

AN STM OBSERVATION OF ADSORPTION OF CuPc ON THE Si(100) SURFACE WITH BI-LINE STRUCTURES

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Received (to be inserted
Revised by publisher)

We report the reaction dynamics of the Bi-line structure (BLS) with copper-phthalocyanine (CuPc) molecules as well as hydrogen and Ag atoms on Si(100) surfaces observed by scanning tunneling microscopy. Co-adsorption of hydrogen and Ag on the Si(100) surface with BLSs brought about agglomeration of Ag atoms on the Si terrace. When CuPc molecules were deposited on the Si(100) surface with BLSs at room temperature, domains with $c(4\times 4)$ periodicity appeared in the terraces near the BLS. When the surface was annealed at 200–400°C, the area of the $c(4\times 4)$ domain was increased. The CuPc molecules, adsorbed on BLS, were possibly dissociated by catalytic reaction of Bi atoms.

1. Introduction

Fabrication of one-dimensional structures is one of promising techniques in making nanoscale devices on the semiconductor surfaces. It is well-known that Bi atoms adsorbed on the Si(100) surface form a long linear structure like a belt.^{1–17} This structure, named as “Bi-line structure (BLS, in short),” consists of two chains of Bi dimers in the topmost layer, and stretches parallel to the $\times 2$ direction of the terrace of the Si(100)(2×1) surface. The BLS is formed by a self-organization mechanism. For applying the BLS to make atomic-scale devices, they should understand not only its formation process

but also its reaction dynamics.

Naitoh et al. observed surface structural changes in the BLS at relatively low hydrogen exposures,⁵ where they showed that Bi-Si bonds in the BLS can be broken by the attack of hydrogen atoms. Itoh et al. found that Ag atoms are preferentially adsorbed on the Si terraces than on the BLS.¹⁸ The BLS was stable over a wide range of surface temperature under the interaction with Ag atoms. However, effects of hydrogen and metal atoms at their co-adsorbed states have not been clarified yet.

In this paper, we report an experiment by scan-

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ning tunneling microscopy (STM) on the reaction of the BLS to the adsorption of various foreign atoms. We observed surface structural changes induced by hydrogen adsorption on the Ag-deposited Si(100) surface with BLSs. Moreover, we investigated the process of adsorption and dissociation of copper-phthalocyanine (CuPc) on the Si(100) surface with BLSs. The CuPc, containing both hydrogen and metal atoms, is a promising material as an organic semiconductor. The fabrication of the CuPc nanostructures on silicon substrates has attracted considerable attention from device-technological and surface-scientific points of view.^{19–22} If above-mentioned BLS can be used as a “template” during the formation of one-dimensional structures of organic molecules such as CuPc, we would open a technology to make new devices. We discuss effects of the CuPc adsorption on the Si(100) surface structure involving BLSs.

2. Experimental

The experiments were carried out in an ultra-high vacuum chamber under a base pressure of 1×10^{-8} Pa. The chamber is equipped with an STM (JEOL JSTM-4500XT), a rear-view low energy electron diffraction (LEED) (VG RVL-900) and sample-preparation facilities including heating and deposition of Bi, Ag and CuPc. The STM images were taken at a condition of negative sample-bias and room temperature. Si(100) samples of the size $1 \times 7 \times 0.38$ mm³ were cut from an n-type wafer (P-doped, 0.015 Ω cm), cleaned in-situ by direct-current heating at 900°C followed by brief flashing at 1200°C. After the cleaning procedure, well-developed STM images and clear (2 \times 1) LEED patterns were observed. The substrate temperature was measured with an optical pyrometer in the range of 200–2000°C. Tips for STM observation were made from tungsten wire (0.3 mm in diameter), which were etched using 2N NaOH in a Pt loop electrode in direct current mode. The tips were baked out before being used for scanning. Bi (99.999 % purity), Ag (99.9999 % purity) or CuPc was deposited from each crucible made of thin Ta foil. The BLSs were produced by the bismuth deposition at 500°C on the Si(100) surface. The STM showed that the lines consisted of two atomic chains in the topmost layer. The LEED pattern for the

Si(100) surface with BLSs showed still (2 \times 1) periodicity. Atomic hydrogen was produced by the decomposition of molecular hydrogen gas on a tungsten filament at 1700 °C located at a distance of 20 cm from the sample. We recorded the H₂ exposure by the B-A gauge, as the actual flux of atomic hydrogen is assumed to be proportional to the exposure.

3. Results and Discussion

Ag atoms of the amount ~ 1 ML were deposited on the BLS/Si(100) surface. A LEED pattern at the surface changed from (2 \times 1) to (1 \times 1) by the Ag deposition. Fig. 1(a) shows an STM image taken after initial deposition of Ag on the Si(100) surface with BLSs. The BLSs are marked by white arrows. Since the BLSs are imaged clearly in Fig. 1(a), we judge that the BLSs are not wetted by the deposited Ag. This coincides with the previous observation by Itoh et al.¹⁸ We exposed this surface to atomic hydrogen with exposures 10–50 L (1 L = 1×10^{-6} Torr s). The (1 \times 1) periodicity in the LEED pattern was not changed by the hydrogen adsorption. Figs. 1(b-d) show STM images of the Ag-deposited BLS/Si(100) surface taken in the course of hydrogen adsorption and annealing. The BLSs in the STM image (Fig. 1(b)) became blurred slightly when hydrogen atoms were dosed at 10 L to the surface corresponding to Fig. 1(a). The STM image from the hydrogen-exposed surface at an exposure of 50 L is shown in Fig. 1(c). We can observe many protrusions on the surface in Figs. 1(b) and 1(c). By increasing the hydrogen exposure, from Fig. 1(b) to Fig. 1(c), the mean size of the protrusions becomes larger and their number increases. Tanaka et al. observed by impact-collision ion scattering spectroscopy that Ag deposition on hydrogen-terminated Si(100) surfaces leads to growth of Ag islands.²³ An STM experiment by Sakurai et al. revealed that Ag atoms diffuse on the Si(100)-(2 \times 1)-H surface and isolated single Ag atoms or Ag clusters are adsorbed on Si dangling-bond sites.²⁴ Taking into account these reports, we speculate that the protrusions on the present surfaces (Fig. 1(c)) correspond to Ag clusters. Further experiments by, e.g., scanning tunneling spectroscopy, are necessary to make clear the real chemical nature of the clusters.

The STM image of the hydrogen-adsorbed Ag/Si(100) surface with BLSs taken after the heat-treatment at 490°C is shown in Fig. 1(d). The BLSs reappeared in the topmost layer in Fig. 1(d). Dimer defects, marked by black arrows, were created in these BLSs. In addition, larger protrusions, covering the surface in Fig. 1(c), disappeared. We propose tentatively the co-adsorption process of Ag and hydrogen as follows. When hydrogen atoms intrude into the Ag/Si(100) surface with BLSs, Ag atoms on the Si terrace are forced to lose bondings with Si and to compose clusters. These clusters are accommodated at sites either in the Si terrace or on the BLSs. The Ag clusters are desorbed from this surface by being annealed at temperatures around 500°C.

CuPc molecules were deposited on the Si(100) surface with BLSs while the sample temperature was maintained at room temperature. Fig. 2(a) shows an STM image taken after CuPc deposition for 30 s on the Si(100) surface with BLSs. The LEED pattern was changed from (2×1) to (1×1) by the CuPc deposition. Looking at a distribution of bright areas in Fig. 2(a), we estimate that CuPc molecules adsorb in the Si terrace more easily than on the BLSs. We can find some patches of the (2×1) substrate structure in Fig. 2(a). This means the Si(100) surface with BLSs was covered only partially with CuPc molecules. Fig. 2(b) shows an STM image taken after CuPc deposition for 60 s on the Si(100) surface with BLSs. Previous STM experiments have demonstrated that metal-phthalocyanine molecules deposited on the Si(100) surface are registered in dangling-bond arrangements of the Si substrate, showing 4-spot images corresponding to their flat molecular structure.^{19,20,25} We can find those bright 4-spot shapes indicated with white arrows in Figs. 2(a) and 2(b). We observed locally a $c(4\times 4)$ structure indicated by the white broken circles in Figs. 2(a) and 2(b). An interpretation of the appearance of the $c(4\times 4)$ structure is given below.

Fig. 3(a) shows an STM image taken after annealing the CuPc-deposited BLS/Si(100) surface at 200°C for 120 s. CuPc-induced bright spots disappeared from the surface by this heating. By annealing further the surface of Fig. 3(a) at 400°C for 120 s we obtained an STM image shown in Fig. 3(b). One can confirm the $c(4\times 4)$ structures developing

in the Si terrace. At least two kinds of possibilities should be considered for generating the $c(4\times 4)$ structure. One is by dissociated Bi atoms from the BLS. The BLS may be cut by hydrogen coming from CuPc molecules and Bi atoms separated from parent BLS may induce the $c(4\times 4)$ reconstruction on the Si terrace. This would correspond to a $c(4\times 4)$ structure observed by Miki et al. at a condition of large Bi flux and high temperatures.³ The other is by dissociated carbon or Cu atoms from CuPc. This may be related to the $c(4\times 4)$ structure observed at Si(100) surfaces when carbon atoms are incorporated on the surface.^{26,27} The former is less probable, because, if the BLS was so unstable and dissociated in the process from Fig. 3(a) to Fig. 3(b), many broken BLSs would be left on the surface, contrary to the STM observation in Fig. 3(b). We speculate that CuPc molecules are partly dissociated by some catalytic behavior of Bi atoms. Single CuPc molecule provides several carbon atoms, and then only small regions with the $c(4\times 4)$ periodicity are formed on the surface. In the annealing process of the CuPc-deposited Si(100) surface with BLSs, carbon atoms supplied by the dissociation of the CuPc molecule migrate easily on the surface, and relatively large regions of the $c(4\times 4)$ structure are formed.

4. Conclusions

We have investigated the reaction dynamics of the BLS with CuPc molecules as well as hydrogen and Ag atoms by STM. Co-adsorption of hydrogen and Ag on the Si(100) surface with BLSs leads to growth of the Ag clusters. When CuPc molecules were deposited on the Si(100) surface with BLSs, domains with $c(4\times 4)$ periodicity appeared on the surface. The CuPc molecules, adsorbed on the Si(100) surface with BLSs, were dissociated by some catalytic reactions of Bi atoms on the surface.

Acknowledgments

This work was supported by a Grant-in Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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