

IV-G Electrical Properties of Organic Semiconductors in Ultrahigh Vacuum

The mechanism of carrier transport in organic semiconductors and carrier injection from metal electrodes becomes the most important subject to be elucidated for high performance organic thin film devices. The electrical properties are modified easily by adsorbed gas molecules, which makes it difficult to obtain reliable experimental results. We have studied intrinsic properties under ultrahigh vacuum conditions to strip away the veil of oxygen.

IV-G-1 Quasi-Intrinsic Semiconducting State of Titanyl-phthalocyanine Films Obtained under Ultrahigh Vacuum Conditions

TADA, Hirokazu; TOUDA, Hiroshi¹; TAKADA, Masaki¹; MATSUSHIGE, Kazumi¹
(¹Kyoto Univ.)

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We investigated electrical properties of titanyl-phthalocyanine (TiOPc) films under ultrahigh vacuum (UHV) conditions to avoid the influence of gas adsorption. The field-effect measurement revealed that TiOPc films exhibited an n-type semiconducting behavior in UHV. The electron mobility at room temperature was $9 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with activation energy of 0.20 eV. The conductivity and carrier density were $9 \times 10^{-8} \text{ Scm}^{-1}$ and $6 \times 10^{16} \text{ cm}^{-3}$, respectively. A clear conversion from n-type to p-type behavior was observed when the film was exposed to oxygen. Strict control of atmosphere made it possible to obtain a quasi-intrinsic state where both p- and n-type conduction appeared simultaneously (Figure 1).

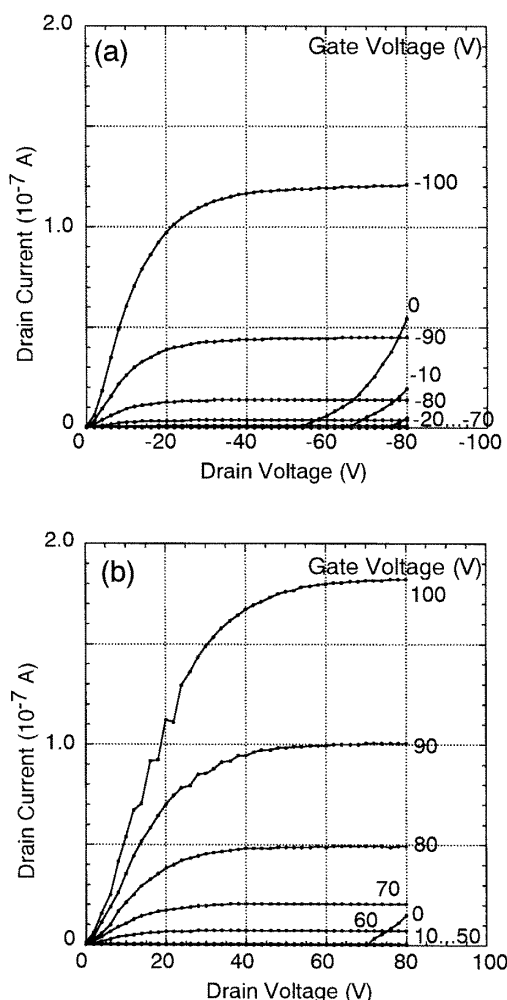


Figure 1. Field-effect transistor characteristics of a TiOPc film measured in a well-controlled atmosphere. Both (a) p-type and (b) n-type conduction appeared simultaneously.

IV-H Preparation and Characterization of Highly Oriented Organic Films

Preparation of ordered and highly-oriented films of organic materials is one of the most promising way not only to improve the characteristics of organic opto-electronic devices such as light emitting diodes, chemical sensors and field effect transistors, but also to study the mechanism of carrier transport and energy transfer in molecular systems. We have established the method of preparation of highly-oriented films on various substrates and studied the correlation between film structure and optical and electrical properties.

IV-H-1 Substrate-Induced Order and Multilayer Epitaxial Growth of Substituted Phthalocyanine Thin Films

SCHLETTWEIN, Derck¹; TADA, Hirokazu; MASHIKO, Shinro²
(¹Bremen Univ.; ²CRL)

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Thin films of hexadecafluorophthalocyaninatooxovanadium ($F_{16}PcVO$) are vapor-deposited under organic molecular beam epitaxy (OMBE) conditions on the (100) surfaces of NaCl, KCl, and KBr and on quartz glass. Beginning at submonolayer coverages and extending to a film thickness of several tens of nanometers the film structure is determined in situ by reflection high energy electron diffraction (RHEED). Following deposition the film morphology is characterized by tapping mode atomic force microscopy (AFM) and chromophore coupling of the molecules within the films is studied by optical absorption spectroscopy. Highly ordered growth of crystalline domains of $F_{16}PcVO$ with dimensions in the micrometer range leading to films of quite uniform thickness is observed. On KBr a commensurate square lattice is seen in RHEED of the first monolayers with the molecules parallel to the substrate surface which is also preserved at higher film thickness. On KCl a surface lattice of the same size is formed which is, however, understood as a result of point-on-line coincidence. Diffraction of transmitted electrons yield a constant three-dimensional crystal structure of the films on KBr and KCl with a tetragonal unit cell of $a = b = 1.47$ nm and $c = 0.62$ nm. On NaCl with its smaller lattice constant no ordered relative orientation is possible and hence an increased part of the film appears amorphous. On quartz glass on the other hand, ordered films are formed with the molecular plane predominantly oriented cofacially parallel to each other and vertical to the surface. Calculations of molecular mechanics as well as of periodic surface potentials are performed to support the proposed structures and to discuss the crystallization in thin films of phthalocyanines and related materials.

IV-H-2 Ordered Growth of Substituted Phthalocyanine Thin Films: Hexadecafluorophthalocyaninatozinc on Alkali Halide (100) and Microstructured Si Surfaces

SCHLETTWEIN, Derck¹; HESSE, Karsten¹; TADA, Hirokazu; MASHIKO, Shinro²; STORM, Uwe¹; BINDER, Joseph¹
(¹Bremen Univ.; ²CRL)

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Physical vapor deposition of hexadecafluorophthalocyaninatozinc ($F_{16}PcZn$) is performed under UHV conditions from monolayer coverages to an average thickness of about 20 nm on the (100) surfaces of NaCl, KCl, and KBr and on quartz glass as well as on microstructured interdigitated electrode arrays on amorphous SiO_2 . UV-vis absorption spectroscopy indicates stacks of cofacial parallel molecules for thin films on SiO_2 and NaCl, whereas a component typical for a head-to-tail arrangement of molecules is detected on KCl and KBr. Atomic force microscopy shows well-defined crystals oriented in a defined azimuth angle relative to the substrate lattice on KCl and KBr, indicating a growth in molecular square lattices parallel to the substrate surface which is confirmed by molecular

mechanics and periodic surface potential calculations. Plateaus of molecules predominantly standing upright on the surface are seen for the films on NaCl and SiO_2 which is confirmed by the relative intensity of optical absorptions and by the electrical conductivity changes observed during growth on SiO_2 . The temperature dependence of the electrical conductivity of films on SiO_2 yields an increase of the thermal activation energy around 200 °C corresponding to a loss in spectral fine structure. A clear correlation is seen between film structure and electrical as well as optical properties of molecular semiconductor thin films.

IV-H-3 Energy Transfer in Highly Oriented Permethyl-Dodecasilane and -Octadecasilane Films

TADA, Hirokazu; TOJO, Tomoaki¹; KAKO, Masahiro²; NAKADAIRA, Yasuhiro²; MATSUSHIGE, Kazumi¹
(¹Kyoto Univ.; ²Univ. Electro-Commun.)

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Heterostructured films of permethyl-dodecasilane (DM12) and permethyl-octadecasilane (DM18) were prepared on silicon and fused quartz plates under ultrahigh vacuum conditions and the films were characterized by optical absorption and photoluminescence spectroscopy, and atomic force microscopy. The molecules were found to form highly oriented films in a layer-by-layer growth mode with their molecular chains perpendicular to the substrate surface. Moreover it was found on the basis of optical measurement that the energy transfer progressed effectively from the optically excited state of DM12 generated by the $\sigma-\sigma^*$ one-electron transition to that of DM18 through the interface between the layers.