Epitaxial growth of \( \alpha \)-copper phthalocyanine crystal on Si(001) substrate by organic molecular beam deposition

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Abstract

Copper phthalocyanine (CuPc) films were grown on Si(001) substrates at temperatures between 483 K and 150 K by organic molecular beam deposition under ultra-high vacuum of \( 1 \times 10^{-5} \) Pa. The X-ray diffraction (XRD) measurement and the atomic force microscope (AFM) lattice image observation revealed that \( \alpha \)-axis oriented \( \alpha \)-CuPc columnar crystals were epitaxially grown on Si(001) at substrate temperature (\( T_s \)) between 363 and 453 K. The \( b \) (\( \perp \)) axis of the \( \alpha \)-CuPc crystal was parallel to the Si [110] (Si [110]). Very smooth \( \alpha \)-CuPc film was also prepared at 150 K. The root-mean-square roughness obtained from the AFM measurement was 0.89 nm. The phase of polymorphs of CuPc was determined by Fourier transform infrared spectroscopy with a standard powder transmission measurement. The electron spin resonance investigation indicates that the molecular plane is tilted at an angle of \( 21 \pm 3 \)° with respect to the substrate surface. A CuPc film was also deposited on the surface of a Langmuir-Blodgett film on glass, and investigated by XRD and AFM. The substrate suppresses the epitaxial columnar crystal growth even at high temperature.

Keywords: Atomic force microscopy; Electron spin resonance; Molecular beam epitaxy; X-ray diffraction

1. Introduction

Much work has been done for copper phthalocyanine (CuPc) films prepared by the vapor deposition process. MoS\textsubscript{2}, graphite and muscovite were used as substrates [1–3]. Growth on Si is important for electronic device applications. Tada et al. [4] reported the Van der Waals epitaxial growth of a vanadyl-phthalocyanine (VOPc) film on Si(111). The substrate surface, which was prepared by Watanabe’s method [5], was atomically flat and terminated homogeneously with monohydride. They succeeded in depositing more than 20 layers. They examined the film growth only with in-situ reflection high-energy electron diffraction (RHEED). No morphological observation was reported.

A phthalocyanine crystalline film is a semiconductor which has potential for many applications, such as an organic applicable for organic solar cell making use of its photo conductivity, photosensitive drum material of a copying machine and a gas sensor utilizing the charge-transfer interaction near the surface [6–8]. A non-crystalline film is not generally suitable for an electronic device application because of its small electron mobility (\( \mu \)) due to the small overlapping integral among molecules (\( J \)). A non-crystalline film is rather preferable for a photochemical hole-burning (PHB) application, because energy transfer among molecules happens too easily in a crystal film, preventing PHB phenomena [9]. Fabrication of a smooth surface is especially important for an optical storage material because the laser beam must be focused on the recording layer without scattering.

Device fabrication on a Si substrate has the advantage of utilizing the highly developed silicon manufacturing technology. The Si(001) surface is expected to allow epitaxial growth of columnar crystals of CuPc because of their good lattice matching. The strong interaction expected between the film and the substrate is effective for realizing a good electronic heterojunction. In this report, we have tried the epitaxial growth of CuPc film and smooth non-crystalline film on
Si(001). Investigation of the crystalline form was performed by X-ray diffraction measurement (XRD) and Fourier transform infrared spectroscopy (FT-IR). FT-IR is adopted for phase identification of CuPc films in this study, although UV-visible light spectroscopy is generally used for it because Si substrate is opaque to the light. The film morphology was observed with atomic force microscope (AFM). The molecular orientation was estimated by electron spin resonance (ESR) measurement.

2. Experimental procedure

The system used for film growth was a molecular-beam epitaxy growth chamber under ultra-high vacuum, modified for organic compounds. The base pressure of the chamber was 1.3 x 10^{-8} Pa, and the pressure during deposition was 1 x 10^{-7} Pa. The surfaces of Si(001) substrates with dimensions of 40 x 40 x 0.5 mm³ were prepared by the UV/HF (ultraviolet light and hydrofluoric acid) treatment developed by Takahagi et al. The treatment gives a hydrogen-terminated clean bare Si surface. Commercially available CuPc powder was used as molecular-beam source after purification by vacuum sublimation. The powder source was heated at between 593 and 533 K for deposition. A quartz oscillator placed beside the substrate was used for thickness monitoring. The calibration of the thickness monitor was performed by spectroscopic ellipsometry (Nikon NPDM-1000). The deposition rate was about 0.2 nm min⁻¹. All films were designed to be deposited about 40 nm thick.

ESR spectra were obtained at X-band with a Brucker ESP-350E spectrometer equipped with an Oxford Instruments ESR 910 liquid-helium-flow cryostat. The measurement was done at 7 K. The magnetic field was measured with a Brucker ER-035M NMR Gaussmeter and the microwave frequency was measured with a Hewlett-Packard 5351B frequency counter. A Brucker IFS-120HR and a Rigaku RAD-C (Cu Kα, 50 kV, 700 mA) were used for the FT-IR and the XRD measurements, respectively.

3. Results and discussion

Fig. 1 is the XRD patterns of the CuPc films prepared at substrate temperatures between 150 K and 483 K. At substrate temperatures higher than 248 K the CuPc films are crystalline, highly oriented to the substrate normal. The film at 483 K consists of the stable β-CuPc form and metastable α-CuPc form. Only the peak corresponding to the α-CuPc form was detected from the films prepared at below 453 K. Strong satellite peaks of α-CuPc (200) are seen in the patterns of the films at 293, 363 and 423 K (Fig. 2(a)). It indicates that a lot of crystallites which are α-axis oriented to the substrate normal are composed of the same numbers of stacked units. The CuPc molecular plane is inclined against the substrate surface while the VOPc molecular plane is parallel to the substrate. From the results of fitting of the Laue function simulation patterns, the numbers of the stacked units along the normal to the substrate surface are 15, 14 and 13, respectively (Fig. 2(b)). The calculated film thicknesses of the films from the α-axis length (2.592 nm) of CuPc were 38.9, 36.2 and 33.6 nm [15]. The thinner was prepared at the higher substrate temperature. It is due to a decrease in sticking probability with the increase in the substrate temperature.

Fig. 3(a)–3(f) are AFM perspective-view images of the CuPc film surface prepared at 453, 423, 363, 293, 248 and 150 K, respectively. Preferred-orientation growth is seen in Fig. 3(a)–3(c). The crystalline columns grow along the [110] direction of the Si(001) surface. Fig. 4(a) is a
Fig. 3. AFM perspective-view images of the CuPc films (deposited thickness, 40 nm) deposited on Si(001) at: (a), 453 K; (b), 423 K; (c), 363 K; (d), 293 K; (e), 248 K; (f), 190 K.

wide-area AFM image (4 × 4 mm²; top view) of the film deposited at 363 K and Fig. 4(b) is the two-dimensional Fourier transform spectrum of the image. A fourfold rotation symmetry seen in Fig. 4(b) clearly shows the existence of the preferred orientation. The high-magnification AFM image of the same surface as Fig. 4(a) is shown in Fig. 5, where stripes with 1.2 nm interval are seen. The interval corresponds to the half length of the \( b \) axis of \( \alpha \)-CuPc. It is believed to be a column of stacked CuPc molecules in the \( b \) axis direction of the \( \alpha \)-type crystal structure. For comparison with the above epitaxial growth, a CuPc film was deposited on the Si(001) surface which was not treated with a hydrofluoric acid solution and covered with native oxide at 363 K. Figs. 6(a) and 6(b) are the AFM image and its two-dimensional Fourier transform spectrum, respectively. There seems no orientation, in spite of the grains shaped similarly to those in Fig. 4(a).

The lattice mismatching between \( \alpha \)-CuPc (\( b = 0.379 \) nm and \( c = 2.392 \) nm) [10] and Si (\( d\{110\} = 0.384 \) nm...
and \(6 \times d_{\langle 110 \rangle} = 2.304 \text{ nm}\) are 1.3% and 3.8%, respectively. They are small enough to be able to form a superlattice comparing to GaAs on Si (4.1%), for example. The difficulty of epitaxial growth over a large area is not therefore due to lattice mismatching. The substrate surface roughness may be the cause. Roughness of the UV/HF-treated Si(001) measured by AFM was about 0.2 nm. Although the surface is flat enough for homoepitaxial growth [16], it may not be enough for perfect heteroepitaxial growth of CuPc film. The molecular diameter of a CuPc is 1.6 nm. It is too large to fill up the unevenness of the substrate surface and too small to absorb it. Use of the off-angle polished Si(001) surface at a few degrees may be effective as with 3C-SiC on Si(111) or GaAs on Si(111), where heteroepitaxial growth is attained by insertion of a buffered layer. An atomic-order flat-surface substrate without offset angle may be also useful, while preparation is not so easy for a Si(001) as for a Si(111) surface [4].

Fig. 3(a)–3(f) shows the grains becoming smaller with decrease of the substrate temperature. The surface
of the film deposited at 150 K is very smooth. The root-mean-square roughness calculated from Fig. 3(f) was 0.89 nm. In order to suppress the crystallization and prepare a smooth CuPc film (roughness is smaller than molecular diameter) the substrate temperature must be cooled down to 150 K while the film of tetraphenylporphyrin, which has four bulky phenyl groups, becomes flat at 248 K [12]. It is probably due to the expected stronger molecular interaction among the CuPc molecules. Formation of such smooth film is important for device preparation. Although no peak is observed in the XRD pattern of the film (Fig. 1), existence of the molecular orientation was confirmed by ESR investigation. Harrison et al. reported the principal axes of the g-tensor (g_l) of the Cu*+, which is the center metal ion, is perpendicular to the molecular plane of CuPc with the value of 2.179 [17]. The parallel component of g value has the maximum value when the static magnetic field is applied parallel to the direction of the principal axis of the g-tensor. A static magnetic field was applied from an arbitrary direction in the substrate plane to the normal to the plane. The angular dependence of the parallel component of the g value was investigated and ∆g (g_l = 2.10) is shown in Fig. 7. It had a maximum at an angle of 69°. The error of the angle which is derived from the sample setting is ±3°. It means that the molecular orientation exists and the molecules are inclined at an angle of 21° ( = 90° - 69°) with respect to the substrate surface. Figs. 8(a)-8(c) show the FT-IR spectra of the film deposited at 150 K, and powder of 3-CuPc and β-CuPc as references, which were confirmed by the XRD measurement [14]. The characteristic peaks of 3- and β-CuPc are seen at 773 and 780 cm⁻¹, respectively. The spectrum of the film resembles that of the 3-CuPc form, although no peak is detected in the XRD pattern. Although the low substrate temperature of 150 K suppresses the crystallization and the film is non-crystalline, the molecules are oriented while keeping a smooth surface.

The hydrogen-terminated Si surface [13] is considered to be a relatively inert substrate for deposition. Stronger interaction between the substrate and molecules may be effective for layer-by-layer growth. A Langmuir–Blodgett film of stearic acid on glass (LBG) was used as a substrate [18]. Fig. 9 shows X-ray diffraction patterns of CuPc film 40 nm thick on a LBG substrate deposited at 323 and 293 K. No diffraction peak of CuPc is observed clearly, while the peak from the Langmuir–Blodgett film is seen. There seems no large difference between the AFM images of the two films. Fig. 10 is the image of the film deposited at 293 K. Instead of the columnar grains seen in Fig. 3, spherical grains of about 50 nm diameter are seen. The LBG substrate, which probably restricts the surface migration of CuPc molecules, suppresses the growth of the columnar crystalline film without substrate cooling. Although a smooth surface film was not obtained here, it may become possible even at room temperature by
4. Conclusion

CuPc films were grown on Si(001) by OMBD at various substrate temperature. The XRD investigation and the AFM lattice image observation revealed that epitaxial growth of χ-CuPc crystals on Si(001) has been achieved successfully for the first time. The b (c) axis of χ-CuPc was parallel to the Si [110] ([110]). A CuPc film with a smooth surface was prepared at 150 K, and the ESR investigation indicates that the molecules were oriented and the molecular plane was tilted at an angle of 21 ± 3° with respect to the substrate surface. CuPc films deposited on Langmuir–Blodgett film did not crystallize even at high substrate temperatures.

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References