Organic Electronic Materials Topical Conference
Room 327 - Session OE+B+EM-TuA

Organic Thin Film Growth
Moderator: N. Karl, Universität Stuttgart, Germany

2:00pm OE+B+EM-TuA1 Structural Characterization of Organic Overlayers Physisorbed on the Surface of Self-Assembled Monolayers (SAMs) of Alkanothiols on Au(111), P. Schwartz, D.J. Lavrich, M.C. Gerstenberg, G. Scoles, Princeton University

INVITED
We have been able to grow well-ordered crystalline monolayers of alkylthiols, and multilayers of dodecanethiol on the surface of alkanethiol SAMs by exposing the surface of the c(4x2) phase of the SAM to the appropriate amount of flux at carefully controlled temperatures. Low energy diffraction shows that all but one of the overlayers proved to be considerably more ordered than the underlying c(4x2) surface as judged by the specular and diffraction peak intensities. While the surfaces of the dodecanethiol overlayers have the same structure whether grown on a C@sub 11@SH or C@sub 10@SH c(4x2), monolayers of C@sub 10@SH on a C@sub 11@SH c(4x2) surface were distinctly different from and of higher quality than monolayers of C@sub 11@SH on a C@sub 11@SH c(4x2) surface. Debye Waller measurements reveal that, besides improving the overall order of the surface, an overlayer has a stiffer surface than the underlying c(4x2) that supports it. Temperature Programmed Desorption experiments have shown that, although the adsorption energy of organic molecules on a gold surface is much greater than that of the bulk heat of vaporization, the adsorption energy of an overlayer on an organic substrate is similar to the bulk value of the overlayer substance as soon as the metal-overlayer distance is greater than 5 Å. To the best of our knowledge, this is the first time that, making use of the great surface specificity of low energy atomic scattering, organic monolayers are structurally characterized after adsorption on an organic substrate of different structure.

2:40pm OE+B+EM-TuA3 Influence of Lattice Misfit on Morphology of Vanadyl-Phthalocyanine Epitaxial Thin Films and Their Growth Mechanisms, S. Nakao, H. Hoshi, K. Ishikawa, H. Takezoe, Tokyo Institute of Technology, Japan

In organic molecular beam epitaxy (MBE) process, the lattice matching condition has been considered not so critical for the epitaxial growth because of the weak interaction between organic molecules and substrates. In fact, however, the morphology of the MBE films depends on the species of substrates. Hence the systematic study for the parameters affecting the MBE growth is required. In this paper, we first demonstrate the influence of lattice misfit on the morphology of vanadyl-phthalocyanine (VOPc) MBE films on alkali-halide (AH) substrates. Substrates with continuously varied lattice constants were prepared by using KCl/KBr mixed crystals, supplying the positive and negative lattice misfit. The domain size of the VOPc MBE film becomes larger as the lattice misfit becomes smaller. This fact indicates that the lattice misfit plays an important roll in organic MBE processes and the smooth large domain could be grown under the zero-misfit condition. We also discuss the growth mechanism in the same system. The reflection high energy electron diffraction (RHEED) study showed that the lattice of the VOPc films is commensurate with that of the substrate in spite of large lattice misfit up to 5%, and then rapidly relaxes to the stable lattice constant independent of lattice misfit. More detailed study of the growth process clarified that the process takes two steps; The 2-dimensional [2-0] tetragonal lattice grows at first and the 3-D monoclinic domains nucleate and grow from the edge of the first layer when the first layer reaches a certain height defined by the lattice misfit. This two-step growth process is thought to be typical in MBE growth of VOPc on AH substrates.

3:00pm OE+B+EM-TuA4 Preferential Orientation of Copper Phthalocyanine Molecular Columns on Vicinal Si(001)-(2x1)-H, M. Nakamura, IRCAT-ATP, Japan; T. Matsunobe, Toray Research Center, Inc., Japan; H. Tokumoto, IRCAT-NAIR, Japan

Fabrication of Pd films on silicon substrates has an advantage in terms of having electrical interfaces with silicon devices. Furthermore, it is a great scientific interest to study organic film growth on various atomically controlled surfaces utilizing well established methods to prepare clean silicon surfaces with a chemical passivation by hydrogen. In our previous work @footnote 1@ we investigated the molecular arrangement of CuPc films on atomically flat Si(001)-(2x1)-H. Atomic force microscopy (AFM) showed that the molecular column laid parallel to the surface, and the

orientational angle between the column and the substrate directions was around 17°. The angle was also supported by molecular mechanics (MM) simulations using simple atom-atom van der Waals potentials. The results suggested that the CuPc crystals were placed so as to make the linear corrugation of the surface parallel to the substrate H rows, although their periods were still incommensurate with each other. In this work, we therefore used vicinal Si(001)-(2x1)-H as substrates which contain atomic steps of approximately 4 nm period to further control the in-plane orientation. A continuous film of which thickness was distributed within 16±2.5 molecular layers was grown at 60°C. 90% of the molecular columns in the film were estimated to be aligned to across the step rows by observing a frictional force image. The preferential orientation is considered to be due to a kind of artificial surface lattices which are formed with the striped ‘effective contact area’ between the rigid Pd crystals and the vicinal surfaces. Detailed discussions and optical property of the films will be presented. @footnote@<br />&nbsp;&nbsp;&nbsp;&nbsp;@footnote 1@M. Nakamura and H. Tokumoto, Surf. Sci. 398 (1998) 143.


There is a growing interest in new organic materials with large second order hyperpolarizabilities, β, for use in nonlinear optical (NLO) devices. In particular, small organic-molecule salts can exhibit very large β, due to their non-centrosymmetric crystal structure. The organometallic charge-transfer salt DAST is an ideally suited material for NLO device applications, having a large electro-optic (EO) coefficient and low dielectric constants, which eventuate in a high figure of merit. Thin films of DAST with very long-range structural ordering were grown by organic vapor phase deposition (OVPD). In this technique vapor transported precursors of the stibazole and methyl-tosylate combine on a substrate in the heated zone of a low pressure, hot wall reactor. This method enables the stoichiometric growth of polar, multiple-component compounds with highly incongruent vapor pressures, which cannot be otherwise deposited by vacuum evaporation. The DAST films were grown on amorphous TiO2 substrates, which was patterned on thermally oxidized [111] Si wafers. The films exhibit very long-range structural ordering, limited only by substrate size. The strong azimudal dependence of the relative second harmonic generation (SHG) efficiencies, together with polarized microscopy studies indicate that the structural ordering extends typically ~2 cm across the substrate surface. Using x-ray diffraction we have identified the films as consisting of the SHG-active crystalline phase of DAST belonging to the monoclinic space group Cc, with a well-defined [001] orientation with respect to the substrate normal. Such very long-range crystalline order is a prerequisite for realizing high-performance, low-loss NLO devices.


Scanning tunneling microscopy (STM) has been used to investigate self-assembled film formation of molecules in single and varied compositions of alkanethiols on Au(111). While the average surface composition of these films typically reflects that of the deposition solution, STM is used to determine the position and motion of these molecules on the surface. We also use STM to measure electron transport through these molecules to ascertain the roles of chain length and chemical contact with the substrate. We discuss how spacer molecules such as adamantane-thiol (C10H15SH) can be used to isolate other molecules for such studies. Our investigation of this system shows that ordered films can be produced from such molecules for this purpose. Unlike alkanethiolate films, this produces structural domain boundaries and other defects that do not involve significant conformation relaxation. In our studies we focus on the modification of self-assembled surfaces to tailor the films to our needs. Our growing abilities to control the placement of molecules within these films are presented.


Control of the molecular-scale structure of multi-component self-assembled of organic thiols on Au(111) can be achieved by selecting a combination of deposition and processing techniques. These include competitive adsorption (growth) and subsequent exchange (modification). The effects of this processing on the molecular-scale structure have been
studied by conventional and AC scanning tunneling microscopy. Lateral epitaxy has been observed where a growing domain of one molecular species is grafted onto an existing crystalline lattice of a different molecular species with no lattice mismatch. In other examples, the limited substrate access afforded by structural defects in the films has been utilized to insert single molecules for further use or study. We also use these mixed composition monolayers to gain insight into the mechanism by which these films can be imaged and the extent to which organic molecules conduct. By analyzing images and local spectra of isolated and aggregated molecules, we can determine the extent to which neighboring molecules contribute to these processes. We believe that none of the structures we obtain are equilibrium structures. We discuss relevant considerations for stabilizing the nanometer-scale structures created.


We present results from a grazing incidence X-ray diffraction study of 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) films deposited on self-assembled monolayers (SAMs) of either decanethiols or 1,6 hexanethiols on Au(111). The aim is to study the effect of changes at the organic-organic interface on the in-plane ordering of PTCDA and the SAM. Changing the number of chemisorbed Sulphur (S) atoms in the layer between the PTCDA and the metallic substrate is of interest in view of the importance of the charge injecting properties of the organic-inorganic interface in organic semiconductor devices. PTCDA is one of the most thoroughly studied van der Waals epitaxial systems. It has previously been shown that under non-equilibrium growth conditions (high incident flux of PTCDA and low substrate temperature) PTCDA layers order parallel to the Au(111) substrate with a well-defined in-plane structure in registry with the underlying substrate. Under the same conditions our first measurements have indicated an unaltered PTCDA in-plane ordering on both thiol SAMs. However, the orientation of the PTCDA in-plane structure changes with respect to the Au surface in both cases. No change in the ordering of the thiols was observed as the PTCDA was deposited. The confined full coverage c(4x2) layer of decanethiols melts at higher temperatures than the unconfined SAM. With melting, the order of the SAM was lost and was not fully recovered upon cooling. However, no significant change was seen in either the out-of-plane or in-plane scattering of PTCDA.

4:40pm OE+Bi+EM-TuA9 The Adsorption of azo Compounds on Si(001), M.D. Ellison, R.J. Hamers, University of Wisconsin, Madison

Recent investigations have demonstrated that unsaturated organic compounds can bond to the Si(001) surface by interaction of the C=C bond with the Si=Si dimers, forming a 4-member Si@sub 2@C@sub 2@ ring at the interface. We have investigated whether analogous reactions can be used to link azo bonds (N=N) to the Si(001) surface using XPS, FTIR, STM, and ab initio calculations. The experimental evidence indicates that the unsaturated N=N bond reacts with a Si=Si dimer in an analogous fashion to a [2+2] cycloaddition reaction, forming a 4-member Si@sub 2@N@sub 2@ ring. Although the thermal [2+2] reaction is forbidden by symmetry considerations, this and other studies have shown the reaction of unsaturated bonds with the Si(001) surface to be quite facile. The facility and selectivity of this reaction reveals the potential of azo compounds to be used in creating ordered organic layers on a Si(001) surface.
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