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 O₂ at a pressure of 10⁻⁴ 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 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 O₂ 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. Once a baseline for the clean BP surface was established, it was dosed with oxygen.

Oxygen-Induced Defects

After dosing O₂ at a pressure of 10⁻⁴ mbar, the BP surface was covered with a relatively high density of new defects (~1.6 defect per 100 nm²) most of which can be sorted into two groups: 1) atom-sized protrusions and 2) depressions of various shapes that range from 1-3 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 O₂-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 O₂-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.

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.

References

5. Liu, Han, et al. ACS nano 4.4 (2014)