Adsorption of cobalt phthalocyanine on a Si(100) surface with Bi-line structures as evaluated by scanning tunneling microscopy

T. Ikari[a], S. Tanaka[b], S. Nakamura[b], M. Naitoh[b,*], S. Nishigaki[b], F. Shoji[c]

[a] *Ube National College of Technology, Ube, 755-8555, Japan*

[b] *Kyushu Institute of Technology, Tobata, Kitakyushu, 804-8550, Japan*

[c] *Kyushu Kyoritsu University, Yahatanishi, Kitakyushu, 807-8585, Japan*

We report the reaction dynamics of cobalt phthalocyanine (CoPc) molecules with Bi-line structures (BLSs) on a Si(100) surface, investigated using scanning tunneling microscopy (STM). When CoPc molecules were deposited on a Si(100) surface with BLSs at room temperature, single-spot protrusions were observed in the STM image instead of four-spot images corresponding to CoPc's flat molecular structure. Moreover, domains with a c(4×4) periodicity appeared on the terraces of the Si(100) surface. This indicates that CoPc molecules may have decomposed on the surface by catalytic reaction with Bi atoms.

PACS: 68.37.Ef; 68.43.Hn

Keywords: STM; Bismuth; Si(100) surface; Surface Structure; Phthalocyanine

E-mail address: naitoh@elcs.kyutech.ac.jp (M. Naitoh).

1. Introduction

There have been many reports of the formation of novel structures on semiconductor surfaces by atomic deposition. Among these, the behavior of Bi atoms on a Si(100) surface has attracted much attention for the ability to form a one-dimensional structure [1-8] and to act as a surfactant in hetero-epitaxial systems such as Ge/Si(100) [9]. Bi atoms adsorbed on a Si(100) surface form a one-dimensional belt-like structure, which has been named the Bi-line structure (BLS). The BLS consists of two neighboring chains of Bi dimers in the topmost layer, and stretches parallel to the ×2 direction of the terraces of the Si(100)(2×1) surface. To apply the BLS to templates in the manufacture of atomic-scale devices, one should understand not only the formation process, but also the reaction dynamics.

Naitoh *et al.* observed surface structure changes in BLS at relatively low hydrogen exposures, where they showed that Bi-Si bonds in the BLS can be broken by the attack of hydrogen atoms [5]. Itoh *et al.* found that Ag atoms are preferentially adsorbed on the Si terraces, rather than on the BLS [10]. The BLS is stable over a wide range of surface temperatures under interaction with Ag atoms. However, the effects of hydrogen and metal atoms in co-adsorbed states have not yet been clarified.

In a previous paper [11], we investigated the processes of adsorption and dissociation of copper-phthalocyanine (CuPc) on a Si(100) surface containing BLSs by scanning tunneling microscopy (STM). Metal phthalocyanine molecules have attracted great technological interest in a wide variety of fields such as chemical sensors, optoelectronic devices, and solar cells [12]. These are organic semiconductors that can be used in well-behaved field effect transistors [13]. They are even expected to serve as two-dimensional insulated quantum wires with a central atomic conductor sheathed in a molecular insulator [13]. If the above-mentioned BLS can be used as a “template” during the formation of one-dimensional structures of organic molecules such as metal phthalocyanine, they would provide a foundation for a very interesting

new device manufacturing technology.

In this paper, we studied the adsorption and dissociation of cobalt-phthalocyanine (CoPc) on a Si(100) surface containing BLSs. CoPc has also attracted much attention for potential application as a low-dimensional molecular magnet due to the magnetic properties of Co atoms [14]. Moreover, it is expected to be useful for the formation of carbon nanotubes [15]. We discuss the effects of CoPc adsorption on a 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 was 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 and CoPc. Si(100) samples of size $1\times7\times0.38$ mm^3 were cut from an *n*-type wafer (P-doped, 0.02 Ωcm), cleaned *in-situ* by direct-current heating at 900^{o}C, followed by a brief flashing at 1200^{o}C. After the cleaning procedure, well-developed STM images and clear (2×1) LEED patterns were observed. The sample temperatures were measured with an optical pyrometer in the range of 200-2000^{o}C. Tips for STM observation were made from tungsten wire (0.3 mm in diameter), 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) or CoPc was deposited from a crucible made of thin Ta foil. The rates of Bi and CoPc deposition were approximately 0.1 and 0.05 ML/min, respectively, where 1 ML was defined as the Si density on the ideal (100) plane.

The BLSs were produced by bismuth deposition of ~0.1 ML at 500^{o}C on the Si(100) surface. The STM revealed that the lines consisted of two atomic chains in the topmost layer. The LEED pattern for the Si(100) surface with BLSs still showed (2×1) periodicity.

3. Results and discussion

We present the reaction dynamics induced by adsorbed CoPc on a Si(100) surface containing BLSs at room temperature. When CoPc molecules were deposited for 30 s on this surface, the LEED pattern of the surface changed from (2×1) to (1×1). Fig. 1(a) shows an STM image of this surface. The BLSs are indicated by white arrows. We observed many bright protrusions in Fig. 1(a), indicated by white squares. The amount of protrusions increased for a CoPc deposition of 60 s, as shown in Fig. 1(b). There were several previous reports that a Co atom located in the center of a CoPc molecule manifests itself as a bright protrusion in STM images, resulting from the relation between the density of states of the STM tips and the electron density in the Co-d orbital [16-18]. The electronic structure and the distribution of spin density for CoPc were found from band structure calculations [19]. Thus, each protrusion with a single bright spot corresponded to a CoPc molecule deposited on the surface. As the sharpness of our STM tips was insufficient, we obtained no five-spot protrusions like those seen in ref. [18] but instead observed protrusions having one bright spot in the STM images.

In Figs. 1(a) and 1(b), there are many protrusions on the Si(100) terrace compared with on the BLSs. This indicates that the sticking coefficient of CoPc molecules on the BLSs is low, or that CoPc molecules decomposed on BLSs. In Figs. 1(a) and 1(b), we see that the Si terraces became disordered. The adsorption of CoPc on the Si(100) surface containing BLSs at room temperature induced the formation of defects in the BLSs, and c(4×4) structures on the Si terrace, indicated by a black arrow and white ovals, respectively. We suppose that the CoPc molecules combined with dangling bonds of the Si(100) terrace atoms after the decomposition of some of the atoms in the CoPc molecules on the Si(100) surface. The decomposition of the BLS arose from the breaking of Bi-Si bonds due to the attack of atomic hydrogen [5]. It is likely that the defects originated with hydrogen atoms from the decomposition of the CoPc

molecules.

Fig. 2 shows an STM image taken after annealing the specimen from Fig. 1(a) for 120 s at 200^{o}C. The amount of defects in the BLSs increased. The defects in the BLSs are probably caused by hydrogen atoms originating from the decomposition of CoPc molecules during the annealing process. In such a process, the top of the BLSs would disintegrate. The number of protrusions in Fig. 2 was about the same order as in Fig. 1(a), because the shape of protrusions in the STM image did not vary with desorption of the outermost atoms in the CoPc molecules.

Fig. 3 shows an STM image taken after annealing the specimen shown in Fig. 2 for 120 s at 400^{o}C. Large protrusions were observed, and the area having c(4×4) structure grew larger in the Si(100) terrace. Palasantzas *et al*. reported an STM experiment on the behavior of deposited Co atoms on H-terminated Si(100)-(2×1) surface at room temperature and during annealing [20]. According to their observations, adsorbed Co atoms on a H/Si(100)-(2×1) surface are imaged as bright spots, and Co atoms deposited on the surface and held at 405^{o}C diffused and assembled to form large islands on the surface. Under our conditions, the CoPc molecules may decompose into several-atoms clusters at 400^{o}C. Then, Co atoms would agglomerate on the surface, which would explain the large protrusions observed in Fig. 3 to be Co islands.

After further annealing the surface of Fig. 3 for 120 s at 500^{o}C, we obtained the STM image shown in Fig. 4. We could not find BLS anywhere on the Si surface. As Bi atoms, either adsorbed or embedded in c(4×4) structures, desorbed from the Si surface, Si (2×1) structures reappeared in the Si terraces. The surface shown in Fig. 4 exhibited a novel c(4×4) structure extending over wide regions of the Si terrace, which was different from the c(4×4) structures of Figs. 1-3. According to the observation by J.Y. Maeng *et al*., a c(4×4) unit cell is oriented perpendicular to the underlying Si dimer rows [21]. The c(4×4) structure in Fig. 4 is similar to the model proposed by J.Y. Maeng. At a substrate temperature of 500^{o}C, hydrogen

atoms desorbed from the surface, but carbon atoms did not. We suggest that the novel c(4×4) structure contains carbon atoms supplied by the decomposition of CoPc molecules. The quantitative measurement of the amount of carbon atoms would be necessary to fully discuss this c(4×4) structure.

When we adsorbed CoPc molecules on a clean (2×1) Si(100) surface, we did not observe c(4×4) structures in the STM images. CoPc molecules may be partly decomposed by catalytic behavior of Bi atoms. A single CoPc molecule could provide several carbon atoms, and then only small regions with c(4×4) periodicity would be formed on the surface. We think that the catalytic reaction of CoPc decomposition is enhanced by the annealing process.

There are larger protrusions in Fig. 4 than in Fig. 3. Thus, the number of decomposed CoPc molecules increased with annealing temperature. The Co atoms supplied by the decomposition of CoPc molecules easily migrate on the surface, and agglomerate to form the clusters.

4. Conclusions

We investigated the reaction dynamics of CoPc molecules with the BLS by STM. When CoPc molecules were deposited on a Si(100) surface containing BLSs at room temperature, single-spot protrusions corresponding to Co atoms located in the middle of CoPc molecules were observed. When the CoPc-deposited surface with BLSs was annealed at 200-400^{o}C, the CoPc molecules decomposed, and Co atoms from decomposed CoPc molecules agglomerated on the surface.

References

[1] M. Naitoh, H. Shimaya, S. Nishigaki, N. Oishi, F. Shoji, Surf. Sci. 377-379 (1997) 899.

[2] M. Naitoh, H. Shimaya, S. Nishigaki, N. Oishi, F. Shoji, Appl. Surf. Sci. 144-145 (1999) 38.

[3] K. Miki, J.H.G. Owen, D.R. Bowler, G.A.D. Briggs, K. Sakamoto, Surf. Sci. 421 (1999) 397.

[4] K. Miki, D.R. Bowler, J.H.G. Owen, G.A.D. Briggs, K. Sakamoto, Phys. Rev. B 59 (1999) 14868.

[5] M. Naitoh, M. Takei, S. Nishigaki, N. Oishi, F. Shoji, Jpn. J. Appl. Phys. 39 (2000) 2793.

[6] M. Shimomura, K. Miki, T. Abukawa, S. Kono, Surf. Sci. 447 (2000) L169.

[7] D.R. Bowler, Phys. Rev. B 62 (2000) 7237.

[8] M. Naitoh, M. Takei, S. Nishigaki, N. Oishi, F. Shoji, Surf. Sci. 482-485 (2001) 1440.

[9] K. Sakamoto, K. Kyoya, K. Miki, H. Matsuhata, T. Sakamoto, Jpn. J. Appl. Phys. 132 (1993) L204.

[10] T. Itoh, S. Kashirajima, M. Naitoh, S. Nishigaki, F. Shoji, Appl. Surf. Sci. 244 (2005) 161.

[11] S. Nakamura, S. Kashirajima, Y. Johdai, Y. Yoshiiwa, M. Naitoh, S. Nishigaki, Y. Shimizu, T. Ikari, F. Shoji, Surf. Rev. Lett. 14 (2007) 957.

[12] X. Lu, K.W. Hipps, X.D. Wang, U. Mazur, J. Am. Chem. Soc. 118 (1996) 7197.

[13] X. Lu, K.W. Hipps, J. Phys. Chem. B 101 (1997) 5391.

[14] A.R. Harutyunyan, Chem. Phys. Lett. 246 (1995) 615.

[15] M. Yudasaka, R. Kikuchi, Y. Ohki, S. Yoshimura, Carbon 35 (1997) 195.

[16] J.G. Hou, A. Zhao, Nano 1 (2006) 15.

[17] K.W. Hipps, X. Lu, X.D. Wang, U. Mazur, J. Phys. Chem. 100 (1996) 11207.

[18] L. Liu, J. Yu, N.O.L. Viernes, J.S. Moore, J.W. Lyding, Surf, Sci. 516 (2002) 118.

[19] B. Białek, I.G. Kim, J.I. Lee, Thin Solid Films 513 (2006) 110.

[20] G. Palasantzas, B. Ilge, J. de Nijs, L.J. Geerligs, Surf. Sci. 412-413 (1998) 509.

[21] J.Y. Maeng, S. Kim, Surf. Sci. 482-485 (2001) 1445.

Figure Captions

Fig. 1. STM images taken after CoPc deposition (a) for 30 s and (b) for 60 s on a Si(100) surface containing BLSs at room temperature. The images were taken sample bias Vs = −2.0 V, tunneling current It = 0.3 nA, and image area S = 44×44 nm^2.

Fig. 2. STM image taken after annealing the specimen from Fig. 1 at 200^oC for 120 s. The image was taken with a sample bias Vs = −2.0 V, tunneling current It = 0.3 nA, and image area S = 44×44 nm^2.

Fig. 3. STM image taken after annealing the specimen from Fig. 2 at 400^oC for 120 s. The image was taken with a sample bias Vs = −2.0 V, tunneling current It = 0.3 nA, and image area S = 44×44 nm^2.

Fig. 4. STM image taken after annealing the specimen from Fig.3 at 500^oC for 120 s. The image was taken with a sample bias Vs = −2.0 V, tunneling current It = 0.3 nA, and image area S = 66×66 nm^2.

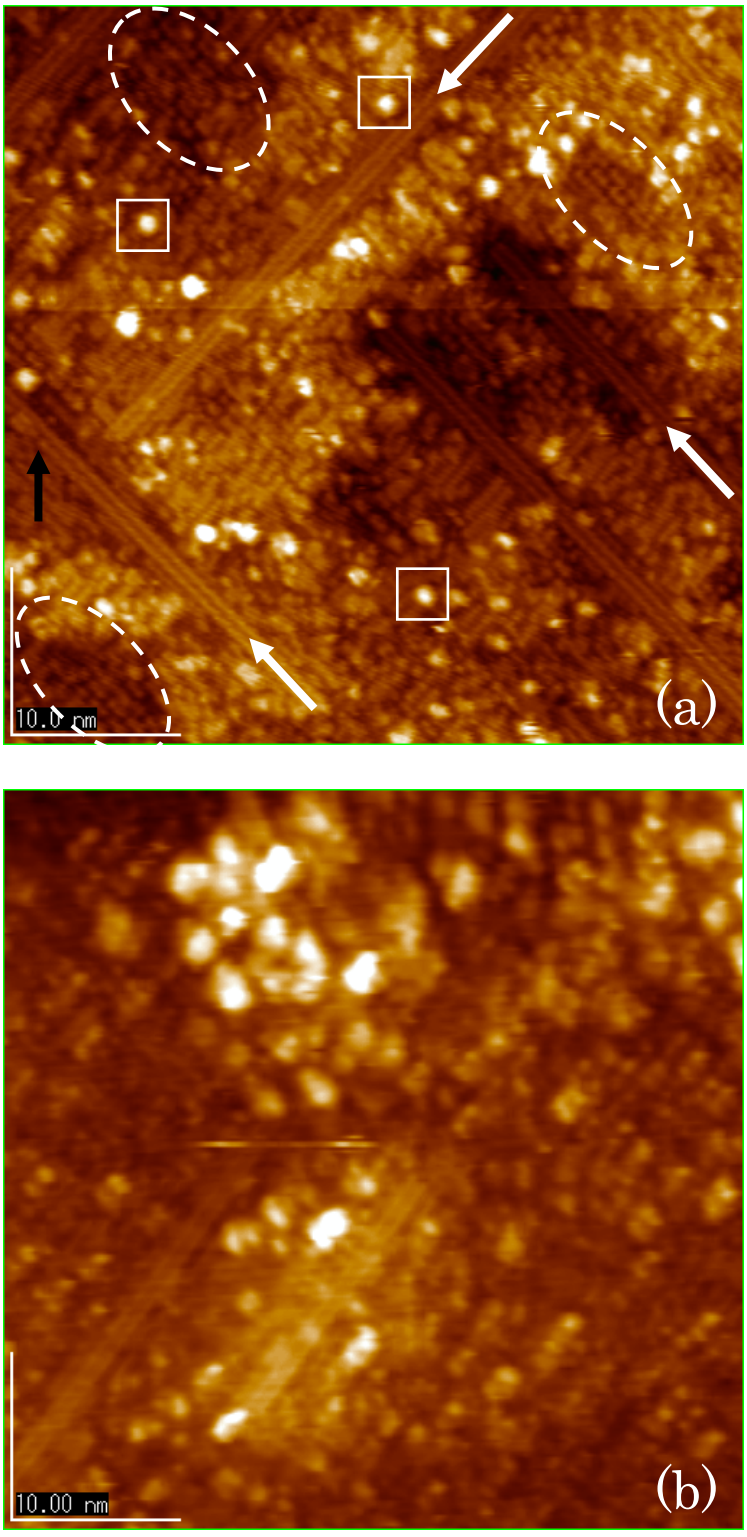

Fig. 1. Ikari et al.

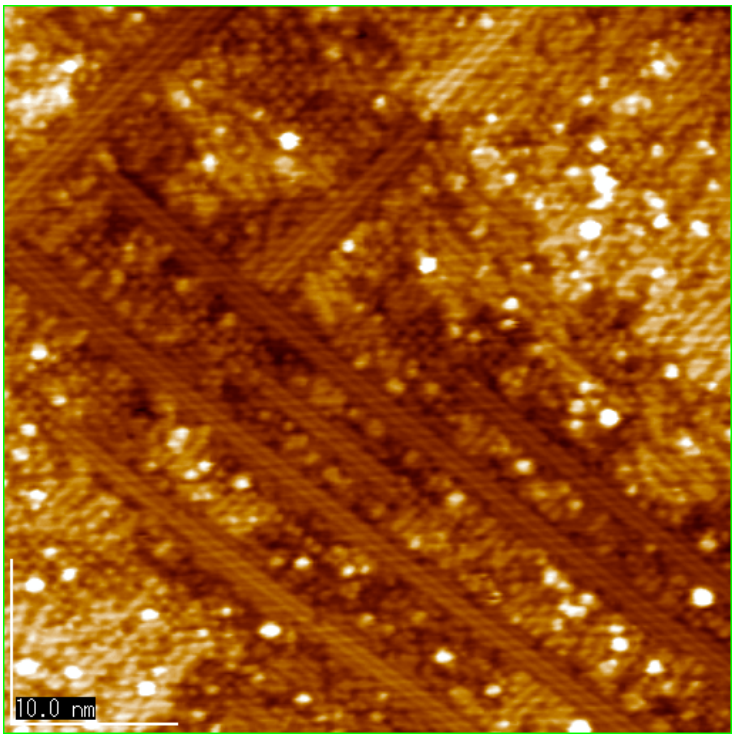

Fig. 2. Ikari et al.

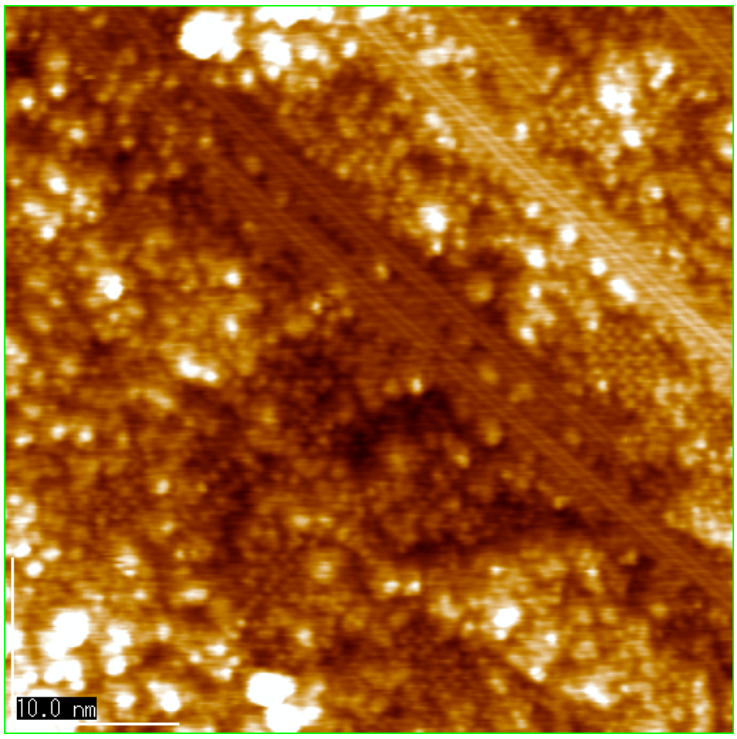

Fig. 3. Ikari et al.

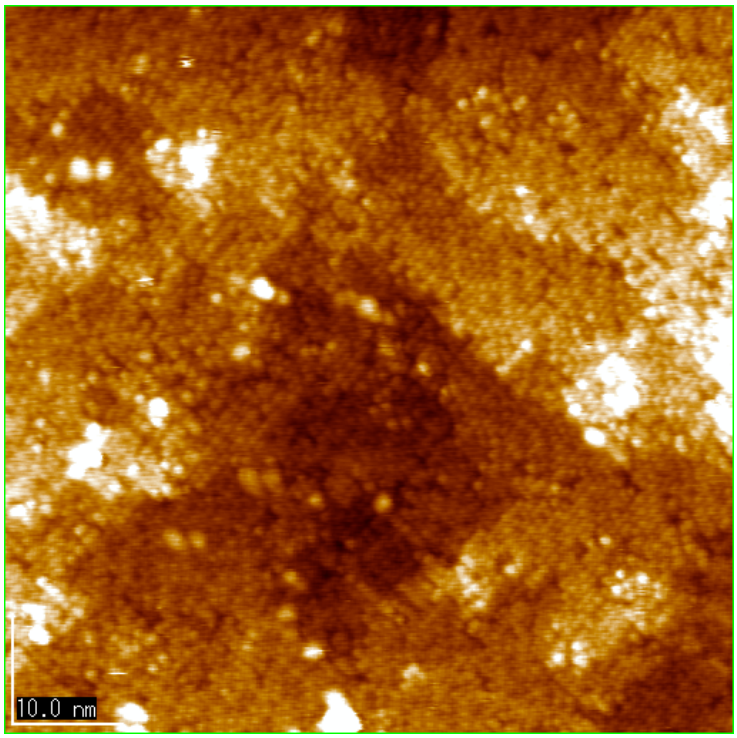

Fig. 4. Ikari et al.