



Photoemission study of copper phthalocyanine growth on hydrogen-terminated surface: Si(100)2 × 1–H



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ABSTRACT

Copper phthalocyanine molecules have grown at room temperature under ultra high vacuum on hydrogen-terminated surface Si(100)2 × 1–H. Chemical and electronic properties of the interface were investigated by ultraviolet and X-ray photoemission spectroscopy (UPS, XPS).

Results: Results indicated the existence of an interfacial dipole of 0.36 ± 0.05 eV and a band bending of 0.40 ± 0.05 eV. These were evidenced by shifts of XPS core levels and change of the vacuum level position. During the growth, the work function was found to decrease from 4.5 eV for the substrate to 3.74 eV for the highest coverage (40 monolayers). This band bending was also due to the shift of the highest occupied molecular orbital.

The interfacial dipole was correlated to a rearrangement of molecules on the surface. An energy level diagram of the interface was deduced from a combination of the XPS and UPS results.

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1. Introduction

Metal phthalocyanines (MePcs'), p-type semiconducting organic molecules, due to their high thermal and chemical stabilities (suitable for thin film preparation [1,2]), have become an important material widely used in optical and electronic device technology. They are used to fabricate light emitting diodes [3], organic field effect transistors [4,5] and organic photovoltaic cells [6]. Recently, the attention has been focused on the fabrication of the transistors based on the copper phthalocyanine (CuPc) thin films, one of the most popular phthalocyanines and crystalline silicon (Si) as a substrate which acts as the insulating layer between the bottom electrode and the active organic semiconducting film on top [7,8].

The range of possible applications of organic electronic devices is strongly dependent on the interfaces between the active organic layer and the substrate or electrodes. Therefore, the understanding of the interface's electronic properties has become important due to their role in the injection of carriers into the organic layer. Many of the studies concerning this topic concentrate on organic-on-metal systems. For example, at the CuPc/Au interface, strong shifts of all electronic levels are present for the early stages of CuPc deposition on Au [9]. Consequently a large interface dipole is present having a value of 1.2 eV. The authors also suggest the presence of band bending. On the other hand, for the CuPc/GeS(110) interface no band bending is present and the determined interface dipole has a value of 0.5 eV.

Gorgoi and Zahn [10] studied the interface formation between CuPc and H–Si(111) and suggest the presence of interface dipole = 0.34 eV and band bending due to the shift (0.4 eV) of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) peaks. They attributed this shift to the rearrangement of molecules on the surface. L. Grzadziel et al., by a photoemission study on Si(111)-native SiO₂/CuPc ultra thin film interface, have deduced the existence of a small interface dipole due to a continuous change of CuPc molecule orientation [11].

In this paper, we focus on X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) studies of the interface formation between CuPc and H–Si(100)2 × 1 as a function of film thickness.

2. Experimental details

Experiments were conducted in an ultra-high vacuum (UHV) system from Omicron Instruments. The sample can be transferred in UHV between a preparation chamber and the analysis chamber equipped with electron and X-ray sources and a hemi-spherical analyzer. The base pressure of the analysis chamber was typically 1×10^{-8} Pa. The sample was single crystal cut from a Si(100) wafer: n-type P-doped with an electron concentration of 10^{15} cm⁻³ and supplied by Siltronix SA. It was cut into stripes with a dimension of 15 mm × 30 mm, then it was degreased with acetone in an ultrasonic bath, rinsed with ethanol and then dried with azote gas. The cut silicon stripes were mounted on the sample holder which is capable of direct current heating. In the UHV system the sample was degassed at 550 °C all the night until the base

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pressure was stable. Repeatedly flashed heating at 1150 °C for 20 s is then performed in order to desorb the native oxide layer and carbon contaminant. Low energy electron diffraction (LEED) was performed on an Omicron SPECTRA system. LEED evidenced a sharp 2×1 pattern and the well known double domain of the Si(100) surface made of rows of Si dimers. After the preparation of a clean surface, passivation with hydrogen was performed in-situ. Hydrogen gas (99.9%) was introduced into the UHV chamber via a leak valve where a tungsten filament was heated at 1800 °C to crack hydrogen molecules into atomic hydrogen. The samples were facing the tungsten filament at an 8 cm distance during the exposure. To prepare a Si(001) 2×1 -H surface, the sample was held at 320 °C while it is exposed to atomic hydrogen at a pressure of 3×10^{-4} Pa for 200 s. The organic material, CuPc (purity 97%), first purified by two cycles of sublimation, was deposited in-situ from a Knudsen cell heated to about 270 °C on the substrate held at room temperature. The flux (around 0.1 monolayer (ML) per min) was determined using a water-cooled quartz crystal thickness monitor (STM-100 Sycon) equipped with an OSC-100A Sycon oscillator. The pressure in the preparation chamber was raised to a maximum of 1×10^{-7} Pa during deposition. X-ray photoelectron spectroscopy measurement is performed by using a conventional Al K α ($h\nu = 1486.6$ eV) photon source (Omicron DAR 400) and a hemispherical electron spectrometer (Omicron EA 125). UPS spectra were recorded by using He I radiation (21.2 eV) line of He discharge lamp and separated in the analyzer. The total energy resolution of the spectrometer was determined by analyzing the width of Ag Fermi edge to be 100 meV (UPS) and 1.42 eV (XPS), respectively. The energy scale was aligned by measuring the Fermi edge (0 eV), as well the Ag3d5/2 emission (368.2 eV) of the silver substrate [12].

The vacuum energy E_{vac} of the samples including substrates was determined by the low kinetic energy cut-off of the UPS spectra [13]. In order to avoid the spectrometer threshold effect, the sample was electronically biased from the ground level. Values for E_{vac} measured from identical samples were consistent within 0.05 eV even when the bias voltage was changed from 0 to -5 V. Photovoltaic effects can be ignored in our UPS measurements because there is no binding energy shift which occurred when the photon intensity of the discharge lamp was changed.

3. Results and discussion

Prior to deposition of CuPc thin films, the hydrogenated surface was investigated with LEED and XPS in order to check its periodicity and to determine its initial state chemistry.

Survey spectrum (the lowest in Fig. 1) exhibited only silicon Si2p and Si2s peaks and indicated neither oxygen nor carbon contaminations which were introduced during the hydrogenation procedure.

Upon further deposition, XPS spectra exhibit (spectra for 1, 10 and 40 ML in Fig. 1) nitrogen, carbon and copper photo-peaks and Auger peaks from the CuPc molecules. The intensity of these features increases with the increase of the deposition amount of the organic molecules while the intensity of silicon Si2p and Si2s peaks decreases. At a very large deposition (40 ML), there are no discernible Si2p and Si2s signals which indicate that the passivated silicon substrate is completely covered by the organic material (the upper spectrum in Fig. 1).

In order to determine the influence of the deposited CuPc layers on the substrate Si2p core level, we investigated the evolution of its binding energy at an increasing amount of molecular coverage (Fig. 2a). We can observe that the Si2p peak shifts by around 0.4 eV towards the higher binding energies. This might indicate a corresponding increase of downward band bending in the substrate at the interface.

The influence of the deposited CuPc layers on molecular core levels is also investigated. We observed a shift of these core levels around 0.4 ± 0.05 eV (Fig. 2b). From 20 ML coverage and above, the pronounced features Cu2p $_{3/2}$, N1s and C1s, typical from the molecular levels, are located respectively at 935.3, 398.9 and 284.6 eV. This

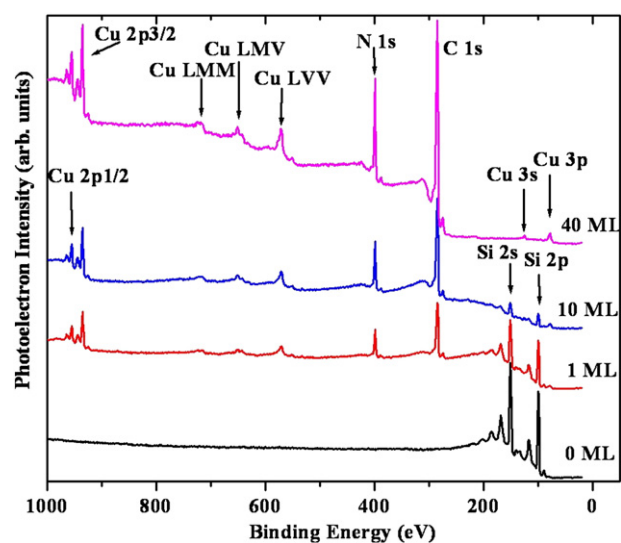


Fig. 1. XPS survey spectra of hydrogen-passivated Si(100) 2×1 -H surface, after 1 ML, 10 ML and 40 ML CuPc coverage.

also might indicate a corresponding increase of downward band bending in the organic film. From Fig. 2, the 0.4 eV shift arises after about 5 ML for Si2p, while it arises after about 15 ML for Cu, C and N lines. This binding energy shift, corresponding to an increase, may be due to relaxation effects of the photo-ionized atom. Because of a relaxation of the positive hole, this occurs by the substrate electrons. From low CuPc coverage, many substrate electrons are involved in bonds with molecules and so the relaxation of substrate Si atoms is weakened. On the contrary, for the CuPc elements, the relaxation decreases normally with coverage. It is more efficient at low coverage and becomes less efficient at higher thickness.

In order to determine the electronic properties of the adsorbed CuPc layers, the UPS measurements were conducted after each deposition. Fig. 3 depicts the thickness dependent ultraviolet photoemission spectra of CuPc deposited on Si(100) 2×1 -H surface. In this figure, the intensity of all peaks was normalized taking into consideration that the highest peak and spectra were shifted to clarity. The lowest spectrum corresponds to the substrate before the organic material deposition. From very low coverage (0.4 ML) of organic material, three features appear at the valence band spectrum. The intensity of the peaks relative to the features from the organic molecules increases with the increase of the coverage. For this initial coverage, photoemission features are located at 0.95, 3.10 and 6.2 eV below the Fermi level. The first peak is relative to the highest occupied molecular orbital (HOMO) of CuPc molecule. With the increase of the coverage, the photoemission features are shifted towards higher binding energies. At the final film thickness of 40 ML, the pronounced features typical from the molecular levels are located at 1.37, 3.5 and 6.65 eV. This corresponds to an energy shift in which the average value is nearly equal to (0.4 ± 0.05) eV. This value is in good agreement with the one obtained by Gorgoi and Zahn [10] for a CuPc layer thickness of 15 nm which is nearly the same as 40 ML (1 ML = 3.4 Å [19]). The binding energies of these characteristic CuPc features are also in reasonable agreement with those observed for the case of CuPc and K-CuPc studied in using photoemission spectroscopy [14].

Fig. 4a depicts magnification of high binding energy cut-off (HBEC) area respectively for substrate, 0.4 ML and 40 ML of CuPc. After the first coverage, the shift of HBEC is 0.22 eV while it is 0.54 eV for the final coverage. This means that the vacuum energy E_{vac} value has undergone a decrease with increasing CuPc coverage. This drop in the E_{vac} value at submonolayer coverage followed by its gradual decrease associated with the peak shifts in UPS and XPS, indicates the existence

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