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## Electronic properties of the diamond films with nitrogen impurities: An x-ray absorption and photoemission spectroscopy study

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X-ray absorption near-edge structure (XANES) measurements have been performed for nitrogen (N) containing diamond films with three different N concentrations at the C *K*-edge using the sample drain current mode. The C *K*-edge XANES spectra of these diamond films resemble that of the pure diamond regardless of the N concentration, which suggests that the overall bonding configuration of the C atom is unaltered. N impurities are found to reduce the intensities of both the  $sp^2$ - and  $sp^3$ -bond derived resonance features in the XANES spectra. The valence-band photoelectron spectra indicate that N atoms cause the broadening of the valence band  $\sigma$ - and  $\pi$ -bond features and the enhancement and reduction of the  $\sigma$ - and  $\pi$ -bond features, respectively. © 2000 American Institute of Physics. [S0003-6951(00)04652-0]

The doping of the diamond film is of both fundamental and technological interests.<sup>1</sup> Several investigations found that boron (B) doping not only improved the quality but also increased the *p*-type conductivity of the diamond film.<sup>2-4</sup> Nitrogen (N) was expected to behave like a donor and was found to enhance the electron emission characteristics in the diamond films.<sup>5,6</sup> Recently, Okano *et al.*<sup>5</sup>, and Geis *et al.*<sup>7</sup> reported that heavily N-doped diamond films had a lower threshold field than those of the B-doped samples suggesting that N impurities play an important role in enhancing the emission properties. In a previous work, we found that B doping induced partial graphitization in some small regions in the diamond films and enhanced the unoccupied  $sp^3$ -bond states of the host atoms surrounding the B impurities.<sup>8</sup> Electron energy loss spectroscopy (EELS),<sup>9-12</sup> x-ray absorption near edge structure (XANES),<sup>10,13</sup> and photoelectron spectroscopy (PES)<sup>14,15</sup> measurements were made on carbon nitride materials. Here, we carry out the C *K*-edge XANES and valence-band PES measurements for the N-containing diamond films with various N concentrations and attempt to understand how the N impurities influence the electronic properties of the diamond films.

The C *K*-edge XANES and valence-band PES measurements were performed using the high-energy spherical grating monochromator (HSGM) and low-energy spherical grating monochromator (LSGM) beamlines, respectively, with an electron-beam energy of 1.5 GeV and maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The spectra of the C *K* edge were measured using the sample drain current mode at room temperature. The typical resolution of the spectra was 0.2 eV for the HSGM beamline. The LSGM beamline for the valence-band PES measurement was under a base pressure of  $\sim 5 \times 10^{-10}$  Torr during the measurements, which has an EAC-125 hemispherical electron energy analyzer. The samples were cleaned by repeated cycles of argon-ion bombardment. Diamond films were grown on silicon substrates by the microwave plasma-enhanced chemical vapor deposition method. Since the N concentration in the diamond film is proportional to the gas-phase urea concentration of the nitrogen source, the variation of the N concentration in the diamond film was obtained by choosing three different urea concentrations of 3, 4, and 5 sccm in the preparation process as described elsewhere.<sup>16</sup> The x-ray diffraction (XRD) measurement was also used to characterize the structure of the films. XRD data analysis indicated that the polycrystalline

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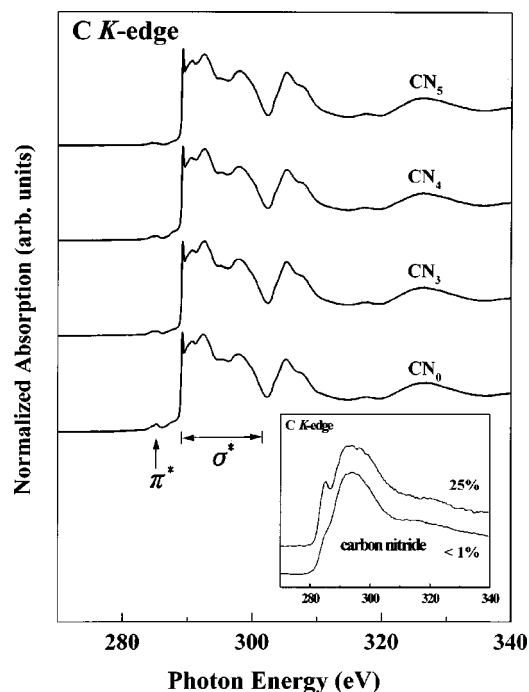


FIG. 1. Normalized C *K*-edge absorption spectra of N-containing and pure diamonds. The inset displays the C *K*-edge EELS spectra of the carbon nitride samples containing less than 1% and 25% of nitrogen (see Ref. 12).

N-containing diamonds have similar crystal symmetries as that of a pure diamond.

Figure 1 displays the C *K*-edge XANES spectra of N-containing and pure diamond films for comparison. The XANES spectra of the N-containing diamond films prepared with urea concentrations of 3, 4, and 5 sccm and the pure diamond film are denoted as CN<sub>3</sub>, CN<sub>4</sub>, CN<sub>5</sub>, and CN<sub>0</sub>, respectively. The spectra were normalized using the incident beam intensity  $I_0$  and keeping the area under the spectra in the energy range between 335 and 345 eV fixed (not fully shown in the figure). 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. The spectra in Fig. 1 reflect transitions from the C1*s* core level to unoccupied *p*-like final states. The spectra of N-containing and pure diamond films clearly display sharp features closely resembling those reported in the earlier works.<sup>8,17,18</sup> The XANES energy range for diamond generally can be divided into two regions characterized by specific features. One is the spike of the C 1*s* core exciton resonance at approximately 289.2 eV. Another is a relatively broad  $\sigma^*$  feature of the  $sp^3$ -bonded carbon atoms in the energy range between about 290 and 302 eV. The relatively small peak at  $\sim 285$  eV is usually attributed to the graphite-like  $\pi^*$  state of the  $sp^2$ -bonded carbon atoms as indicated in Fig. 1. The spectral lineshapes in the C *K*-edge XANES spectra of these N-containing and pure diamond films appear to be nearly identical regardless of the different N concentrations, which indicates that adding N atoms in diamond does not significantly alter the overall local environment of the C atom. The inset of Fig. 1 displays the C *K*-edge EELS spectra of two carbon nitride samples containing 25% and less than 1% of nitrogen, respectively.<sup>12</sup> These two spectra are very different from those of the N-containing

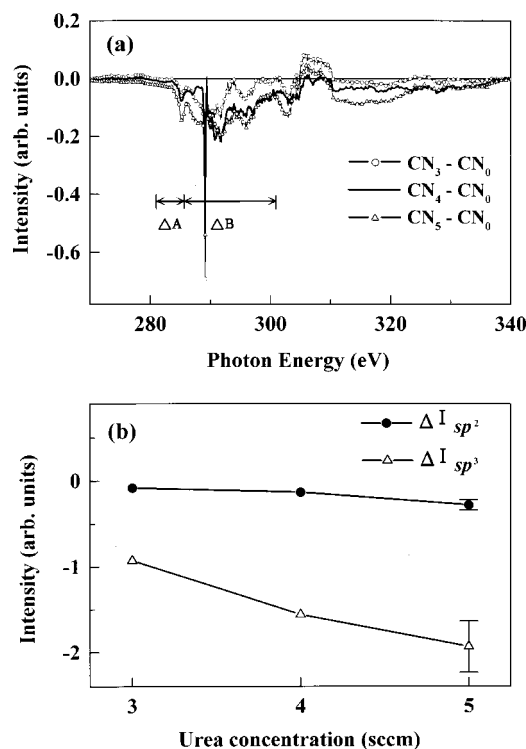


FIG. 2. (a) The C *K*-edge difference intensity curves between N-containing and pure diamonds. (b) A plot of the integrated difference intensity curves,  $\Delta I_{sp^2}$  and  $\Delta I_{sp^3}$ , over  $\Delta A(\pi^*)$  and  $\Delta B(\sigma^*)$  regions, respectively, vs the N concentration.

diamond films shown in Fig. 1, which indicates that the local bonding configuration of the C atom in N-containing diamond films differ from that of the carbon nitride. In other words, the bonding configuration between the N impurity and the surrounding host C atoms are different from those in the carbon nitride, i.e., the N impurities seem not likely to be substitutional in the diamond films used in our study.

Figure 2(a) shows the difference intensity curves between the C *K*-edge XANES spectra of the three N-containing diamond samples and that of the pure diamond sample. Integration 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. 2(b) as  $\Delta I_{sp^2}$  and  $\Delta I_{sp^3}$ , respectively.  $\Delta I_{sp^2}$  and  $\Delta I_{sp^3}$  represent N-impurity-induced reduction of the absorption of x-ray by the electrons transit from the C1*s* core state to the unoccupied  $sp^2$ - and  $sp^3$ -bond states, respectively. Figure 2(b) shows that  $\Delta I_{sp^2}$  decreases slightly with the N concentration. In conjunction with the trend of the diminishing  $\pi^*$  feature shown in Fig. 2(a), one can conclude that N impurities suppress the formation of the small quantity of  $sp^2$  bonds in the diamond films, which may exist in the grain boundary regions or on the surface. This is reasonable because N atoms tend to form strong covalent bonds with neighboring host atoms with the directional *p* orbitals, which may destabilize the planar  $sp^2$  bonding in the diamond films. The same chemical or bonding property of the N atoms may enhance the *p*-orbital content in the occupied  $sp^3$ -bond derived states in the N-containing diamond films. Consequently, the *p*-orbital content in the unoccupied  $sp^3$ -bond derived states (or anti-bonding  $sp^3$  states) will be depleted, so that  $\Delta I_{sp^3}$  decreases substantially with the increase of the N concentration as

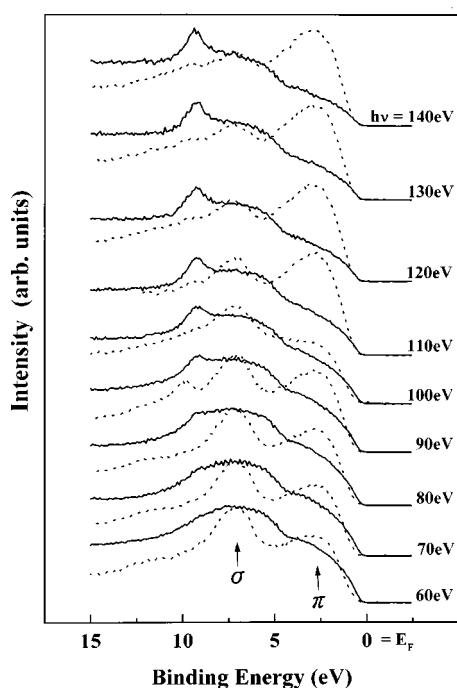


FIG. 3. Representative valence-band PES spectra of  $CN_0$  (dashed lines) and  $CN_5$  (solid lines) at various photon energies between 60 and 140 eV.

shown in Fig. 2(b). The present result is in contrast with that of the B-containing diamond films, in which the B impurities enhance the number of unoccupied  $sp^2$ - and  $sp^3$ -bond states.

Figure 3 shows the valence-band PES spectra of  $CN_0$  and  $CN_5$  for various photon energies between 60 and 140 eV. The height of the maximum intensity has been normalized to unity for comparison. The  $CN_0$  spectra basically show two main features predominantly associated with the C– $\pi$ - and  $\sigma$ -bond states,<sup>14,15,19</sup> respectively, in the 0–5 and 6–9 eV regions. The dependence of the spectra on the photon energy indicates that the lower-binding-energy  $\sigma$ -bond feature is gradually suppressed for higher photon energies. Since the lower-energy initial states are more localized and the higher-energy final empty states are more extended, it is understandable that the dipole-transition matrix element and consequently the transition probability for this feature become diminished relative to that of the  $\pi$ -bond feature for higher photon energies. There are substantial differences between the  $CN_0$  and  $CN_5$  spectra as shown in Fig. 3. The  $CN_5$  spectra show strong broadening of both  $\sigma$ - and  $\pi$ -bond features, which can be attributed to a strong C–N hybridization. Besides broadening Fig. 3 also shows that the  $\sigma$ - and  $\pi$ -bond features in the PES spectra of  $CN_5$  are enhanced and reduced, respectively, relative to those in the  $CN_0$  spectra. The enhancement of the lower-binding-energy  $\sigma$ -bond feature reflects that N orbitals have larger binding energies than those of C orbitals. In Fig. 3, an additional feature emerges around 9.3 eV in the  $CN_5$  spectra for photon energies higher than

about 80 eV. N impurities in diamond films seem to induce additional delocalized valence-band states. A valence-band electron absorbing a high energy photon will transit to a highly extended final state. The transition probability will be larger for a delocalized than for a localized initial state.

In summary, the comparison between the C  $K$ -edge XANES spectra N-containing diamond films and those of the carbon nitride samples suggests that the local bonding configuration of the host C atoms surrounding the N impurity in the diamond film is very different from that in the carbon nitride. An analysis of the C  $K$ -edge XANES spectra of N-containing diamond films shows that N impurities reduce the number of unoccupied  $sp^3$  states. Our valence-band PES measurements show that N impurities cause the broadening of the  $\sigma$ - and  $\pi$ -bond features and the enhancement and reduction of the  $\sigma$ - and  $\pi$ -bond features, respectively.

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