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InSb–TiOPc interfaces: Band alignment, ordering and structure dependent HOMO splitting

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ABSTRACT

Thin films of titanyl phthalocyanine (TiOPc) have been adsorbed on InSb(1 1 1) (3 × 3) and InSb(1 0 0) *c*(8 × 2) surfaces and studied with respect to their electronic structure using photoemission (PES), density functional theory (DFT) and scanning tunneling microscopy (STM). The interface chemical interaction is weak in both cases; no adsorbate induced surface band bending is observed and the energy level alignment across the interface is determined by the original position of the substrate Fermi level and the charge neutrality level of the molecule.

Room temperature adsorption results in disordered films on both surfaces. The behaviors after annealing are different; on InSb(1 0 0) well-ordered molecular chains form along and on top of the In-rows, whereas on (1 1 1) no long range order is observed. The disorder leads to intermolecular interactions between the titanyl group and neighboring benzene rings leading to a split of TiOPc HOMO (highest occupied molecular orbital) by as much as 0.8 eV.

1. Introduction

Phthalocyanines (Pc) are used in organic opto-electronics devices, organic light emitting devices (OLED), field effect transistors, photovoltaics and also as dye in dye-sensitized nano structured solar cells [1–17]. Pc are chemically and thermally stable, and can appear both as p-type and n-type semiconductors with properties that depend on the chemical structure in the molecular centre and periphery. In technical applications the interface quality and structure is crucial for optimum device performance. Atomic structure, chemical abruptness and energy level alignment at interfaces play key roles on electronic transport properties. Much work has been performed on the (1 0 0) surfaces of InAs and InSb [18–20] in part thanks to their surface reconstruction with long atomic lines along the surface separated by 16–18 Å [21], which may be utilized as templates for one dimensional ordering. Fewer studies are found on (1 1 1) surfaces of these materials. However, both H_2Pc and CuPc are known to form nice ordered layers on InSb(1 1 1)A and InAs(1 1 1)A where a $(\sqrt{12} \times \sqrt{12})R30^\circ$ reconstruction is found for the first ML on both surfaces [22,23]. The band alignment of thin CuPc layers grown on InSb(1 1 1)A, displayed a nested arrangement with the molecular band gap surrounding the substrate band gap, with the substrate Fermi level (E_F) 0.2 eV up in the conduction band and the HOMO 1.19 eV below E_F [24].

Titanyl phthalocyanine (TiOPc) is pyramid-shaped molecule with an oxygen in the apex and a concave base plane consisting of the organic ring. The Ti is positioned between the phthalocyanine centre and the oxygen [25]. The partly ionic Ti–O bond results in a 1.8 D electric dipole [26]. TiOPc is a semiconductor that changes from n-type to p-type upon oxygen exposure, making it useful in gas sensing applications [27–29]. The electronic properties of TiOPc have been investigated previously using ultraviolet photoelectron spectroscopy (UPS) [26,28,30], X-ray absorption and emission spectroscopy [31,32] and resonant photoelectron spectroscopy [33]. On weakly interacting substrates such as highly oriented pyrolytic graphite (HOPG) TiOPc adsorb in bi-layer islands, with the oxygen pointing towards the bi-layer centre [34]. Prolonged thermal treatment can, at least up to one monolayer (ML), redistribute the adsorbate to a single layer with oxygen atoms facing outward evidenced by UPS and Penning ionization electron spectroscopy investigations. Upon further deposition the bi-layer forms again [35–37]. The different organisations lead to a splitting of the HOMO by 0.21 eV [30].

On ZnO(0 0 0 1), ordered adsorption was found in low energy electron diffraction (LEED) where a 1 × 1 pattern from the clean surface is changed to a 2 × 1 pattern upon exposure to TiOPc

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[38]. The observed splitting of HOMO by ~0.8 eV was assigned to different adsorption geometries on the surface. The Fermi level was pinned by the LUMO giving rise to a 0.5 eV up-ward band bending at the surface, determined from the shift of the O1s bulk component [38].

In this paper we study surface order and energy level alignment in a weakly interacting system; TiOPc films grown on two different InSb surfaces using photoelectron spectroscopy (PES), density functional theory (DFT) and scanning tunneling microscopy (STM).

2. Experimental

The STM measurements were performed using an Omicron VT-STM in constant current mode at room temperature. The STM chamber also houses LEED optics, sample cleaning and the phthalocyanine source. An electrochemically etched tungsten tip was used and positive bias corresponds to tunneling into empty surface states. Calibration of the STM-images were done by measuring the distance between adjacent In-rows in the [1 1 0] direction; 18.3 Å.

Photoelectron spectroscopy experiments were performed at beam line I511 at MAX-lab in Sweden. I511 is an undulator-based beam line equipped with a Scienta SES-200 hemispherical electron analyzer, rotatable around the axis of the photon beam. The photon energy ranges from 100 to 1200 eV. In connection with the photoemission chamber is a preparation chamber equipped with LEED, mass spectrometer, sample cleaning and evaporation cell. Details of the I511 set-up have been presented previously [39]. The core level spectra were recorded at room temperature, in normal emission and grazing incidence (approximately 80° off-normal) of the photons. The resolution of the PE spectra was better than 170 meV for N1s, 100 meV for C1s and ~30 meV for In4d, Sb4d and valence band spectra. All spectra are intensity normalized to the background. The Fermi level, measured on a Ta foil in electric contact with the sample, was used as binding energy reference. The core levels are analyzed by a curve fitting procedure using Voigt functions and a Shirley background. In order to avoid beam damage in the organic thin film, the sample was scanned during exposure to the synchrotron light.

InSb(1 1 1)B samples were cut from n-type (Te 2.3–3.6 × 10^{15} cm^{-3}) wafers, oriented to ±0.1° off the (1 1 1) plane, supplied by Wafer Tech. Ltd., UK. In order to prepare a well-defined (3 × 3) reconstructed surface, the samples were Ar^+ sputtered for several cycles with subsequent annealing to 600–700 K. This treatment resulted in large terraces and a sharp (3 × 3) LEED pattern. InSb(1 0 0) samples were cut from undoped wafers supplied by Wafer Tech. Ltd., UK. The samples were repeatedly Ar^+-sputtered and annealed to about 675 K until a sharp $c(8 \times 2)$ LEED pattern was obtained. This procedure resulted in a clean and well-ordered surface with several hundred nanometres wide terraces as seen in STM.

A home-made Knudsen-type cell consisting of a quartz tube resistively heated by a W wire was used to evaporate TiOPc, purchased from Sigma–Aldrich at 95% purity. The powder was used after thorough outgassing for several hours in front of a mass spectrometer until the levels of impurities (mainly water) had decreased below the detection limit. A thermocouple was attached to the outside of the crucible to monitor the temperature.

Determination of surface coverage in the photoemission experiments is done by comparing the intensity of the C1s and substrate core levels with other similar systems measured at the same beamline [20,38,40], together with the attenuation of the substrate Sb4d core level intensity below an approximately 10 Å thick film (~5 ML). The In4d signal is obscured by the appearance of molecular orbitals in the same binding energy region, and cannot be used for this purpose. In the STM experiments the coverage (at low coverage) was estimated from the surface area covered and the measured thickness of the molecular film.

3. Theoretical methods

Calculations were performed using Gaussian 03 [41] code at the DFT level and employing the hybrid functional B3LYP [42], with the double *z* with polarization 6-31G(d, p) basis set. The dimer structures (A and B in Fig. 7) were geometry optimized, while the structure C was chosen to model a disordered adsorption. The density of states obtained for the three dimers were convoluted with a Gaussian profile of 1.0 eV to simplify the comparison with the experimental results. We also report DOS convoluted with a 0.05 eV Gaussian to highlight the single features.

4. Results and discussion

After room temperature deposition of TiOPc on InSb(1 0 0) no long range order was observed with STM. However, annealing at ~600 K improves the order drastically, as shown in Fig. 1a (430 × 225 Å^2) and Fig. 1b (2030 × 1020 Å^2). Both images are from the same preparation (initial coverage ~1 ML) and recorded at −3.0 V and 37 pA. Molecular lines grow along the substrate, centred on-top of the In-rows, in agreement with other Pc's on this surface [18–20,43]. These lines are up to several hundred nanometres long, typically one molecule high (2.2 Å), but frequently decorated by additional molecules (4.5 Å height above the first layer molecules). This height could be due to double layer adsorption or adsorption with the molecular plane tilted with respect to the surface plane. Often, but not always, these second layer molecules appear smaller (in width) than the first layer molecule, thus indicating a tilted adsorption. Although the preferred adsorption site is on the indium rows, it is not possible to tell whether the molecules adsorb oxygen-up or oxygen-down. We can only resolve the typical [18–20,43] four-leaf clover like structure, which is due to tunneling from the outer benzene rings of the molecule.

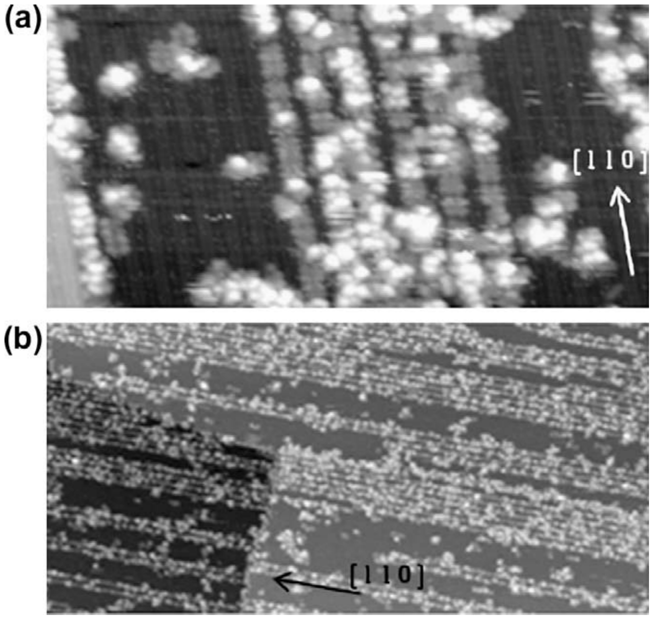

Fig. 1. STM-images of TiOPc on InSb(1 0 0) $c(8 \times 2)$ after annealing to 600 K in (a) 430 × 225 Å^2, −3.0 V, 37 pA and (b) 2030 × 1020 Å^2, −3.0 V, 37 pA. Molecular lines grow along the In-rows of the substrate. Note that the scan direction in the two images is rotated with respect to each other.