Adsorption of Benzenethiol and 1,4-Benzenedithiol on the Si(111)-7 × 7 Surface

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Benzenethiol- and 1,4-benzenedithiol-adsorbed Si(111)-7 × 7 surfaces were studied by using scanning tunneling microscopy and synchrotron radiation photoemission spectroscopy, which showed that benzenethiol molecules were adsorbed on Si adatoms with upright structures and 1,4-benzenedithiol molecules on two adjacent Si adatoms with a bridging structure. At the initial stage, the adsorptions can be understood by a dissociative process between sulfur and hydrogen on the Si atoms. Here, sulfur bonds to the electrophilic adatoms while hydrogen bonds to neighboring nucleophilic restatoms. On the other hand, this adsorption mechanism during the initial stage does not apply at higher exposures of molecules, as is noticed from the photoemission spectra.

I. INTRODUCTION

Interactions of multifunctional molecules on solid surfaces have been an essential issue in molecular devices, electrochemistry, interfacial physics, and materials science [1]. C. Joachim *et al.* suggested some candidates as potentially applicable molecules in scaling down electronic devices to a nano scale such as molecular wires and switches [2]. In recent years, a junction system, such as an organic molecule-metal-semiconductor, has been tried. For example, Y. P. Zhang *et al.* showed that 1,4-benzenedimethanethiol and thiophene molecules could be selectively attached on a Cu nanostructure self-assembled on the Si(111)-7 × 7 surface [3]. In fact, the Si(111) surface has many advantages for this application because the surface tends to make a well-ordered nanostructure through reactions with the adsorbate(s) [4]. On the other hand, the Si(111)-7 × 7 surface consists of a charge-asymmetric adatom-restatom pair which behaves as an electrophile-nucleophile pair

[5]. The adatom-restatom pair prefers to attract various molecular functional groups: dissociative adsorptions of thiol(-SH) and alcohol(-OH) and cycloadditional reactions of unsaturated hydrocarbons [6–10]. This naturally leads to a question as to whether the reactions of the functional molecules on surface Si atoms can be safely ruled out when the molecules are introduced to a metal-induced Si(111) template. Therefore, the interactions of functional molecules with the Si(111)-7 × 7 surface is strongly related to the molecular manipulation on the semiconductor surfaces.

In case of a thiophene molecule containing a sulfur atom and two π-bonds by four unsaturated hydrocarbon atoms, the surface reaction occurs through the formation of the di-σ bonds of Si-C. This results in a [4+2] cycloadditional reaction, as observed for 1,3-butadiene and benzene molecules [3,8,9]. This means that a lone pair of sulfur atoms does not play an important role in the adsorption process in comparison with the π-bonds of carbon atoms. Most of the molecules suggested by C. Joachim *et al.*, however, have both thiol (-SH) and unsaturated hydrocarbons [2]. Among them, benzenethiol (C_6H_5-SH) and 1,4-benzenedithiol (SH-C_6H_4-SH) molecules are particularly interesting because they

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are the simplest and most fundamental molecules of applicable materials [11]. Therefore, we expect a study of the structures of the molecule-adsorbed Si surfaces and their reaction mechanisms not only provides useful information but also help make visibility of molecular applications wider through an understanding of the selectivity between multi-functional groups.

The experiments on the selectivity of molecules possessing bi-functional (benzenethiol) or multi-functional (1,4-benzenedithiol) groups on Si surfaces were performed by using scanning tunneling microscopy (STM) and synchrotron radiation photoemission spectroscopy (SRPES). As a result, surface Si atoms prefer the -SH of the molecules to a π-conjugated aromatic group. S bonds to a charge-deficient adatom while H bonds to a neighboring charge-rich restatom, which is suggested as the adsorption mechanism during the initial stage. Besides, benzenethiol molecules adsorb on Si adatoms with upright structures and 1,4-benzenedithiol molecules adsorb on two adjacent Si adatoms with a bridging structure. Furthermore, the adsorption mechanism for high exposures of the molecules is different from the one during the initial stage, as is noticed from the PES results.

II. EXPERIMENTS

STM images were acquired using a commercial variable-temperature STM (Omicron, Germany) with a base pressure below 1×10^{-10} Torr. All STM images shown here were measured with a constant current of 1.0 nA, and the purities of benzenethiol and 1,4-benzenedithiol were checked using a quadrupole mass analyzer (QMA). The base pressure of the vacuum system was lower than 1×10^{-10} Torr. High resolution PES experiments using synchrotron radiation for the valence band were performed at the 7B1 beamline of the Pohang Accelerator Laboratory (PAL). The energy resolution was about $\sim$100 meV taken with $h\nu = 40$ eV.

A boron-doped Si(111) wafer ($5 - 12$ Ωcm) was degassed at 800 °C for several hours and repeatedly annealed to 1250 °C by direct-current heating to obtain a clean 7×7 surface. The cleanliness of the 7×7 surface was checked by using Low Energy Electron Diffraction (LEED) and SRPES, which showed no trace of contamination and large peak intensities for the surface components. The benzenethiol and the 1,4-benzenedithiol from Sigma-Aldrich were purified by prolonged pumping before use on the clean Si(111)-7×7 surface. Dosing was performed from a backfilled gas line into the chamber. The exposure was recorded in langmuir (1 L = 10^{-6} Torr·s).

III. RESULTS AND DISCUSSION

Fig. 1 shows STM images for empty states of the Si(111)-7×7 surface after it is exposed to 0.1 L ben-
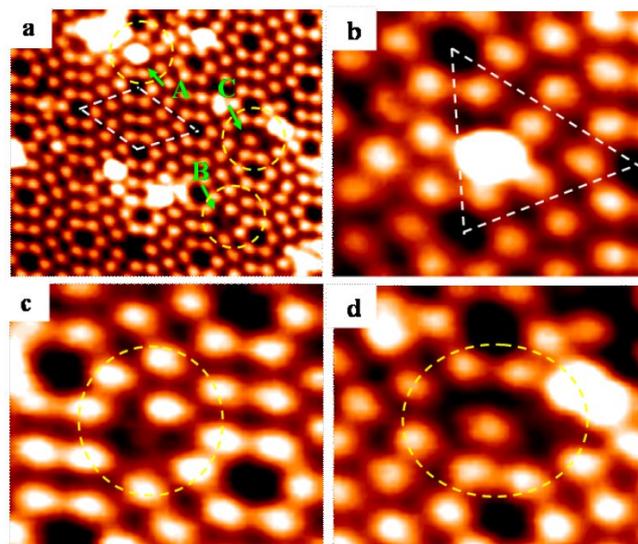

Fig. 1. (a) STM image ($V_s = +2.5$, $I = 1$ nA) of the Si(111)-7×7 surface following room-temperature 0.1-L exposure to benzenethiol, where the white dashed areas denote the unit cell of Si(111)-7×7 surface and arrows A-C indicate the different molecule-derived species on the surface. (b)-(d) show magnified images of A, B, and C, respectively.

zenethiol at room temperature. The Si(111)-7×7 surface is composed of 12 adatoms and 6 restatoms in the unit cell, based on the dimer-adatom-stacking fault (DAS) model [5]. The bright small protrusions in the STM image acquired at $V_s = +2.5$ V originate from Si adatoms with unsaturated dangling bonds [8,12]. In the STM Image, the majority of adsorption sites appear as a large brighter protrusion indicated by the arrow A (Fig. 1(b)). These protrusions shift toward the edge of the triangular half unit cell, leaving the other sides darker. On the other hand, two different adsorption sites, the dark site indicated by the arrow B (Fig. 1(c)) and the elliptical protrusion indicated by the arrow C (Fig. 1(d)), were observed to be minor. These features look very similar to those with 1,3-butadiene additions on the Si(111)-7×7 surface in our previous work, which implies that the chemical reactions at the B and the C sites occur through the [4+2]-like cycloaddition with adatom-restatom and adatom-adatom pairs, respectively [8]. Thus, the B and the C sites are considered to originate from Si adatom bonding to benzenethiol molecules rather than defects. This is because the characteristic STM images of dark sites due to defects were observed; generally, the STM images of dark sites should not be changed by varying the bias voltage from 0.5 to 2.5 V. Thus, a reasonable origin of the images seems to be the cycloadditional reaction, where two carbon atoms of a benzene ring make di-σ bonds (Si-C) with surface Si atoms. Previous works, reporting that a benzene ring is reactive on a Si surface, also support this [9]. These cycloadditional reactions are not, however, the major reaction on the surface. For a
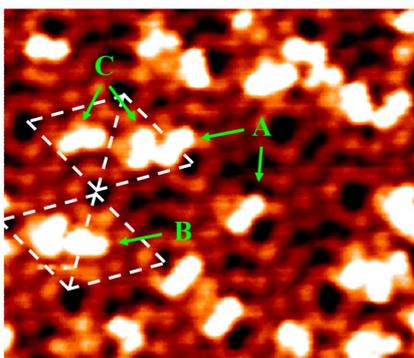
Fig. 2. STM image ($V_s = +2.5$ V, $I = 1$ nA) of the Si(111)-7 × 7 surface following room-temperature 0.1-L exposure to 1,4-benzenedithiol, where the white dashed areas denote the unit cell of the Si(111)-7 × 7 surface and arrows A-C indicate the different molecule-derived species on the surface, on-top site of corner adatom pair-bridging adjacent half unit cells, center adatom pair-bridging adjacent half unit cells, and corner adatom pair in the half unit cell, respectively.

comparison with the reactions of benzenethiol molecules, 1,4-benzenedithiol molecules were also investigated under the same condition.

As Fig. 2 shows, 1,4-benzenedithiol molecules on the Si(111)-7 × 7 surface were obviously imaged as prolonged ellipse protrusions and seem to react with two adjacent adatoms: the on-top sites (A) of a corner adatom-adatom pair bridging adjacent half unit cells, (B) of a center adatom-adatom pair bridging adjacent half unit cells and (C) of a corner adatom-adatom pair in a half unit cell. The size of the ellipse is almost twice as large as the size of A in Fig. 1. Besides, as Figs. 1(c)-(d) show, it does not make sense that the prolonged elliptical protrusion images are due to cycloadditional reactions. If both sulfur atoms react with two adatom sites, the π-conjugated aromatic group of a 1,4-benzenedithiol molecule on the Si surface may not efficiently play the role as a functional group with the Si(111)-7 × 7 in comparison with its thiol group. In order to confirm whether the thiol group really reacts with the Si surface, we performed SRPES experiments.

Fig. 3 shows Si $2p$ PE spectra with benzenethiol and 1,4-benzenedithiol exposures of 60 and 30 L, respectively. The spectra were taken at an emission angle of 60° and a photon energy of 130 eV to achieve a surface-sensitive spectrum. The Si 2p spectrum of benzenethiol moleculres (Fig. 3(b)) is very analogous to one of 1,4-benzenedithiol molecules (Fig. 3(c)). The labels indicate each component obtained by decomposing with a curve fitting analysis: the adatom A, the restatom R, the bulk B, the dimer D, the pedestal P, and the surface S components induced by the adsorption of the molecules [13, 14]. By comparing the spectrum for the clean Si surface (Fig. 3(a)) with the spectra of benzenethiol- and 1,4-benzenedithiol-adsorbed Si surfaces, several significant differences are observed. The R and the A components
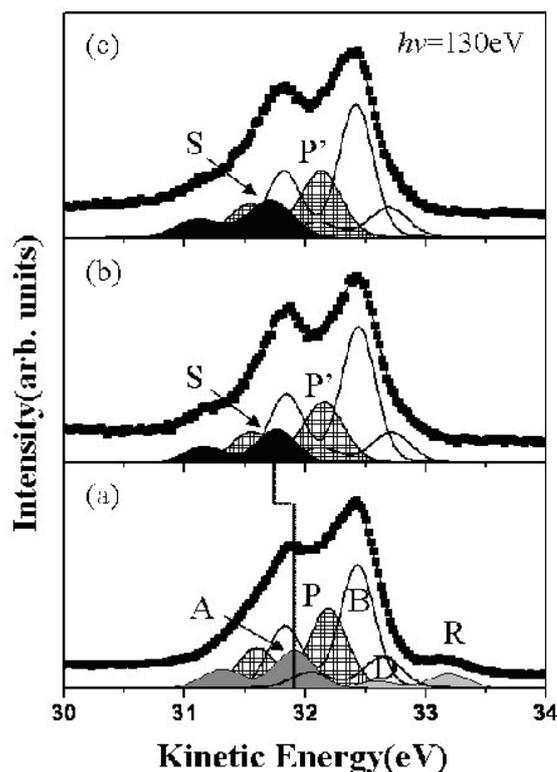

Fig. 3. Si 2p core-level spectra obtained after exposing the Si(111) 7 × 7 surface to the molecules at room-temperature: (a) clean Si(111) 7 × 7, (b) 60 L exposure of benzenthiol and (c) 30 L exposure of 1,4-benzenedithiol. The photon energy(hv) and the emission angle were 130 eV and 60°, respectively. The denoted labels indicate each components by curve fitting; A-adatom, R-restatom, B-bulk, D-dimer, P (P')-pedestal and S-surface component induced by the adsorbed molecules.

disappear, and the S component appears simultaneously. The S component is located at a higher binding energy by 0.7 eV relative to the binding energy of the bulk component. The S peak shifts probably due to a change in the charge distribution around a particular surface atom [14,15]. This can be explained by surface Si atoms bonding to sulfur atoms having much higher electronegativity than bulk Si atoms. Thus, this peak is induced by a Si atom bonding with sulfur atom whereas a chemical shift by Si-C or Si-H is in the range between 0.2 to 0.4 eV. Besides, the quantity of the S component is the same as that of the A component, which can be explained by a sulfur atom reacting with a Si adatom. On the other hand, the full width at half maximum (FWHM) of the P component for the clean Si surface becomes a little wider after saturation with the molecules. This feature may be due to a restatom reacting with a hydrogen atom or to a cycloadditional reaction with a benzene ring [14]. However, the ratio of the cycloadditional reaction with the benzene ring can be ignored. Otherwise, the S component should be much smaller and the P' component should be much higher because of competition
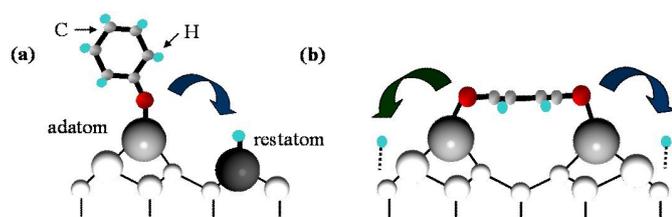
Scheme 1. Proposed molecular adsorption structures; (a) upright structure of benzenethiol on adatom-restatom pair and (b) bridging structure of 1,4-benzenedithiol on two adjacent Si adatoms. Processes of hydrogen dissociative adsorption are shown by curved arrows.

between the formation of a Si adatom-sulfur atom bond and the [4+2] cyclic formation of a Si adatom-C bond. Therefore, the origin of the FWHM broadening of the P' component is the adsorption of a hydrogen atom on a surface Si atom. Unfortunately, an accurate determination is beyond our experimental resolution. Returning to Fig. 1(b), the small dark area at the upper side of the brighter protrusion may introduce a Si restatom saturated by hydrogen atoms. The sulfur atoms of these molecules are nucleophilic, and the hydrogen of -SH is electrophilic. This leads to the conclusion that the sulfur atom easily attaches to a charge-deficient adatom and the hydrogen atom prefers to attach to a charge-rich restatom. Therefore, the appearance of the feature related to the Si-S bond indicates a dissociative adsorption on the Si adatom. Besides, the hydrogen atom reacts with a Si restatom. This interpretation allows us to understand easily that benzenethiol and 1,4-benzenedithiol molecules form upright and bridging structures, respectively, on two adjacent Si adatoms. These results are consistent with our STM interpretation. Scheme 1 shows a schematic diagram of the adsorption structures: (a) the upright structure for a benznethiol molecule and (b) the bridging structure for a 1,4-benzenedithiol molecule.

As observed in STM and PES studies for small exposure, the thiol group is much more reactive with the Si(111)-7 × 7 surface than the carbon benzene ring. The sulfur atom bonds to a charge-deficient adatom, and the hydrogen atom bonds to a neighboring charge-rich restatom, which is suggested as an adsorption mechanism during the initial stage. In comparison, the adsorption mechanism after saturating the restatom with hydrogen atoms should be different from the adsorption mechanism during the initial stage because of no being available for excess hydrogen atoms decomposed from thiol groups (Fig. 3). One possibility is H2 molecular desorbed from the Si surface into vacuum, and another is diffusion of hydrogen atoms into the Si bulk.

IV. CONCLUSION

The experiments for room-temperature benzenethiol and 1,4-benzenedithiol adsorptions on the Si(111)-7 × 7

surface suggest that the surface Si atoms prefers the -SH of the molecules to π-conjugated aromatic groups. In addition, the sulfur atom bonds to an electrophilic adatom, and the hydrogen atom bonds to a neighboring nucleophilic restatom during the initial stage. Besides, as Scheme 1 shows, (a) benzenethiol molecules adsorb on Si adatoms with an upright structure and (b) 1,4-benzenedithiol molecules adsorb on two adjacent Si adatoms with a bridging structure. Although another possible adsorption mechanism at high exposures requires further work, we expect a study on the selectivity of molecules possessing bi- or multi-functional groups on a Si surface to provide very useful information for applications such as molecular devices.

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