Initial Stage of Molecular Adsorption on Si(100) and H-terminated Si(100) Investigated by UHV-STM(STM,Si(001))

Initial Stage of Molecular Adsorption on Si(100) and H-terminated Si(100) Investigated by UHV-STM

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We have investigated the initial stage of adsorption of a conjugated aromatic compound, 1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB), on the clean Si(100)-2 × 1 surface and the hydrogen terminated Si(100)-2 × 1-H surface by ultra-high-vacuum (UHV) scanning tunneling microscopy (STM). We found adsorbed molecules cannot migrate on the chemically active Si(100)-2 × 1 surface, while they can migrate on the chemically inactive hydrogen terminated Si(100)-2 × 1-H surface until they are trapped to hydrogen-missing dangling bonds. On the clean Si(100)-2 × 1, we observed four different adsorption directions. An individual molecule appears as two or three bright spots, the brightness and distance between bright spots varying for different cases. Through structural analysis and bias-voltage-dependent STM images, we conclude that the electronic states of Si dimers modulated by the adsorbed molecules are observed instead of the molecules themselves. A simple estimation by considering only the molecular size and shape reproduces the distribution of four different kinds of adsorption structures we observed.

KEYWORDS: initial stage of adsorption, conjugated aromatic compound, Si(100), hydrogen terminated Si(100), scanning tunneling microscopy

1. Introduction

A number of crystalline state organic photoreactions have been reported to date in which several examples date a hundred years back. Among these reactions, topochemical photopolymerization which was first established by Hasegawa *et al.* in 1967 has been widely investigated [1]. Topochemical photopolymerization is a kind of solid-state polymerization caused by ultraviolet (UV) irradiation. As shown in Fig. 1(a), for example, the monomer crystal of a conjugated aromatic compound, 1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB), affords a linear polymer having the recurring cyclobutane structure with a 1,3-trans configuration and 1,4-arylene units alternately in the chain. According to the topochemical concept, the reaction tends to occur with a minimum of atomic and molecular motion. More preciously, in the α-type crystal, the double bonds of neighboring molecules should be arranged in parallel and make contact at a distance of 3.6-4.1 Å (topochemical principle) [2].

Although the understanding of this principle has been established by X-ray diffraction study *etc.* [3], there exists a strong want to obtain the microscopic information on this polymerization in real space. Scanning tunneling microscopy (STM) [4] has a large potential of detecting the structural change before and after polymerization. In addition, some spectroscopic method such as scanning tunneling spectroscopy (STS) may tell us a microscopic mechanism of a polymerization process in principle.

So far, we have investigated the ultra-thin films of P2VB molecules on several kinds of substrate, such as highly oriented pyrolytic graphite (HOPG) [5], Cu(111),
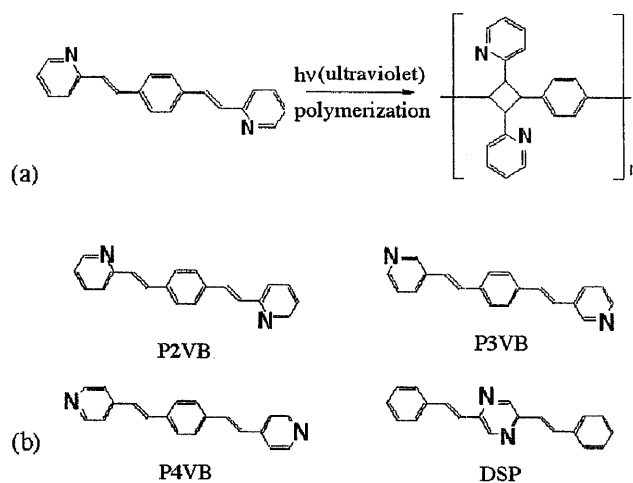

Figure 1. (a) Chemical structures of P2VB and poly-P2VB obtained by irradiating UV light to its monomer-crystal. (b) Similar derivatives with P2VB, where the locations of nitrogen atoms are different from each other.

Ag(100) [6], and Au(111) [7], by STM. In the case of the first layer of the P2VB thin film on these substrates, molecular ordering tends to become the γ-form partly because of strong interactions between molecules and substrates. Thus, polymerization does not take place due to the topochemical principle [2].

In this study, ultra-high-vacuum (UHV) STM was applied to observe the initial stage of adsorption of P2VB individual molecules on a Si(100) surface. This surface

was selected as a substrate because (1) a clean Si(100) surface can be easily obtained by merely a series of heatings, (2) several research reports on the adsorption of organic molecules on Si(100) surface have been published [8–10], and (3) the future development of molecular devices may be based on Si(100) or Si(111) surfaces. We show how molecules interact with a chemically active surface and how we interpret STM images of the molecule. For comparison, molecular adsorption behaviors on hydrogen terminated Si(100)–2 × 1–H surface is also discussed.

2. Experimental

Silicon samples, which were cut from a commercial Si(100) wafer (n type, 0.007–0.013 $\Omega \cdot$cm), were introduced into the UHV preparation chamber and a series of resistive heatings up to 1260°C following the overnight outgassing at 700°C was conducted to obtain a clean Si(100)–2 × 1 surface. The pressure of the preparation chamber was kept below 2×10^{-10} Torr during the final cleaning procedure.

After introducing the Si(100)–2 × 1 substrate into the STM chamber, we checked the clean surface by STM. Then we deposited P2VB molecules, using a homemade doser, which was made of tantalum. The base pressure of the STM chamber was kept below 5×10^{-11} Torr and the pressure increase during the deposition of molecules was less than 1×10^{-11} Torr. In this condition, a few dozen P2VB molecules adsorbed on the area of 400×400 Å^2 for 20 min deposition, which corresponds to about 10^{-5} ML (1 ML in this paper refers to 6.78×10^{14} cm^{-2}; the number of Si atoms on the ideal bulk-terminated Si(100) surface).

In order to prepare a hydrogen terminated Si(100)–2 × 1–H surface, atomic hydrogen was made from hydrogen gas molecules using a homemade doser and impinged to the Si(100)–2 × 1 surface whose temperature was kept at approximately 350–400°C. The hydrogen flux is estimated to be 3×10^{-2} ML/s and the density of dangling bonds (missing hydrogen defects) is controlled by the impinging period. The detailed condition of making hydrogen terminated Si(100)–2 × 1–H was reported previously [11]. According to this report, we can obtain a hydrogen terminated Si(100)–2 × 1–H monohydride phase in this condition.

Scanning tips electrochemically etched from ⟨111⟩ oriented single crystal W wires were used. Each tip apex was cleaned and shaped into hemisphere using field ion microscope (FIM) [12, 13] in $situ$ in the preparation chamber. The base pressure of the STM chamber was kept below 7×10^{-11} Torr during the STM observation. The STM images presented here were taken at a sample bias voltage V_{sample} ranging -2.0–$+2.0$ V and a constant tunneling current I_t of 20 pA.

3. Results and Discussions

3.1 Adsorbed structures of P2VB molecules on Si(100)
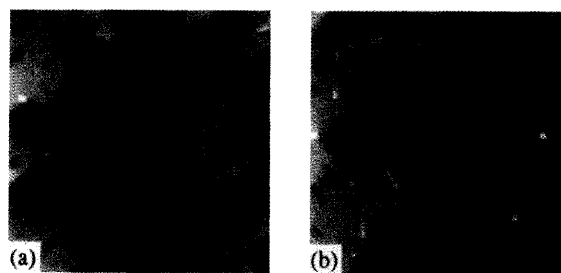
Figures 2(a) and (b) show STM images of the Si(100)–

Figure 2. STM images of Si(100)–2 × 1 (a) clean and (b) with 2×10^{-5} ML P2VB molecules. For both images, the scan size is 400×400 Å^2 and $V_{sample} = -2.0$ V.

2 × 1 surface before and after deposition of P2VB molecules. In Fig. 2(a), we observe Si dimer rows of the clean Si(100)–2 × 1, while P2VB molecules are visible in Fig. 2(b). The coverage of adsorbed P2VB molecules was 1×10^{-5} ML. We note that the individual molecules adsorb randomly and stably on the surface, indicating that the molecules cannot migrate long distances on this chemically active surface. Hence, strong interaction between Si dangling bonds and molecules may cause chemisorption of P2VB molecules on the Si(100) surface.

In Fig. 3(a)–(d), four different directions of P2VB molecular adsorption were observed: (a) and (d) inclined to dimer rows, (b) along a dimer row, and (c) perpen-
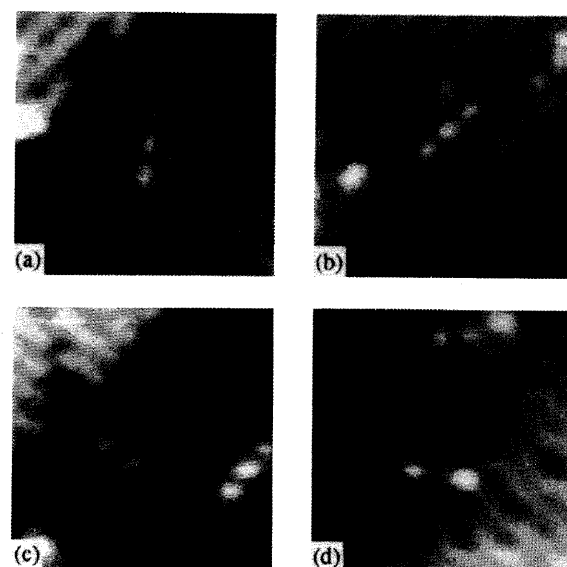

Figure 3. STM images of four different directions of P2VB molecular adsorption. A molecule adsorbs (a) and (d) inclined to dimer rows, (b) along a dimer row, and (c) perpendicular to dimer rows. The scan size is 70×70 Å^2 and $V_{sample} = -2.0$ V for all images.
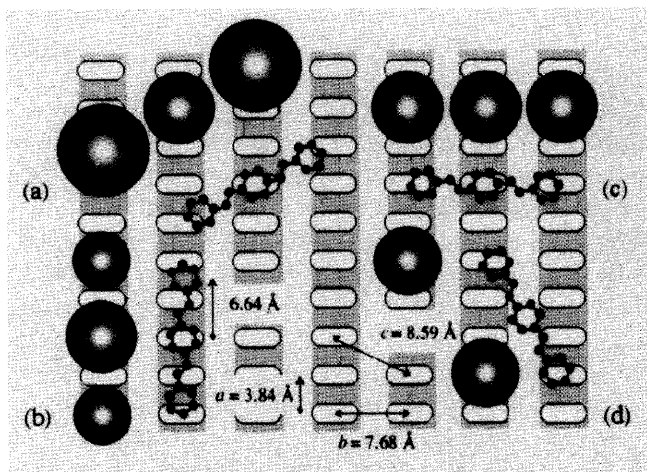
Figure 4. Comparison between the structure obtained by STM and possible interpretations of the adsorption site for all cases. This figure also presents dimensions of the Si(100)–2 × 1 surface and P2VB molecule.

Figure 5. Bias-dependent STM images of a P2VB molecule adsorbed along a dimer row. The scan size is identical, 110×110 Å^2, while V_{sample} is -2.0 V for (a) and $+2.0$ V for (b). In (a), the molecule can be observed as three bright spots, while the bright spots disappear in (b), as indicated by the arrow.

dicular to dimer rows. We observed no other adsorption direction. Note that a molecule is imaged as three bright spots, except in the case of (d). Because of the adsorbed structure appearing in (d), a simple explanation that these bright spots correspond to three aromatic rings included in a P2VB molecule is not valid.

In order to investigate these adsorption structures in detail, we determined adsorption sites precisely with respect to the Si(100) dimer. Figure 4 shows the adsorption sites determined. In this figure, dimensions of Si(100)–2 × 1 surface and P2VB molecule are also presented. For example, in the case of the molecule adsorbed inclined to dimer rows (Fig. 4(a)), the distance between two bright spots is $(1.00 \pm 0.05)c$, where c is one of the unit lengths introduced in Fig. 4. Furtheremore, in the case of the molecule adsorbed along a dimer row (Fig. 4(b)), the distance between two bright spots is $(2.05 \pm 0.07)a$ ($a = 3.84$ Å is the unit distance of the Si(100) surface). Since the distance between two aromatic rings in a P2VB molecule is 6.64 Å, we conclude that the bright spots are located on the Si dimers rather than on the aromatic rings. Other two adsorption structures can be fully understood in a similar manner. For all cases, the Si dimers that strongly interact with aromatic rings of a molecule are visible as bright spots.

Figure 5 shows bias-dependent STM images of a P2VB molecule adsorbed along a dimer row. The imaging areas of Figs. 5(a) and (b) are almost identical. On the other hand, sample bias voltages are reversed; $V_{sample} = -2.0$ V for (a) and $+2.0$ V for (b). In Fig. 5(a), a molecule appears as three bright spots. But, the P2VB molecule does not form bright spots; only a darker spot is visible in Fig. 5(b) as indicated by the arrow.

In some cases, the bias voltage dependence may be explained by the original electronic states of an adsorbate, such as the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). Indeed, some researchers have succeeded in their interpre-
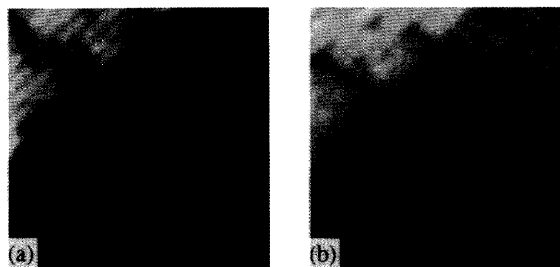
tation of adsorbed molecules on several kinds of substrate based on this explanation [14, 15]. But, there exist some cases in which the LUMO and HOMO themselves are not observed. Some researchers used theoretical approaches to explain the imaging mechanism of adsorbates such as resonant tunneling [16] and through-bond tunneling [17]. In the case of low bias voltages, mixed electronic states of an adsorbate near the Fermi level of a substrate may be detected resulting from the many-body effect [18]. The imaging mechanism of adsorbed molecules is still controversial. We, hence, do not intend to give any general explanation in this paper, but will discuss some possibilities below. First, please note the comparison between the observed structure and the results of Hükkel molecular orbital (HMO) calculation, as shown in Fig. 6. It can easily be discerned that the calculated orbitals do not coincide with the observed structure. Furtheremore, this idea can be easily discarded becase the brightness and distance between bright spots varying for different cases. The existence of the adsorbed structure appearing in Fig. 3(d) also denies this idea, where a molecule is visible as only two bright spots.

Recalling the observed results that the locations of the bright spots coincide fully with that of Si dimers, it can be mentioned that we observed the electronic states of Si(100) dimer modulated by the adsorbed molecule, rather than the molecule itself. The distinct bright spots appearing in Fig. 3 and Fig. 5(a) correspond to the enhanced occupied electronic states of Si dimers, while the empty states of the Si dimer are reduced as shown in Fig. 5(b). This result may suggest the possible interaction mechanism between Si dimers and molecules that the molecular orbital of an aromatic ring interacts with dangling bonds on the Si dimer, forming new electronic states just below the Fermi level. Another possibility is that the dangling-bond states are rearranged by molecular adsorption and the Si dimers become rich with covalent electrons, similar to the case of the interaction between π-bond and alkali metals [19, 20]. The possibility of some charge transfer resulting in the change of the electronic states of Si dimers also cannot be de-
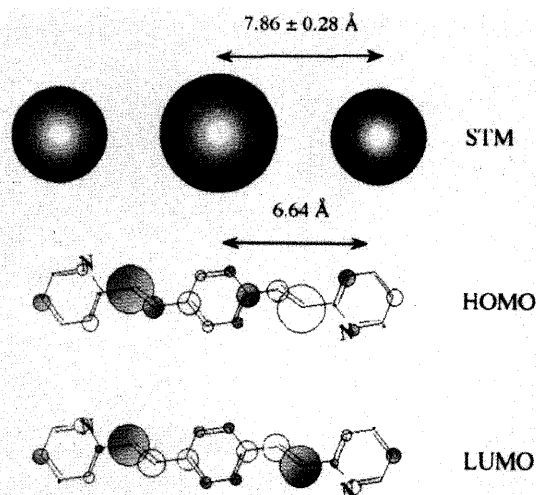
Figure 6. Comparison of the obtained electronic structure and eigen states of P2VB (HOMO and LUMO). The calculated orbitals do not always coincide with the observed structure.

nied [10]. Similarly, our preliminary molecular orbital calculation shows that the direct chemical bonding between carbon atom and silicon atom forms upon adsorption of benzene on Si(100) surface. Thus, we propose the STM bright spots reflect the silocon dangling bonds chemisorbed with carbon/nitrogen atoms of P2VB [21].

Additional evidence of the modulation of the electronic states of Si dimers by adsorbed molecules can be seen in Fig. 3(a). We can see the buckling of the dimers within a range of a few dimers near the adsorbed molecule, as indicated by the arrow. This result implies that the adsorption stabilizes buckling of dimers similar to the case of alkali adsorption or presence of some defects on the surface [19, 22, 23].

We also observe different contrasts of the bright spots for the four types of adsorption structures (see Figs. 3 and 4). As explained above, for example, the molecule along a dimer row appears as three bright spots: the center spot, which interacts with a benzene ring, is brightest. In the case of the molecule perpendicular to the dimer rows, however, three spots of equal brightness are visible. Although we observe the modulated electronic states of Si dimers as discussed above, we do not fully understand the origin of this contrast. The small difference in the interacting area may cause the difference in the appearance of the observed structures, or some charge transfer from Si dangling bond to nitrogen atom existing in the prydine ring may dominate the interaction strength. To investigate such a charge transfer mechanism, similar derivatives such as shown in Fig. 1(b) are under study, where the locations of nitrogen atoms are different from each other.

3.2 Initial stage of adsorption of P2VB molecules

As shown in Fig. 3, there exist four stable adsorption structures of P2VB molecules. We noticed that the different adsorption directions appear with different probabilities. The distribution of adsorption structures we observed is summarized in Table 1. This anisotropy in the initial stage of adsorption can be explained by considering the strong interaction between a molecule and Si dimers. We assume that a molecule adsorbs on a Si dimer at its end first and it falls toward the Si(100) surface in random directions of almost equal probability. When the molecule lies on the Si surface, it can rotate only small angles with its fixed end as a rotation center, until it finds one of the stable adsorption structures. The interaction of the center benzene ring of the P2VB molecule with the Si dimer is considered to be the most important factor.

In this model, the ratio of each divided area shown in Fig. 7 corresponds to the probability of finding a molecule in each area divided by the boundary lines also shown in Fig. 7. The position of the boundary lines are determined so that the center benzene ring overlaps with the corresponding Si dimer for each adsorption structure. The boundary position between two neighboring areas is adjusted to the middle, if they overlap each other. The calculated probabilities are also summarized in Table 1. This simple estimation seems to reproduce the experimental results very well, indicating that the initial stage of adsorption of P2VB molecules is dominated merely by the molecular size and shape. Accordingly, the interaction of the P2VB molecules with the Si dimers is strong enough to prevent surface migration of the molecule.

3.3 Adsorbed structures of P2VB molecules on hydrogen terminated Si(100)

Recent development of STM and its use for atom manipulation [24] has opened up a new field in basic science and technology. For example, a nanoscale device made of atom wires and a switching atom, Atom Relay Transistor (ART), proposed by Wada et al. [25], is one of the most promisng application realized by such methods. For a step of realizing nanoscale devices, we have chosen the hydrogen terminated Si(100)-2 × 1-H surface as a starting substrate. This surface has been systematically studied by STM and the 2 × 1-H monohydride surface structure is well established [26]. The hydrogen terminated Si surface is one of the promising substrates for atomic scale fabrication and nanoscale devices be-

Table 1
The measured and the calculated distributions for the initial stage of adsorption.

	measured (%)[a]	calculated (%)
Inclined	50 ± 10	40
Parallel	25 ± 8	25
Perpendicular	15 ± 7	15
2 bright spots	10 ± 6	20

a) The number of sample points is about a hundred and the probable errors employ a confidence limit of 95 %.
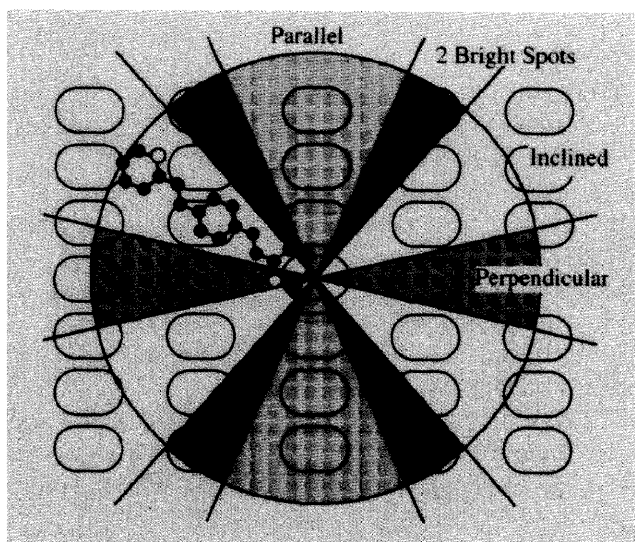
Figure 7.   Schematic showing a simple calculation method for obtaining the distribution of the initial stage of adsorption. In this model, the size of each divided area corresponds to the probability of finding a molecule in each area.

Figure 8. STM images of hydrogen terminated Si(100) surface (a) before and (b) after P2VB molecular adsorption. V_{sample} is -2.0 V for both images. (a) 0.006 ML hydrogen-missing dangling bonds are visible as protrutions.. (b) The preferencial adsorption of P2VB molecules takes place. The density of adsorbed molecules is about 0.003 ML.

cause of the following properties; (a) Hydrogen atoms on the surface can be desorbed by using tunneling current of STM and nanoscale dangling bond patterning has been demonstrated [27]. (b) Atomically flat surface is routinely obtained. (c) The bulk conductivity can be reduced enough for characterizing physical properties (conductivity, for instance) of the atom structures by using a low dopant level and/or reducing the temperature of the sample. (d) Surface states resulted from the dangling bonds of the Si dimers are passivated by hydrogen adsorption. (e) The surface is less reactive and can be kept clean (even for several days) in UHV. (f) Reactivity to some of the metal atoms are low enough and the surface mobility of those metal atoms are expected to be high [28]. Adsorption of the Ga on the clean Si(100)–2 × 1 surface was studied by STM and formation of the Ga dimer rows on the surface was reported after annealing the surface at 750K [29].

In our previois paper [11], we reported on the STM observation of the Ga atoms thermally deposited on the hydrogen terminated Si(100)–2 × 1–H surface. We showed that the Ga atoms preferentially adsorb on the dangling bonds left on the surface as missing hydrogen defects. Furtheremore, this selectivity is used to demonstrate a noble method of fabricating *atomic* Ga wires on the Si(100) surface by adsorbing Ga atoms on to the dangling bond wire.

In this section, a similar example for the future development are shown, where the formation of molecular wire instead of Ga wire will be proposed. In particular, if P2VB molecule is adopted for the sorce of the molecular wire, *in situ* observation of polymerization process may be achieved. However, in this paper, only the preferencial adsorption to hydrogen-missing dangling bonds on the hydrogen terminated Si(100)–2 × 1 surface is
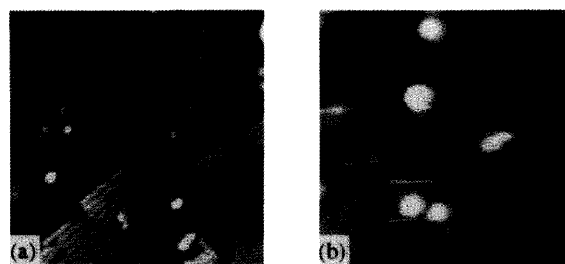
presented as follows. Figure 8(a) shows a high resolution STM image of the hydrogen terminated Si(100)–2 × 1–H monohydride phase. Although the surface states of the dangling bonds of Si dimers are passivated by hydrogen adsorption, we can observe similar dimer rows to the case of the clean Si(100)–2×1 surface. Several dangling bonds are observed as protrusions, since the hydrogen atoms are missing and dangling-bond states near the Fermi level are recovered [26]. The density of dangling bonds (missing hydrogen defects) is about 0.006 ML. On the other hand, Fig. 8(b) shows an STM image of the hydrogen terminated Si(100)–2 × 1–H after P2VB molecular adsorption. We can see larger protrusions than those appearing in Fig. 8(a). These larger protrusions obviously correspond to the enhanced electronic states of Si dangling bonds by molecular adsorption, same with the case of the molecular adsorption to the clean Si(100)–2 × 1 surface as described in the previous section and the case of the metal, Ga, adsorption to hydrogen-missing dangling bonds on the hydrogen terminated Si(100)–2×1–H surface [11]. Hence, we can expect that the thermally deposited P2VB molecules preferentially adsorb on the hydrogen-missing dangling bonds. Counting both the densities of hydrogen-missing dangling bonds and adsorbed molecules confirms this idea. In Fig. 8(b), the density of dangling bonds is about 0.003 ML, half of the case of Fig. 8(a). In addition, the density of molecules is also 0.003 ML. Hence, the density of dangling bonds is effectively reduced by molecular adsorption. Thus, molecules can migrate on the chemically inactive hydrogen terminated Si(100)–2 × 1–H surface until they are trapped to hydrogen-missing dangling bonds, where preferencial adsorption of molecules occurs.

4. Conclusion

P2VB molecule was adsorbed on the clean Si(100)–2 × 1 and the hydrogen terminated Si(100)–2 × 1–H surfaces in UHV and was investigated by UHV-STM. On the clean Si(100)–2 × 1, four different adsorption direc-

tions were observed. We found adsorbed molecules cannot migrate on the chemically active Si surface, while they can migrate on the chemically inactive hydrogen terminated Si(100)–2 × 1–H surface until they are trapped to hydrogen-missing dangling bonds. Through structural analysis and bias-voltage-dependent STM images, we conclude that the electronic states of Si(100) dimer modulated by the adsorbed molecule, rather than the molecule itself are observed by STM, where the occupied states of Si dimer are enhanced by the molecular adsorption, while its empty states are reduced. Initial stage of adsorption of this molecule onto the clean Si(100)–2×1 surface is explained by considering the molecular size and shape and strong interaction between the molecule and the Si dimers.

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