Vol 18 No 5, May 2009
1674-1056/2009/18(05)/2041-07
Chinese Physics B
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and IOP Publishing Ltd

Electronic properties of hydrogen- and oxygen-terminated diamond surfaces exposed to the air*

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(Received 17 October 2008; revised manuscript received 30 November 2008)

The electronic properties of hydrogen- and oxygen-terminated diamond surfaces exposed to the air are investigated by scanning probe microscopy (SPM). The results indicate that for the hydrogen-terminated diamond surface a shallow acceptor above the valence-band-maximum (VBM) appears in the band gap. However, the oxygen-terminated diamond film exhibits a high resistivity with a wide band gap. Based on the density-functional-theory, the densities of states, corresponding to molecular adsorbate in hydrogenated and oxygenated diamond (100) surfaces, are studied. The results show that the shallow acceptor in the band gap for the hydrogen-terminated diamond film can be attributed to the interaction between the surface C–H bonding orbitals and the adsorbate molecules, while for the oxygen-terminated diamond film, the interaction between the surface C–O bonding orbitals and the adsorbate molecules can induce occupied states in the valence-band.

Keywords: hydrogen-termination, oxygen-termination, electronic properties, diamond film
PACC: 7360J, 0779, 8265M

1. Introduction

Diamond film is especially attractive due to its outstanding electronic properties.[1−3] In addition to bulk properties, a high surface electronic conductivity has been detected in a hydrogen-terminated diamond surface.[4−6] The hydrogen termination can be obtained by exposing diamond to a hydrogen-plasma. After treating in oxygen-plasma or boiling in strong acid, the diamond surface becomes oxygen-terminated. In contrast, an oxygen-terminated diamond surface is strongly resistive.[7,8] Thus, in-plane electronic devices using diamond films can be realized by controlling the surface termination.

Concerning the origin of the high surface conductivity for hydrogenated diamond film, several controversial models have been proposed, ranging from hydrogen induced surface acceptors[9] to an acceptor subsurface region created by incorporation of hydrogen[10] or even to a buried acceptor layer.[11] Recently, another possible explanation of the surface high conductivity for hydrogenated diamond film was proposed by Maier *et al* [12] and further supported by Nebel *et al* [13] and Rezek *et al* [14] separately. Their results indicated that the chemisorbed hydrogen was necessary for high surface conductivity, but adsorbed species when exposed to air were also required. Up to now, however, little is known about the details of the electronic structures of the diamond films exposed to the air, and the effects of the surface adsorbates are still under debate.[12,15]

In the present paper, we report on the electronic structures of the hydrogenated and the oxygenated diamond films exposed to the air by scanning probe microscopy (SPM). By means of the *ab initio* method, the densities of states, corresponding to the adsorbates on surface-terminated diamond (100) films, are also investigated. The results reveal that for hydrogenated diamond film, a shallow acceptor above the valence-band-maximum (VBM) appears in the band gap, arising from the interaction between the surface C–H bonding orbitals and adsorbate molecule, while the oxygenated diamond (100) surface is still highly resistive when exposed to an adsorbate molecule.

*Project supported by the National Natural Science Foundation of China (Grant No 50675112), National Basic Research Program of China (Grant No 2007CB707702), and the China Postdoctoral Science Foundation (Grant No 20070410515).
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2. Experiment

The diamond films were deposited on low-resistivity silicon (p-type) substrates from a hot-filament activated methane hydrogen gas mixture at a pressure of 6.66×10^3 Pa. The filament was at 2500 °C and substrates were at 830 °C. The mixture flow rate was 5 L/min, and the growth rate was 0.24 μm/h. A continuous film of diamond was obtained after a 15 hour growth. The film resistance was measured in a solid-state arrangement to be in the range of 10–100 Ω.

For hydrogenation, the deposited diamond surface was exposed to a microwave hydrogen plasma at about 800 °C for ten minutes after annealing in ultra high vacuum (UHV) at 1100 °C. In order to obtain an oxygen-terminated diamond film, the hydrogenated diamond film was boiled for one hour in a solution of HNO_3/H_2SO_4 (concentration ratio=1:3) at 350 °C. The obtained diamond films with treated surfaces were characterized by x-ray photoelectron spectroscopy (XPS) and contact angle measurement. Using the SPM, the spectrum curves for tunnelling current versus voltage ($I-V$) were investigated.

All the calculations in the present work were performed by using the CASTEP code based on the density-functional-theory. The electron-ion interaction was described by ultra-soft pseudopotentials in real space. The generalized gradient approximation (GGA) given by Perdew–Wang PW91 for the exchange-correlation potentials was employed. In all the calculations, the wave functions were expanded into plane waves up to a cutoff energy of 300eV. For the Brillouin-zone integrations, a 4×4×1 grid of Monkhorst–Pack special points was used. The optimization of the atomic coordinates continued until the total energy was converged within 10^{-6} eV/atom.

Probably the most important surface for CVD diamond samples is (100), due to the large facets of this orientation in a high-quality material. With exposure to the air, the diamond surface would be physisorbed by active molecules. CO_3H^- is a kind of adsorbate molecule suggested by Ristein *et al*,[16] which originates from reactions of atmospheric CO_2 in solution. Thus, in the present paper, C(100) orientation is used to represent the diamond surface and the CO_3H molecule is adopted as a surface adsorbate. The diamond surfaces are modelled with a finite slab composed of ten layers, each with eight C atoms. At the top and the bottom of the slab, the C atom layers are covered with one layer of hydrogen or oxygen atoms. To avoid repulsive interactions, a vacuum layer of 1.5 nm is adopted. During the calculations, all the atoms are allowed to relax freely. The 1s orbitals of C, O are frozen in the core, while the other orbitals of C, O and H are considered as valence shells. To investigate the adsorbate molecule, a 1.5 nm cubic box is used to isolate the molecule in vacuum.

3. Results and discussion

3.1. Electronic properties of surface-terminated diamond films

In order to evaluate the as-prepared diamond samples, XPS spectra were measured, and the results are presented in Fig.1. For the oxygen-terminated diamond film, the O 1s/C 1s atomic concentration ratio is about 14.2 at % as calculated from the relevant peak area in the recorded spectrum divided by an appropriate bulk atomic sensitivity factor. This value is comparable with the reported values for the diamond surfaces treated by other oxidization methods, such as by the O-plasma treatment and the anodic treatment.[17] In contrast, The O 1s/C 1s ratio is smaller than 2.0 at %, and the O KLL Auger peak is undetectable for the hydrogen-terminated diamond film. The oxygen amount for the hydrogen-terminated sample in our paper is also comparable with those for the hydrogenated diamond film after exposure to water (about 0.9 at %)[18] and air (1±0.3 at %).[19] Taking into account the XPS detection depth of about 2–3 nm, the oxygen amount is very tiny, even though the samples were stored in the air. Apart from the oxygen and hydrogen, both the diamond surfaces appear to be very clean and without detectable impurities. In order to further examine the H-plasma treated diamond surface, water contact angles of the two diamond films with treated surfaces were measured. The hydrogen-terminated diamond film shows a water contact angle of 92.5°, which is expected for a surface terminated with the C–H groups. This value is close to published values.[20,21] A significant decrease of water contact angle is observed to be 1.6° for the oxygen-terminated diamond film. This oxygenated wetting angle is slightly higher than that obtained by Yagi *et al* (0.6°).[20] It is, however, much lower than other reported values,[21−23] which range remarkably from 4° to 64.7°. The great difference between the results can be probably attributed to the different oxygenation methods,[20,23] the surface topography,[21,22] and the sp3/sp2 ratio.[21]

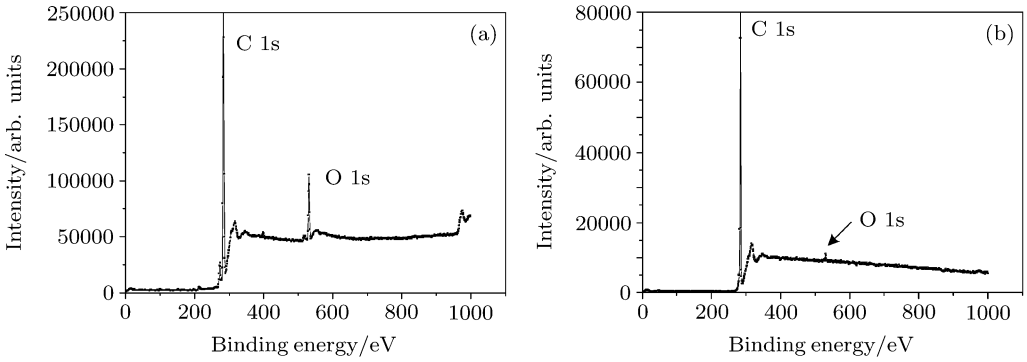


Fig.1. XPS spectra of (a) oxygen-terminated and (b) hydrogen-terminated diamond films.

The morphologies of the hydrogen-terminated and oxygen-terminated diamond films were recorded by SPM as shown in Fig.2. The results indicate that the two types of diamond surfaces both have complete crystal grains and clear grain boundaries. The surface roughnesses of the hydrogen-terminated and oxygen-terminated diamond films are 47.52 nm and 49.03 nm, respectively. There is little variation in the images of the two surfaces. $I - V$ spectroscopy curves for the hydrogenated and oxygenated diamond films were measured at the constant height mode at room temperature and under ambient atmosphere conditions. To rule out the influence of the grain boundary, the measuring points were adopted at the peak positions of the crystalline grains for the two surface-terminated diamond films (point 1 in Figs.2(a) and 2(b)) as shown in Fig.3. It can be found that for the hydrogen-terminated diamond film, the potential range corresponding to a low tunnelling current is narrow. Beyond this range, the tunnelling current between the film and the probe tip increases significantly as the applied bias increases. In contrast, the tunnelling current between the oxygen-terminated diamond film and the scanning probe tip is close to zero in a much wider potential range. This implies that the hydrogenated diamond film has a better surface conductivity than the oxygenated one. Noting that for the hydrogen-terminated diamond film the tunnelling current at the negative bias is a little larger than that at the positive bias, it follows that the surface energy bands of the hydrogen-terminated diamond film bend upwards and the hydrogen-terminated diamond surface exhibits a p-type conductivity.[24]

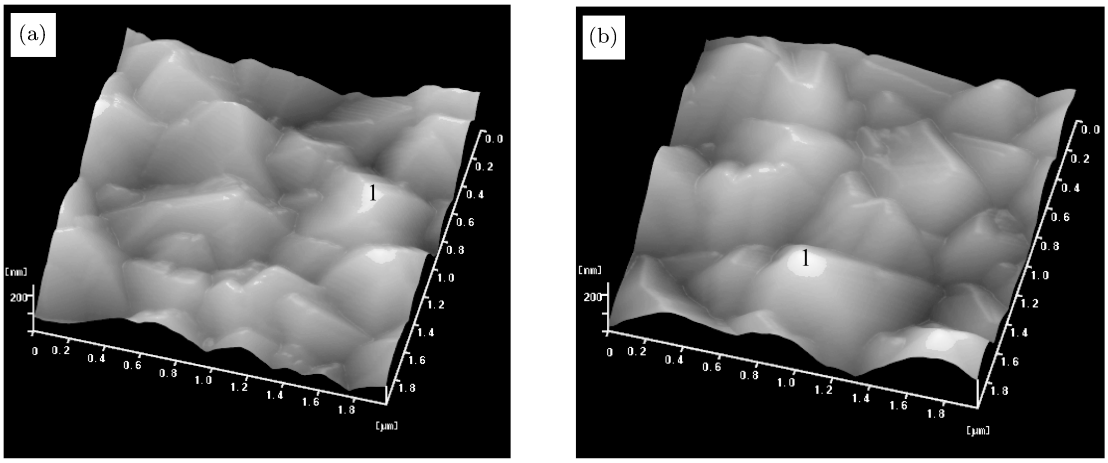


Fig.2. SPM images of (a) oxygen-terminated and (b) hydrogen-terminated diamond films.

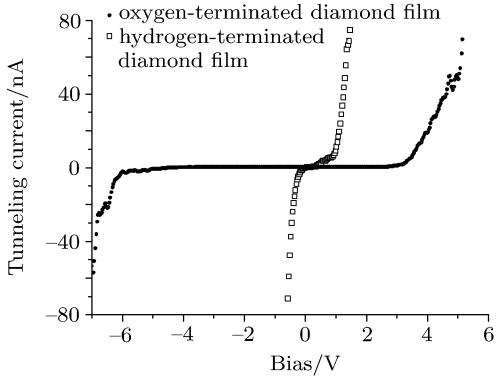


Fig.3. $I-V$ spectroscopy curves of oxygen-terminated and hydrogen-terminated diamond films.

To further investigate the electronic structures of the surface-terminated diamond films, the originally recorded $I-V$ curves were differentiated numerically to obtain the $\mathrm{d}I/\mathrm{d}V$ spectra as revealed in Figs.4(a) and 4(b). The $\mathrm{d}I/\mathrm{d}V$ spectrum, corresponding to the hydrogen-terminated diamond film, indicates that the surface exhibits a p-type conductivity with a band gap width of about 0.8 eV and an empty surface state at 0.4 eV existing in the band gap located above the VBM. Additionally, it could be found that the Fermi level (represented as 0 eV) shifts into the valence-band, which is probably induced by the upward bending of the surface energy bands. However, the oxygen-terminated diamond film with a wide and clean band gap (about 5.5 eV) is highly resistive. For the hydrogen-terminated diamond, the band gap structure obtained by SPM in our paper is similar to the results from other groups by using STM, and they each show a narrow energy gap (even no energy gap) with strong empty surface states above the VBM. Since they can act as traps for valence-band electrons, they facilitate a high conductivity.

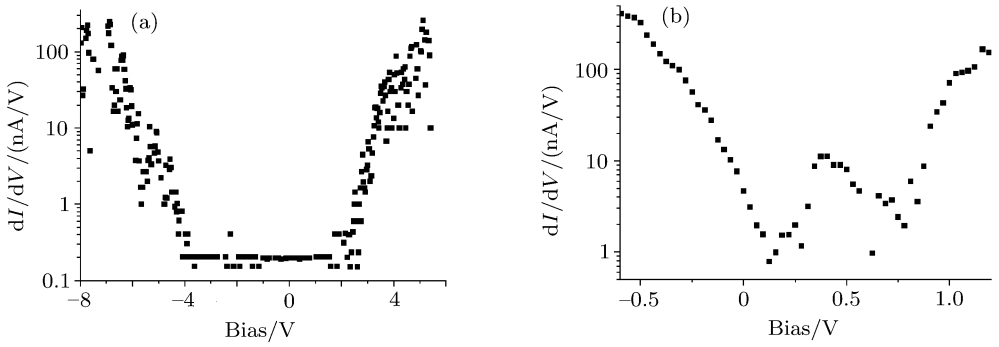


Fig.4. $\mathrm{d}I/\mathrm{d}V$ spectroscopy curves of (a) oxygen-terminated and (b) hydrogen-terminated diamond films.

3.2. Origin of the shallow acceptor of hydrogen-terminated diamond surface

Some researchers[25,26] presumed that the interactions between subsurface hydrogen and defects would perhaps contribute to the high surface conductivity. According to the previous report,[27] the subsurface hydrogen would effuse out at about 500 °C, and the hydrogen atoms, chemisorbed on the diamond surface, would start to be desorbed at about 700 °C. However, the oxidization process in our experiments was kept at 350 °C. At such a low temperature, effusion of the subsurface hydrogen is impossible. It follows that the hydrogenated and oxygenated diamond samples prepared in our experiments have similar subsurface components, both incorporating many hydrogen atoms in them. Our experimental results indicate that the hydrogen-terminated diamond sample exhibits a high surface conductivity with a shallow acceptor in its band gap, whereas the oxygen-terminated diamond sample shows a high resistivity. So, it seems that the subsurface hydrogen has little effect on the p-type surface conductivity.

Many reports[28−30] have demonstrated that monohydrogenated diamond (100) surface (C(100)-2×1:H) and oxygenated diamond (100) surface with

ether structure (oxygen sites on bridge of carbons, C(100)-1×1:O-BR) are more stable than the other configurations of the hydrogenated and oxygenated diamond (100) surfaces, respectively. The equilibrium geometries of C(100)-2×1:H and C(100)-1×1:O-BR were investigated in this paper, and the obtained results are in good agreement with the previous results obtained by the *ab initio* local-density approximation (LDA)[31,32] and tight-binding molecular dynamics.[33] This verifies the reasonableness of our computational model and selected parameters.

The calculated densities of states for a CO_3H molecule, C(100)-2×1:H surface and C(100)-1×1:O-BR surface were shown in Figs.5(a), 5(b) and 5(c) respectively. It can be found that for the CO_3H molecule, the band gap between its highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level is wider than 5 eV. At the positions of HOMO level (0 and −0.64 eV), there exist occupied states arising from the O 2p orbitals. For the C(100)-2×1:H, no shallow acceptor appears in its band gap. This can be interpreted as follows: when the hydrogen atoms cover the dangling bonds of the surface C atoms, the C–C π bond breaks and only C–C σ bond exists.[32] Thus, the surface states induced by C–C π bond in the band gap of the bare C(100)-2×1 surface disappear after the surface is covered with the hydrogen atoms. The result in our work conflicts with the experimental results from Kawanada *et al*,[9] but it is consistent with other results.[32,34] This is perhaps because Kawanada *et al* did not rule out the effects of surface adsorption during the experiment. With regard to the C(100)-1×1:O-BR surface, there exists a strong state deep in the valence band at −22 eV, which can be attributed to the C 2s and C 2p hybrid orbital induced by O 2s. In the case of the occupied states from −3.3 eV to −8 eV, the densities of states have contribution from the O 2p and C 2p bonding orbitals. Strong surface states near the valence-band-maximum (VBM) (−0.5 eV to −2 eV) in this case, originate mainly from the non-bonded O lone pairs. Additionally, there is a strong unoccupied state in the conductive band at 4.8 eV. It is induced by the O 2p and the C 2p antibonding orbitals.[35,36] Similar to the C(100)-2×1:H surface, no surface state appears in its band gap.

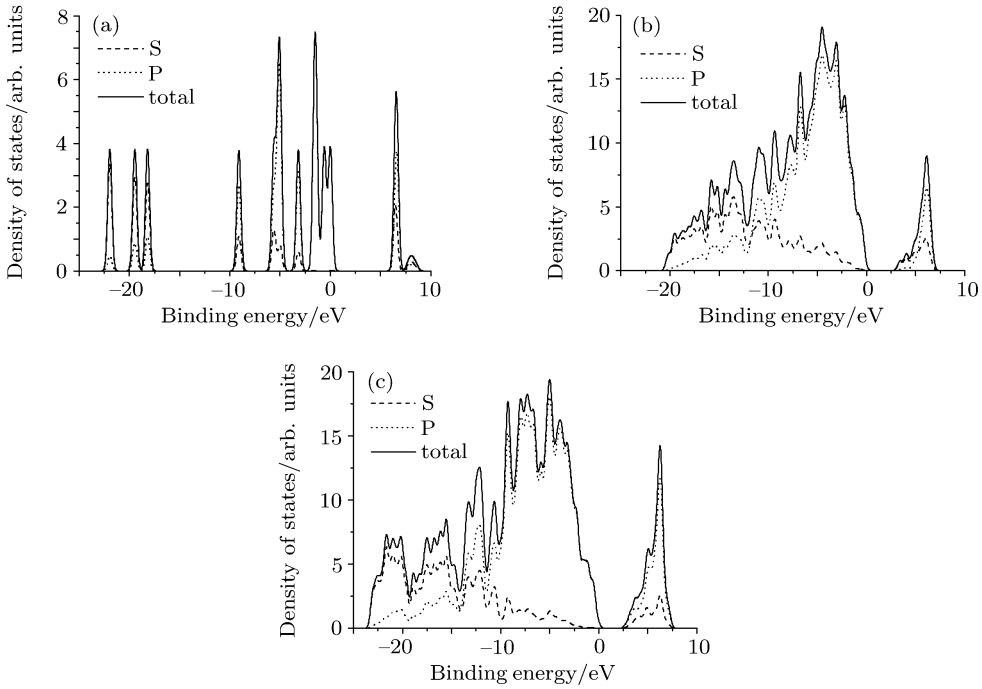


Fig.5. Densities of states for (a) CO_3H molecule, (b) C(100)-2×1:H surface and (c) C(100)-1×1:O-BR surface, where 0 eV is the position of HOMO level for CO_3H molecule and the VBM for diamond surfaces.

For the hydrogenated diamond (100) surface physisorbed with CO_3H molecule, its density of states is shown in Fig.6(a). Compared with the density of states for the hydrogenated diamond (100) surface without adsorbate, the density of states for the hydrogenated diamond (100) surface with adsorbate has a significant change in its band gap, where a shallow acceptor at the position of about 0.4 eV above the VBM appears. To investigate the

origin of the surface state, the electron distributions at this binding energy are shown in Fig.6(b). It indicates that the shallow acceptor is induced by the interaction between the C–H σ bond and non-bonded O 2p orbitals of CO_3H molecule, particularly in the case where O atoms are close to the hydrogenated diamond surface.

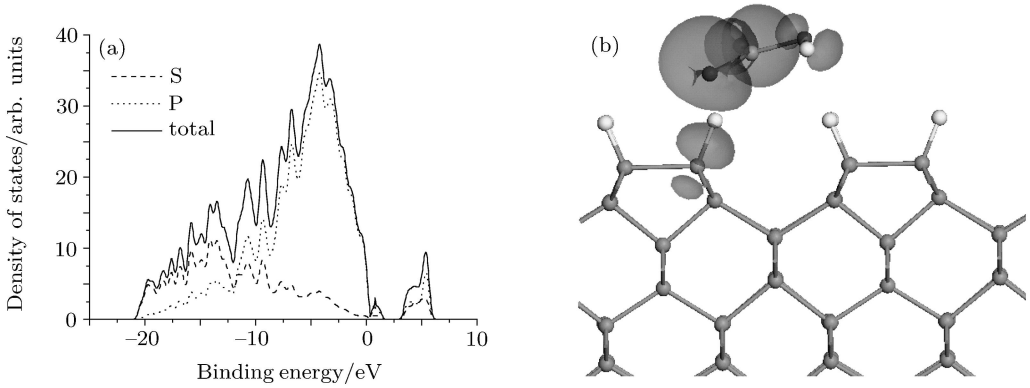


Fig.6. (a) Densities of states and (b) the electron distributions at 0.4 eV above valence band maximum for the C(100)-2×1:H surface physisorbed with a CO_3H molecule, where 0 eV is the position of VBM.

For the oxygenated diamond (100) surface physisorbed with the CO_3H molecule, its density of states is shown in Fig.7(a). At the −0.8 eV below the VBM, there is an occupied state arising from the interaction between the O 2p orbitals of the CO_3H molecule and the CO orbital of the oxygenated diamond surface as revealed by the electron distributions shown in Fig.7(b). The band gap of the oxygenated diamond (100) surface physisorbed with CO_3H molecule is clear and wide, different from that of the hydrogenated diamond (100) surface physisorbed with the CO_3H molecule. This implies that surface adsorbate has no influence on the surface conductivity of oxygenated diamond film.

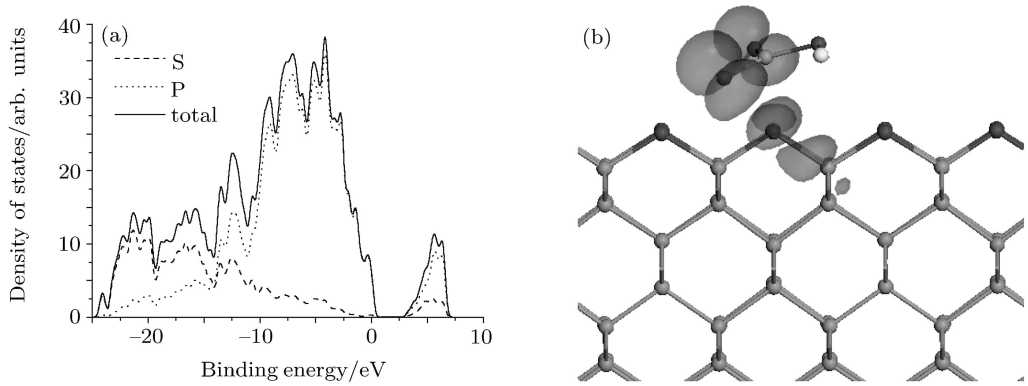


Fig.7. (a) Densities of states and (b) the electron distributions at −0.8 eV above valence band maximum for a C(100)-1×1:O-BR surface physisorbed with a CO_3H molecule, where 0 eV is the position of VBM.

When the diamond film is exposed to the air, a tiny diamond/solution electrochemical system is actually constructed. According to the recent results given by Nebel *et al*,[13] if the hydrogen-terminated diamond film is immersed into redox electrolyte solutions with chemical potentials below the VBM, the diamond surface would undergo an insulator–metal transition. However, when the diamond surface is oxidized, the transition does not happen. This is consistent with our computational result. For the VBM of the hydrogenated diamond (100) surface, which is higher than the chemical potential of the CO_3H molecule, the non-bonded O 2p orbitals of the CO_3H molecule extracts the electrons from the hydrogenated diamond surface, then holes remain in the diamond surface and so a shallow acceptor appears there. While the VBM of

the oxygenated diamond (100) surface is lower than the chemical potential of CO_3H molecule, the interaction between CO_3H molecule and the CO orbitals cannot lead to pulling an electron out of the VBM of the diamond surface.

4. Conclusions

The hydrogen-terminated diamond film with exposure to the air exhibits a shallow acceptor above the VBM in the band gap. The shallow acceptor can be attributed to the interaction between non-bonded O 2p orbitals of the CO_3H molecule and C–H bond of the diamond surface. The oxygen-terminated diamond film remains a wide and clean band gap after exposure to the air. The interaction between the O 2p orbitals of the CO_3H molecule and CO orbital of the oxygenated diamond surface would induce the occupied states in the valence-band.

Acknowledgement

The authors thank the Department of Material Engineering of Tsinghua University, China, for the supercomputing facilities.

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