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May 24-28, 2004

SYMPOSIUM E

Organic field-effect transistor:
towards molecular scale

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E-MRS 2004 SPRING MEETING

SYMPOSIUM E

Tuesday, May 25, 2004

Morning

Session I : Materials and devices I

- E-I.1** 9:00 -Invited- GRAPHENE MOLECULES AS SEMICONDUCTORS FOR FETs
Mark D. Watson and **Klaus Müllen**, Max-Planck-Institute for Polymer Research, Mainz, Germany
This presentation is based on three central points:
Polymer synthesis is able to produce all sorts of coil structures and topologies derived from them such as stars and brushes, but disc-like polymers with two-dimensional molecular forms are unknown;
Graphite, a single sheet of which can be viewed as a 2D-macromolecule, is an attractive material for solid-state physics, especially in view of its allotropes such as fullerene and nanotubes, but is hardly a definable objective for polymer synthesis; Polycyclic aromatic hydrocarbons (PAHs) have played a central role in the development of organic chemistry, but possess no polymer analogs. We demonstrate practical routes to make extremely large PAHs, which act as structurally defined processable graphite molecules. Connected with the synthesis is the attainment of complex supramolecular architectures by processing from solution or from the melt. In this way a hierarchy of structures is developed, which leads from single molecules and their visualization towards, for example, epitaxially ordered multilayers, fibres and films, containing perfect columnar arrangements of discotic molecules. This organisation produces remarkable physical properties, which are responsible for very high charge carrier mobilities in photoconduction and efficient energy conversion in solar cells. Other possible applications include efficient lithium storage or selective thermolytic conversion of PAHs into novel carbon nano- and microtubes.
- E-I.2** 9:40 INCREASED MOBILITY FROM LINEAR TO STAR-SHAPED BRANCHED THIOPHENE-BASED POLYMERS IN ORGANIC FIELD EFFECT TRANSISTORS
B. Pépin Donat(a), S. Panozzo(b), J-C. Vial(b), C. Bégnié(c), Y. Sansom(c), F. Rieutord(d), (a)Laboratoire de Physique des Métaux Synthétiques, UMR CEA-CNRS-Univ.-J. Fourier N° 5819, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France, (b)Laboratoire de Spectrométrie Physique, Université Joseph Fourier Grenoble 1 CNRS (UMR C5588), 140 avenue de la Physique, B.P. 87, 38402 Saint Martin d'Hères cedex, France, (c)Laboratoire NM, SP2M, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble cedex, France, (d)Laboratoire de Physico-chimie Moléculaire, UMR CEA-CNRS-Univ.-J. Fourier N° 5819, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France
Field effect mobilities in star-shaped polybranched poly(octylthiophene) systems were studied on spin coated films. The systems consist in non regioregular poly(octylthiophene) chain segments connected by various trithienylbenzenes of functionality f equal to 3 or 6. These systems exhibit a two-order higher mobility than the related linear non regioregular poly(octylthiophene)s. By changing the length and regioregularity of the poly(octylthiophene) chain segment between adjacent crosslinks and the nature of the crosslink, we demonstrate the crucial role of the local star-shaped structure on the mobility. In the large range of studied systems (linear or star-shaped, non regioregular or regioregular), we observe a clear correlation between mobility and charge delocalisation in film (characterised by the energy of UV-Vis. transition). The increased delocalisation and mobility in the non regioregular star-shaped systems is attributed to a specific self organisation induced by the local star-shaped structure. This assumption is supported by Atomic Force Microscopy (AFM) observations and X Ray Reflectivity measurements which reveal a specific structure.
- E-I.3** 10:00 LOW BAND GAP DONOR-ACCEPTOR-DONOR POLYMERS FOR INFRA-RED ELECTROLUMINESCENCE AND TRANSISTORS
M. Chen(a), E. Perzon(b), N. Robinson(a), M. Andersson(b), S. Marcinkevicius(c), M. Fahlman(a), M. Andersson(b) and M. Berggren(a), Linköping University, Sweden
A conjugated polymer consisting of fluorene units and low bandgap donor-acceptor-donor (D-A-D) units is reported. The D-A-D segment includes two electron-donating thiophene rings combined with a thiadiazolo-quinoxaline unit. The resulting polymer has a band gap of 1.3 eV. We will present spectroscopic data together with results achieved from solid state devices including this low band gap polymer as the active layer. For instance, the absorption spectrum of the polymer peaks at around 800nm and the corresponding electroluminescence spectra peaks at 1000 nm. Also, transistors have been made including this material and the resulting hole mobility value and the transistor IV characteristics will be presented. Conjugated polymers, designed after the D-A-D criteria, are of general interest since they can provide light emission in the near-infrared region, are promising materials for transistors and offer red-shifted light absorption in photovoltaic devices.
- E-I.4** 10:20 AMBIPOLAR ORGANIC HETEROSTRUCTURE FIELD-EFFECT TRANSISTOR
Constance Rost, David J. Gundlach, Siegfried Karg, Walter Riess, IBM Research GmbH, Säumerstrasse 4, 8803 Rüschlikon, Switzerland
Organic field-effect transistors (OFETs) containing a single material as active layer generally function either as p- or n-channel device. Therefore, ambipolar device operation over a wide range of operating voltages is difficult to realize. Here, we present a highly asymmetric heterostructure OFET architecture using the hole

transport material pentacene and the electron transport material N,N'-dibutylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C13H27). Efficient charge carrier injection is achieved by using Au as bottom contact for hole injection into pentacene and Mg as top contact for electron injection into PTCDI-C13H27. The device characteristic of this asymmetric heterostructure shows all features of ambipolar operation. For example, for small VDS a typical transistor characteristic with a linear and saturation region is observed. For large VDS, the current increases due to additional injection of charge carriers of opposite sign from the drain contact. In that regime, both types of charge carriers are present in the device. Thus, the thin film transistor can be operated in a mixed state in which both electron and hole currents are injected into the device and where the double injection regime is controlled by the gate voltage. Replacing the non-emitting pentacene with an efficient fluorescent hole transporting material results in a light-emitting field-effect transistor.

10:40

BREAK

Session II : Electronics at the molecular scale I

- E-II.1** 11:00 -Invited- MOLECULAR LANDERS AS PROTOTYPES OF SINGLE MOLECULAR DEVICES: SYNTHESIS, CONFORMATION, CONDUCTANCE, SURFACE RESTRUCTURING AND CONTACT
André Gourdon, NanoSciences Group, CEMES-CNRS, BP4347, 29 Rue J. Marvig, 31055 Toulouse Cedex 04, France
A prerequisite to the use of single molecules as active devices in future molecular-scale electronics is the description and understanding of the important parameters controlling the device properties: molecular conformation, surface structure, molecule-metal electronic coupling, contact resistance etc. It implies to perform experiments in ultra-clean conditions and in a "planar geometry" in which the studied molecular device is parallel to the substrate so that the electronic and geometrical parameters can be described at sub-molecular level. The only currently available tool giving access to these parameters in a fully controlled way is the UHV Scanning Tunneling Microscope, which allows in the same time imaging of the molecules, electrical and spectroscopic investigations and single-molecule manipulation. The main drawback of this technique is the requirement of a conductive substrate implying strong electronic interactions with the molecule, especially the unsaturated organic cores required for long distance electron transport. With these constraints in mind we have designed specific families of molecules, named "molecular landers", in which the active part is electronically decoupled from the metallic substrate by spacers UHV Scanning Tunneling Microscopy experiments on these landers have allowed us to measure single molecule conductance, contact resistance with an electrode, to perform molecular manipulation, conformational changes and molecular switching. We also have shown that some of these landers could be used to restructure surfaces or metallic steps edges to create 2 or 3 atoms wide metallic wires.
- E-II.2** 11:40 SINGLE-CRYSTAL ORGANIC FIELD EFFECT TRANSISTORS BASED ON TETRATHIAFULVALENE DERIVATIVES
M. Mas-Torrent(a), M. Durkut(a), P. Hadley(a), X. Ribas(b), C. Rovira(b), (a)Department of NanoScience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands, (b)Institut de Ciència de Materials de Barcelona, Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
The processing characteristics of organic semiconductors make them potentially useful for electronic applications where low-cost, large area coverage, and structural flexibility are required. The highest mobilities have been reported for crystals of pentacene (1.5 cm²/Vs)[1] and rubrene (8 cm²/Vs), [2] which were grown from the vapor phase in long and complex experiments. Recently, we reported on the field effect hole mobility in single crystals of the organic semiconductor dithiophene-tetrathiafulvalene (DT-TTF) grown by drop casting, a very simple method. [3] The maximum mobility observed in these crystals was as high as 1.4 cm²/Vs. Herein, we present our latter results with DT-TTF single crystal transistors as well as the transport measurements of various tetrathiafulvalene derivatives. The high mobility of this family of compounds combined with the simple processing required makes them very good candidate materials for electronic applications. References: [1] Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* 2002, 14, 99-117. [2] Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* 1998, 72, 1854-1856. [3] Mas-Torrent, M.; Durkut, M.; Hadley, P.; Ribas, X.; Rovira, C. *J. Am. Chem. Soc.* 2004, 3, in press.
- E-II.3** 12:00 STM/STS ON SELF-ORGANIZING 3D HYBRID NANOSTRUCTURES
Elena Mena-Osteritz and Peter Bäuerle, Dept. of Organic Chemistry II, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
The well-defined molecular structure of pi-conjugated linear and macrocyclic Thiophenes allows their self-organisation on substrates. Moreover the semiconductor properties of such a family of organic compounds will play an essential role as key components for coming nanoelectronic devices and as modular building blocks for the assembly of new materials and supramolecular chemistry. However, the assembly of molecular materials in nanoscale architectures will be a crucial step for the future molecular scale electronics. On the other side due to their toroidal structure, pi-conjugated macrocycles could represent intriguing "molecular circuits" which would additionally include sites for recognition and selective complexation. In this contribution we will present the different 2D-arrangements of the first fully conjugated macrocycles (cyclo[n]thiophene) at the liquid/HOPG interface revealed by in-situ scanning tunnelling microscopy (STM). The data will be analysed with the help of theoretical conformational and MO analyses. By means of STM, we also investigated epitaxy and interactions of C60-fullerenes with 2D crystalline monolayers of cyclo[12]thiophene resulting in perfectly ordered 1:1 complexes. STM-analyses of the nature, specificity and dynamics of the complexation process taking place at the surface, supported by theoretical calculations, as well as Scanning Tunneling Spectroscopy (STS) analyses of these "molecular diodes" will be discussed.

Tuesday, May 25, 2004

Afternoon

Session III : Fabrication techniques I

- E-III.1** 14:00 -Invited- NOVEL MATERIALS FOR DRY PRINTING ELECTRONIC DEVICES
Graciela B. Blanchet(a), J.A. Rogers(b), C.P. Nuckolls(c), G.D. Jaycox(a), M. Lefenfeld(c) and Yieh-Lin Loo(d), (a)DuPont Central Research and Development, Wilmington DE 19880, USA, (b)University of Illinois, Urbana Champaign, USA, (c)Columbia University, New York NY 10027, USA, (d)University of Texas, Houston TX, USA
 The field of organic electronics offers the possibility for the design of lightweight and flexible systems with large area coverage, properties not easily achievable with standard silicon technologies, and at potentially lower manufacturing costs. DuPont's approach to the fabrication of organic electronic devices is thermal transfer, a laser assisted imaging technique appropriate for early commercialization. Since complex multi-layer circuits are fabricated by the sequential printing of solid films, material options are considerably broadened and stringent solvent compatibility issues faced by "wet" techniques like micro-contact printing and ink jet are effectively circumvented.
 We continue to focus on the development of conducting and semiconducting organic composites that allow for the printing of active and passive electronic devices at good process speeds and at high resolutions. The feasibility of using our laser ablation technique for the large area printing of organic electronic devices was recently demonstrated by fabricating a 32" diagonal thin, flexible and ultra-light weight organic transistor array backplane.
- E-III.2** 14:40 STRUCTURE-PERFORMANCE RELATIONSHIP IN PENTACENE/AL₂O₃ THIN-FILM TRANSISTORS
W. Kalb(a), P. Lang(b), M. Mottaghi(b), H. Aubin(c), G. Horowitz(b) and M. Wuttig(a), (a)I. Physikalisches Institut (IA), RWTH Aachen, 52056 Aachen, Germany, (b)ITODYS, CNRS-UMR 7086, Université Denis-Diderot, 1 rue Guy de la Brosse, 75005 Paris, France, (c)Laboratoire de Physique Quantique, CNRS-UPR A0005, ESPCI, 10 rue Vauquelin, 75231 Paris, France
 Pentacene-based thin-film transistors were fabricated on alumina substrates with gold top-contact source and drain electrodes. The growth mechanism of the pentacene film was followed by atomic force microscopy (AFM). On some devices, the alumina surface was modified with fatty acid self-assembled monolayers prior to pentacene deposition. On sub-monolayer films, the growth is found to be two-dimensional on bare alumina, while it turns to three-dimensional in the case of surface-modified substrates. The average grain size is around a few hundreds of nanometers in both cases. On bare alumina the growth mechanisms turns to three dimensional on subsequent layers, with the emergence of dendritic grains with an average diameter of a few micrometers. The variation of the mobility as a function of thickness was deduced from an analysis of the gate voltage dependent mobility. On thick films, mobility is higher on films grown on surface-modified alumina, while it becomes higher on thin films deposited on bare alumina. This finding seems in good agreement with the respective growth mechanisms.
- E-III.3** 15:00 TEMPLATE GROWTH OF CONJUGATED ORGANIC LAYERS ONTO LOCAL OXIDE NANOPATTERNS
R. García, M. Tello, Instituto de Microelectrónica de Madrid, CSIC, 28760 Tres Cantos, Madrid, Spain, F. Biscarini, M. Murgia, CNR-ISMN Sez. Bologna, 40129 Bologna, Italy
 In this contribution we present a process for nanoscale fabrication of ordered monolayer films of conjugated organic molecules. The process makes possible to grow sexithiophene monolayers (T6) at precise locations on a silicon substrate with a high degree of order while preserving the orientation of growth. The process is based on the integration of local oxidation nanolithography of the substrate and template growth of the molecular thin film. The former is used to fabricate silicon oxide arrays of parallel lines of 30-50 nm in width and several microns in length. Template growth arises from the interplay between kinetic growth parameters and preferential interactions with the patterned surface. The result is a monolayer film of organic molecules that conformally mimicks the features of the fabricated motives.
- E-III.4** 15:20 SELF-ORGANIZATION OF PHTHALOCYANINES ON AL₂O₃(11-20) IN ALIGNED AND ORDERED FILMS
E. Barrera(a), J.O. Ossó(b), F. Schreiber(c), D.G. de Oteyza(a), M.I Alonso(b), M. Garriga(b), H. Dosch (a,d), (a)Max-Planck-Institut fuer Metallforschung, Heisenbergstr.1, 70569 Stuttgart, Germany, (b)Institut de Ciència de Materials de Barcelona CSIC, 08190 Bellaterra, Spain, (c)Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, U.K., (d)Institut fuer Theoretische und Angewandte Physik, Universität Stuttgart, 70550 Stuttgart, Germany
 The controlled growth of ordered organic films is prerequisite for the development of organic electronic devices. One of the challenges is to achieve films with defined in-plane structure, that is, to avoid the formation of randomly oriented azimuthal domains. We show that F16CuPc molecules self-organize on Al₂O₃ (11-20) substrates forming unidirectionally oriented needle-like structures. X-ray diffraction reveals a highly ordered layered structure with the (001) plane parallel to the surface. The morphology, investigated by Atomic Force Microscopy (AFM), is smooth and consists of long (microns) and narrow (tens of nm) needle-like terraces unidirectionally aligned along one of the main crystallographic directions of the Al₂O₃ (11-20) surface. High resolution AFM images reveal in-plane molecular order with the molecular stacking direction parallel to the needle-like terraces. Spectroscopic ellipsometry shows that these films exhibit anisotropic optical properties correlated with the molecular arrangement.
- 15:40 **BREAK**

Session IV : Electronics at the molecular scale II

- E-IV.1** 16:00 -Invited- SELF-ASSEMBLED MOLECULAR RECTIFYING DIODES ON SILICON: EXPERIMENTAL AND THEORETICAL STUDIES
S. Lenfant, D. Vuillaume, C. Krzeminski, G. Allan, **C. Delerue**, Institut d'Electronique, de Micro-électronique et de Nanotechnologie (IEMN), Département ISEN, 41 boulevard Vauban, 59046, Lille Cedex, France
Following the predictions of Aviram and Ratner [1], recent works have demonstrated the possibility to make rectifying diodes with molecular mono-layers, using molecules containing donor and acceptor moieties linked by a short or bridge [2-5]. This approach requires important efforts to synthesize the molecules and to make the mono-layers. Thus simplified schemes are highly desirable. In this work, we report such a simplified method based on the fabrication of self-assembled mono-layers (SAM) with only one donor group and an alkyl chain. We present physical characterizations of the structures, transport measurements and theoretical calculations to simulate the systems [6].
We use a chemical functionalization of the end-groups of alkyltrichlorosilane SAMs to fabricate insulator/semiconductor (called -) heterostructures at a molecular level on silicon substrates. We characterize the structural properties of these SAM's by FTIR, wettability and ellipsometry before the electrical measurements. Current rectification is observed for the electronic transport through these functionalized SAM's embedded in a Si(n⁻-type)/ - /metal junction, with rectification ratio up to about 37 and threshold voltages of in the range -0.3 to -0.9 V (negative voltage applied on a top electrode). Self-consistent tight binding calculations of the density of states for these Si/ - systems show that the rectification occurs due to a resonant tunneling transport through the HOMO level of the conjugated group. The position of the HOMO with respect to the Fermi energies of the electrode is determined experimentally from the fit of a simple analytical model of the current-voltage curve [6] and from photo-current. A good agreement is found with our theoretical calculations for the different end-groups.
[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277-283 (1974).
[2] R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, and G. J. Ashwell, J. Am. Chem. Soc. **119**, 10455-10466 (1997).
[3] R. M. Metzger, T. Xu, and I. R. Peterson, J. Phys. Chem. B **105**, 7280-7290 (2001).
[4] D. Vuillaume, B. Chen, and R. M. Metzger, Langmuir **15**, 4011-4017 (1999).
[5] C. Krzeminski, G. Allan, C. Delerue, D. Vuillaume, and R. M. Metzger, Phys. Rev. B **64**, 085405 (2001).
[6] I.R. Peterson, D. Vuillaume and R.M. Metzger, J. Phys. Chem. A **19**, 4702-4707 (2001).
[7] S. Lenfant, C. Krzeminski, C. Delerue, G. Allan, and D. Vuillaume, Nano. Lett. **3**, 741 (2003).
- E-IV.2** 16:40 ELECTRICAL TRANSPORT OF METAL-MOLECULES-METAL NANOFUNCTIONS
C. Vanoni(a), S. Tsujino(a), A. Weber(a), J. Lehmann(a), L. Heyderman(a), C. David(a), J. Gobrecht(a), T.A. Jung(a), C. Schonenberger(b), (a)Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, (b)Nanocenter Basel, Institute of Physics, Klingelbergstrasse 82, 4056 Basel, Switzerland
The experimental determination of electron transport through molecules is a fundamental challenge with importance for opto- /electronic device applications. Here we present a fabrication process derived from silicon process technology, which obtains electrode-molecules-electrode nanofunctions with well-defined gap spacing and definition by angle deposition. The process has been established, and a large number of nanofunctions with varied gap spacing have been produced. For electrically open devices a resistance in the GOhm range has been obtained for the smallest typical gap of ~50 nm. We anticipate a further decrease of this value by process optimisations. In a first experiment to explore molecular transport, the junctions are modified by subsequent homogenous nucleation of ad-layer islands on the insulating substrate surrounding the gap. The low bias conductance of the devices is measured before and after adsorption of 1,4-Benzenedimethanethiol. Preliminary results show a correlation between the amount of nucleated metal and the increase of the conductivity upon molecular adsorption. This result is consistent with the picture of a granular film linked by "conductive" molecules, a concept which shall be further exploited.
- E-IV.3** 17:00 PROTOTYPICAL SINGLE MOLECULE TRANSISTORS WITH SUPRAMOLECULAR GATES
E. Jäckel, J.P. Rabe, Humboldt University Berlin, Department of Physics, Newtonstr. 14, 12489 Berlin, Germany; M.D. Watson, University of Kentucky, Department of Chemistry, Lexington KY 40506-0055, USA, and K. Müllen, Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
Electron transport through single molecules has attracted much interest due to the ambitious goal of nanometer-scale electronics. Hybrid-molecular diodes whose current-voltage characteristics are determined by a single molecule in a well controlled gap with dimensions on the order of one nanometer can be realised using a scanning tunnelling microscope (STM) or nanofabricated metal or break junctions. Field effect transistors have been fabricated with carbon nanotubes and single molecules. The electrodes, however, were macro- or mesoscopic and not readily scalable to nanoscale dimensions. Here we present a prototypical three-terminal device, in which the current through a hybrid-molecular diode is modified by nanometer-sized charge transfer complexes covalently linked to the molecule in the STM junction. Since the complexes are formed by electron acceptors covalently bound to the molecule in the gap, and electron donors coming from the ambient fluid, this set-up represents a chemical field effect transistor based on a single molecule with nanometer-sized gate. The gating effect is explained by a interface dipole model.
- E-IV.4** 17:20 NANOWIRES OF EDT(CONHMe)₂ AND (TMTSF)₂CIO₄
C. Colin(a), C. Pasquier(a), P. Auban-Senzier(a), S.A. Baudron(b), P. Batail(b), J. Fraxedas(c), (a)Laboratoire de Physique des Solides, UMR8502, Centre Universitaire, 91405 Orsay, France, (b)Laboratoire Chimie Inorganique, Matériaux et Interfaces, FRE2447, Université d'Angers, Bâtiment K, 2 Boulevard Lavoisier,

49045 Angers, France, (c)Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

Single crystalline nanowires of the one-dimensional monomolecular, neutral and insulating compound, EDT(CONHMe)₂ and of the prototypical organic superconductor (TMTSF)₂ClO₄ are shown to develop readily out of acetonitrile solutions. Electrical characterization of the narrow crystals of the latter compound will be presented. First attempts at constructing an organic field effect transistors (OFETs) based on the former EDT(CONHMe)₂ single crystalline nanowires as the electron channel will be presented. Perspectives on the use of single crystalline charge transfer salts as the channel medium for the making of OFET will be discussed.

Wednesday, May 26, 2004

Afternoon

Session V : Characterization and multifunctional applications I

- E-V.1** 14:00 -Invited- **A MICROSCOPIC VIEW OF CHARGE TRANSPORT IN POLYMER TRANSISTORS**
Lukas Bürgi, Tim Richards, Richard H. Friend, and Henning Sirringhaus, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K., *present address: CSEM SA, Badenerstrasse 569, 8048 Zürich, Switzerland
Although organic transistors have witnessed a rapid improvement in performance over the last decade, [1] the present understanding of many aspects of their complex device physics – such as the charge carrier injection process or charge trapping at the semiconductor-insulator interface – is far from being complete. Here, we explore the physics of polymer field-effect transistors on down to nanometer length-scales by means of scanning-probe microscopy based techniques.[2] Such a microscopic approach yields very valuable complementary information about device operation as well as charge transport and is of special importance in view of the ongoing miniaturization of organic electronics. In particular, we will discuss the formation of the accumulation layer on the basis of time-resolved local potential measurements. We will also concentrate on very direct and accurate measurements of the contact resistance, which allow important conclusions about the charge injection/extraction process at the source/drain electrode to be drawn. Finally, we will address charge-trapping in polymer field-effect transistors. A novel technique whereby light is coupled into a scanning force microscope is used for a direct spectroscopic investigation of trap-states at the polymer/insulator interface.
[1] G. Gelinck *et al.*, Nature Materials **3**, 106 (2004)
[2] L. Bürgi, H. Sirringhaus, and R.H. Friend, Applied Physics Letters **80**, 2913 (2002)
- E-V.2** 14:40 **STM/STS STUDIES OF POLY(3-ALKYLTHIOPHENE)S : MODEL SYSTEMS FOR PLASTIC ELECTRONICS**
M. Brun(a), R. Payerne(b), P. Rannou(b), R. Baptist(a), B. Grévin(b), (a)LETI-DTS CEA-Grenoble, 17 rue des Martyrs 38054 Grenoble Cedex 9, France, (b)Laboratoire de Physique des Métaux Synthétiques, UMR5819-SPRAM (CEA-CNRS-Univ.Grenoble I), DRFMC CEA-Grenoble, 17 rue des Martyrs 38054 Grenoble Cedex 9, France
Pi-conjugated polymers such as poly(3-alkylthiophene)s (P3ATs) are promising materials for the development of plastic electronics. Understanding their self-assembly in thin film is crucial to improve our understanding of their electronic transport properties. Scanning Tunneling Microscopy (and related spectroscopy : STM/STS) is a powerful tool for studying the structural organization and the electronic properties of these polymers. We present STM studies on two regioregular P3ATs, namely poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly(3-dodecylthiophene-2,5-diyl) (P3DDT), 2D thin films cast on HOPG. Both polymers self-assemble into a “close packing” morphology in which alkyl side-chains interdigitate to form crystalline monodomains of ca. 15-25 nm. A discussion of structural parameters (polycrystalline vs amorphous domains, domain sizes, interfaces and folds) will be given by comparing images obtained on P3HT and P3DDT. We will demonstrate how variation of casting conditions and ex situ post-annealing procedures can be used to significantly reduce disorder which can negatively impact P3ATs’ electronic transport properties. Moreover, we will discuss STM results on P3DDT monolayers, showing the coexistence of the “close packed” phase together with a new long range ordered phase. Finally, low current (pA range) STS imaging on P3DDT monolayers will be reported. A strong contrast between P3DDT and HOPG is observed on the mesoscopic scale. Its origins and a discussion of the corresponding I(V) curves will be presented.
- E-V.3** 15:00 -Invited- **IN SITU ELECTRICAL CHARACTERIZATION OF ORGANIC THIN FILM TRANSISTORS**
T. Muck, V. Wagner, School of Engineering and Science, International University Bremen, Campus Ring 8, 28759 Bremen, Germany, U. Bass, M. Leufgen, J. Geurts, L.W. Molenkamp, Physikalisches Institut, EP 3, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
The aim of this study was to determine the conducting channel thickness in the active layer of organic field transistors (OFET). Transport properties of OFETs are critically influenced by the active layer and its interface to the insulator and drain/source contacts. For a better understanding of the active layer we measured the electrical properties of the devices in situ during film growth. This provides an insight into the dependence of charge mobility on film thickness, especially in the first monolayers, while avoiding any contamination effects. We used pre-patterned templates with channel lengths from 50 μm down to 1 μm . Deposition of the active material was performed by organic molecular beam deposition in ultra high vacuum. As organic material dihexylquaterthiophene (DH4T) was used. By characterizing the organic transistor at different film thicknesses in the monolayer range we observe a step like behavior of the charge mobility. It starts at approx. one monolayer and immediately saturates. Additional monolayers do not increase the performance. Besides, temperature dependence is observed, which reflects e.g. transport mechanisms and effects of the structural phase transition of DH4T.
- 15:20 **BREAK**

Session VI : Characterization and multifunctional applications II

- E-VI.1** 15:40 **AVOIDING HOLE TRAPPING IN PARTIALLY DISORDERED TETRACENE AND PERYLENE THIN FILMS**
R. Friedlein, C. Süss and W.R. Salaneck, Department of Physics (IFM), Linköping University, 58183 Linköping, Sweden
Using a combination of photoelectron spectroscopy and laser optical excitations it is shown that trapping of holes in partially-disordered thin films of polycyclic aromatic hydrocarbons is avoided by changing the

macroscopic polarizability. The local polarizability depends on the concentration of negative and positive charge carriers and can be optimized either by illumination or by a balanced injection. In particular, upon illumination of Li-intercalated perylene and tetracene, the energy of such hole states can be shifted by up to 0.5 eV and even above the substrate Fermi level. The occurrence of spectral weight above the Fermi level in those systems is therefore related to conducting states but not to a metallic behavior.

- E-VI.2** 16:00 **STUDY OF THE MOBILITY ANISOTROPY USING THE ORGANIC TRANSISTOR WITH A DIAGONAL DEVICE CONFIGURATION**
T. Kamata, M. Yoshida, S. Uemura, S. Hoshino, N. Takada, T. Kodzasa, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan
It has been generally recognized that the active layer of an organic transistor should be prepared by a highly ordered thin film to obtain high transistor performance, thus the anisotropy of the field effect mobility is a very important factor to control the device performance. In this study, we have examined to estimate the mobility anisotropy (horizontal and vertical) using our newly developed device structure and studied the effect on the device performance. We have designed an organic field effect transistor with a diagonal configuration of source and drain electrodes, named as the Top and bottom contact (TBC) configuration. It is formed with a combination of the top contact type electrode and the bottom contact type electrode in a device. The source and drain electrodes are arranged diagonally through the organic semiconductor layer. The channel of the device is basically formed at the interface between the semiconductor layer and the gate insulator layer. However, there is a vertical carrier transportation path that is almost same length with the channel length in this device. Therefore, the vertical mobility seems to strongly affect on the total device performance. We have prepared pentacene FET with the TBC configuration and examined horizontal and vertical mobility in the device. The horizontal field effect mobility was estimated to be ca. 10-1 cm²/Vs. On the other hand, the vertical field effect mobility was estimated to be ca. 10-3 cm²/Vs. These results indicate that the total device mobility in the FET device with a vertical path such as a top contact configuration or a vertical configuration receives a great influence from the vertical mobility of the organic semiconductor layer.
- E-VI.3** 16:20 **INTERFACE STUDY OF LANGMUIR-SCHÄFER CONJUGATED POLYMER THIN FILM TRANSISTORS**
L. Torsi(a), B. Pignataro(b), G.M. Farinola(a), M.C. Tanese(a), D. Colangiuli(a), S. Conoci(c), L. Valli(e), S. Casilli(e), F. Babudri(d), F. Naso(d) and P.G. Zambonin(a), (a)Dipartimento di Chimica, Università degli Studi di Bari, Bari, Italy, (b)Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Catania, Italy, (c)Si optic & post Silicon Technologies Corporate R&D, STMicroelectronics, Catania, Italy, (d)CNR ICCOM Sezione di Bari, Dipartimento di Chimica, Università degli Studi di Bari, Bari, Italy, (e)Dipartimento di Ingegneria dell'Innovazione, Università degli Studi di Lecce, Lecce, Italy
The control of the structure and of the physico-chemical properties of the interface between the organic active layer and the gate dielectric is critical for the realization of high performance organic thin film transistors (OTFTs). Langmuir-Schäfer (LS) deposition technique of conjugated polymers is particularly suitable to achieve this control as the molecules can be transferred layer by layer as very thin films by finely tuning the thermodynamic conditions. In this work, thin films (1-30 layers) of poly[1,4-(2,5-dicycloxyphenylene)-2,5-thiophene] have been transferred by LS on a SiO₂ gate dielectric. The physico-chemical properties of these interfaces have been studied as a function of the film thickness by different surface-sensitive tools including Scanning Probe Microscopies, Contact Angle, X-Rays photoelectron spectroscopy, Ellipsometry, Reflectance UV-Vis and IR Spectroscopy. OTFTs have been fabricated in a standard bottom gate configuration with the Langmuir-Schäfer or cast thin films as active layer. The carrier mobility, extracted from the device current-voltage characteristics, has been found to be strongly dependent on the structural properties of the first polymer layers at the gate/polymer interface.
- E-VI.4** 16:40 **TRANSPORT LAYER IN ORGANIC THIN FILM TRANSISTORS**
Franco Dinelli, Mauro Murgia, Jean Francois Moulin, Fabio Biscarini, CNR, Istituto per lo Studio dei Materiali Nanostrutturati, Bologna, Italy, and Dago de Leeuw, Philips Laboratories, Eindhoven, The Netherlands
In Organic Thin Film Transistors, charge transport is expected to occur in the near proximity of the dielectric layer. Predictions based on continuous models sustain that the carrier distribution is mainly limited to the first few nanometers.¹ However no experimental evidence has been yet provided on where transport actually occurs and on the physical size of the accumulation layer. In this work, hole mobility of π -Sexithienyl films is studied as a function of the coverage. For a layered morphology with molecules nearly perpendicular to the substrate, the charge mobility rapidly increases with increasing coverage and saturates at around two monolayers. This demonstrates that the first two molecular layers next to the dielectric interface are mainly active in charge transport. A quantitative analysis of spatial correlations shows that the second layer is very important as it provides efficient percolation pathways for carriers generated both in the first and second layer. The upper layers do not actively contribute either because their domains are smaller than the ones in the second layer or because the carrier density is negligible.² Effects due to variations in substrate temperature and molecular rate are also presented. It is shown that, at low rate, a sharp increase in mobility occurs at around 55°C. This effect is possibly associated with a phase transition. [1] G. Horowitz et al., Adv. Mat. 10, 923 (1998) [2] F. Dinelli et al., Phys. Rev. Lett. (submitted 2003)

17:00 – 19:00

POSTER SESSION

- E/P.01** **TRANSIENT ELECTROLUMINESCENCE IN (ALQ+TPD) ALLOY LIGHT EMITTING DIODES**
V.V.N. Ravi Kishore, Meghan P. Patankar, N. Periasamy and K.L. Narasimhan, Tata Institute of Fundamental Research, Colaba, Mumbai 400 005, India
In this paper, we report on transient electroluminescence (EL) in (TPD+Alq) alloy material and compare it with results on a standard device. The device structure for the standard device is ITO/TPD/Alq/cathode. The alloy device has a similar structure

-ITO/TPD/ Alloy /Alq / cathode. The transient EL is characterized by two times- onset delay time t_d which is the delay for the onset of the EL after application of the voltage pulse and t_r the response time the time for the luminescence to attain steady state. The response time for the standard sample is typically about 15 ms. This increases to about 100-200 ms in the alloy sample. We show that this is a direct consequence of increased disorder in the alloy sample. The alloy sample also has strong memory effects absent in the standard sample. By studying both the EL and the current transient, we show that the memory effects arise due to the presence of deep traps in the alloy sample. This is also supported by studies of the temperature dependence of the transient electroluminescence in these samples.

E/P.02

EXPLORING THE SCALING OF ORGANIC TRANSISTORS

Yuanjia Zhang(a), Jason R. Petta(b), D.C. Ralph(b), George G. Malliaras(a), (a)Department of Materials Science and Engineering, Cornell University, Ithaca, NY, USA, (b)Department of Physics, Cornell University, Ithaca NY, USA

The use of organic thin film transistors OTFTs has raised a large interest in emerging electronic technologies where large area coverage and low cost are required. The current delivered by a TFT is inversely proportional to the channel length L , and that motivated studies of OTFTs with submicron channel lengths. Past work has shown the characteristics of the TFTs to degrade when L is below 100nm, due to either poor charge injection at metal/organic semiconductor interface [1] or "punch-through" effects [2]. To explore whether those effects impose the inherent limitation in the performance of nanoscale organic transistors, we combined state-of-the-art e-beam lithography with organic semiconductor deposition techniques to fabricate organic field-effect transistors with channel lengths down to 30 nm. The current-voltage characteristics of the devices exhibited the behavior expected for p-channel TFTs and scaled gracefully with channel length and width. That result showed that it is possible to realize functional organic transistors with channel lengths at least down to 30 nm [3]. [1] E. L. Granstrom, C. D. Frisbie, J. Phys. Chem. B 103, 8842 (1999). [2] M.D. Austin, S.Y. Chou, Appl. Phys. Lett. 81, 4431 (2002). [3] Y. Zhang, J.T. Petta, D. Ralph and G.G. Malliaras, Adv. Mater. 15, 1632 (2003).

E/P.03

THEORETICAL APPROACH FOR SUPRAMOLECULAR DEVICES BASED ON PHTHALOCYANINE DIMER

Hiroshi Mizuseki, Hidetoshi Baba, Rodion V. Belosludov, Amir A. Farajian and Yoshiyuki Kawazoe, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Molecular devices is a potential candidate for the next step towards nanoelectronic technology (1). A great deal of experimental work has been carried out to demonstrate an element of such an electronic device using either a single- or a finite-number of small organic molecules. Phthalocyanine possesses good electron-donating properties due to its large easily ionized π -electron system and many different metal phthalocyanines are available. In this study, we propose that useful physical properties, such as spintronics, could be created combining two phthalocyanine molecules containing 3d transition metal atoms. We have analyzed the spatial extent of the frontier orbitals (HOMO and LUMO) and estimate the electronic transport through phthalocyanine dimer by Green's function approach. This study was performed through Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government. (1) A. Aviram and M. A. Ratner, Chem. Phys. Lett. Vol. 29 (1974) 277.

E/P.04

CHARACTERISTICS OF THE PENTACENE THIN FILM TRANSISTOR WITH A HIGH-k Gd₂O₃ GATE INSULATOR

S.J. Kang, D.S. Park, H.J. Kim, K.B. Chung, Y.K. Choi, M.H. Jang, M. Noh, C.N. Whang, Institute of Physics and Applied Physics, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea

Pentacene is a promising material in the field of organic semiconductor. Though the mobility of a pentacene thin film transistor is comparable to that of amorphous Si-based devices, its device performance is still insufficient for achieving applicable organic semiconductor device. We used thin high-k Gd₂O₃ layer as a gate insulator that was grown on a heavily doped Si substrate by ion beam assisted deposition (IBAD). The crystalline quality of Gd₂O₃ layer was characterized by in-situ reflection high-energy electron diffraction (RHEED). The preferentially oriented high quality pentacene thin film was prepared on the gate oxide layer by thermal evaporation in ultra-high vacuum and thin gold layer was used as an electrode. The pentacene film was characterized by using the high-resolution synchrotron X-ray Diffraction (XRD) facility at the Pohang Light Source (PLS) and atomic force microscopy. We present the device properties when the SiO₂ gate insulator is replaced with Gd₂O₃ in the pentacene thin film transistor.

E/P.05

ELECTRICAL CHARACTERIZATION OF PENTACENE THIN-FILM TRANSISTORS WITH POLYMERIC GATE DIELECTRIC

J. Puigdollers, C. Voz, I. Martín, M. Vetter, A. Orpella, R. Alcubilla, Dept Enginyeria Electronica, Universitat Politècnica Catalunya, Barcelona 08034, Spain

The performance of organic thin-film transistors (OTFTs) using small molecules has considerably improved during the last years. In particular, the use of pentacene as a semiconductor material has allowed the fabrication of devices with field effect mobilities values comparable to those obtained with hydrogenated amorphous silicon. Although the most usual gate dielectric used to fabricate pentacene TFTs is thermally grown silicon dioxide or silicon nitride deposited by PECVD, the use of polymeric materials which can be spin cast or dip coated are more desirable. In this paper we present results concerning the electrical characterization of pentacene TFTs obtained using polymethyl methacrylate (PMMA) as a gate dielectric [1]. The maximum process temperature was 170°C, which corresponds to the baking of the PMMA. These devices present good electrical characteristics with field-effect mobilities of 0.01 cm²/V·s and low threshold voltages (-15 V). The analysis of the output and transfer characteristics measured at moderate temperatures (300 ? 360 K) evidence that the field-effect mobility presents a thermally activated behaviour. The dependence of the activation energy of the field-effect mobility as a function of the gate-source voltage is also studied. [1] ?Pentacene thin-film transistors with polymeric gate dielectric?, J. Puigdollers, C. Voz, A. Orpella, R. Quidant, I. Martín, M. Vetter and R. Alcubilla. Organic Electronics, In Press

E/P.06

FROM DISULFIDE PHYSISORPTION TO THIOLATE-INTERFACE FORMATION: CHEMISORPTION INDUCED EVOLUTION OF INTERFACE ELECTRONIC PROPERTIES IN THE DIMETHYL-DISULFIDE/AU(111) SYSTEM

Valentina De Renzi, Diego Marchetto, Roberto Biagi and Umberto del Pennino, INFN -National research Center on nanoStructures and bioSystems at Surfaces (S3) and Universita' di Modena e Reggio Emilia, Italy

The lineup of the molecular electronic levels relative to the metal Fermi level is a crucial issue in the determination of charge injection and transport properties of devices based on organic-metal interfaces. In this work, we study by means of combined High-Resolution Electron-Energy Loss (HREELS), X-ray and Ultraviolet Photoemission Spectroscopies (XPS and UPS) the evolution of the interface electronic properties of the methylthiolate/Au(111) model system upon formation of a chemisorbed state. Low-temperature (100 K) deposition of dimethyl-disulfide is found to produce a weakly-bound metastable adsorption state of the intact disulfide molecule, characterized by a S 2p core level binding energy of 163.8 eV and a low-energy S-Au

vibrational stretching mode at 15 meV. The temperature-dependent evolution of this weakly-bound phase into the commonly-observed chemisorbed methylthiolate phase (S2p at 162.2 eV binding energy) is monitored by the transformation of the low-energy S-Au feature into the thiolate-characteristic 30 meV S-Au mode. Parallel UPS measurements provide evidence for a chemisorption-induced modification of the interface electronic properties. In particular, a 0.5 eV shift of the molecular levels toward lower binding energy is observed in concomitance with bond formation, accompanied by a corresponding (0.5 eV) work function change. The implication of these results on the current understanding of the mechanism controlling molecular level alignment at organic/metal interfaces is also discussed.

E/P.07

HYBRID MEMORY DEVICES BASED ON PENTACENE AND METALLIC NANOPARTICLES

A.M. Molloy, M.C. Petty, C. Pearson, School of Engineering Centre for Molecular & Nanoscale Electronics, University of Durham DH1 1LE, U.K.

Flash memory devices are playing an increasingly important role in microelectronics technology. Nanoflash memory devices show a promising possibility in scaling down the device size using nanoparticles in place of a floating gate. Organic transistors based on pentacene have been widely reported in literature around the world and have been shown to work as a plausible additional technology. In previous work, we have described a memory structure based on silicon and Langmuir-Blodgett (LB) films of functionalized gold nanoparticles [1]. Here, we report preliminary current versus voltage and capacitance versus voltage data on a similar device based on the organic semiconductor pentacene. It is hoped that such a structure could form the basis of a low-cost nanoflash organic memory. [1] Paul, S.; Pearson, C.; Molloy A.; Cousins, M. A.; Green M.; Koliopoulou, S.; Dimitrakis, P.; Normand, P.; Tsoukalas, D.; Petty, M. C. Nano Letters 2003, 3, 533

E/P.08

CHARACTERIZATION OF POLYMERIC METAL-INSULATOR-SEMICONDUCTOR DIODES

Silviu Greco, Markus Bronner, Andreas Opitz, Wolfgang Brütting, Experimentalphysik IV, Universität Augsburg, 86135 Augsburg, Germany

Metal-insulator-semiconductor (MIS) diodes are the two-terminal pendants of thin film transistors sharing the same basic layer structure. However, instead of the current-voltage characteristics one has to study the capacitance-frequency and capacitance-voltage behavior, which can give information about mobile charges and trapping processes in these devices. We have investigated MIS structures based on poly(alkyl-thiophene) as semiconductor which were fabricated on glass substrates with polymeric insulator layers and compared their response to devices fabricated on Si/SiO₂ substrates. From capacitance-voltage measurements the acceptor dopant concentration is determined for different preparation conditions. Typically these measurements show hysteresis between forward and reverse bias sweeps. We have investigated this behavior as a function of external parameters like sweep speed and temperature and discuss their possible origin. The analysis of the frequency response using appropriate equivalent circuits allows the extraction of material parameters, like conductivity and charge carrier mobility, which are compared to data obtained on thin film transistor structures.

E/P.09

EFFECT OF MOLECULAR WEIGHT AND ANNEALING OF POLY(3-HEXYLTHIOPHENE)S ON THE PERFORMANCE OF ORGANIC FIELD EFFECT TRANSISTORS

Dieter Neher, Achmad Zen, Frank Jaiser, University of Potsdam, Institute of Physics, Am Neuen Palais 10, 14469 Potsdam, Germany, Jens Pflaum, Stephan Hirschmann, University of Stuttgart, Institute of Physics, Pfaffenwaldring 57, 70569 Stuttgart, Germany, Jürgen P. Rabe, Wei Zhuang, Humboldt University, Department of Physics, Newtonstr. 15, 12489 Berlin, Germany, Ullrich Scherf, Udom Asawapirom, University of Wuppertal, Macromolecular Chemistry, Gauss-Str.20, 42097 Wuppertal, Germany

The optical, structural and electrical properties of thin layers made from poly(3-hexylthiophene) (P3HT) samples of different molecular weight are presented. The solid state absorption spectra of these layers exhibit a significant blue-shift with decreasing molecular weight. This effect is attributed to a larger distortion of the P3HT backbone in the low-molecular weight P3HT chains. Transistors prepared from all P3HT fractions exhibit well-behaved output characteristics. As reported in a previous paper by Kline et al., the mobilities of these layers are a strong function of the molecular weight, with the largest mobility found for the largest molecular weight. Atomic force microscopy (AFM) studies reveal a complex polycrystalline morphology which changes considerably upon annealing. X-ray studies show the occurrence of a layered phase for all P3HT fractions, especially after annealing at 150 °C. However, there is no clear correlation between the differences in the transport properties and the data from structural investigations. In order to reveal the processes limiting the mobility in these layers, the transistor properties were investigated as a function of temperature. The mobility decreases continuously with increasing temperatures, with the same trend pronounced thermochromic effects of the P3HT films occur. From this we conclude that at higher temperatures, the polymer chains adopt a more twisted, disordered conformation, leading to a more hindered interchain charge transport. We, finally, conclude that the conformation of the polymer backbone rather than the crystallinity of the layers is the most crucial parameters controlling the mobility in these P3HT layers.

E/P.10

SYNTHESIS AND PATTERNING OF FUNCTIONALIZED POLYANILINES

M. Massi(a), M. Facchini(a), M. Cavallini(a), F. Biscarini(a), S. Stagni(b) and A. Palazzi(b), (a)CNR – ISMN Sez. Bologna, via Gobetti 101, 40129 Bologna, Italy, (b)Dipartimento di Chimica Fisica ed Inorganica, Univ. di Bologna, V.le Risorgimento 4, 40136 Bologna, Italy

Polyaniline (PANI) is a very interesting material for organic thin film transistors. Protonated PANI exhibits a conductivity of the order of 1 S cm⁻¹, and is thus a promising candidate for electrodes and vias in integrated circuits of plastic electronics [1]. The most severe limitation is its insolubility, and the effort spent up to date in order to obtain more processable forms [2] yields PANI that are much less performant in terms of conductivity. In this work, we present a route towards the creation of three dimensional networks of conductive PANI based on the chemical modification of the chain structure with organic functional groups together with the application of bottom up fabrication techniques. We have synthesized polyanilines starting from ortho-substituted anilines, with COOH or CH₂OH groups, in order to have soluble PANI and to limit the disorder introduced due to the sterical hindrance. We deposit the solution onto silicon substrates patterned with a complementary chemical motif, to obtain PANI structures following the template features. Moreover, we explore the possibility to deposit PANI in microchannels using a microfluidic approach. References: [1] J. Stejskal, Pure Appl. Chem., 2002, 74, 857. [2] J. Prokeš, I. Křivka, J. Stejskal, Polymer International, 1997, 43, 117.

E/P.11

STRUCTURAL EFFECTS ON THE CHARACTERISTICS OF ORGANIC FIELD EFFECT TRANSISTORS BASED ON NEW OLIGOTHIOPHENE DERIVATIVES

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Groupe Systèmes Conjugués Linéaires, CIMMA, UMR CNRS 6200, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France

This paper reports on a comparative investigation of a new series of oligothiophene derivatives as active semiconductor in organic field effect transistors (OFET). Quater- and sexithiophenes end-capped with linear hexyl chains or fused phenyl rings have been synthesized. Bottom contact OFET were processed with these molecules and their performances were compared as a function of the nature of molecules. The oligomers were deposited by vacuum evaporation onto pre-processed substrates. Highly doped Silicon was used as gate covered with 200 nm thermal SiO₂. Ti/Au were used as source and drain electrodes. The thickness of the oligomer films was 80 nm. The analysis of the characteristics of the various devices shows that the nature and the number of the end group exert a considerable influence on the field effect mobility of the resulting devices. Our results have been discussed in terms of steric interactions and also on the basis of the influence of the end group in the oligothiophene on the molecular arrangement on the surface of the substrate.

E/P.12

ELECTRODE MODIFICATION FOR IMPROVING SEMICONDUCTOR/METAL INTERFACES IN ORGANIC THIN FILM TRANSISTORS

M. Massi, F. Dinelli and F. Biscarini, CNR – Istituto per lo Studio dei Materiali Nanostrutturati Via Gobetti 101, 40129 Bologna, Italy

Organic Thin Film Transistors are typically fabricated in a bottom-electrode configuration where the semiconducting thin film is deposited on top of the electrodes. A major problem is represented by the difficulty of interfacing the organic semiconductor and the metal electrode [1]. A high contact resistance, with a behaviour resembling a Schottky diode, lowers significantly the effective mobility of the devices. Herein, we present a study of the modification of gold electrodes with self-assembly monolayers (SAM) [2] using alkyl and ω -carboxy-alkyl thiols of various chain lengths. Pentacene thin films (10 nm thickness) are grown by means of Organic Molecular Beam Deposition. In the channel, the film morphology is independent of the electrode treatment. On the treated electrodes, however, Pentacene grows orderly with stacking molecular domains instead of tridimensional grains as on bare gold. The electrical behaviour is highly sensitive to the termination and chain length. An ohmic interface with the lowest contact resistance is obtained when using alkyl thiols with $n=8$. Molecules with polar heads worsen the performances with respect to the untreated devices. We suggest that SAMs may act at two levels: lowering the effective barrier to carrier injection, and promoting better nucleation and growth of semiconductor domains at the electrode interfaces. References: [1] H. Klauk et al. Sol. St. Elect. 47, 297 (2003). [2] C. D. Dimitrakopolous and P. R. L. Malenfant, Adv. Mater. 14, 99 (2002).

E/P.13

ALL POLYMER TRANSISTOR STRUCTURES: SPECTROMICROSCOPY, KELVIN-AFM AND ELECTRICAL CHARACTERISATION

K. Müller, C. Schwietz, Yevgen Burkov, A. Goryachko, D. Schmeisser, Brandenburgische Technische Universität Cottbus, Angewandte Physik-Sensorik, 03013 Cottbus, P.O.Box 101344, Germany

In order to optimize organic field effect transistors, the characterization of surfaces in terms of their roughness or chemical composition is important. We report on high resolution microscopic mapping of organic thin film transistors by photoemission electron microscopy (PEEM) and Kelvin-AFM. It was shown that PEEM is able to characterize the surface morphology (roughness), the chemical homogeneity or the composition of structures in between the source and drain electrodes. Mapping of surface potentials, especially at the interface electrode/channel is possible. The characterization at applied voltages is also shown. With this two independent methods, Kelvin-AFM- and PEEM mapping of work function, we are able to confirm the results, for example, taken by PEEM. And in addition, a separation from morphology dependent surface potentials or lateral distributions of work function should be possible. The devices, prepared as top and bottom-gate-structures, will be furthermore characterized by electrical measurements, for example, their transfer and output characteristics. The influence of different materials for the gate dielectric layer on $C(V)$, effects like hysteresis or the reproducibility will be analyzed.

E/P.14

INFLUENCE OF SPACE CHARGE AND TRAP-FILLING ON THE ELECTRICAL PROPERTIES OF ORGANIC THIN FILM FIELD-EFFECT TRANSISTORS

M. Koehler, Departamento de Engenharia Elétrica, Universidade Federal do Paraná, 81531-990 Curitiba, PR Brazil and I. Biaggio, Department of Physics, Lehigh University, Bethlehem PA 18015, USA

We review the basic electrical properties of an organic insulator in a planar field-effect-transistor (FET) applying the surface charge formalism. This approach includes the charge carriers injected by the source and drain contacts under the influence of both the gate voltage and the source-drain voltage. We show that the current saturation behavior for higher source-drain voltages is influenced by the space-charge limited conduction near the drain electrode. Space-charge effects can explain some electrical properties of organic FETs (OFETs) that cannot be described by conventional FET model. We predict a strong dependence of the current on the applied voltage even in the so-called "saturation region", and show that it becomes the dominant contribution for short channel devices. This effect decreases, however, when the organic layer is very thin. If charge carrier traps are present, the channel conduction can follow a trap-filling transition with increasing gate voltage. This transition produces a sharp variation of the effective mobility with the gate voltage and induces a strong dependence of the apparent threshold voltage on the temperature. We demonstrate that this trap-filling transition can explain mobility measurements performed in OFETs.

E/P.15

NEW INSIGHT IN π -SEXITHIENYL THIN FILM GROWTH

Franco Dinelli, Maria Antonietta Loi, Enrico Da Como, Jean Francois Moulin, Mauro Murgia, Michele Muccini, Fabio Biscarini, CNR – Istituto per lo Studio dei Materiali Nanostrutturati, Bologna, Italy and Jiang Wei, Peter Kingshott, The Danish Polymer Centre, Risoe National Laboratory, Denmark

A complete description of the early stages of π -Sexithienyl film growth by UHV vapour deposition has been obtained by a series of complementary techniques, namely AFM, Confocal Laser Scanning Microscopy (CLSM) and Time-of-flight Secondary Ion Mass Spectroscopy (ToF-SIMS). In the case of coverage below one monolayer, AFM images show flat domains having a thickness compatible with that of standing molecules. CLSM confirms this hypothesis and further evidences that, on thermal silicon oxide, the domains are surrounded with molecules lying flat on the substrate. Spatially resolved ToF-SIMS, which allows mapping the molecular density over the substrate, also proves the presence of flat molecules on other substrates, such HMDS-treated silicon oxide. Thicker films present a layered morphology and photoluminescence locally similar to that of single crystals. On the basis of these results we propose the following mechanism for thin film formation: the molecules firstly land flat on the substrate and some of them eventually nucleate domains with a molecular orientation perpendicular to the substrate. These domains grow at the expense of the surrounding film, finally leading to a complete layer of standing

molecules. We suggest that this mechanism is at the origin of the problems encountered in the formation of metal/organic interfaces in bottom electrode Thin Film Transistors. [1] E. Da Como et al., This Conference.

E/P.16

PATTERN FORMATION IN PARA-QUATERPHENYL FILM GROWTH ON GOLD SUBSTRATES

G. Hlawacek, C. Teichert, Institute of Physics, University of Leoben, 8700 Leoben, Austria, S. Müllegger, R. Resel, A. Winkler, Institute of Solid State Physics, Graz University of Technology, 8010 Graz, Austria

Polycrystalline films of conjugated organic semiconductors offer attractive potential for optoelectronic applications. Controlling the film morphology is essential for preparing tailored thin films for optimized devices. Here, we use atomic-force microscopy (AFM) to investigate the morphology of 4P films deposited under UHV conditions onto different gold surfaces. Thick (200 nm) and thin (30 nm) films of para-quaterphenyl have been investigated on an Au(111) single crystal substrate. Individual rod like 4P crystallites as well as chains of rod like and tetragonal crystallites were observed on the thick film. For the thin film, fan like arrangements of 4P chains and bent 4P chains with a distinct height distribution were found. To study the effect of different surface orientations on shape and arrangement of the crystallites, a 30 nm 4P film has been deposited on a polycrystalline Au foil. On individual gold grains, preferential orientations of the 4P crystallite chains can be found. The orientation of the chains is linked to the crystallographic orientation of the underlying Au grains. Occasionally, the chains grow across grain boundaries. In addition, growth hillocks with 1.8 nm high terraces of upright standing 4P molecules are observed.

E/P.17

IMPACT OF SUBSTRATE TEMPERATURE AND DEPOSITION RATE ON THE NUCLEATION AND GROWTH OF PENTACENE THIN FILMS ON SILICON OXIDE

Pratontep Sirapat, Martin Brinkmann, Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg, France, Frank Nüesch and Libéro Zuppiroli, LOMM-IMX-EPFL, Swiss National Institute of Technology, 1015, Lausanne, Switzerland

We present an extensive study of the growth in the early stages of pentacene thin films by vacuum deposition on silicon oxide, using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). The morphology of the pentacene film is found to be strongly dependent on various deposition parameters (deposition rate, substrate temperature and film thickness). Both, substrate temperature and deposition rate are key parameters which control the nucleation density in the sub-monolayer regime, hence, transport properties in the first layer of the OFETs. The maximum number of pentacene islands per unit area scales almost linearly with the deposition rate and follows an Arrhenius law with an activation energy of 0.8eV. A mechanism of homogeneous nucleation followed by diffusive growth accounts for this behaviour and allows us to estimate the critical nucleus size of the pentacene islands. The results obtained from the statistical analysis of the island size distribution are fully consistent with a phenomenological capture zone model. The validity of this model depends on the extent of re-evaporation of pentacene ad-molecules during deposition, which is moderated by the deposition rate. In addition, we demonstrate that the rate-dependence of island nucleation density of the pentacene islands has important implications on the density of grain boundaries, which plays an essential role in the transport mechanism.

Thursday, May 27, 2004

Morning

Session VII : Materials and devices II

E-VII.1 08:40 -Invited- DESIGNING IMPROVED THIOPHENE-BASED MATERIALS FOR FIELD-EFFECT TRANSISTORS: WHY? AND HOW?

G. Barbarella, Consiglio Nazionale Ricerche (ISOF), Via Gobetti 101, 40129 Bologna, Italy

Improving the processibility, the self-assembly properties, the morphology characteristics and the charge carrier mobilities of organic semiconductors for field-effect transistors (FETs) are some of the many problems that are currently being faced in order to realize the promise of 'plastic electronics'. Recently, thiophene oligomers have been demonstrated to reach FET charge mobility values of the order of $1 \text{ cm}^2/\text{V}\cdot\text{s}$, attained so far only by pentacene. For thiophene-based compounds - already known for their chemical stability and easy property tunability via organic synthesis - good p-type, n-type and ambipolar charge carrier mobilities, bright electroluminescence, optical gain and lasing properties, morphological stability and even high self-affinity have been demonstrated in the last few years. All these results suggest the possibility to develop an 'all-thiophene' type of plastic electronics. Why not? It would be intriguing from a fundamental point of view: the same basic molecular structure with different functionalities incorporated depending on the task to be accomplished. It would also be of interest with regard to ease of manufacturing, low costs and material compatibility. Central to achieving this goal is the understanding and the control of the forces presiding over the self-organization of thiophene-based oligomers and polymers in the solid state. In this framework, the efforts made at CNR in Bologna to obtain suitable thiophene-based materials for FETs will be described.

E-VII.2 09:20 NEW DITHIENO[3,2-B:2',3'-D]THIOPHENE OLIGOMERS AS PROMISING MATERIALS FOR ORGANIC FIELD-EFFECT TRANSISTOR APPLICATIONS

M.D. Iosip(b,c), S. Destri(a) and M. Pasini(a), (a)Istituto per lo Studio delle Macromolecole, CNR, via E. Bassini 15, Milan, Italy, (b)Dipartimento di Scienza dei Materiali, Università Milano Bicocca, Via Cozzi 53, Milan, Italy and (c)Institute of Macromolecular Chemistry, Aleea Gr.Ghica Voda, 41A, Iasi, Romania

Oligomers containing thiophene have been dominated as the active organic materials for organic field-effect transistors (OFET) applications and exhibit high field-effect charge mobility, which have been associated with both, the π -stacking and macroscopic highly ordered thiophene-based oligomer films. We designed and synthesized new organic semiconductors for OFET applications using the fused thiophene derivative, dithieno[3,2-b:2',3'-d]thiophene, in the core of the molecules. The choosing of dithieno[3,2-b:2',3'-d]thiophene as the central unit of our molecules is motivated by some demonstrated advantageous characteristics, such as: low oxidation potential, high conjugation between the monomer units, and high degree of interchain conformational order which could favor an efficient intra and interchain charge transport. The target co-oligomers based on dithienothiophene and thiophene or fluorene derivatives have been obtained by Suzuki coupling reaction. Electrochemical characterization of these molecules as films evidenced that their oxidation is reversible, a condition almost necessary in order to have an active material for OFET. The values of the ionization potential demonstrate that these materials match very well with the work-function electrodes, gold or platinum. A closely packed face to face or face-on stacking in cast films and high ordered vacuum-evaporated films are expected. Measurements of hole field-effect mobility are in progress.

E-VII.3 09:40 ORGANIC FET DEVICES: STRUCTURE-PROPERTY RELATIONSHIP IN EVAPORATED FILMS OF THREE FLUORENONE DERIVATIVES

W. Porzio, S. Destri, M. Pasini, U.Giovanella, T. Motta, Istituto per lo studio delle Macromolecole of C.N.R., via E.Bassini 15, 20133 Milano, Italy, D. Natali(a,b), M. Sampietro(a,b), L. Franco(a), (a)Dipartimento di Elettronica e Informazione Politecnico di Milano p.za L. da Vinci 32, 20133 Milano, Italy, (b)Istituto Nazionale Fisica Nucleare, sez. di Milano, via Celoria 16, 20133 Milano Italy

The address of the solid state aggregation, orientation, and morphology determines the overall charge mobility, key-factor in the fabrication of FET devices based on molecular crystals. In the optimization of the device, these factors have to be carefully evaluated and balanced, hence a deep knowledge of solid state of all polymorphs in which the considered molecule can crystallise is a prerequisite in the choice of suitable active molecules. We have studied the role of the fluorenone moiety, more stable than fluorene, in a series of three thiophene-derivative based molecules, as active layers in FET devices, prepared by high vacuum evaporation onto patterned substrates. The detailed structural and morphological characterizations of the active films- up to 50 nm thick- evidencing the peculiar packing contribution of fluorenone, can not fully account for the huge difference in mobility, ranging from 10^{-9} up to $10^{-3} \text{ cm}^2 (\text{Vs})^{-1}$. It turns out that relative building-block connectivity has a strong influence on transport properties: the presence of the fluorenone moieties at both ends of the molecule is a necessary but not sufficient condition for achieving good carrier mobility. These results drive the future optimization of organic FET based on such molecules.

10:00

BREAK

Session VIII : Fabrication techniques II

E-VIII.1 10:20 -Invited- THE WAVE-PRINTER: TOWARDS LARGE-AREA, MULTILAYER SOFT LITHOGRAPHY
Michel M.J. Decré, Research Laboratories Eindhoven, Royal Philips Electronics, Prof. Holstlaan 4 (WAG01), 5656 AA Eindhoven, The Netherlands

While soft lithography has previously been reported for patterning electrodes for semiconducting polymer transistors, an accurate and up-scalable multilayer manufacturing technique for large area printable electronics is still lacking. This is due to the combined difficulties of single layer distortion control, multilayer alignment, contact control and defect management. We present our analysis of some mechanical

constraints put on large area soft lithography, particularly those deriving from low filling ratios where printed features of small size are located far from each other, that has lead us to the conclusion that one must abandon conventional printing approaches.

A new printing concept, termed "wave-printing", is described that addresses the discussed mechanical constraints and holds the promise of easy alignment and up-scalability. In "microcontact wave-printing", the microstructured rubber stamp (Sylgard 184) is brought in contact with the substrate using a pneumatic pressure wave, that travels across the substrate to achieve complete printing. Since the pressure applied during printing is lower than 10 kPa, very low filling ratios are achieved without unwanted squeezing contact. We present our prototype wave-printer and discuss results of multilayer microcontact printing on gold. Micron-size features were printed on 150 mm wafers with multilayer alignments better than 2 micron.

We realized polymer MISFETs on 150 mm substrates. The finest features in these devices, i.e. finger width and distance of the source and drain electrodes are formed using microcontact printing. Transistors with channel length ranging from 20 to 1 micron have been made and analyzed. Their performance is equal to devices made using standard photolithography, demonstrating that wave microcontact printing offers a viable route to low-cost manufacturing of organic transistors.

E-VIII.2 11:00 -Invited-

BOTTOM-UP NANOFABRICATION OF MATERIALS FOR ORGANIC ELECTRONICS

Massimiliano Cavallini, CNR-ISMN Sez. Bologna, Via P. Gobetti 101, 40129 Bologna, Italy

I will present novel bottom-up fabrication techniques for organic nanostructures discovered and developed in our group. The first process, termed lithographically controlled wetting (LCW), allows us to pattern soluble materials with nanometer-sized structures in single step and in a few seconds. In LCW, capillary forces drive a solution, initially spread on a substrate, to be pinned to the protrusions of a stamp placed on top at a controlled distance. The menisci formed confine deposition and consequent self-organization phenomena, like ripening or dewetting, under the protrusions. We demonstrate patterning nanostructures like droplets, stripes and fibers, with size feature less than 100 nm, for a variety of materials relevant to organic electronics: conjugated oligomers and polymers, coordination compounds, rotaxanes, liquid crystals and molecular magnets. In the second part, a new property of triggered self-organization of a supra-molecular thin solid film into nanostructure arrays at well-defined positions will be shown to yield less than 50 nm size structures like dots and wires at 100 nm pitch. In the third part we show some results of parallel local oxidation technique of silicon wafers, and other technologically relevant substrates, and the local electro chemical transformation of self-assembly monolayers, as first steps towards template growth and constructive lithography.

E-VIII.3 11:40

POLYMER FIELD EFFECT TRANSISTORS FABRICATED BY DEWETTING

J.Z. Wang, Z.H. Zheng, H. Siringhaus, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.

Manufacturing of high performance electronic devices with micrometer or even submicrometer dimension by solution processing and direct printing requires the ability to accurately control flow and spreading of functional liquid inks on surfaces. This can be achieved with the help of surface energy patterns causing inks to be repelled and dewet from pre-defined regions of the substrate. To exploit this principle for the fabrication of submicrometer device structures, a detailed understanding of the factors causing ink droplets to dewet on patterned surfaces is required. Here we study the influence of solution viscosity, ink volume, and contact angle on the process of dewetting of inkjet printed droplets of a water-based conducting polymer from hydrophobic surface energy barriers of different geometries. For surface energy barriers with a finite thickness of 30-80 nm higher resolution patterning was achieved than for monolayer thick barriers. We demonstrate polymer field-effect transistor (FET) devices with channel length of 500 nm fabricated by surface energy assisted inkjet printing.

E-VIII.4 12:00

SUMBE BASED ORGANIC THIN FILM TRANSISTORS

F. De Angelis(a), T. Toccoli(b), A. Pallaoro(b), N. Coppedè(b), L. Mariucci(a), G. Fortunato(a) and S. Iannotta(b), (a)CNR-IFN, via Cineto Romano 42, 00156 Roma, Italy, (b)CNR-IFN, Sezione di Trento, Via sommarive 18, 38050 Povo di Trento, Italy

We report on structural and electrical properties of pentacene thin film transistors fabricated by the novel SUMBE technique. As previously shown SuMBE, through the control on the molecular precursors in the beam, allows improving the quality of the semi conducting thin films compared to more standard OMBE growth. The surface morphology of pentacene films with different deposition parameters was characterized by AFM measurements. Optimised parameters result in large grain (>2 micrometer) polycrystalline pentacene films. The TFTs were fabricated on heavily doped Si wafer which served also as gate electrode. A thermally grown silicon dioxide layer (80 nm thick) was used as gate dielectric. Two contact configurations have been considered: 1) bottom (BC) with gold source and drain (S/D) contacts deposited on the SiO₂ gate dielectric prior to the active layer deposition; 2) top S/D (TC) with gold S/D contacts evaporated through a shadow mask on top of pentacene active layer. The shadow mask, made of plexiglass foil defined channel lengths of 10 and 20 micrometer and contact width of 200 micrometer. Electrical measurements on TC-TFT show field effect mobilities of 0.5 cm²/Vs and subthreshold slope of 1.2 V/dec. Output characteristics exhibit good linearity at low drain voltages, indicating low contact resistance. Lower field effect mobilities have been observed in BC-TFT. AFM shows the presence of large crystalline grains in the centre of the channel, whereas smaller grains are observed at the Au S/D contacts.

12:20

LUNCH

Thursday, May 27, 2004

Afternoon

Session IX : Nanoscale devices

- E-IX.1** 14:00 -Invited- NANOSCALE ORGANIC TRANSISTORS
Yuanjia Zhang, **George G. Malliaras**, Department of Materials Science and Engineering, Cornell University; Jason Petta, Daniel C. Ralph, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, USA
Organic field-effect transistors with channel lengths down to several nanometers were made. The fabrication involved coupling state-of-the-art e-beam lithography with organic semi-conductor deposition techniques. The source and drain electrodes were fabricated using a three-step e-beam lithography process, and various processes were developed to pattern the organic semiconductor and achieve electrical isolation of individual transistors. Pentacene films were used as a benchmark, and their growth in the confined geometry of the channel was investigated. These organic transistors allow studies of charge injection and transport in organic semiconductors at the nanometer length scale.
- E-IX.2** 14:40 -Invited- ENGINEERING MOLECULES-SURFACES INTERACTIONS FOR MOLECULAR ELECTRONICS
J.P. Bourgoin, Laboratoire d'Electronique Moléculaire, CEA Saclay France, Together with F. Armand, S. Auvray, J. Borghetti, P. Chenevier, V. Derycke, S. Gazeau, A. Filoramo, L. Goux-Capes, M. Goffman, R. Lefevre, M. Lambert, S. Palacin, L. Patrone
During the last five years, Molecular Electronics has seen very significant advances and raised prospects of mid-term applications[1,2]. In this review, after a short introduction, the focus will be on self-assembly. Self-assembly is generally considered as the way of choice for the fabrication of future molecular electronics circuits. Self-assembling molecules into devices has been used during the last few years with the aim to engineer i) metal-molecule interfaces to improve their transport properties and ii) molecule-surface interactions to localize the self-assembly of the molecules-including carbon nanotubes.
In this lecture, recent results from our group and others will be used to illustrate these two axes. After a presentation of different means that can be used to measure the transport properties of a single molecule, the relationship between the molecular structure and the transport properties will be discussed. It will be shown that the metal - molecule coupling plays a key role[3]. This will be illustrated based on combined Photoelectron Spectroscopy-STM experiments where similar conjugated molecules with different endgroups have been systematically compared⁴. The realisation of devices based on single or a few molecules will then be presented
In a second part[4], it will be shown how carbon nanotubes (NTs) known to give rise to high performance devices[5,6], can be self-assembled at predefined location of a substrate using for example a localized functionalization of the substrate by a self-assembled monolayer[7]. The FET devices prepared in that way are functional with state-of-the-art performances[8]. The role played by the environment (including that of the self-assembled monolayer directing the deposition of the NTs and that of molecules adsorbed on the NTs) on the devices characteristics will be discussed. Finally, the improvements of the self-assembling technique using the recognition properties of biomolecules will be presented.
The conclusion will open the discussion about the future developments of molecular electronics at the circuit and system levels.
[1]A. Nitzan and M. Ratner, Science 300 (2003)1384
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[3]J.P. Bourgoin in "Interacting Electrons in Nanostructures", H. Schoeller, R. Haug eds.Lectures Notes in Physics, Springer, Berlin 2001
[4]L. Patrone, F. Armand, S. Palacin, J. Charlier, J. Lagoute, T. Zambelli, S. Gauthier, H. Tang and J.P. Bourgoin, Physical Review Letters (2003), 91(9) 96802
[5]S. J. Wind, J. Appenzeller, R. Martel, V. Derycke, and Ph. Avouris, Appl. Phys. Lett. 80 (2002) 3818
[6]A. Javey et al, Nature 424(2003) 654
[7]K.H. Choi, J.P. Bourgoin, S. Auvray, D. Esteve, G. S. Duesberg, S. Roth and M. Burghard, Surf. Sci. 462,195 (2000).
[8]E. Valentin, S. Auvray, J. Goethals, J. Lewenstein, L. Capes, A. Filoramo, A. Ribayrol, R. Tsui, J.P. Bourgoin, J.N. Patillon, Microelectronic engineering 61-62, 491 (2002).
- E-IX.3** 15:20 MORPHOLOGY STRUCTURE AND CONDUCTION PROPERTIES OF ISOLATED ISLANDS OF PENTACENE . APPLICATION IN ORGANIC THIN FILM TRANSISTORS
K. Lmimouni, T. Heim, C. Dufour, D. Vuillaume, IEMN- UMR CNRS 8520, BP69, Avenue Poincaré, 59652 Villeneuve d'Ascq, France
In the last few years, there has been a growing interest on pentacene based Organic Thin Film Transistors because of their unique physical properties and potential use for a wide range of applications, ranging from Active Matrix addressing in flat panel displays to chemical sensors. In this work we focus on OTFT made with a very thin active layer of pentacene, typically a few monolayers. We describe the realization of these devices with a special attention to the pentacene vacuum deposition made at a rate as low as $3 \cdot 10^{-2}$ Å/s. The growth of isolated islands of pentacene is also described. We investigate the morphology, the structure and the conduction properties of these isolated pentacene domains using AFM and EFM measurements. Nano-OTFT, with channel length as small as 50nm, are made by electron beam lithography to measure field effects on these structures. We also use FIB to connect a single, isolated, pentacene domain between two electrodes and to measure its transport properties (e.g as function of the number of pentacene monolayers in the domain).
- E-IX.4** 15:40 OPTIMIZED SUB-MICRON ORGANIC THIN-FILM TRANSISTORS: THE INFLUENCE OF CONTACTS AND OXIDE THICKNESS

M. Leufgen, U. Bass, T. Borzenko, G. Schmidt, J. Geurts, L.W. Molenkamp, Universität Würzburg, Physikalisches Institut (EPIII), Am Hubland, 97074 Würzburg, Germany, T. Muck, V. Wagner, International University Bremen, Campus Ring 8, 28759 Bremen, Germany

For future low cost electronics, high-performance organic thin-film transistors (OTFT) are highly desirable. One possible route towards device optimization is the downscaling of the channel length L into the sub-micron regime which allows higher operation frequency, better integration and large currents. Reducing the channel length decreases the effect of grain boundaries on transport in polycrystalline organic films, but in return the metal-organic contact resistance becomes more important. We present a systematic study of transistors based on vacuum-deposited dihexylquaterthiophene (DH4T), a n-type Si gate, SiO₂ insulator layer and metal drain/source contacts with L from 50 μm down to 50 nm. To analyze the contact resistance, we varied the contact metal (Ti/Au, Ti/Pt and Pd). We observe a strong influence of the thickness of the Ti adhesion layer on the contact resistance for Ti/Au contacts. The best contacts are obtained using Pd, but we find that chemical processing of Pd containing devices is cumbersome. Sub-micron devices require a thinner insulator layer to maintain proper scaling of the ratio between longitudinal and transversal electrical field in the channel. Thus, we studied devices fabricated on wafers with SiO₂ thicknesses ranging from 200 nm down to 30 nm. For 30 nm oxide layers our devices show standard FET characteristics (i.e. no short-channel effects), a high carrier mobility of about 2×10^{-2} cm²/Vs and an on/off-ratio of 10⁵ for channel lengths down to 200 nm. Below 200 nm the field-effect is still observed, but the transistor performance decreases and short-channel effects become observable. The work was supported by the European Union, project Mona-Lisa (G5RD-CT-2000-00349).

16:00

BREAK

Session X : Materials and devices III

- E-X.1** 16:20 -Invited- PENTACENE THIN FILM TRANSISTORS - SUBSTRATES, STABILITY, AND OPERATING VOLTAGE
Marcus Halik, Hagen Klauk, Ute Zschieschang, Günter Schmid, Christine Dehm, Infineon Technologies, New Memory Platforms, Materials and Technology, Paul-Gossen-Str. 100, 91052 Erlangen, Germany
Targeting cost-sensitive applications, we have developed a robust process for organic TFTs and circuits on various inexpensive substrates including glass, plastics and paper. The TFTs built in this technology have large on / off current ratios of 10⁵ - 10⁶ and a carrier mobility of 0.01-0.3 cm² / V s. Corresponding ring oscillators have a signal propagation delay of 22 μs per stage on plastics and 10 msec on paper, respectively. To evaluate the operational and environmental stability of our organics TFTs, we have investigated 32 substrates after treatment under different conditions, e.g. elevated temperatures, increased humidity, repeated thermal cycling, and operational stress. It could be demonstrated that TFTs and circuits operate after cycling in a temperature range between 20 and 80 °C without significant degradation. Ring oscillators can be operated continuously for several hours without change undergoing more than 10⁷ switching cycles. Also, the performance of the TFTs remains virtually unchanged when stored for more than 12 months under ambient conditions. To reduce the operating voltage and make organic electronics suitable for low power applications we have developed pentacene TFTs with an ultra thin molecular self assembled monolayer gate dielectric. With a gate dielectric thickness of 2.5 nm, TFTs can be operated with supply voltages as low as 2V while exhibiting excellent subthreshold swing (100 to 200 mV/decade), large carrier mobility (1 cm²/Vs), and low gate leakage (<100 pA). These self assembled monolayer dielectrics are sufficiently robust to permit the use of standard photolithographic and wet chemical etching techniques.
- E-X.2** 17:00 PENTACENE FIELD EFFECT TRANSISTORS WITH POLYMER/ HIGH-K OXIDE GATE DIELECTRIC
Jacques Tardy and Anne-Laure Deman, Ecole Centrale de Lyon and CNRS Laboratoire d'Electronique, Optoélectronique et Microsystèmes (LEOM), 36 avenue Guy de Collogue, 69134 Ecully cedex, France
We report on the fabrication of pentacene field effect transistors with a gate dielectric made of a bilayer of Ta₂O₅ and PMMA (poly(methyl methacrylate)). Ta₂O₅ is used for its high dielectric constant (~30) which enables operating voltages much lower than with conventional oxides as SiO₂. We actually report saturation regime operating voltage as low as 1.5V. As high-k oxides are usually somewhat leaky rather poor on/off ratio are observed with Ta₂O₅. In order to overcome this drawback, a films of PMMA has been spun on the evaporated Ta₂O₅ film. With the bilayer gate dielectric, a drastic reduction of the gate leakage has then be observed (2 orders of magnitude) and on/off ratio of 3x10⁵ were obtained. Furthermore, the field effect mobility is strongly improved with PMMA attributed to a surface smoothing effect of PMMA. The influence of PMMA thickness was investigated (between 15 and 250 nm) and an optimised thickness of 35 nm was found for which the mobility, the on/off ratio and the voltage to get the saturation regime were respectively 0.3 cm² V⁻¹ s⁻¹, 2.7x10⁵ and 10 V.
- E-X.3** 17:20 INFLUENCE OF THE GATE DIELECTRIC ON THE PERFORMANCE OF PENTACENE THIN FILM TRANSISTORS
D. Knipp(a,b), R.A. Street(b), A.R. Völkel(b), P. Kumar(a), (a)International University Bremen, Department of Science and Engineering, 28219 Bremen, Germany, (b)Palo Alto Research Center, Electronic Materials Laboratory, Palo Alto CA 94304, USA
The electronic transport of pentacene thin film transistors (TFTs) on organic and inorganic large area compatible dielectrics were investigated. The influence of the gate dielectric on the morphology of the pentacene films and the device performance of the TFTs were studied. The poly crystalline films were prepared by thermal evaporation on top of plasma enhanced chemical vapor deposited (PECVD) silicon nitride and spin-casted benzocyclobutene (BCB) and poly-vinyl phenol (PVP) dielectrics. Careful control of the preparation conditions of the dielectric and the pentacene films lead to TFTs with mobilities of ~0.4 cm²/Vs on the different dielectrics. The mobility on organic dielectrics is comparable with the mobilities observed for inorganic dielectrics like thermal oxide and silicon nitride. The subthreshold slope of TFTs on

PVP is improved by a factor of 2-3 comparing the slope with the best results observed for inorganic dielectrics (considering the thickness and the dielectric constant of the dielectric). Subthreshold slopes of 0.4V/decade were measured for 200nm thick PVP films. Furthermore, the TFTs on PVP exhibit threshold voltages very close to 0V. The results reveal that the pentacene molecules tend to align better on smooth PVP surfaces than on the inorganic surfaces, which might lead to better structural order within the first monolayers. The influence of the organic dielectric on the device performance and the electronic transport will be discussed.

Friday, May 28, 2004

Morning

Session XI : Characterization and multifunctional applications III

- E-XI.1** 08:40 **PHOTOINDUCED CHARGE TRANSPORT IN POLYMER FIELD EFFECT TRANSISTORS**
S. Dutta and K.S. Narayan, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India
Recent observations on optical effects of poly(3-alkylthiophene)-field effect transistors (FETs) have explored intriguing phenomena both from the perspective of understanding the nature of electrical transport as well as from a technological standpoint [1,2]. A remarkable increase in drain-source conductance of these polymer-FETs upon illumination of light is observed even at low intensity [1]. The relaxation of the photoinduced conductance upon termination of light is a gradual non-exponential process and portrays a persistent behavior with discernible gate voltage dependence in such a system. The slow relaxation process cannot be physically explained by the processes leading to a parallel recombination, but is attributed to the model based on serial relaxation dynamics, due to hierarchy of systems with increasing spatial separation of the photo generated negative and positive charges [2]. The huge photo-multiplication during light exposure, followed by a slow relaxation upon termination of light can be exploited to store the charges in the system. We demonstrate the write, store, repeated-read and erase operations using the combination of the gate voltage and incident light source over a temperature range of 10 K - 200 K. The entire process can be understood on the basis of a built-in field developed in the channel region due to the redistribution of the photoinduced charge carriers. These studies of optically induced effects indicate possibility to design efficient FET characteristics by introducing an additional top gate arrangement.
References: [1] K. S. Narayan and N. Kumar, Appl. Phys. Lett. 79, 1891 (2001). [2] S. Dutta and K. S. Narayan, Phys. Rev. B 68, 125208 (2003).
- E-XI.2** 09:00 **CHARGE TRANSFER AS A METHOD TO OPTIMIZE ORGANIC TFT PERFORMANCE**
K.P. Pernstich, D. Oberhoff, D.J. Gundlach, B. Batlogg, Laboratory for Solid State Physics, ETH Zurich, Switzerland
We report on the device characteristics of top contact pentacene (Pc) thin film transistors (TFTs) fabricated on heavily doped and oxidized silicon wafers with modified Pc/SiO₂ and Pc/source (S) and drain (D) contact interfaces. Self-assembled monolayers (SAMs) of various organosilanes with functional groups having different charge withdrawing and accepting properties are used to modify the SiO₂ surface prior to the Pc deposition. The threshold voltage (V_t) and the subthreshold behavior are strongly influenced by the partial transfer of charge between the channel and the SAM. The shift in V_t is independent of the film morphology. The hole mobility shows some dependence on the functionality of the SAM but varies by less than an order of magnitude. The injection properties of the gold S/D contacts were modified by depositing a thin layer of the charge transfer (CT) complex tetracyanoquinodimethane (TCNQ) prior to depositing the gold. As reported for quaterthiophene TFTs [1], the use of TCNQ is expected to increase the hole density at the contacts. This is consistent with our initial measurements which show a reduced contact resistance at low drain-to-source voltages using TCNQ. The use of molecules with CT properties to tailor the interface properties provides a powerful method for investigating basic charge injection and transport in organic semiconductors and may prove technologically relevant. [1] F. Garnier, Chemical Physics 227 (1998) 253-262
- E-XI.3** 09:20 **MOLECULAR ORIENTATION IN ULTRATHIN FILMS OF a-SEXITHIENYL ON SILICON DIOXIDE**
E. Da Como, M.A. Loi, F. Dinelli, M. Murgia, J.F. Moulin, F. Biscarini, R. Zamboni, M. Muccini, C.N.R. Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Bologna division, Via Gobetti 101, 40129 Bologna, Italy
Among organic semiconductors a-Sexithienyl (T6) has emerged as one of the most interesting materials because of its appealing charge transport properties and its successful application in thin films Field Effect Transistors (FET)[1]. The physical properties, and in particular the charge transport properties, of T6 in the solid state can be strongly anisotropic depending on the molecular organization. Therefore, detailed morphological and structural studies of thin films are relevant for understanding and optimising the FET performances. Knowledge about the molecular organization in thin films can be obtained through cross-correlation of photophysical and morphological investigations. A setup based on a confocal laser scanning microscope that is able to perform simultaneously photoluminescence (PL) microscopy and time resolved PL spectroscopy with 200 nm in plane spatial resolution has been implemented[2]. Here we report a combined AFM and confocal microscopy and spectroscopy investigation of the molecular organization in ultrathin films of T6 grown by ultra high vacuum sublimation on silicon dioxide. The correlation between topography, PL microscopy and spatially resolved PL allows to determine the molecular orientation in ultrathin films of T6. We demonstrate that in the early stages of growth of T6 on silicon dioxide, a sub-nanometer thick layer is formed, where T6 molecules lie flat on the surface. [1] A. Dodabalapur, L. Torsi, H.E. Katz, Science 268, 270, 1995 [2] M.A. Loi, E. Da Como, R. Zamboni, M. Muccini, Synth. Met. 139, 687, 2003
- E-XI.4** 09:40 **TRANSIENT PHOTOCURRENTS IN OLIGOTHIOPHENE-BASED ULTRATHIN FILM TRANSISTORS**
E. Pavlica and R. Hudej and G. Bratina, Nova Gorica Polytechnic, Vipavska 13, 5001 Nova Gorica, Slovenia and M. Leufgen and U. Bass and J. Geurts and L.W. Molenkamp, Universitaet Wuerzburg, Physikalisches Institut (EPIII), Am Hubland, 97074 Wuerzburg, Germany and T. Muck and V. Wagner, International University Bremen, Campus Ring 8, 28759 Bremen, Germany
The transient photocurrent(TPC) measurements were performed of the organic field-effect transistors consisting of 10nm of dihexylquaterthiophene(DH4T),vacuum evaporated on OTS threated SiO₂ surface of n-Si substrate.The measurements were performed in the temperature range of 20K-300K using 5ns laser pulse excitation of 460nm.The voltage was connected between the source and drain contacts and the illumination

was performed face-on. We have examined the samples with the channel lengths of 1 μ m, 2 μ m and 4 μ m. We observed TPC responses with maximum length of approx. 30 ns. The TPC response exhibits two peaks whose relative intensity is strongly field and temperature dependent. At high electric field and high temperatures the initial fast rise in current is dominated by a broader feature located approximately 10 ns after the onset of the current. The lineshape of the I(t) curve at low fields and/or low temperatures is consistent with the behavior of photoinduced carriers in the presence of energetic and positional disorder. For the bias range explored we observe no dependence of the transit time on the electric field. Moreover the use of the classical expression for charge mobility, yields mobilities that are an order of magnitude larger than the mobilities obtained from the DC transport measurements. This argues for the limited region of nonnegligible electric field within the organic layer. The drift current of the photoinduced carriers is only present in a relatively narrow region near the collecting metallic contact. The extent of this region is independent on the channel length, and must be determined by the microscopic interface environment at the metallic contact. Work supported by the 5th FW program, project MONA-LISA, Project Contract Number: G5RD-CT-2000-00349

10:00

BREAK

Session XII : Characterization and multifunctional applications IV

- E-XII.1** 10:20 -Invited- **MULTIFUNCTIONAL ORGANIC DEVICES: AMBIPOLAR LIGHT-EMITTING ORGANIC TRANSISTORS**
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 Organic thin-film devices such as Light-Emitting Diodes (OLEDs), Field-Effect Transistors (OFETs) and Solar Cells (OSCs) have successfully been developed. Among the advantages of organic materials, which include low-cost processing and mechanical flexibility, multifunctionality is particularly appealing as it may lead to novel applications. Combining light-emission with electrical switching capability in a single device may be relevant for existing applications as Active Matrix Displays and to develop new device concepts. Therefore light-emitting field-effect transistors (LEFET) are attracting increasing interest due to the advantages offered by the transistor device structure with respect to the OLED structure. In an ambipolar LEFET the gate voltage would improve charge injection, the balance of the electron and hole currents, and would tune the location of the emitting zone within the transistor channel. The recently reported light-emitting OFETs based on tetracene thin films are, however, unipolar. The optoelectronic characteristics of unipolar tetracene-based light-emitting transistors will be reviewed and the charge trapping processes that prevent ambipolarity will be analyzed. We will report on the first LEFET, which combines ambipolar current characteristics with light emission modulated by both the drain and gate voltage. We will discuss the optoelectronic characteristics of the materials and the thin-film processing employed for this model structure ambipolar LEFET in order to gain general knowledge on the materials and device architecture requirements.
- E-XII.2** 11:00 **ELECTRONIC COUPLING IN HIGHLY ORDERED PHTHALOCYANINE THIN FILMS: INFLUENCE OF CHEMICAL SUBSTITUTION AND PREPARATION CONDITIONS**
 Christine Mattheus(a), Wilfried Michaelis(a,b), Christian Kelting(a) and **Derck Schlettwein(a,c)**, (a) Carl-von-Ossietzky-University Oldenburg, Institute of Pure and Applied Chemistry, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany, (b)present address: University of Bremen, Institute of Organic and Macromolecular Chemistry, Leobener Str. NW 2, 28334 Bremen, Germany, (c)present address: Justus-Liebig-University Giessen, Institute of Applied Physics, Heinrich-Buff-Ring 16, 35392 Gießen, 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 SiO₂, 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, e.g., ultrathin conductive films could be prepared and implications are discussed for their application in organic field effect transistors and chemical sensors.
- E-XII.3** 11:20 **CHARGE NEUTRALITY LEVEL AND INDUCED DENSITY OF INTERFACE STATES: ENERGY LEVEL ALIGNMENT IN METAL/ORGANIC INTERFACES**
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 Understanding the energy level alignment at metal/organic semiconductor interfaces is essential for the design of new organic-based devices. Although different mechanisms have been proposed [1], this issue is not yet well understood. In this communication, we explore several non-reactive metal/organic interfaces (such as PTCDA/Au, PTCBI/Au and CBP/Au) within the Induced Density of Interface (or virtual) States (IDIS) model [2]. Using a DFT method adapted to highly correlated electron systems [3], we calculate the Charge Neutrality Levels (CNL) of the organic molecules and the interface Fermi levels for their contact with

a Au(111) surface. We show that, although the chemical interaction between the metal and the organic semiconductor is weak, it creates an IDIS in the organic energy gap that is large enough to pin the Fermi level near the CNL. Our results show excellent agreement with experimental EF positions. We conclude that the concepts of Charge Neutrality Level and Induced Density of Interface States can explain the energy level alignment in metal/organic interfaces. The mechanism associated with the formation of Schottky barriers formation at these interfaces is the charge transfer between the metal and the organic semiconductor: this creates an electrostatic interface dipole which tends to align the metal Fermi level and the organic CNL.

E-XII.4 11:40

OXYGEN-INDUCED EFFECTS ON THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF POLYHEXYLTHIOPHENES IN SOLUTION AND THIN FILMS

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Poly(3-hexylthiophene) (P3HT) is used as active material for organic field effect transistors (OFETs). Oxygen is detrimental to the performance of OFETs due to reversible charge carrier production and irreversible (photo-)oxidation. In order to elucidate the mechanisms of these processes, we studied the photophysics and photochemistry of P3HT in solution and thin films by UV/Vis absorption and fluorescence spectroscopy. The results are compared to those obtained for oligothiophenes. In solution, reversible and irreversible fluorescence quenching (FQ) by oxygen is observed. Reversible FQ is due to physical quenching of excited singlet states. Irreversible FQ is due to loss of absorption during photodecomposition of P3HT. The solvent dependence of the reaction rate supposes that singlet oxygen is involved in this process. The sensitivity towards photooxidation increases on going from oligothiophenes via regiorandom P3HT to regioregular P3HT. In thin films, reversible FQ consists of two components, which rise with different rates upon oxygen admission to the sample. While the fast component is due to collisional quenching of excited states, the slow component is caused by the formation of mobile charge carriers, as shown by the concomitant increase of photoconductivity. Irreversible FQ is highly efficient, due to diffusion of excited singlet states to photooxidation products, which act as quenchers. Water enhances the photooxidation rate, but is inactive in the absence of oxygen.