Electronic Structure of MePc/Si(100) Surface Studied Using Metastable-Atom Induced Electron Spectroscopy*

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Metal phthalocyanines (MePc) have unique features applicable to the field of electronics and optics. In this study, we observe the surface electronic structure of MePc (Me = Cu, Zn) adsorbed Si(100) using metastable-atom induced electron spectroscopy (MIES). MePc molecules are deposited for less than 2000 s in vacuum at room temperature. At the initial adsorption of the MePc, each molecule lays flat on the substrate and the center metal atom is on top. This orientation of the adsorbed molecules gradually changed with an increase in the deposition time of the MePc. When the MePc covered surface was annealed by direct current heating at 800°C or below, the molecules started to decompose and desorbed from the Si(100) surface. However, Cu atoms remained on the surface. We discuss the adsorption structure based on the deposition time and behavior of the MePc molecule with annealing.

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I. INTRODUCTION

Metal phthalocyanines (MePc) have unique features for applications in the field of electronics and optics. For example, they can be employed in various devices such as solar batteries, sensors, and fuel cells. These features of MePc are attributed to the atomic bonding state and the molecular structure. The adsorption structures of MePc have already been observed on single crystal substrates using a scanning tunneling microscope (STM) [1, 2]. STM results were reported that the orientation of the adsorbed MePc depends on the structure of the substrate surface. The surface electronic structures of CuPc and ZnPc were calculated using theoretical methods such as density functional theory (DFT) [3–6]. These results showed partial density of states for each atom in the CuPc and ZnPc molecules.

In this study, we measure the surface electronic structure of MePc (Me = Cu, Zn) adsorbed Si(100) using metastable-atom induced electron spectroscopy (MIES). The MIES technique provides accurate measurements at the outermost surface. The detailed surface electronic structures obtained by MIES revealed the influence of the amount of adsorbed MePc molecules to their orientation on the surface. Moreover, we observed desorption and decomposition of MePc molecules at higher substrate annealing temperatures.

II. EXPERIMENTAL

The experimental setup comprised a helium metastable atom (He^*) source, rear-view low energy electron diffraction (LEED) optics, retarding field energy analyzer, quadrupole mass spectrometer, and MePc evaporators. The base pressure was approximately 1.0×10^{-7} Pa. Helium atoms were excited to the metastable states by hot-cathode low voltage discharge. The discharge was pulsed so that the fast photons and the slow He^* in the incident beam could be distinguished based on time of flight using a time-resolved detection technique. The raw data obtained by the retarding field energy analyzer, which integrated energy distributions, were differentiated numerically to yield MIES and UPS spectra. In MIES, the de-excitation of metastable atoms proceeds through different channels depending on the relation of the work function at the surface. At high work function surfaces such as clean Si(100) in Fig. 1(a), He^* undergoes resonance ionization followed by Auger neutralization (RI+AN). The AN process takes place close to the topmost layers, and the MIES spectrum reflects a convolution of partial density of states at the surface.

The sample was a Si(100) substrate of P-doped n-type, cleaned in vacuum by direct-current Joule heating. A Si(100) clean surface was confirmed by a double-domain (2×1) LEED pattern. The sample temperatures were measured with an optical pyrometer (200–1600°C). Cu or Zn phthalocyanine powder was inserted into the evaporator crucible. This crucible was heated by direct current to deposit MePc molecules at room temperature. We did not measure the amount of adsorbed MePc molecules; instead, we determined its index based on the deposition time. To determine the coverage or film thickness, observations using analytical techniques are necessary. During sample surface preparation, outgassing products of rel-

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FIG. 1. Series of MIES spectra obtained for the CuPc/Si(100) surface: (a) clean Si(100), (b1–b5) CuPc deposition time up to 2130 s.

atively lightweight atoms and molecules were monitored using the quadrupole mass spectrometer.

III. RESULTS AND DISCUSSIONS

A. CuPc/Si(100) surface

We measured the MIES spectra for clean and CuPc deposited Si(100) surfaces up to the deposition time of 2130 s at room temperature. Figure 1 shows a series of MIES spectra for the CuPc/Si(100) surface. In Fig. 1(a), at the Si(100) clean surface, the peak P_1 at 8.4 eV can be assigned to the Si-3p state. The peak at around 11.5 eV in Fig. 1(b3), labeled P_2 , is due to electron emission from the Cu induced states [7]. The theoretical calculations about the partial density of states of each atom composing the CuPc molecule were reported by some researchers [3, 4]. We referred to these calculations for interpreting the origins of peak structures. The shoulder S_1 at 9–12 eV contained electron emissions for each atom (Cu, N, and C) in the CuPc molecule. The intensity of peak P_2 decreased with increasing CuPc deposition time. The peak structure S_2 at 5–8 eV originated from the electron emissions induced C atoms in CuPc. In the MIES spectrum (b5), S_2 made a significant contribution while the intensity of P_2 decreased. This result implies that the CuPc adsorption structure changed from flat depending on the CuPc deposition time [8]. Namely, the adsorbed CuPc molecule lied flat on the substrate keeping the Cu atom on top at the initial stage of CuPc adsorption. However, at higher coverage, because He^* de-excited around C atoms at the outermost position in CuPc, electron emission due to C induced states increased. It was possible that CuPc molecules were tilted upwards on the Si(100)

FIG. 2. Series of MIES spectra obtained for CuPc/Si(100) surface with annealing: (a) clean Si(100), (b) CuPc_2130 s/Si(100), (c1–c3) annealed at 1000°C and below.

surface.

Figure 2 shows a series of MIES spectra for the CuPc adsorbed Si(100) surface at different annealing temperatures. When the CuPc/Si(100) surface was annealed at 400–1000°C, peaks P_1 and P_2 reappeared slightly with an increase in the annealing temperature. After annealing at 1000°C for 3 min, the shape of several peaks were con-

FIG. 3. Series of MIES spectra obtained for ZnPc/Si(100) surface: (a) clean Si(100), (b1–b9) ZnPc deposition time up to 2000 s.

FIG. 4. Series of MIES spectra obtained for ZnPc/Si(100) surface with annealing: (a) clean Si(100), (b) ZnPc-2000 s/Si(100), (c1–c4) annealed at 1000°C and below.

firmed clearly in the spectrum (c2). As the pyrrole rings and aromatic rings in phthalocyanine were decomposed by annealing, the light elements (N, C, and H) preferentially desorbed from the surface. Therefore, electron emissions were derived from residual Cu and C atoms or bare Si atoms. We found that Cu atoms remained on the Si(100) surface with annealing at 1000°C or less.

B. ZnPc/Si(100) surface

The MIES spectra obtained for the ZnPc deposited Si(100) surface are shown in Fig. 3. The interpretation for our MIES spectra was derived from the previously reported theoretical and experimental results of the surface electronic structures of the ZnPc molecule [5, 6, 9]. In Fig. 3(a), peak P_1 was induced by a Si-3p state. The spectrum (a) for the Si clean surface exhibited peak positions for Si induced states were identical to its in Fig. 1(a). The shape of this spectrum in the low energy region reflects the influence of the secondary electrons. For a ZnPc

deposition time of 80 s, peak P_2 caused by the electron emissions from the Zn atom appeared. As the spectrum (b4) reflects the density of states originating from the Si substrate, ZnPc molecules could not fully cover the surface but laid flat on keeping the Zn atom on-top. In Fig. 3(b5–b9), the shoulder structure S_1 and the peak P_3 at around 6.5 eV appeared. S_1 contains the electron emissions for each atom (N and C) in the ZnPc molecule. Peak P_3 originated from the C atom. The intensity of P_3 increased with ZnPc deposition time. These results suggested that the molecular plane of adsorbed ZnPc stood upright. The behavior of ZnPc on the Si(100) surface was similar to that of the CuPc.

After 2000 s ZnPc deposition, the ZnPc/Si(100) sample (Fig. 3(b9)) was annealed at 300–1000°C. Fig. 4 shows a series of MIES spectra for ZnPc adsorbed Si(100) surface with annealing temperatures. In Fig. 4(c1), the intensity of peaks P_2 induced by Zn decreased slightly and a new peak P_1' containing electron emission due to Si induced states was observed at around 7.8 eV after annealing at 300°C. This result suggests that ZnPc molecule started to decompose and the Zn atom desorbed from the surface at relatively low temperatures. When the ZnPc/Si(100) surface was annealed at 1000°C for 19 min, the position of peak P_1' shifted to a higher energy. The intensity of P_1 recovered, and P_2 vanished in Fig. 4(c4). This MIES spectrum was roughly similar to that obtained for the Si clean surface indicating almost complete desorption of ZnPc and its decomposed species from the surface.

IV. CONCLUSIONS

We measured the surface electronic structure of MePc (Me = Cu, Zn) adsorbed Si(100) using MIES. The MePc absorption structures depend on deposition time. At the initial adsorption of MePc, molecules laid flat on the substrate, keeping metal atoms on top of the surface. With increasing MePc deposition time, the orientation of MePc molecule became upright. It was found that even low temperature annealing triggered the decomposition of CuPc molecules. Then, the decomposed Cu atoms were directly bonded to the Si subsurface by high temperature annealing. Therefore, Cu atoms were not completely removed from the surface. In the case of the ZnPc adsorbed Si(100) surface, ZnPc started to desorb from the surface with low temperature annealing and finally desorbed approximately at 1000°C with the other decomposed elements.

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