

Adsorption study of copper phthalocyanine on Si(111)($\sqrt{3} \times \sqrt{3}$)R30° Ag surface



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ABSTRACT

The adsorption of copper phthalocyanine (CuPc) molecules on Si(111)($\sqrt{3} \times \sqrt{3}$)R30° Ag surface is studied at room temperature under ultra high vacuum. Crystallographic, chemical and electronic properties of the interface are investigated by low energy electron diffraction (LEED), ultraviolet and X-ray photoemission spectroscopies (UPS, XPS) and X-ray photoemission diffraction (XPD). LEED and XPD results indicate that after one monolayer deposition the molecular layer is highly ordered with a flat lying adsorption configuration. The corresponding pattern reveals the coexistence of three symmetrically equivalent orientations of molecules with respect to the substrate. XPS core level spectra of the substrate reveal that there is no discernible chemical interaction between molecules and substrate; however there is evidence of Fermi level movement. During the growth, the work function was found to decrease from 4.90 eV for the clean substrate to 4.35 eV for the highest coverage (60 monolayers). Within a thickness of two monolayer deposition an interface dipole of 0.35 eV and a band bending of 0.2 eV have been found. UPS spectra indicate the existence of a band bending of the highest occupied molecular orbital (HOMO) of 0.55 eV. The changes in the work function, in the Fermi level position and in the HOMO state have been used to determine the energy level alignment at the interface.

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1. Introduction

The study of interfaces between thin films of organic materials and inorganic surfaces has increased in intensity over the last few years. Among organic materials, semiconducting metal-phthalocyanines (MPcs⁺), represent one of the most interesting candidates due to their high thermal and chemical stability allowing the formation of many organized thin films important for optic or molecular electronic applications such as light emitting diodes [1], organic field effect transistors [2,3] and organic photovoltaic cells [4]. It is now well-established that physical phenomena taking place at the molecule-electrode interface largely influence the performance of electronic devices. This includes, for instance, charge injection mechanisms, contacts and carrier recombination [5–7].

Many studies concentrate on organic on metal interfaces. For example, in the case of CuPc deposition on Au(100) [8], a large interface dipole of 1.2 eV is measured while band bending in the organic semiconductor is very small. Baran et al. [9] have carried out a comparative study of the adsorption of three phthalocyanine molecules

CoPc, SnPc, and PbPc on Ag(111) surface using a range of experimental techniques in particular scanning tunneling microscopy (STM) coupled with density functional theory (DFT) calculations. They have shown that in all cases, the adsorption is driven by the interaction of the central metal with the Ag(111) surface, but only SnPc forms long range ordered domains. Neither PbPc nor CoPc forms a well-ordered monolayer on Ag(111) via the deposition and annealing procedures (substrate held at 300°C). CoPc molecules form a locally ordered monolayer. The lack of order in the case of PbPc is due to a strong interaction between the central Pb atom and the Ag(111) surface, leading to the formation of Pb–Ag surface alloy. This is confirmed by X-ray photoemission spectroscopy (XPS) where a shift from an apparent oxidation state of +2 to 0 is measured. Furthermore charge transfers from the substrate to MPcs are frequently observed by ultra-violet photoemission spectroscopy (UPS), for example in the case of CoPc on Au(100) [10]. This results in the formation of an interface dipole.

The adsorption of organic molecules on Si(111)($\sqrt{3} \times \sqrt{3}$)R30° Ag surface has been less studied. This surface, shown schematically in Fig. 1, is described by the honeycomb chain trimer (HCT) model with a full silver monolayer [11]. Few organic molecules have been studied on this surface such as fullerene, pentacene, cobalt phthalocyanine (CoPc), PTCDA and zinc phthalocyanine (ZnPc)

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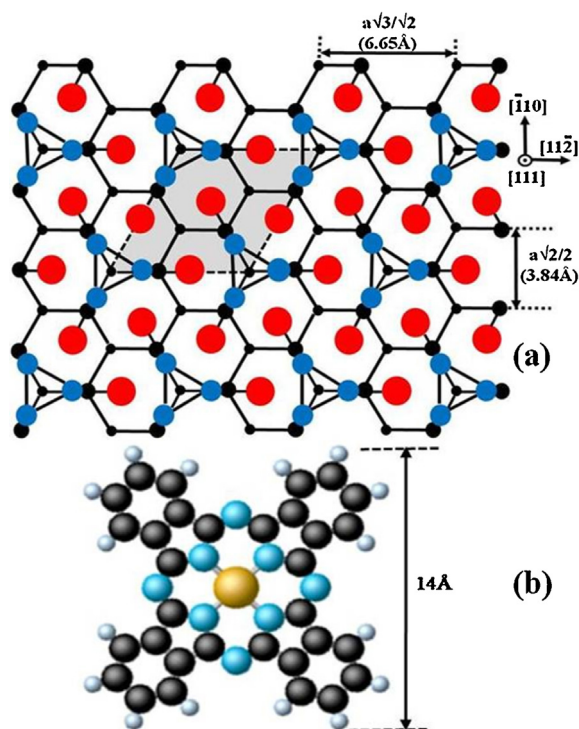


Fig. 1. (a) Top view of a HCT model for Si(111)($\sqrt{3} \times \sqrt{3}$)R30°Ag surface. The largest circles (in red color) represent Ag atoms. The unit cell of the surface is marked. (b) Atomic model of the copper phthalocyanine molecule CuC₃₂N₈H₁₆. Both molecule and substrate are in the same scale. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[12–16]. In the case of fullerenes [12], pentacene [13], CoPc [15] and ZnPc [16] STM studies have shown that highly ordered molecular layers can be formed. In the case of pentacene, the electronic structure of the surface has been studied by Photoelectron spectroscopies (PES). An interface dipole of 0.35 eV is observed together with a modification of the C 1s peak indicating different adsorption sites for the molecules [14].

In this paper, we present growth study of CuPc deposited on Si(111)($\sqrt{3} \times \sqrt{3}$)R30°Ag, in the 1–60 monolayer (ML) range. Structural characterization, obtained by low energy electron diffraction (LEED) and XPD, is combined to UPS and XPS measurements. The results suggest that CuPc molecules are oriented parallel to the substrate.

2. Experimental details

Experiments are performed 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 hemispherical analyzer. The base pressure of the analysis chamber is typically around 1×10^{-10} mbar. The sample is a single crystal cut from a Si(111) wafer: p-type B-doped with an electron concentration of 10^{16} cm^{-3} and supplied by Siltronic SA. It is cut into stripes with a dimension of $5 \text{ mm} \times 15 \text{ mm}$, then it is degreased with acetone in an ultrasonic bath, rinsed with ethanol and then dried with nitrogen gas. The cut silicon stripes are mounted on the sample holder which is capable of direct current heating. In UHV system, the samples are first degassed at 600 °C for about 10 h. Repeatedly flashed heating at 1250 °C for 20 s are then performed in order to desorb the native oxide layer and carbon contaminants. Low energy electron diffraction (Omicron SPECTRA-LEED) evidenced a sharp (7×7) pattern. The cleanliness of Si(111)-(7 × 7) surface is

checked by XPS before preparation of the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°Ag surface. Silver 5 N (Goodfellow Metals) is evaporated from a molybdenum crucible onto the Si substrate maintained at 500 °C during the deposition. The organic material, CuPc (purity 97%), first purified by two cycles of thermal gradient sublimation [17] is 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) is 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 raises to a maximum of 1×10^{-9} mbar during deposition. X-ray photoelectron spectroscopy (XPS) measurement is performed by using a conventional Al K α ($h\nu = 1486.6 \text{ eV}$) photon source (Omicron DAR 400) and a hemispherical electron spectrometer (Omicron EA 125) (pass energies 100 eV and 20 eV). UPS spectra are recorded by using He I radiation (21.2 eV) line of He discharge lamp and separated in the analyzer (pass energy 5 eV). The energy scale was aligned by measuring the Fermi edge (0 eV), as well the Ag3d_{5/2} emission (368.2 eV) of the silver substrate [18].

The vacuum energy E_{vac} of the samples including substrates is determined by the low kinetic energy cut-off of the UPS spectra [19]. In order to avoid the spectrometer threshold effect, the sample is electronically biased from the ground level. Values for E_{vac} measured from identical samples are consistent within 0.05 eV.

The XPD technique in performing an angular scan of the photoelectron intensity from specific core levels, like in the present case Si 2p, Cu 2p_{3/2}, N 1s, and C 1s. The XPD patterns are obtained with a 100 eV pass energy by scanning the polar angle, defined as the angle between the normal to the substrate and the direction of the electron analyzer. The crystallographic XPD technique is therefore a probe of the local atomic environment of the emitting atom. During the present experiment, the entrance slit of photoelectrons in the analyser is kept at its lowest value, corresponding to an entrance angle of 3° for photoelectrons. The polar angle is varied in steps of 2° by rotating the sample-holder around an axis perpendicular to the chosen azimuthal plane.

3. Results and discussion

Prior to the deposition of CuPc thin films, the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°Ag surface is investigated with LEED, XPS and UPS in order to check its periodicity and to determine its initial chemical and electronic properties. Fig. 2 shows the evolution of LEED patterns recorded for the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°Ag surface in the course of the sample preparation. While the usual (7×7) reconstruction is obtained for clean Si(111) surface (Fig. 2a), LEED diagram obtained after one monolayer silver indicates the well known ($\sqrt{3} \times \sqrt{3}$)R30° pattern (Fig. 2b). After one monolayer of CuPc deposited at room temperature, LEED pattern evolves to the pattern represented in Fig. 2c. This pattern, collected with beam energy of 11 eV due to the large lattice spacing of CuPc molecules, demonstrates three concentric rings, two of which have twelve spots and one has twenty four spots. The form of this pattern is similar to those from CuPc films on Ag(111) [20] and FePc on Ag(111) [21]. This confirms that the Pc ligand π system is lying flat on the surface. The LEED pattern can be indexed as three identically sized unit cells rotated by 120° with respect to each other (Fig. 2d). The rotation appears to be 30° because the phthalocyanine lattice has a four-fold symmetry. Similar patterns were observed and similar conclusions were made recently even for non planar Pc molecules as vanadium oxide phthalocyanine (VOPc) on Au(111) [22]. The similar intensity of spots in each ring, suggests that the three orientations belong to three domains which have comparable molecular populations on the surface as it was confirmed by Rochford et al. [22]. By considering the three-fold symmetry of the substrate, the form of the

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