Molecular arrangement of copper phthalocyanine on hydrogen-terminated Si(111): Influence of surface roughness

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The molecular arrangement of copper phthalocyanine (CuPc) crystals on hydrogen-terminated Si(111) surfaces was investigated by using both scanning probe microscopy and x-ray diffraction in terms of influence of the surface roughness. On a rough surface with a root-mean-square roughness of 0.20 nm, the molecules were stacked so as to form an α crystal where the molecular column was parallel to the surface. On the other hand, a new crystal form with its column exactly perpendicular to the Si(111) plane was grown on an atomically flat surface. In this case, the molecules were stacked perpendicular to the substrate with the underlying molecules situated directly below. These molecular arrangements were independent of the growth temperature in the range of 60–180 °C. On the atomically flat surfaces, the strong interactive force between the surface and the planar CuPc molecule may result in the new growth behavior. © 1996 American Vacuum Society.

I. INTRODUCTION

Metal phthalocyanine (Pc) thin films have been studied extensively due to their potential property as electronic or optoelectronic materials and possible application for fabricating functional nanostructures on solid surfaces. Metal Pc are found to be semiconductive molecular crystals having several polymorphs which determine the energy state, the band gap, and the anisotropy of electrical conductivity. In order to examine the molecular arrangement and crystal orientation, vacuum-deposited films were prepared on various substrate materials; however, very few reports stated the influence of the surface morphology of the substrate. Tada and co-workers reported that vanadyl phthalocyanine (VOPc) and chloroaluminum phthalocyanine (AlPcCl) grew epitaxially with their molecular columns perpendicular to the flat hydrogen-terminated Si(111) substrate {Si(111)−H}, which was flattened by boiling-water etching, but not on relatively rough Si(111)−H or Si(100)−H. Recently, in the case of the copper phthalocyanine (CuPc), it was found to grow epitaxially even on the relatively rough Si(100)−H at 90–180 °C. Since the CuPc is a planar molecule in contrast to the VOPc and AlPcCl with the pyramidal shape, we expect a different and simplified growth behavior.

In the present study we grew the CuPc crystals by molecular-beam deposition at various substrate temperatures on both the rough and flat Si(111)−H surfaces. Molecular arrangement of the crystals was examined by using scanning probe microscopy and x-ray diffraction (XRD). The influence of the surface roughness on the crystal growth is discussed.

II. EXPERIMENT

A Si(111) wafer with 0.5° off angle was used as the substrate. The wafer was thermally annealed to form 500-nm-thick oxide film. It was then cut into small pieces and cleaned by dipping into boiling acids, $H_2SO_4:H_2O_2:H_2O=1:1:3$ and $HCl:H_2O_2:H_2O=1:1:4$, successively. A rough silicon substrate was prepared by removing the oxide layer using 1% aqueous HF, while a flat substrate was prepared by immersing the rough substrate into 40% aqueous $NH_4F$ for 15 min. The substrates were introduced into a load-lock chamber for CuPc film deposition after rinsing in ultrapure water for 10 s. CuPc films were grown by molecular-beam deposition. The base pressure of the chamber was $1.3\times10^{-8}$ Pa and the working pressure was kept below $1\times10^{-7}$ Pa during the film growth. Commercially available powder of CuPc was preheated at 350 °C for 10 h in low vacuum before putting in a K cell, which was then heated up at 200 °C for more than 12 h in the K cell with a differential pumping system. The molecular flux was kept constant, which corresponds to the average growth rate of 0.1–0.15 nm/min. The substrate temperature $T_s$ was varied in the range of 60–220 °C. Atomic force microscopy (AFM) measurement was carried out in air for macroscopic imaging and in nitrogen atmosphere for molecular imaging. Triangular-shaped silicon nitride cantilevers with a stiffness of 0.09 N/m were used to obtain molecular images. The
ultrahigh-vacuum scanning tunneling microscopy (UHV STM) was measured by using electrochemically etched tungsten tips. XRD was measured with a Cu Ka x-ray source.

III. RESULTS AND DISCUSSION

The surface roughnesses of the two kinds of substrates were examined by AFM. Figures 1(a) and 1(b) show the topographic images of the rough and flat surfaces, respectively. The rough surface is characterized by the randomly distributed corrugation with a root-mean-square (rms) roughness of 0.20 nm, which is typical for a Si surface treated by the 1% HF solution. In contrast, well-ordered atomic steps and flat terraces are clearly observed on the flat surface without significant vacancies, of which rms roughness is 0.12 nm. It has been clarified that the hydrogen-terminated silicon surface prepared by HF etching is chemically inactive, and that the etching of Si(111) surface by basic HF solutions with pH=8 produces ideal monohydride termination and atomically flat surfaces consisting of well-ordered atomic steps. Accordingly, both surfaces are fully terminated by hydrogen although they have morphological differences. The CuPc molecules can adsorb on these surfaces without dissociation due to the inactivity, and the interactive force between the molecule and the substrate is considered to be van der Waals in nature.

Figure 2 shows wide-area AFM images of the CuPc films grown on both the rough and flat surfaces at various T_s. The average thicknesses of these films were ~20 nm. Small grains of less than 1 μm in length are grown densely on the rough surfaces as seen in Figs. 2(a) and 2(b), while large isolated islands of more than 10 μm in length on the flat surfaces as seen in Figs. 2(c) and 2(d). On the rough surfaces, each grain does not have particular shape at T_s=60 °C (a), but ~1-μm-long rodlike grains with sixfold symmetry appear at T_s=140 °C (b). On the flat surface, the leaflike dendrites are seen at T_s=60 °C (c), and long styluslike islands clearly appear at T_s=180 °C (d). Typical heights of the islands were 50 nm for T_s=60 °C and 400 nm T_s=180 °C. From the island shapes, the film growth seems to be unaffected by the atomic steps, which are expected to exist at 50 nm intervals in the direction of the broken lines as shown in (c) and (d). The films did not grow at T_s>140 °C on the rough surfaces and T_s>180 °C on the flat surfaces. In the plain area of the flat samples, the atomic images on the Si(111)-1×1-H were observed with a few isolated CuPc molecules by STM. In addition, SiH fragment ion intensity measured by time-of-flight secondary-ion-mass spectrometry (TOF-SIMS) was almost equal to that from the original Si(111)–H surface. These facts indicate that the original hydrogen-terminated silicon surface remains even after the film growth. It is remarkable that the average thicknesses of all samples obtained by large-area topographic images, optical microscope observations, and spectroscopic ellipsometry were within the range of 13–21 nm, in spite of the wide variation of crystal shape. The deviation of the average thickness tends to become small when the molecular density of the film, which depends on the crystal form described later, is taken into account. This means that the total amount of CuPc molecules is nearly independent of either the substrate temperature or the surface roughness, and that the CuPc molecules migrate over 100 μm on the flat surface at T_s=140 °C which is estimated from the distance between neighboring crystals of 200 μm.

XRD patterns of the films deposited at T_s=60, 100, 140, and 180 °C on the rough surfaces are shown in Fig. 3. A peak corresponding to (200) diffraction of the α-form crystal, which is the stable crystal form at T_s<200 °C, appears at T_s=60–140 °C as indicated by an arrow. The other peaks originate from the silicon substrate. The α-axis orientation of the α-form crystal and rodlike appearances as in Fig. 2(b) are consistent with the previous results in the case of
CuPc/Si(100)–H. Accordingly, the $b$ axis or molecular column axis of $\alpha$-form crystal lies parallel to the surface $\{1\overline{1}0\}$ direction. The molecular arrangement and crystal orientation are schematically shown in Fig. 4. In this figure, the lattice constants and the molecular packing of the $\alpha$ form crystal are taken from a previous report. The $(010)$ spacing of $\alpha$-form CuPc is only 1.3% smaller than that of Si$(1\overline{1}0)$. This lattice mismatch is considered to be small enough to accomplish the epitaxial-like crystal growth.

On the flat surfaces, a sharp intense peak appeared in the XRD patterns as shown in Fig. 5, which corresponds to 0.322 nm interplanar spacing. The peak was observed for all films with considerably strong intensity. This diffraction peak was carefully examined by changing the tilting angle of the sample from $-20^\circ$ to $20^\circ$ under various in-plane rotational angles in XRD geometry. From these measurements it was found that the 0.322 nm diffraction peak was exactly parallel to the substrate $(111)$ diffraction and the tilting-angle dependence was as sharp as the substrate diffraction. In the case of vacuum deposited CuPc, either $\alpha$, $\beta$, or $\delta$ crystal form has been reported so far, however, none of these have the strong 0.322 nm spacing diffraction. These suggest that the molecules are stacked straight along the Si$(111)$ normal with the molecular planes parallel to the Si$(111)$ plane as schematically shown in Fig. 6(b).

The isolated CuPc crystal grown on the flat surface at $T_s \geq 140^\circ$ C has wide and flat faces on its top which are parallel to the substrate surface. Figure 7 shows the high-resolution frictional force image taken on the top face of a typical crystal grown at higher $T_s$ where the local thickness is...
100 nm. Brighter means larger frictional force in the figure. A higher scanning rate was used to suppress the distortion of the image caused by the thermal drift. Similar lattice images were observed also by STM even on top faces of thicker crystals. In this figure, we can see oblique lattice formed by square-shaped brighter parts. Each bright part seems to coincide with single CuPc molecule in respect to the size and the shape of its van der Waals surface, which indicates that this image exhibits molecular arrangement of the CuPc crystal. By measuring the image of a triangular etch pit near the CuPc crystal which occasionally appears on this silicon surface and is to be surrounded by steps along the [110] direction, we can determine the relative orientations of the molecular arrangement with the substrate, which is shown in Fig. 6(a). Here, the center Cu atom of the every other molecule for each lattice direction is placed on top of the surface H atom so as to realize the periodicity of the image shown in Fig. 7. The corresponding lattice constants $a$ and $c$ are 1.57 and 1.50 nm, and the angle $\beta$ between $a$ and $c$ is 98.7°, which agrees with the measured values 1.54 nm, 1.55 nm, and 104°, respectively, within 5% error. We determined lattice constants by taking images in a similar way on many different crystals grown at 140 and 180 °C. These observations revealed that there exist several types of CuPc unit cells of which lattice constants of the models are as follows: $\{a$ (nm), $c$ (nm), $\beta$ (°)$\} = \{1.45, 1.57, 101.2\}, \{1.45, 1.38, 99.4\}, \{1.57, 1.38, 93.7\}, \{1.64, 1.38, 100.1\}$. These are consistent with a model that either every or every other neighboring molecule adsorbs on the equivalent site on the Si(111)–H as expected from Fig. 6(a). All observed lattices were assigned to these five models within a few percent error. Furthermore, facets with a tilting angle of about $12 \pm 1^\circ$ with respect to the substrate surface appear frequently on these crystals. The angle agrees with the (110) or (011) plane of this monoclinic crystal model of which $a$ or $c$ ranging 1.38–1.64 nm and $b=0.322$ nm.

From these XRD and AFM observations, we can conclude that the film on the flat surface is a new polymorph where the molecules are stacked cofacially as shown schematically in Figs. 6(a) and 6(b). This type of molecular arrangement has not been clearly confirmed for the thin films of planar Pc such as CuPc excepting the case of iodine-doped Pc. The intermolecular distance of 0.322 nm along the column axis is narrower than that of other forms, which suggests that the higher electric conductance along the axis is expected due to the stronger correlation between the face-to-face stacked molecular orbitals. The island growth of this system is not necessarily a disadvantage for application of the material. We expect that it is possible to form nanometer-sized structure at a selected position by controlling the large-scale surface migration of the molecule.

Finally, we propose a mechanism of the growth mode difference induced by the surface roughness. Basically, it is considered that there are four kinds of interactive forces which mainly drive the film growth in this system:

(i) molecule/molecule interaction to stack them face to face which is emphasized by the conjugated $\pi$ orbitals;
(ii) molecule/surface interaction which varies much depending on the substrate;
(iii) column-side/surface interaction which is proportional to the column size; and
(iv) column-side/column-side interaction which is also proportional to the column size.

It is easy to recognize that the force (i) is generally large considering that the vapor pressure of this material is extremely low. In the case of force (i) $\gg$ force (ii), the film grows as follows: The stacking proceeds primarily due to the larger force (i) and forms a longer column; then the increase of the column length makes the forces (iii) and (iv) larger than force (ii); finally, large columns fall down to be parallel to the surface. This may be the case for the film growth on the rough Si(111)–H surface. On the other hand, in the case of force (i) $\approx$ force (ii), the film grows as follows: The CuPc molecules condense keeping the molecular planes parallel to the surface due to the larger force (i) and (ii) than force (iii); the column length increases depending on the growing island size, which makes the forces (iii) and (iv) larger; finally the large force (iv) helps to form two-dimensional lattices as shown in Fig. 7 but the force (iii) does not work because the large force (ii) prevents the molecular column from falling down in contrast to the former case. This may be the case on the flat Si(111)–H surface. As a consequence, the $\alpha$ form is not the most favorable arrangement on this surface.

IV. CONCLUSION

The molecular arrangement of CuPc film was found to be strongly affected by the microroughness of the substrate surfaces. CuPc crystals with the molecular column parallel to the surface were grown on the rough surface having randomly distributed corrugation. The molecules are condensed in an $\alpha$-form crystal with its column axis parallel to the [110]
direction of the Si(111) surface. On the other hand, a new crystal form with its column exactly perpendicular to the Si(111) plane was grown on the flat surface which exhibited well-ordered atomic steps and flat terraces without defects. The molecules were stacked cofacially in this case. We proposed a mechanism describing how the different structures grow on both of these surfaces.

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