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Electronic and bonding structures of amorphous Si–C–N thin films by x-ray absorption spectroscopy

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X-ray absorption near edge structure (XANES) spectra of hard amorphous *a*-Si–C–N thin films with various compositions were measured at the C and N *K*-edge using sample drain current and fluorescent modes. The C *K*-edge XANES spectra of *a*-Si–C–N contain a relatively large $1s \rightarrow \pi^*$ peak, indicating that a substantial percentage of carbon atoms in the *a*-Si–C–N films have sp^2 or graphite-like bonding. Both the observed sp^2 intensity and the Young's modulus decrease with an increase in the carbon content. For N *K*-edge XANES spectra of the *a*-Si–C–N films we find the emergence of a sharp peak near the threshold when the carbon content is larger than between 9% and 36%, which indicates that carbon and nitrogen atoms tend to form local graphitic carbon nitride. © 2001 American Institute of Physics. [DOI: 10.1063/1.1409275]

Carbon-related amorphous materials are important materials of fundamental and technological interest.¹ Amorphous silicon carbon nitride (*a*-Si–C–N) exhibits superior properties to those of the conventional materials; it has excellent properties such as high oxidation resistance, a wide band gap, and promising mechanical and thermal properties.^{1,2} Previous C, N, and Si *K*-edge x-ray absorption measurements and first-principles calculation showed that crystalline (*c*)-Si–C–N thin film has a proportional combination of local Si–N and Si–C bonds around the Si atoms.³ X-ray absorption near edge structure (XANES) measurements for *c*- and *a*-Si–C–N showed that the binding energies of excited electrons were higher and that the spectral features were broader in the amorphous phase than in the crystalline phase.⁴ More recently, surface acoustic wave spectroscopy measurements showed that both the Young's modulus and the mass density decreased as the carbon content increased in *a*-Si–C–N films.⁵ Although the XANES technique⁶ has been used to study the characteristics of *a*-Si–C–N films the local electronic and bonding structures related to the mechanical properties of hard *a*-Si–C–N films have not been examined. Thus we have carried out this study to analyze the C and N *K*-edge x-ray absorption spectra and the local electronic and bonding structures in ternary *a*-Si–C–N systems.

C and N *K*-edge XANES measurements were carried out

for *a*-Si–C–N films and for chemical vapor deposition (CVD) grown diamond, graphite, polycrystalline α -Si₃N₄, and β -SiC films, which were used as references, using a high-energy spherical grating monochromator (HSGM) and wide-range beamlines. The beamlines had an electron-beam energy of 1.5 GeV and a maximum stored current of 200 mA and were located at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The C *K*-edge XANES spectra were measured using the sample drain current mode. All fluorescence measurements of the N *K*-edge XANES spectra were performed using a seven-element Ge detector. The *a*-Si–C–N films, with their various compositions listed in Table I, were deposited by ion beam sputtering. The Young's modulus and the density were observed to decrease from 260 ± 15 to 85 ± 12 GPa and from 3.4 ± 0.2 to 2.4 ± 0.3 g/cm³, respectively, as the carbon content of the films was increased from 0% to 68%. Details of the preparation

TABLE I. Compositions and elastic properties of *a*-Si–C–N films obtained by ion beam sputtering.

Sample No.	Composition (%)				Thickness (mm)	Young's modulus (GPa)	Density (g/cm ³)
	C	N	Si	O			
IC102	0	49	44	7	0.79 ± 0.05	260 ± 15	3.4 ± 0.2
IC56	9	39	44	8	0.31 ± 0.03	255 ± 25	3.4 ± 0.2
IC48	36	24	29	11	0.30 ± 0.03	220 ± 30	3.2 ± 0.4
IC101	49	21	20	10	0.25 ± 0.03	130 ± 20	2.6 ± 0.5
IC103	68	22	9	1	0.54 ± 0.01	85 ± 12	2.4 ± 0.3

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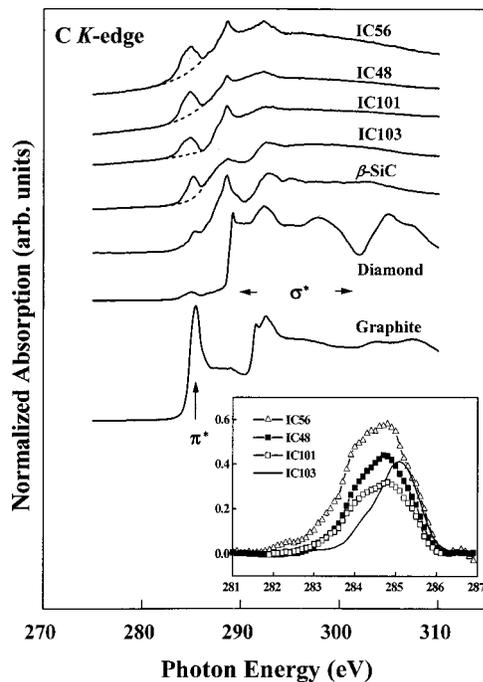


FIG. 1. Normalized C *K*-edge absorption spectra of *a*-Si-C-N, β -SiC, diamond, and graphite. The inset shows enlargement of the π^* feature after background subtraction.

procedure for other compounds are described elsewhere.⁵

Figure 1 compares the C *K*-edge XANES spectra of *a*-Si-C-N, β -SiC, CVD-grown diamond, and graphite. Following pre-edge background subtraction, the spectra were normalized using the incident beam intensity I_0 and by keeping the area under the spectra in the energy range between 315 and 325 eV fixed (not shown completely in Fig. 1). According to the dipole-transition selection rule, the spectra in Fig. 1 are due to transitions from the carbon 1*s* core level to the *p*-like final states above the Fermi level. The general C *K*-edge XANES spectra of the *a*-Si-C-N films, which reflect local environments of the carbon atoms, seem different from those of the diamond and graphite but quite similar to that of β -SiC. The XANES energy range for the diamond is typically divided into two regions characterized by (1) the spike of the C 1*s* core exciton resonance at approximately 289.2 eV, and (2) a relatively broad σ^* feature of the sp^3 -bonded carbon occurring between about 290 and 302 eV.^{7,8} The relatively weak (strong) peak at ~284.5 (285) eV in the diamond (graphite) spectrum shown in Fig. 1 can be assigned to the π^* states of sp^2 -bonded carbon.⁹ The pre-edge π^* peak at ~284.5 eV in the *a*-Si-C-N spectra exhibits not only greater intensity but also a slight shift toward the lower energy side by 0.2–0.6 eV relative to that in the β -SiC spectrum. The lack of long-range order in the amorphous compound has long been understood to cause the excited electrons to be more localized near the core hole. The localization enhances electron–hole interaction and increases the binding energy of the excited electrons.^{10–12} The inset of Fig. 1 displays the π^* peaks for several carbon contents after a background best fit with Gaussian curves, shown by the dashed lines, was subtracted. The inset of Fig. 1 shows that the intensities and widths of the π^* peak decrease and that its position shifts toward the higher energy side as the carbon content increases. The relatively large π^* peak shows that a

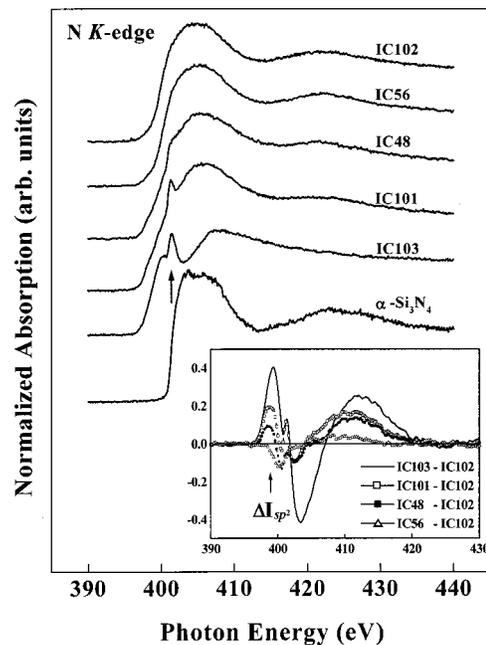


FIG. 2. Normalized fluorescence-yield N *K*-edge absorption spectra of *a*-Si-C-N and α -Si₃N₄. The inset shows the difference curves between the spectra of the *a*-Si-C-N films and those of the carbon-free sample for four different carbon contents.

substantial percentage of carbon atoms in the *a*-Si-C-N films have graphite-like sp^2 bonding.

Figure 2 shows the normalized N *K*-edge XANES spectra of *a*-Si-C-N and α -Si₃N₄. The spectra of the low-carbon-content *a*-Si-C-N are quite similar to those of α -Si₃N₄ except that the threshold is 1–3 eV lower and the width of the feature near the threshold is broader. The similarity among the spectra of low-carbon-content *a*-Si-C-N, α -Si₃N₄, and *c*-Si-C-N suggests that the local environments of nitrogen atoms are generally similar in these materials.³ The shifts of the threshold in the *a*-Si-C-N spectra toward lower energies relative to that in the α -Si₃N₄ spectrum may be attributed to disorder-induced bond length deviations that broaden the unoccupied N 2*p* band, so that the edge extends into lower energy side. The spectra of *a*-Si-C-N with a higher carbon or lower nitrogen content contain a sharp peak (marked by the vertical arrow) at ~401.4 eV near the threshold, and are similar to the spectra of the amorphous carbon nitride films.¹³ The sharp peaks were assigned to the π^* states of the sp^2 C–N bonds (a nitrogen atom bounded to trigonal carbon atoms).^{14–16} The inset of Fig. 2 shows the difference curves of the N *K*-edge XANES spectra of *a*-Si-C-N relative to those of the carbon-free sample (No. IC102). The region between ~396 and 402 eV contains an enlarged sharp peak. The intensity of the sharp peak shown as ΔI_{sp^2} in the inset increases with the carbon content. The emergence of the sharp peak at ~401.4 eV when the carbon content is larger than between 9% and 36% suggests that carbon and nitrogen atoms in *a*-Si-C-N tend to form local graphitic carbon nitride.

The enlarged carbon sp^2 -bond features between 282 and 286 eV in the C *K*-edge XANES spectra are shown in the inset of Fig. 1. The intensities were integrated to qualitatively show the dependence of the π^* feature of the carbon sp^2 bond on the carbon and nitrogen contents in the

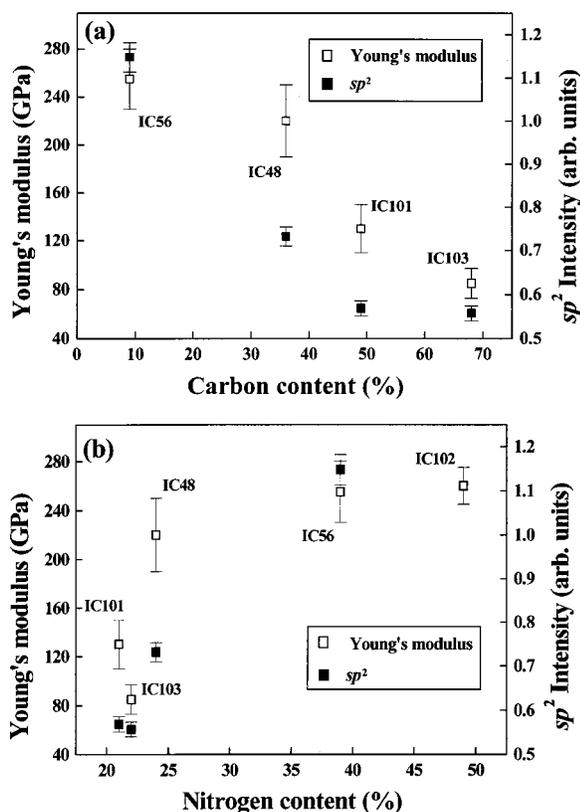


FIG. 3. (a), (b) Young's modulus and the integrated intensity of the *sp*²-bond feature at the *K* edge as functions of the carbon and nitrogen contents, respectively, for the *a*-Si-C-N films.

a-Si-C-N films. Figure 3(a) and 3(b) compare the Young's moduli given in Table I and the integrated intensities of the *sp*²-bond feature as functions of the carbon and nitrogen contents, respectively. Figure 3(a) shows that both the Young's modulus and the integrated intensity of the carbon *sp*²-bond feature decrease as the carbon content increases. It is generally thought that, in carbon-related materials, the *sp*³- and *sp*²-bonded carbon contribute to the hardness and softness of the materials, respectively. On this line of thought, our observed decrease of the intensity of the *sp*²-bond feature will indicate the softening of *a*-Si-C-N with an increase of the carbon content, which is opposite to the trend suggested by the measured Young's moduli. The concept of softening of the carbon-related materials by the *sp*²-bonded carbon is based on the softness of the graphite, which has an extended layered structure with very weak bonding between the layers. However, in amorphous carbon-related materials, there is no such extended or long-range *sp*² layer and no weak bonding between the layers. Thus, the local *sp*² bonding in amorphous carbon-related materials does not necessarily lead to the softening of the materials. Figure 3(b) shows that both the Young's modulus and the integrated intensity of the carbon *sp*²-bond feature increase with an increase of the nitrogen content. Based on studies of amorphous carbon nitride films, carbon atoms were observed to form *sp*² C-N bonds with nitrogen atoms¹⁴⁻¹⁶ as men-

tioned in the previous paragraph. From this finding, our result suggests that the increased intensity of the *sp*²-bond feature is due to an increase of the number of graphitic C-N bonds. Table I and Fig. 3(b) show that the *a*-Si-C-N film with zero carbon and the largest nitrogen contents, which does not have any *sp*² C-N bond, has the largest Young's modulus. Then the Young's modulus decreases with a decrease of the nitrogen content. Thus, the Young's modulus or the hardness of the *a*-Si-C-N film seems to predominantly depend on nitrogen not on carbon. We have not studied *a*-Si-C-N films with small nitrogen contents, which can be regarded as N doping of *a*-Si-C films. However, if our result is extrapolated to the small nitrogen content, our result may be related to previous experimental findings of the enhancement of the carbon *sp*²-bond feature by nitrogen in N-doped tetrahedral bonded amorphous carbon films^{17,18} and in theoretical calculations for a wide range of stoichiometries in the amorphous carbon nitride system.¹⁹

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¹ *Proceedings of the 10th European Conference on Diamond, Diamond-like Materials, Carbon Nanotubes, Nitrides, Nitrides and Silicon Carbide*, edited by J. Robertson, H. Güttler, H. Kawarada, and Z. Sitar, 1999.

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