Atomic Scale Investigation of Oxidation at the Black Phosphorus Surface

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Abstract

The oxidation of bulk black phosphorus (BP) is investigated using scanning tunneling microscopy/spectroscopy (STM/S). Dosing O_2 at a pressure of 10^{-5} mbar for 1 minute creates two new types of defects on the surface. We identify these defects as atomic oxygen and phosphorus multivacancies using STM/S simulations. In addition to the physical changes to the surface, the electronic structure is also drastically altered by the introduction of oxygen. The band gap of BP, which is normally 300 meV, is lifted due to dosing. This change to the electronic structure is reversible by removing defects from a localized region with the STM tip. These are the first experimental results showing the atomic-scale oxidation of BP, an important step toward understanding the degradation process.

Oxygen Dosing

To ensure that the surface was pristine prior to O_2 dosing, we first cleaved the BP crystal in UHV. Figure 1a shows a freshly-cleaved BP surface with atomic rows spanning diagonally across the image. Native defects are present in the freshly-cleaved crystal surface, the most common of which image as protrusions with a lateral size of several nanometers, like the one imaged in Figure 1a. These defects have an extended, anisotropic electronic signature and appear as either ellipses or dumbbells depending on the tunneling conditions and have previously been identified as single phosphorus vacancies.[1-3] Once a baseline for the clean BP surface was established, it was dosed with oxygen.

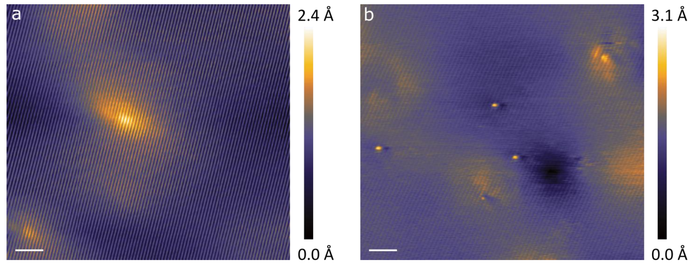

Figure 1: a) Typical native defects found in UHV cleaved black phosphorus. b) After dosing O_2 two new types of defects appear on the surface. Imaging parameters for (a) and (b) -300 mV, 150 pA. Scale bar is 3 nm in both

Oxygen-Induced Defects

After dosing O_2 at a pressure of 10^{-5} mbar, the BP surface was covered with a relatively high density of new defects (~1.6 defect sites per 100 nm^2) most of which can be sorted into two groups: 1) atom-sized protrusions and 2) depressions of various shapes that range from 1-3.5 nm across. Both types of oxygen-induced defects are shown in Figure 1b along with a single vacancy in the upper right corner. Figure 2 shows a comparison of O_2-induced defects at positive and negative imaging bias. Although individual defects vary in appearance as the polarity of the tunneling bias is reversed, their general structure and contrast remains constant. The observation that both types of O_2-induced defects maintain their contrast at positive and negative imaging bias distinguishes them from lattice oxygen defects reported in the literature. High resolution views in Figure 2c-d show atomic rows near depressions that vary in shape and size. These images show that the STM is primarily sensitive to the top row of atoms, as indicated by the lattice overlay.

References

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Oxygen lifts the **band gap** on the surface of **black phosphorus**

Dangling atomic oxygen is the most **favorable** oxygen defect

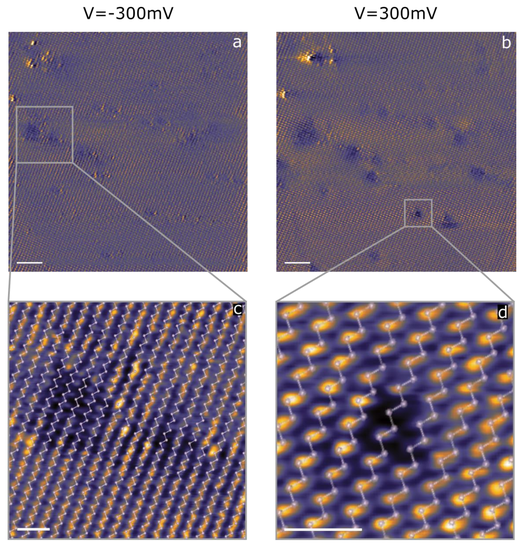

Figure 2: STM images of the same region showing the surface with a high density of oxygen-induced defects. Extended depressions and localized protrusions are shown at both negative bias (a) and positive bias (b). Enlarged images are shown in (c) and (d) with a lattice overlay. For clarity, only the top atoms of the surface layer of BP are presented. Tunneling conditions: (a,c) -300 mV, 150 pA (b,d) 300 mV, 150 pA. Scale bar is 4 nm in (a) and (b), and 1 nm in (c) and (d).

Electronic Changes

STS measurements, which probe the local density of states (LDOS), reveal a significant and uniform change to the electronic structure of the BP surface after oxygen dosing, shown in Figure 3. STS of freshly cleaved BP (blue curve in Figure 3a) shows a band gap of ~300 meV, matching expectation for bulk BP, and p-doping, which is explained by the abundant native single vacancies.[4,5] After oxygen dosing, the LDOS is metallic with small peaks and dips, and no evidence of a band gap (red curve in Figure 3a). The are small variations in the LDOS dependent on the proximity to defects (gray scale curves in Figure 3a), but the general shape and metallic structure is independent of location.

Due to the interaction between the STM tip and the surface, the applied bias can cause defects to become mobile.[6] We were able to use STM manipulation to remove defects from an 80 nm wide O_2-dosed region by repeatedly scanning at 300 mV, 150 pA (Figure 3d,e). The LDOS of the defect-free region is similar to undosed BP (Figure 3c), most notably: the band gap is restored.

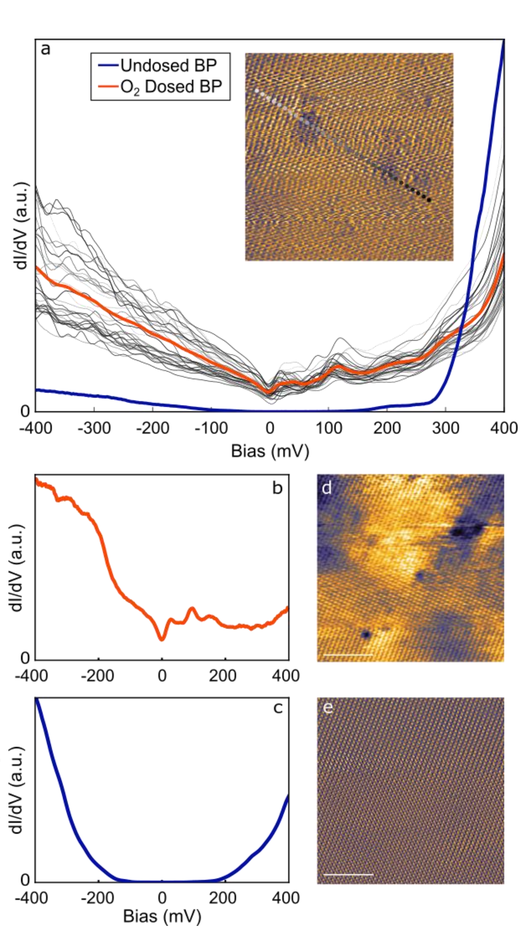

Figure 3: Changes to LDOS by oxygen dosing. a) Typical dI/dV spectroscopy on UHV cleaved BP shown in blue. After dosing the surface with oxygen, the gray scale curves show the spatial dependence of the LDOS with the colors corresponding to the locations on the inset STM topograph. Their average is shown in red. The dosed curves have been multiplied by a factor of 40 to compensate for the increased set point bias of 500mV. dI/dV spectroscopy and corresponding STM topograph (b,d) after the oxygen dose (c,e) after clearing the surface. Tunneling conditions: (a) undosed: 300 mV, 150 pA dosed: 500 mV, 150 pA (b) 500 mV, 150 pA (c) -300 mV, 150 pA (d) 500 mV, 150 pA (e) 300 mV, 150 pA. Scale bar is 5 nm in d and e.

Defect Identification

The dark defects in Figure 2 appear as depressions of different shapes and sizes at both positive and negative bias. Multivacancies are the simplest explanation of this defect type, consistent with the interpretation that atoms are missing from the atomic rows in Figure 2c and d. This interpretation is supported by DFT simulations of STM multivacancies, shown in Figure 4. In these simulations, multivacancies of phosphorus atoms appear as depressions at both positive and negative bias and are found to have a relatively low formation energy. All other potential oxygen-induced defect configurations we investigated are inconsistent with the experimental findings.
The localized protrusions, which also maintain contrast when reversing the polarity of imaging bias, are best identified as chemisorbed dangling O atoms using DFT STM simulations. Dangling oxygen are the lowest energy oxygen defect in BP. Additionally, its creation is an exothermic reaction, even at the expense of separating the O=O bond.

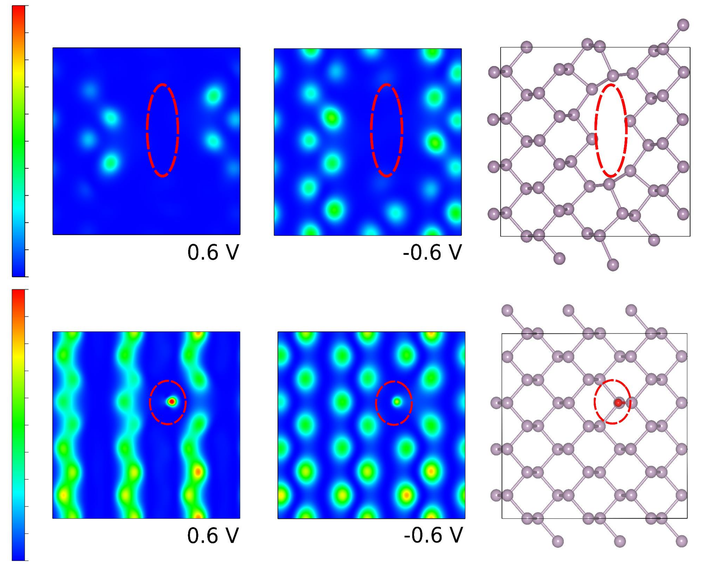

Figure 4: DFT simulated STM images of the phosphorene (010) surface with (a) phosphorus multivacancies and (b) dangling O atom under positive (left column) and negative (middle column) imaging bias voltages. The corresponding structures are shown in the right column.

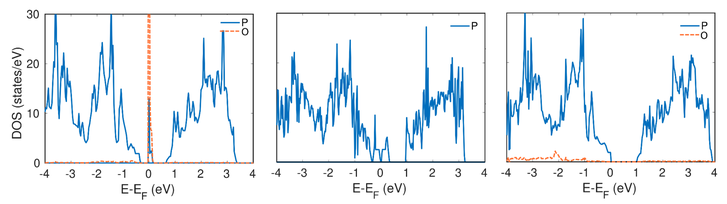

Figure 5: DFT calculated density of states (DOS) of (a) molecular oxygen unbonded to the surface, (b) phosphorus multivacancies (c) dangling O atom attached to the top row of the BP slab.

Conclusion

We have experimentally shown the initial stages of black phosphorus oxidation at the atomic scale. There is a significant change to the DOS which completely lifts the band gap. This alteration of the electronic structure is caused by the addition of defects to the surface. Although the new defects consist of atomic oxygen bonded to the surface, multivacancies in the phosphorus, and physisorbed molecular oxygen, only the vacancies and the molecular oxygen impact the DOS. The change in DOS is reversible by removing the defects from a region. This significant change in both the physical and electronic structure during oxidation provides insight to the degradation process when BP is exposed to ambient conditions.