

Density Functional Calculation of the 0.5ML-Terminated Allyl Mercaptan/Si(100)-(2 × 1) Surface *

TANG Chun-Mei(唐春梅)^{1,2}, DENG Kai-Ming(邓开明)^{1,2**}, CHEN Xuan(陈宣)^{1,2},
XIAO Chuan-Yun(肖传云)^{1,2}, LIU Yu-Zhen(刘玉真)^{1,2}, LI Qun-Xiang(李群祥)²

¹Department of Applied Physics, Nanjing University of Science and Technology, Nanjing 210094

²Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026

(Received 6 February 2009)

The structural and electronic properties of the 0.5 ML-terminated allyl mercaptan (ALM)/Si(100)-(2 × 1) surface are studied using the density functional method. The calculated absorption energy of the ALM molecule on the 0.5 ML-terminated ALM/Si(100)-(2 × 1) surface is 3.36 eV, implying that adsorption is strongly favorable. The electronic structure calculations show that the ALM/Si(100)-(2 × 1), the clean Si(100)-(2 × 1), and the fully-terminated H/Si(100)-(2 × 1) surfaces have the nature of an indirect band gap semiconductor. The highest occupied molecular orbital is dominated by the ALM, confirming the mechanism proposed by Hossain for its chain reaction.

PACS: 68.43.Bc, 71.20.-b, 71.15.Mb

The interaction of organic molecules with semiconductor surfaces, particularly the Si(100) surface, is a topic of great interest, since it represents the first stage of technologically relevant processes such as the growth of silicon carbide, a very promising semiconductor material,^[1] and the fabrication of organic layers with controllable physical and chemical functionality^[2] suitable for applications in nonlinear optics, thin-film displays, molecular electronics, etc.

The reconstructed (100) silicon surface seems to be particularly suitable to couple the carbon atoms of organic molecules.^[3] Since the surface reactivity is essentially ruled by the presence of dangling bonds on the surface, most experiments have been carried out using hydrogen terminated Si(100)-(2 × 1) substrates, in order to prevent spurious oxidation processes.^[4] A Si(100) surface has Si dimers formed by the pairing of adjacent Si atoms during the (2 × 1) reconstruction, and the bonding within the dimer can be described, at least formally, as a σ bond and a weak π bond. The unsaturated hydrocarbons chemisorb on the Si(100)-(2 × 1) surface through interaction between the p bond of the molecule and the p bond of the Si dimer, and the adsorption usually gives rise to the breaking of the p bond and then the formation of a new Si-C σ bond.^[5]

It is reported that one adsorbed hydrogen from a dimer on the H-terminated Si(100)-(2 × 1) substrate can be removed using a scanning tunneling microscopy (STM) tip.^[6] On the other hand, styrene (CH₂=CH-C₆H₅),^[4] vinyl ferrocene,^[7] and long-chain alkenes (C₈-C₁₄) can induce the growth of self-directed molecular nanowires along the dimer rows on the H-

terminated Si(100)-(2 × 1) surface. The chemisorption of these organic molecules on Si(100)-(2 × 1) surface has been the subject of numerous studies, motivated by fundamental issues concerning, for example, the understanding of the reconstruction of semiconductor surfaces as well as more technological reasons, related to passivation, heteroepitaxy and growth. The adsorption processes on the Si(100)-(2 × 1) surface, which is widely used in the microelectronics industry, have been particularly investigated. For example, Hossain *et al.*^[8] have found that allyl mercaptan (ALM), CH₂=CH-CH₂-SH is a good candidate for growing molecular lines across the dimer rows on the H/Si(100)-(2 × 1) surface, whereas propylene (CH₂=S-CH₃) and allyl methyl sulfide (CH₂=CH-CH₂-S-CH₃) do not show any line growth. Therefore, the -SH group in ALM seems to play an important role in the stabilization of the intermediate radical, which has been reported to be the key for the successful growth of the molecular line.^[9] To the best of our knowledge, there is no theoretical research on the 0.5 ML-covered ALM/Si(100)-(2 × 1) surface so far. Thus, the study of its geometric and electronic structures is desired.

In this Letter, density functional calculations^[10,11] are carried out using the projected augmented wave (PAW)^[12] pseudopotentials as implemented in the VASP code. The Perdew-Burke-Ernzerh (PBE) form^[13] of the generalized gradient approximation (GGA)^[14] for exchange and correlation functionals is employed. Generally, a kinetic energy cutoff of 500 eV and a k -point mesh of 10 × 10 × 1 (Γ point included) are found to be sufficient to achieve convergence of the

*Supported by the National Natural Science Foundation of China under Grant No 10174039, the Natural Science Foundation of Jiangsu Province under Grant No BK2002099.

**Email: kmdeng@mail.njust.edu.cn

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energy within the order of 10^{-4} eV per atom. A unit cell of (2×1) is used. ALM molecules are adsorbed to Si-Si dimers on one surface of the slab, and all the dangling bonds on both the top and bottom layers are saturated by two hydrogens per Si atom. All atoms but the bottom four Si layers held at bulk positions are relaxed by a conjugate-gradient algorithm^[15] until the change in energy upon ionic displacement is below 10^{-3} eV.

For the periodically repeated artificial slab, two surfaces will strongly interact both via the bulk and via vacuum on the condition that there are few slab layers or a reduced vacuum. The spurious interaction leads to a splitting of the two surface states.^[16] On the other hand, moderately increasing the vacuum separation and slab thickness would greatly increase the computational burden. In order to select suitable sizes of the slab and vacuum, the work function^[17] (WF) of the slab and the electric field gradient (EFG) of the surface atoms should be calculated.^[18] In general, the EFG of the surface atom should converge for the slab thickness upon a sufficient vacuum space, while the WF should converge for the vacuum thickness upon a sufficient slab space. The WF is defined as follows: $WF = V_c - E_f$, where V_c is the Coulomb potential at the center of the vacuum, and E_f represents the Fermi energy of the slab. The calculations show that, when the slab and vacuum thicknesses are equal to 20.51 Å (13 Si slab layers) and 24 Å, respectively, both the EFG and WF will converge well. Therefore, the values of 20.51 and 24 Å for the slab and vacuum thickness are adopted in the following calculations.

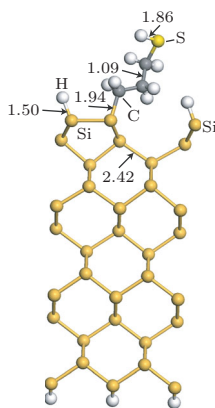


Fig. 1. Optimized structure of the 0.5 ML terminated ALM/Si(100)- (2×1) surface.

In order to check the reliability of our computational method as well as to obtain the results of the Si-Si and the Si-H bond lengths for comparison, we first took the calculation on the full-terminated H/Si(100)- (2×1) surface. The hydrogen adsorption saturates all surface dangling bonds and results in a symmetric Si-Si dimer configuration with the bond length of 2.42 Å on the top layer, close to the calculated value of 2.39 Å obtained by Kresse *et al.*^[19] and that of the 2.40 Å

obtained by Krüger *et al.*^[20] The Si-H bond length is 1.51 Å, close to the theoretical result of 1.49 Å obtained by Ciston *et al.*^[21] using a full-potential all-electron code, and within the standard error of the experiment of $1.51(\pm 0.01)$ Å.^[21] These indicate that the calculation method used here is reliable.

Figure 1 shows the optimized structure of the 0.5ML-terminated ALM/Si(100)- (2×1) surface based on the STM image.^[8] The ALM molecule, bonded to the Si atom, is oriented perpendicularly to the dimer row. The calculated bond length of the Si-Si dimer is 2.42 Å, the same as the Si-Si bond length on the full-terminated H/Si(100)- (2×1) surface. The Si-H bond length is 1.50 Å, similar to the value 1.51 Å on the full-terminated H/Si(100)- (2×1) surface. Those indicate that the bond lengths of the Si-Si and the Si-H are insensitive to the absorbed molecule. The calculated Si-C bond length is 1.94 Å, similar to the calculated one 1.89 Å in the case of the C_4H_7N molecule adsorbed on the Si(100) surface,^[22] and 1.89 Å in the case of the CH_3CN molecule adsorbed on the Si(001) surface.^[16] Meanwhile, the calculated C-H bond length of 1.09 Å is in good agreement with the calculated value of 1.11 Å in the case of the CH_3-CH molecule adsorbed on the Si(001) surface.^[23] The computed S-H bond length of 1.86 Å, is similar to 1.89 Å^[24] in the case of the H_2S molecule adsorbed on the Si(001) surface.

The adsorption energy of the ALM molecule on the Si(100)- (2×1) surface at the 0.5 ML coverage is calculated to test if the adsorption reaction is feasible. The adsorption energy is defined as^[25–27]:

$$E_{\text{ads}} = (E_{\text{H/Si(100)-(2} \times 1)} + E_{\text{ALM}}) - E_{\text{ALM/Si(100)-(2} \times 1)}, \quad (1)$$

where $E_{\text{H/Si(100)-(2} \times 1)}$, E_{ALM} , and $E_{\text{ALM/Si(100)-(2} \times 1)}$ are respectively the total energies of the 0.5ML-terminated H/Si(100)- (2×1) , the isolated ALM molecule, and the 0.5ML-covered ALM/Si(100) surfaces in a supercell. If the adsorption energy is greater than zero, the reaction will be exothermic. The higher the adsorption energy, the greater the stability of the system.^[25–27] The calculated adsorption energy of the ALM molecule on the 0.5ML-terminated H/Si(100)- (2×1) surface is 3.36 eV, thus the adsorption reaction is highly exothermic. The value is comparable not only to that in the case of the small organic molecules absorbed on metal surfaces, for example, the adsorption energy for the thiophene adsorbed on the Ni(110) surface is 3.74 eV,^[27] and that for the thiophene adsorbed on the surface Ni(100) is 2.88 eV,^[25] but also to the calculated value for the methyl chloride adsorbed on the Si(001) surface, from 1.92 to 4.11 eV upon increasing coverage from 0.125 to 1 ML using the same formula^[26] as ours. Therefore, the adsorption of ALM on the Si(100)- (2×1) surface is strongly favorable from the energy viewpoint.

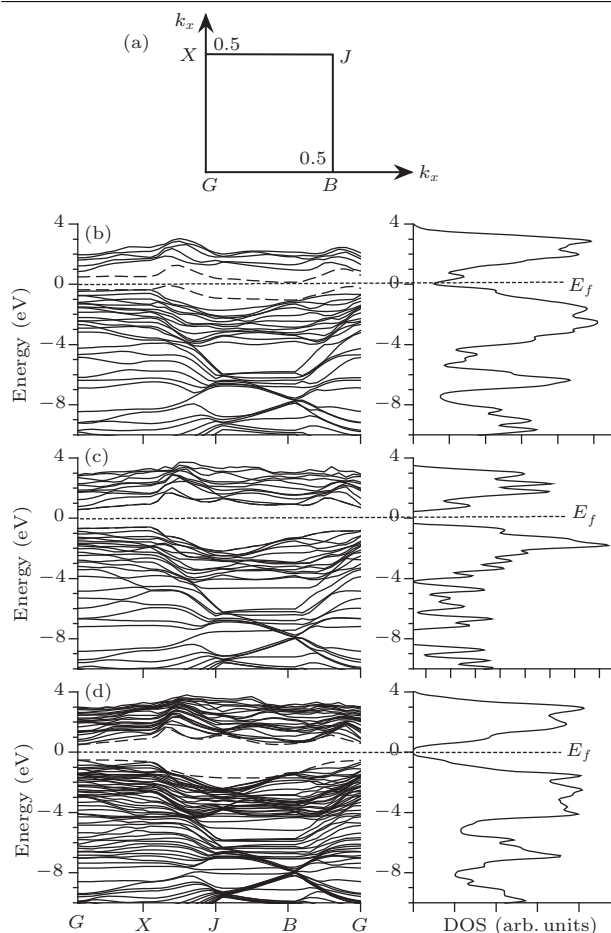


Fig. 2. (a) Primitive cubic Brillouin zone. The energy bands and the total density of states for (b) the Si(100)-(2 × 1) clean surface, (c) the hydrogen full-terminated Si(100)-(2 × 1) surface, and (d) the 0.5 ML-terminated ALM/Si(100)-(2 × 1).

Figure 2 shows (a) the surface Brillouin zone of Si(100)-(2 × 1), as well as the energy bands and the total density of states (TDOSs) for (b) the Si(100)-(2 × 1) clean surface, (c) the full hydrogen covered Si(100)-(2 × 1) surface, and (d) the 0.5 ML-terminated ALM/Si(100)-(2 × 1) surface. The Fermi energy levels are taken as zero. The dashed lines above and below the Fermi energy are the energy bands at the bottom of the conduction band and the top of the valence band, respectively. The DOS is obtained by a Lorentzian extension of the discrete energy levels with weights being the orbital populations in the levels and a summation over them. It is easy to find from the figure that the bottom of the conduction band and the top of the valence band of each surface are situated at the different K points. In addition, there is no energy band across the Fermi level, therefore all of them have the nature of an indirect band gap semiconductor, corresponding to the zero DOS at their Fermi levels. The band gap of the 0.5 ML ALM/Si(100)-(2 × 1) is 1.01 eV, much larger than that of 0.24 eV for the clean Si(100)-(2 × 1), but smaller than that of 1.27 eV for the full hydrogen covered Si(100)-(2 × 1).

surface. Therefore, when the ALMs partially replace the hydrogens to form the 0.5 ML ALM/Si(100)-(2 × 1) surface, it will decrease the band gap of the surface.

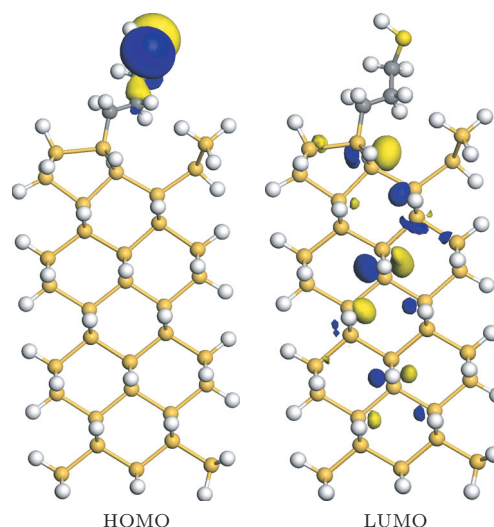


Fig. 3. Iso-density surfaces of the HOMO and the LUMO for the 0.5 ML-terminated ALM/Si(100)-(2 × 1).

In order to understand the electronic properties near the Fermi level, we pay particular attention to the regions around the Fermi level. Figure 3 shows the iso-density surfaces of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), where the dark and light grays represent the negative and positive wave functions respectively. It is clear from the figure that the HOMO is dominated by the ALM, particularly localized at the -SH group. Therefore, electron detachment should occur at the -SH group, confirming the mechanism for the chain reaction of the ALM proposed by Hossain *et al.*^[8] that the radical centered at carbon can be transferred on sulfur through tautomerism, resulting in a thiyl radical, which is expected to be stable enough to remove a hydrogen from the substrate, forming a 0.5 monolayer (ML)-terminated ALM/Si(100)-(2 × 1) surface. Therefore, the -SH group, different from propylene ($\text{CH}_2=\text{S}-\text{CH}_3$) and allyl methyl sulfide ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{S}-\text{CH}_3$), seems to play an important role in the stabilization of the intermediate radical in ALM,^[8] whereas the LUMO has the features of the Si-Si dimers on the ALM/Si(100)-(2 × 1) surface, indicating that electron attachment should happen at the Si-Si dimers.

In summary, the structural and electronic properties of the 0.5 ML-terminated ALM/Si(100)-(2 × 1) surface have been studied using the generalized gradient approximation based on density functional theory. The geometric optimizations show that the natures of the Si-Si and Si-H bonds are not sensitive to the adsorbed molecule. The calculated absorption energy of the ALM molecule on the Si(100)-(2 × 1) surface is 3.36 eV, indicating that the adsorption is strongly fa-

vorable from the energy viewpoint. By analyzing the energy bands and the total densities of states of the Si(100)-(2 × 1) clean surface, the full hydrogen terminated Si(100)-(2 × 1) surface, and the 0.5 ML-covered ALM/Si(100)-(2 × 1) surface, we find that all of them have the nature of an indirect band gap semiconductor. It is known from the iso-density surface that the highest occupied molecular orbital is dominated by the ALM, confirming the mechanism for its chain reaction.

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