

Anchoring phthalocyanine molecules on the 6H-SiC(0001)3×3 surface

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The adsorption of individual metal-free phthalocyanine molecules on the 6H-SiC(0001)3×3 surface was studied using the scanning tunneling microscope supported by density functional theory calculations. Phthalocyanine molecules were found to be chemisorbed through a reaction of two conjugated imide groups with two silicon adatoms. This type of anchoring opens numerous perspectives for the organic functionalization of a biocompatible wide band gap semiconductor.

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Functionalization of wide band gap semiconductor surfaces such as silicon carbide (SiC) and diamond with organic molecules is an important issue for the development of biosensors¹⁻⁵ and optoelectronic devices.^{6,7} Indeed, silicon carbide and diamond have substantial advantages over other common semiconductors since they are biocompatible, transparent and have outstanding mechanical properties. Biocompatible semiconductor materials could be the basis for implantable biosensors or other electrical components *in vivo*. Until now the functionalization strategies for diamond surfaces have relied on the cycloaddition of a C=C bond.^{5,8,9} Concerning the SiC, it has been difficult to find suitable molecules involving the appropriate chemical group susceptible to act as an anchor. Recently, on the cubic-SiC(001), the adsorption of simple CH₃X-like organic molecules was studied from *ab initio* calculations.¹⁰ On the 3×3 hexagonal reconstruction, a recent x-ray photoelectron spectroscopy and low energy electron diffraction (LEED) investigation of the adsorption of pyrrole molecules¹¹ shows that the bonding through the dissociation of a N-H bond is favorable. Until now there have been no atomic-scale studies of adsorbed organic molecules on SiC surfaces.

In this letter, we investigate at the atomic scale the anchoring of metal-free phthalocyanine (H₂Pc) molecules on a 6H-SiC(0001)3×3 substrate with the scanning tunneling microscope (STM) at room temperature under ultrahigh vacuum (UHV) conditions. The 3×3 reconstruction¹²⁻¹⁴ exhibits dangling bonds (DB's) located on the top of pyramid-like structures separated by about 9 Å from each other.¹² Here, we take advantage of this very low DB density and of the high spatial resolution of the STM to explore in detail the adsorption configuration of individual H₂Pc molecules on this surface. The adsorption configuration is found to involve two Si-N bonds whereas the phenyl groups do not show any apparent chemical interaction. Starting from these experimental data, the energetics and structure of the corresponding adsorption configuration are calculated using density functional theory (DFT).

Experiments were performed using a room temperature UHV STM apparatus. N-doped 6H-SiC(0001) single-crystal wafers with a free carrier concentration in the range of 3

× 10¹⁸ cm⁻³ were used. After outgassing, the SiC sample was heated at 1100 °C, to remove the native oxide and other impurities. It was then annealed at 650 °C for a few minutes under a silicon flux which led to a well reconstructed 3×3 surface, as indicated by a sharp LEED pattern. High purity (99%) H₂Pc powder supplied by Aldrich was used. Prior to sublimation, the evaporant was outgassed at a temperature slightly above the temperature used for deposition. During exposure, H₂Pc molecules were evaporated at about 250 °C, while the substrate was held at room temperature.

Figure 1 shows a STM topography of individual H₂Pc molecules deposited on the 6H-SiC(0001)3×3. The three-fold symmetry of the 3×3 reconstruction gives rise to three possible equivalent molecular orientations, as can be seen in the topography.

Figure 2 shows an enlarged STM topography of a single H₂Pc molecule on SiC and a model of the corresponding surface structure and molecular adsorption geometry. The

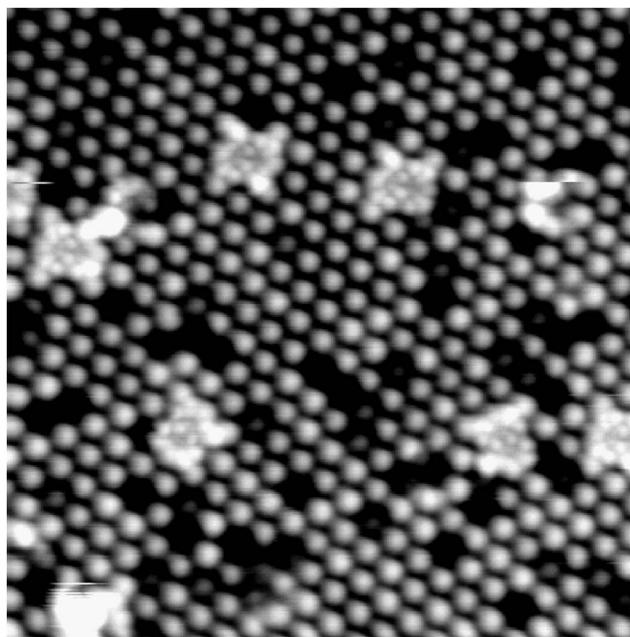


FIG. 1. 20×20 nm² STM image of individual H₂Pc molecules on 6H-SiC(0001)3×3 recorded at a sample bias $V=-2.0$ V and a tunnel current $I=0.3$ nA.

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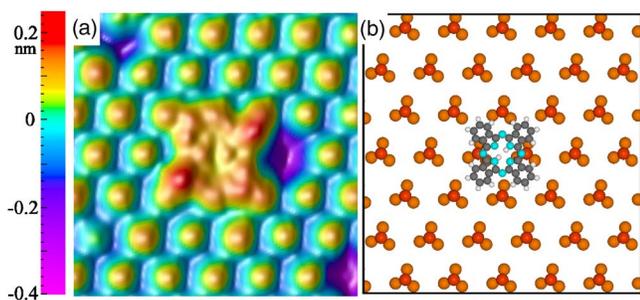


FIG. 2. (Color online) (a) Typical molecule topography. $5 \times 5 \text{ nm}^2$, $(V, I) = (-2.0 \text{ V}, 0.3 \text{ nA})$. (b) The associated adsorption model shows the molecule and the top two Silicon layers of the surface (adatoms and trimers).

molecular adsorption geometry is deduced from the symmetry and the position of the molecular envelope relative to the Si adatoms. The STM topographies of all molecules show very similar internal molecular structures. The slight differences between various molecules are attributed to surface defects close to the molecules or structural modifications of the surface beneath the molecule.

From examination of the position of the molecule relative to the Si adatoms (Fig. 2), we deduce that the interaction of the H_2Pc molecule with the SiC surface could proceed by the reaction of the conjugated imide nitrogens (N1 and N2) with two silicon adatoms, as shown in Fig. 3. The reaction mechanism can be assimilated to a $[10+2]$ cycloaddition though only partially since the two silicon adatoms are separated by about 9 \AA . The reaction may be concerted or proceed in two steps. First, a Si–N bond is formed, giving rise to a radical intermediate state stabilized by the conjugated system, followed by the formation of the second Si–N bond. A two step cycloaddition reaction via a radical intermediate has been observed in solution chemistry.¹⁵ The N1 and N2 lone pairs are not thought to play any role since the relative orientation of the nitrogen lone pairs and the sp^3 -like silicon orbital is not favorable for chemical bond formation when the molecule lies parallel to the surface. The chemical adsorption mechanism shown in Fig. 3 seems to be favorable for several reasons: (i) the associated electronic rearrangement gives rise to a final state in which the adsorbed molecule is uncharged and contains no radical (Fig. 3), (ii) the Si–N bond is known to be chemically stable (silizane, Si_3N_4), (iii) the N–N distance in the free molecule (6.71 \AA) is close enough to the Si–Si distance on the surface (9.29 \AA) to enable bond formation with the two silicon adatoms, and (iv) the other silicon DB's are too far away to have any interaction with the molecule or to play any role.

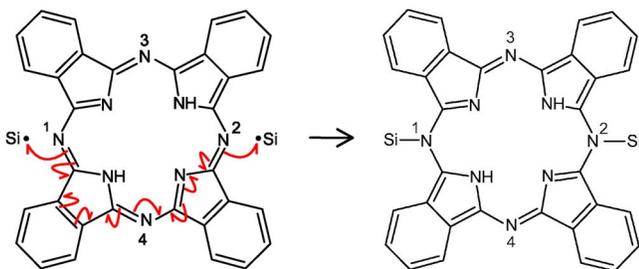


FIG. 3. (Color online) Adsorption model of the phthalocyanine molecule showing the electronic rearrangement. Two silicon DB's of the SiC surface form covalent Si–N bonds with two conjugated nitrogen atoms of the molecule.

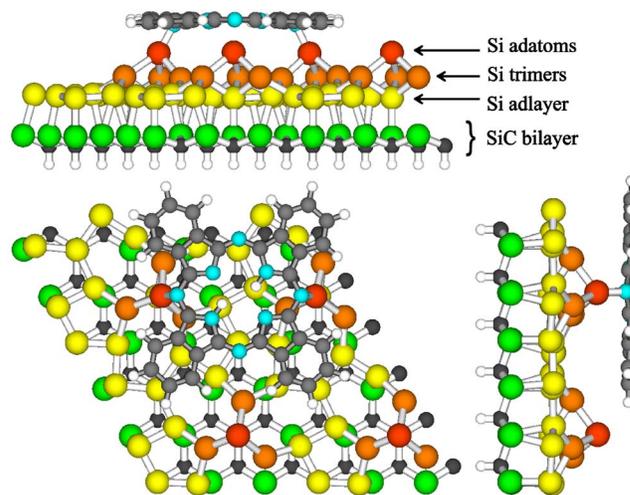


FIG. 4. (Color online) Top and two side views of the optimized configuration of the unit cluster.

To corroborate this model and provide further insights into the adsorption properties, the atomic structure and adsorption energy were investigated within the periodic DFT using the VASP code^{16–18} in generalized gradient approximation (GGA) and ultrasoft pseudopotentials.^{19,20} The Brillouin zone was sampled using a single \mathbf{k} point at the Γ point which is a reasonable choice given the large size of the chosen supercell. The $6H\text{-SiC}(0001)3 \times 3$ surface is modeled by a periodic slab involving six layers (three layers for the reconstruction, one bilayer of SiC, and one layer of hydrogen atoms). H atoms are added on the back side to saturate DB's. The total number of atoms in the unit cluster is 218. The theoretical bulk silicon carbide lattice parameter (4.38 \AA) is used and the vacuum region along the z direction (normal to the surface) is equal to 12 \AA . The four top layers were allowed to relax and the residual forces on the atoms are lower than 0.05 eV/\AA .

The optimized adsorption geometry indicates an elongation of the molecule, the N1–N2 distance extended from 6.71 to 7.16 \AA and the Si–Si distance contracted from 9.29 to 8.85 \AA with the Si–N bonds 1.88 \AA in length. A smaller contraction is observed in the orthogonal direction, the N3–N4 distance varied from 6.71 to 6.48 \AA . However, the planar structure is preserved, as shown in Fig. 4. The adsorption energy was calculated to be -1.36 eV . This relatively small binding energy indicates that the probable adsorption process involves the formation of two Si–N bonds weakened slightly by the molecule surface distortion. This also explains the tip induced diffusion of the molecule that was occasionally observed, as shown in the topography of Fig. 5, where the STM scans line by line from the bottom to the top. In the bottom half of the image, the molecule is adsorbed through the adatoms Si1 and Si2 [Fig. 5(b)]. When the tip reaches the middle of the topography marked with the arrow, the molecule moves to the adsorption geometry depicted in Fig. 5(c). The movement is similar to a rotation of the molecule around the remaining Si2–N bond promoted by the rupture of the Si1–N bond. In all cases, the molecule rotates by 60° around one silicon DB and no direct translation has been observed, thus confirming the adsorption model proposed in Fig. 3.

In conclusion, we have reported a STM study of organic molecules deposited on the $6H\text{-SiC}(0001)3 \times 3$ surface.

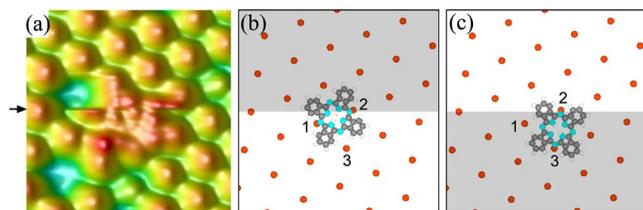


FIG. 5. (Color online) STM topography showing a tip induced motion of a molecule during the scan. $4 \times 4 \text{ nm}^2$, $(V, I) = (-2.0 \text{ V}, 0.3 \text{ nA})$. A discontinuity is visible in the middle of the topography (a). The corresponding molecule positions in the lower and upper parts of the topography are schematized in (b) and (c) showing a rotation around the Si₂-N bond.

STM topographies of phthalocyanines with high spatial resolution enable a determination of a molecular adsorption configuration in which only two DB's of the SiC surface are involved in the formation of covalent Si-N bonds with two nitrogen atoms of the molecules. This configuration arises from the reaction of two conjugated imide groups in the molecule. This model is supported by periodic DFT-GGA calculations of the atomic structure and the adsorption energy. We emphasize that the adsorption of organic molecules on $6H\text{-SiC}(0001)3 \times 3$ is markedly different from other semiconductor surfaces. In the latter case, molecular chemisorption is usually related to the close proximity of two unsaturated DB's or weak π bonds. This enables, in particular, an even number of electrons to be involved during the molecular adsorption. This explains, for example, the adsorption of a number of organic molecules on the $(100)2 \times 1$ reconstructed Si, Ge, and C surfaces through molecular dissociation²¹⁻²³ or $[2+2]$ and $[4+2]$ cycloadditions.^{8,9,21,23,24} In the case of $6H\text{-SiC}(0001)3 \times 3$, the DB's are far apart, making these adsorption processes very unlikely. Nevertheless we have found that the adsorption of organic molecules is possible provided the molecule contains two *reactive* and *conjugated* chemical groups separated by the *appropriate distance*. This opens up interesting perspectives to anchor organic molecules on SiC surfaces and explore the properties of such hybrid systems for bioengineering and optoelectronics.

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