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Adsorption of Cu phthalocyanine on Pt modified Ge(001): A scanning tunneling microscopy study

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The adsorption configurations of copper phthalocyanine (CuPc) molecules on platinum-modified Ge(001) have been studied using scanning tunneling microscopy. After deposition at room temperature and cooling down to 77 K the CuPc molecules are still dynamic. However, after annealing at 550 ± 50 K, the adsorption configurations of the CuPc molecules change and the CuPc molecules do not exhibit any dynamics at 77 K. This is indicative of a transition from a physisorbed to a chemisorbed state. We suggest that during annealing, the CuPc molecule binds with the substrate dimers via a cycloaddition reaction. Atomic models are proposed for the different adsorption configurations.

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I. INTRODUCTION

The phthalocyanine (Pc) molecules have recently attracted a substantial amount of attention in the field of nanoscience. Their electrical, physical, and optical properties can be manipulated by the large variety of substitutes that can be attached to the basic Pc structure.[1,2] Additionally, it is possible to incorporate about 70 different metals in the center of the Pc molecule giving even more freedom to tailor its properties.[1] The flexibility of these molecules has already resulted in a wide variety of Pc-based devices such as gas sensors,[3] field effect transistors,[4] light-emitting devices,[5] and solar cells.[6] Understanding the interaction of phthalocyanines with semiconductor surfaces is a prerequisite for finding their potential applications in electronics and nanotechnology.

The selected molecule in this research is the Cu-phthalocyanine (CuPc). The Cu, with oxidation state of 2+, makes two coordinated covalent and two covalent bonds with the Pc ring which has an oxidation state of 2−. The Cu ion is small enough to fit in the cavity of the Pc molecule, making CuPc a planar, fourfold symmetric molecule.

Self-assembly does not occur on every type of surface, and it is dependent on the relative strength of the molecule-molecule and molecule-substrate interactions.[7–9] For Si and Ge surfaces where the molecule-substrate interaction is dominant, the molecules will lie flat down, but in a disordered fashion. Ordered films on these surfaces can be obtained by passivating the dangling bonds with hydrogen.[9]

In this research we have chosen the platinum-modified Ge(001) surface[10,11] as a substrate for the adsorption of CuPc molecules. The platinum-modified Ge(001) surface is an ideal template for molecular electronics due to the presence of densely packed arrays of nanowires. Mastering and understanding the adsorption of the technologically interesting CuPc molecules on these templates can pave the way toward new possibilities in molecular electronics. As will be shown, the complexity of this surface along with the peculiar structure of this molecule leads to a rich variety of adsorption configurations.

II. EXPERIMENTAL PROCEDURE

The sample was cut from an intrinsic Ge(001) wafer and cleaned in an isopropanol ultrasonic path prior to insertion in the vacuum chamber. The background pressures of the preparation chamber and the scanning tunnel microscope (STM) chamber were kept below 5×10^{-11} mbar throughout the experiment. Subsequently, the surface was cleaned by cycles of Ar-ion bombardment and annealing at 1100 ± 25 K by direct current heating. The cleanliness of the surface was checked by STM. After obtaining an ordered $(2 \times 1)/c(4 \times 2)$ Ge(001) surface,[12] a fraction of a monolayer of Pt was deposited. By applying an annealing cycle at 1100 ± 25 K, the surface undergoes a dramatic morphological transition. More details about the fabrication process, the atomic structure and electronic properties of this surface can be found elsewhere.[10,11]

The CuPc was deposited using a Knudsen cell with a quartz crucible. The used CuPc was >99% pure. The sample was directly facing the Knudsen cell's outlet at a distance of about 2 cm. During the deposition the temperature of the Knudsen cell was kept at 573 ± 5 K and the pressure in the preparation chamber was 4×10^{-9} mbar. During the deposition the sample was at room temperature. Subsequently, the sample was transferred to the STM chamber and cooled down to 77 K.

III. RESULTS AND DISCUSSION

In order to obtain a fractional coverage of CuPc on Pt/Ge(001), we increased the CuPc deposition time step by step. After each deposition step the surface was checked by STM. Figure 1 shows an overview of the Pt/Ge(001) surface after a total deposition time of 990 s. The Pt/Ge(001) surface consists of three different regions known as α terraces, β terraces, and nanowires.[10,11] The individual CuPc molecules appear as bright spots. We never observed any evidence for the formation of ordered domains of molecules.

It can be seen that the β terrace has a higher CuPc coverage than the nanowire regions. The highest coverage is, however, found on the α terraces. On these terraces the in-

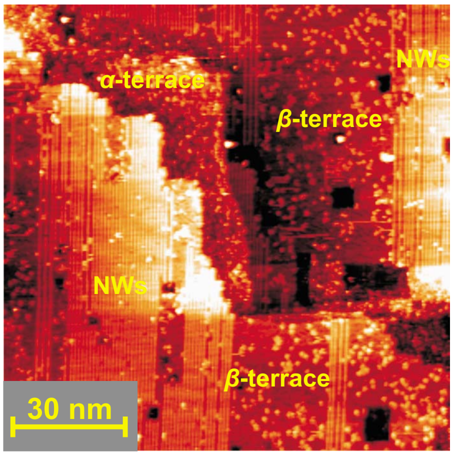

FIG. 1. (Color online) An STM image of Pt-modified Ge(001) surface after 990 s deposition of CuPc molecules at room temperature. The temperature of the Knudsen cell was 573 K. The image is recorded at 77 K with a sample bias of +1.5 V and 0.2 nA tunnel current.

dividual CuPc molecules are hardly recognizable, which might be caused by the disordered nature of the α terraces or the rich variety of adsorption configurations.

Figure 2 shows three examples of CuPc molecules on a β terrace at different sample biases. In column (A), the angle between the axis of the molecule and the substrate dimer rows, θ, is 0° ± 5° (see Fig. 3 for a definition of θ). We will refer to this configuration as the (+) configuration. Column (B) shows another CuPc molecule with an angle, θ, of 45 ± 5°. This configuration will be referred as the (×) configuration. Even though we have observed some molecules with different angles on the surface—e.g., the one shown in column (C)—the majority of the molecules are found in the (×) and (+) configurations.

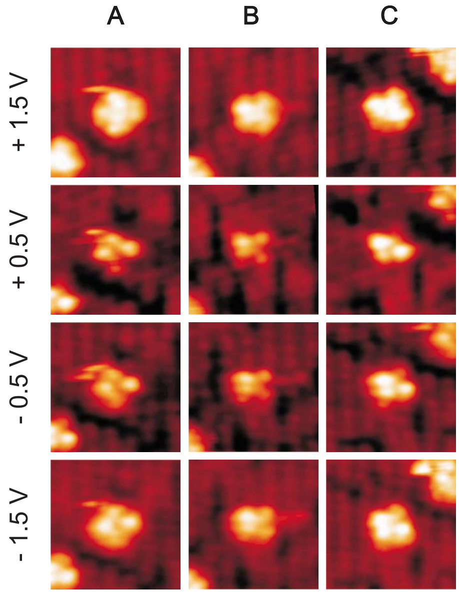

FIG. 2. (Color online) Three different adsorption configurations of CuPc molecules on a β terrace at different sample biases. The two main configurations, (+) and (×), are shown in (A) and (B), respectively. (C) shows an exception. The size of the images is 5.2×5.2 nm^2 and the tunnel current was 0.2 nA.

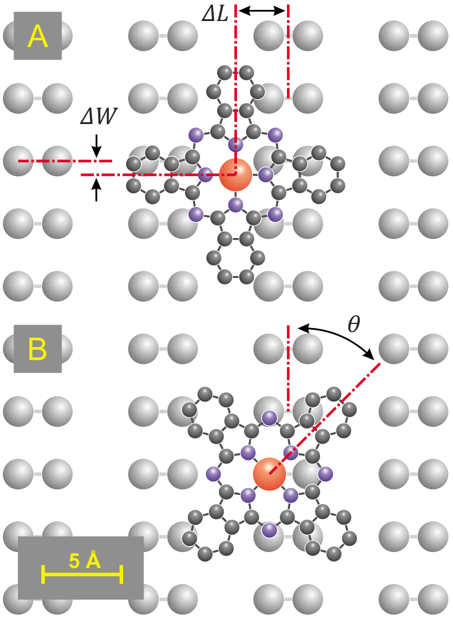

FIG. 3. (Color online) Schematic representation of the two main CuPc adsorption configurations on a β terrace: (A) the (+) configuration with $\theta=0°\pm5°$, (B) the (×) configuration with $\theta=45°\pm5°$. The carbon (C), nitrogen (N), and copper (Cu) atoms of the CuPc molecule are represented by small black, blue, and big red circles, respectively. The shown CuPc molecules are depicted using the equilibrium structure of CuPc molecule at its free form.

In all cases the molecules have a cloverlike appearance with four distinct lobes. For the (+) configuration, the molecules look symmetric at 1.5 V biases while at biases lower than 0.5 V the horizontal lobes become brighter. For the (×) configuration shown in column (B), the left side of the molecule looks brighter at both polarities. For the case shown in column (C), there is a reversal of brightness of two of the four lobes when the polarity is changed (see Fig. 2).

The free CuPc molecule is fully symmetric with four identical lobes. Apparently, the adsorption of the molecule on the surface can break its symmetry. In all cases, the center of the molecule appears dimmer than the four lobes. It has been proposed that this is because the d_{zz} orbital of the Cu^{2+} core—which is pointing out of the plane of the molecule—is fully occupied and lies about 2 eV below the highest occupied molecular orbital, hence the core of the molecule appears as a depression at low biases.[13]

Figure 3 shows the schematic representation of the (+) or (×) configuration. Note that in the STM images the dimer rows appear as dark lines at positive sample biases while they appear as bright lines at negative sample biases. For the (+) configuration, the distance between the center of the molecule and the center of its adjacent dimer row—indicated by ΔL in Fig. 3—is 3.3 ± 0.5 Å. The lateral distance between the center of the molecule and the axis of its nearest dimer—indicated by ΔW in Fig. 3—is 0.9 ± 0.5 Å. For the (×) configuration, these values are $\Delta L=1.2\pm0.5$ Å and $\Delta W=0.0\pm0.5$ Å, respectively.

The (+) configuration has been observed previously for several metal phthalocyanines on Ge(001) and Si(001).[14–18]

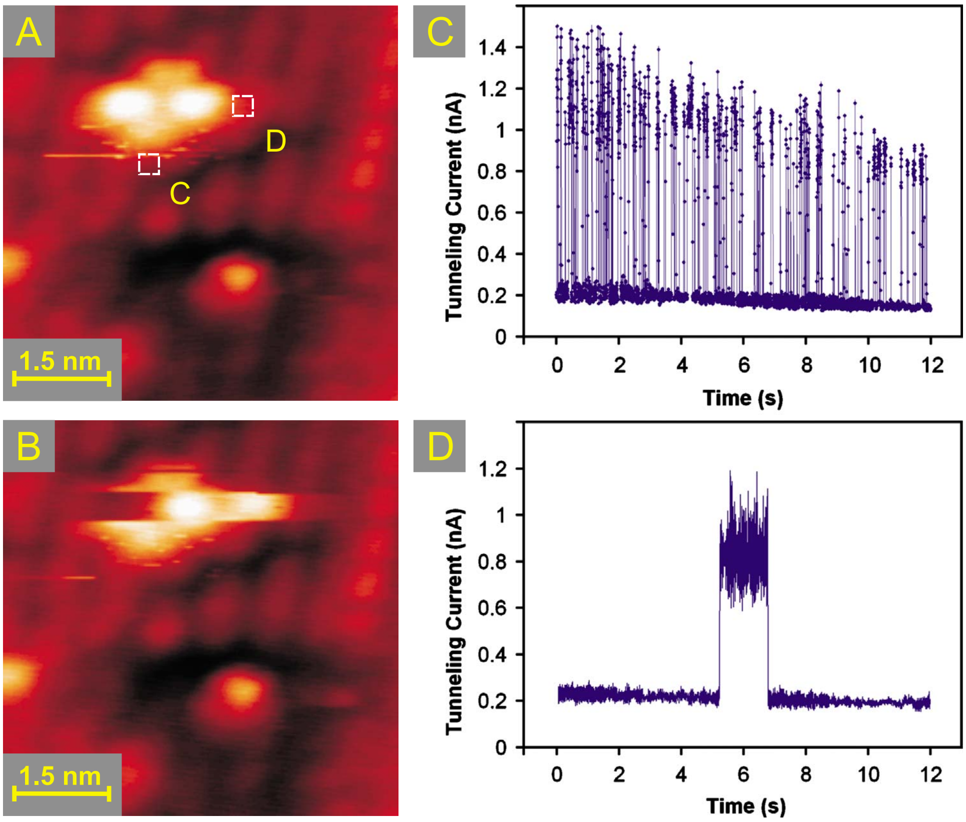

FIG. 4. (Color online) (A) and (B) show two consecutive images of an (+) CuPc molecule on a β terrace. (C) and (D) show $I(t)$ traces recorded at the points indicated in image (A). Sample bias is -1.5 V and the set current is 0.2 nA.

In all of these cases the center of the molecule was reported to be either exactly at the middle of the trough between the substrate dimer rows or exactly at the middle of a substrate dimer row. Our results, however, reveal that the center of the CuPc molecules is slightly displaced from the middle of the troughs. This can be related to the fact that the β terrace is comprised of mixed Pt-Ge and Ge-Ge dimers.[10,11] No $(\times)$ configuration has been reported in Refs. 14–18. However, the $(\times)$ configuration has been observed for adsorbed CoPc molecules on Si(001).[19] Surprisingly no (+) adsorption configuration has been reported for this system.

The molecules exhibit a significant amount of dynamics at 77 K. The fuzzy feature seen in Fig. 2(A) just above the upper left of a (+) CuPc molecule is an indication its dynamic behavior. Apparently, the top lobe has some degree of freedom while the center of the molecule remains fixed. Additionally, our observations have revealed that both the (+) and $(\times)$ CuPc molecules can diffuse on a β terrace.

In order to obtain a better understanding of the dynamic behavior of CuPc we have performed time-resolved STM measurements.[20] Figures 4(A) and 4(B) show two consecutive images of a (+) CuPc molecule exhibiting dynamic motion on a β terrace. In Fig. 4(A) the lower lobe has a fuzzy appearance. This is not the case for the other three lobes. Figure 4(B) shows the lateral hopping of the molecule perpendicular to the substrate dimer rows. Two time traces have been taken at locations C and D, as indicated in Fig. 4(A).

The results are depicted in Figs. 4(C) and 4(D). Time trace (C) suggests that the molecule is switching back and forth between two states. The high-current state, however, seems to be less well defined than the low-current state. The mean residence time in the high and low current states is measured to be 27 ms and 85 ms, respectively. The average switching frequency is 8.8 Hz.

The $I(t)$-curve recorded at position D is very different. No fast switching process is visible in this graph, so the bright lobe close to point D seems to be static. However, the presence of a sudden jump in the current at ~5 s indicates the

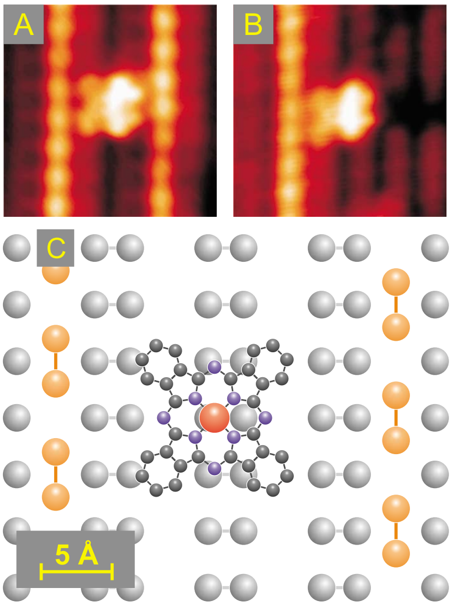

FIG. 5. (Color online) (A) STM images of CuPc molecules adsorbed in a 2.4-nm-wide trough (B) and at the boundary of a nanowire patch and a β terrace. The image sizes are 5×5 nm^2, the sample bias is $+1.5$ V and the tunnel current is 0.2 nA. In (C) a schematic of the CuPc molecule in image (A) is shown.

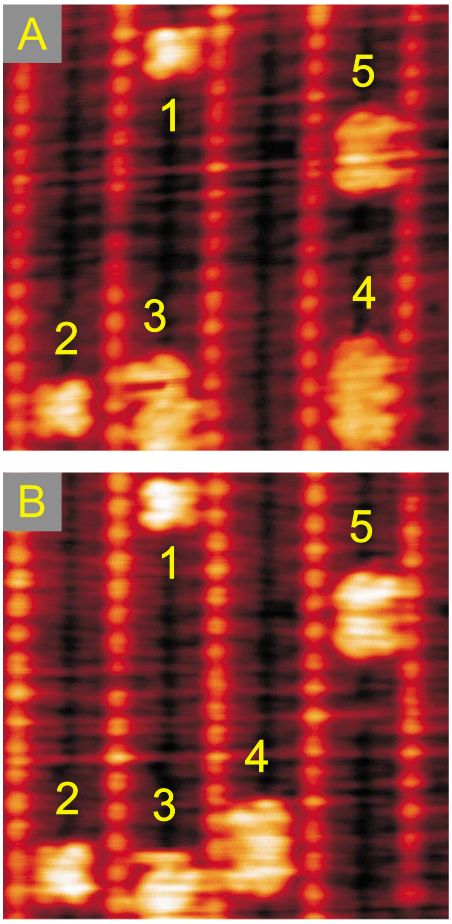

FIG. 6. (Color online) (A) and (B) show two consecutive images of several CuPc molecules adsorbed in 2.4-nm-wide troughs. The image size is 11×11 nm^2. The sample bias is 1.45 V and the tunnel current is 0.2 nA.

transformation of the molecule to another state. This is most probably due to a lateral diffusion event of the molecule, similar to what is observed in Fig. 4(B).

As mentioned before, the molecules seem to have a smaller tendency to adsorb on the nanowires. In most cases, the spacing between the nanowires is 1.6 nm.[10] We could not observe any stable configuration neither on top nor in between the nanowires. However, a small fraction of the nanowires are separated 2.4 nm apart, which is apparently large enough for the adsorption a CuPc molecule in the trough.

Figure 5(A) shows an example of a CuPc molecule adsorbed in a 2.4-nm-wide trough. The corresponding configuration is shown schematically in Fig. 5(C). This configuration is very comparable to a $(\times)$ configuration on a β terrace. However, ΔL in this case has a value of only 0.7 ± 0.5 Å, which is most likely due to the presence of nanowires in its close proximity. The two right-hand side lobes of the molecule look brighter and each of them seems to consist of two smaller lobes. The left side lobes look dimmer and they do not show any substructure. Figure 5(B) shows another molecule at the boundary of a nanowire patch and a β terrace. The absence of a nanowire at the right-hand side of the CuPc molecule in Fig. 5(B) is most likely responsible for its sheared configuration.

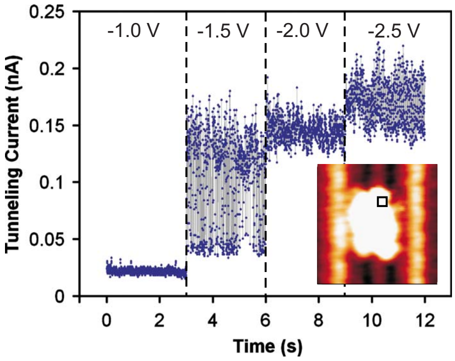

FIG. 7. (Color online) $I(t)$ curve recorded on a dynamic CuPc molecule in a 2.4-nm-wide trough. The location of the tip is indicated in the inset. Different voltage pulses have been applied during the measurements. The size of the inset is 3.6×3.6 nm^2, and it has been recorded at 1.5 V and 0.2nA. The same settings were also used as the initial settings of the $I(t)$ trace.

Similar to the β terrace, the CuPc molecules also exhibit dynamics in a 2.4-nm-wide trough. Figure 6 shows two consecutive images of several CuPc molecules in 2.4-nm-wide troughs. The molecules indicated by 1 and 2 are stable and show no dynamics. The other molecules, however, exhibit a fast back and forth hopping along the trough, which makes their appearance more elongated than the immobile ones. Additionally, the molecule indicated by 4, jumps to its left-hand side trough. It is not clear yet why some molecules are mobile and others are not.

In Fig. 7 the dynamics of a CuPc molecule at different sample biases is studied. The insets show a dynamic molecule with an elongated appearance, similar to the molecule 5 in Fig. 6. For this measurement, the tip has been placed on the marked position in the inset, the feedback loop has been turned off, the bias has been changed in a stepwise fashion, and the current has been recorded as a function of time. Each step in the tunneling current is due to an increase in the applied bias.

Generally, an increase in the tunneling current leads to an increase in its noise level. The discreteness of the electric charge and the random nature of the tunneling process generates a noise, the so-called shot noise, that has a spectral density that is proportional to the average tunnel current.[21,22] However, we see a violation of this trend at -1.5 V bias. Despite the fact that the tunneling current during the -1.5 V pulse is lower than the current at -2.0 V and -2.5 V pulses, the noise level is clearly higher at -1.5 V. This is an indication of tip-induced dynamic behavior of the molecule at -1.5 V.

A closer look to the current-time trace during the -1.0 V, -2.0 V, and -2.5 V pulses reveals that the data points seem to be distributed randomly along the current axis. Interestingly, however, the data points during the -1.5 V pulse have an inhomogeneous distribution with clear maxima at the lowest and highest currents. The latter provides further evidence that the increased noise level during the -1.5 V pulse is due to hopping of the molecule between two states. Therefore, we suggest that -1.5 V matches with one of the electronic states of the CuPc molecule and electron detachment

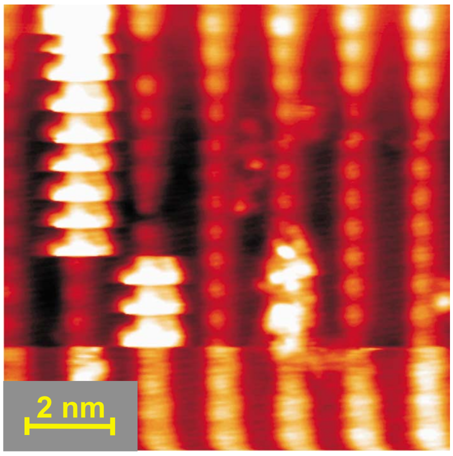

FIG. 8. (Color online) STM-induced motion of a CuPc molecule adsorbed on a nanowire. The image is recorded at 1.5 V and 0.5 nA.

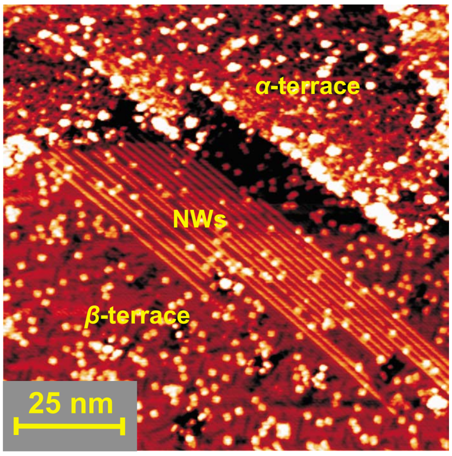

FIG. 9. (Color online) An STM image of Pt-modified Ge(001) after 1890 s deposition of CuPc followed by 5 min annealing at 550±50 K. The image has been recorded at +1.5 V sample bias and 0.2 nA tunnel current.

from this electronic state is responsible for the observed dynamics. Careful analysis of Fig. 7 shows that the residence times in the high and low current states is less than the time resolution of our measurements (3 ms).

As mentioned before, our experiments did not reveal any stable CuPc configuration on top of the nanowires. It seems that even if a CuPc molecule adsorbs on the nanowires it can be easily removed when the STM tip is scanning across the molecule. In Fig. 8, the STM tip is dragging a CuPc molecule along a nanowire. The fast scanning direction is perpendicular to the nanowires and the slow scanning direction is from bottom to top. The picture shows several CuPc hopping events along the nanowires and in one case the molecule is transferred to an adjacent nanowire. We believe that the bonding between the CuPc molecule and a nanowire is so weak that the molecule can easily be displaced by the STM tip.

In order to study the surface at a higher coverage of molecules, we applied an additional 900 s deposition cycle, which resulted in a total deposition time of 1890 s. After this second adsorption experiment, the surface was found to be covered with a disordered layer of CuPc molecules. Subsequently, this sample was annealed by direct current heating at 550±50 K for 5 min. This temperature is below the thermal dissociation temperature of CuPc molecule, i.e., ~973 K.[23] Figure 9 shows an overview of the surface after this annealing step. The majority of the molecules have been desorbed from the surface. This time, however, we have a comparable concentration of molecules on α terraces, β terraces, and nanowires. The molecules show up as bright spots. In contrast to the β terraces and nanowires, the α terraces still look disordered and the molecules have a spherical shape, rather than the regular cloverlike appearance.

After the annealing process we could not find any evidence for dynamics or diffusion of the CuPc molecules on any of the three regions. This suggests that the bonding be-

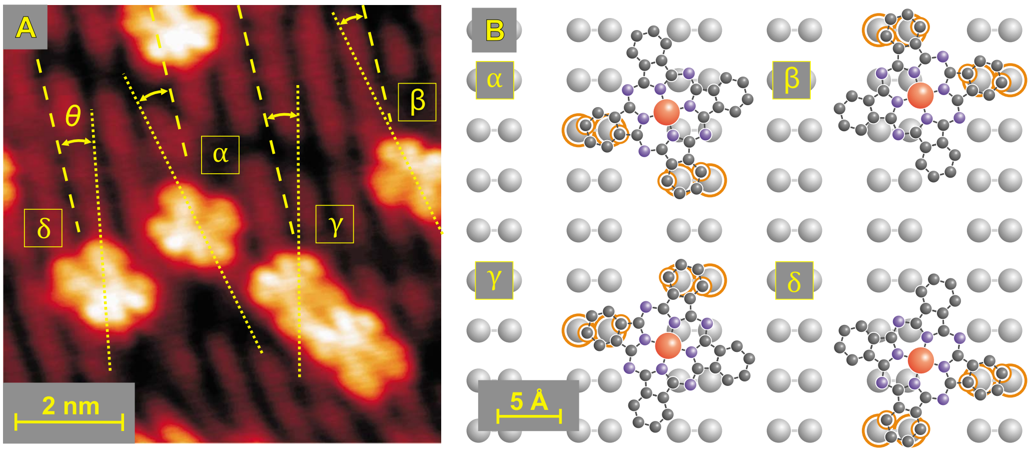

FIG. 10. (Color online) (A) Closeup view of CuPc molecules on a β terrace after 5 min of annealing at 550±50 K. The image is recorded at +1.5 V bias and 0.2 nA tunnel current at 77 K. The axes of molecules are shown by dotted lines and the dashed lines are positioned on top of the substrate dimer rows. (B) Ball-and-stick models of CuPc molecules marked in (A). The assumed reacting carbon atoms of the CuPc molecules and the underlying substrate dimers are marked by additional rings. The position of molecule has been adjusted to give the best fit between the highlighted carbon and substrate atoms. The shown configurations are corresponding to $\theta = \pm 15°$, $\Delta L = 2.1$ Å, and $\Delta W = 1.6$ Å.

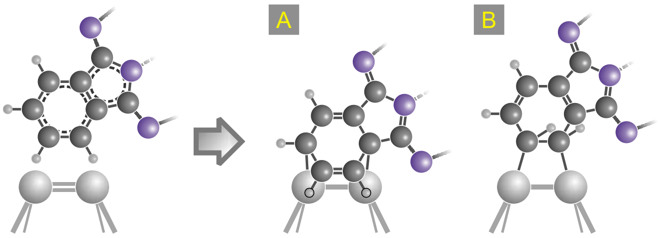

FIG. 11. (Color online) Two possible cycloaddition reaction pathways resulting in a bond between a CuPc arm and a dimer.

tween the molecule and the substrate is stronger than before the annealing step.

Figure 10(A) shows a closeup view of CuPc molecules on a β terrace at 77 K. Surprisingly, all the molecules show a different configuration compared to what was observed before the annealing step. In all cases, the axes of molecules make an angle of $|\theta|=12°\pm5°$ with the substrate dimer rows. The molecules (α) and (β) have a negative angle while the (γ) and (δ) have a positive angle. The lower lobes of (α) and (δ) are brighter than the others and each of these lobes seems to consist of two smaller lobes. For (β) and (γ) this is just the other way around. The relative coordinates (see Fig. 3) of the molecules are $\Delta L=1.8\pm0.5$ Å and $\Delta W=1.3\pm0.5$ Å. Hence the adsorption configurations have changed upon annealing.

A careful analysis of the images reveals that the ends of the arms of the molecules are located on top of substrate dimers. Figure 10(B) shows the proposed models for adsorption configurations of the CuPc molecules shown in Fig. 10(A).

It is known that an unsaturated organic molecule can react with the dangling bonds of a semiconductor surface. In one specific type of reaction, known as cycloaddition reaction, the molecule makes a cyclic bond with the substrate which reduces the multiplicity of an unsaturated bond of the molecule.[24–27] Figure 11 shows two possible pathways for such a reaction between a substrate dimer and the arm of a CuPc molecule. Note that this reaction will break the symmetry of the molecule and the molecule will convert to one of its conjugated states. Reaction (A) is energetically more favorable than (B) since it leads to less stress in the substrate dimer (see Fig. 11).

Figure 10(B) shows the cases where both of the CuPc arms make bonds via reaction type (A) and the deformation of the molecule due to the bond formation has been ignored. However, we cannot exclude that reaction type (B) occurs, so there are, in principle, four slightly different adsorption configurations, namely AA, AB, BA, and BB. Each of these configurations leads to a slightly different adsorption configuration.

The brighter lobes of the CuPc molecules in Fig. 10(A) correspond to the bonded arms while the dimmer lobes correspond to the free arms shown in Fig. 10(B). The bonded lobes exhibit a substructure while the free lobes appear larger and more blurry. This is consistent with the fact that the bonded arms are better fixed while the free arms have higher degree of freedom.

As already pointed out, we have found a higher density of CuPc molecules on the nanowires after annealing (see Fig. 9). Figure 12(A) shows a closeup view of a few CuPc molecules adsorbed on nanowires and their corresponding models are shown in Fig. 12(B). The CuPc molecule indicated by (α) is located in a 2.4-nm-wide trough. This molecule clearly has a different configuration from the one shown in Fig. 5(A). One of the lobes is located on the nanowire and looks significantly brighter than the others. The corresponding model of (α) in Fig. 12(B) shows that this molecule has probably no bond with the nanowire and has anchored itself to the substrate dimers in the trough. One of the two free lobes lies on the nanowire. This probably leads to the bright appearance.

The CuPc molecule indicated by (β) is also located in a 2.4-nm-wide trough. However, this molecule does not show any bright lobe. The corresponding model of (β) shows that indeed all the lobes of molecule are lying flat down in the trough. It should be pointed out that in contrast to the CuPc molecules in Fig. 10 no bright lobes are observed. Moreover, the CuPc molecule in Fig. 12(A) looks a little distorted. We

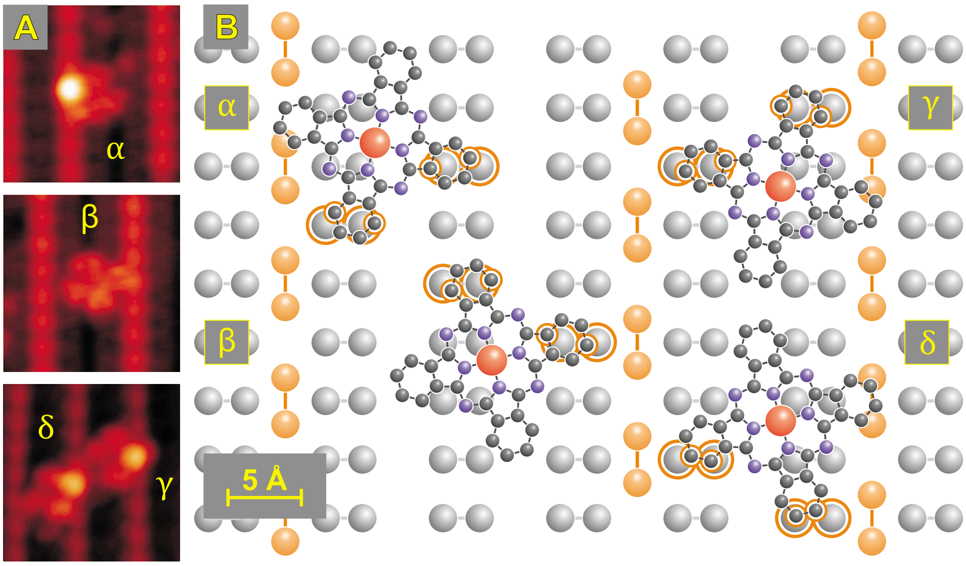

FIG. 12. (Color online) (A) CuPc molecules adsorbed in 2.4-nm-wide troughs (α and β) and two CuPc molecules adsorbed in a 1.6-nm-wide trough (γ and δ). Image size of 4.6×4.6 nm^2, sample bias is 1.5 V and tunnel current is 0.2 nA. (B) Ball-and-stick models for the CuPc molecules shown in (B). The carbon atoms and the substrate atoms that are most likely involved in the cycloaddition reaction are highlighted with additional circles.

believe that these differences are due to the presence of the nanowires and confinement of the adsorbed molecule in the trough region.

Furthermore, we observed many stable CuPc molecules on the nanowires that are 1.6 nm apart. Two examples are indicated by (γ) and (δ) in Fig. 12(A). There molecules also reveal a single bright lobe on the nanowire. The anchoring mechanism is similar to the other cases discussed above. Note, however, that for the lower molecule the best fit is obtained if the two arms of the CuPc molecule are anchored via reaction type (B) in Fig. 11.

IV. CONCLUSIONS

The adsorption of CuPc molecules on Pt-modified Ge(001) has been studied using STM at 77 K. We have proposed models for the adsorption configurations of the CuPc molecules after deposition at room temperature and subsequent annealing at 550 K. After deposition at room temperature, the CuPc molecules exhibit dynamics. The dynamics of molecules is bias dependent. However, after annealing no dynamics has been observed. We suggest that this is caused by a transition from a physisorbed configuration to a chemisorbed configuration. The chemisorbed CuPc molecules bind with the substrate dimers via a cycloaddition reaction.

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