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Description	

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Stable alignment of 4,4”-diamino-*p*-terphenyl chemically adsorbed on a Si(001)-(2×1) surface observed by scanning tunneling microscopy

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Abstract

Low coverages of 4,4”-diamino-*p*-terphenyl (DAT) molecules deposited on a Si(001)-(2×1) surface in ultrahigh vacuum at room temperature were observed by scanning tunneling microscopy (STM). The linear framework of DAT, consisting of a central benzene ring, two phenyl rings (terphenyl) and two amino groups at both ends, mostly lay down laterally on the surface. The majority of DATs were tilted at about 17° with respect to the direction of a Si dimer row on the surface, though a variety of DAT configuration with different angles was found by STM. The histograms of the tilted angles showed that the most frequent angle was 17°. The apparent height of DAT tilted at 17° looked hollow at the center and lower than that of other configurations of DAT in STM images. This indicates that the DAT tends to take a double arched shape at the tilted angle of 17° in a stable conformation with butterfly-like bonding through the central benzene ring to a Si dimer as well as the two amino groups bonded to respective Si atoms on the dimer row.

Keywords: molecule; diamino-*p*-terphenyl; silicon; butterfly bonding; scanning tunneling microscopy

1. Introduction

Organic molecular electronics has attracted much interest to fabricate innovative products with high performance at low cost, and furthermore to open novel architecture for future device processes [1]. Fundamental and promising molecular devices have been developed, for example, such as charge-based memory [2], configurational switch and memory [3], molecular resonant tunneling diodes [4,5], and molecular transistors [6]. To improve their characteristic performance, the conformational alignments and bonding states of individual organic molecules in the devices are crucial. Selection and preparation of molecule-binding substrates also dominate the performance, and a wide-ranging survey for the molecule-substrate combination is indispensable.

Silicon (Si) substrates for deposition of organic molecules are of great interest to realize novel functionalized devices not only from a viewpoint of industrial application based on silicon technology but also of basic science [7,8]. A large number of reports have been published to reveal the adsorption configuration and to control the alignments of organic molecules on well-defined silicon surfaces [9]; for example, amino-terminated organic monolayers on hydrogen-terminated silicon surfaces [10] and covalently modified silicon surfaces [11]. In fabrication of stable molecular layers chemically bonded to silicon substrates, amino groups in the molecules possibly play important roles, because a N atom in the amino group with a lone pair of electrons can firmly interact with silicon substrates and act as an electron donor; distinct chemical and electrical properties are expected. Electronic and vibrational spectroscopies showed that a basic molecule of NH_3 deposited Si(001)-(2×1) surfaces comprised coadsorbed NH_2 and H at room temperature [12-15]. Though an early study using scanning tunneling microscopy (STM) discussed the adsorption in terms of subsurface atomic N and adsorbed H on it [16], at present it is accepted that NH_2 and H species are adsorbed on Si dimers on a clean Si(001)-(2×1) surface [17]. In general, amino groups react to silicon surfaces through the dissociation of H from them at room temperature [7].

For a molecule with amino groups deposited on silicon, Nishimura et al. [18] examined

4,4”-diamino-*p*-terphenyl (DAT) molecules on a Si(111)-(7×7) surface at room temperature using X-ray photoelectron spectroscopy (XPS) and STM. Figure 1 shows the chemical structure of DAT consisting of a linear but twisted three-benzene chain (π-conjugated), i.e., terphenyl, and two amino groups at the two ends of the chain. DAT is a monomer used to synthesize a conjugated polymer by vapor deposition polymerization through the amino groups [19]. At low coverages of DAT, the authors found that the DAT was chemically bonded to the silicon surface through one amino group at one end of the DAT even at room temperature, and the other amino group was not bonded to the surface, resulting in the main framework of DAT standing at a slant onto the Si(111) surface. Meanwhile, to form ordered molecular multi-layers over long distances through π-π stacking interaction, the molecules lying-down parallel to their substrate is preferable, which are profitable to light-emitting and photovoltaic molecular devices [20]. Their lying-down configuration in the layers can be triggered at the interface between the first layer molecules and the substrate. Since the reconstructed Si(001)-(2×1) surface has a number of Si dangling bonds larger than that of the Si(111)-(7×7) surface per unit area, the molecules with π orbitals deposited on the Si(001)-(2×1) surface can take a diversity of alignments on it, possibly leading to their lying-down configuration. In this study, we examine the adsorption of DAT on the Si(001)-(2×1) surface at room temperature by STM to pursue its stable alignment.

2. Experimental

Experiments were conducted in ultrahigh vacuum (UHV) using a home-built STM system in a main vacuum chamber with a base pressure of 2×10^{-11} Torr, which was connected to a preparation vacuum chamber with a base pressure of a low of 10^{-10} Torr through gate valves; this was the same setup as in ref. 18. The preparation chamber was equipped with a molecule deposition apparatus consisting of a tungsten carbide crucible wound with a sheath heater with a thermocouple, a water cooling jacket, and a mechanical shutter between the crucible and a substrate. The crucible temperature was controlled by a digital controller (LT350, CHINO Corp.).

A cut of 2×12×0.35 mm^3 from a B-doped Si(001) wafer with a resistivity of 0.01-0.02 Ω·cm was used as a substrate. The substrate was cleaned by ultrasonic bath of acetone and an ozone cleaner (NL-UV253, Nippon Laser & Electronics Lab). Next, the substrate was introduced to the main chamber, followed by resistively heating at 873 K for 12 h for degassing and subsequent flashing at 1473 K for 1 min. Finally it was cooled to room temperature at a rate of about 0.5 degree/s, leading to a clean Si(001)-(2×1) surface.

DAT from Lancaster Synthesis was used after it was purified three times by train sublimation method [21]. The DAT was evaporated by heating the crucible containing the DAT at a temperature of 418 to 433 K, which was below the DAT melting temperature of ~510 K, accompanied by a rise of pressure below 10^{-9} Torr in the preparation chamber. The substrate temperature was room temperature (not controlled intentionally). The DAT coverage was monitored by a quartz thickness monitor (CRTM-9000, ULVAC, Inc.), and controlled by the mechanical shutter, which was opened for a few to 10 sec. The STM images were acquired at a constant current of 0.05 to 0.1 nA and a tip bias voltage of +1.5 V (filled state) with electrochemically etched [111]-oriented single crystal W tips [22], which were cleaned in UHV by heating before STM scanning [23,24]. Furthermore, we annealed the samples at a substrate temperature of 423 for 10 min by passing a DC current into the substrate after DAT deposition to examine the change in DAT configuration on the Si(001) surface.

3. Results and Discussion

Fig. 2(a) shows a typical STM image of a clean Si(001)-(2×1) surface with Si dimer rows and single atomic-height steps. Fig. 2(b)-(d) show STM images of Si(001)-(2×1) surfaces covered with DAT molecules at different amounts; the shutter opening time for the sample in (c) and (d) was two and five times longer than that in (b), respectively. Bright protrusions were found on the Si dimer rows in Fig. 2(b)-(d), and the shapes of protrusions were mostly elongated. Since the number of protrusions increased with extending shutter opening time, the protrusions were attributed to

DAT molecules. The increase in the number of protrusions had also been confirmed using the same setup for DAT on a Si(111)-(7×7) surface, and the origin of protrusion had been attributed to each DAT molecule by XPS analysis [18]. Assuming that each protrusion on the Si(001)-(2×1) surface corresponds to one DAT molecule, the deposition amount in (b), (c) and (d) was calibrated to ~0.02, 0.04 and 0.1 molecule/nm^2, respectively. The length of elongated ones was roughly close to that of DAT, ~1.5 nm. This was different from that of DAT standing at a slant on the Si(111)-(7×7) surface imaged as spherical ones of ~1 nm in diameter [18]. It is presumable that the elongated shape corresponded to each DAT with the linear framework of terphenyl lying-down laterally on the Si(001) surface, although the shape was not unique probably due to a variety of adsorption configurations of the DAT on it.

Some elongated protrusions looked tilting with respect to the direction of the underlying Si dimer row with several specific angles. The tilted angle of the majority of elongated protrusions was about 17°, denoted by white arrows in Fig. 2(b). Other angles were about 8° and 0°, denoted by black and white arrow heads, respectively, in Fig. 2(b). The protrusions at the angle of 17° usually possessed two, or occasionally three bumps depending on the tip conditions. The protrusions at 8° possessed one or two bumps, and almost the protrusions at 0° possessed one bump. Fig. 3 shows the STM images of the typical protrusions enlarged from Fig. 2(c), where they are denoted by arrows A, B, and C, as well as the line profiles along the elongated protrusions. The image in Fig. 2(c) was obtained without any accidental tip change. The averaged top height of profiles at 17° was about 0.08 nm, ranged from 0.06 to 0.13 nm, which was measured from the top of the Si dimer. The averaged height at 8° was about 0.1 nm, ranged from 0.06 to 0.13 nm, and the height at 0° was 0.14 nm, ranged from 0.09 to 0.18 nm, respectively. The protrusions with the height above 0.12 nm exhibited one bump, while the protrusions below 0.1 nm tended to have two bumps. The variety of their height and the number of bumps indicated the variation of the chemical configuration of DAT on the Si(001) surface. The appearance change in terms of the number of bumps should be related to the chemical conformation of DAT as well as the chemical bonds between DAT and Si dimers,

because the tunneling conductance possibly changes locally in the electronic states of the chemical bonds. In addition, it is noted that the dark areas on Si dimer rows near the ends of DAT were possibly ascribed to Si atoms terminated with H atoms, which were dissociated from the amino groups of DAT on the adsorption.

The frequency of the tilted angles of about 250 protrusions on samples with coverage of ~0.04 molecule/nm^2 was statistically counted, and the histogram of the angles was made, as shown in Fig. 4. The histogram exhibits three main tilted angles with widths of their distributions: the majority region peaked at 17°, ranged from 14° to 21°, the second region around 8°, ranged from 7° to 11°, and the third region ranged from 0° to 4°. The frequency of protrusions at about 17° was the largest (more than 50%). After annealing at 423 K for 10 min, the number at the tilted angled of 17° was still the most abundant. This implies that the configuration of the protrusion at 17° was so stable probably due to the chemical bonding of the DAT to the Si(001)-(2×1) surface.

Oda conducted the density functional theory (DFT) calculations for stable alignment of DAT on a Si(001)-(2×1) surface with the tilted angles of 17° and 0° [25]. The total energy for configuration at 17° and 0° was -2.34 eV and -1.66 eV, respectively, referring to the total energy of 0.0 eV for a system consisting of a Si(001)-(2×1) surface and a DAT molecule separated from the surface. The difference in the total energy by 0.68 eV indicates that the configuration of DAT at 17° was stable. Fig. 5 shows the intuitive models of DAT configurations, not calculated to be optimized; the models at 17° and 0° were reproduced from the optimized configurations in ref. 25. The stability at 17° was ascribed to three chemical bonds to the silicon surface: each of two amino groups at both ends of a DAT covalently bonds to a Si atom of a dimer, and the center benzene ring forms a butterfly-like bond [26] with a Si dimer. Noted that the two amino groups are bonded to respective Si atoms on the opposite sides of the same dimer row. Consequently, since the DAT takes the so-called butterfly configuration of a double arch shape on the Si(001) surface, the double arch is seemingly imaged as two bright bumps in the STM images. Each bright bump of the DAT looked slightly shifted outward to the position of the amino group possibly owing to the change in the

electronic states caused by the chemical bonding between the amino group and the underneath Si atom.

For a model of the DAT with the tilted angle of 0° (Fig. 5(c)), while the two amino groups at both ends of the DAT are bonded to respective Si atoms on the one side of a Si dimer row, there is no butterfly-like bond, resulting in an upward arch of the main framework of the DAT. Accordingly, the protrusion with the tilted angle of 0° possibly looked one bump at its center. For the protrusion with the tilted angle of 8°, since one bump was observed, it is reasonable to interpret the DAT structure as the arch similar to that for 0°. Here a model for 8°, in Fig. 5(b), is proposed using analogy of the model for 0° but the two amino groups chemically bonded to respective Si atoms on the opposite sides of a Si dimer row. Experimentally the line profile of DAT at 0° showed higher at the center than that at 8°, as shown in Fig. 3. Since the separation of chemical bonds of amino groups to the Si atoms in the model at 0° is slightly closer than that for 8°, the compression for 0° possibly makes the framework of DAT bent more upward than that for 8°.

Here we discuss the conformational relationship among the configurations with the three tilted angles. As the first adsorption step of a randomly-oriented DAT as vapor onto the Si(001) surface, it is likely that one amino group of DAT is covalently bonded to a Si atom of a dimer through H-dissociated bond formation. After the one end of the DAT is anchored at the Si atom through the amino group, the DAT is thermally vibrating and rotating around the Si atom until the other amino group of DAT is bonded to another Si atom. This Si atom is one of the Si dimer separated by a distance of four-Si dimer interval along a Si dimer row from the initially anchoring Si atom, since the distance is very close to the length of a DAT, resulting in an arched conformation of DAT, as shown in Fig. 5. There are two possibilities to select the one Si atom out of the Si dimer: one is on the same side of the dimer row with the initially anchoring Si atom, and the other is on the opposite side of the dimer row, corresponding to the configuration of the tilted angle of 0° and 8°, respectively. The buckling arch of DAT more likely transforms to the butterfly-like double-arched structure at the tilted angle of 17° through the chemical bonding of the center benzene ring to a Si

dimer. This binding energy should exceed the strained energy of the double-arched structure, leading to the more stable configuration of the DAT at 17° on the Si(001)-(2×1) surface.

4. Conclusions

The DAT molecules deposited on a Si(001)-(2×1) surface at room temperature, and subsequently annealed, were observed by STM. A number of elongated protrusions tilted at an angle of about 17° with respect to the Si dimer row were observed. Those corresponded to DAT molecules lying-down laterally on the surface, which looked lower than other protrusions and mostly two bumps in the STM images. The appearance of protrusions of DAT in the STM images supported the models for 17° and 0°, proposed by Oda; the DATs chemically bonded to the Si(001)-(2×1) surface with butterfly-shaped bonding for 17°, which is more stable than that with the arched framework of DAT for 0°. This study also indicated that DAT deposited at room temperature can take a variety of chemical configuration, and post annealing possibly promotes the ordering of DAT overlayers based on the configuration with a tilted angle of 17° on the Si(001)-(2×1) surface.

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Figure captions

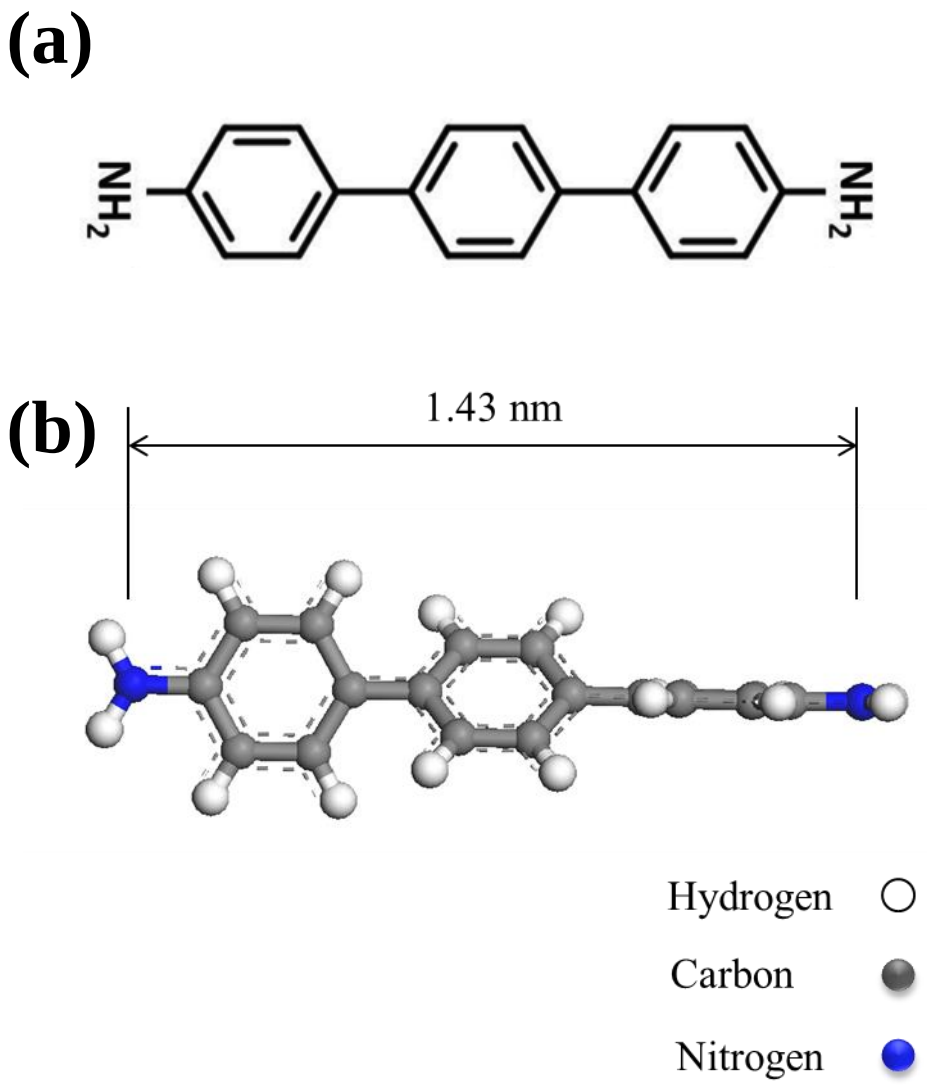
Fig. 1. (a) Chemical structure and (b) optimized structure of DAT using Material Studio [27].

Fig. 2. STM images taken at I_{tunnel} = 0.1 nA, V_{tip} = +1.5 V. (a) a clean Si(001)-(2×1), (b) DAT deposited on the Si(001)-(2×1) at room temperature with a coverage of ~0.02 molecule/nm^2. The white arrows denote the protrusions with a tilted angle of 17°, black and white arrow heads denote 8° and 0°, respectively. (c) ~0.04 molecule/nm^2 and (d) ~0.1 molecule/nm^2. Scanning area: 35×35 nm^2 for (a), (c) and (d), and 18×18 nm^2 for (b).

Fig. 3. STM images of typical protrusions with (a) a tilted angle of 17°, (b) 8° and (c) 0° in the left panels, which were enlarged from Fig. 2(b) with arrows A, B and C indicating the respective protrusions. The pixel numbers are 26×35. The white lines indicate the Si dimer rows in the center panels. The line profiles along red lines in the center panels are shown in right panels.

Fig. 4. Histogram of the tilted angle of a DAT molecule with respect to the direction of dimer row of Si(001)-(2×1).

Fig. 5. Top and side view of models for chemical bonding configurations of a DAT on the Si(001)-(2×1) (a) for a tilted angle of 17°, (b) 8°, and (c) 0°. The models in (a) and (c) were reproduced from those in ref. 25. The Si atoms near the amino groups of DATs are depicted to be terminated with the H atoms dissociated from the amino groups.



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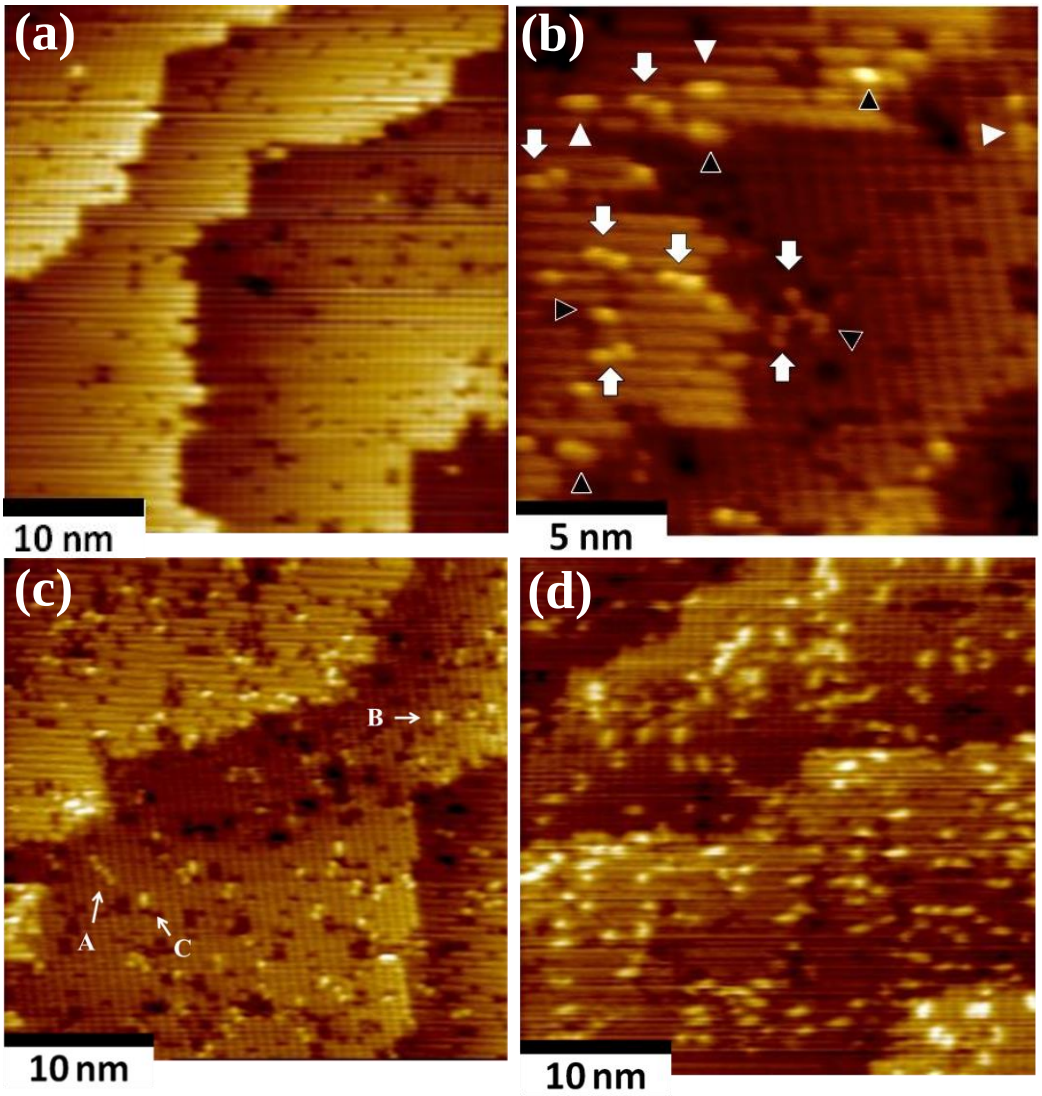

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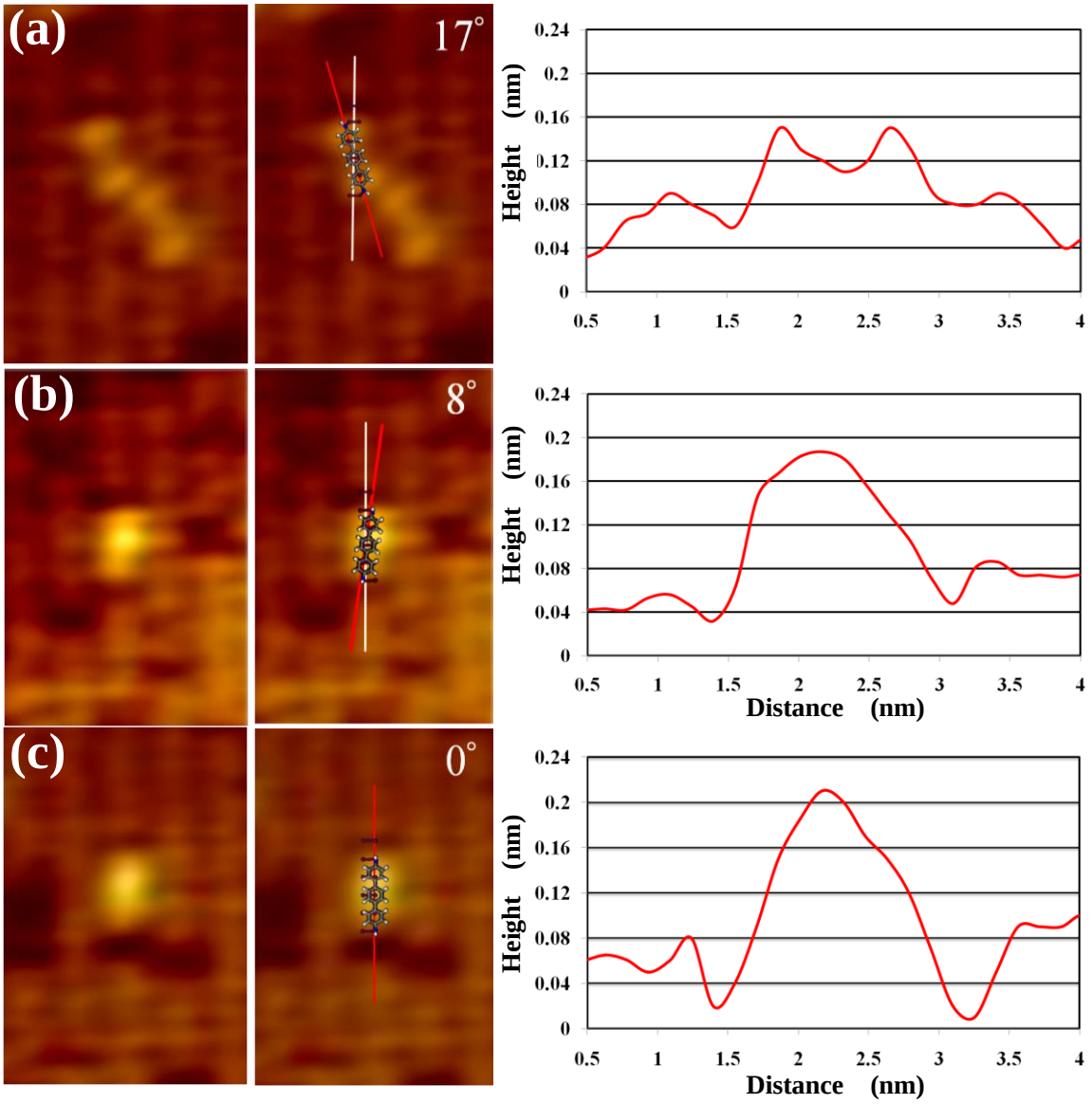

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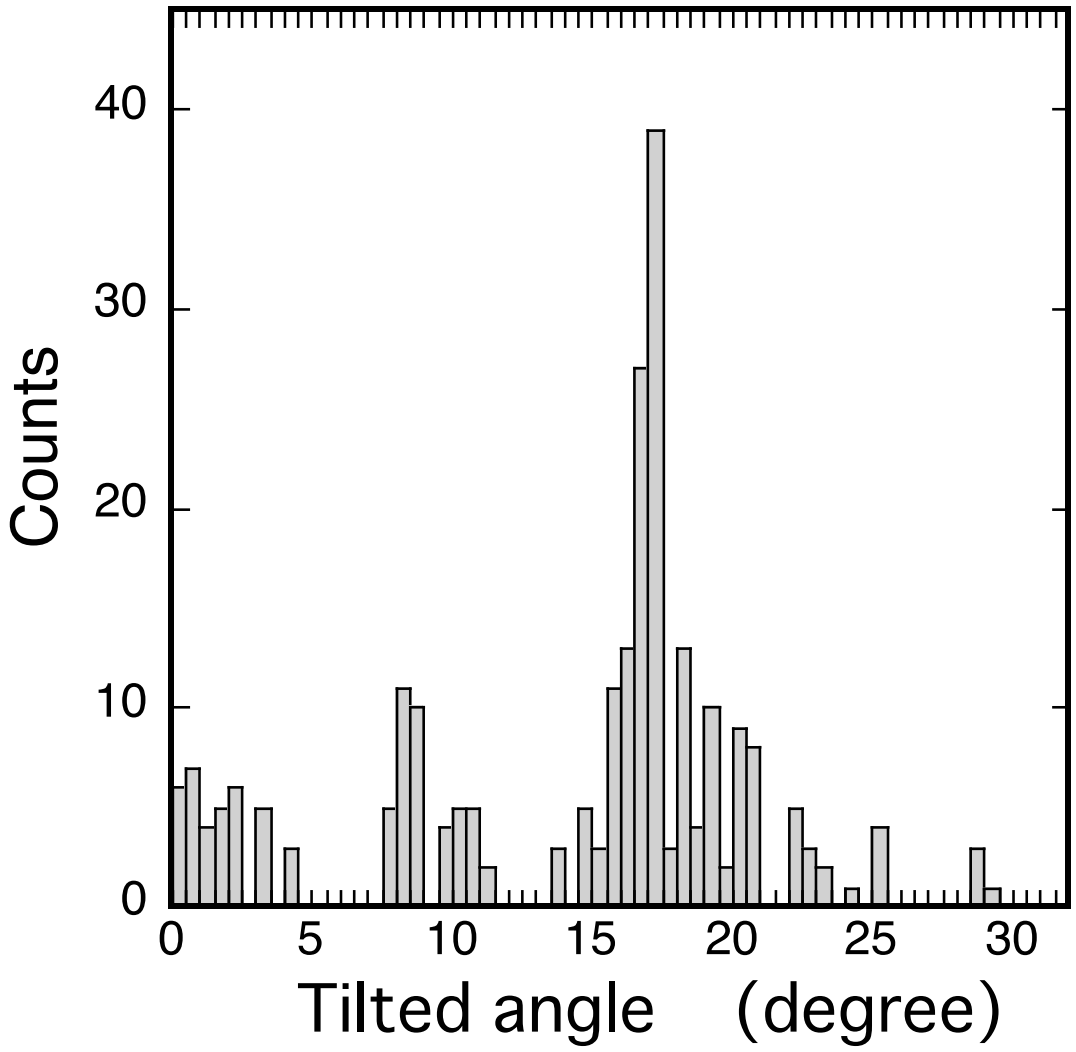

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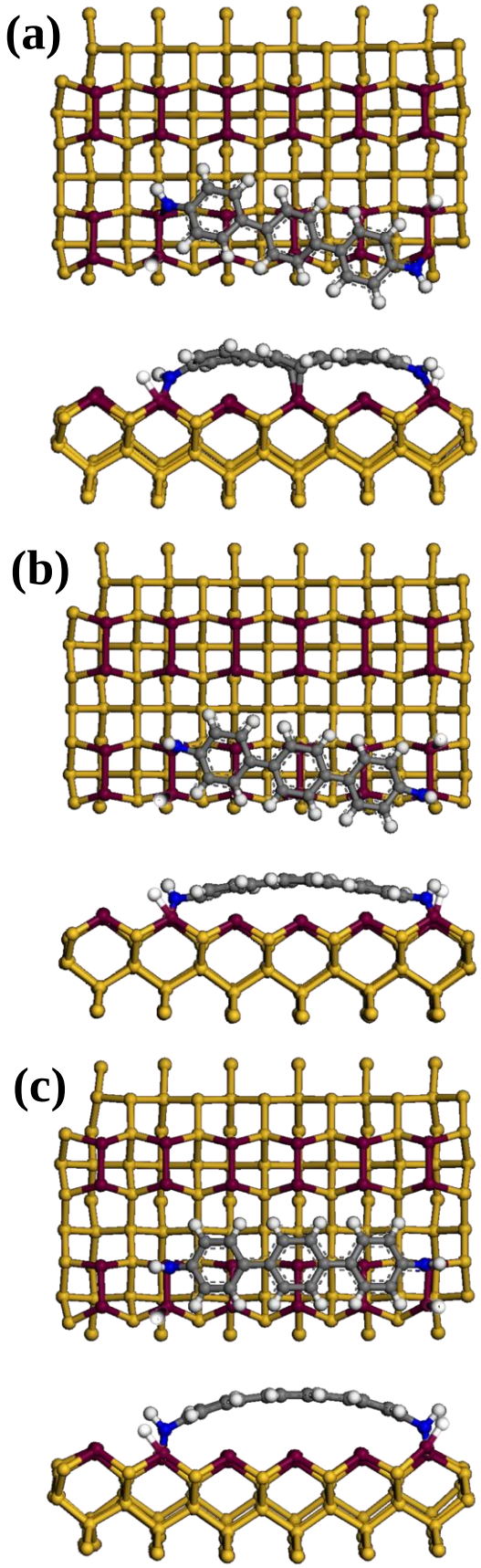

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