single crystals. The (time-resolved) PL-spectra show no significant trap contributions. Possibilities to use this growth technique for the preparation of high quality organic films are discussed. Supported by the DFG.
- P/P05** EFFICIENT ENERGY TRANSFER IN ORGANIC THIN FILMS BY ULTRA-HIGH VACUUM EVAPORATION  
W. Porzio, U. Giovanella, M. Pasini, C. Botta, S. Destri, Istituto per lo Studio delle Macromolecole (ISMAR-CNR), via E. Bassini 15, 20133 Milano Italy  
The energy transfer in organics assumes relevance in optimising the performance of many LED devices. Ultra high vacuum evaporation is nowadays an ideal technique to build up proper active layers either in multi layered or in co-evaporated films. We have chosen two oligomers displaying the appropriate absorption/emission windows, in fact the emission maximum of the first, a dithienyl-fluorene derivative, is centred in the region where the absorption of the second, tetrahexylsexithophene, is large, hence guaranteeing a complete Förster transfer even at low content of the latter. Optical microscopy investigations together with XRD analysis allowed us to get insight onto both the structure orientation and the morphology of the film components. The optical aspects of this thin layers, 15 nm thick, are also discussed and compared with the mono-component films obtained in the same conditions. LED prototypes were prepared and compared with analogous devices obtained by spin-coating technique. The intimate structure/morphology can readily account for the better performance of LED devices obtained by high-vacuum evaporation.

- P/P06** ELECTRON TRANSPORT PROPERTIES OF OXADIAZOLE DERIVATIVE  
L.G. Gasanova, A.Z. Abasova, A.G. Kyazym-zade, V.M. Salmanov, A.A. Agayeva, Baku State University, Physics Semiconductor, Z. Khalilov Str. 23, 370145 Baku, Azerbaijan  
 By time-of flight photocurrent techniques, hole transport has been investigated in vapor deposited films of the title compound. The samples are fabricated from a binary solid solution of charge transporting molecule dispersed in inert polymeric binder. The deposition of PBD layer, a semitransparent indium tin oxide (ITO) layers were vapor deposited on the free surface. Titanium oxide phthalocyanides (TiOPc) as the photoemitting layer were used. Aluminum electrodes are the second contact. Thickness of the doped polymer films were about 20 nm. Photoexcitation of the TiOPc emitter layer was accomplished by 3 ns exposures of 724 nm radiation derived from a dye laser (PRA, LN-107). The photocurrent transient was measured with a transient digital system (Board Master 800 AB I 8). In this report the spectral response, the drift mobilities and the photocurrent transient measured investigated experimentally. The spectrum response TiOPc layers are about 400-900 nm. The maximum of photosensitivity used films corresponds to 724 nm that determined a choice of dye laser radiation with suitable wavelength. The measurement of transit time dependence of electric field E illustrates that for TiOPc layers the transit time is reduced by increasing of the E. For  $E_{max}=1.15 \times 10^5$  V/cm correlate with  $\tau=5 \times 10^{-7}$  s. These values of the transit time are much less than those for other disordered materials, using for electrophotography application. At the room temperature the field dependence of the charge carries mobility indicates that this dependence can be best described by an exponential dependence on the square root of the electric field. The predicted field dependence is very similar to the Poole-Frenkel behavior frequently observed in transport measurements of doped polymers.
- P/P07** HIGH RESOLUTION STM STUDY OF THE INTERACTION OF SEXIPHENYL WITH AN OXYGEN PASSIVATED NI (110) SURFACE  
G. Koller, F.P. Netzer, M.G. Ramsey, Institut für Experimentalphysik, Karl-Franzens Universitaet Graz,, Universitaetsplatz 5, 8010 Graz, Austria  
 The interaction of semiconducting organic oligomers with ferromagnetic surfaces is of interest in view of prospective future applications of hybrid organic-magnetic tunnelling devices. The stability of organic layers sandwiched between two ferromagnetic metals, as required in such devices, is determined to a large extent by the organic/metal interface. This is a crucial issue because ferromagnetic metal surfaces are very reactive, leading to a break-up of organic molecules at the interface. This can be avoided by a suitable passivation of the metal surface. In this work we have used the oxygen passivated Ni (110) (2x1)O reconstruction as a substrate to study the coupling of sexiphenyl molecules. We have used LEED, AES and STM to reveal the structure and molecular orientation of the sexiphenyl molecules. STM images have been obtained with submolecular resolution allowing to identify the individual phenyl rings of the sexiphenyl molecule. The orientation of the molecules with respect to the reconstructed substrate has thus been determined: the alignment along four preferential directions has been detected. Apart from planar, flat lying molecules, molecules with partly tilted phenyl rings could also be visualized in one particular direction. The sexiphenyl molecules desorb with partial decomposition at ~ 450 K leaving some residues in form of molecular fragments and carbonaceous decomposition products at the surface, which have been imaged in the STM.
- P/P08** ON THE MECHANISM OF ELECTRICAL CONDUCTION IN SOME NEW SYNTHESIZED ORGANIC SALTS IN THIN FILMS  
 I. Druta(a), L. Leontie(b), R. Alupoae(a), G.I. Rusu(b), (a)Faculty of Chemistry, "Al. I. Cuza" University, 11 Carol I Boulevard, 6600 Iasi, Romania, (b)Faculty of Physics, "Al. I. Cuza" University, 11 Carol I Boulevard, 6600 Iasi, Romania  
 The temperature dependence of electrical conductivity,  $\sigma$ , and Seebeck coefficient,  $\alpha$ , for investigated compounds (N-(p-R-phenacyl)-1,10-phenanthroline bromides), were studied on thin film samples ( $d=0.51-1.76 \mu\text{m}$ ) deposited from dimethylformamide solutions onto glass substrates.  
 The sample surface was examined by means of AFM and optical microscopy techniques. The shape of the temperature dependences of  $\sigma$  and  $\alpha$  are typical for semiconducting materials. The investigated organic films show a p-type conduction. Using these dependences, the values of some characteristic parameters for respective compounds have been determined. The activation energy of electrical conduction ranged from 0.68 eV and 1.78 eV. Some correlations between these values and molecular structure of the compounds are established. The model based on band gap representation could be suitable for the study of electronic transport mechanism in investigated compounds.
- P/P09** PENTACENE THIN-FILM TRANSISTORS WITH POLYMERIC GATE DIELECTRIC  
J. Puigdollers, C. Voz, A. Orpella, I. Martín, M. Vetter, R. Alcubilla, Universitat Politècnica de Catalunya, Departament d'Enginyeria Electrònica, C/ Jordi Girona 1-3, Mòdul C4, Barcelona-08034, Spain  
 Organic thin-film transistors have been obtained using a polymeric gate dielectric. The semiconductor layer was a pentacene thin-film obtained by thermal evaporation in high-vacuum, at a deposition rate of 25 Å/s. The thickness of the pentacene layer was about 800 nm. The microstructure of the pentacene films was studied by X-Ray Diffraction and Atomic Force Microscopy. Crystalline silicon and Kapton were used as substrates. The gate dielectric was formed by spin coating the substrates with polymethyl methacrylate (PMMA). The thickness of the PMMA layer was about 700 nm. The drain and source electrodes were defined by evaporating gold through a shadow mask. These devices presented a channel length and width of 120 and 600 microns respectively. The maximum process temperature was 170°C, which corresponds to the baking of PMMA.  
 The TFTs presented good electrical performances with field-effect mobilities around 0.01 cm<sup>2</sup>/V·s and negative low threshold voltages (<-15 V). The ON/OFF current ratio was about 10<sup>3</sup> (when V<sub>gs</sub> changes from ?20 to 20 V). The devices showed a subthreshold slope of about 2.1 V/decade at V<sub>ds</sub> = -5 V.

- P/P10** ACCURACY OF THICKNESS MEASUREMENTS BY QUARTZ MICROBALANCE DURING ORGANIC MOLECULAR BEAM DEPOSITION OF THIN FILMS  
M. Campione, A. Borghesi, E. Pinotti, A. Sassella, INFN and Università degli Studi di Milano Bicocca, Dipartimento di Scienza dei Materiali, Via Cozzi 53, 20125 Milano, Italy  
The problem of monitoring in-situ the film thickness by a quartz microbalance during vacuum deposition of organic molecular semiconductors is here addressed by setting a procedure for sensor calibration based on comparison with ex-situ atomic force microscopy measurements. The procedure is applied to the growth of molecular thin films on silica and some physical parameters of the material are deduced.
- P/P11** GROWTH AND CHARACTERIZATION OF SOME DOPED ORGANIC SEMICONDUCTOR CRYSTALS  
Anca Stanculescu(a), Florian Stanculescu(b), Laura Tugulea(b), Marcela Socol(a), (a)National Institute of Materials Physics, Bucharest-Magurele, Romania, (b)University of Bucharest, Faculty of Physics, Bucharest-Magurele, Romania  
Organic crystalline compounds are a new class of materials for optical, photoconductive, electric and electronic applications. The solid state properties of aromatic substituted derivatives compounds are strongly influenced by the modus of molecular packing, the nature of the substituents groups or side chains and the presence of dopants.  
This paper presents some investigations on highly doped molecular semiconductor crystals growth process from the melt by a Bridgman-Stockbarger method. We have obtained organic crystals of benzil doped with elementary sodium and silver, meta-dinitrobenzene crystals doped with elementary iodine and benzil and benzil doped with meta-dinitrobenzene. To grow crystals we have used organic compounds of high purity obtained by a melting zone refining process. For every mentioned host (organic)/guest (inorganic, organic) we have evaluated the parameters defining the growth process (furnace's hot zone temperature, gradient at the growth interface and moving speed of the interface solid/melt in the thermal gradient) in order to control the crystallization and improve the optical quality. The influence of the dopant on the optical properties of the host organic material was investigated by Optical Spectroscopy compared with the optical properties of the same undoped bulk material. Measurements have been done on bulk samples, polished wafers with thickness between 0.5 and 3.5 mm cutted from above grown crystalline ingots.
- P/P12** A WAY TO IMPROVE THE CRYSTALLOGRAPHIC QUALITY OF DOPED CRYSTALS GROWN USING BRIDGMAN-STOCKBARGER METHOD  
Monica M. Mihailovici, Department of Mathematics, West University Timisoara, Romania, Agneta M. Balint, Department of Physics, West University Timisoara, Romania, Stefan Balint, Department of Mathematics, West University Timisoara, Romania  
The aim of this paper is to simulate, using a complex mathematical model, the growth process of doped crystals using Bridgman-Stockbarger technique, and to show that it is possible to improve the quality of the grown crystal by using adequate initial conditions. The mathematical model takes into account the unsteady thermal convection in the melt, the decrease of the melt length in the ampoule, the rejection of the dopant at the interface, and the precrystallization-zone. Numerical computations have shown that, if the initial dopant distribution is uniform, axial and radial segregation in the grown crystal will be important. Therefore, in order to reduce the compositional non-uniformity and to obtain an almost constant prescribed dopant concentration of value 1 on an important fraction of the grown crystal, non-uniform initial dopant repartitions, suitable for the environment in which the growth process takes place, can be used. In this paper we show numerically, how the quality of a doped crystal grown in strictly zero-gravity and low gravity conditions, respectively, can be improved when initial non-uniform dopant repartitions, given by explicit formulas, are used. Numerical computations are made for Ga-doped Ge crystals.
- P/P13** OMBE SYSTEM AND INITIAL STUDIES OF ORGANIC LAYER GROWTH  
M. Andreasson, P. Wellmann and T.G. Andersson, Applied semiconductor physics, Division of Microelectronics and Nanoscience, Mina Department of Physics and Engineering Physics, Chalmers University of Technology and Göteborg University, 412 96 Göteborg, Sweden  
Organic, semiconductor materials are promising for new nm-scale devices. To fully understand such semiconductors, the growth and characterization of the materials are important. In this work three subjects have been investigated and described: the construction of an organic molecular beam epitaxy (OMBE) machine, control of beam flux, and finally the initial growth studies on different substrates. The OMBE has been connected to an existing III-V semiconductor MBE system. The OMBE system has ports for three MBE evaporation sources and also contains reflection high energy electron diffraction (RHEED), film thickness monitor, quadrupole mass spectrometer and substrate heater. The OMBE system will be described including growth of GaAs and transferring between the two systems. The organic material used was 3,4,9,10-tetra carboxylic perylene 3,4,9,10-dianhydride (PTCDA). The powdered raw organic material was purified by a gradient sublimation technique in a glass tube under high vacuum conditions. In order to grow well controlled organic films and multilayer structures, both film thickness and composition must be well controlled. Control of the beam flux was achieved by use of beam gauge and a QCM thickness monitor. By growing a layer under known conditions on a masked sample, the absolute thickness was obtained from which beam flux and thickness monitor were calibrated. The variables for growth control have been molecular flux and substrate temperature. The substrates used were glass, indium-tin-oxide (ITO), passivated silicon and in-situ grown GaAs. The crystallinity of the surface and the initial growth was monitored by RHEED. The morphology of thick films were characterised by AFM and SEM.

- P/P14** CONDUCTIVITY AND CATHODOLUMINESCENCE OF COMPOSITE POLYMER FILMS WITH NANOPARTICLES OF V2O5  
Sergey Svechnikov, Petro Smertenko, Larysa Fenenko, Institute of Semiconductors Physics NASU, 45 prospekt Nauki, 03028 Kyiv, Ukraine, Vitaliy Pokhodenko, Nikolay Guba, Ludmila Grebinskaja, L.V. Pisarzhevski Institute of Physical Chemistry NASU, 31 prospekt Nauki, 03029 Kyiv, Ukraine, Michael Hietschold, Falk Mueller, Chemnitz University of Technology, Institute of Physics, 70 Reichenhainer Str., 09126 Chemnitz, Germany  
The sandwich-structures on the base of carbazol contained polymer films of poly(N-epoxypropylcarbazol) and poly(3,6-di-Br-N-polyepoxypropylcarbazol) vanadium oxide (V2O5) and their composites were studied. The features of these structures conductivity in dark conditions and under illumination of white light was analysed. The effect of illumination and V2O5 content in the composite was scrutinized. The cathodoluminescence of investigated films is obtained in visible range. The mechanisms of injection, recombination and charge flow of charge carriers are considered.
- P/P15** REAL-TIME X-RAY AND KINETIC MONTE-CARLO STUDY OF THE TEMPERATURE-DEPENDENT 2D-3D TRANSITION IN THE GROWTH OF PTCDA ON Ag(111)  
B. Krause(a), E. Schreiber(a,b,c), H. Dosch(a,b), A. Pimpinelli(d), and O.H. Seeck(e), (a)Max-Planck-Institut fuer Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany, (2)Institut fuer Theoretische und Angewandte Physik, Universitaet Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany, (3)new address: Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QZ, U.K., (d)LASMEA, Universite Blaise Pascal - Clermont 2, Les Cezeaux, 63177 Aubiere Cedex, France, (e)IFF, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany  
PTCDA (3,4,9,10-perylene-tetracarboxylic dianhydride) on Ag(111) is widely studied and considered a model for organic epitaxy. Nevertheless, several complications are encountered during the growth, such as (partial) dewetting and a competition of different structural phases [1]. We present a real-time x-ray scattering study of the growth modes of PTCDA on Ag(111) and find a temperature-dependent transition from layer-by-layer growth to islanding. The transition smears out for low substrate temperatures, T, implying that the degree of the layer-by-layer growth of the wetting layer decreases with decreasing T. This behavior is been analyzed quantitatively and reproduced by kinetic Monte Carlo simulations. The role of the different diffusion barriers and the consequences for the understanding of organic molecular beam epitaxy are discussed. [1] B. Krause, A. C. Duerr, K. A. Ritley, H. Dosch, and D. Smilgies, Phys. Rev. B 66 (2002), 235404; and references therein
- P/P16** A STUDY OF DEPOSITED INDIUM-THIN-OXIDE(ITO) FILM CHARACTERISTICS USING AN OXYGEN ION BEAM ASSISTED DEPOSITION(IBAD) TECHNIQUE FOR ORGANIC ELECTROLUMINESCENT DEVICE (OLED) FABRICATION  
N.G. Cho, D.W. Kim and G.Y. Yeom, Dept. of Materials Engineering, Sungkyunkwan Univ., Kyunggi-do, 440-746 Suwon Korea, Y.W. Ko, J.H. Lee, Electronics and Telecommunications Research Institute (ETRI), 305-350 Taejon, Korea  
To fabricate active matrix organic electroluminescent devices (OLED), a transparent conducting material such as indium tin oxide(ITO) has to be deposited on the organic material of the devices and the organic materials are easily damaged by the oxygen atom, ion bombardment, heating, etc. during the deposition processing of ITO. Also electrical property control has difficulties by oxidation of thin film electrode. When a conventional ITO deposition technique such as sputter deposition were used, there are difficult to maintain both electrical conductivity and transparency of ITO without generating damages to OLED. Therefore, in this study, a dual oxygen ion beam assisted evaporator system has been used to deposit ITO films on the OLED to investigate as a possible transparent and conductive ITO deposition technique without generating damage to OLED. The characteristics of the deposited ITO was investigated using a four-point probe and a UV-spectrometer to measure the resistivity and transmittance of ITO films, respectively. In this work, the thickness of deposited ITO film was 120 nm and had lower than 70 $\Omega$ /sq; of sheet resistance with over 90% of transmittance in 550 nm region. Also, to investigate the ion flux damage, C-V characteristics were measured as a function of incidence assisted ion beam angles and current-voltage(I-V) characteristics of the fabricated OLED with the ITO electrode were measured by HP-4145A semiconductor parameter analyzer. The change of surface roughness after ITO deposition was investigated using an atomic force microscopy(AFM).
- P/P17** AN STM STUDY OF ORGANIC MOLECULES IN MIXED PHASES: PTCDA AND CUPC ON CU(111)  
Christian Bobisch, Amin Bannani, Thorsten Wagner, Rolf Moeller, University of Essen, Germany  
In this work we will report on the mixed monolayer formed by the organic molecules 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and copper-phthalocyanine (CuPC). The binary molecule film has been prepared in UHV by molecular beam epitaxy while the substrate was held at room temperature. The amount of each species was an equivalent of 0.7 monolayers. Afterwards the sample was tempered by a linear temperature ramp ending at 450K. STM measurements reveal two ordered mixed structures. One phase consists of an oblique unit cell "Mickey-Mouse" -phase consisting of one CuPC- and two PTCDA-molecules, hence a ratio of 1:2. The other regular unit cell contains two CuPC- and six PTCDA-molecules yielding a ratio of 1:3. Subsequent temper procedures showed a domination of the "Mickey-Mouse" -phase. At temperatures higher than 550K the ordering is destroyed.
- P/P18** THREE DIMENSIONAL GROWTH OF ORGANIC NANOCRYSTALS: A STM STUDY  
Amin Bannani, Christian Bobisch, Thorsten Wagner, Rolf Moeller, University of Essen, Germany  
An equivalent of ten monolayers of PTCDA (3,4,9,10-perylene-tetra-carboxylic-dianhydride) was deposited by OMBE on a Cu(111) single crystal. Annealing up to 520K leads to the formation of three dimensional PTCDA nanocrystals. These crystals were investigated by a home built STM, optimized for low tunnelling currents down to 1pA. Molecular resolution could be achieved as well on the top layer as on the slopes of the crystal consisting of 90 up to 100 molecular layers. It was possible to obtain the three-dimensional structure by evaluating the shift for each crystal-line relative to the unit cell in the top layer. It is found, that the structure of the nanocrystals differs from the known bulk structures. The analysis was extended to PTCDA crystals found on different substrates, like Au(111) and Cu(110).

- P/P19** SCANNING TUNNELING SPECTROSCOPY AT ORGANIC FILMS: PTCDA AND CUPC ON CU(111)  
Thorsten Wagner, Amin Bannani, Christian Bobisch, Rolf Moeller, University of Essen, Germany  
 This work focuses on spectroscopic measurements by STS on thin organic films formed by 3,4,9,10-perylene-tetracarboxylic-dianhydrid (PTCDA) and copper-phthalocyanine (CuPC). The thin films have been prepared by in situ vapour deposition on a Cu(111) single crystal surface under UHV conditions. The homogeneous systems of either PTCDA or CuPC reveal only a little signal in the dI/dV mapping due to different coverages on the substrate. However the dI/dV measurements provide a clear chemical contrast between the two types of molecules. This facilitates the identification of the various unit cells for the mixed phase.
- P/P20** CANCELLED
- P/P21** GROWTH OF DAST THIN FILMS CRYSTALS  
B. Ruiz, S. Manetta, P. Laveant, M. Zgonik, P. Günter, ETH Zuerich, Switzerland  
 Recently many efforts have been focused on synthesizing and growing organic crystals for nonlinear optical applications. For potential applications in integrated optics, molecules with high nonlinearities and thin monocrystalline films are needed. Therefore, we focus on DAST (4'-dimethylamino-N-methyl-4-stilbazolium tosylate) which offers high second order nonlinear optical and electro-optical coefficients being respectively 10 times and twice as large as those of inorganic LiNbO<sub>3</sub> crystals [1,2].  
 Using different thin films methods such as the traveling cell technique or the capillary method, we describe the nucleation and growth thermodynamics in solution. The monocrystals obtained are typically 1mm<sup>2</sup> with a thickness of about 40 microns. The main experimental parameters for bidimensional growth are discussed and first promising results are presented.  
 [1] F. Pan, G. Knöpfle, Ch. Bosshard, S. Follonier, R. Spreiter, M. S. Wong and P. Günter, Appl. Phys. Lett. 69 (1). 1 July 1996, 13-15.  
 [2] S. Manetta, M. Ehrensperger, Ch. Bosshard and P. Günter, C. R. Physique 3 (2002) 449-462.
- P/P22** MOLECULAR ORDERING IN ULTRATHIN PENTACENE FILMS  
 Bert Nickel(a), Ricardo Ruiz(b), Richard F. Haglund Jr.(b), Leonard C. Feldman(b), Giacinto Scoles(a), (a)Princeton University, Department of Chemistry, Princeton NJ 08544, USA, (b)Vanderbilt University, Dept. of Physics and Astronomy, Nashville TN 37235, USA  
 Molecular ordering is of primary interest in organic thin film science. Since most conjugated organic crystals exhibit highly anisotropic transport properties, a high degree of control in molecular ordering is desirable for key applications such as organic thin film transistors (OTFTs). To model relevant electronic properties, detailed information about the molecular arrangements is crucial. Here, we report a synchrotron X-ray surface Bragg scattering study of submono- and multilayer pentacene films on oxidized and reduced Si surfaces. From these measurements, we have been able to determine the lateral unit cell dimension of the so-called thin film phase. The molecular arrangement of submonolayer films as a function of the deposition temperature and rate are also reported. Complementary atomic force microscopy measurements have been performed to link the structural properties with island size and shape.
- P/P23** THERMAL TREATMENT OF THE PENTACENE THIN FILM TRANSISTOR EVAPORATED IN THE ULTRA HIGH VACUUM  
S.J. Kang, D.S. Park, H.J. Kim, M. Noh, C.N. Whang, Institute of Physics and Applied Physics & ASSRC, Yonsei University, Seoul, Korea  
 Pentacene is one of the promising materials for the development of applicable organic semiconductor device. However, the mobility is still low at the polycrystalline pentacene thin film to be a competitor of Si-based semiconductor. It is helpful to enhance the mobility that controlling the size of grain and the orient of structure. We prepared preferentially oriented high quality pentacene thin film via thermal evaporation in ultra-high vacuum. And we have done thermal treatment to change the size of pentacene grain and the roughness of the organic-metal interface. We used the High Resolution synchrotron X-ray Diffraction at the PLS to obtain the roughness, thickness and density of the pentacene thin film from reflectivity. We also used the Atomic Force Microscopy to characterize the film. We compared the roughness and domain size obtained from the simulations of the X-ray Diffraction data and the Atomic Force Microscopy observations. Our investigation results of the electrical properties on the organic thin film transistor will be presented.
- P/P24** STRUCTURE, MORPHOLOGY AND OPTICAL PROPERTIES OF ORGANIC - ORGANIC HETEROSTRUCTURES  
 J.O. Osso(a,b), F. Schreiber(a,b,c), E. Barrena(a), M. Garriga(b), M.I. Alonso(b), H. Dosch(a,d), (a)Max-Planck-Institut fuer Metallforschung, 70569 Stuttgart, Germany, (b)Institut de Ciencia de Materials de Barcelona CSIC, 0819 Bellaterra, Spain, (c)Physical and Theoretical Chemistry Laboratory, University of Oxford, OX13QZ Oxford, U.K., d)Institut fuer Theoretische und Angewandte Physik, Universitaet Stuttgart, 70550 Stuttgart, Germany  
 The controlled preparation and the understanding of the resulting functional properties of organic-organic heterostructures such as doublelayers of multilayers is a challenging task. Nevertheless, the organic-organic interface is a key element for several organic device structures such as OLEDs, and its understanding is mandatory for technological progress. Several studies have been devoted to the investigation of the electronic properties of such interfaces, but the structure, morphology, and interdiffusion at the organic-organic interface is not well understood. We have investigated organic bilayers of the compounds copper-hexadecafluorophthalocyanine (F<sub>16</sub>CuPc) and diindenoperylene (DIP) grown by OMBD on oxidized Si(100) and Al<sub>2</sub>O<sub>3</sub>. For both compounds the behavior of the individual films is well characterized [1,2]. The optical properties of the bilayers were investigated by spectroscopic ellipsometry and related to the structural properties probed by x-ray diffraction. The optical and electronic properties of the films, depend strongly on the final structure of the individual layers. While in the case of DIP on F<sub>16</sub>CuPc the properties of the bilayer system can be directly compared to the single layer case, F<sub>16</sub>CuPc on DIP appears to exhibit significant deviations. The implications for the preparation of organic heterostructures are discussed.  
 [1] Osso et al., Adv. Funct. Mat. 12 (2002) 455  
 [2] Duerr et al., Appl. Phys. Lett. 81 (2002) 2276; Phys. Rev. Lett. 90 (2003) 016104

**P/P25**

**GROWTH OF ORGANIC SEMICONDUCTOR THIN FILMS ON STEPPED SAPPHIRE SURFACES**

J.O. Osso(a,b), E. Barrena(a), F. Schreiber(a,c,d), M. Garriga(b), M.I. Alonso(b), H. Dosch(a,d), (a)Max-Planck-Institut fuer Metallforschung, 70569 Stuttgart, Germany, (b)Institut de Ciencia de Materials de Barcelona CSIC, 0819 Bellaterra, Spain, (c)Physical and Theoretical Chemistry Laboratory, University of Oxford, OX13QZ Oxford, U.K., (d)Institut fuer Theoretische und Angewandte Physik, Universitaet Stuttgart, 70550 Stuttgart, Germany

Controlled in-plane alignment is one of challenges in the growth of organic semiconductors. We have recently demonstrated the concept of using stepped sapphire substrates to suppress the evolution of azimuthal domains for the growth of phthalocyanine thin films [1]. Here we present a study of the growth, structure, and optical properties of highly ordered organic thin films of diindenoperylene (DIP) on vicinal Al<sub>2</sub>O<sub>3</sub>(11-20) surfaces. The nucleation of the organic films at the step edges is investigated at different growth stages by atomic force microscopy (AFM). When surface diffusion is enhanced, large crystallites are obtained, all oriented in one azimuthal direction. High resolution AFM images allow to determine the in-plane structure of the film and their orientation relative to the substrate. Interestingly, when two facet steps join to form a single one, spiral growth is observed in the molecular film. The preferred orientation of the films facilitates the study of the intrinsic structural and optical properties of this system. [1] Osso et al., Adv. Funct. Mat. 12 (2002) 455

**P/P26**

**STRUCTURAL CHARACTERIZATION OF POLYCRYSTALLINE  $\alpha,\omega$ -DIHEXYL QUATERTHIOPHENE THIN FILMS BY TRANSMISSION ELECTRON MICROSCOPY**

M. Campione, A. Borghesi, M. Moret, A. Sassella INFN and Università degli Studi di Milano Bicocca, Dipartimento di Scienza dei Materiali, Via Cozzi 53, 20125 Milano, Italy, B. Lotz, A. Thierry, Institute Charles Sadron - CNRS, 6 rue du Boussingault, 67083 Strasbourg, France

alpha,omega-dihexylquaterthiophene thin films have been deposited by ultra-high vacuum sublimation on silica and potassium acid phthalate substrates. The influence of the substrate on the structure of the films are investigated by transmission electron microscopy and the results are compared with the morphological and optical properties of the same samples.

**P/P27**

**ORDERED ORGANIC THIN FILMS MADE BY SUPERSONIC MOLECULAR BEAM EPITAXY**

K. Walzer

Wednesday, June 11, 2003  
Mercredi 11 juin 2003

Afternoon  
Après-midi

Session II: High quality molecular films by OMBE and related techniques  
(continued)

Session Chair: J. Rabe

- P-II.08** 14:20 -Invited- STM STUDIES OF ORGANIC MULTILAYERS  
**Rolf Möller**
- P-II.09** 15:00 -Invited- GROWTH PHENOMENA IN CONJUGATED MOLECULAR MOLECULAR THIN FILMS FOR ORGANIC ELECTRONICS  
**Fabio Biscarini**, Consiglio Nazionale delle Ricerche - ISMN, Sezione di Bologna, Via P. Gobetti 101, 40129 Bologna, Italy  
Oligomer thin films, mainly sexithienyl and its derivatives, can give rise to a variety of architectures, according to the growth conditions. In order to control transport properties, it is crucial to control not only molecular order, but also the morphology and the spatial correlations at larger lengthscales. In thin films grown by ultra-high vacuum sublimation in an Organic Molecular Beam Deposition, the large variety of morphologies is mainly determined by the kinetic control during growth, and by the nature of the substrate which determines nucleation density and domain shape and orientation. These aspects are discussed in the case of technologically relevant systems, such as silicon oxide (bare or coated with a primer) and transistor channels. Another important aspect is the control of size and dimensionality of conjugated nanostructures, which is often hindered by coarsening phenomena. Here we show how three different approaches: growth onto nano-fabricated templates, stamp-assisted deposition, and thermally and mechanically induced dewetting can be useful to fabricate in a genuine bottom up fashion islands, droplets, fibrils just a few monolayer thin and with a characteristic sizes from microns to nanometers. This work was partially supported by EU-Projects Growth-MONA LISA and RTN LAMINATE.
- P-II.10** 15:40 INFLUENCE OF THE MOLECULAR STRUCTURE ON THE GROWTH AND THE MORPHOLOGY OF OLIGOTHIOPHENE BASED THIN FILMS  
**J. Ackermann**(a,b), C. Videlot(a), P. Dumas(b), H. Oughaddou(a), P. Raynal(a), A. El Kassmi(a), S. Safarov(b), P. Blanchard(c), J. Roncali(c), F. Fages(a), (a)LMMB, UMR CNRS 6114, Faculté des Sciences de Luminy, Marseille, France, (b)GEPC, UMR CNRS 6631, Faculté des Sciences de Luminy, Marseille, France, (c)IMMO, UMR CNRS 6501, Université d'Angers, Angers, France  
Organic semiconductors represent very promising materials for application in field-effect transistors (FETs), light emitting diodes (LEDs) and solar cells. The electronic properties of organic semiconductor thin films depend strongly on their morphology. The self-assembling properties of the molecules given by their structure present the most powerful parameter to control the morphology. In this study the influence of the molecular structure on the growth and the morphology of thin films has been investigated. Thin films has been deposited under high vacuum (10<sup>-6</sup> mbar) on passivated Si(100), SiO<sub>2</sub> and ITO. Classical oligothiophenes (4T, 8T, DH4T&#8230;) as well as oligothiophene based block-oligomers (BV2TVB, 2TVBV2T, 4T3V, DH4T3V) were investigated. The growth of the organic thin films deposited at different substrate temperatures has been studied by AFM. By producing organic field effect transistors charge carrier mobilities were determined and put into relation with observed film morphology. The results clearly demonstrate the impact of molecular structure on the self-organisation of the molecules and thus on the electronic properties of thin films. Small alterations of the molecule structure were found to give rise to complete changes in the morphology accompanied by a change of several orders of magnitude in the mobility of charge carriers. In particular the planarity of the molecular has been identified as important parameter in order to form highly crystalline thin film even on rough substrates like ITO.
- P-II.11** 16:00 NUCLEATION GROWTH REGIME OF OLIGOTHIOPHENE THIN FILMS: AN ATOMIC FORCE MICROSCOPY STUDY  
**M. Campione**, A. Borghesi, M. Moret, A. Sassella, INFN and Università degli Studi di Milano Bicocca, Dipartimento di Scienza dei Materiali, Via Cozzi 53, 20125 Milano, Italy  
An ex-situ atomic force microscopy low resolution analysis has been carried out with the scope to study the dynamics of the nucleation process in thin films of quaterthiophene obtained by molecular beam deposition. The effects of the competition between heterogeneous and homogeneous nucleation on the diffusion and aggregation processes of the deposited molecules are discussed through the investigation of the dynamic and scaling behavior of the separation and size distribution of nuclei.
- 16:20 **BREAK**

Session Chair: E. Umbach

**P-II.12** 16:40

EPITAXIAL GROWTH OF OLIGO-PHENYLENES ON Al(111) AND Au(111) SURFACES

R. Resel, I. Salzmann, T. Haber, S. Müllegger, A. Winkler, Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria, C. Teichert, G. Hlawacek Institute of Physics, University Leoben, Austria, B. Winter, J. Ivanco, M. Ramsey, Institute of Experimental Physics, University Graz, Austria

This study deals with the structural and morphological properties of sexiphenyl on a Al(111) surface and of quaterphenyl on a Au(111) surface. In both cases the film was prepared with MBE keeping the temperature of the substrate around 300K, the average thickness of the films was 30nm. The films were investigated by Atomic Force Microscopy (AFM) and by X-ray diffraction - pole figure (XRD-PF) technique.

The AFM studies reveal island type formation of the molecules. The XRD-PF studies reveal a crystalline state of the molecular material with a defined orientation of the crystallites relative to the metal (111) surface. In case of sexiphenyl on Al(111) the molecules are oriented with their molecular planes parallel to the (111) surface. Totally twelve different alignments of the sexiphenyl crystallites are observed, due to the threefold symmetry of the Al(111) surface, four independent types of epitaxial growth could be identified. The common feature of these four types of epitaxial order is that the long molecular axis of sexiphenyl is aligned along a azimuthal direction (e.g. [1-10]) on the Al(111) surface. From this fact, we conclude that even within the first monolayer formation the molecules are aligned in identical direction. The situation for the quaterphenyl on Au(111) is similar, except that the long molecular axis of the molecule is aligned parallel and perpendicular to the azimuthal directions, resulting in totally 24 different alignments of the quaterphenyl crystallites on the Au(111) surface.

**P-II.13** 17:00

GROWTH EXPONENTS AND RAPID ROUGHENING FOR DIINDENOPERYLENE THIN FILMS

A.C. Duerr(a), F. Schreiber(a,b,c), K.A. Ritley(a), V. Kruppa(a), J. Krug(d), H. Dosch(a,b) and B. Struth(e), (a)Max-Planck-Institut fuer Metallforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany, (b)Universitaet Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany,(c){new address}: University of Oxford, South Parks Road, Oxford OX1 3QZ, U.K., (d)Fachbereich Physik, Universitaet Essen, 45117 Essen, Germany, (e)ESRF, BP 220, 38043 Grenoble Cedex, France

Scaling laws are very powerful tools to analyze growth phenomena [1], but only little is known about the behavior of organic systems. We report the independent determination of the scaling exponents  $\alpha$ ,  $\beta$ , and  $1/z$  in highly ordered thin films of the organic molecule diindenoperylene (DIP) deposited on silicon-dioxide under UHV-conditions. Non-contact AFM, x-ray reflectivity, and diffuse x-ray scattering were employed. The surface roughness displays power law scaling over more than two orders of magnitude in film thickness. We obtained  $\alpha = 0.684 \pm 0.06$  for the roughness exponent,  $\beta = 0.748 \pm 0.05$  for the growth exponent and  $1/z = 0.92 \pm 0.20$  for the inverse dynamic exponent [2]. Exceeding the random deposition limit  $\beta_{RD} = 0.5$  and commonly expected values of  $1/z$ , the derived exponents point to an unusually rapid growth of vertical roughness and lateral correlations. We suggest that they could be related to lateral inhomogeneities arising from the formation of grain boundaries between tilt-domains of the DIP-film in the early stages of growth. The general implications of the results for other organic thin-film systems are discussed.

[1] J. Krug, Adv. Phys. 46 (1997), 139

[2] A. C. Duerr, F. Schreiber, K. A. Ritley, V. Kruppa, J. Krug, H. Dosch, and B. Struth, Phys Rev. Lett. 90 (2003), 016104

**P-II.14** 17:20

NUCLEATION, GROWTH AND SCALING OF PENTACENE FILMS ON OXIDIZED Si SUBSTRATES

Ricardo Ruiz(a), Bert Nickel(b), Richard F. Haglund Jr.(a), Leonard C. Feldman(a), Giacinto Scoles(b), (a)Vanderbilt University, Dept. of Physics and Astronomy, Nashville TN 37235, USA, (b)Princeton University, Department of Chemistry, Princeton NJ 08544, USA

Organic/inorganic interfaces play a crucial role in the rapidly growing field of molecular electronics. Even though huge progress has been achieved in the understanding of electronic transport in conjugated molecular materials, a complete theory of nucleation, growth and film morphology for organic materials deposited on inorganic substrates has yet to be formulated.

We report a systematic study involving complementary techniques, such as atomic force microscopy (AFM) and synchrotron X-ray scattering, to apply a diffusion model in the growth of pentacene films on oxidized Si substrates. We employ dynamic scaling theory that has been applied in the past to inorganic materials to model the island size distribution, critical cluster size and island correlations. The scaling behavior of the island size distribution of pentacene in the aggregation regime (0.1 to 0.5 monolayers) indicates that surface diffusion laws govern the system. The particular distribution of the scaling function suggests that the minimum number of molecules that conform a stable nucleus is 4. The island-island correlation length and the scaling of the structure factor of the film density were also measured using AFM and diffuse X-ray scattering, with consistent results between the two methods; the experiments are also in agreement with dynamic scaling theories for diffusion limited systems. The structure factor can be described as the product of two functions: the single island form factor and the spatial distribution of the islands. The present work demonstrates that it is possible to apply existing diffusion models to organic/inorganic interfaces even though conventional concepts like lattice mismatch and strong covalent bonding are not applicable.

Thursday, June 12, 2003  
Jeudi 12 juin 2003

Morning  
Matin

Session III: Electronic properties of crystals and films  
Session Chair: F. Biscarini (tentative)

- P-III.1** 8:40 -Invited- DIRECT AND INVERSE PHOTOEMISSION SPECTROSCOPY OF ORGANIC MOLECULAR FILMS AND INTERFACES  
**A. Kahn**, Dept. Electrical Engineering, Princeton University, Princeton NJ 08544, USA  
Surface electron spectroscopies are exceedingly important to obtain basic information, at the molecular level, on the electronic structure and chemistry of organic molecular films. This talk reviews recent work done on films of  $\pi$ -conjugated molecules of interest for organic-based devices such as organic light emitting diodes. The techniques used are ultra-violet photoemission, X-ray photoemission and inverse photoemission spectroscopies (UPS, XPS, IPES) for investigating valence states, core levels and empty states, respectively. The first part of the talk reviews basic but crucial concepts relevant to the proper understanding of, and correct application of spectroscopic techniques on, these highly correlated systems: polarization effects in the bulk vs. interfaces, and the single-particle, or transport, gap [1]. We show how the single particle gap is measured and used to estimate the large exciton binding energy in molecular solids [2]. The second part of the talk looks at the role of these spectroscopies in understanding interface electronic structures, i.e. injection barriers at metal-organic or organic-organic interfaces. In particular, UPS and XPS are shown to play a central role in the investigation of molecular level alignment at metal/organic interfaces [3]. Finally, we review the role of UPS and IPES in understanding electrical doping in these materials [4].  
[1] Tsiper et al. Chem. Phys. Lett. **360**, 47 (2002);  
[2] Hill et al. Chem. Phys. Lett. **327**, 181 (2000);  
[3] Shen et al. Organic Electronics, **2**, 89 (2001);  
[4] Gao et al. Appl. Phys. Lett., **79**, 4040 (2001)
- P-III.2** 9:20 BAND ALIGNMENT ON A NANOSCOPICALLY PATTERNED INORGANIC-ORGANIC INTERFACE  
**G. Koller**, F.P. Netzer, M.G. Ramsey, Institut für Experimentalphysik, Karl-Franzens Universitaet Graz, Universitaetsplatz 5, 8010 Graz, Austria  
Large organic molecules have attracted interest not only for their present day applications in light emitting devices but also for use in prospective nanoelectronic devices. One important parameter for the functioning of organic electronic devices in general is the barrier to charge injection. We therefore investigated the band alignment of an organic semiconductor on a nanoscopically patterned surface, specifically bithiophene on a Cu-O substrate, from submonolayer coverages to thin molecular films, using ultraviolet photoelectron spectroscopy and work function measurements. The Cu (110) - (2x1)O stripe phase, which is used as a substrate, consists of alternating stripes of clean and oxygen passivated copper with respective stripe diameters of three to four times the molecular length. The results show that in the first two molecular monolayers the electronic bands are aligned by the local surface potential of the individual stripes, which differs by 1 eV. This results in a superposition of UPS spectra from the two regions, which can be clearly identified. The nanoscopic substrate pattern is therefore imprinted into the molecular film. For thicker layers, however, the band alignment is determined by the average interface dipole potential, as demonstrated by a uniform UPS spectrum.
- P-III.3** 9:40 GROWTH OF CRYSTALLINE SEXIPHENYL FILMS WITH DIFFERENT CONFORMATIONS AND ELECTRONIC STRUCTURE  
**J. Ivanco**, **B. Winter**, F.P. Netzer and **M.G. Ramsey**, Institut für Experimentalphysik, Karl-Franzen-Universität Graz, Austria  
It will be shown that crystalline para-sexiphenyl films can be grown with significantly different molecular conformations and concomitant electronic structures. The in situ growth of sexiphenyl (6P) films on Al(111) has been studied with particular emphasis on the structure and electronic structure of the resulting films as evidenced by low energy electron diffraction (LEED) and angle resolved ultra-violet photoemission spectroscopy (ARUPS) and supported by ex-situ AFM and XRD measurements. On atomically clean Al(111) different crystalline films grow at both room and elevated substrate temperature despite having identical first monolayers. For growth at elevated temperatures the molecules are oriented with their molecular axes near perpendicular to the substrate and have a p-band structure typical of that reported for solid sexiphenyl in the literature. This electronic structure is associated with 6P with a high p conjugation due to removal of the inter-ring twist (torsional) angle. In contrast, it is found that for the highly crystalline 6P films grown at RT the molecules are oriented parallel to the substrate and have a smaller p-band energy spread and a 0.6 eV higher ionisation potential. The valence band electronic structure is identical to that of gas phase 6P implying that crystalline films with a high (40°) torsional angle can be grown and such semiconductor materials cannot be assumed to be made up of rigid rod like molecules. The influence of the details of the substrate interaction on the type of films that grow will be discussed as well as the significance of the type of film on device properties.

10:00

**BREAK**

## Session Chair: A. Thierry

- P-III.4** 10:40 ELECTRONIC PROPERTIES OF HIGHLY ORDERED ORGANIC ULTRATHIN FILMS STUDIED BY SCANNING TUNNELING SPECTROSCOPY  
Michael Toerker(a), Torsten Fritz(b), Holger Proehl(b), Rafael Gutierrez(c), Frank Großmann(c), Rüdiger Schmidt(c), (a)Fraunhofer Institut für Photonische Mikrosysteme, Grenzstr. 28, 01109 Dresden, Germany, (b)TU Dresden, Institut für Angewandte Photophysik, 01062 Dresden, Germany, (c)TU Dresden, Institut für Theoretische Physik, 01062 Dresden, Germany  
Highly ordered organic thin films on Au(100) single crystals have been investigated by Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) at room temperature. Firstly, the organic dye molecule perylene-tetracarboxylic-dianhydride (PTCDA) has been deposited as a sub-monolayer covering. I-V spectroscopy at a fixed tip to sample distance performed alternately on uncovered areas of the Au(100) surface and on PTCDA islands are compared. Secondly, scanning tunneling spectroscopy (STS) measurements on highly ordered double layers of the planar organic molecule hexa-peri-hexabenzocoronene (HBC) on Au(100) are presented. These measurements are compared to a theoretical characterization of the electronic conductance based on a combination of the Landauer transport formalism with a density-functional-parametrized tight-binding scheme within the Local Density Approximation (LDA).
- P-III.5** 10:40 MEASUREMENT OF CARRIER TRANSPORT AND INJECTION IN METAL-FREE TETRAPHENYLPORPHYRIN  
E. Pinotti, M. Cartotti, A. Sassella, and A. Borghesi, INFN and University of Milano Bicocca, Department of Materials Science, via R. Cozzi 53, 20125 Milano, Italy  
Carrier transport and charge injection are studied in metal-semiconductor structures employing metal-free tetraphenylporphyrin (H2-TPP) as the organic semiconductor. H2-TPP is deposited on an indium tin oxide (ITO) substrate into an apparatus for molecular beam epitaxy of organic materials, and aluminum is employed as the top electrode. The ITO/H2-TPP/Al structures thus obtained are investigated by a large-signal capacitance-voltage method, and transport and charge injection are simultaneously measured. At low electrical fields a space-charge limited transport is found, with a mobility value substantially higher than the ones previously reported in literature. Moreover, the device behavior is symmetrical, notwithstanding the different energy barriers between H2-TPP and Al, and H2-TPP and ITO interfaces. At higher electric fields the transport regime becomes Schottky-barrier limited, with the asymmetry expected from the energy difference between the two contact metals. The charge injected into the device behaves symmetrically at low fields, and shows a peak at the transition voltage between the space-charge and the Schottky regime, both in the positive and negative bias direction. Several mechanisms potentially producing this behavior (interface trapping, injection into conduction bands and chemical reactions), are discussed.
- P-III.6** 11:00 PERYLENE THIN FILMS FOR ORGANIC FIELD EFFECT TRANSISTORS: IMPORTANCE OF GROWTH PARAMETERS INVESTIGATED BY X-RAY ABSORPTION SPECTROSCOPY  
M.B. Casu, A. Schöll, D. Hübner, Y. Zou, K. R. Bauchspiess, C. Heske and E. Umbach, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany  
We have investigated thin films of perylene, one of the promising candidates as active material in an organic field effect transistor (OFET), deposited on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) by means of near-edge X-ray absorption fine structure spectroscopy (NEXAFS). A highly ordered thin (5 Å) layer of Al<sub>2</sub>O<sub>3</sub>, which is used to simulate the insulating layer in an OFET, was obtained by controlled oxidation of a Ni<sub>3</sub>Al(111) single crystal. Thin films of perylene were grown in-situ by organic molecular beam deposition, under strictly controlled evaporation conditions in order to obtain well-ordered films. The NEXAFS experiments were performed at BESSY (Berlin, Germany) at the UE52-PGM beamline, using variable photon beam polarisation. We have studied the influence of the growth parameters on the molecular orientation and on the electronic fine structure. We find that it is possible to tune the molecular orientation of perylene by using different sets of growth parameters. In particular, the molecules stand upright if, keeping the substrate at room temperature, a high deposition rate is chosen. This result has large technological relevance since it promises that perylene can be used for OFETs in a film structure with maximal p-orbital overlap. Furthermore, it demonstrates that perylene/Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) is a suitable organic/insulator/substrate model system for developing optimised FETs based on organic materials.
- P-III.7** 11:20 ELECTRICAL PROPERTIES OF ORGANIC THIN-FILM TRANSISTORS BASED ON PENTACENE DEPOSITED AT VARIOUS SUBSTRATE TEMPERATURE  
Jiyoul Lee and Seongil Im, Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea  
We report on the electrical properties of pentacene based organic thin film transistors (OTFTs), where active pentacene channel layers have been deposited with a fixed deposition rate of 1 Å/sec at various substrate temperatures ; RT, 60, 90, and 120 °C. The crystalline quality or molecular ordering of the pentacene layers were found to degrade with the substrate temperature while their field effect hole mobilities were maintained to be ~0.15 cm<sup>2</sup>/Vs as measured from OTFTs fabricated using a 270 nm - thick AlO<sub>x</sub> gate dielectric film. More details on the relationship between substrate temperature and the field mobility of pentacene TFTs will be discussed in this paper.

**P-III.8** 11:40

**ANALYSIS OF DEEP TRAPS IN 4,4'-BIS(4-DIMETHYLAMINOSTYRYL BENZENE) BASED LIGHT EMITTING DIODE DEVICES**

P. Lévêque, T.P. Nguyen, P. Le Rendu, Laboratoire de Physique Cristalline, Université de Nantes, France and O. Gaudin, R.B. Jackman, University College London, Torrington Place, London, U.K.

In this work, we have investigated the deep traps that exist within the active layer of organic light emitting diodes by the charge-based Deep Level Transient Spectroscopy (Q-DLTS) technique. The active layer of the devices investigated was 4,4'-bis(4-dimethylaminostyryl benzene) (DMSAB), a poly(p-phenylene vinylene) (PPV) derivative containing amine groups. The structures used were indium-tin-oxide (ITO)/DMSAB/MgAg. The comparison of results obtained on LEDs based on PPV and on DMSAB may give some information about the nature of the defects associated with the deep traps. Traps with an emission rate of  $\sim 11 \text{ s}^{-1}$  at 300 K were detected in both PPV and DMSAB based devices. They were identified as the contribution of two different traps in PPV based devices: an electron trap with an activation energy of  $\sim 0.41 \text{ eV}$  and a capture cross section of the order of  $10^{-19} \text{ cm}^2$  and a bulk acceptor-like hole trap with an activation energy of  $\sim 0.5 \text{ eV}$  and a capture cross section of the order of  $10^{-17} \text{ cm}^2$ . Another trap with an emission rate of  $\sim 5000 \text{ s}^{-1}$  was detected only in DMSAB based devices. This hole trap has an activation energy of  $\sim 0.38 \text{ eV}$  and a capture cross section of the order of  $5 \times 10^{-17} \text{ cm}^2$ .

12:00

**LUNCH**

Thursday, June 12, 2003  
Jeudi 12 juin 2003

Afternoon  
Après-midi

Session IV: Optical properties of crystals and films

Session Chair: P. Petelenz

- P-IV.1** 14:20 -Invited- THE APPLICATION OF REFLECTANCE ANISOTROPY SPECTROSCOPY TO ORGANICS DEPOSITION  
**Claudio Goletti**, Dipartimento di Fisica and Unità INFM, Università di Roma "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Roma, Italy  
The use of molecular materials in electronic devices is strongly developing nowadays, thanks to technologies that enable their integration with inorganic electronics in new hybrid materials, whose unique electronic and optical properties could originate disrupting applications. The need for a deeper characterization of organic layers has favored the development of new, highly controlled deposition techniques of organics in Ultra-High-Vacuum, mimicking what happened for Molecular Beam Epitaxy (MBE) of inorganic semiconductors. As MBE, also Organic MBE (OMBE) needs techniques capable to characterize in situ and in real time the deposited layers: the analogy with inorganic deposition shows that optical techniques represent a highly efficient opportunity. For this aim, Reflectance Anisotropy Spectroscopy (RAS) has been recently applied to organic layers, showing that spectra are reliably connected to the electronic properties of the molecule and to the morphological characteristics of the layer. In particular, RAS capabilities have been successfully applied to a class of solid-state materials, as Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) films, having an increasing importance in molecular materials applications. The results have clearly demonstrated that RAS is now ready for being applied to monitor the OMBE growth, most probably going through a success similar to the one already experienced in inorganic growth.
- P-IV.2** 15:00 -Invited- ANISOTROPIC OPTICAL FUNCTIONS OF OLIGOTHIOPHENE SINGLE CRYSTALS  
**S. Tavazzi**, INFM and Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Via Cozzi 53, 20125 Milano, Italy  
For the study of molecular crystals, oligothiophenes are often considered as representative of a large group of solids which crystallize in the monoclinic structure. Among possible techniques for investigating their properties, optical measurements are of fundamental interest, since a large amount of information can be obtained from them, e.g. the polarization of the exciton bands, their Davydov splitting, the influence of the macroscopic longitudinal fields. Polarized transmission and reflection spectra of oligothiophene single crystals and thin films are reported in the spectral region from 2.5 eV up to 6 eV, where several bands are detected, with their own polarization; in particular, directional dispersion is found for the excitonic band at lowest energy. The results are discussed in the framework of the macroscopic theory of the optical properties of anisotropic crystals and the complex dielectric tensor is modeled, thus giving some insight of the oligothiophene microscopic properties.
- P-IV.3** 15:40 PHOTOLUMINESCENCE PROPERTIES OF ORDERED AND ORIENTATIONALLY DISORDERED SOLID STATE OLIGOTHIOPHENES  
**E. Meinardi**, M. Cerminara, A. Sassella, A. Borghesi, R. Tubino, Università Milano-Bicocca, Via Cozzi 55, Milano, Italy and S. Blumstengel, Humboldt-Universität zu Berlin, Invalidenstrasse 110, Berlin, Germany  
The optical properties of quaterthiophene (4T) films grown on silica substrates have been studied and related to the presence of perfectly crystalline and orientationally disordered domains. The translational order is always retained, however in the latter case each molecule can assume two non-equivalent orientations, because 4T molecules lack a reflection symmetry plane perpendicular to the long molecular axis. The electronic state energies are almost configuration independent but the selection rules for the transitions from excited states towards the ground state are completely different in well-oriented and orientationally disordered domains. All observed photoluminescence spectral features of high-quality films (presence/absence of PL purely electronic transition, peak width, relative intensity of the vibronic replica, PL temperature dependence) are interpreted in terms of intrinsic emissions from these two kinds of aggregates. The model of chiral and achiral pinwheel aggregates provides theoretical support to this picture.

**P-IV.4** 16:00

**OXYGEN-INDUCED QUENCHING OF PHOTOEXCITED STATES IN POLYTHIOPHENE FILMS**

L. Lüer, H.-J. Egelhaaf, D. Oelkrug, Inst. for Physical and Theoretical Chemistry, Auf der Morgenstelle 8, 72076 Tübingen, Germany, G. Cerullo, G. Lanzani, Istituto Nazionale per la Fisica della Materia, Politecnico di Milano, Milano, Italy, B.-H. Huisman, D. de Leeuw, Philips Research Laboratories, Eindhoven, The Netherlands

Oxygen causes reversible and irreversible detrimental effects to the performance of organic (opto-) electronic devices. In order to get some insight into the mechanisms of these effects, we investigated the kinetics of fluorescence quenching (FQ) in thin films ( $d = 100$  nm) of regioregular polyalkylthiophenes upon exposure to oxygen.

The kinetics of FQ consists of a slow and a fast reversible component as well as an irreversible component. The fast reversible component leads to a loss of fluorescence intensity of appr. 2 % at an oxygen partial pressure of 1 bar within milliseconds. It is independent of the intensity of the exciting light and is ascribed to collisional quenching after oxygen diffusion into the bulk of the film. The slow reversible component, whose amplitude depends on light intensity, occurs on a timescale of minutes. It is assigned to the formation of charge transfer complexes between excited singlet states of polythiophene and oxygen. Femtosecond pump-probe experiments show enhanced decay rates of charged photoexcitations under oxygen. The increase of the decay rates shows the same dependence on exposure time to oxygen as the amplitude of the slow reversible component of FQ. Irreversible FQ is due to photooxidation of the polymer chains. The products of photo-oxidation act as traps for the highly mobile excitation energy and thus lead to efficient FQ, although hardly any loss of conjugation is visible in the absorption spectra of the films.

16:20

**BREAK**

Session Chair: S. Iannotta

**P-IV.5** 16:40

**INFLUENCE OF MOLECULAR ANISOTROPY ON THE OPTICAL PROPERTIES OF NANOCRYSTALLINE FILMS OF  $\pi$ -CONJUGATED SYSTEMS**

G. Weiser and S. Möller, Physics Dept., University of Marburg, 35032 Marburg, Germany

Electrons of  $\pi$ -conjugated bonds, confined to the small volume of a molecule or polymer chain, show strong electron correlation effects which results in unique linear and non-linear optical properties. A single exciton acquires much of the oscillator strength of  $\pi$ - $\pi^*$  transitions and splits away from higher excited states. If excited in a solid these large transition dipoles create a strong polarization field that is essential in understanding the optical spectra. In case of anisotropic crystals the position of absorption peaks depends on the orientation of the wavevector of light and may deviate from exciton energies by 1eV. While such polariton effects are well understood in single crystals they generate new effects in films of nanocrystalline domains, like broad and featureless bands of excessive absorption. However, a non-linear dielectric response like electroabsorption still resolves the spectral features arising from excitons. By comparing spectra of nanocrystalline films of  $\alpha$ -sexithiophene (T6) with those of a single crystal we demonstrate that the striking differences do not result from a different electronic structure or different dielectric response of the molecules but from the modification of the local field by coherently coupled transition dipoles and show that excess absorption is related to the mesoscopic size of anisotropic crystals. Similar behaviour will be presented for films T4 and PTCDA.

[1] L. Dähne, A. Horvath, G. Weiser, Chem. Phys. 196, 307 (1995)

**P-IV.6** 17:00

**OPTICAL PROPERTIES OF ORDERED ULTRATHIN FILMS OF THE ORGANIC SEMICONDUCTOR PERYLENE-3,4,9,10-TETRACARBOXYLIC-3,4,9,10-DIANHYDRIDE (PTCDA)**

H. Proehl, R. Nitsche, S. Mannsfeld, T. Diemel and T. Fritz Institut für Angewandte Photophysik, TU-Dresden, 01062 Dresden, Germany

Research activity on molecular solids revealed a wide range of interesting properties, emerging industrial interest, with real applications at the horizon. High quality samples, precise structural data, and a detailed understanding of the physical properties of thin films and their interfaces are essential. In this respect, the use of highly controlled growth techniques like Organic Molecular Beam Epitaxy/Deposition (OMBE/OMBD) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, therefore displaying well defined physical properties. Here we will discuss the special optical properties of ultrathin films of PTCDA, an archetypal organic semiconductor. Highly ordered organic thin films on a gold single crystal have been prepared by means of OMBE with submonolayer to multilayer coverage. All films were structurally characterized by Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED), clearly indicating epitaxial "point-on-line" growth. In situ Differential Reflectance Spectroscopy (DRS, a variant of reflection absorption spectroscopy) has been applied to measure the optical characteristics of those films. The results clearly show that ultrathin layers have different optical properties as compared to thicker films, which match the results known for long from polycrystalline samples. The results are compared to ordered thin films grown on mica to discuss the influence of different substrates on the growth mode, which ranges from Stranski-Krastanov to van der Merve (layer-by-layer) growth.

**P-IV.7** 17:20

TIME-RESOLVED PHOTOLUMINESCENCE IN PTCDA SINGLE CRYSTALS: EVIDENCE FOR RECOMBINATION VIA FRENKEL EXCITONS, CHARGE TRANSFER STATES, AND EXCIMERS

R. Scholz(a), A.Yu. Kobitski(a,b), I. Vragovic(a), H.P. Wagner(a,c) and D.R.T. Zahn(a), (a)Institut für Physik, Technische Universität Chemnitz, Germany, (b)Abteilung Biophysik, Universität Ulm, Germany, (c)Department of Physics, University of Cincinnati, USA

The radiative recombination channels in  $\alpha$ -PTCDA are analysed with time-resolved PL techniques in the 100 ns range between temperatures of  $T=10$  K and  $T=300$  K [1-3]. These PL spectra are interpreted with model calculations based on the transfer of Frenkel excitons [4] and with time-dependent density functional theory applied to different molecular dimer geometries [3]. At low temperature, the lineshape and radiative lifetime of the most important PL channel [1] can be assigned quantitatively to a vertical transition from the indirect minimum of the Frenkel exciton dispersion towards the electronic ground state [4]. In an intermediate regime below about  $T=100$  K, charge transfer states involving an anionic and a cationic molecule dominate the PL spectra [2,3]. Radiative recombination from an excimer state in a stack geometry has a rather weak temperature dependence, and due to non-radiative quenching of the other PL channels, this excimer produces the most important PL band above about  $T=200$  K [2,3].

[1] A.Yu. Kobitski, R. Scholz, I. Vragovic, H.P. Wagner, and D.R.T. Zahn, Phys. Rev. B 66, 153204 (2002).

[2] A.Yu. Kobitski, R. Scholz, D.R.T. Zahn, and H.P. Wagner, submitted to Phys. Rev. B (2003).

[3] R. Scholz, A.Yu. Kobitski, I. Vragovic, T.U. Kampen, D.R.T. Zahn, and H.P. Wagner, Proc. 26th Int. Conf. Phys. Semicond. (2002).

[4] R. Scholz, I. Vragovic, A.Yu. Kobitski, M. Schreiber, H.P. Wagner, and D.R.T. Zahn, phys. stat. sol. (b) 234, 402 (2002).

**P-IV.8** 17:40

INFLUENCE OF MOLECULAR ORGANIZATION IN THE EMISSION PROPERTIES OF LANGMUIR-BLODGETT FILMS OF TWO DIFFERENT PERYLENE TETRACARBOXYLIC DIIMIDE DERIVATIVES

T. Del Caño(a), V. Parra(a), M.L. Rodríguez-Méndez(a), R. Aroca(b), J.A. De Saja(a), (a)Física de la Materia Condensada, Facultad de Ciencias, Universidad de Valladolid Prado de la Magdalena s/n 47011 Valladolid, Spain, (b)Materials and Surface Group, School of Physical Sciences, University of Windsor, 4012 Sunset Ave, Windsor On. N9B 3P4, Canada

The absorption and emission properties of Langmuir-Blodgett films of two different perylene tetracarboxylic diimide derivatives, Bis(neopentylimido)perylene and Bis (n-propylimido)perylene, are studied in the search of new organic emitters. The surface pressure-area isotherms ( $\pi$ -A) of the Langmuir monolayers were recorded in order to optimize the best transfer conditions. It is found from the area per molecule values extracted from the isotherms analysis that the molecules are tilted on the water subphase for both dyes, and this orientation seems to be preserved during the transfer of the monolayers to different substrates. Film structure and molecular organization in the films is extracted from transmission and reflection-absorption Infrared Spectroscopy (RAIRS) and atomic force microscopy (AFM). The differences in emission properties of both dyes are correlated with the degree of aggregations and molecular stacking in the films. Finally the effect of thermal annealing and solvent vapours on the films structure was examined.

Friday, June 13, 2003  
Vendredi 13 juin 2003

Morning  
Matin

Session V: Modelling of the growth mechanisms and properties of molecular  
crystalline materials

Session Chair: G. Weiser

- P-V.1** 8:40 -Invited- TEXTURAL DISORDER IN ABSORPTION AND ELECTRO- ABSORPTION SPECTROSCOPY  
**P. Petelenz**, M. Andrzejak and M. Slawik, Department of Theoretical Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland  
Although textural disorder affects directly only a small fraction of the molecules contained in a polycrystalline sample, it gives rise to considerable broadening of the absorption spectrum. This is a consequence of the terms in bulk exciton energy which are attributable to the influence of the mesoscopic boundaries of each individual crystallite and are non-analytic at  $k=0$ , depending on the direction of the wave vector. In a polycrystalline sample the differently oriented microcrystals absorb at different energies --- hence the broadening. As the interaction depends on the square of the transition dipole moment, the effect is not negligible only for intense Frenkel transitions, such as that observed in sexithiophene. Yet, for this same system the substantial difference between the electro-absorption (EA) spectra of the single crystal and of a film, both dominated by the charge-transfer (CT) excitons, demonstrates that also these latter states turn out to be sensitive to textural disorder, although their transition dipole moments are quite small. Direct calculations allow one to explain this effect by direction-dependent shifts in the CT manifold due to the off-diagonal coupling to Frenkel excitons, whose energies depend on crystallite orientation as indicated above. The conclusions are supported by complete theoretical reproduction of the experimental spectra of the sexithiophene crystal and film.
- P-V.2** 9:20 -Invited- ADVANCE MODELLING OF ORGANIC-INORGANIC HETEROEPITAXY  
**S. Mannsfeld**, T. Fritz, Institut für Angewandte Photophysik, Technische Universität Dresden, 01062 Dresden, Germany  
The complicated balance of forces leading to highly ordered OMBE (Organic molecular beam epitaxy) films on inorganic crystalline substrates requires a sophisticated model in order to understand the experimentally observed layer structure. The use of atom-atom potential methods with molecular force field parameters is a realistic approach of modeling the energetics for an OMBE layer. However, the computational effort of the potential energy calculation prevents its use for realistically large molecular domains with tens of thousand atoms, including the required number of substrate atoms.  
Nevertheless, the molecules in OMBE layers are often lying flat on the substrate. Hence, the potential functions of rigid molecules on a rigid substrate lattice describing both, the intermolecular interactions and the molecule-substrate interactions, can be expressed as a potential function dependent on only three parameters. By utilizing pre-calculated interaction potential tables and suitable interpolation methods we can, therefore, speed up the calculation remarkably.  
This technique allows us to minimize the total interfacial energy in large molecular domains (~1000 molecules), thereby predicting a favorable layer structure for a given adsorbate-substrate combination. Here, we compare experimental data from OMBE layers on graphite with the results from the respective calculations. We will further demonstrate the validity of the assumption that the so-called point-on-line epitaxy, as suggested for various OMBE systems, is related to an energetic gain per molecule.
- P-V.3** 10:00 -Invited- FRENKEL AND CHARGE-TRANSFER EXCITONS IN QUASI-ONE-DIMENSIONAL MOLECULAR CRYSTALS  
**M. Hoffmann**, Institut für Angewandte Photophysik, TU Dresden, 01062 Dresden, Germany and Z.G. Soos, Department of Chemistry, Princeton University, Princeton NJ 08544, USA  
We discuss the excited state structure of one-component quasi-one-dimensional molecular crystals. Our underlying model includes Frenkel exciton transfer, mixing of Frenkel and charge-transfer (CT) excitons and linear coupling of both excitons to one internal molecular vibration. This model is used to describe optical spectra of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) and MePTCDI (N-N'-dimethylperylene-3,4,9,10-dicarboximide).  
The excited Frenkel-CT-vibronic states of the model Hamiltonian are investigated by numerical diagonalization. For this, we represent the Hamiltonian in a displaced oscillator (Lang-Firsov) basis and use a problem-adapted truncation scheme for the phonon basis. Thus, the complete optical spectrum becomes accessible for weak up to intermediate electronic coupling [1]. We demonstrate how the characteristic vibronic progression of isolated molecules is changed upon aggregation for various Frenkel and CT exciton coupling situations. Evaluation of the electronic character of the eigenstates allows to relate their complicated structure to the basic electronic interactions. Thus, the main features in crystal absorption spectra of the model compounds can be interpreted. [1] M. Hoffmann and Z. G. Soos, Phys. Rev. B 66(2002) 24305.

10:40

**BREAK**

**P-V.4** 11:20 -Invited-

**EFFECT OF CHAIN PACKING ON THE OPTICAL AND TRANSPORT PROPERTIES OF CRYSTALLINE ORGANIC SEMICONDUCTORS: AN AB INITIO INVESTIGATION**

Alice Ruini(a), Giovanni Bussi(a), Andrea Ferretti(a), Marilia J. Caldas(a,b) and Elisa Molinari(a), (a)INFM National Center on nanoStructures and bioSystems at Surfaces (S3) and Dipartimento di Fisica, Università di Modena e Reggio Emilia, Italy, (b)Instituto de Fisica, Universidade de Sao Paulo, Brazil

We investigate the effect of solid-state chain packing on both optical and transport properties for a prototype polymer, poly(paraphenylenevinylene) (PPV), that is considered in different possible crystalline packings. The optical behaviour of PPV is explored through an ab-initio density matrix scheme, that allows us to include electron-hole interaction on top of a density functional theory calculation. We find [1] that the details of crystalline arrangement dramatically alter the optical properties and lead to a richer excitonic structure: each excitonic state splits in two direct components (with electron and hole on the same chain), and the optical inactivity of the lowest component crucially quenches the photoluminescence efficiency. Moreover, the transport properties of PPV have been investigated [2] by converting the band-structure problem to a tight-binding formulation; this approach provides a first-principles determination of the transfer integrals, which are found to be a crucial quantity to appreciate the important effect of crystalline aggregation on conduction properties. Our results suggest that control of interchain interaction a tunable parameter to design efficient optoelectronic devices.

[1] Alice Ruini, Marilia J. Caldas, Giovanni Bussi, and Elisa Molinari, Phys. Rev. Lett. 88, 206403 (2002).

[2] Andrea Ferretti, Alice Ruini, Elisa Molinari, and Marilia J. Caldas, Phys. Rev. Lett. in press (2003).

**P-V.5** 11:40

**EFFECTS OF INTERMOLECULAR INTERACTIONS ON PHOTOLUMINESCENCE EFFICIENCY IN CRYSTALLINE THIOPHENE-S-S-DIOXIDE MOLECULAR SEMICONDUCTOR**

F. Della Sala, G. Gigli, M. Anni, D. Pisignano, R. Cingolani, National Nanotechnology Laboratories of INFM, G. Barbarella, L. Favaretto, G. Sotgiu, Consiglio Nazionale Ricerche, ICoCEA, E. Tedesco, K. Harris, School of Chemistry, University of Birmingham, L. Antolini, Dipartimento di Chimica, Università di Modena e Reggio Emilia, Italy

In the context of organic molecular semiconductors, thiophene derivatives are relevant for the high chemical stability, the excellent transport properties and for the wide color tunability, although, their use as active materials for light-emitting diode has been limited by the relatively poor photoluminescence (PL) quantum efficiency. However thiophene-S,S-dioxide and dithieno-thiophene-S,S-dioxide derivatives can show high PL quantum efficiency in the solid-state up to 70%, and has larger electronic affinity with favour the electron injection. Thus these materials represent an important class of molecular semiconductor for optoelectronic applications. We here investigate their supramolecular organization using X-ray structure. The role of the crystalline structure on solid-state PL quantum efficiency is investigated by calculating intermolecular interactions using the INDO/S quantum chemistry approach. The exciton resonance interaction is calculated exactly (i.e. without the dipole-dipole approximation) and the role of charge-transfer pairs is considered by evaluating the electron and hole transfer integrals. Experimental PL efficiency trends can be justified by these theoretical investigations.

## Session VI: Chemistry-related aspects of organic crystalline materials

Session Chair: H. Klapper

- P-VI.1** 12:00 -Invited- **PROPERTIES AND ORIGIN OF THE SUPRAMOLECULAR ORDERING IN NONLINEAR OPTICAL THIN FILMS BASED ON A SPECIALLY DESIGNED CHROMOPHORE**  
**Ali N. Rashid**, Nonlinear Optics Laboratory, Institute of Quantum Electronics, Swiss Federal Institute of Technology, ETH-Hönggerberg, 8093 Zürich, Switzerland  
Thin films based on acentric supramolecular assemblies of organic conjugated molecules are very attractive for a multitude of information processing and photonic applications. While major advances have been made towards achieving this goal, one of the problems that remain to be solved is that of thickness control. In this contribution, a simple and effective method will be described for the growth of acentric supramolecular self-assembled thin films with stable directional ordering perpendicular to the surface of the substrate. This method, which involves the evaporation under vacuum of well-designed molecules onto cleaned amorphous glass substrates, takes advantage of the control offered by vapor deposition techniques over the thickness of the films grown while directional hydrogen bonding ensures that the acentric ordering is maintained over a large thickness.
- P-VI.2** 12:40 **THE ROLE OF IMPURITIES ON QUATERTHIOPHENE PHOTOLUMINESCENCE**  
**S. Trabaton**(a), A. Borghesi(a), S. Laera(b), M. Moret(b), A. Papagni(a), (a)INFM and Università Milano-Bicocca, Dipartimento di Scienza dei Materiali Via Cozzi 53, 20125 Milano, Italy, (b)Università Milano-Bicocca, Dipartimento di Scienza dei Materiali Via Cozzi 53, 20125 Milano, Italy  
The presence of two independent vibronic series in photoluminescence (PL) emission spectra of ultrathin films of quaterthiophene (4T), grown by molecular beam deposition, was previously associated with emission from two different species. The first series originating at 2,52 eV, is related to localised states like disordered 4T and the second one, originating at 2,43 eV was related to crystalline 4T, the real origin being at 2,61 eV, detectable only at temperatures lower than 20K. Considering the fact that the intensity of the first vibronic series fades on going on with the number of films grown with the same starting material, the presence of impurities which act as traps of 4T excitation is suggested here. Thus, proceeding from quaterthiophene synthesis to chemical and physical analysis, we will demonstrate that the PL series originating at 2,52 eV is the contribution from a-monobromoquaterthiophene (Br4T). The presence of Br4T is consistent with the synthesis utilized and confirmed by thin layer chromatography and mass spectrometry. From nuclear magnetic resonance the 4T chemical purity is determined higher than 99%. As expected the presence of Br4T is not visible in the absorption spectra of 4T films at room temperature, but it may be clearly evident in PL emission spectra at low temperature as the mentioned PL series. To confirm this hypothesis we have synthesised Br4T and compared the PL emission of Br4T films with that rising at 2,52 eV in the 4T spectra.
- P-VI.3** 13:00 **HIGHLY- ORDERED GROWTH OF PERFLUORINATED PHTHALOCYANINES: INFLUENCE OF CHEMICAL SUBSTITUTION AND CHOICE OF SUBSTRATES**  
W. Michaelis(a), K. Hesse(b), C. Kelting(a) and D. Schlettwein(a), (a) Physical Chemistry 1, Department of Chemistry, University of Oldenburg, PO Box 2503, 26111 Oldenburg, Germany, (b) PicoRapid, Fahrenheitstrasse 1, 28359 Bremen, Germany  
In the search of suitable organic n- conductors to complement the well- known examples of p- conducting layers, perfluorinated phthalocyanines appeared as promising candidates that are easily reduced and can act as organic n- conductors. To further exploit their potential as electrode material, the film growth and structure of films has been studied in detail:  
Films were prepared by physical vapor deposition on amorphous SiO<sub>2</sub>, mica, polymeric substrates and alkali halides. To avoid interaction with ambient atmosphere and to allow an analysis during subsequent deposition from the monolayer range to about 100 nm, most experiments were performed in situ. Optical absorption spectroscopy was used to analyze the orientation of chromophores relative to each other (coupling of transition dipoles) and relative to the substrate plane (integral absorbance). Reflection high energy electron diffraction (RHEED) allowed to determine the organic crystal lattice relative to a given substrate lattice. The observed structure was also confirmed by transmission electron diffraction (TEM) of individual islands after their removal from the substrate. Electrical conduction measurements provided insight into the formation of conducting pathways during film growth and hence enabled us to determine the growth mode (layers vs. islands). Subsequent atomic force microscopy (AFM) confirmed the assignments. A clear influence of the substrate on the film growth was observed, but also of different central groups (VO, Cu, Zn) in the given ligand system of the perfluorinated phthalocyanine. By these means, ultrathin conductive films could be prepared and implications are discussed for their application in organic field effect transistors or chemical sensors.
- 13:20 **CLOSING REMARKS (J. Rabe, T. Fritz)**