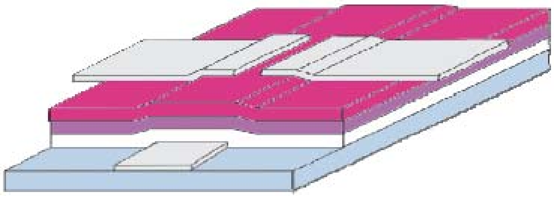
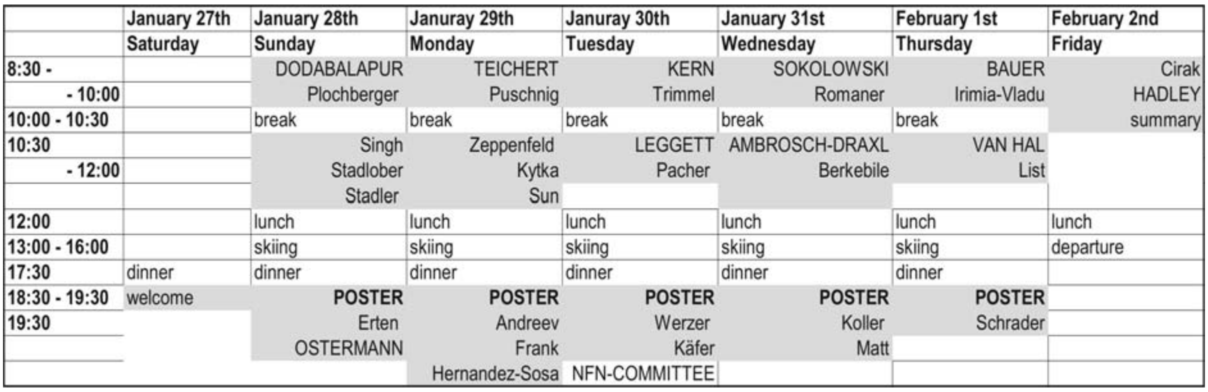


scientific programme

winterschool on organic electronics
27 January – 2 February 2007, Planneralm, Austria

National Research Network (NFN)

„Interface Controlled and Functionalised Organic Films”



	January 27th	January 28th	Januray 29th	Januray 30th	January 31st	February 1st	February 2nd
	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
8:30 -		DODABALAPUR	TEICHERT	KERN	SOKOLOWSKI	BAUER	Cirak
- 10:00		Plochberger	Puschnig	Trimmel	Romaner	Irimia-Vladu	HADLEY
10:00 - 10:30		break	break	break	break	break	summary
10:30		Singh	Zeppenfeld	LEGGETT	AMBROSCH-DRAXL	VAN HAL	
- 12:00		Stadlober	Kytka	Pacher	Berkebile	List	
		Stadler	Sun				
12:00		lunch	lunch	lunch	lunch	lunch	lunch
13:00 - 16:00		skiing	skiing	skiing	skiing	skiing	departure
17:30	dinner	dinner	dinner	dinner	dinner	dinner	
18:30 - 19:30	welcome	POSTER	POSTER	POSTER	POSTER	POSTER	
19:30		Erten	Andreev	Werzer	Koller	Schrader	
		OSTERMANN	Frank	Käfer	Matt		
			Hernandez-Sosa	NFN-COMMITTEE			

Sunday, 28th January 2007

chairman: Helmut Sitter, speaker of the NFN, Johannes Kepler University Linz
8:30 – 9:30
Ananth Dodabalapur, University of Texas, Austin
Organic thin film transistors: history and current developments
9:30 – 10:00
Birgit Plochberger, Johannes Kepler University Linz
Barium doped C_{60} for field effect transistors

10:00 – 10:30 coffee break

10:30 - 11:00
Birendra Singh, Johannes Kepler University Linz
N-channel field effect transistors and ring oscillators based on epitaxially grown C_{60} fullerene films
11:00 – 11:30
Barbara Stadlober, Institute of Nanostructured Materials and Photonics, Weiz
Scaling laws in organic thin film transistors
11:30 – 12:00
Philipp Stadler, Johannes Kepler University Linz
Hysteresis in organic field effect transistors

18:30 – 19:30 POSTER

chairman: Serdar N. Sariciftci, Johannes Kepler University Linz
19:30 – 20:00
Sule Erten, Ege University, Izmir
Air-stable and soluble derivatives of perylene and naphthalene diimide for n-channel organic semiconductors
20:00 – 21:00
Timm Ostermann, Johannes Kepler University Linz
Device and electronic circuit modelling
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Monday, 29th Janury, 2007

chairman: Claudia Ambrosch-Draxl, University of Leoben
8:30 - 9:30
Christian Teichert, University of Leoben
Application of atomic force microscopy techniques for surface analysis
9:30 – 10:00
Peter Puschnig, University of Leoben
Cohesive and surface energies of organic molecular crystals

10:00 – 10:30 coffee break

10:30 – 11:00
Peter Zeppenfeld, Johannes Kepler University Linz
Characterisation of organic thin films by optical means
11:00 – 11:30
Milan Kytka, Slovak University of Technology Bratislava
Ellipsometry on the amorphous rubrene thin films
11:30 – 12:00
Lidong Sun, Johannes Kepler University Linz
Growth of sexithiophene (6T) films studied by RDS

18:30 – 19:30 POSTER

chairman: Adi Winkler, Graz University of Technology
19:30 – 20:00
Andrej Andreev, University of Leoben
Para-sexiphenyl thin films grown on KCl substrates
20:00 – 20:30
Paul Frank, Graz University of Technology
Tailoring of ultrathin hexaphenyl films on mica(001) through surface modifications
20:30 – 21:00
Gerardo Hernandez Sosa, Johannes Kepler University Linz
New crystalline phase of sexiphenyl needles on mica??

Tuesday, 30th January 2007

chairman: Dieter Meissner, Johannes Kepler University Linz
8:30 – 9:30
Wolfgang Kern, Graz University of Technology
Surface chemistry and lithographic patterning for organic electronics
9:30 – 10:00
Gregor Trimmel, Graz University of Technology
Photoreactions in thin organic films based on the photoisomerisation of benzyl thiocyanates and aromatic esters

10:00 – 10:30 coffee break

10:30 – 11:30
Graham Leggett, University of Sheffield
Patterning of self-assembled monolayers
11:30-12:00
Peter Pacher, Graz University of Technology
Thin reactive layers for ammonia detection with organic thin film transistors

18:30 – 19:30 POSTER

chairman: Christian Teichert, University of Leoben
19:30 – 20:00
Oliver Werzer, Graz University of Technology
Pentacene monolayers and submonolayers on silicon oxide: a combined x-ray reflectivity and AFM study
20:00 – 20:30
Daniel Käfer, Ruhr-University Bochum
Improving performance of pentacene OFETs using aromatic thiols

20:30
Meeting of the NFN steering committee
only for project leaders of the National Research Network

Wednesday, 31st January 2007

chairman: Egbert Zojer, Graz University of Technology
8:30 – 9:30
Moritz Sokolowski, University Bonn
Surface science with organic molecules
9:30 – 10:00
Lorenz Romaner, Graz University of Technology
Adsorption of F4TCNQ on Cu(111): a combined experimental and theoretical study

10:00 – 10:30 coffee break

10:30 – 11:30
Claudia Ambrosch-Draxl, University of Leoben
How to calculate the electronic structure of organic semiconductors
11:30 – 12:00
Stephen Berkebile, Karl Franzens University Graz
Inter- and intramolecular dispersion in a highly ordered organic molecular crystal

18:30 – 19:30 POSTER

chairman: Wolfgang Kern, Graz University of Technology
19:30 – 20:00
Georg Koller, Karl Franzens University Graz
Heteroepitaxy of organic-organic nanostructures: fundamental aspects of growth and electronic structure
20:00 – 20:30
Gebhart Matt, University of Applied Sciences, Wels
Treshold phenomena in C_{60}-fullerene based field effect transistor

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Thursday, 1st Februry 2007

chairman: Michael Ramsey, Karl Franzens University Graz
8:30 – 9:30
Siegfried Bauer, Johannes Kepler University Linz
Electret, ferroelectret and ferroelectric organic field effect transistors: devices and applications
9:30 – 10:00
Mihai Irimia-Vladu, Johannes Kepler University Linz
Low frequency dielectric spectroscopy of polyvinylalcohle gate dielectrics

10:00 – 10:30 coffee break

10:30 – 11:30
Paul van Hal, Philips Research Laboratories Eindhoven
Large area molecular electronics
11:30 – 12:00
Emil List, Graz University of Technology
All solution processed organic field effect transistors

18:30 – 19:30 POSTER

chairman: Peter Zeppenfeld, Johannes Kepler University Linz
19:30 – 20:00
Sigurd Schrader, University of Applied Sciences Wildau
Thermally stimulated relaxation in organic molecular solids

Friday, 2nd Februray 2007

<u>chairman:</u> Siegfried Bauer, Johannes Kepler University Linz
8:30 – 9:00
Julius Cirak, Slovak University of Technology Bratislava
Perspectives of Langumir Blodgett layers for molecular electronics
9:00 – 10:00
Peter Hadley, Graz University of Technology
New approaches for inorganic and organic electronic devices

POSTER:
Sunday, 28th January – Thursday, 1st Februray 2007
18:30 – 19:30

Anja Haase, Institute for Nanostructured Materials and Photonics, Weiz
Low voltage organic thin film transistors

Valeriy Yashchuk, National University of Kiev
The functional properties of the biopolymers connected with the electronic excitations energy transfer

Valeriy Yashchuk, National University of Kiev
New molecular functional structures based on the DNA fragments with neutral and charged excitons energy transfer for organic nanoelectronics

Martin Egginger, Johannes Kepler University Linz
Ionic impurities in PVA gate dielectrics cause hysteresis in organic field effect transistors

Thomas Grießer, Graz University of Technology
Photolithographic patterning of polymer surfaces based on the photo-Fries rearrangement: selective post-exposure reactions

Martin Kaltenbrunner, Christoph Keplinger, Johannes Kepler University Linz
Multifunctional ferroelectric polymer – piezoelectric ceramic nano-composites for flexible skin-like electronics

Veronika Proschek, Graz University of Technology
Chemical surface reaction of 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane with ammonia: a combined experimental and theoretical study

Thomas Höfler, Graz University of Technology
Kinetic investigation of aryl esters undergoing a photo-Fries rearrangement

Alexandra Lex, Graz University of Technology
New photosensitive silane molecule for photochemical patterning of thin layers

Joshi Siddarth, University Siegen
Structutre and crystallinity studies of poly(3-hexylthiophene) based OFET layers

Piet Reuter, Graz University of Technology
Electrical probing and manipulation of small structures

Markus Koini, Graz University of Technology
Epitaxial order of sexithiophene on Cu(110) - (2x1) O stripe phase and clean Cu(110)

Dimitrii Nabok, University of Leoben
Cohesive and surface energies of organic molecular crystals

Martin Oehzelt, Karl Franzens University Graz
Molecular organisation : the role of substrate interaction

Priya Sony, University of Leoben
Adsorption of thiophene on Cu(110) – (2x1) O

Gregor Hlawacek, University Leoben
Following self-organized growth of 6P thin films by low energy electron microscopy

Quan Shen, University of Leoben
Morphologic characterisation of organosilane self-asembled monolayers on SiO_2

Shaima'a M. Abd Al-Baqi, Johannes Kepler University Linz
Rubrene epitaxial layers for organic TFT's grown by hot wall epitaxy

Konstantiyn Grytsenko, Institute of Semiconductor Physics, Kyiv
Oriented growth of organic films onto aligned PTFE surfaces

Anna Track, Graz University of Technology & Karl Franzens University Graz
Theoretical studies on an organic / metal interface: CO on Cu(111)

Adolf Winkler, Graz University of Technology
Fundamental aspects of oligo-phenylen adsorption and thin film layer growth on gold surfaces

Klaus Duncker, Martin Luther University Halle
Thin films of sexithiophene on Ag(100) and Au(111) – a combined STM and LEED study

Organic thin film transistors: history and current developments

Ananth Dodabalapur

The University of Texas at Austin

This presentation will describe the history and important developments in organic/polymer transistors, including materials, performance levels, fabrication methods and device structures. First, the most important classes of materials will be reviewed along with performance figures. The important phenomena involved in charge transport (both steady-state) and dynamic will be described so as to represent current understanding. The scaling behaviour and properties of small geometry organic transistors will be surveyed. The second part of the talk will begin with a discussion on organic transistor speeds and what sort of circuits can be built with them. This will lead to a discussion of applications for organic transistors including electronic paper, displays, RFID tags, and in sensors/actuators.

Barium doped C_{60} for Field-Effect-Transistors

B. Plochberger[1]*, *H. Sitter*[1], *B.Th. Singh*[2], *N.S. Sariciftci*[2], *G. Hernandez-Sosa*[1], *P. Bauer*[3], *R. Kolarova*[3]

[1] *Institute of semiconductors and solid state physics, University Linz, Austria*
[2] *Institute of organic solar cells (LIOS) - Institute of physical chemistry, University Linz, Austria*
[3] *Institute of Experimental Physics, University Linz, Austria*

Research in Organic Field-Effect Transistors (OFETs) resulted in very interesting devices such as displays, all organic integrated circuits, ect. The efforts to increase the charge carrier mobility in OFETs with n-type organic materials have been difficult due to several physical reasons; rapid degradation under ambient conditions and electron transport properties are sensitive to the purity of the crystal [1]. Among the n-type organic semiconductors, C_{60} shows the highest obtained mobilities of up to 0.6 $cm^2V^{-1}s^{-1}$ [2].

In this work the electron mobility in hot wall epitaxially grown barium doped C_{60} based field-effect transistors was studied as a function of the growth parameters. The electrical active layers were deposited on a staggered glass, ITO (gate) and BCB (dielectric material) substrate. The contacts were evaporated through a shadow mask and subsequently the transistor characteristic was determined based on IEEE standard 1620. To control the influence of the surface morphology and dopant distribution on the OFET performance, additional AFM and Rutherford Backscattering, Polarization, FITR measurements were performed.

OFETs fabricated from pristine C_{60} layers show that the first few monolayers of the electrical active layer at the interface to the dielectric layer dominate the carrier transport [3] while the upper layers are less relevant for the transport properties, but act more as a protecting cap. In this case carrier mobilities in the range of 0,1-1 $cm^2V^{-1}s^{-1}$ were obtained. To further improve the mobility it was tried on one hand to optimise the substrate temperature or on the other hand to dope the C_{60} layers with different concentrations of barium. Typical results for Ba doped C_{60} OFETs are shown in figure 1. From plot $\sqrt{I_D}$ versus V_G the threshold voltage was determined. Figure 2 shows the mobility versus the gate voltage. Using the IEEE standards a mobility of μ=4-6$cm^2V^{-1}s^{-1}$ was determined, which is to our knowledge the best value reported so far for C_{60} based OFETs.

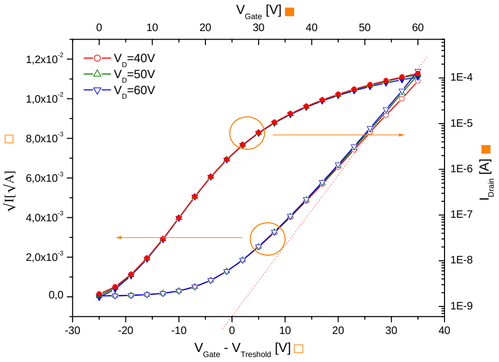

Figure 1: Transfer characteristics of barium doped C_{60} OFET: semilogarithmic plot of I_D versus V_G (top and right axis), $V_G - V_T$ versus $\sqrt{I_D}$ (bottom and left axis).

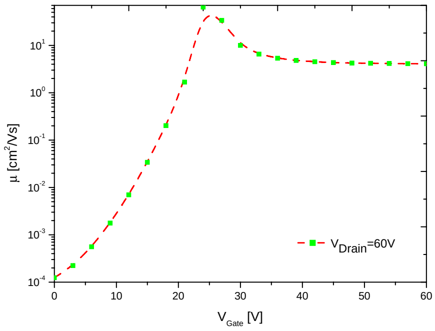

Figure 2: Mobility μ versus V_G of a barium doped C_{60} OFET based dielectric BCB

The dependence of the mobility related to doping concentration as well as to substrate temperature will be discussed.

References

[1] R.G. Kepler.
Physical Review, (119):1226, 1960.

[2] S. Mori A. Fujiwara Y. Iwasa S. Kobayashi, T. Takenobu.
Appl. Phys. Lett., (82):4581, 2003.

[3] G.J.Matt S. Guenes N.S. Sariciftci A. Montaigne A. Andreev H. Sitter R. Schwoediauer S. Bauer Th. B. Singh, N. Marjanovic.
High-mobility n-channel organic field-effect transistors based on epitaxially grown C_{60} films.
Organic Electronics 6, (288):105–110, 2005.

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[*] Email: plochi@nme.at

N-channel field-effect transistors and ring oscillators based on epitaxially grown C_{60} fullerene films

Th. B. Singh,[a] Thomas D. Anthopoulos,[b] H. Yang,[c] L. Yang,[d] N. Marjanovic,[a] N. S. Sariciftci,[a] M. Cölle,[e] Dago M. de Leeuw,[e] A. Montaigne Ramil,[f] B. Plochberger,[f] and H. Sitter[f]

[a] Linz Institute of Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria E-mail: birendra.singh@jku.at
[b] Department of Physics, Blackett Laboratory,Imperial College London
London SW7 2BW, UK
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110 8th Street, Troy, NY 12180, USA
[d] National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, USA
[e] Philips Research Laboratories, High Tech Campus 4, 5656 AE
Eindhoven, The Netherlands
[f] Institute of Semiconductors and Solid State Physics, Johannes
Kepler University Linz, A- 4040. Linz , Austria

We report on organic n-channel field-effect transistors and circuits based on epitaxially grown C_{60} films. Discrete top-contact transistors employing evaporated gold source-drain contacts and divinyltetramethyldisiloxane-bis(benzocyclobutene) as gate dielectric show maximum electron mobility in the range 3 - 6 cm^2/Vs. By integrating a number of C_{60} transistors we are able to fabricate unipolar ring oscillators with maximum operating frequency of 30 kHz and a corresponding stage delay of 2.3 μs. To our knowledge this is the fastest n-type organic circuit reported to date. From an extensive study of film morphology (See Figure 1) and crystallinity of the fullerene films using atomic force microscopy and grazing-incidence X-ray diffraction, authors experimentally established a correlation of crystallinity of the film and charge carrier mobility. Higher substrate temperature leads to single crystal-like faceted fullerene crystals.

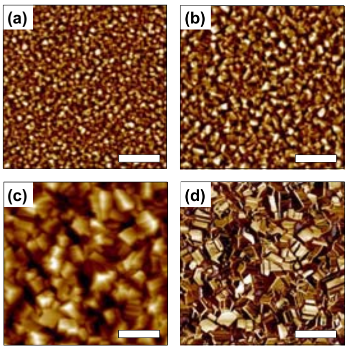

Figure 1. AFM topographic (a-c) and phase (d) images for 100-nm-thick C60 fullerene films deposited on SiO2/Si substrates kept at different TDs: (a) 25 °C, (b) 120 °C, and (c, d) 250 °C. (All scale bar represents 1 μm.)

Scaling Laws in Organic Thin Film Transistors

B. Stadlober[1], U. Haas[1], H. Gold[1], A. Haase[1], C. Auner[1], G. Jakopic[1], and G. Leising [1,2]
1) *Institute of Nanostructured Materials and Photonics, Joanneum Research, Austria*
2) *Institute of Solid State Physic, Graz University of Technology*

High performance organic thin film transistors (OTFTs) can be fabricated only by carefully controlling all relevant device parameters, which are the morphology of the organic semiconductor, the thickness, density and dielectric constant of the organic gate dielectric and the contact resistance. We have produced a large number of pentacene OTFTs by varying the gate dielectric, decreasing the thickness of the dielectric layer to values below 150nm and by reducing the contact resistance. In addition, we have quantitatively studied the growth process of pentacene on different dielectrics for different temperature regimes. It turned out, that high-mobility pentacene OTFTs ($\mu>0.1$ cm^2/Vs) with operation voltages well below 5V can be produced by minimizing the dielectric film thickness, the contact resistance and optimizing the pentacene morphology. The miniaturization of the critical dimensions down to the subµm-regime by means of nanoimprint lithography in conjunction with investigations of short-channel effects is another prerequisit for a deeper understanding of OTFTs. We report on the scaling behaviour of the charge carrier mobility, the device resistance and the device behaviour in the subthreshold regime.

Hysteresis in Organic Field Effect Transistors

P. Stadler[1] (a), T. B. Singh(a), R. Schwödiauer(b), S. Bauer(b), J. G. Grote(c) and N. S. Sariciftci(a)
(a) *Institute of Organic Solar Cells, Johannes Kepler University Linz, Austria*
(b) *Institute of Soft Matter Physics, Johannes Kepler University Linz, Austria*
(c) *Materials & Manufacturing Directorate, Air Force Research Laboratory, AFRL/MLPS, Wright-Patterson Air Force Base, Ohio USA …*

In organic field effect transistors (OFETs) the gate dielectric plays a crucial role - highly insulating thin film polymer layers are key-components in state of the art organic transistor devices. When replacing the polymer layer by introducing solution-processed thin film surfactant-modified biopolymer Desoxyribonucleic Acid (DNA) as gate dielectric [1], transistor-characteristics are changed towards remanence-like hystheresis behaviours. The hysteresis-loops probed in bio-organic field effect transistors (BiOFETs) derived from DNA and fullerene derivatives form bistable states which can be used for memory devices at low operating voltage regime compared to similar organic thin film transistors using polymers as gate insulator. Bulk-interface interactions have been reported in various space-charge electrets without ferroelectric-like properties [2] and - in the case of DNA - are probed with sandwich devices of pristine biopolymer (Metal-Insulator-Metal) as well as sandwich devices with biopolymer and semiconducting fullerene derivative (Metal-Insulator-Semiconductor-Metal) and bottom gate – top electrode OFET devices itself.

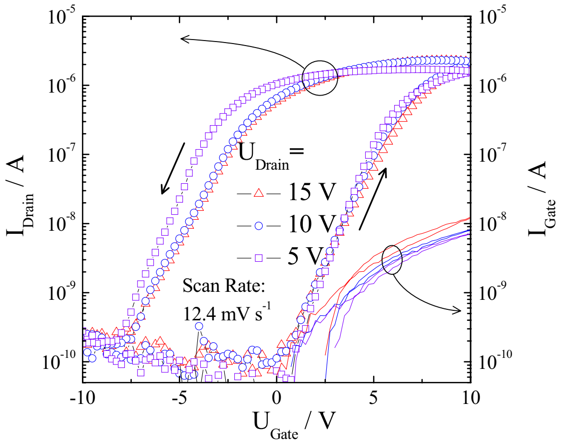

Figure 1 Transfer characteristics of BiOFET: Measurements performed with scan rate of 12.4 mV s^{-1}.

[1] T. B. Singh, N. Marjanovic, G. J. Matt, N. S. Sariciftci, R. Schwödiauer and S. Bauer, Appl. Phys. Lett. **85**, 5409 (2004).
[2] P. Author4, Author5, J. Appl. Phys. **45**, 323 (2002).

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[1] Philipp.Stadler@jku.at

Air-stable and Soluble Derivatives of Perylene and Naphthalene Diimide for n-channel Organic Semiconductors

S. Erten,[a,b] Th. B. Singh,[a], N. S. Sariciftci,[a] S. Icli,[b]

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[b] Ege University, Solar Energy Institute, 35100, Bornova-Izmir, TURKEY E-mail: sule.erten@ege.edu.tr

Solution-processed n-type organic field-effect transistors (OFETs) have been fabricated using soluble derivatives of perylene diimide and naphthalene diimide with chemical structure as shown in Figure 1. We report the synthesis of the organic semiconductors and the fabrication of bottom gate OFET devices using solution-processed organic dielectrics. Surface morphology studies reveal films with layered textures and liquid crystalline-like structure. Devices show field-effect electron mobilities of 10^{-2} cm^2/Vs and 10^{-3} cm^2/Vs for N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide-NDI I under inert conditions and in air, respectively. N,N'-bis-(1-pentyl)hexyl-3,4,9,10-perylene diimide-PDI-4 shows mobility of 5 x 10^{-4} cm^2/Vs. Organic field-effect transistors based on N,N'-bis(dehydroabietyl)-3,4,9,10-perylene diimide-PDI-1 derivative exhibit ambipolar transport.

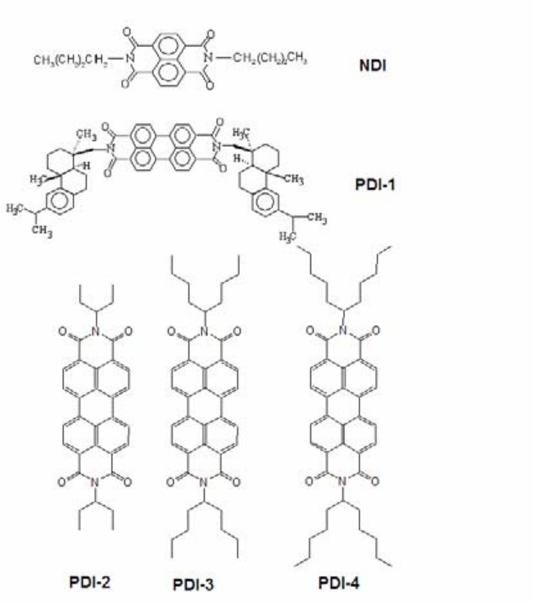

Figure 1: Chemical structure (a) N,N'-bis-butyl-1,4,5,8-naphthalene diimide-NDI (b) N,N'-bis-dehydroabietyl-3,4,9,10-perylenediimide-PDI-1 (c) N,N'-bis-(1-ethyl)propyl-3,4,9,10- perylene diimide-PDI-2, (d) N,N'-bis-(1-butyl)pentyl-3,4,9,10-perylene diimide-PDI-3 (e) N,N'-bis-(1-pentyl)hexyl-3,4,9,10-perylene diimide-PDI-4.

Tutorial: Device and electronic circuit modeling

T.Ostermann
Institute for Integrated Circuits, University of Linz, Austria

The aim of the tutorial is to present a detailed overview regarding device modeling as well as circuit modeling. In the first part of the tutorial different aspects of device modeling will be considered. The auditors will learn about the different ways to model devices as well as the background of these approaches. Not only for circuit description/simulation but with the main focus on the use of device models for later circuit simulations. The second and larger part of the tutorial concentrates on modeling aspects regarding complete electronic circuits. These circuits could consists of only a few devices up to circuits with huge numbers of devices. But with reference to polymer devices, the circuit part will have his main focus on the special needs of smaller circuits. Here analog as well as digital circuits will be considered and the tutorial will show the differences but also the similarities in modeling of those topologies.

Application of atomic force microscopy techniques for surface analysis*

C. Teichert[1] (a)
Institute of Physics, Montanuniversität Leoben, Austria

Among scanning probe microscopy techniques, atomic-force microscopy (AFM) has become a powerful tool to characterize surface morphologies on the nanometer scale which is in contrast to scanning tunneling microscopy applicable to all material classes. According to the measurement principle of AFM, where a sharp probe at the end of a cantilever is scanned across the sample surface, the recorded "image" represents a three-dimensional topography z(x,y).

Illustrated by examples from the wonderful world of self-organized semiconductor nanostructures (both organic and inorganic ones), this tutorial will demonstrate how the morphological image z(x,y) can be quantitatively analyzed in terms of surface roughness, size and 3D shape of individual nanostructures as well as integral information (mean values and distribution functions) in the case of nanostructure arrays.

Information on lateral nanostructure size, uniformity and arrangement can be easily accessed by analyzing the two-dimensional power spectral density of roughness and the analysis of the two-dimensional histogram of the orientations of local surface normals yields integral information on facet orientations of the nanocrystals (Fig. 1). Finally, the average nanostructure height is obtained from the height histogram of the AFM image. The influence of probe dimensions and other imaging artifacts on the corresponding results as well as inadequate image processing will be discussed. It will be shown how the AFM based morphology analysis is used to derive information on molecular processes in the growth of organic thin films.

Besides morphological analysis, AFM allows also to obtain a materials contrast on the nanometer scale as will be demonstrated by phase imaging and friction force microscopy of organic thin films. In an outlook, the capabilities of conducting AFM (C-AFM) to investigate electric properties of thin films and nanostructures will be briefly presented.

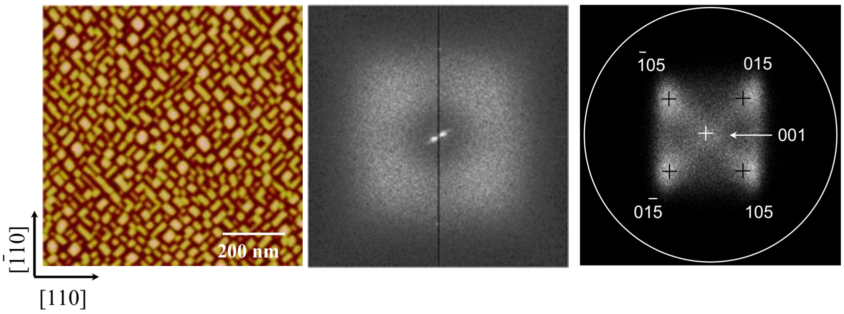

Figure 1. Topography image (left), 2D power spectrum (center), and facet analysis (right)

[1] C. Teichert, Phys. Rep. **365** (2002) 335.
[2] G. Hlawacek, et al., phys. stat. sol. **a 202** (2005) 2376.
[3] C. Teichert, et al., Appl. Phys. **A 82** (2006) 665.

* Research has been performed in the framework of the FWF National Research Network "Interface controlled and Functionalised Organic Films" (S9707-N08) in collaboration with A. Andreev, G. Hlawacek, C. Hofer, Y. Hou, and S. Kremmer.

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[1] teichert@unileoben.ac.at.com
http://www.unileoben.ac.at/~spmgroup/

COHESIVE AND SURFACE ENERGIES OF ORGANIC MOLECULAR CRYSTALS

D. Nabok, P. Puschnig, and C. Ambrosch-Draxl
Chair for Atomistic Modelling and Design of Materials , University of Leoben, Austria

The cohesive and surface energies of the oligo-acene, oligo-phenyl and oligo-thiophene series are computed. The calculations are performed using an ab-initio pseudo-potential planewave approach where different approximations for the exchange-correlation potential, i.e. the local density approximation (LDA) and the generalized gradient approximation (GGA), have been tested. We have computed surface energies for the (100), (010), (001), (110), and (1-10) planes in the acenes, phenylenes and thiophenes. Moreover the energies of the experimentally observed 6P high index surfaces (-312), (-302), (-211) and (-111) are calculated.

We demonstrate that GGA calculations for the cohesive energy can be corrected for the missing non-local correlations by adding an empirical formula taking care of van der Waals interactions. This leads to cohesive energies of oligo-acenes in good agreement with experiment, and shows that it is a very promising approach for the calculation of cohesive energies and surface energies of organic molecular crystals.

CHARACTERIZATION OF ORGANIC THIN FILMS BY OPTICAL MEANS

K. Maschek, Y. Hu, L.D. Sun, M. Hohage and P. Zeppenfeld[1]
Institut für Experimentalphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria

Thin films of organic molecules have been studied extensively in recent years, due to their interesting electronic and optical properties exploited in electronic and opto-electronic devices such as OLEDs, OFETs or organic solar cells. On the other hand, it is known that the electronic, transport and optical properties of thin organic films may crucially depend on the structure and morphology of these films and their interfaces.

Therefore, it is quite important to understand the relationship between the thin film structure and morphology and the ensuing electronic and optical properties, preferably by monitoring them in an in-situ and online fashion during the growth or fabrication process.

We will demonstrate that reflectance difference spectroscopy (RDS), provides a powerful means to investigate the structure and growth of thin organic films and, at the same time, study the evolution of the electronic and optical properties in situ and with submonolayer sensitivity.

As examples, we discuss the growth of para-sexiphenyl (p-6P) on Cu and TiO_2 surfaces [1,2]. We illustrate how the growth mode and structural parameters like the orientation of the molecules can be inferred from RD spectra probing both substrate and thin film related optical transitions. The shift, broadening and splitting of the characteristic HOMO-LUMO transitions were monitored during growth and are related to changes in the electronic structure arising from the interaction of the molecules in the organic layer or from conformational changes within the individual molecules.

The RDS method also allows to resolve the fine structure of the main optical transitions, resulting from the strong electron phonon coupling in these films and to study its thickness and temperature dependence. Finally, structural phase transitions can be detected both as a function of coverage (i.e., during growth) and as a function of temperature.

Being a purely optical probe, RDS is not limited to UHV related fabrication processes but could, for instance, be applied to monitor the deposition from solution or to study organic thin film devices during operation.

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[2] L.D. Sun, M. Hohage, P. Zeppenfeld, S. Berkebile, G. Koller, F.P. Netzer, M.G. Ramsey, Appl. Phys. Lett. **88**, 121913 (2006).

Collaboration with M.G. Ramsey and his colleagues at the University Graz is gratefully acknowledged. The work is supported by the Austrian Science Fund (FWF) through projects P15963-N08 and S9002-N02.

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ELLIPSOMETRY ON THE AMORPHOUS RUBRENE THIN FILMS

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Many organic materials with delocalized π-electron systems exhibit significant potential for electronic and optoelectronic applications [1]. Rubrene molecule ($C_{42}H_{28}$, 5,6,11,12-tetraphenylnapthacene) belongs to a group of small organic molecules with promising properties, which found use in organic light emitting diodes (as a red dopant) and organic field effect transistors. We demonstrate the use of spectroscopic ellipsometry as a non-invasive in-situ technique for rubrene thin films. The films were prepared by organic molecular beam epitaxy on Si-waver with native or thermal oxide at room temperature. The ellipsometric parameters ψ and Δ was acquired by ellipsometer Woollam M-2000® (rotating compensator) with CCD-based detection system in range from 1.25 to 5 eV. Since rubrene grows in non-crystalline films [2][3], we employed an isotropic model. The commercial software WVASE® applied with general oscillation model or method for mean square error (MSE) calculation with fixed thickness was used. The data there were converted to the *complex dielectric function*. These two methods represent powerful tool for data analysis and error visualization.

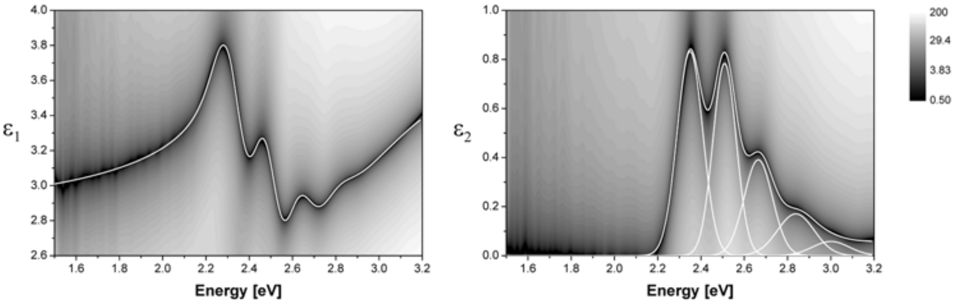

Figure 1. Dielectric function $\varepsilon_1+i\varepsilon_2$ of amorphous rubrene thin film (low MSE denote high probability of dielectric function and white line denote fit with general oscillation model in WVASE®)

The growth of rubrene thin films exhibits non-crystalline structure with anomalous roughness [2], on the other side it exhibit high affinity on oxygen [4]. Relatively wide spectral range and fast acquisition allowed to use this technique as a key for investigation of kinetics in *thin film growth* and *oxidation* under controlled condition.

[1] F. Schreiber. Physica Status Solidi A. **201**, 1037 (2004)
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[4] R. M. Hochstrasser, M. Ritchie. Trans. Faraday Soc. **52**, 1363 (1956)

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Growth of sexithiophene (6T) films studied by RDS

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Reflectance difference spectroscopy (RDS) measures the difference of the normal-incidence optical reflectivity for two mutually perpendicular orientations of the polarization vector as a function of the photon energy. As a linear differential optical method, RDS is extremely sensitive to any kind of optical transition which is polarization dependent [1], from single molecule excitation to excitons of molecular aggregates. Here, we report our *in-situ* RDS investigation of 6T film growth on anisotropic substrates, namely Cu(110)-(2x1)O and $TiO_2(110)$. The orientation of 6T molecule and optical property of 6T thin film have been monitored over the entire range of the film thickness up to several nm. At submonolayer coverage, the optical property of the film is close to that of single molecule. However, already when the thickness of the film approach to one completed monolayer, exitonic state represented by Davydov splitting sets in. Following the evolution of RD spectrum, the growth mode and the film morphology can be deduced. As an example, the difference of imaginary part of dielectric function obtained from RD spectra recorded during 6T deposition on Cu(110)-(2x1)O is shown in Fig. 1. 6T grows on Cu(110)-(2x1)O maintains their orientation in wetting layer, i.e., all molecules in the film are uniaxially aligned with their long molecular axes parallel to the Cu–O rows and to the Cu substrate surface. The result agrees very well with the grazing-incidence X-ray diffraction (GID) studies [2]. Similar growth mode has been observed also for the 6T growth on $TiO_2(110)$ at liquid nitrogen temperature. Whereas the 6T growth on $TiO_2(110)$ at room temperature shows a different behavior. The detail will be discussed by comparing with the results obtained by other complementary methods.

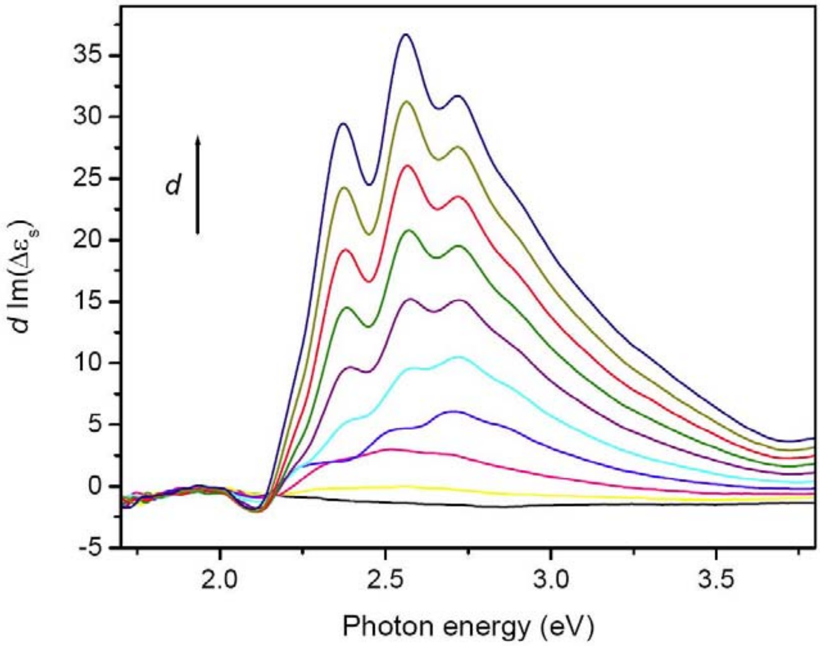

Fig.1: The anisotropy of imaginary part of dielectric function scaled by film thickness *d* obtained from RD spectra recorded during 6T deposition on Cu(110)-(2x1)O up to a film thickness of 2 nm.

[1] L.D. Sun, M. Hohage, P. Zeppenfeld, S. Berkebile, G. Koller, F.P. Netzer, M.G. Ramsey, Appl. Phys. Lett. 88, 121913 (2006).

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PARA-SEXIPHENYL THIN FILMS GROWN ON KCL SUBSTRATES

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Para-sexiphenyl (6P) is a blue light emitting organic semiconductor widely investigated for optoelectronic applications, like organic light emitting diodes and lasers [1,2]. Especially, 6P thin films grown on mica(001) and KCl(001) substrates show large morphological and optical anisotropy, which makes them attractive for nano-scale photonic devices. In this work, we focus on the growth of 6P on KCl(001) substrates, in order to find the parameters controlling film morphology, structure and quality. Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD) and were mainly used for characterization. In addition, spectroscopic methods, as steady-state photoluminescence (PL) and time-resolved PL monitored at different temperatures and delay times, have been utilized to get information on the deep traps defects in the films.

It is shown that the growth process of 6P on KCl(001) is quite complex and can be divided preliminary in two steps. The initial growth stage is characterized by the formation of long needle-like crystallites (built of 6P molecules lying with their long axes flat on the substrate surface), generating a rectangular network in accordance with the substrate surface symmetry. With increasing coverage, terraced crystalline mounds composed of upright standing molecules start to develop between the needles. These mounds are clearly formed due to repeated 2D nucleation of 6P molecules. Consequently, all terraces found are on average about 2.6 nm high, which corresponds to one monolayer of standing 6P molecules. Subsequent growth is characterized by a coexistence of the constantly growing needles and mounds. By means of phase imaging in AFM tapping mode, it is demonstrated that both needle-like crystallites and flat terraced mounds grow directly on the substrate surface, i.e., there is no wetting layer formed during the deposition of 6P on KCl(001).

Time-resolved PL studies have shown that, as in 6P films on mica, the emission spectra also contain two different components - a conventional structured spectrum due to intrinsic excitons and a very broad red-shifted band ascribed to some kind of defects. The latter band can be distinguished in delayed fluorescence spectra of the studied films. It is remarkable, however, that the relative intensity of the defect band is much weaker in the films grown on KCl substrates comparing to that on mica ones. This finding implies that the defect band is rather sensitive to the type of substrate and hence supports an idea of structural origin of the defect states. We also discuss a correlation between growth condition of 6P and a relative intensity of the defect PL band.

[1] G. Leising, S. Tasch, F. Meghdadi, at al., Synth. Met. **81**(2/3), 185 (1996)
[2] A. Andreev, F. Quochi, F. Cordella, et al., J. Appl. Phys. **99**, 034305 (2006).

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TAILORING OF ULTRA THIN HEXAPHENYL FILMS ON MICA (001) THROUGH SURFACE MODIFICATIONS

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In this contribution we focus on the hexaphenyl (6P) ultra thin film growth on mica (001), which was investigated by surface science methods. Mica was cleaved under ambient atmosphere conditions with a scotch tape in order to get a "clean" surface. The 6P films were prepared by vacuum evaporation under ultra high vacuum (UHV) conditions. Thermal desorption spectroscopy (TDS) was used to get information on the monolayer formation. X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) were used to characterize the mica surface before 6P thin film deposition. TDS, XPS and LEED were carried out in a vacuum chamber under UHV conditions. The grown films were investigated ex-situ by atomic force microscopy (AFM).
First, the 6P film growth on the freshly cleaved mica surface was investigated. In the multilayer regime (film thickness>0.4nm), 6P forms needle-like islands. These structures have already been shown in the literature previously. TDS now allowed for the first time to investigate the monolayer regime (film thickness<0.4nm), and thus to draw conclusions on the existence of a monolayer, a so-called wetting-layer. TDS-measurements show that there is a monolayer of hexaphenyl on freshly cleaved mica.
In the multilayer regime, the morphology of the needles at different film thickness and different adsorption temperatures was investigated by AFM. Additionally, so-called "XPS vs. Temp" measurements were carried out, where the sample was investigated by XPS during heating, yielding additional information on needle formation and needle morphology.
The main goal of this work was, however, to tailor the 6P layer growth by surface modifications. Basically, modifications can be realized through a change in surface composition or in surface structure. For this purpose, the surface was covered with a carbon layer (change of surface composition) via X-ray induced dissociation of 6P and sputtered (change of surface structure) using low energy Ar^+ ion beams, respectively. TDS and AFM investigations showed a significant change in monolayer formation, from flat laying molecules on the freshly cleaved and untreated mica surface to upright standing molecules on the carbon covered as well as on the sputtered mica surface (see Fig.1).

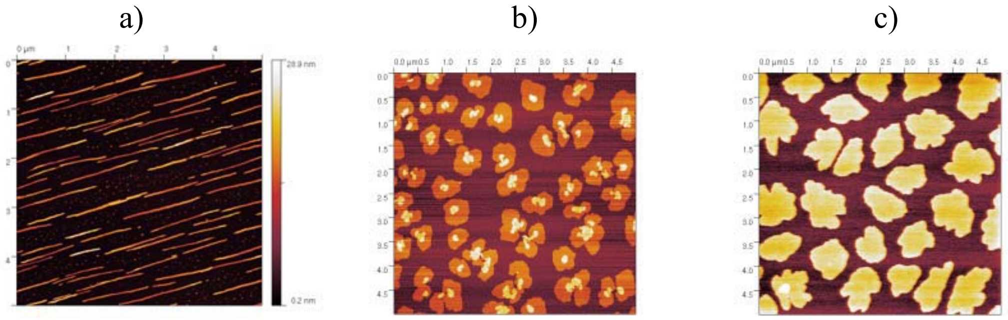

Fig.1: 1nm 6P on a) freshly cleaved mica, b) carbon covered mica, c) sputtered mica

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NEW CRYSTALINE PHASE OF PSP NEEDELS ON MICA?

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On this work we show evidence of a new morphology of psp (Parasexiphenyl) grown on muscovite mica by Hot wall epitaxy (HWE). As we can appreciate from figure 1d this new structures show a rectangular cross section contrasting with the semicircular one of the structures that usually are obtained [1]. This fact implies a different packing of the molecules which will have a consequence on the physical properties of the structures. We can also observe from fig.1c that the width of the needles is uniform. Moreover, the steep walls and sharp ends would be an advantage when we use the fibers as waveguides or resonators for lasing [2].

We will also like to discuss the conditions we need for a reproducible growth and the possible reasons for the change of morphology.

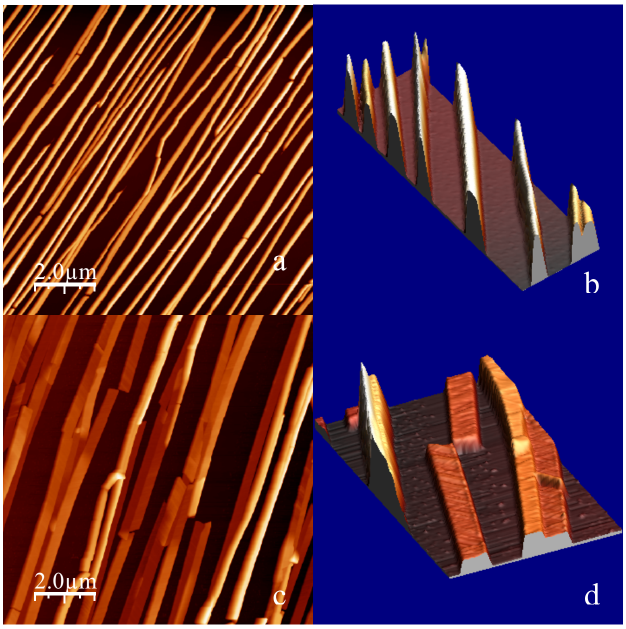

Figure 1. AFM images of psp needles on mica. a and b typical morphology. c and d new morphology.

[1] A.Andreev et.al. Adv.Mater. **45** (2002) 629.
[2] F.Quochi et. al. Appl.Phys.Lett. 84(2004)4454

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Surface chemistry and lithographic patterning for organic electronics

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This contributions presents an overview on lithographic patterning strategies for thin films and surface layers. Both the chemical approaches for resist materials (positive and negative toned recording materials) as well as current lithographic techniques will be discussed. Photolithographic processes with resolutions in the micrometer and sub-micrometer scale as well as lithography with X-ray and e-beam techniques will be described and characteristic examples will be given. Applications for optical and electronic devices are demonstrated together with the underlying chemical processes.

The second part of this lecture focuses on the surface chemistry of polymers and surface layers. Strategies for immobilizing molecules and nano-particles at surfaces will be shown, and useful concepts for the surface functionalization of organic layers, e.g. by UV-assisted processes, will be presented.

This lecture aims at physicists and chemists who wish to learn more about the chemistry and the applications of functional surfaces and the patterning of organic resist materials.

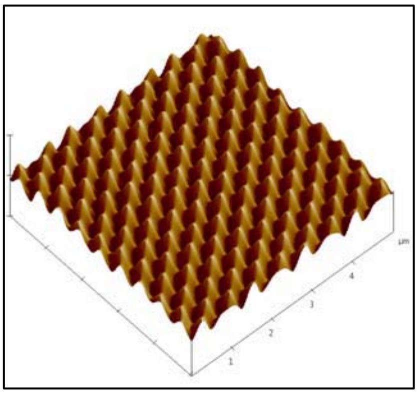

Figure 1. Triple surface relief grating inscribed with UV interference lithography in a layer of poly(styrene-co-4-vinylbenzyl thiocyanate) [1] [2]

[1] T. Kavc, G. Langer, W. Kern, G. Kranzelbinder, E. Toussaere, G. A. Turnbull, I. D. W. Samuel, K. F. Iskra, T. Neger, A. Pogantsch, *„Index and relief gratings in polymer films for organic DFB lasers"*, Chemistry of Materials **14**, 4178-4185 (2002)
[2] D. Wright, E. Brasselet, J. Zyss, G. Langer, A. Pogantsch, F.F. Iskra, T. Neger, W. Kern, „*Multiple Grating Organic Distributed Feedback Lasers*", Opt. Express **12**, 325 (2004)

Photoreactions in thin organic films based on the photoisomerisation of benzyl thiocyanates and aromatic esters.

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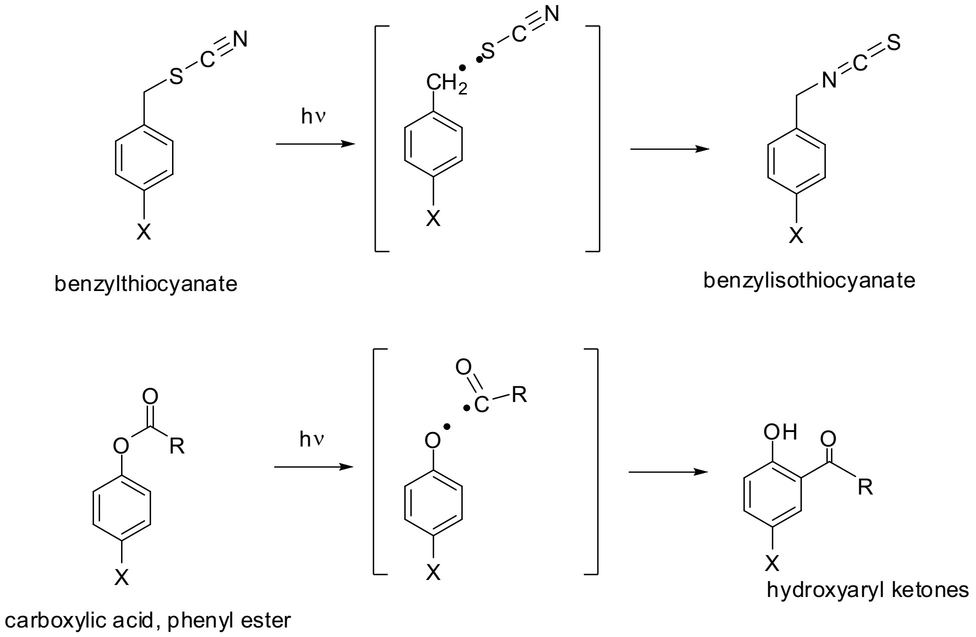
Modification of thin surfaces layers by UV-light-induced reactions allows lateral patterning by lithographic techniques. In the first part, the principle of the two investigated photoreactions – the photoisomerisation of benzylthiocyanat and of aryl esters of carboxylic acids (the so called photo-Fries reaction), see Scheme 1 – will be demonstrated for thin polymeric films. Both photoreactions cause a change in the refractive index of the polymer and in addition lead to a modification in the chemical reactivity in the UV-illuminated areas. The latter effect can be used for reactions that selectively take part in these regions and a variety of molecules can be immobilized in such a way. The photoreactions were followed by FT-IR- and UV-VIS spectroscopy, and ellipsometric measurements.

In the second part, we present the principle how these photoreactions can be transferred to organic molecular surface layers. First examples of photoreactive silanes on SiO_2 surfaces and functional thiols on gold surfaces will be demonstrated.



Scheme 1: Photoisomerisation of benzylthiocyanates and carboxylic acid, arylestes. X denotes a polymerisable group (e.g. X = vinyl), the polymer backbone, or an anchoring group for inorganic surfaces (X = thiol, trichlorosilyl, triethoxysiliyl)

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Patterning of Self-assembled Monolayers

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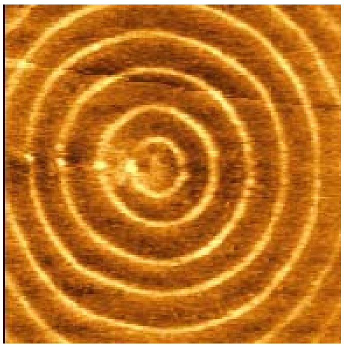
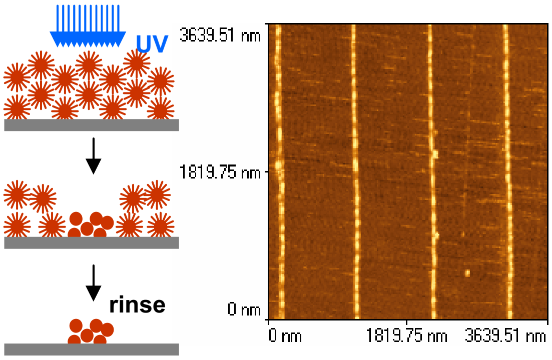
One of the outstanding challenges in molecular nanoscience is the development of techniques that span the divide from top-down (lithographic) and bottom-up (synthetic) fabrication techniques. While for inorganic materials the fabrication of sub-10 nm structures is now feasible using electron beam lithography, the state of the art is very much less well advanced for organic materials. There is a critical length regime, from about 100 nm to the size of a single macromolecule, in which there are currently no established tools for the manipulation of molecular structure. Self-assembled monolayers (SAMs) have attracted a great deal of interest as templates for the fabrication of molecular nanostructures, and this lecture will review methods for their lateral organization. We will focus particularly on the archetypal SAM system, monolayers of alkanethiols on gold surfaces, and explore methods for their patterning on both the micrometre and the nanometre scale.

We will begin by looking at the most widely used tool for SAM patterning, microcontact printing (μCP). We will consider the basic process, including the fabrication of stamps, and illustrate the capabilities of μCP by exploring its applications to problems in the fabrication of metallic structures and in biology. We will briefly examine the wider field of “soft lithography” which has developed from μCP. Alternative approaches to micrometre-scale patterning will be explored, including photopatterning methods.



Concentric rings of carboxylic acid groups formed in a chloromethyl-phenylsilane monolayer by scanning near-field photolithography

Nanometre scale patterning of SAMs may be accomplished using electron beam and scanning probe methods. We will look briefly at electron beam lithography of SAMs. While there have been some impressive successes, electron beam methods have not yet demonstrated widespread utility in SAM patterning. However, scanning probe microscopy-based methods have attracted a great deal of interest. We will look in more detail at four methods that have emerged in recent years and which offer very high lateral resolution: local oxidation lithography, dip-pen nanolithography, nanoshaving/nanografting and near-field optical lithography. In each case we will examine the basic mechanism of monolayer modification, the general scope offered for the control of chemistry, the resolution limit and the factors that determine performance, and we will consider applications of the methods to molecular patterning. We will explore the prospects offered by scanning probe-based methods for spanning the divide between top-down and bottom-up fabrication, and the prospects for their widespread adoption by researchers in molecular electronics and related disciplines.



Gold nanowires of width 60 nm formed by scanning near-field photolithography of thiol-capped gold nanoparticles

THIN REACTIVE LAYERS FOR AMMONIA DETECTION WITH ORGANIC THIN FILM TRANSISTORS

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In this contribution we discuss the influence of reactive thin layers on the device performance of organic thin film transistors (OTFTs). The CSTS layer (2-(4-Chlorosulfonylphenyl)-ethyltrichlorosilane, Fig. 1.a.) is characterized by thickness measurements from a best curve fit to a grazing incidence X-ray reflection measurement. Reflection absorption infrared spectroscopy (RAIRS) is used to study the chemical reaction of CSTS with ammonia gas (NH_3). Density functional theory calculations are presented to explain the origin of the observed peaks and peak shifts of the RAIRS spectra. They are found to be in good agreement with our experimental data and show in conjunction with the experiment that the reaction shown in Fig. 1.a. takes place. XPS studies on samples before and after NH_3 exposure are a further proof for this reaction to happen.

Particular attention is paid to how such thin films can be used as sensitizers, which translate interaction with an analyte into a modification of OTFT characteristics. Two basic experiments are conducted: First the CSTS layer is directly exposed to NH_3 before spincoating P3HT as the organic semiconductor (termed *direct exposure*) and secondly the finished OTFT is exposed to NH_3 *(indirect exposure)* as shown in Fig. 1.a. The actual effect on the transfer characteristics is found to be huge and similar in both cases: The turn on voltage shifts from large positive values to negative values (see Fig. 1.b. for direct and Fig. 1.c. for indirect exposure).

We believe that this novel sensor concept can open new routes for the design and the optimization in the field of organic sensors.

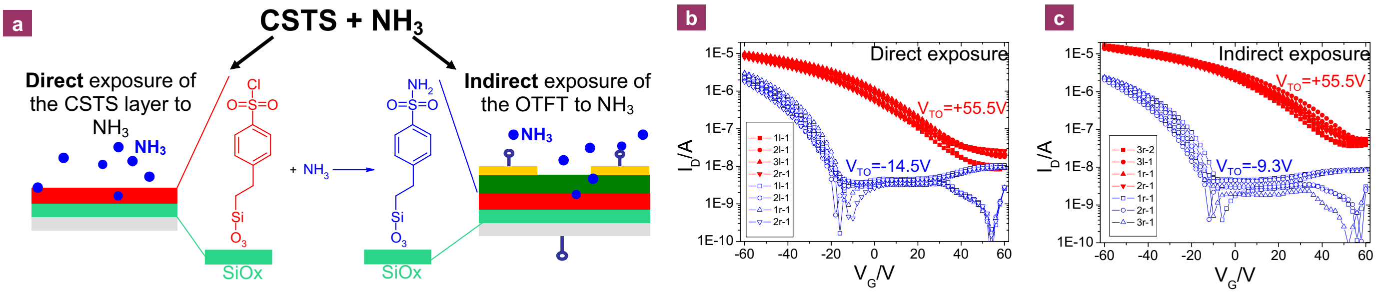

Figure 1: Reaction of the CSTS layer and the effect to device characteristics.

a. Schematics of the chemical reaction of the CSTS layer with ammonia gas (NH_3). Upon direct exposure the CSTS layer reacts with NH_3 before deposition of the organic semiconductor (OSC), while upon indirect exposure the reaction takes place after this deposition and thus NH_3 has to diffuse through the OSC.
b. Shift of the transfer characteristics of four devices before (closed red symbols) and after (blue open symbols) direct exposure to NH_3
c. same as b. for indirect exposure

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Pentacene monolayers and submonolayers on silicon oxide: a combined X-ray reflectivity and AFM study

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A deeper understanding of organic film growth from the first monolayer to the bulk phase is of great interest for scientific and commercial application since the electronic properties are strongly correlated with structural and morphological properties within the first few monolayers. Polymorphism is present in pentacene film but the reason is still unknown.

Pentacene thin films were prepared by physical vapor deposition onto thermal oxidized silicon. The deposition was performed under a high vacuum; substrate temperatures are varied for different samples. Films with different coverage's were produced starting with a nominal coverage of 0.3nm (mass equivalent), 0.6nm, 0.9nm, 1.2nm, 2.4nm 3.6nm and 4.8nm.

Atomic force microscopy measurements were performed to obtain surface structure, layer thickness and coverage. Additional x-ray reflectivity (XRR) measurements were performed to achieve information on the number of pentacene layers, layer thickness of each layer and the interface behavior from adjacent monolayers. Additional the electron density distribution within the film is determined giving the information about the packing or coverage within a layer.

The results reveal that the AFM results are in good agreement with XRR results concerning the coverage for all investigated samples. Additional a wetting layer is observed by XRR with a layer thickness of about 6Å for all samples. A layer by layer growth with 15.4 Å is not observed for the first monolayers.

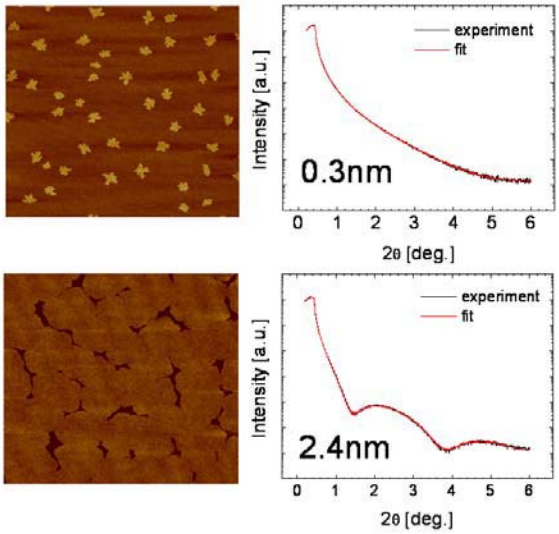

Figure: AFM and XRR results for 0.3nm (top) and 2.4 nm (bottom) coverage

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Improving performance of pentacene OFETs using aromatic thiols

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In addition to tailoring mechanical and chemical surface properties self-assembled monolayers (SAMs) have also attracted significant interest in connection with studies on molecular electronics or as contact primers for organic electronic devices. The high electrical conductivity required for the latter applications has favored the use of aromatic SAMs which generally reveal a more complex ordering mechanism as compared to aliphatic SAMs. While an improved ordering has been achieved by using additional alkyl-units within the backbone this in turn reduces the conductivity and increases the band gap of the molecular film.

In a comprehensive multi-technique study (based on NEXAFS, TDS, STM and LEED measurements) we have investigated the formation, molecular structure and thermal stability of acene-based SAMs on gold. [1] It will be shown that varying the anchor group from anthracene-2-thiol to anthracene-2-selenol yielded higher ordering of these films on Au(111) as needed for the use as template in an organic field-effect transistor.

Because of its high charge carrier mobility and the ability to form (poly-)crystalline films pentacene is still one of the most promising organic semiconductor for the fabrication of such devices. The growth and evolution of pentacene films on gold which is commonly used as electrode material have been studied. By combining complementary techniques including STM, AFM, SEM, NEXAFS, and XRD the molecular orientation, crystalline structure and morphology of the organic films were characterized as a function of film thickness and growth parameters (temperature and rate) for different gold substrates ranging from Au(111) single crystals to poly-crystalline gold.

On clean gold surfaces the first monolayer forms a chemisorbed wetting layer with planar adsorption geometry while subsequent growth is characterized by a pronounced dewetting and formation of needle-like islands where molecules adopt a bulk-like upright orientation. At very large deposition rates rather disordered films are formed where this molecular reorientation is quenched. A distinctly different growth scenario was observed for gold surfaces which had been modified before by a SAM. In that case no planar oriented seed-layer is formed and pentacene molecules grow immediately in an upright orientation in quasi layer-by-layer fashion without any dewetting yielding rather smooth films.

Possible reasons for the different growth mechanism will be discussed and the consequences for the use of pentacene films in organic field-effect transistors will be illustrated using devices with channel lengths of $L<4\mu m$ and pre-treatment of the electrodes with alkanethiols and aromatic thiols compared to an untreated device. Besides morphological changes also the electrical properties of such devices differ drastically. [2] A reduction of the threshold voltage from about $V_T=2V$ for untreated transistors to -0.9V for transistors with SAM modified electrodes was found. Using aliphatic SAMs a poor on/off ratio of about 10^2 was obtained due to their low conductivity, whereas aromatic SAMs yielded an enhancement by four orders of magnitude. In the latter case a subthreshold swing as low as 0.55 V/decade is achieved which corresponds to a trap density reduced by one order of magnitude compared to the reference sample with pentacene on bare gold electrodes.

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[2] C. Bock, D.V. Pham, U. Kunze, D. Käfer, G. Witte, Ch. Wöll, J. Appl. Phys. **100**, 114517 (2006).

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Surface science with organic molecules

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Thin semiconducting films of vacuum deposited large organic molecules are successfully used in organic electronic devices. However, besides chemical properties of the individual molecules and chemical purity, the performance of the films concerning charge transport or optical properties is strongly determined by the interfaces to the underlying substrate or the electrodes. In particular structural and morphological properties are strongly templated from the interfaces, which can lead to film properties significantly differing from those of the corresponding molecular crystals.

In this talk, details of chemical bonding, ordering and film growth of large π-conjugated molecules on well defined surfaces will be reported. A particular focus will be given on the electronic and structural properties of the first surface bonded layer, which are decisive for further film growth and the interfacial electronic barriers. From a number of examples it will be demonstrated that structural and chemical details of the adsorbate/substrate combination can lead to large variety of growth scenarios and variations in the resulting film properties.

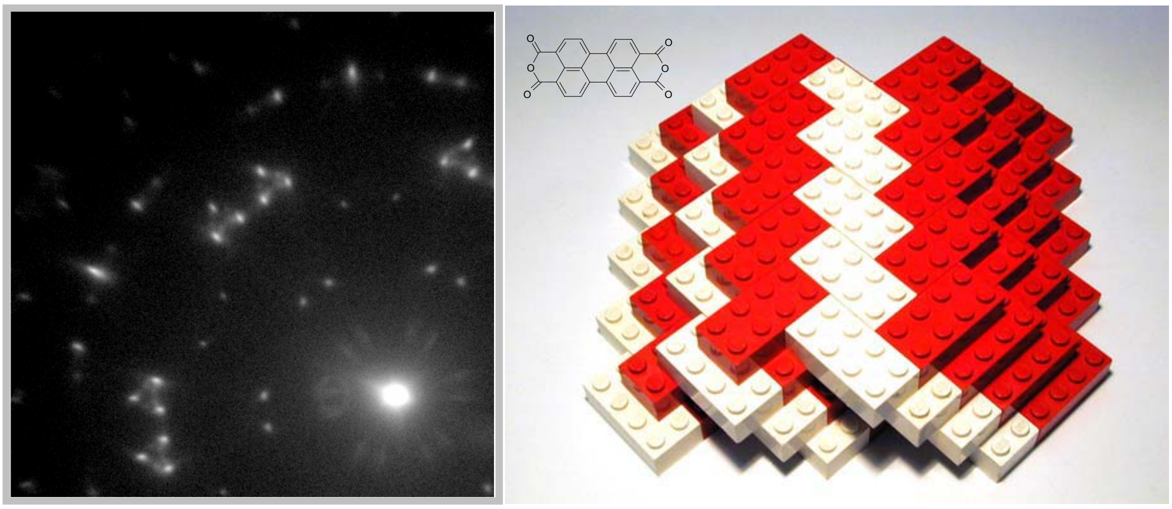

Figure 1. High resolution LEED pattern (25 eV) of a thick PTCDA film grown on the Ag(111) surface and corresponding model [1].

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[3] A. Hauschild et al., Phys. Rev. Lett. **94** (2005) 036106; Hauschild et al., Reply, Phys. Rev. Lett. **95** (2005) 209602.

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Adsorption of F4TCNQ on Cu {111}: a combined experimental and theoretical study

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The physical and chemical properties of organic/metal interfaces are of high interest for the understanding of molecular monolayer formation, workfunction modification of metals, injection barrier tuning in electronic devices, chemical sensing and molecular electronics.

We present results for the molecule F4TCNQ adsorbed onto the copper {111} surface. The electronic properties and atomic distances to the surface were determined by ultraviolet photoelectron spectroscopy (UPS) and the X-ray standing wave (XSW) method.

To gain insight into the nature of the bonding between metal and molecule, the interface was modeled by means of density functional theory based bandstructure calculations using the VASP code. This allows for a precise analysis of the charge forward donation from the lone pairs of the molecule to the metallic states, together with the back donation from the metal into the LUMO of the molecule. The density of states belonging to the molecule and the geometric distortion can be directly compared to the UPS and XSW data. The rearrangement of charges is, furthermore, investigated in real space where a dipole layer is seen to be formed upon adsorption. Together with the intrisinc dipole layer of the molecule, the total workfunction of the surface can be obtained.

HOW TO CALCULATE THE ELECTRONIC STRUCTURE OF ORGANIC SEMICONDUCTORS?

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This tutorial should give an introduction into electronic structure calculations in general, and the specific features related to organic semiconductors in particular. The concept of density functional theory (DFT) will be introduced, which is not only the basis for all modern band structure codes, but has turned out to be a very powerful tool in computational solid state theory and materials science. It will be shown, which properties can be obtained, and how well they compare to their experimental counterparts. The computational effort of such calculations will be discussed as well as their limitations. All examples will be chosen from the topics investigated within the NFN.

Inter- and intramolecular dispersion in a highly ordered organic molecular crystal

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The inter- and intramolecular dispersion in organic molecular crystals have been predicted by theory, but never measured to a satisfying degree. Further, organic pi-conjugated molecules, as they are intrinsically one-dimensional objects with a well-defined number of repeating units, serve as a simple model for understanding what happens to the basic electronic structure in systems of limited size and low dimensions. Here, the band structure of a highly ordered and crystalline para-sexiphenyl (6P) film has been measured using angle-resolved photoemission spectroscopy (ARUPS) in the three directions important to charge transport in organic devices. The ARUPS behavior reveals both strong intermolecular dispersion perpendicular to the molecular axis and intramolecular dispersion along the axis of the molecules. The data will be shown to be in very good agreement with calculations in terms of the extent of the band dispersion, the ARUPS intensity and the k-spread of the peaks associated with quantum size effects. Supported by the Austrian Science Funds (FWF).

Heteroepitaxy of organic-organic-nanostructures: fundamental aspects of growth and electronic structure

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The potential of organic semiconductors as active materials in devices such as organic light emitting devices, organic field effect transistors, photovoltaic cells and sensors has attracted basic scientific as well as technological interest. These devices often consist of a multiplicity of organic layers, thus making the understanding of the organic interface and organic-on-organic growth a scientifically and technologically important issue. On the one hand details of the interfaces are important for charge injection, while the films morphology and crystallinity together with the molecular/crystallite orientation determine charge transport and light emission/absorption characteristics. To optimise device performance these key factors need to be controlled for the specific device as OLEDs, OFETs and photovoltaic cells have different requirements.

Here we report the growth of epitaxially ordered heterostructures of sexithiophene (6T), sexiphenyl (6P) and pentacene (5A). We have produced crystalline films, where the molecules are either exclusively parallel or near perpendicular to the inorganic supports. These crystalline films are then used as substrates for the 6P, 6T, 5A heterostructures. The geometric structure and morphology of these heterostructures was obtained from near edge x-ray absorption fine structure spectroscopy, synchrotron radiation x-ray diffraction and atomic force microscopy studies, together with the electronic band alignment at the organic interface, as measured with photoemission. We find that the orientation of the molecules in the organic substrate film determines not only the orientation in the heterolayer, but also leads to a second film which is crystalline with a well defined epitaxial relationship. This demonstrates that highly oriented crystalline molecular films provide excellent, stable templates for organic heteroepitaxial growth. However, our results clearly show that the epitaxial growth of organics on organics cannot be simply understood in terms of lattice match, but appears to be mainly driven by the alignment of the overlayer molecules with respect to the substrate molecules [1, 2].

Supported by the Austrian Science Foundation (FWF).

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Threshold phenomena in C_{60}–Fullerene based field effect transistors

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At this converence, we present results on organic field effect transistors (OFET) based on C_{60} grown on top of organic dielectrics divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) using hot wall epitaxy (HWE). The HWE can be maintained to operate close to the thermodynamic equilibrium. Consequently the molecule can find the most suitable arrangement before being condensed, resulting in highly ordered structures of the deposited layer [1]. The controlled growth conditions ensures the preparation of a defined C_{60} thin film morphology with a low total number of traps. Optimization of the growth–parameters enhances the drain–source current to values up to 98.9 mA at a drain–source voltage of 100 V and at a gate–source voltage of 75 V [2]. The current–densities reported here, are two order in magnitude higher as those achieved from similar prepared devices. A detailed analysis including the properties of the interface between C_{60} and the dielectric as well as the transport properties of the crystalline C_{60} thin–film will be outlined.

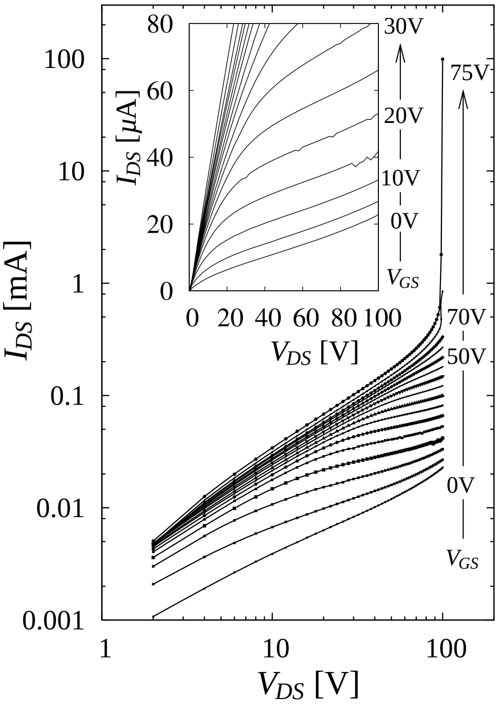

FIG. 1: Double logarithmic presentation of a $I_{DS}(V_{DS})$ C_{60}–FET characteristics in accumulation mode. The C_{60} was grown using HWE on top of the organic dielectric BCB.

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ELECTRET, FERROELECTRET AND FERROELECTRIC ORGANIC FIELD-EFFECT TRANSISTORS: DEVICES AND APPLICATIONS

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Electrets, ferroelectrets and ferroelectric polymers belong to the class of dielectric materials with quasi-permanent excess charges, oriented molecular dipoles or ferroelectric polarization. Their use in organic field effect transistors (OFET's) was first demonstrated in 2003 by Katz et al. to produce OFET's with floating gate-like effects [1]. Currently, such materials are at the heart of many applications, from nonvolatile memory elements to sensors for wearable electronics and prosthethic skin. In the tutorial, the basic features of electret materials are discussed, starting with space charge electrets with excess charge carriers trapped for long times on the order of decades at room temperature. Space charge electrets in OFET's produce not only memory elements, but also transistors with an adjustable threshold voltage, useful in unipolar logic elements. "Ferroelectrets" are internally charged soft foams, with highly anisotropic voids dispersed throughout the polymer film. Their name stems from the analogy to ferroelectric materials, and to charge storing electrets. Ferroelectrets provide a new class of ferroic materials, and are stimuli responsive, since they react sensitively with a strong electrical signal output to mechanical pressure changes. The piezoelectric effect in ferroelectrets is characterized by large piezoelectric d_{33} tensor elements on the order of several 100 pC/N, comparable to numbers obtained with currently employed, lead containing ceramics. In comparison to the ferroelectric ceramics, ferroelectrets are "green materials", based on non-toxic components. Ferroelectrets are therefore soft electroactive foams for transducers, in ferroelectret field effect transistors they can be employed as touch sensors, in pressure activated switches, as well as in microphones. Semicrystalline ferroelectric polymers show a ferroelectric polarization in the crystalline part and are therefore interesting for non-volatile memories, but also for infrared sensors based on their pyroelectric response.

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LOW FREQUENCY DIELECTRIC SPECTROSCOPY OF POLY VINYL ALCOHOL GATE DIELECTRICS

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Polyvinylalcohol (PVA) is a water soluble dielectric polymer widely employed as gate dielectric in organic field effect transistors (OFET). Depending on the preparation route of PVA, the resulting dielectric film may contain ionic impurities, yielding OFET's with a pronounced hysteresis in the transfer and output characteristics [1]. In order to reveal the influence of ionic impurities on the dielectric properties of PVA, dielectric spectroscopy is performed in the frequency range between 5×10^{-4} Hz to 10^{4} Hz on commercially available PVA's, on dialysis grade PVA and on PVA films with added impurities of sodium acetate. Films cast at room temperature on a glass substrate with an evaporated Al or Au electrode are dried under argon in a glovebox, before a top electrode is deposited to form a metal-insulator-metal capacitor structure. In order to reveal a possible influence of blocking Al electrodes on the dielectric spectra, samples have been also prepared with non-blocking Au electrodes. Results obtained from dielectric spectroscopy on PVA MIM samples are correlated with results on PVA metal insulator semiconductor MIS devices, as well as with transfer and output characteristics measurements on PVA based OFET's.
At room temperature, dielectric measurements on PVA MIM samples do not show a dielectric loss peak, however, a clear loss peak is found at elevated temperatures above 50°C, which shifts towards larger frequencies with increasing temperature. When the temperature of the film is lowered, the PVA films show similar dielectric properties, indicating reversible changes in the film. However, after exposing the film to temperatures above the glass transition of PVA an irreversible change in the dielectric loss spectra is observed, suggesting recrystallization of the film. The effect of adding (sodium acetate) or removing ionic impurities by dialysis is also evident in the dielectric loss spectra. The dielectric measurements also correlate well with measurements on PVA based MIS and OFET structures, thereby providing an explanation of the hysteresis phenomena frequently observed in such devices.

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Large-Area Molecular Electronics

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Understanding charge transport through a single molecule is crucial for the development of new organic devices. Both improved device performance via surface modification of electrodes as well as miniaturization of devices demand knowledge on the molecular level.

Interesting studies have been performed to study molecular transport using a variety of techniques, i.e. mechanical breakjunctions, CP-AFM, STM, etc. Recently, Reed and coworkers[I] showed an important step for molecular junctions using inverted nanopores of 1500 nm^2. In 2006, large-area molecular junctions in the vertical interconnects of a photoresist layer with diameters ranging from 1 - 100 µm have been reported.[II] The advantage of these molecular junctions concerns the reliability of the measurements and the high yield. All studies have in common the use of molecules, which self assemble onto a metal surface; often alkane(di)thiols are used as the self-assembled monolayers (SAMs).

In this presentation, the manufacturing and characterization of large-area molecular junctions will be discussed. Initially, simple alkanedithiols are used as SAMs to benchmark the large-area molecular junctions.

The SAM is placed between a gold bottom electrode and a highly conductive polymer top electrode, i.e. poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid) (PEDOT:PSS). On top of this water-based polymer, gold is evaporated. The additional PEDOT:PSS layer prevents direct electrical shorts upon applying the metal top electrode.

Discrete large-area tunnel junctions can relatively simple be manufactured using patterning of the bottom gold electrode and deposition of the metal top electrode via a shadow mask. At Philips, a technology has been developed to up-scale these large-area tunnel junctions onto 6-inch wafers and to integrate them (Figure 1). To that end, also the top electrode has to be patterned via lithograpy.

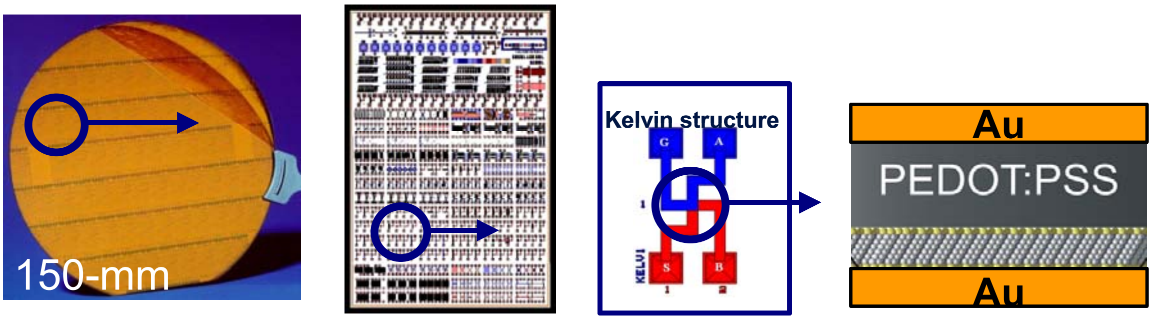

Figure 1. Large-area molecular junctions, i.e. Au / SAM / PEDOT:PSS / Au, on a 6-inch wafer.

The conductivity for alkanedithiols is shown to be scalable with the area size, independent of temperature, and exponential dependent on the length of the SAM. Hence, charge transport is regarded as a tunneling process, and can reasonably be well described using the Simmons model. The charge transport is governed by the chemisorbed gold-SAM bottom contact, the SAM itself, and the physisorbed SAM-PEDOT top contact. In the future, incorporation of functional SAMs could result in self-assembled molecular electronics, like rectifying diodes, memories and/or photoswitches.

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[1] paul.van.hal@philips.com
[I] Reed et al., *Science* **278** 1997, 252
[II] Akkerman et al, *Nature* **441** 2006, 69

Direct ink-jet printing of Ag-Cu nanoparticle and Ag-precursor based electrodes for OFET applications

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Two novel metallic inkjet printable materials are studies: i.) a soluble organic silver-precursor and ii.) a silver-copper nanoparticle based dispersion. Both materials reveal largely metallic properties of the cured materials, compared with respect to OFET performance. The presented results show that commercially available solution processable metals are definitely becoming an alternative to doped conjugated polymers in many organic electronics applications.

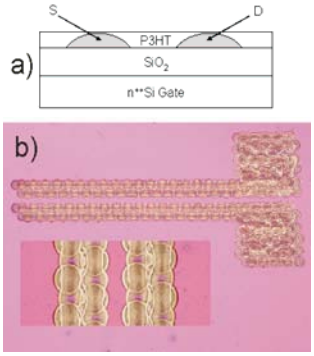

Figure 1: Printed organic FET

[1] Stefan Gamerith, Andreas Klug, Horst Scheiber, Ullrich Scherf, Erik Moderegger, Emil J.W. List, Advanced Functional Materials, (in print)

THERMALLY STIMULATED RELAXATION IN ORGANIC MOLECULAR SOLIDS

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Molecular solids are usually formed from organic polymers, oligomers or low-molecular organic compounds. Processes like thermal charge carrier generation, release of carriers from traps or molecular motion, which are taking place in these solids are activated processes. The time constants of these processes show a pronounced temperature dependence characterised by a constant or temperature dependent activation energy as a fundamental quantity describing these processes.

In the situation of a frozen-in process the principle of "Thermal Stimulation" (TS) can be used to accelerate the relaxation and to make the process detectable by an appropriate technique during the time of experiment. Due to that, the whole relaxation strength of the process can contribute to the detected signal which makes the thermally stimulated techniques to be more sensitive than isothermal techniques.

Among the TS-techniques, thermoluminescence (TL) is an important technique to study release of carriers from traps where they are immobilised prior to the experiment. The population of carrier traps can be created by various processes, e.g. by cosmic radiation which has importance for archeological dating of insulating natural materials, by illumination with UV light, x-rays, γ-rays, electron beams or field injection at low temperature in case of synthetic materials like organic semiconductors which are mainly discussed here. After thermal release at rising temperature the carriers can recombine radiatively at recombination centres. The detected luminescence intensity is a measure for the density of traps, and of trapped carriers. At distinct temperatures the detected signals form characteristic peaks. Their maximum temperature and the shape of the peaks are related to the activation energy of the involved process. In case of a response formed by multiple overlapping signals arising from processes which are distributed in activation energy, the shape parameter of their energy distribution can also be extracted from the experimental data. The area of the peak is related to the density of released carriers. Therefore, a detailed TL peak analysis provides all the essential parameters to understand trapping and detrapping processes in the investigated molecular solids.

In case of electrical detection using capacitor sample geometry, various processes connected with charge redistribution in organic solids can be studied by observing the flow of mirror charges in the external measuring circuit. This includes dipole relaxation and charge transport.

Among the different measuring techniques which allow the investigation of these processes including impedance spectroscopy, isothermal polarisation or isothermal depolarisation, the techniques like thermally stimulated polarisation (TSPC) or depolarisation currents (TSDC) are having the highest sensitivity, and resolution power towards overlapping relaxation processes. As mentioned above these methods rely on the fact that activated processes like dipole reorientation or charge release can be stimulated by gradual increase of the detection temperature during the measurement. Starting from a frozen-in state after a formation process the whole number of oriented dipoles or trapped charges can be released during the relatively short time of experiment.

Combined studies of TL response and of the field and thickness dependence of TSDC and TSPC signals allow to discriminate between charge transport and dipole relaxation phenomena.

Application of the described techniques to materials used for fabrication of organic light-emitting devices (OLEDs), thin-film transistors (TFTs)/organic field-effect transistors (OFETs) or organic solar cells (OSCs) provide all information necessary for a detailed understanding of charge transport in these devices

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PERSPECTIVES OF LB LAYERS FOR MOLECULAR ELECTRONICS

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Conjugated polymers, oligomers, or fused aromatics have been envisioned as a viable alternative to more traditional, mainstream solid state devices based on inorganic materials. The unique processing performance of these structures suggests that they can be competitive candidates for existing or novel devices requiring large area processing, and especially low cost. Such applications include switching devices for active matrix flat panel displays, organic light emitting diodes, or "electronic paper" displays. Additionally, sensors, low-end smart cards, prototype all-polymer integrated circuits have been demonstrated.

In this context, the method used for the fabrication of the active organic layer is relevant in determining the device performance. The Langmuir-Blodgett deposition provides the possibility to build a molecular system in the layer-by-layer manner and has proven itself to be useful in constructing new supramolecular architectures. The control of thickness can be achieved at the molecular level and, moreover, the preferential orientation of the organic molecules is reached with respect to the dipping direction during the transfer of the monolayer from the water surface [1]. The organization in various molecular systems fabricated by the LB technique has been revealed by X-ray diffraction, reflection, GISAXS, TEM, SEM.

The molecular conformation and ordering in monomolecular layers were identified by electrical properties of monolayer constituting molecules using the detection of Maxwell's displacement currents flowing through a metal electrode / air-gap insulating layer / Langmuir monolayer situated on a water surface or on a solid substrate.

The complex study on amphiphilic poly(3-alkyl-thiophene) having polar metoxy chain ends is presented. It involves the investigation of monolayer properties at the air/water interface supported by results of computer simulation, structural studies by X-ray diffraction. The LB films showed photoluminescence and electroluminiscence at RT. The changes in the emission energy spectra could be tuned by varying applied voltage [2].

The thiophene LB layers were also used to prepare surface modified ion-selective microelectrodes for improving sensitivity and selectivity in voltammetric detection of electrically active species in solutions [3].

Among fused-ring polycyclic aromatic hydrocarbons pentacene is very attractive due to its high field-effect mobility values. However, defects and impurities play a dominant role in determining the properties. MDC showed the presence of molecular order in the Langmuir film and the recorded high values of molecular dipole moment indicate defects states. The existence of pentacene defects in LB films was verified by charge deep-level transient spectroscopy. Semi-empirical calculations (PM3) of pentacene molecule and its defect forms show that hydrogen-, oxygen-, and hydroxide- defects are possible and stable. All the defects have an impact on electronic structure of the molecule and, thus, on electron density or molecular dipole moment. The evaluation of the dipole moment from MDC measurements is essential for identification of the different defect states.

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[3] K**.** Gmucová, D. Barančok, J. Cirák, P. Tomčík, acta phys. slov. 53, 105 –110 (2003)

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New approaches for inorganic and organic electronic devices

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Silicon is the dominant technology for information processing devices. For high performance applications like microprocessors, no other technology even comes close to delivering the same performance. Silicon produces the fastest circuits, the densest circuits, and the cheapest transistors. One of the weaknesses of silicon technology is that an integrated circuit costs roughly €100/cm^2. This is too expensive for applications where a large area is desired such as displays or sensors. Organic electronics have traditionally been used to make cheap, large-area circuits because simpler processes can be used to fabricate devices. Organic devices are typically orders of magnitude slower than silicon but in applications like RFID tags, displays, solar cells, and disposable (medical) sensors, they can sometimes provide sufficient performance at lower cost. However, recent developments in nanoelectronics are challenging the role of organic electronics in large scale applications. Carbon nanotubes and semiconducting nanowires have the electronic performance of silicon but can be dispersed in solution and can be used in process technologies that are similar to those used with organic electronic materials. This lecture will explain the differences in how charge moves through organic conductors and inorganic conductors and what advantages and disadvantages different materials have. The status of solution processible inorganic materials such as carbon nanotube ink and spin-on silicon will be reviewed and compared to organic electronic materials.

[1] Some of the arguments that will be presented can be found in: P. Hadley, Bottom-up Nanoelectronics, European Microwave Week 2004 Conference Proceedings (ISBN 1-58053-994-7), pp. 141 - 145 (2004).
http://lamp.tu-graz.ac.at/~hadley/publications/microwave/eumw2004.pdf

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Low Voltage Organic Thin Film Transitors

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Low voltage organic thin film transistors are a stringent requirement for the use of OTFTs in electronic circuits especially in combination with sensors. The organic semiconductor pentacene is still the most promising candidate for high performance OTFTs due to its excellent physical properties and its good environmental stability.

To fabricate OTFTs with a driving voltage below 5 Volts, we utilized a double-layer dielectric technique using a combination of inorganic and organic dielectric thin layers. Due to low leakage currents and a quite perfect growth of the pentacene thin films on the organic dielectric, we could achieve carrier mobilities of up to 1 cm^2/Vs, low threshold voltages around -1V, and an excellent subthreshold swing.

Several combinations of organic and inorganic dielectric materials have been investigated and a comparison of the relevant transistor properties in dependence on gate dielectric materials and dielectric thickness will be presented.

THE FUNCTIONAL PROPERTIES OF THE BIOPOLYMERS CONNECTED WITH THE ELECTRONIC EXCITATIONS ENERGY TRANSFER

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The nucleic acids (DNA and RNA) are the vitally important macromolecules for all live creatures that immediately participate in the storage, transfer and realization of genetic information. The intensive investigations of them have been carried out since the middle of XX century. Unfortunately the spectral properties of the DNA and RNA have not been investigated completely for the understanding of the absorbing and emitting centers nature. In the talk, the spectral properties, energy structure and electronic processes in the DNA, RNA, double-stranded polymer poly(dAdT)$_2$, oligomer d(CCCGGGTTTAAA), trimer d(ATC), dimers d(AT) and d(AG), monomers dGMP, dAMP, dCMP, dTMP, rGMP, rAMP, rCMP, rUMP and rIMP were studied. The DNA fluorescence is close to linear combination of guanine and cytidine emissions and connected to greater extent with singlet energy transfer to these bases. Main attention paid to the DNA phosphorescence that is associated with adenosine-thymidine-sequences. The spectral investigations show these sequences are the traps of triplet excitations in the DNA as well as the synthetic compounds poly(dAdT)$_2$, d(CCCGGGTTTAAA), d(ATC) and d(AT) specially designed and synthesized [1]. This gives the possibility to propose these short DNA-fragments as well as more long DNA-fragments to be used for nanoelectronic devices design. The triplet energy transfer to the traps (mentioned above) and adenine bases (that are most photostable) leads to the DNA self-protection against damage induced by electronic excitations of the DNA.

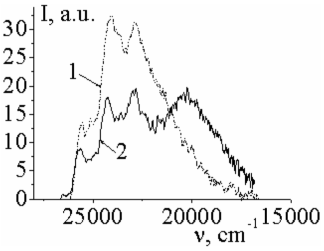

Figure 2. phosphorescence spectra of rAMP (1) and RNA (2)

In contrast to the DNA the RNA phosphorescence is connected with other type centers. The comparison of the phosphorescence spectra of the RNA and the ribonucleotides (Fig. 2) shows the one of the main triplet excitations traps in the RNA is adenosine base.

[1] V. Yashchuk, V. Kudrya, M. Losytskyy, H. Suga, T. Ohul'chanskyy // J. Mol. Liq. **127**, Iss.1-3, 79 (2006).

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NEW MOLECULAR FUNCTIONAL STRUCTURES BASED ON THE DNA FRAGMENTS WITH NEUTRAL AND CHARGED EXCITATIONS ENERGY TRANSFER FOR ORGANIC NANOELECTRONICS

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Now in the modern electronics world the problem of development of the electronics basic elementary functional units of molecular (nano-) sizes has sharply appeared and requires for technological development. The use of nanostructures based on organic π-electron-containing functional compounds that possess the predetermined energy structure and, as the result, the properties of predicted unidirect excitations conductivity is actually for the nanoelectronic basic elements creature. In the talk, the results of the design, synthesis and investigations of the compounds (possessing such type conductivity) containing several (up to 12) π-electron systems (including nucleotides-containing systems – the short DNA-fragments) are reported. The spectral investigations results of the synthetic DNA-fragments are compared with the results obtained on DNA. The predicted processes of unidirect triplet electronic excitations transfer in all investigated compounds were proved. The nature of the electronic excitations traps in the compounds investigated is discussed. Main attention paid to the nature of triplet excitations traps in several DNA-fragments: the spectral investigations show the adenosine-thymidine-sequences are such traps in these compounds as well as the DNA (Fig. 1) [1].

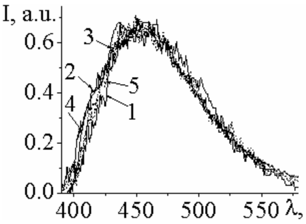

Figure 1. phosphorescence spectra of poly$(dAdT)_2$ (1), d(CCCGGGTTTAA) (2), DNA (3), d(AT) (4) and d(ATC) (5)

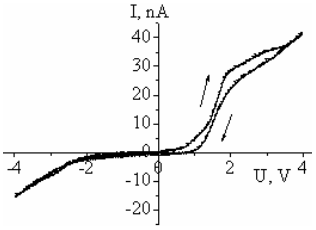

Figure 2. I(U) characteristic of π-electron-containing polymer-gilded film

The existence of the energy levels lowering from chromophore to chromophore along the molecular system gives the ground to predict not only unidirect neutral excitation transfer but unidirect charge carrier current. Really the «diode» I(U) characteristic for metal-organic system of gold islands connected by π-electron-containing molecules was observed (Fig. 2). This gives the possibility to propose these compounds to be used for nanoelectronic devices design. The computer simulations of electronic excitations passing through the oligomer functional macromolecule taking into account reverse exciton currents show such type macromolecules are perspective for applying in nanoelectronics.

[1] V. Yashchuk, V. Kudrya, M. Losytskyy, H. Suga, T. Ohul'chanskyy // J. Mol. Liq. **127**, Iss.1-3, 79 (2006).

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IONIC IMPURITIES IN PVA GATE DIELECTRICS CAUSE HYSTERESIS IN ORGANIC FIELD EFFECT TRANSISTORS

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Hysteresis is a well known phenomenon in the electrical characteristics of organic field effect transistors (OFETs) using polyvinylalcohol (PVA) as dielectric material [1]. It was already proposed that mobile ionic impurities in the PVA might be the reason for the observed hystersis effect [2]. A side-product (approx. 50 mass%) of PVA is sodium acetate, an ionic salt. This salt is removed after the production, but some residue is left. We further cleaned the received PVA (Mowiol from Kuraray Specialities Europe GmbH, Dr. Robert Fuss) by dialysis. This cleaned PVA (“dialysis grade”) was used as dielectric layer in our OFETs:
PVA films cast from aqueous solution at room temperature on a glass substrate with an evaporated Al electrode are dried under argon in a glovebox at 60°C, before a layer of semiconducting C_{60} is evaporated. The OFET device is finished by depositing a lithiumfluoride / aluminium top electrode. Comparing the transfer characteristic curves of OFETs using the “as received” PVA with the dialysis grade PVA shows a dramatic decrease in the hysteresis behaviour. With intentionally added impurities of sodium acetate into the dialysis grade PVA the hysteresis is observed again and can even be enlarged (Fig. 1).
Investigating the temperature dependence and the scanning speed of the hysteresis also supports the theory that mobile ions in PVA cause the observed hysteresis behaviour.
The OFET measurements also correlate well with dielectric sprectroscopy measurements on PVA based MIS and MIM structures, thereby providing an explanation of the hysteresis phenomena frequently observed in such devices.

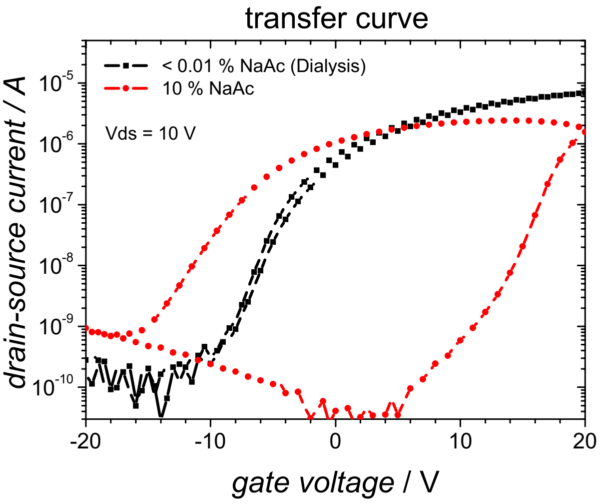

Figure 1. Transfer charcteristics of the investigated Al / PVA / C_{60} / LiF / Al OFETs using dialysis grade PVA and PVA with 10% sodium acetate added.

[1] Th. B. Singh et al., Appl. Phys. Lett. **85**, 5409 (2004).
[2] Th. B. Singh et al., IEEE Trans. Dielectr. Electr. Ins. **13**, 5, 1082 (2006).

Work partially supported by the FWF within the NFN “Interface controlled and functionalized organic films”.

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Photolithographic patterning of polymer surfaces based on the photo-Fries rearrangement: selective post-exposure reactions

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In this study we report on lithographic patterning based on the photo-Fries rearrangement in combination with post-exposure reactions to obtain structured functional polymer surfaces. Polymers with aromatic ester groups undergo an acyl-shift to the corresponding ortho- and para-hydroxylketones upon UV-irradiation. This reaction, the so called photo-Fries-rearrangement, causes large changes in the surface polarity of the polymer due to the formation of aromatic hydroxyl groups.

We prepared poly(endo,exo- bicyclo [2.2.2]hept-5-ene-2,3-dicarboxylic acid, diphenyl ester) (Poly-1) by ring opening metathesis polymerization. This polymer undergoes the photo-rearrangement by illumination with UV-light of 254 nm, as displayed in Figure 1. [1] The formed aromatic hydroxyl groups can be used for post modification reactions, e.g with dansyl chloride, a highly fluorescent dye. Figure 2 shows an example of this reaction after illumination through a contact mask. Other possibilities are reactions with FeCl3 or with carboxylic acid chloride. Also the carbonyl-group can be used for selective modification reactions, e.g. with derivatives of hydrazine to give hydrozones.

All these post modification reactions allow an additional change in the surface polarity as well as the introduction of different functionalities onto the polymer surface.

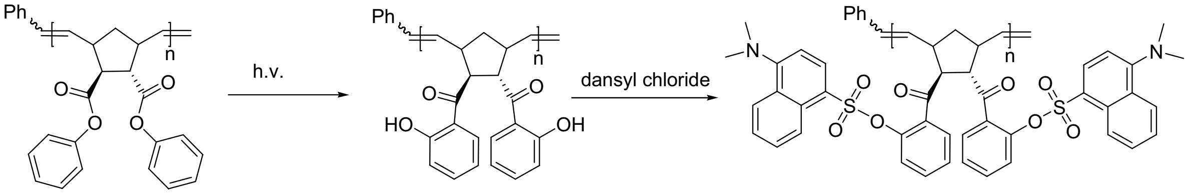

Figure 1: Poly-1 before and after illumination followed by post modification with dansyl chloride

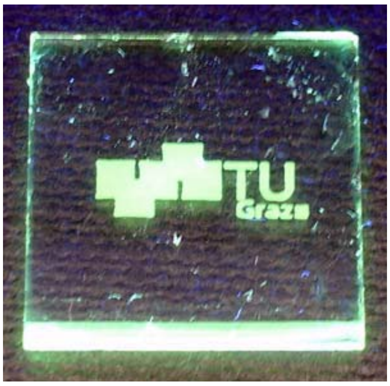

Figure 2: Image of a surface of poly-1 after UV irradiation and subsequent modification with dansyl chloride (the sample was illuminated with 302 nm while taking the photograph, the overall sample size is 1.5x1.5 cm).

[1] T. Höfler, T. Grießer, X. Gstrein, G. Trimmel, G. Jakopic and W. Kern (submitted to Polymer)

MULTIFUNCTIONAL FERROELECTRIC POLYMER - PIEZOELECTRIC CERAMIC NANO-COMPOSITES FOR FLEXIBLE SKIN-LIKE ELECTRONICS

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[(c)] *University of Cambridge, NanoScience, 11 JJ Thomson Avenue, Madingley Road, Cambridge CB3 0FF, U.K.*
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The technology for wearable electronics and prosthethic skin is advancing rapidly. Flexible and even stretchable backplane circuits based on amorphous silicon or organic thin film transistors may be employed in wearable pressure and temperature sensitive networks. Lightweight, compliant and large area sensor films that react sensitively to either pressure or temperature changes are required for such applications. These now have become available in the form of ferroelectrets and multifunctional ferroelectric polymer – piezoelectric ceramic nano-composites. Such materials exhibit strong piezo- and pyroelectric responses after poling. By employing a sophisticated two-step poling process, the polymer ceramic nano-composites can be tailored to react only to pressure changes (piezoelectric mode) or only to temperature changes (pyroelectric mode). Here we describe the flexible thin film transistors, the ferroelectret foils and the multifunctional polymer – ceramic nano-composites, their combination and the application of the circuits in temperature and pressure sensors on the same backplane.

Work partially supported by the FWF within the NFN “Interface controlled and functionalized organic films”

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Chemical Surface Reaction of 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane with Ammonia: A Combined Experimental and Theoretical Study

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Sensing with organic devices in organic thin film transistor OTFT is becoming highly interesting. A reactive thin layer assembled between the silicon oxide and the active layer in OTFTs influences the characteristics of an OTFT and changes it again after the sensing reaction.

In this contribution, the reaction of 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane (CSTS) on silicon oxide with ammonia gas (NH_3) (Fig. 1) is discussed to get a deeper understanding of the sensing process in related devices. The chlorine at the end group of the CSTS is replaced by NH_2 after exposure to NH_3 under desorption of HCl. Infrared reflection-absorption spectra (IRRAS) on thin layers and transmission infrared spectra on thick films are measured before and after the reaction with NH_3. Density functional theory DFT calculations on an isolated CSTS molecule are used to assign the experimental peaks to molecular vibrations and their changes as a result of the chemical reaction. The focus of this contribution lies on the shift of the asymmetric O=S=O vibrational mode. The calculated DFT spectra are in good agreement with the experimental results.

A further proof of the chemical reaction of CSTS with NH_3 can be derived from X-ray photoelectron spectra (XPS). The spectra show a Cl_{2p} peak at a binding energy of 198 eV before the exposure to NH_3. This peak disappears after the reaction with NH_3 and is replaced by a N_{1s} peak at a binding energy of 397 eV.

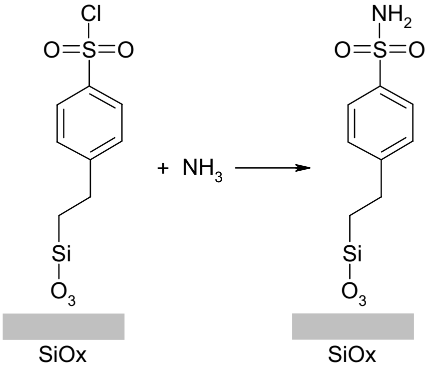

Fig. 1: CSTS reaction with ammonia gas

Kinetic investigation of aryl esters undergoing a photo-Fries rearrangement

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As demonstrated in previous works [1] the photo-Fries reaction causes a large increase of the refractive index (between +0.03 and +0.05) in polymeric materials. In order to learn more about the reaction products of this UV-induced rearrangement, low-molecular-weight model compounds were irradiated in solution and in solid state. Aryl esters such as naphtalene-1-carboxylic acid phenyl ester and naphthalene-1-carboxylic acid *p*-tolylester were UV illuminated at wavelengths 254 nm and 313 nm. The kinetics of the photorearrangement was monitored by FTIR spectroscopy. The individual reaction products and their relative amounts were determined by GC-MS. The results are important to understand the photoreactions in UV-sensitive surface layers and thin films.

[1] UV reactive polymers for refractive index modulation based on the photo-Fries rearrangement, T. Höfler, T. Grießer, X. Gstrein, G. Trimmel, G. Jakopic and W. Kern, manuscript submitted to Polymer (Sept. 2006)

NEW PHOTOSENSITIVE SILANE MOLECULE FOR PHOTOCHEMICAL PATTERNING OF THIN LAYERS

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In this contribution we report on the synthesis and characterization of the new bifunctional molecule (4-thiocyanatomethyl)phenyltrimethoxysilane containing the photosensitive benzyl thiocyanate group as well as the anchoring group trimethoxy silane. The molecule was characterized by NMR-, UV-VIS, and FTIR spectroscopy. The benzyl thiocyanate group undergoes a photoisomerization to the benzyl isothiocyanate group when exposed to UV light. This photoinduced isomerization causes a change of the refractive index. In addition, the obtained benzyl isothiocyanate group is chemically more reactive than the thiocyanate and post modification reactions can be selectively carried out in the illuminated areas. The photoisomerization and the modification reaction with propylamine have been demonstrated using FTIR-spectroscopy on a thin layer of this molecule (see Figure 1).
The new molecule is able to form monolayers and thin layers on siliconoxide due to the trimethoxy silane group which can react with surface Si-OH-groups. The layer formation, the photoreaction as well as the postmodification were investigated by atomic force microscopy (AFM), by X-ray reflectivity (XRR) and by reflection absorption infrared spectroscopy (RAIRS).

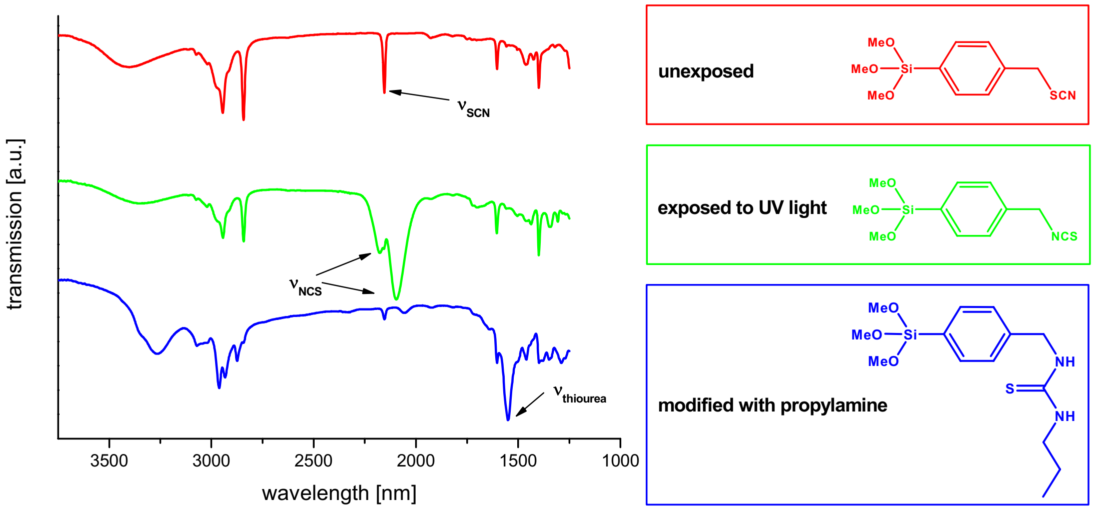

Figure 1. (4-thiocyanatomethyl)phenyltrimethoxysilane unexposed (red), after exposure to UV light (green) and after reaction with propylamine (blue).

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Structure and crystallinity studies of Poly(3-hexylthiophene) based OFET layers

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For few decades, there has been considerable interest in using organic semiconducting materials (polymers, oligomers) as the active component in organic field effect transistors (OFETs). This is mainly due to the fact that organic materials offer some advantages compared to the inorganic counterparts. Organic material is highly-soluble and can be easily processed using spin casting and printing technique, providing the possibility for the large-area electronic application. Poly (3-hexylthiophene) P3HT is one of the most promising π-conjugated polymers used in polymer-electronics and exhibits relatively high charge carrier mobility.

However, up-to now the correlation between the surface morphology and the charge-carrier mobility in P3HT is still not well-understood. Our studies are focussed on the investigation of the structural order [1] and the degree of crystallinity of semi-crystalline thin films (thickness ~ 10-50 nm) of low-and high-molecular weights of P3HTs by using X-ray scattering techniques.

For detailed studies, grazing incidence X-ray diffraction (GID) [2, 3,] has been employed in order to determine the vertical and lateral structures of P3HT films. Based on the additional investigations using atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-ray measurements, we concluded that the thin film of low molecular weight fraction samples consist of highly ordered crystallites with ribbon- or whiskers- like structures embedded in an amorphous matrix. Further, the smaller charge-carrier mobility in low-M_w films is mainly due to the charge-carriers are scattered around the amorphous region. In contrast, the higher mobility in high-M_w fraction can be explained by the fact that high M_w fraction consists of small partially-ordered domains, with average width smaller than the chain length. Thus, chains either are fold back, extend into the disordered phase, or interconnect neighbouring domains, which led to an efficient interchain transport. Also, we have determined the degree of crystallinity for low-and- high molecular weight fractions utilising Ruland's method [4] indicating the increase of degree of crystallinity with increasing the concentration of the samples. Temperature and thickness dependent study of the inter-planer distances 'd' of the P3HT thin films have shown that the 'd' spacing increases with temperature and depending on layer thickness. Temperature dependent out-of-plane measurements indicate that the structure order peaks intensity is decreasing at elevated temperatures and the temperature where the intensity disappears completely can be associated to the melting point of the material. The melting temperature was found to depend on the thickness of the sample, indicating a strong substrate-layer interaction.

1. A. Zen et al., Macromolecules, 39 (2006) 2162.
2. R. J. Kline et. al., Nature materials, 5 (2006) 222.
3. A. Zen et al., Adv. Funct. Mater. 14 (2004) 757.
4. W. Ruland, Acta Cryst., 14 (1961) 1180.

Electrical probing and manipulation of small structures

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Sharp metal tips with a radius of about 50 nm can be made by electrochemical etching. In our probe station, up to six probes can be independently manipulated with a joystick with about 1 nm resolution. The probes can be used to make electrical measurements or force measurements. They can be used to modify the sample by scratching or pushing structures, small particles or carbon nanotubes around. By bringing a tip very close to a conducting surface it is also possible to generate a spark that ablates material away. Craters with diameters between 200 nm and 5 microns can be made. These probes are being used to construct and to measure the characteristics of nanodevices.

Epitaxial order of sexithiophene on Cu(110)-(2x1)O stripe phase and clean Cu(110)

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The crystal structure of sexithiophene (6T) films were investigated on a Cu(110)-(2x1)O stripe phase substrate, where approximately 50% of the surface was covered with Cu(110)-(2x1)O. The stripes with a width of approx. 60 Å consist of oxygen rows which are running along the stripes. The gap between two oxygen rows is 5.10 Å. The second substrate was clean Cu(110). Both samples were prepared by molecular beam deposition in ultra high vacuum and investigated by x-ray diffraction (XRD) methods using specular scans and polefigures. All observed diffraction features could be indexed within one crystal structure. The unit cell dimensions of this phase are: $a = 44.7086$ Å, $b = 7.8513$ Å, $c = 6.0292$ Å, $\alpha = \gamma = 90°$, $\beta = 90.76°$.
On the stripe phase surface, all orientations found in the 150 Å thick film, are aligned either edge-on or flat-on relative to the substrate surface. The quantitatively dominating orientation (A) adjusts its (020) – plane parallel to the substrate surface. The long molecular axes follow the oxygen corrugated surface direction, namely $[001]_{Cu}$. In contrast to this, orientation (B) and (C) (contact plane (-411) and (-421), respectively) align their long molecular axes along $[1\text{-}10]_{Cu}$, which is perpendicular to the long molecular axes of orientation (A).
On the clean copper surface, also three orientations could be identified. Orientation (A) is following now the intrinsic corrugation of the pure copper surface, which is $[1\text{-}10]_{Cu}$, with an angular in-plane offset of about 5° from $[1\text{-}10]_{Cu}$. Orientation (B) was found in an equal orientation like on the stripe phase sample. Additionally, an upright standing orientation with contact plane (100) was found (orientation S).
The experimental results of both samples reveal, that orientation (B) grows identically on both substrates, therefore we conclude, that (B) grows on clean Cu(110). Orientation (A) aligns the long molecular axis along the oxygen rows on the stripe phase and along $[1\text{-}10]_{Cu}$ on the clean substrate. This implies the assumption, that (A) grows on the oxygen rows of the stripe phase surface. In principle we can say, that all lying orientations, namely (A), (B) and (C), grow along corrugated directions. The epitaxy of the crystal growth is dominated by the corrugation of the surface. It seems that the tilt of orientation (A) of about 5° in-plane symmetrically off $[1\text{-}10]_{Cu}$ is a consequence preferred alignment of 6T in the first monolayer.

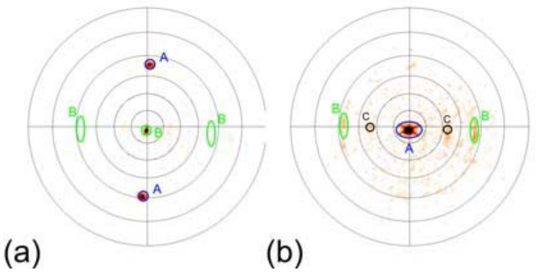

Figure 1. -411 polefigure (a) and 020 polefigure (b) of 6T on Cu(110)-(2x1)O stripe phase

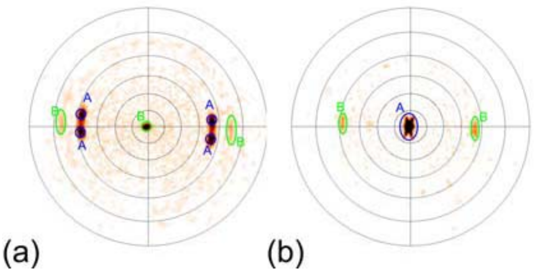

Figure 2. -411 polefigure (a) and 020 polefigure (b) of 6T on clean Cu(110)

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COHESIVE AND SURFACE ENERGIES OF ORGANIC MOLECULAR CRYSTALS

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The cohesive and surface energies of the oligo-acene, oligo-phenyl and oligo-thiophene series are computed. The calculations are performed using the pseudo-potential planewave code where different approximations for the exchange-correlation potential, i.e. the local density approximation (LDA) and the generalized gradient approximation (GGA), have been tested. We have computed surface energies for the (100), (010), (001), (110), and (1-10) planes in the acenes, phenylenes and thiophenes. Moreover the energies of experimental observed 6P high index (-312), (-302), (-211) and (-111) surfaces are calculated.

We demonstrate that GGA calculations for the cohesive energy can be corrected for the missing non-local correlations by adding an empirical formula taking care of van der Waals interactions. This leads to cohesive energies of oligo-acenes in good agreement with experiment, and shows that is a very promising approach for the calculation of cohesive energies and surface energies of organic molecular crystals.

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MOLECULAR ORGANIZATION: THE ROLE OF SUBSTRATE INTERACTION

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The significance of the interface chemistry on the structure of the first monolayer of adsorbed organic molecules is investigated by LT-STM (low temperature – scanning tunnelling microscopy), NEXAFS (near edge x-ray absorption fine structure) and ARUPS (angle resolved ultraviolet photoelectron spectroscopy). The influence of the surface chemistry is studied by means of the clean Cu(110), the oxygen reconstructed Cu(110) p(2x1)O (Cu-O) and the intermediate striped copper oxygen single crystal surfaces. The three different adsorption geometries of para-sexiphenyl (6P) that can be generated depend on the exact nature of the interaction with the substrate. On the fully reconstructed Cu-O surface the molecules are uniaxially oriented by the substrate, having a corrugation with weak chemical interactions. This leads to a perfectly ordered two-dimensional lattice whose formation is dominated by attractive intermolecular interactions. The resulting layer is a contracted 6P(20$\underline{3}$) bulk crystal plane which is modified due to the constraints of commensurability and only possible because of the flexibility of the Van der Waals interaction. To reach commensurability the 6P molecules are more densely packed on the Cu-O surface than in the bulk crystal structure, with the stress released by tilting the molecular planes. NEXAFS measurements could determine the different structures in the monolayer in terms of molecular tilt angles. On clean copper the molecules lie flat on the surface and align either parallel or perpendicular to the copper rows depending on whether there are Cu-O strings present on the Cu terraces or not. In contrast to the Cu-O surface, on clean copper a stronger chemical bond, involving backdonation from the substrate, is observed. This in turn results in repulsive intermolecular interactions and a quasi-ordered monolayer, reminiscent of a smectic liquid crystal phase. Finally, the registry of the molecules is determined and their diffusion barrier anisotropy probed with molecular manipulation.

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Adsorption of thiophene on Cu(110) and Cu(110)-(2x1)O

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Various oligomers have come up as potential candidates for both, electronic and opto-electronic devices like OFETs, OLEDs, *etc*. Such applications are usually based on thin films grown on top of metal substrates. Due to the anisotropy of these materials one of the major questions in this context is, how the molecules are arranged on the surface. From the theoretical point of view, mainly the bulk properties of oganic molecular crystals have been studied, while thin organic films, their terminations, and interfaces are hardly explored. In the present work, we perform density-functional calculations to study the relaxation and orientation of organic molecules on metallic surfaces. To this extent, we first investigate the relaxation of the pure Cu(110) and the Cu(110)-(2x1)O surfaces. In a next step, we study, how a molecule is adsorbed. In this presentation, we will mainly focus on thiophene, where the adsorption energy corresponding to various positions and orientations of the molecule is calculated on the search for the most favourable adsorption site. Thereby we focus on the role of the exchange-correlation potential including van der Waals interaction. We also address the question, how sensitively the adsoption energy depends on surface relaxation effects.

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Following self-organized growth of 6P thin Films by Low Energy Electron Microscopy

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Para-sexiphenyl (6P) is an important member of the group of small molecule optically active organic semiconductors that have shown a high potential for FETs and blue LEDs and lasers. For all these applications the control of molecular orientation as well as film morphology [1,2] and quality [3] is important. For light emitting or wave guiding applications, molecules with their long molecular axis parallel to the substrate are appropriate. This conformation is found in the -- for 6P typical -- needle or chain like morphology. Here, a Low Energy Electron Microscope (LEEM) was used to in situ follow the growth of 6P thin Films. As substrate $TiO_2(110)$-(1x1) was used. The substrate was selected because recent studies [1, 4] suggest complex and rather unexpected growth scenarios. For Films grown on TiO_2 a stripped Film morphology controlled by anisotropic diffusion has been found for high temperature growth. Low temperature growth leads to a morphology characterized by 1D needles. In situ growth investigations possible with LEEM should allow a deeper understanding of the processes involved.

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Morphologic characterization of organosilane self-assembled monolayers on SiO_2

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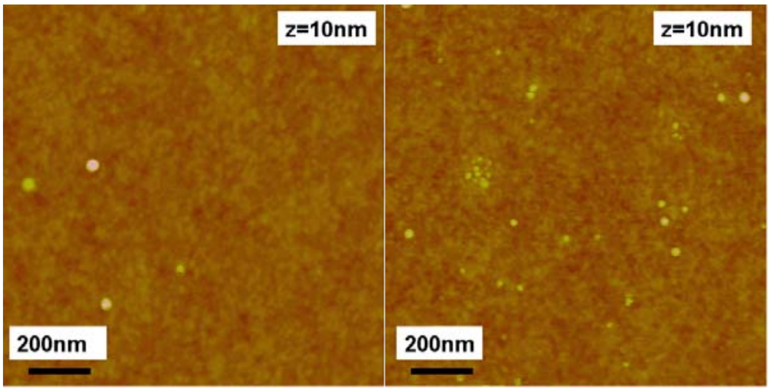
Abstract:

Self-assembled monolayers (SAMs) are molecular aggregates that are spontaneously formed by the adsorption of amphifunctional molecules on a solid surface. The smooth and robust monolayer where all molecules have the same orientation and conformation can serve as appropriate substrate layers for organic thin films. Since the SAMs end group can be tailored to have specific chemical properties, the wetting and the adsorption behavior of the surface can be controlled to allow the preparation of high quality organic devices. Here, we apply ex situ atomic force microscopy to study the surface morphology of organosilane SAMs deposited on silicon oxide substrate. An island-like structure (densely-packed molecular aggregates) of the SAM was observed and the thickness of the SAM could be measured. In addition Friction Force Measurements were used to obtain a material contrast between the substrate and the film.

Supported by Austrian Science Fund FWF National Research Network "Interface controlled and Functionalised Organic Films" (S9707-N08)



1 µm AFM images showing a CSTS (rms=0.2 nm) and a PFDTS SAM (rms=0.3 nm)

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Rubrene Epitaxial Layers for Organic TFT's Grown by Hot Wall Epitaxy

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I will report on my Ph.D.project that has been done during the last six months which included constructing a new hot wall epitaxy equipment and purifying of rubrene ($C_{42}H_{28}$). My future work is to continue constructing the equipment and starting to evaporate rubrene which has been choosen as an organic material to fabricate thin film transistors (TFTs). Further more I plan to apply an electric field to the mica substrate to influence the orientation of the rubrene molcules during deposition. I plan to examine diffirent kinds of substrates and dielectric materials to obtain a good characteristrics of TFT.
I will show also state of the art concerning rubrene TFTs:

a) Rubrene single crystals were used to fabricate FET by applying the air-gap field-effect technique. Intrinsic (not limited by statistic disorder) polaronic transport was realized on the surface of rubrene crystals over a wide temperature range. The signatures of this intrinsic transport are the anisotropy of the carrier mobility and the growth of carrier mobility (μ) with cooling. Anisotropy of μ vanishes in the activation regime at low temperatures, where the transport is dominated by shallow traps.

b)The growth of well-oriented crystalline films of rubrene on SiO_2 and Au(111) substrates was achieved by employing ''hot wall'' deposition whereas organic molecular beam deposition (OMBD) only yields rather amorphous layers or poly-crystalline dendritic networks at elevated temperatures. This pronounced difference in film growth is related to the conformational change of rubrene molecules involving a loss of chirality upon crystallization and the enhanced diffusion which becomes possible at high temperature and large vapor pressure. Moreover, it was demonstrated that the crystalline rubrene films reveal an enhanced thermal and chemical stability as compared to the OMBD grown films.

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ORIENTED GROWTH OF ORGANIC FILMS ONTO ALIGNED PTFE SURFACE

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Aligned layers were prepared by evaporation of polytetrafluoroethylene (PTFE) in vacuum with subsequent rubbing by a cloth [1]. Films of pentacene (PN), 5,5`-di(9,9`-di-(butyl)-fluorene')-2,2`-bithiophene (DBFBT) and several squaraine dyes (SQ) were deposited onto PTFE layers using evaporation in vacuum. SQ compounds both methyl and ethyl substituted formed oriented films with a dichroic ratio of about 5. PN and DBFBT also revealed oriented growth on PTFE layer. The elevation of substrate temperature from 20^0C to 75^0C increased film ordering. The PTFE film with the highest surface ridges (and grooves) led to the smallest degree of ordering. Methyl-substituted OHSQ revealed second harmonic generation [2], while ethyl-substituted SQ and SQ without OH groups have no SHG.

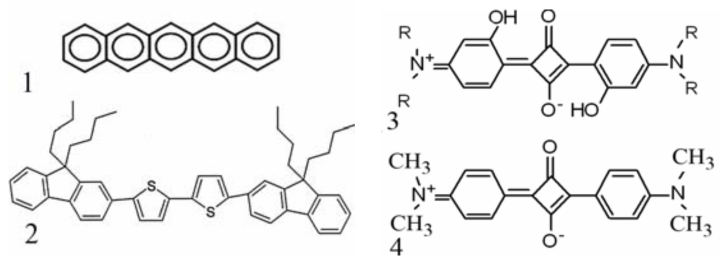

Figure 1. Chemical structure: 1 - PN, 2 – DBFBT, 3 - squaraine dye with OH-groups, where R – were methyl and ethyl groups, 4 - squaraine dye without OH-groups with methyl groups.

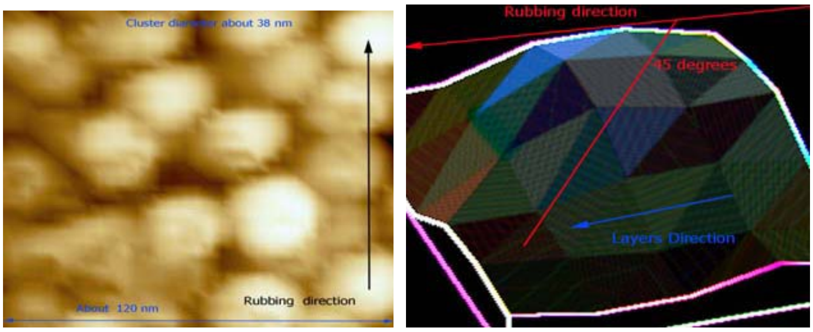

Figure 2. AFM images of the OHSQ surface, grown on the PTFE aligned layer.

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Theoretical studies on an organic/metal interface: CO on Cu(111)

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The energetic and physical properties of metal/organic interfaces are of high interest for the understanding of molecular monolayer formation, work function modification and injection barrier tuning in electronic devices.

On the poster, we study the chemisorption of CO on Cu(111) using the band structure code VASP, which is a plane-wave based density functional theory method.

We investigated the work function modification, the charge rearrangement and the formation of dipole layers for the CO molecule in the on-top and hcp hollow site (Figure 1).

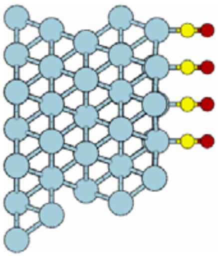

Figure 1: Geometry of on top adsorbed CO on Cu(111)

Furthermore, we show which molecular levels are involved in the interactions between Cu(111) and CO. The nature of the chemical bond is investigated in terms of forward and back donation.

Finally the packing density is varied, which allows an investigation of the depolarization effects occurring at the interface.

FUNDAMENTAL ASPECTS OF OLIGO-PHENYLEN ADSORPTION AND THIN FILM LAYER GROWTH ON GOLD SURFACES

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In this contribution we present a comprehensive experimental study on the adsorption of p-quaterphenyl and p-sexiphenyl on gold surfaces. In particular, we focus on the correlation between the monolayer structure and energetics and the multilayer structure and morphology. We demonstrate that the organic thin films can be intentionally tailored by the geometry and the chemical composition of the substrate. Most investigations were performed on the Au(111) surface, but re-crystallized gold foils were also used as substrates, which offer a convenient way to study the influence of different substrate geometries in parallel. With respect to surface impurities the influence of carbon on the film growth will be discussed. For the investigations of the submonolayer, monolayer and ultra-thin multilayer films we have applied thermal desorption spectroscopy (TDS), low energy electron spectroscopy (LEED) and X-ray photo electron spectroscopy (XPS). For thicker films (up to 30 nm) we have additionally applied XRD, SEM, AFM and NEXAFS. This made it possible to obtain a quite complete understanding of the interface between the substrates and the oligo-phenylen films.

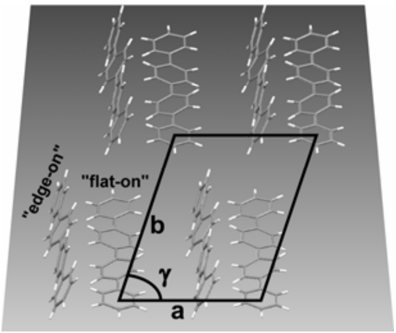

Fig.1 Molecular packing of p-quaterphenyl on Au(111)

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Thin films of sexithiophene on Ag(100)and Au(111) -- a combined STM and LEED study

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In the fast growing field of molecular electronics huge progress has been achieved over the last years. However, many aspects regarding the growth mode of the first organic layers on metal and oxide substrates and their interface structure are still unclear and need to be clarified in order to better understand and improve the contact conditions and the properties of thin film devices.

Variable temperature scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) have been used to study the morphology of the first few monolayers of α-sexithiophene (6T) on Ag(100) and Au(111)at room and elevated temperatures. The 6T molecules have been sublimated onto the surfaces from a homebuilt Knudsen cell at a base pressure of 1 x 10^{-10}mbar.

STM images with sub molecular resolution reveal long range ordered domains of flat lying molecules on both substrates with domain diameters up to 100 nm. On Ag(100) five different structures have been observed depending on the coverage, whereas on Au(111) only one dominant structure shows up in STM and LEED.

As 6T molecules are chiral upon adsorption on a surface, in all but one structure chiral self recognition leads to homochiral domains. Either left or right handed molecules form parallel rows of close packed molecules. The superstructures will be discussed in the context of point on line arrangement of the adlayer. Three domains, one on Au (111) and two on Ag(100), are represented by unit cells with a single molecule, another one consists of paired molecules leading to two molecules per unit cell. Only one heterochiral domain structure with four molecules in the unit cell is found on the Ag(100) surfaces. The molecules form left or right handed pairs that arrange in rows of alternating chirality. Most remarkably this structure is connected with a cis-trans isomerisation of all molecules between the second and third thiophene ring .

On Au(111) additionally to the molecular superstructures the interaction between adsorbed molecules and substrate becomes visible, as the herringbone reconstruction of the clean surface is still visible at monolayer coverage and appears to be stretched by about 9 % with respect to the clean surface.

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