Surface Structures of Black Phosphorus Investigated with Scanning Tunneling Microscopy

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The atomic and electronic structures of the black phosphorus surface are investigated by means of scanning tunneling microscopy (STM) combined with density functional theory (DFT) calculations for the first time. STM measurements reveal that the atoms on the surface occupy almost the same sites that they would have in bulk, except for a little relaxation perpendicular to the surface, which causes the atoms to take two types of positions (P1 and P2) with a contrast visible in the STM images. DFT calculations indicate that the small difference in height of 0.02 Å between atoms at P1 and P2 position breaks the symmetry, leading to an apparent discrimination of electronic structures. The bias-dependent variation of the contrast between P1 and P2 in the STM images is consistent with the DFT simulations.

Introduction

As a layer-structured and narrow-gap elemental semiconductor,[1] black phosphorus (BP hereafter) has received more attention in recent years.[2–5] As the most stable form among many allotropes of phosphorus, BP has novel structural properties.[6,7] A single layer of BP consists of 3-fold coordinated phosphorus atoms arranged in a honeycomb network, which is very similar to graphene.[8–10] The investigations of bulk BP crystal have shown many interesting physical properties. For instance, a sequence of structural phase transformations was found in the system,[11,12] and the T_c of its superconductivity can even be higher than 10 K under high pressure.[13,14] The electrical resistivity and magnetoresistivity are dependent on temperature.[15–17] The application of BP has already made great progress.[3] Moreover, unlike the majority of other semiconductor surfaces, the absence of dangling bonds makes it possible to grow ordered molecular films or nanostructures on a BP surface that remain difficult on a clean semiconductor surface.[18] However, until now there has been no report on the study of BP surface structure or the electronic structure on the surface since it was first synthesized in 1914.[19]

In this work, we report on the first scanning tunneling microscopy (STM) investigation and density functional theory (DFT) calculations for the BP(010) surface. Direct STM observations clearly confirm the stability of BP surfaces. Only a slight relaxation in the perpendicular direction was observed in STM images. DFT calculations reveal the details of the BP surface and interpret the STM observations well. A high resolution STM image was obtained, which might show the atoms of the second layer.

Experimental and Calculational Details

The BP crystal was synthesized under high pressure and high temperature (HPHT) conditions with red phosphorus as a starting material, as previously reported.[20] The experiment was performed with an ultrahigh vacuum low temperature STM system (Unisoku) with a base pressure of 1×10^{-10} mbar. To obtain a fresh BP surface, nitrocellulose was dropped on the surface.

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TABLE 1: Measured Surface Lattice Constants and Theoretical Optimized Results Together with Previous Data of Bulk BP

reported by Morita[7]	measured from STM images	theoretical optimized results
$a = 3.313$ Å	$a = 3.33$ Å	$a = 3.28$ Å
$b = 10.473$ Å		$b = 10.37$ Å
$c = 4.374$ Å	$c = 4.33$ Å	$c = 4.35$ Å
$d_1 = 2.222$ Å, $\alpha_1 = 96.5°$		
$d_2 = 2.777$ Å, $\alpha_2 = 101.9°$		

After solidification, it was peeled off in dry nitrogen gas. The freshly cleaved surface was transferred into the STM chamber immediately and slowly cooled down to 77 or 4.3 K. The STM measurements were performed with mechanically cut Pt−Ir tips. The images were taken in constant-current mode, and all given voltages are referred to the sample.

In addition to the STM experiments, DFT calculations were performed by using the Vienna ab initio simulation package (VASP). Local density approximation (LDA) was applied for the exchange-correlation functional and projector augmented wave (PAW) approximation for the electron−core interaction. The energy cutoff for plane wave basis was set to 400 eV. The optimized lattice constants are $\mathbf{a} = 3.28$ Å, $\mathbf{b} = 10.37$ Å. and $\mathbf{c} = 4.35$ Å (Table 1), slightly smaller than the experimental values. This is due to the use of LDA, which usually underestimates the lattice. Then, 6-layer phosphorus and 17 Å vacuum were used to model the BP surface. The periodic boundary condition was used for all three dimensions. When optimizing the geometric structure, the lowest two layers of P were fixed, while other atoms were allowed to relax until the force acting on each relaxed atom was less than 0.01 eV/Å.

Results and Discussion

Bulk BP at ambient pressure has an orthorhombic form. The unit cell consists of puckered layers parallel to the *ac* plane, as shown in Figure 1(c). In a single puckered layer, the P atoms are arranged in a honeycomb network similar to that of a graphene layer, but with the two atoms in the unit cell "staggered" into two different planes, as can be appreciated in a side view [Figure 1(b)]. Every P atom in a puckered layer
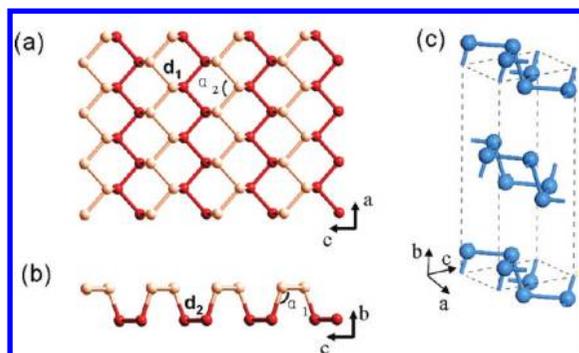
Figure 1. (a) and (b) Projections of a single layer BP on the *ac* and *bc* plane. The upper and lower atoms are presented in pink and red, respectively. (c) Schematic illustration of unit cell, showing a shift of *a*/2 units between adjacent layers.

covalently bonds with its three nearest neighbors via 3p orbitals, leaving a lone electron pair.[21,22] Thus each atom is chemically saturated. The bond lengths d_1 and d_2 are very close to each other and the bond angles α_1 and α_2 are close to a right angle (see Table 1). The projections of a single layer on the *ac* and *bc* plane are shown in Figure 1, parts (a) and (b), where the upper and lower atoms in a single puckered layer are depicted in orange and red, respectively. The schematic illustration of the unit cell shows that every layer overlaps the second layer and is shifted by **a**/2 units. Since each P atom is chemically saturated within a puckered layer, the interactions between neighboring layers are of van der Waals type in character. Therefore, our cleaving process exclusively leads to the achievement of fresh BP(010) surface.

Figure 2(a) shows a large-scale STM image of BP with atomic resolution. As an upper atom sits just directly above a lower one in a puckered layer, it is hard to detect the lower atoms using STM. Generally, the STM image of BP surface is an array of zigzag chains composed only of the upper atoms. A close-up image [Figure 2(b)] reveals some detailed features of the surface. All atoms almost hold their original sites, as shown in the STM images. A rectangular unit cell is marked by blue lines in the STM image, in which the arrows (**a**, **c**) represent the unit cell vectors. The length of **a** and **c** measured from the STM image are 4.33 Å and 3.3 Å, respectively, in good agreement with the reported values of bulk BP (Table 1).[7] The images acquired either at 300 K or 77 K display the same results (not shown). Besides, even after annealed to ~400 K, the surface still retains its structure. The absence of significant reconstruction of BP surfaces illustrates their chemically saturated nature, in contrast to silicon surfaces with abundant dangling bonds and HOPG surfaces with extended in-plane π-electron. Nevertheless, there is a slight difference in brightness and size between the atoms in the two different positions in a zigzag chain, labeled as P1 and P2 (P1 for brighter atoms and P2 for darker ones) in Figure 2(b). A missing P2 atom is indicated by a white dashed circle. Interestingly, due to the charge redistribution, the nearest P2 atom in the neighboring zigzag chain, indicated by the white arrow in Figure 2(b), appears brighter than P1 atoms, in contrast to other P2 atoms.

Figure 3(a) shows the STM image at the sample bias $U = -0.315$ V. It is seen that the contrast between P1 and P2 atoms is more distinct compared with the image at $U = -1.3$ V [(Figure 3(b)]. Line profiles [Figure 3(c−d)] reveal that the difference in apparent height of P1 and P2 atoms reaches up to ~100 pm for $U = -0.315$ V, whereas several picometers for $U = -1.3$ V. This bias-dependent behavior suggests different electronic structures of P1 and P2 atoms.
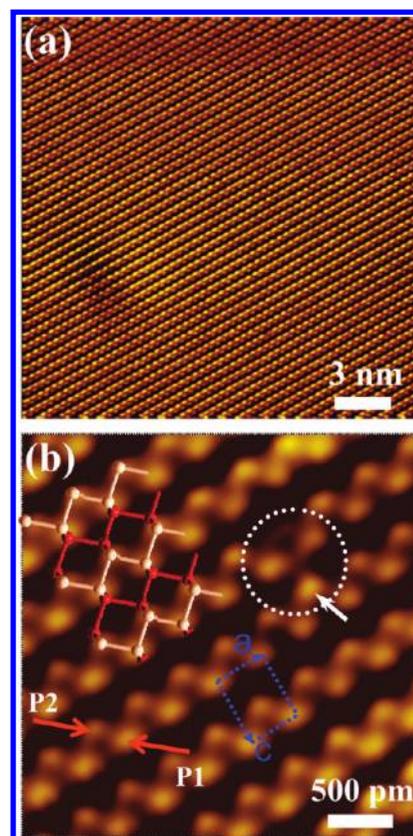

Figure 2. (a) Large-scale STM image of BP surface with atomic resolution. (b) Close-up showing that only the upper atoms of the topmost puckered layer can be seen with no reconstructions. The unit cell is indicated by blue dashed lines and a vacancy is marked by a green dashed circle. There is a contrast between the two rows in the same zigzag chain, indicated by red arrows and labeled as P1 and P2, respectively. Scanning parameters: (a) $U = -0.315$ V, $I = 157$ pA, (b) $U = -1.3$ V, $I = 157$ pA. Images were taken at 4.3 K.

From DFT calculations, we found that the P1 and P2 atoms are almost on the same plane, with only 0.02 Å difference in the perpendicular direction, as shown in the optimized structural model [Figure 4(a)]. However, further calculations of the electronic structures indicate that this small buckling breaks the symmetry and induces the notable difference of the electronic structure between P1 and P2 atoms. Using the Tersoff approximation,[23] we simulated the STM image. At $U = -0.3$ V [Figure 4(b)], the two P atoms show an obvious difference with one large and bright and the other one small and gray. However, for a higher sample bias of $U = -1.3$ V, P1 and P2 atoms are only show a slight difference, as seen in the simulated STM image in Figure 4(d). These results are in good agreement with the experimental STM topographies (Figure 3). Moreover, Differential conductance dI/dV spectra were measured on the surface. An average curve over different atoms of the surface is shown in Figure 4(c). The band gap in the spectrum is about 0.4 eV, slightly larger than the reported value of bulk material. The peak at −0.17 V is probably due to a surface state.

It is well-known that a sharper tip would increase spatial resolution remarkably in STM experiments. For instance, Wang et al. reported that the rest atom of Si (111)−7 × 7 surface can only be imaged by a sharp tip with radius smaller than 1 nm.[24] In our study, a high resolution STM image of BP surface was also acquired, as shown in Figure 5(a). There is an extra spot in every hole of the zigzag chain indicated by the arrow. Recalling that in BP crystal, every layer overlaps the second layer and is shifted by **a**/2 units. We tentatively assign these
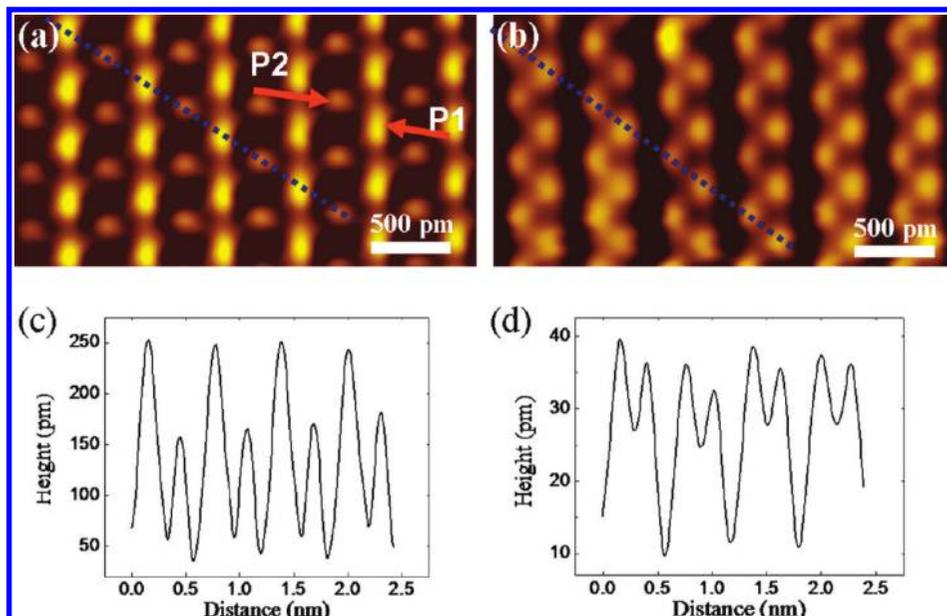
Figure 3. (a,b) STM images with sample bias $U = -0.315$ and -1.3 V, and $I = 157$ and 122 pA, respectively. Images were taken at 4.3 K. (c,d) Line profiles along the dashed lines in (a,b), showing a remarkable bias- dependent contrast.
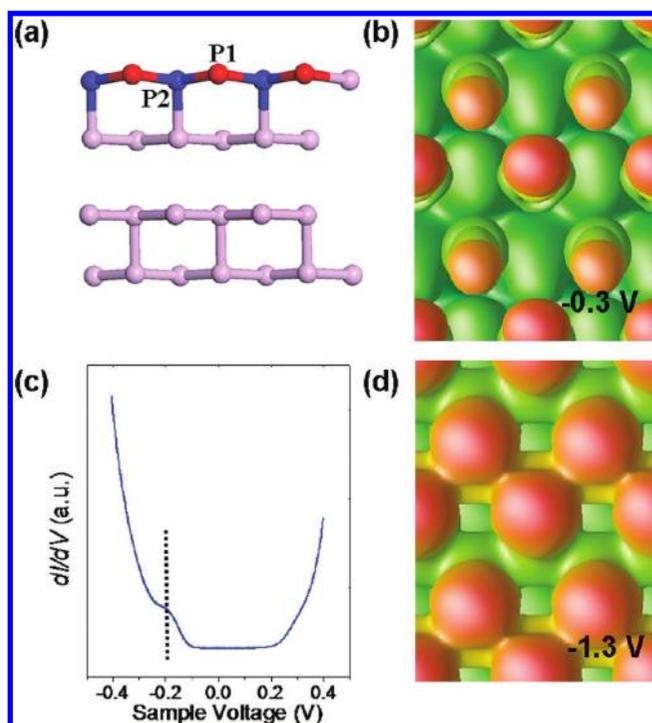

Figure 4. (a) Structure of BP surface after geometric optimization by DFT calculations, showing a small difference in perpendicular direction between P1 (red) and P2 (blue) atoms. (b) and (d) Simulated STM images at $U = -0.3$ and -1.3 V, respectively. (c) Differential conductance dI/dV spectra of the surface, the dashed line shows a surface state at -0.17 V.

extra spots to the second layer atoms. The corresponding structural model is shown in Figure 5(b). The solid green and dashed black rectangles in the STM image and the corresponding diagram indicates the unit cells of the top and second layer, respectively. In the second layer, only half as many of the atoms can be observed clearly—that is, only the ones below P2 atoms and marked by the blue arrow. (Only half of the atoms in the first layer can be seen and only one-fourth of those in the second layer appear.) The others under the P1 atoms are indistinguishable with P1 atoms of the top layer. This results in the significant
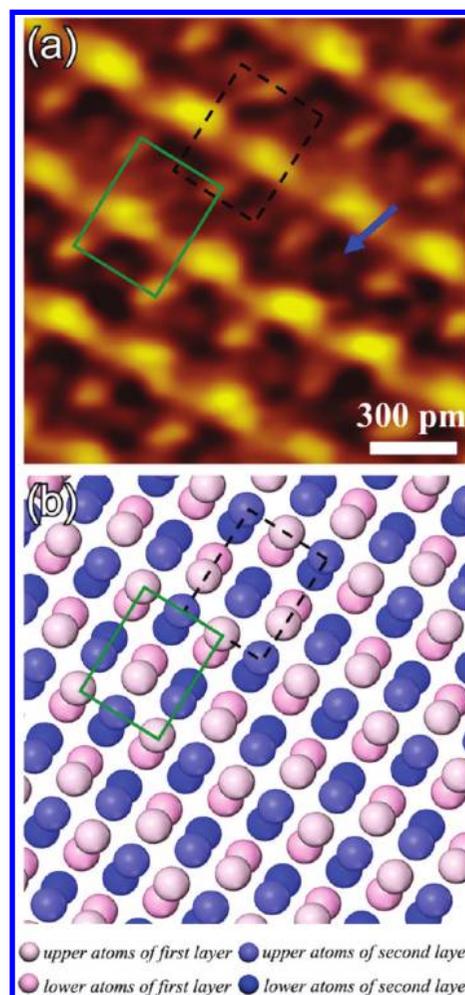

Figure 5. (a) High resolution image of BP surface taken at 77 K. The spot indicated by the blue arrow is assigned to atoms of the second layer. Unit cells of the first and second layers are indicated by green solid and black dashed rectangles, respectively. (b) Projection of two adjacent puckered layers on the *ac* plane. Scanning parameters: $U = -0.348$ V, $I = 398$ pA.

distortion of the rows consisted of P1 atoms, whereas the contrast between P1 and P2 atoms remains. However, considering that the second-layer is about 5 Å below the top layer, it might be difficult to "see" the second-layer atoms with STM. Thus, the possible origination of the extra spots from the local extension of the density of states of the first layer cannot be excluded. To clarify this issue, further experiments and calculations are underway.

Conclusions

We studied the atomic and electronic structures of the BP surface with STM for the first time. In most cases, only the upper atoms in the topmost layer can be imaged. The surface lattice remains unchanged with bulk material at room temperature, 77 K and 4.3 K, even after annealing to 400 K. DFT calculations point to a slight relaxation in the perpendicular direction, causing atoms to take two types of positions with a significant difference of electronic structure. Furthermore, the bias-dependent contrast between the atoms in the two positions in the same zigzag chain was well explained by the DFT calculations. Our results indicate that the BP surface is quite different from HOPG and some of the semiconductor surfaces, showing ideal stability. This study is believed to spark significant research interest in exploring the physicochemical properties of this special layered semiconductor material.

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JP907062N