X-ray-absorption studies of boron-doped diamond films

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X-ray-absorption near-edge structure (XANES) measurements have been performed for a variety of boron-doped and undoped diamond films at the C K edge using the sample drain current mode. The C K-edge XANES spectra of B-doped diamonds resemble that of the undoped diamond regardless of the B concentration, which suggests that the overall bonding configuration of the C atom is unaltered. B impurities are found to enhance both the sp^3- and sp^2-bond derived resonance features in the XANES spectra. © *1999 American Institute of Physics.* [S0003-6951(99)05138-4]

Diamond has received extensive theoretical and experimental investigations because of its important technological applications and unique structural and electronic properties.[1] Particular attention has been focused on the modification of the electrical properties by boron (B) doping of chemical vapor deposited (CVD) diamond films for device applications.[2] Based on the observation that the ratio of the intensities of sp^3- and sp^2-bond derived Raman spectral features increased with the B concentration, Nishimura, Das, and Glass[2] and Won *et al.*[3] concluded that the diamond crystal quality is improved by B doping. On the other hand, Bohr found that at very high B additions during the diamond growth the population of the sp^2 bonds, i.e., graphitization, was enhanced.[4] This controversy was argued to be due to insufficient accuracy for the Raman spectroscopy technique to resolve sp^2- and sp^3-bond contributions in carbon materials.[5] Based on the x-ray diffraction measurements that the lattice parameter of B-doped diamonds are close to that of the undoped diamond, Spitsyn, Bouilov, and Derjaguin argued that B impurities are interstitial.[6] On the contrary, based on the x-ray diffraction measurements that the doping of B always induced an increase of the lattice parameter, Brunet *et al.*[7] argued that B impurities are substitutional. To help resolve these controversies, we carry out measurements of the C K-edge x-ray-absorption near-edge structure (XANES) for B-doped diamonds with various B concentrations. XANES is highly sensitive to the local environment around the absorbing atom and can be used as a fingerprint of the chemical bonding state in these B-doped diamonds.[5,8]

The C K-edge x-ray-absorption spectra of CVD-grown B-doped and undoped diamonds were measured using the high-energy spherical grating monochromator (HSGM)

beamline with an electron-beam energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The spectra were measured using the sample drain current modes at room temperature. Photon energies for the C K-edge XANES spectra were calibrated using bulk diamond.[9] The typical resolution of the spectra was 0.2 eV for the HSGM beamline. Diamond films were grown on silicon substrates by the microwave plasma-enhanced chemical vapor deposition method. Boron concentration (3, 6, and 9 sccm) in the diamond films was varied in proportion to the $B(CH_3O)_3$ concentration in the CH_4/H_2 plasma, as described elsewhere.[10] The x-ray diffraction (XRD) measurement was also used to characterize the structure of the films. XRD data analysis indicated that polycrystalline B-doped diamonds have similar crystal symmetries to that of undoped diamond. The high-resolution XRD spectra of B-doped diamonds with B concentrations of 3, 6, and 9 sccm are denoted as CB_3, CB_6, and CB_9, respectively, as shown in Fig. 1. They exhibit a prominent peak for diamond (111), which resembles that of the undoped diamond denoted as CB_0. The diamond (111) peak shifts towards the smaller-angle side with the increase of the B concentration, which corresponds to an increase of the overall lattice parameter of the films with the increase of the B concentration, as shown in the inset of Fig. 1. The increase of the lattice parameter is not linear and seems to saturate at 3.580 Å, which is about 0.3%, or 0.013 Å, larger than that of the undoped diamond. The increase of the lattice parameter agrees with the x-ray diffraction measurements of Brunet *et al.*[7] If the B impurities are located at the substitutional sites and the B atom has the same size as that of the C atom, the lattice parameter would remain the same as that of the undoped diamond. However, since the B–C bond length (about 1.6 Å),[11] is slightly larger than the C–C bond length

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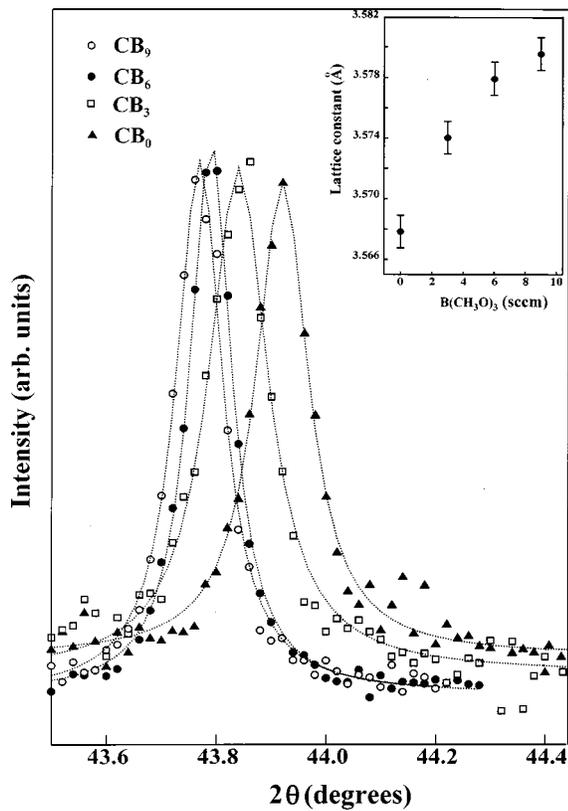
FIG. 1. Representative x-ray diffraction spectra of B-doped and undoped diamonds. The inset is the lattice parameter vs B concentration in B-doped and undoped diamonds.

FIG. 2. Normalized C K-edge absorption spectra of B-doped and undoped diamonds. The inset shows the normalized C K-edge absorption spectra of B_4C (from Ref. 15).

(about 1.5 Å),[11] substitutional B impurities can cause the increase of the lattice parameter in B-doped diamonds. On the other hand, interstitial B impurities can push apart neighboring host atoms and can also cause an increase of the lattice parameter. Thus, the lattice-parameter measurement is not useful for determining whether B impurities are interstitial or substitutional. The increase of the lattice parameter may also be contributed by B-impurity induced graphitization because graphite has a density, 2.30–2.72 g/cm^3, smaller than that of diamond, 3.51 g/cm^3.

Figure 2 displays the C K-edge XANES spectra of B-doped and undoped diamonds for comparison. The spectra were normalized using the incident beam intensity I_0 and keeping the area under the spectra in the energy range between 314 and 335 eV fixed. For x-ray energies in the XANES region, the excited photoelectron undergoes a transition from a core level to an unoccupied final state determined by the dipole-transition selection rule. According to Fig. 2, the spectra reflect transitions from the carbon $1s$ core level to p-like final states in the unoccupied states above the Fermi level. The spectra of B-doped and undoped diamonds clearly display sharp features which closely resemble that reported in earlier works for diamond.[9,12] The XANES energy range for diamond generally can be divided into two regions characterized by specific features. One is the spike of the C $1s$ core exciton resonance at approximately 289.2 eV. Another is a relatively broad σ^* feature in the energy range between about 290 and 302 eV for the sp^3-bonded carbon. The relatively small peak at ~285 eV can be attributed to the graphite-like π^* state of sp^2-bonded carbon, as indicated in Fig. 2.[13,14] The spectral line shapes in the C K-edge XANES
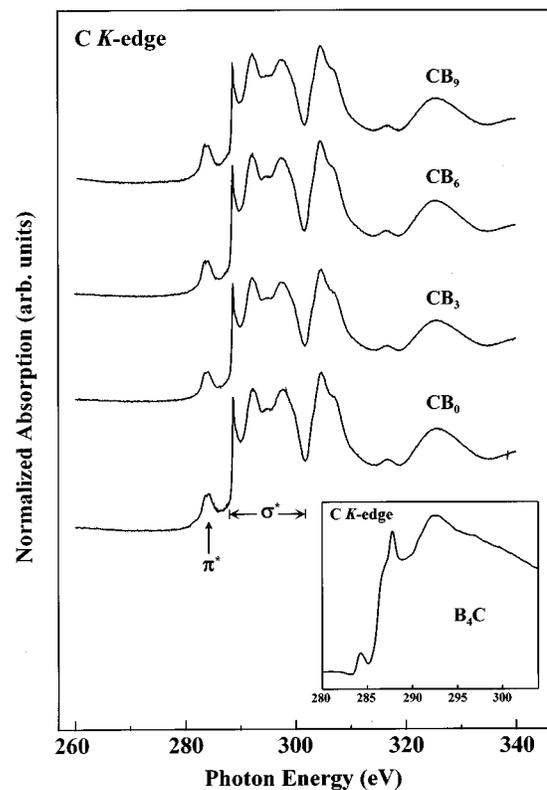
spectra of these B-doped and undoped diamonds appear to be nearly identical regardless of the different B content, which indicates that the doping of B atoms in diamond does not significantly alter the overall local environment of the C atom. This property suggests that the B impurities are substitutional not interstitial for the following reasons. When the B impurity is located at the substitutional site, the perturbation to the host periodic potential is the difference potential between the atomic potentials of the B atom and the host atom substituted by it. The difference potential is small, so that the band structure approximately remains the same except the addition of an impurity level. If B is a shallow acceptor, the impurity level lies slightly above the valence-band maximum, which is about 5.4 eV below the conduction-band minimum. The acceptor-impurity level is occupied at room temperature and is not detectable by XANES. On the other hand, if the B impurity is located at the interstitial site, the perturbation to the host periodic potential is the total B atomic potential. The atomic potential is large and will change greatly the electronic structure and bonding configuration of neighboring host atoms, especially when the B–C bond strength is comparable with that of the C–C bond (diatomic bond strengths of B–C and C–C bonds are 4.64 and 6.29 eV,[11] respectively). Thus, the measured XANES spectrum should be altered significantly by interstitial B impurities unless the B concentration is too small to be detected. The inset of Fig. 2 displays the C K-edge XANES spectrum of B_4C. This spectrum is contributed to by the carbon atoms associated with the C–B–C linear chains in the icosahedra.[15] The conduction band shown in the C K-edge spectrum of B_4C is very different from those of B-doped and

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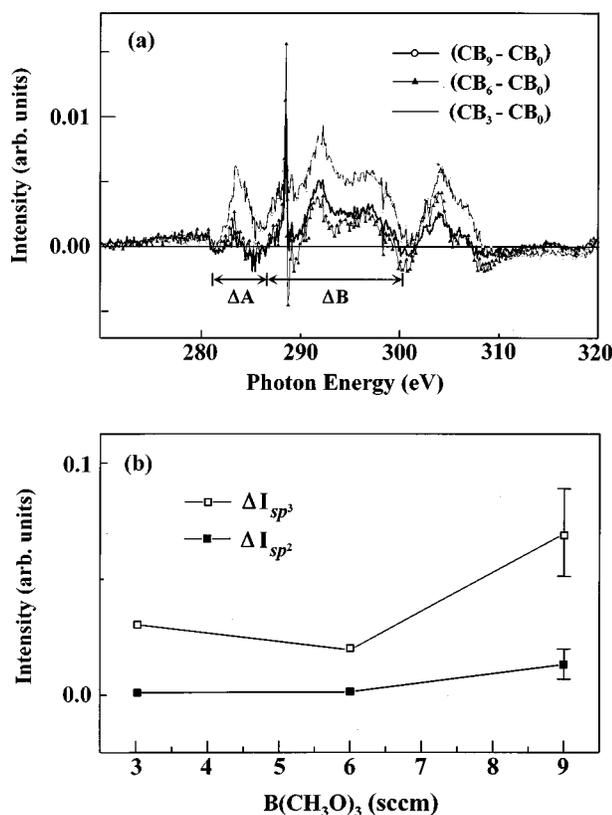
FIG. 3. (a) C *K*-edge difference intensity curves between B-doped and undoped diamonds. (b) Plot of integrated difference intensity curves of ΔI_{sp2} and ΔI_{sp3}, over $\Delta A(\pi^*)$ and $\Delta B(\sigma^*)$ regions, respectively, vs the B concentration.

undoped diamonds, which indicates that the local bonding configuration of the C atom in B-doped diamonds even with a high B concentration is not B_4C like, i.e., it does not have a linear C–B–C bond arrangement. This property further supports the argument that B impurities are substitutional not interstitial because an interstitial B impurity can form a linear C–B–C bond arrangement.

Figure 3(a) shows the difference curves of the C *K*-edge XANES spectra of the three B-doped diamonds with respect to the undoped diamond. Integrations of the intensities over $\Delta A(\pi^*)$ (between 281.6 and 286.1 eV) and $\Delta B(\sigma^*)$ (between 286.1 and 300.7 eV) regions are plotted in Fig. 3(b) as ΔI_{sp2} and ΔI_{sp3}, respectively. ΔI_{sp2} and ΔI_{sp3} represent enhanced absorption of the x ray by the electron transit from the C 1s core state to unoccupied sp^2- and sp^3-bond states, respectively. ΔI_{sp2} and ΔI_{sp3} can be caused by the B-impurity induced increase of sp^2 or sp^3 bonds or an enhancement of the dipole-transition probability. Since the numbers of C atoms is not increased by B doping, the numbers of sp^2 and sp^3 bonds cannot both increase. The enhancement of the dipole-transition probability must be at least the partial cause of the increase of either ΔI_{sp3} or ΔI_{sp2}. The B atom is known to be an acceptor in diamond. Thus, it is negatively charged. B ions can polarize the electronic distributions in surrounding C atoms by their Coulomb potentials. The polarization will enhance the dipole-

transition probability because the dipole operator is a polarization operator. This effect will be more important for the insulating sp^3-bond states than for the itinerant graphite-like sp^2-bond states, which can be shielded by the screening effect. Thus, the B-impurity induced increase of ΔI_{sp3} may be due to the enhanced dipole-transition probability between the C 1s core state and the unoccupied sp^3-bond states. As for the small increase of ΔI_{sp2}, it can be attributed to the B-impurity induced conversion of sp^3 bonds to sp^2 bonds in some small regions of the films. Note that as an acceptor the B atom takes an electron away from the sp^3 bond that requires the occupation by all four electrons in each C atom. Thus, B impurities can destabilize some sp^3 bonds and convert them to sp^2 bonds. This is a unique property of carbon materials because the graphite structure with the sp^2 bonding is the thermodynamically most stable structure of carbon. Our argument is consistent with the finding of Bohr that high B additions during diamond growth produce an increased graphite component.[4]

In summary, analyses of x-ray diffraction data and C *K*-edge XANES spectra indicate that B impurities doped in diamond are substitutional not interstitial. Analysis of the changes of the XANES spectra of B-doped diamonds with respect to that of the undoped diamond indicates that B impurities may induce partial graphitization in some small regions of the films and enhance the dipole-transition probability between the C 1s core state and the unoccupied sp^3-bond states of the host atoms surrounding the B impurity.

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