

# STM Study of *trans*-Stilbene Self-Organized on the Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$ Surface

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The interfacial structures of *trans*-stilbene (TSB) on Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$  were studied by low-temperature scanning tunneling microscopy (LT-STM) in ultrahigh vacuum (UHV). Stilbene overlayers were prepared by vapor deposition at a substrate temperature of 200 K and imaged after the samples were cooled to 100 K. High-resolution images allow the identification of individual molecules, with TSB appearing with a distinctive dumbbell shape. From in situ observation of the substrate lattice, the TSB monolayers were found to form a ( $2 \times 1$ ) structure. Due to the excellent matching of unit cell length for Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$  to the molecular length of TSB, the interaction between TSB and the substrate surface plays the controlling role in influencing the structure of the TSB overlayers. A model for the unit cell of TSB monolayers is proposed and discussed.

## 1. Introduction

Self-ordered monolayers formed by organic molecules on inorganic substrates are of considerable importance in various technical applications. In particular, the order of surface organic molecules has a significant impact on important properties such as charge transport between molecules, charge injection, wetting, friction, and optical properties. The surface-induced order of organic molecules can also affect the bulk over comparatively large distances, influencing their structure and electrooptical properties.<sup>1</sup> Thus, understanding how functionalized organic molecules order at surfaces is crucial for optimizing their use in the application. The study of ordering of an organic material at a solid surface is, however, difficult due to the presence of the substrate. Scanning tunneling microscopy (STM), due to its ability to directly image the surface structure with molecular, and often, atomic resolution, has emerged as a powerful tool to examine the orientations, packing arrangements, and even internal structures of organic molecules on conductive surfaces.<sup>2</sup> In this study, we report on self-ordering of *trans*-1,2-diphenylethylene (*trans*-stilbene, TSB) on the Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$  surface studied with low-temperature STM (LT-STM).

Stilbenoid compounds have been studied for more than 60 years,<sup>3,4</sup> because of their important role in many areas of chemistry as well as their impact on materials technology. Stilbene, in particular, can be considered as a

prototypical molecule for studying photochemical reactions with potential in the development of data storage media. When irradiated with UV light, stilbene molecules can undergo a *trans*-to-*cis* isomerization reaction. The *cis*-stilbenes revert to the more stable *trans* form through irradiation at a different wavelength of UV light. Photoisomerization of stilbene in solution has been well studied and reviewed by Waldeck.<sup>4</sup> However, relatively little work has been performed on the photoisomerization-induced structural change on surfaces.<sup>5</sup> In this work, we study the surface structure of TSB adsorbed on Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$ . The main focus is to investigate how the interactions between adsorbed molecules and between surface adsorbates and substrate influence the surface structure. This study thus lays the foundation for later photochemical studies of these isomers on the surface.

To investigate the adsorption behavior of organic molecules by STM, conductive substrates are required. The noble metal/elemental semiconductor surfaces, possessing manifestly metallic property under specific reconstruction, are important platforms of both scientific and technological interest.<sup>6,7</sup> We have chosen Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$  (denoted as the Ag/Ge(111)- $\sqrt{3}$  surface hereafter) because it is one of the most intriguing and well-characterized metal–semiconductor surfaces. The study of detailed atomic structure for metal deposited on semiconductor surfaces is important to understanding the interface properties such as Schottky barrier formation, surface states, and electronic properties of each reconstruction.<sup>8</sup> In particular, Ag/Si(111) and its resemblant interface, Ag/Ge(111), have received considerable attention. Both these systems follow the Stranski–Krastanov growth mode<sup>7</sup> with Ag growing epitaxially to form a  $\sqrt{3} \times \sqrt{3}$  $R30^\circ$  structured layer and thus are well-defined models for such studies. The atomic arrangement of the Ag/Ge(111)- $\sqrt{3}$  surface has been resolved as a honeycomb

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chained trimer (HCT) structure<sup>8,9</sup> based on the strong resemblance of the STM images obtained on this surface to that for the Ag/Si(111)-( $\sqrt{3} \times \sqrt{3}$ )R30° surface. The HCT model has a missing-top-layer Ge(111) surface with a top Ag layer arranged in a honeycomb configuration. An important feature of the Ag/Ge(111)- $\sqrt{3}$  surface is that the lattice constant of the surface unit cell ( $\sim 6.5$  Å) is nearly equal to the distance between the centers of the two benzene rings in TSB. This makes Ag/Ge(111)- $\sqrt{3}$  a good candidate for a substrate for TSB self-organization. More detailed discussion of Ag/Ge(111)- $\sqrt{3}$  is given in section 3.2.1.

In this paper, we present an STM study of *trans*-stilbenes (TSB) self-organized on Ag/Ge(111)- $\sqrt{3}$ . TSB can be reproducibly observed with a high spatial resolution. In particular, the molecular images have distinct shapes that permit easy identification of two isomers and their molecular arrangements on the surface. Furthermore, the simultaneous observation of substrate lattice and the TSB molecules allows the direct determination of the TSB orientation relative to the substrate as well as their registry on Ag/Ge(111)- $\sqrt{3}$ . The structural models corresponding to various STM images for the adlayers of TSB on Ag/Ge(111)- $\sqrt{3}$  are then proposed and discussed.

## 2. Experimental Section

The experiments were carried out in a dual-chamber ultrahigh vacuum (UHV) system consisting of a variable-temperature STM (VT-STM; Omicron Vakuum Physik) chamber and a sample preparation/surface analysis chamber. This second chamber is equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), a quadrupole mass spectrometer (QMS), and an ion sputtering gun for both substrate cleaning and STM tip bombardment. Both chambers are maintained at a base pressure of less than  $2 \times 10^{-10}$  Torr. The design allows both tip and sample transfer throughout the system with a load lock preventing the need to break vacuum when introducing/removing samples to and from UHV.

The Ge samples ( $2 \times 10 \times 0.37$  mm<sup>3</sup>) used in this study were cut from a single crystal, n-type ( $<0.4$  ohm-cm) Ge(111) wafer. Prior to mounting the Ge sample on a sample holder, the crystal was degassed by ultrasonic cleaning in acetone. The sample was heated resistively. Surface temperature was monitored by infrared pyrometers. The Ge sample was degassed overnight at a temperature of  $\sim 700$  K once it was introduced into the UHV chamber. Before each experiment, the Ge(111) surface was cleaned by Ar<sup>+</sup> ion bombardment (1 keV, 5 min, current  $\sim 35$  mA) followed by annealing to 1100 K to remove any contamination and to smooth the surface. The bombardment–annealing cycles were repeated until a sharp  $c(2 \times 8)$  LEED pattern was obtained, which indicated the formation of large domains. The surfaces were also subsequently characterized by using STM imaging that also showed large  $c(2 \times 8)$  terraces (500–1500 Å) coexisting with small  $c(4 \times 2)$  and  $p(2 \times 2)$  domains.

The tungsten tips used in the STM experiments were electrochemically etched in an aqueous solution of KOH (1 N) followed by in vacuo cleaning using electron bombardment and heating with tungsten hot filament. All the STM images were recorded in constant current mode. The tunneling conditions have been optimized in order to attain the highest resolution. Unless otherwise specified, the voltage,  $V$ , corresponds to the sample bias with respect to the tip. STM images have been slightly filtered to remove dominant acoustic noise, to offset small inclination, and to enhance the image contrast. Image distortion was also corrected using built-in computer software to normalize the measured lattice parameters to the values proposed by the theoretical model. To calibrate STM images for adsorbed TSB, the concurrently measured underlying Ag/Ge(111)- $\sqrt{3}$  lattice was fit to an ideal honeycomb chain structure. STM images were obtained many times with different imaging conditions to confirm the results.

A homemade Ag source evaporator was built for the deposition of Ag. The deposition rate was approximately 0.1 ML/min with the substrate held at an elevated temperature of 620 K, followed by postannealing to 673 K. To reduce the thermal drift, the prepared Ag/Ge(111) surfaces were maintained at room temperature (RT) for at least 3 h prior to STM measurements. The Ag coverages were estimated from AES measurements. *trans*-Stilbene was shielded from light to prevent photoisomerization and was purified by outgassing for more than 24 h before it was introduced into the UHV chamber. It was then admitted to the UHV chamber via a leak valve and deposited onto the surface in a line-of-sight configuration from a sample cell kept at  $\sim 450$  K. A more detailed description of the crystal mounting and the surface temperature measurement/calibration can be found in another work.<sup>10</sup>

## 3. Results and Discussion

**3.1. Structure Characterization of the Ag/Ge(111)-( $\sqrt{3} \times \sqrt{3}$ )R30° Surface by STM.** Before presenting the results concerning the TSB adsorbate layer, we begin with a brief description of structure characterization of the substrate surface prepared by Ag vapor deposition onto Ge(111)- $c(2 \times 8)$ . After introducing the Ge(111) sample into the vacuum chamber and cleaning it by bombardment–annealing cycles, a  $c(2 \times 8)$  reconstructed surface was obtained. When the Ag is deposited onto a Ge(111) surface and annealed to between 500 and 770 K, the surface transforms to one of several various unit cell structures. At low coverages, the Ag/Ge(111) forms a  $(4 \times 4)$  structure, coexisting with large terraces of  $c(2 \times 8)$  domains. The domain boundaries between these two structures have been identified as a  $(3 \times 1)$  reconstruction.<sup>11</sup> With higher coverages, the  $(4 \times 4)$  reconstruction begins to transform into the  $(\sqrt{3} \times \sqrt{3})$  structure, and the reconstruction is complete at a Ag coverage around 1 ML. Although Ag/Ge(111) reconstructed surfaces have been investigated by many research groups<sup>8,11,12</sup> using various surface analysis techniques, their exact geometric structures and the coverages for structure evolution still remain controversial. We have reexamined the structures of Ag/Ge surfaces, from submonolayer to monolayer, using LT-STM.<sup>10</sup> High-resolution images of three reconstructed surface structures,  $(3 \times 1)$ ,  $(4 \times 4)$ , and  $(\sqrt{3} \times \sqrt{3})$ , were observed with distinct atomic arrangements. The structure and unit cell parameters of the  $(\sqrt{3} \times \sqrt{3})$  surface, which is the substrate for TSB adsorption, will be discussed in detail.

When Ag is deposited to coverage above 0.25 ML followed by annealing to 500 K, the  $(4 \times 4)$  reconstruction begins to transform into the  $(\sqrt{3} \times \sqrt{3})$  structure. Figure 1a shows an empty state image of the  $\sqrt{3}$  phase at a positive bias of 0.36 V after the Ag/Ge(111) surface had slowly cooled to room temperature. Similar to Ag/Si(111)- $\sqrt{3}$ , the Ag/Ge(111)- $\sqrt{3}$  surface is found to form the well-known honeycomb chained trimer (HCT) structure in which a missing-top-layer Ge(111) surface with a top Ag layer was arranged in a honeycomb configuration.<sup>6,8,9,13–18</sup>

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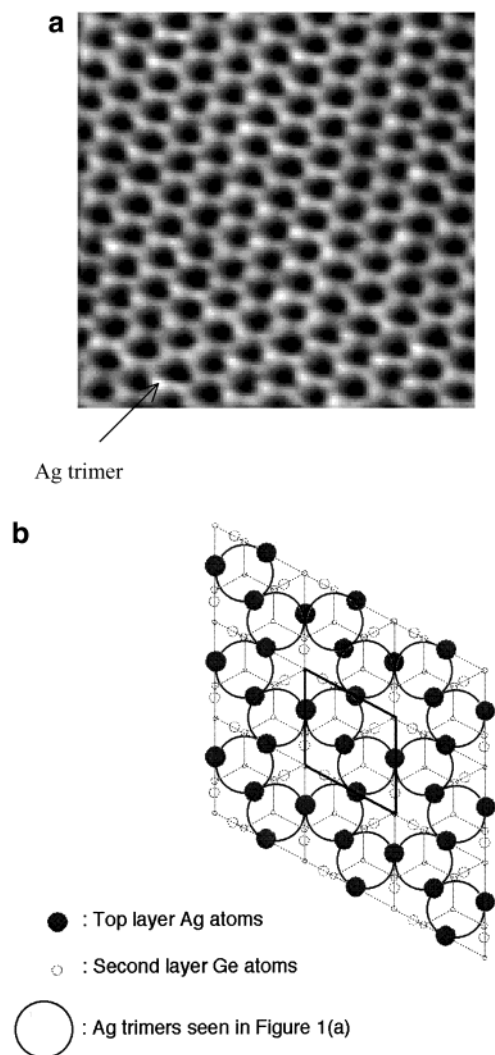
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**Figure 1.** (a) An  $8 \times 8 \text{ nm}^2$  empty state STM image of Ag/Ge(111)- $\sqrt{3}$  taken at positive bias of 0.36 V and 0.5 nA. (b) Geometrical structure of the HCT model for Ag/Ge(111)- $\sqrt{3}$ . The unit cell is outlined by a rhombus circled with a heavy line. One of the Ag trimers is pointed out by an arrow.

While the individual Ag atoms cannot be resolved, the maxima of bright spots correspond to centers of the Ag trimers. The HCT model of the  $(\sqrt{3} \times \sqrt{3})$  structure is shown in Figure 1b. This structure is derived by reconstruction of the first-layer Ge atoms to form trimers so that two of three broken bonds originally formed on the ideal Ge(111) surface can be stabilized. The remaining dangling bonds are terminated by forming covalent bonds with the adsorbed Ag atoms in positions slightly distorted from a regular triangular lattice, and thus, the surface reactivity is greatly reduced. According to the model in Figure 1b, the lattice parameter of the surface unit cell is commensurate with the distance between two alternative Ag trimers in a honeycomb ring. The distance between the alternative Ag trimers, corresponding to unit cell length of Ag/Ge(111)- $\sqrt{3}$ , was measured to be  $(6.7 \pm 0.2) \text{ \AA}$ . It is important to note that this distance is comparable to the distance between the centers of two benzene rings in TSB (see below). The match of lattice spacing makes Ag/Ge(111)- $\sqrt{3}$  an ideal substrate for TSB self-organization. In addition, in contrast to the large corrugation on

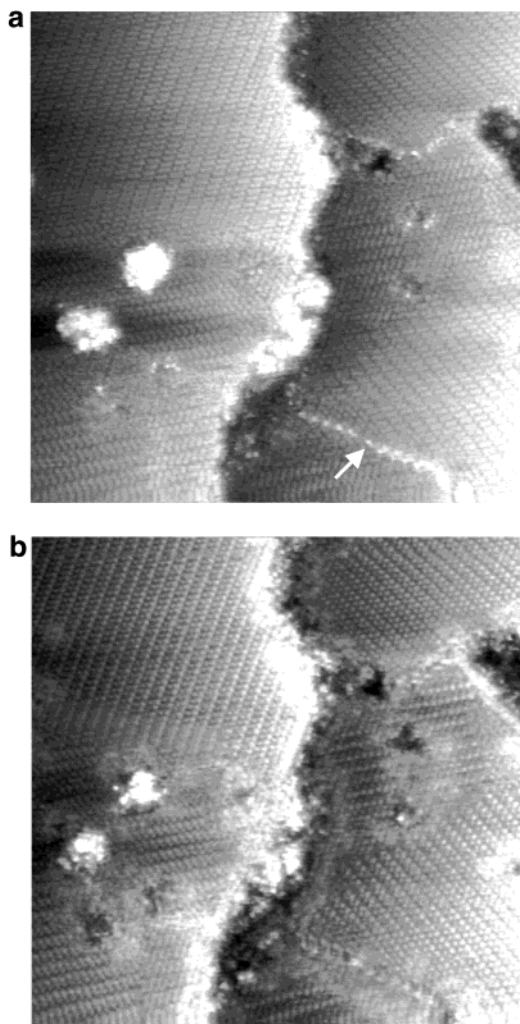
the bare Ge(111) surface resulting from the reconstruction of top two layers, the Ag layer on Ag/Ge(111)- $\sqrt{3}$  only reconstructs with lateral displacements<sup>9</sup> that result in a small variation of the corrugation profile. This provides an opportunity to image the molecules with a minimal substrate perturbation. The  $\sqrt{3} \times \sqrt{3}$  reconstruction was observed at silver coverages above 0.25 ML on Ge(111) and appeared completed at a silver coverage of 1 ML.<sup>10</sup> The average size of atomically flat terraces for Ag/Ge(111)- $\sqrt{3}$  obtained in this work is at least  $50 \times 50 \text{ nm}^2$ . Weiering and Carpinelli have investigated the electronic properties of the Ag-induced reconstructions.<sup>6</sup> It was found that the  $(3 \times 1)$  and  $(4 \times 4)$  reconstructions are nonmetallic, with band gaps larger than that of bulk Ge. The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  reconstruction, on the other hand, is metallic with a small tunneling gap based on CITS (current imaging tunneling spectroscopy) data.<sup>6</sup> There is sufficient conductivity to allow the Ag/Ge(111)- $\sqrt{3}$  surface to serve as an appropriate material for STM imaging. The Ag/Ge(111)- $\sqrt{3}$  surface was thus prepared and used as the substrate for the study of adsorption and self-organization of TSB.

**3.2. Adsorption and Self-Organization of *trans*-Stilbene on Ag/Ge(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ .**

**3.2.1. STM Observation of *trans*-Stilbene Self-Organized on Ag/Ge(111)- $\sqrt{3}$ .** STM study of the TSB adsorption on the Ag/Ge(111)- $\sqrt{3}$  surface was performed in the range of 0.25–2 L exposures of TSB. The dosing of TSB was confirmed by background measurement using a mass spectrometer during exposure. An Auger spectrometer also detected a strong carbon signal at 272 eV. A major obstacle in the STM studies of organic molecules is the thermally activated diffusion of the molecules on the surface that could sometimes seriously degrade the STM resolution. Therefore, we immobilized the TSB molecules by reducing substrate temperature to 100 K after deposition. We used LT-STM to image the TSB overlayer on Ag/Ge(111)- $\sqrt{3}$  under the ultrahigh vacuum (UHV) environment. Figure 2 shows a pair of STM images in an area of  $50 \times 50 \text{ nm}^2$  for 1 L (close to 1 monolayer (ML)) of TSB molecules adsorbed under UHV condition on the Ag/Ge(111)- $\sqrt{3}$  surface at a substrate temperature of  $\sim 200 \text{ K}$ . After TSB exposure, the sample was quickly (less than 30 s) transferred to the STM stage for further cooling to 100 K, at which the STM image was made. Therefore, the temperature rise of the substrate during transfer should be small. These images were taken in parallel, tunneling into the sample while rastering in one direction, and out of the sample while rastering in the other at a tunneling current of 0.05 nA. The left panel (a) shows the filled states image and the right panel (b) shows the empty state image at sample bias  $-1.3 \text{ V}$  and  $+0.97 \text{ V}$ , respectively. The TSB coverage was estimated from STM images and was defined to 1 ML as the coverage corresponding to the saturated molecular structure shown in Figure 2. In this study, it was not possible to obtain STM image of the ordered TSB overlayer on the Ag/Ge(111)- $\sqrt{3}$  surface at room temperature even after saturating the surface with molecules. Instead, images taken at room temperature show randomly distributed molecular bumps with no discernible structure pattern. We attribute this to insufficient stability of molecular adsorbates, which is caused by the high mobility of the TSB molecules on the substrate surface at room temperature. In addition, the tip can also exert significant forces, both van der Waals and electrostatic, on the molecules that can cause molecular motion during

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**Figure 2.** The  $50 \times 50 \text{ nm}^2$  (a) filled state ( $-1.3 \text{ V}$ ,  $0.05 \text{ nA}$ ) and (b) empty state ( $0.97 \text{ V}$ ,  $0.05 \text{ nA}$ ) images of TSB monolayer adsorbed on Ag/Ge(111)- $\sqrt{3}$ . The line formed by small bright dots indicated by the arrow in (a) is a substrate domain boundary.

imaging.<sup>19,20</sup> Therefore, to alleviate such molecular diffusion, we performed STM imaging of TSB at low temperature. The result shown in Figure 2 reveals that the thermal motion is greatly suppressed at 100 K. Imaging with molecular resolution is also possible even at low coverages. The molecular arrangements observed at 100 K represent thermodynamically stable structures that could be imaged continuously over periods of several hours. Stable well-resolved STM images were normally obtained 2 h after deposition, at which time thermal equilibrium exists and the self-ordering is complete. We noticed that, even for higher TSB exposures, only a monolayer of TSB adlayer was observed. None of the images indicate the formation of TSB multilayers on Ag/Ge(111)- $\sqrt{3}$  under such dosing conditions. This result suggests that TSB multilayer cannot be formed on Ag/Ge(111)- $\sqrt{3}$  at  $\sim 200 \text{ K}$ .

The atomically flat terraces are now covered with orderly packed TSB monolayer. As shown in Figure 2, the molecular structure appears in the image as parallel stripes aligned along three equivalent directions on the surface, which are rotated by  $120^\circ$ . It is apparent that the

molecules are aligned along three dominant directions, which are defined by the surface unit cell vectors of the substrate. This result demonstrates that the self-ordering of TSB on Ag/Ge(111)- $\sqrt{3}$  is well correlated with the substrate lattice. It also suggests that the intermolecular interaction of TSB could be weaker than the interaction with substrate that therefore plays the dominant role in influencing the structure of the monolayers. If the force between the molecules is stronger than the substrate–molecule interactions, an arbitrary order with respect to the substrate should be the consequence. The self-assembled monolayer is well ordered over tens of nanometers. The domain size is variable with an average diameter of 30 nm, usually containing around 1000 molecules. Several defects and disordered areas are also observed for the TSB assembly, especially in the boundary region of different TSB domains. These regions account for  $\sim 5\%$  of the area on the images. Although molecular vacancies sometimes appear (not shown), the formed two-dimensional networks are reproducibly observed in large areas, indicating a high stability of this self-assembly configuration.

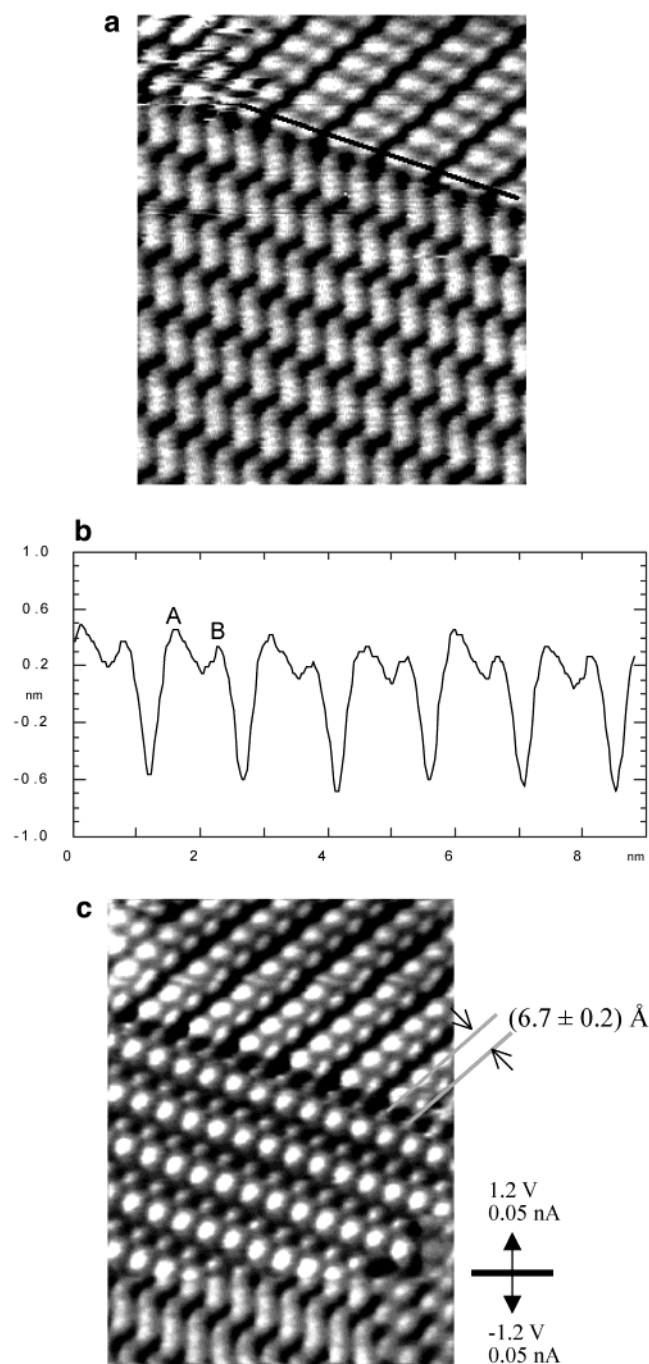
Detailed structure and orientation of TSB molecules in the adlayer are seen in a high-resolution STM image ( $-1.2 \text{ V}$ ,  $0.05 \text{ nA}$ ) as shown in Figure 3a. It can be seen that each TSB molecule in most of our STM images appears as a dumbbell shape with two lobes corresponding to two benzene rings at the trans position of the double bond at the molecular center. Similar molecular features have been observed for azobenzene derivatives on graphite surface.<sup>21</sup> Very occasionally, with a particularly good tip, high-resolution STM images showed the double bond feature in the center of two bright spots. For a better interpretation of the STM images, the dimensions of the molecule can be useful. For this purpose, we have calculated the structure of TSB isolated molecule via a geometrical optimization by the HyperChem program using a semi-empirical approach with AM1 force field. The calculated molecular dimensions of the TSB are about 11.5 and 3.1 Å along the long and short molecular axes, respectively, as shown in Figure 4a. The distance between the centers of the two benzene rings is  $\sim 6.5 \text{ Å}$ . Notice that, from the side view of the optimized configuration (Figure 4b), the two benzene rings in TSB are not on the same plane, but with a distortion angle of  $\sim 5^\circ$ . This may be the reason the observed image in the upper part of Figure 3a displays two unequal lobes in the dumbbell image. Based on this molecular model, the bright patchy features making up chains in Figure 3a correspond to individual TSB molecules. The molecular length along the long axis and the width of dumbbell approximately match the molecular dimensions shown in Figure 4a. Note that the detailed molecular shapes for TSB located on the upper right of Figure 3a differ from those in the lower part of the image where the TSB molecules are oriented in different directions. When the tip scanning direction is approximately perpendicular to the long axis of the TSB molecule, it may disturb the molecule more easily. Therefore, for TSB adsorbed in different orientations, altered molecular images were observed. Another method to confirm the TSB adsorption was to flash the sample to 600 K, where all the TSB molecules desorbed from Ag/Ge(111)- $\sqrt{3}$  and some of them were detected in situ by mass spectrometer.

The orientation of TSB overlayer with respect to the substrate was carefully examined. We found that all TSB molecules have identical and well-defined orientations, which are entirely lined up with the Ag/Ge(111)- $\sqrt{3}$

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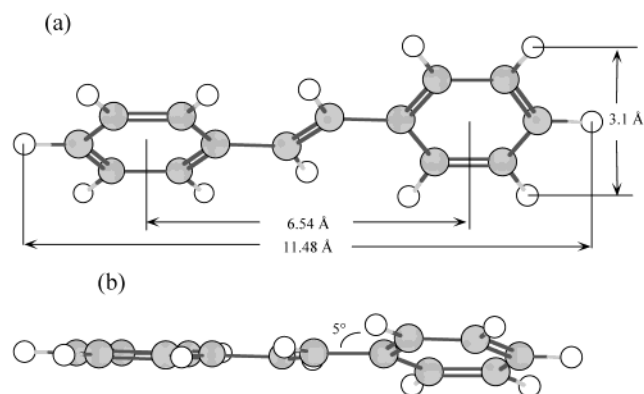
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**Figure 3.** (a) A  $9 \times 11 \text{ nm}^2$  high-resolution STM image ( $-1.2 \text{ V}$ ,  $0.05 \text{ nA}$ ) of TSB monolayer adsorbed on  $\text{Ag/Ge(111)-}\sqrt{3}$ . (b) The cross-section profile shows the corrugation along the straight line drawn in (a). (c) A  $9 \times 12 \text{ nm}^2$  STM image of TSB monolayer on  $\text{Ag/Ge(111)-}\sqrt{3}$  with tip bias changed from negative ( $-1.2 \text{ V}$ ,  $0.05 \text{ nA}$ ) to positive ( $1.2 \text{ V}$ ,  $0.05 \text{ nA}$ ) during the STM scan, as indicated by the arrows.

lattice. Further evidence for this point is given in the next section. The corrugation profile shown in Figure 3b is the cross section taken along the line drawn in Figure 3a. Under the present experimental condition, the averaged corrugation height for each molecule was ca.  $0.5 \text{ nm}$ . By measuring the relative height at the vacancy sites, it was estimated that TSB is about  $1\text{--}2 \text{ \AA}$  above the substrate, which is typical for a  $\pi$ -bonded system lying flat on the substrate surface, as measured by STM.<sup>2,22</sup> Note, however, that the corrugation height for one of the benzene rings



**Figure 4.** Top view (a) and side view (b) of optimized molecular structure of TSB and its dimension calculated by HyperChem program.

is slightly larger than that for the other. To confirm this observation, we have repeated the imaging of TSB right after Figure 3a with tip bias changed from negative to positive during the STM scan, indicated by the arrow shown in Figure 3c. Under this condition, the empty state of TSB ( $V_B < 0$ ) adlayer is measured. The set of two spots for each molecule is again attributed to two benzene rings. The difference of contrast in terms of brightness and size for the two benzene lobes is more discernible. Even the seriously drifted molecular image shown in the lower domain of the filled state image (Figure 3a) can now be resolved. It should be noted that the TSB molecules are physisorbed on  $\text{Ag/Ge(111)-}\sqrt{3}$ , since neither the LEED patterns nor STM molecular images can be observed at the deposition temperature of  $200 \text{ K}$  due to the high mobility of adsorbed TSB at this temperature. According to Hansma and Tersoff, an STM image is sensitive to electron density at the Fermi level rather than to total charge density.<sup>23</sup> For a physisorption system, the adsorbate should make no contribution to the local density of states at the Fermi level. Eigler et al. have proved that a rare gas atom, such as Xe, adsorbed on a  $\text{Ni(110)}$  surface can cause the local state density at the Fermi level to protrude much further out to the vacuum side of the atom and therefore the adsorbed Xe can be imaged by STM.<sup>24</sup>

On the other hand, Smith et al. proposed that STM images reflect the electron density of the molecular orbitals (MOs) of the adsorbates.<sup>25</sup> Therefore, it is reasonable to concentrate on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the adsorbates. We have used the HyperChem program (semiempirical, AM1) to calculate the electron density contours of the HOMO (Figure 5a) and LUMO (Figure 5b) for isolated TSB molecules, assuming no significant electron perturbation caused by the adsorbate–substrate interaction. The result shows that the highest electron density for HOMO is uniformly distributed over the whole TSB molecule. The electron density for LUMO, on the other hand, shows two distinct lobes on two sides of the molecular center with almost equal electron density. This result is not completely consistent with STM observation in terms of the dissimilar intensity in the two benzene lobes observed in the images. Note that this calculation does not consider the effect of molecular adsorption to a substrate or the presence of a tip. For

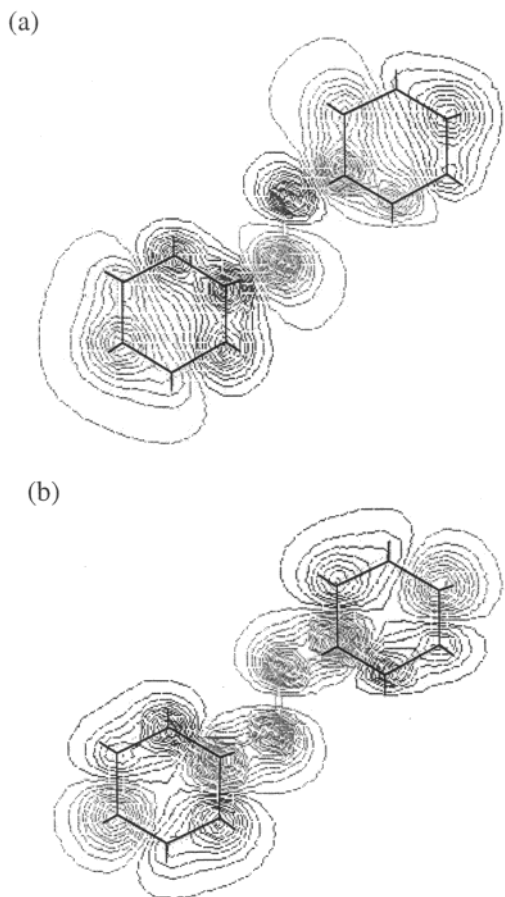
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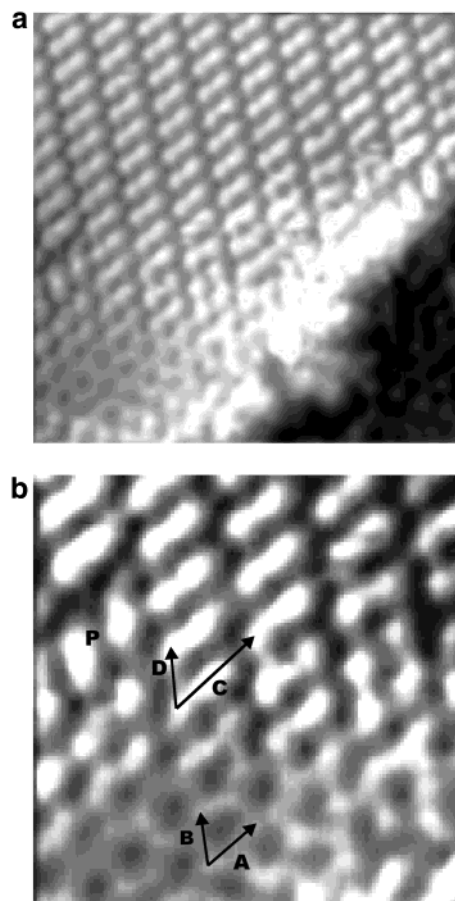
**Figure 5.** Electron density contours of the HOMO (a) and LUMO (b) of free-standing TSB molecule calculated by HyperChem program using semiempirical approach with AM1 force field.

example, changing the tip bias may induce a local molecular conformation change and/or a local molecular rotation. Since an STM image is the convolution of topography and surface electronic structure, it is postulated that the two benzene rings of TSB are adsorbed either at different binding sites or with different geometric configurations. Due to the lattice match of TSB with Ag/Ge(111)- $\sqrt{3}$ , the former possibility seems unsupported. Champagne et al. have concluded that TSB is planar in the ground state under ultracold jet conditions with no excess vibrational energy.<sup>26</sup> There is additional experimental evidence, however, based on features of the vibrational spectrum of stilbene in solids, liquid, and gas phase, that is consistent with an out-of-plane C1-phenyl torsional angle of 5° as shown in Figure 4b.<sup>4,27,28</sup> Based on our STM result, the TSB should have nonplanar configuration when adsorbed on Ag/Ge(111)- $\sqrt{3}$ . We also noted that the distance between two corrugation maxima (A and B, Figure 3b) corresponding to two benzene lobes was measured to be  $7.6 \pm 0.5$  Å, slightly larger than what would be expected from HyperChem calculation (6.5 Å). As mentioned earlier, STM images result from the convolution of electron density, surface topography, and tip profile. The STM imaged charge position would be, sometimes, not exactly equal to the atomic position.

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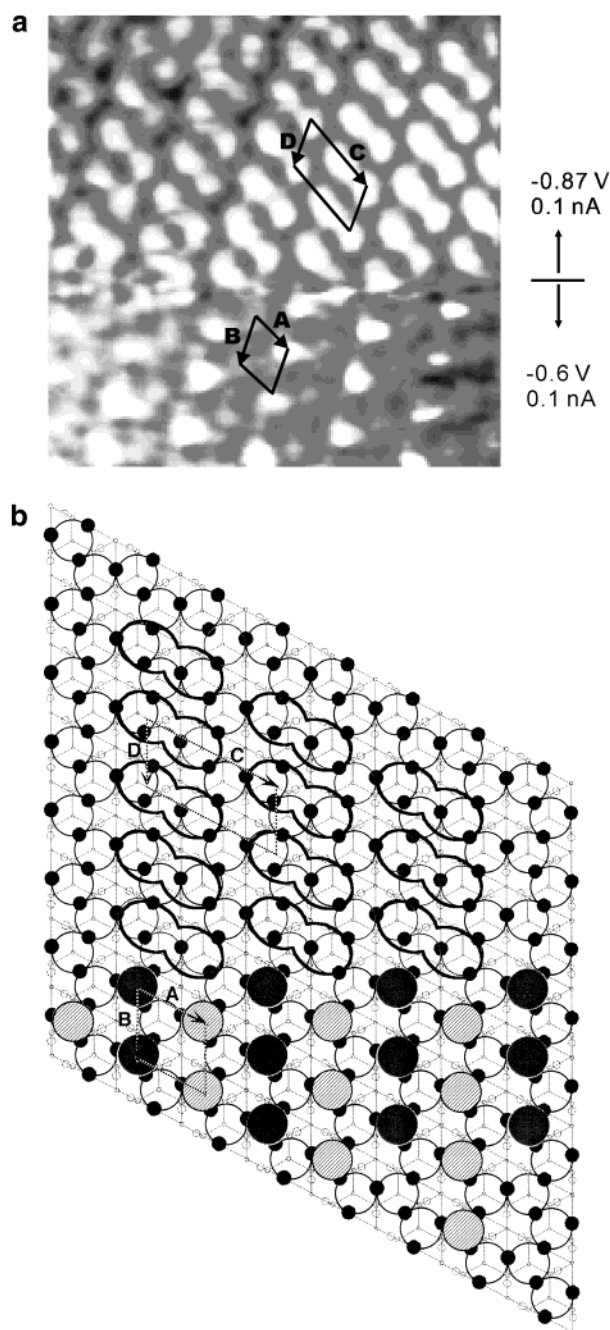
**Figure 6.** (a) A  $10 \times 10$  nm<sup>2</sup> STM image acquired at 100 K for 0.5 ML of TSB adsorbed on Ag/Ge(111)- $\sqrt{3}$ . The scanning condition is -1.1 V and 0.05 nA. (b) Expanded STM image in an area of  $5 \times 5$  nm<sup>2</sup> of the left lower part image of (a).

**3.2.2. Registry and the Unit Cell Structure of trans-Stilbene Self-Organized on Ag/Ge(111)- $\sqrt{3}$ .** The dimensions of the structures in the STM images can be used to develop structural models for a molecule-substrate system. If the substrate surface atoms can be observed simultaneously, the registry, i.e., the molecular adsorption site and its unit cell structure, can be strictly determined. Figure 6a is an STM image made for 0.5 ML of TSB adsorbed on Ag/Ge(111)- $\sqrt{3}$ . A single TSB domain, along with part of the bare substrate shown in the lower left corner of Figure 6a, was observed. Molecular vacancy sometimes appears (not shown in this image), though the formed two-dimensional networks are reproducibly observed in large areas even at coverages below 1 ML. Obviously, the TSB molecules segregate to form large domains upon adsorption on Ag/Ge(111)- $\sqrt{3}$  under the experimental condition. In addition to the well-resolved molecular structures of TSB, the substrate lattice shown as a honeycomb chain in the lower left corner of Figure 6a was observed as well. The left lower part of the image shown in Figure 6a was enlarged to yield the image shown in Figure 6b. Some TSB molecules, marked as "P" in the image, show the same corrugation height as the majority, and are sparsely distributed on the Ag/Ge(111)- $\sqrt{3}$  surface, and at the domain edges, with molecular orientation parallel to the lamellar axes. This kind of "overlayer defects" was observed mostly along domain edges or step edges. The substrate unit cell vectors are indicated as **A** and **B**. We found that all molecules with few exceptions are oriented with the long axis along the vector **A** of the

substrate unit cell. The molecular rows, on the other hand, are aligned along another substrate unit cell vector **B**. The overlayer unit cell vectors are shown as **C** and **D** in Figure 6a. The average intermolecular distances are  $12.5 \pm 0.5$  and  $6.5 \pm 0.4$  Å along the directions of **C** and **D**, respectively. The length of substrate unit cell found in the previous section is 6.5 Å; therefore, we conclude that the adsorbed TSB molecules form a  $(2 \times 1)$  structure on Ag/Ge(111)- $\sqrt{3}$ .

The packing arrangement of TSB on Ag/Ge(111)- $\sqrt{3}$  can also be determined by in situ comparison with the underlying substrate lattice that can be made visible by lowering the bias voltage. Figure 7a shows another STM image for 1 ML of TSB adsorbed on Ag/Ge(111)- $\sqrt{3}$ . The tip bias is altered during the scan so that the TSB molecule (upper part) and the substrate atoms (lower part) can be observed in one image. Since reduction of the bias voltage at a constant current corresponds to a decrease in distance between the tip and the sample,<sup>29</sup> the substrate lattice can be imaged as well. The unit cell of the TSB adlayer can be identified in Figure 7a as the parallelogram formed from vectors **C** and **D**. These results are in good agreement with that from partial coverage (Figure 6a) and confirm the so-called  $(2 \times 1)$  unit cell for TSB adlayer on Ag/Ge(111)- $\sqrt{3}$ . The structural model based on Figure 7a is illustrated in Figure 7b. This kind of registry model can also be deduced from the image for the partially covered surface (Figure 6a), which shows simultaneously the TSB domains and the bare surface. It is important to note, however, that the Ag trimers of Ag/Ge(111)- $\sqrt{3}$  imaged under such a condition show a different feature from what would be expected for TSB-free Ag/Ge(111)- $\sqrt{3}$  (Figure 1a). As denoted by solid gray circles and striped circles in Figure 7b, only part of the Ag trimers with different contrast intensity can be observed. This is believed to be due to the different interaction between aromatic rings and Ag trimers. As pointed out previously, two benzene rings of TSB do not subsist in the same plane after adsorption on Ag/Ge(111)- $\sqrt{3}$ , and this may lead to different effects on the electronic structures of the underlying Ag trimers. The substrate unit cell is shown by two vectors, **A** and **B** in Figure 7b. Further decrease of bias voltage to  $-0.3$  V, an image similar to Figure 1a with equal contrast intensity for all the Ag trimers can be observed.

For TSB adsorption on Ag/Ge(111)- $\sqrt{3}$  at 200 K, the STM images shows an ordered pattern of structure for TSB adlayer upon cooling to 100 K. However, it is found that annealing the as-dosed TSB/Ag/Ge(111)- $\sqrt{3}$  sample to room temperature, even briefly, would lead to significant change of the structure of TSB overlayer. Figure 8 is an STM image in a relatively large area of  $100 \times 100$  nm<sup>2</sup>, taken with a tunneling parameter of  $-1.0$  V and 0.09 nA at 100 K for depositing 0.5 ML of TSB on Ag/Ge(111)- $\sqrt{3}$  followed by annealing to  $\sim 300$  K. It was seen that the coverage of TSB decreases to less than 0.3 ML, indicating desorption of TSB from Ag/Ge(111)- $\sqrt{3}$  during the heating process. The TSB molecules remaining on the surface tend to cluster preferentially near step edges. This behavior is not unexpected since substrate steps are well-known to act as preferential binding sites for atoms and molecules.<sup>30–36</sup> There are triangular features with contrast



**Figure 7.** (a)  $6 \times 6$  nm<sup>2</sup> STM image of 1 ML of TSB adsorbed on Ag/Ge(111)- $\sqrt{3}$ . The tip bias is altered during the scan so that the TSB molecule (upper part,  $-0.9$  V, 0.1 nA) and the substrate atoms (lower part,  $-0.6$  V, 0.1 nA) can be observed in one image. (b) Structural model for TSB monolayer on Ag/Ge(111)- $\sqrt{3}$ . The solid gray circles and striped circles represent the visible Ag trimer with different contrast intensity.

depression in the center distributed at irregular intervals on the terrace. The size and shape of these triangles suggest the “intracluster self-organization” of TSB mol-

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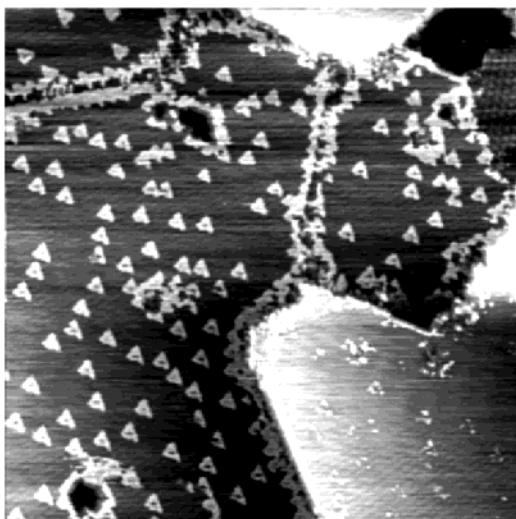
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**Figure 8.** STM image in a relatively large area of  $100 \times 100$  nm<sup>2</sup>, taken with tunneling parameter of  $-1.0$  V and  $0.09$  nA at  $100$  K for  $0.5$  ML of TSB on Ag/Ge(111)- $\sqrt{3}$  which was annealed to  $\sim 300$  K to desorb most TSB.

ecules on Ag/Ge(111)- $\sqrt{3}$ , resulting in an ensemble of molecular clusters with uniform size/structure but with random spatial distribution. These triangles are supramolecular clusters of TSB, mostly trimers, nucleating on the substrate terrace with a height equal to that of a single TSB molecule. The size for each side of triangle is  $\sim 14$  Å. The symmetry of the trimer reflects, approximately, the 3-fold symmetry of the underlying substrate. In other words, the trimer configuration for low coverages of TSB on Ag/Ge(111)- $\sqrt{3}$  is again dominated by the substrate lattice. The population of TSB trimer is preferentially localized near the step edges, suggesting that the trimer formation may be predominated on the defect site. If we prepare low coverages ( $\approx 0.3$  ML) of TSB/Ag/Ge(111)- $\sqrt{3}$  by exposing the substrate surface to a smaller amount of TSB at  $200$  K, the STM images show aggregated ( $2 \times 1$ ) domains after cooling to  $100$  K (no annealing before the cooling procedure). The trimer configuration of deposit-annealing TSB/Ag/Ge(111)- $\sqrt{3}$  surface is thus assigned to be a low coverage phase. Since the in situ imaging of

the underlying substrate lattice failed in this case, the registry cannot be absolutely decided. Presumably, each trimer is surrounded by three TSB molecules oriented in three equivalent directions on the surface,  $120^\circ$  apart, with an adsorption site the same as that of monolayer coverage. This model provides good qualitative explanations for the stability of the TSB trimer and its strong size selection. A more definitive determination of surface structure of TSB trimer on Ag/Ge(111)- $\sqrt{3}$  will require further experimental and theoretical work.

#### 4. Conclusions

We have studied the adsorption of *trans*-stilbene (TSB) on Ag/Ge(111)- $\sqrt{3}$  using low-temperature STM in an ultrahigh vacuum environment. Molecularly resolved STM images of well-ordered adsorbates could be obtained for TSB. The TSB molecules showed the appearance of dumbbell shapes. The images revealed two clear lobes corresponding to the two benzene rings at the trans positions of the double bond at the molecular center. The difference of contrast in terms of brightness and size for the two benzene lobes was explained by the nonplanar configuration for TSB on Ag/Ge(111)- $\sqrt{3}$ . Self-ordering of TSB on Ag/Ge(111)- $\sqrt{3}$  is well correlated with the substrate lattice. It suggests that the intermolecular interaction of TSB molecules could be weaker than the interaction with the substrate which therefore controls the structure of the monolayers. The packing arrangement of TSB on Ag/Ge(111)- $\sqrt{3}$  was determined either by in situ comparison with the underlying substrate lattice that can become visible through lowering the bias voltage or by a  $0.5$  ML TSB image that shows the coexistence of TSB domains and the partial bare surface. We conclude that the adsorbed TSB molecules form a ( $2 \times 1$ ) structure on Ag/Ge(111)- $\sqrt{3}$ . A structural model based on a direct comparison of STM images between the TSB and bare substrate lattice is presented.

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