

# Threshold of photoelectron emission from $CN_x$ films deposited at room temperature and at 500 °C

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The threshold of photoelectron emission was measured for amorphous  $CN_x$  films deposited at room temperature (RT) and at 500 °C. The  $x$  values of the films deposited at RT and at 500 °C by magnetron sputtering of a graphite target in a mixed  $N_2/Ar$  gas were 0.6 and 0.3, respectively. Ratios of the  $sp^2$ - to  $sp^3$ -hybridized components of both C and N for the film deposited at 500 °C were larger by  $\approx 4$  times than those for the film deposited at RT. The onsets of the electron emission by photon irradiation were 5.0 and 4.7 eV for the films deposited at RT and at 500 °C, respectively. © 2004 American Institute of Physics. [DOI: 10.1063/1.1787907]

Electronic properties of amorphous  $CN_x$  films with different ratios of the  $sp^2$ - to  $sp^3$ -hybridized components are of great interest for applications in the electron emission devices such as electron-beam sources and flat-panel displays.<sup>1</sup> It is well known that hydrogen termination for diamond surfaces brings about an enhanced electron emission by irradiation of photons or electrons,<sup>2,3</sup> which must be beneficial for practical device applications by applying a field. We expect that a  $CN_x$  film with a relatively large value of the  $sp^2$  to  $sp^3$  ratio shows a small energy barrier for the electron emission, which is promising for the device applications similar to the diamondlike carbon films.<sup>4</sup>

The  $\beta$ - $C_3N_4$  phase with a very high elastic bulk modulus<sup>5</sup> forms very small crystallites and is immersed in the  $sp^2$ -bonded amorphous  $CN_x$  matrix.<sup>6,7</sup> The bonding configurations leading to a high bulk modulus material are C, having four neighbors as in diamond ( $sp^3$  bonding), and N, having three neighbors in a planar geometry ( $sp^2$  bonding with a lone pair). However, this is one of the many possibilities available for the  $CN_x$  compounds. A new group, called a fullerene-like CN, has been found in the amorphous  $CN_x$  films when high substrate temperatures were used and relatively high N contents were achieved.<sup>8,9</sup> Sjöström *et al.*<sup>10</sup> reported that a fullerene-like microstructure was formed due to a cross-linking between the two  $sp^2$  hybridized  $CN_x$  layers by bucking around pentagons for the amorphous  $CN_x$  ( $x=0.2$ ) film, which has a distorted graphitelike microstructure consisting of buckled and curved basal planes. A semiempirical, pseudopotential model-cluster calculation of N substitution for C in graphite revealed that the clusters, including 96 C atoms, are plane for the N concentrations up to  $[N]/[C] \sim 0.2$ , and the bucking develops in the clusters above the concentration.<sup>11</sup> The energy gap between the lowest unoccupied molecular orbital and the highest occupied molecular

orbital decreased with increasing the N content from 1.8 eV for the pure carbon cluster to 0.18 eV for the saturated  $[N]/[C]=1$  cluster due to the filling of the conduction-band states. As the N content increases, electrons fill the antibonding  $\pi^*$  states above the Fermi energy of graphite. The bucking of the structure by a N incorporation for concentrations above  $[N]/[C] \sim 0.2$  leads to the localization of the electrons into a lone-pair orbital of the N-substituted graphitelike clusters. Therefore, an increase of the  $sp^2$ -hybridized CN bond lowers the energy barrier for electron emission when the amorphous  $CN_x$  film was deposited at high substrate temperatures.

The amorphous  $CN_x$  films used in this experiment were deposited on an  $n$ -type Si(100) substrates at room temperature (RT) and at 500 °C by magnetron sputtering of a graphite target with four nines purity in a  $N_2/Ar=5/3$  gas, at a pressure of 10 Pa. The thickness of the films deposited at RT and at 500 °C were approximately 500 and 300 nm, respectively. A Surface Science Laboratory SSX-100 spectrometer with a monochromatized Al  $K\alpha$  source was employed to obtain a core-level electron spectra of the film in the analyzer chamber with a base pressure of  $1.3 \times 10^{-8}$  Pa. The N 1s and C 1s spectra of the films are shown in Figs. 1(a) and 1(b). The  $x$  values estimated from the data were 0.6 and 0.3 for the films deposited at RT and at 500 °C, respectively. As shown in Figs. 2(a) and 2(b), the N 1s and C 1s spectra of the film deposited at 500 °C can be partitioned into the peaks originated from the  $sp^3$ - and  $sp^2$ -hybridized CN bonds and others, as pointed out by Marton *et al.*<sup>12,13</sup> The  $sp^3$ -hybridized CN bond corresponds to both the N 1s peak centered at 398.3 eV and the C 1s peak at 287.7 eV, whereas the  $sp^2$  hybridized CN bond relates to the N 1s peak at 400.0 eV and the C 1s peak at 285.9 eV.<sup>14</sup> The ratios of the  $sp^2$ - to  $sp^3$ -hybridized components for N of the films deposited at RT and at 500 °C were 0.2 and 0.8, respectively. The ratios of the  $sp^2$ - to  $sp^3$ -hybridized components for C of the films deposited at RT and at 500 °C were 1.2 and 5.2, respectively. The  $sp^2$  to

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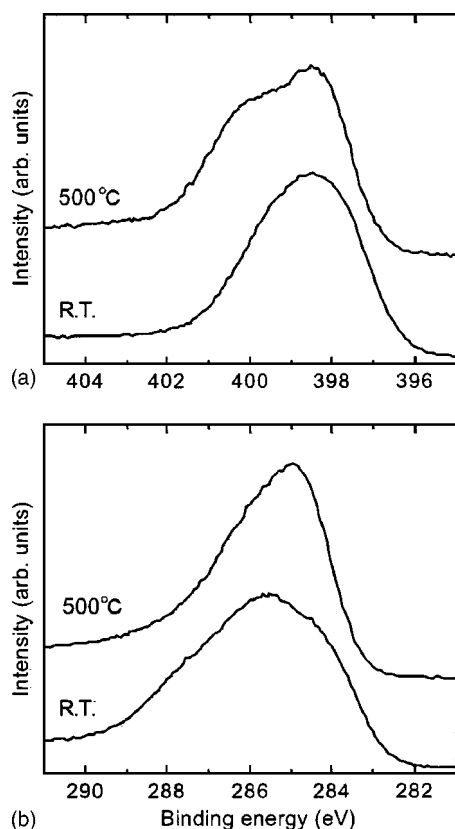


FIG. 1. N 1s (a) and C 1s (b) electron spectra of the films deposited at RT and at 500 °C. The spectra were normalized to the same maximum intensity.

$sp^3$  ratios of both C and N for the film deposited at 500 °C were larger by  $\approx 4$  times than those for the film deposited at RT. The substrate temperature, 500 °C, was high enough to obtain a larger fraction of the  $sp^2$ -hybridized CN bonds. Thus, we measured the threshold energy of the electron emission from a photoirradiated surface of the amorphous  $CN_x$  films with the low and high  $sp^2$  to  $sp^3$  ratios.

We used a modified photoemission electron microscope for the measurement.<sup>15</sup> The wavelength of ultraviolet rays ( $\lambda=195\sim 350$  nm) from a D<sub>2</sub>-lamp was swept by a Shimadzu UV-3100PC monochromator with an energy resolution of 0.1 nm. The sample surface set in the chamber at a pressure below  $1\times 10^{-7}$  Pa was irradiated by the monochromatized photons ( $h\nu=3.6\sim 6.3$  eV). The bright spots that appeared on the fluorescent screen, which correspond to the particular numbers of the ejected electrons, were counted by using the CCD camera. The background counts were lessened by improving the spatial discrimination characteristics of the microscope and by using the chromatic aberration of silica lens at the wavelength of the threshold of photoelectron emission.

As shown in the inset of Fig. 3, the onset of electron transition from the valence band to the conduction band by a photon irradiation started at 1.8 and 1.0 eV for the films deposited at RT and at 500 °C, respectively. This trend with increasing the  $sp^2$  to  $sp^3$  ratio matches for the filling of the antibonding  $\pi^*$  states above the Fermi level.<sup>11</sup> As shown in Fig. 3, the threshold the photoelectron emission of the films deposited at RT and at 500 °C were 5.0 and 4.7 eV, respec-

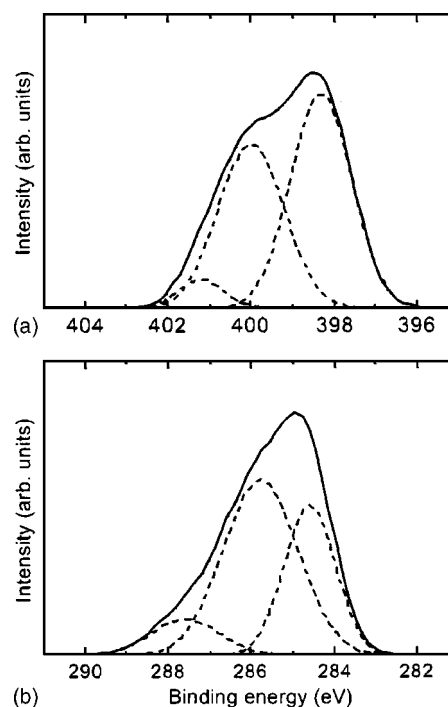


FIG. 2. N 1s (a) and C 1s (b) electron spectra of the film deposited at 500 °C. A linear-type background has been subtracted, and the Gaussian function was used for fitting. The linewidth of the resolved N 1s peaks at 398.3 and 400.0 eV were 1.5 and 1.6 eV, respectively. The linewidth of the resolved C 1s peaks at 284.6, 285.9, and 287.7 eV were 1.2, 1.8, and 1.7, respectively.

tively. The film deposited at RT showed a gradual increase of the emitted photoelectrons with increasing the photon energy above 5.0 eV. The intensity of the photoelectron emission from the film deposited at 500 °C was larger than that from the film deposited at RT. For the film deposited at 500 °C, we have observed a steeply increased photoelectron emission at  $\sim 5.2$  eV. At  $\sim 5.2$  eV, the photoelectron intensity differs by almost two to three orders of magnitude. Such lowered threshold energy and enhanced intensity of the photoelectron

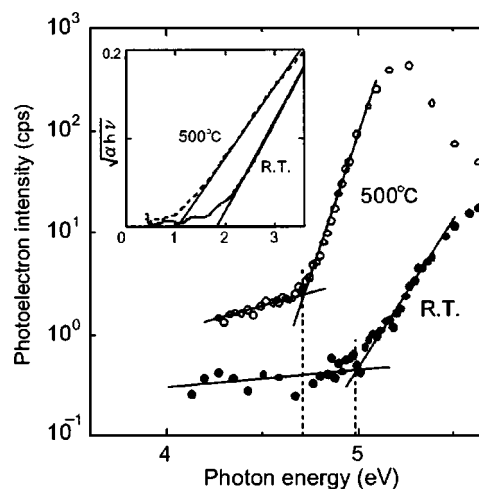


FIG. 3. Photon-energy dependence of the electrons ejected from the films deposited at RT and at 500 °C. The reproducible data were obtained after three times of cleaning of the surface by an Ar<sup>+</sup> sputtering at 0.25 keV. Inset: Onset of optical transition of the films deposited at RT and at 500 °C. Unit of the vertical axis  $(\alpha h\nu)^{1/2}$  is (eV/nm)<sup>1/2</sup>.

emission for the film deposited at 500 °C are characteristics of the lowered energy barrier for the electron emission from the amorphous  $\text{CN}_x$  film with a high  $sp^2$  to  $sp^3$  ratio. The lower threshold energy of the photoelectron emission (4.7 eV) observed for the film with high  $sp^2$  to  $sp^3$  ratios of both C (0.8) and N (5.2), which can be attributed to the localized electrons in a lone-pair orbital of N substituted for C in graphitelike clusters, is beneficial for practical device applications by applying a field.

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<sup>13</sup>The N 1s peak centered at 402.0 eV and the C 1s peaks at 284.6 and 289.5 eV are resulted from the N–O or N–N bonds, adventitious carbon, and C–O bond, respectively. The C 1s peak observed additionally at 283.6 eV for the film deposited at RT was due to the adsorbed carbon atoms on the surface.

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