SCANNING TUNNELING MICROSCOPE STUDY OF BORON-DOPED HIGHLY ORIENTED PYROLYTIC GRAPHITE

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Introduction

Atomically resolved scanning tunneling microscopy (STM) results are shown for substitutionally doped boron atoms in the hexagonal carbon network of highly oriented pyrolytic graphite (HOPG). STM images of boron-doped HOPG reveal not only a clear change in the electronic structure of the surface graphene network, but also directly affecting the electronic structure of the second and even of the third graphene layer from the HOPG surface which is very exceptional for STM measurements. The boron atom site in the graphene network appears as the brightest area in the image including the 6 adjacent carbon atoms which have a relatively higher intensity than normal carbon atoms in the STM image.

Experimental

The rectangular HOPG samples, with dimensions of 10 mm x 10 mm x 5 mm (thickness), were mixed with B_4C powder and heat treated at 2500□ for 1hr in an Ar atmosphere by a graphite resistance furnace as reported elsewhere[3]. For STM measurements, the samples were examined using a Nanoscope E instrument (Digital Instruments Inc.) in an ordinary ambient atmosphere at 25□. STM images with atomic resolution were obtained in the constant current mode by using commercially available Pt-Ir tips from Digital Instruments Inc. The images were obtained with a set-point current of 1nA and a bias voltage of 20mV. All STM images in the present paper were filtered by the spectrum 2D method[1].

Results and Discussion

Figure 1 shows the STM image of a three-dimensional surface plot with a scan range of 5 nm and its sectional analysis of a B-doped HOPG graphene surface. As is generally known, β-site carbon atoms are revealed in the STM image, which are located just on the centers of the hexagonal carbon rings of the adjacent graphene layer in the hexagonal graphite crystal[2].

At the B-doped HOPG graphene surface, four substituted boron atoms with the highest intensity electron groups (a-d) are found in the image. Each bright area consists of the boron atoms with the highest electron density located in the center of six surrounding medium intensity sites, corresponding to the carbon atoms. Also the electron density distribution of a substituting boron atom and of the surrounding 6 carbon atoms clearly appears in the three-dimensional surface plot (Fig. 1 insert). The substituting boron atom shows the highest electron density in the center. The six carbon atoms closest to the boron atom also show a higher electron density than the next neighborβ-site carbon atoms. Namely, the substituted boron atoms are seen here to affect the electronic structure of the adjacent 6 β-site carbon atoms.

The closest distance between the β-site carbon atoms observed in the section analysis of the STM image is measured to be 0.246 nm for pristine HOPG. On the other hand, the distance between boron and carbon atoms located at β-sites measured in the section analysis of the STM image is 0.276 ± 0.005 nm, as shown in the insert to Fig. 1. This distance is slightly longer in comparison to the corresponding distance in the pristine HOPG (0.246 nm). This trend in the expansion of the B-C bond distance is consistent with previously reported results[3].

As shown in Figure 2, the highest occupied molecular orbital density is at the center of the cluster model where the boron atom is located. The highest density part is surrounded by a smaller density part showing a hexagonal shape. This is similar to the STM image shown in Figure 1, where a high electron density is observed at the center surrounded by a hexagonal high-density part. From the calculation, we can also conclude that a boron atom is placed at the center where the highest electron density is observed.

Figure 3 shows a schematic model for boron-substituted graphite. The average distance between the

boron and adjacent carbon (C_1) atoms on β-sites, as measured in the STM image, is 0.276 ±0.005 nm, as described above. The bond distance between the boron and adjacent carbon atoms is calculated to be 0.159 nm from 0.276 nm for the β-site B-C distance. The distance between C_1-C_1 is measured in the STM to be also 0.276 nm. Therefore, this result indicates that the substituted boron might be located at a slightly higher position than the surrounding carbon atoms in the basal plane of HOPG. The substitution of boron should slightly deform the flatness of basal plane. C. T. Hach et at. reported similar results, that the bond distance between boron and carbon atoms is 0.154 nm for hexane and 0.152 nm for $B_2C_{52}H_{18}$[3]. By restricting the measured bond length between the B-C atoms obtained, we have simulated the optimized structure of a graphene sheet. An improper torsion angle (B at the apex) is calculated to be 164º as shown in Figure 3 insert, while the original plane is almost flat with an angle of 179º

The electronic structure is also modified largely by B-doping, as shown by susceptibility measurement. Namely, both atomically and electronically the graphite planes can be tailor-made, and the boron doping can contribute to controlling the properties of the hexagonal carbon network in order to modify its properties relative to ideal graphite.

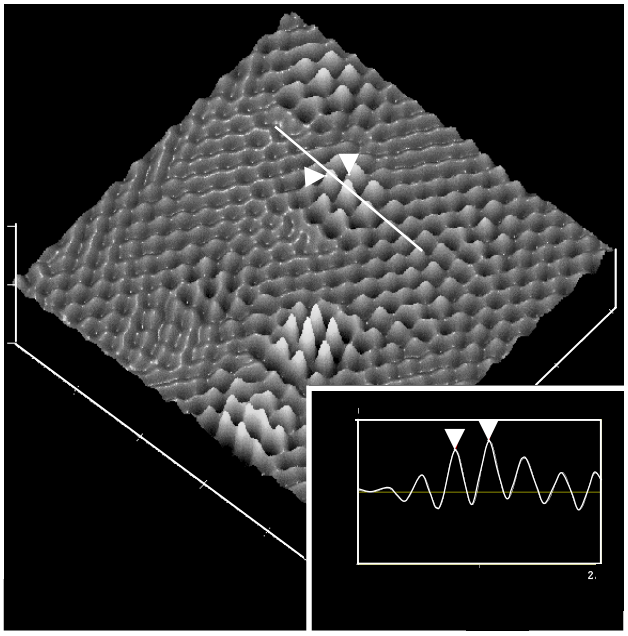


Fig. 1. STM image of a three-dimensional surface plot and the section analysis corresponding to the indicated line (see insets) of the B-doped HOPG graphene surface.

Fig. 2. 3D plot of the highest occupied molecular orbital for the boron-doped graphene sheet model.

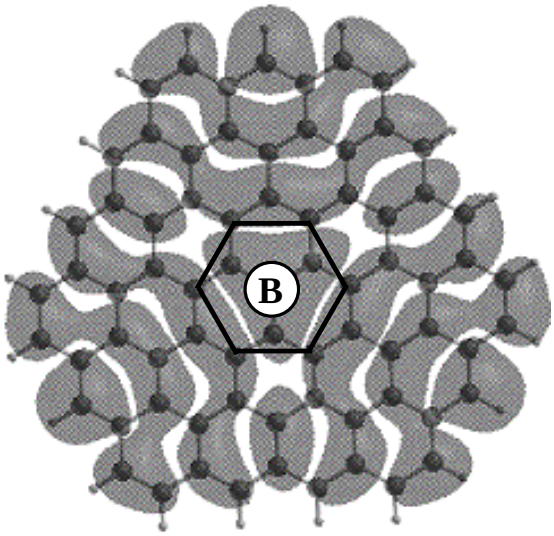
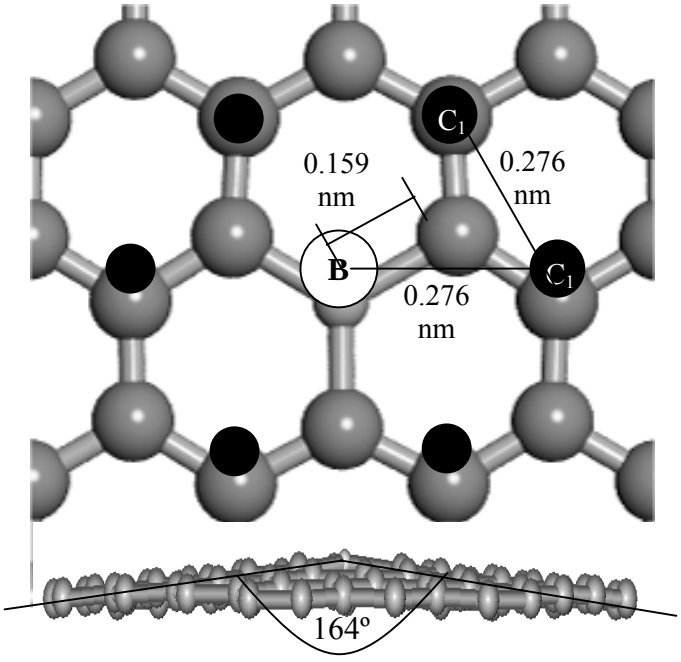


Fig. 3. Schematic model of the top view (a) and the side view (b) for a boron-substituted graphene sheet based on the



measured dimensions of B-C_1 and C_1-C_1.

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