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Electronic and atomic structures of Si–C–N thin film by X-ray-absorption spectroscopy¹

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Abstract

This study measures X-ray absorption spectra of crystalline (c)-Si–C–N thin film at the C and Si *K*-edge using the sample drain current mode, and at the N *K*-edge using the fluorescent mode. A resonance peak resembling the C 1s core exciton in CVD-diamond/Si is observed, and a broad feature occurring in the energy range between ~290 and 300 eV can be assigned to the antibonding C 2p–Si 3sp hybridized states and the C 2p–N 2sp hybridized states as well. Analysis of the N *K*-edge near edge absorption spectra reveals a similar feature in c-Si–C–N and a-Si₃N₄, suggesting that nitrogen atoms generally have similar local environment in these two materials. Moreover, results obtained from Si *K*-edge absorption spectra for c-Si–C–N demonstrate a proportional combination of local Si–N and Si–C bonds, associated with the local tetrahedral C–Si–N₃ as well as the long-range ordered atomic structure around Si atoms. © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

Silicon carbide (Si–C) and silicon nitride (Si–N) are highly promising for wide applications in mechanics, optics and electronics [1]. Carbon nitride (C–N), another binary compound, has recently also received extensive attention owing to its potential

applications in new hard materials [2]. The importance of Si–C and Si–N as well as the hypothetical C–N binary systems suggested that the ternary Si–C–N system may be similarly important. However, detailed analyses of the local electronic and atomic structures of this ternary system have seldom been performed. Recently, Gheorghiu et al. [3] and Ténégal et al. [4] have reported Si *K*-edge extended X-ray absorption fine structure (EXAFS) studies of nanometric Si–C–N powders. However, they obtained different atomic structures. Gheorghiu et al. suggested the existence of

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a local C–Si–N₃ arrangement around Si atoms, which is in contrast to the Si atoms randomly linked together through the C–N network proposed by Ténégat et al. Trying to clarify this discrepancy, we have performed an analysis of C, N, and Si *K*-edge X-ray absorption spectra for the *c*-Si–C–N thin film.

2. Experiment

The C, N, and Si *K*-edge X-ray absorption spectra of the *c*-Si–C–N thin film with that of chemical-vapor-deposition (CVD)-grown diamond on Si substrate, α -Si₃N₄ powders, and thin film β -SiC and *c*-Si(100) as references were measured using the high-energy spherical grating monochromator (HSGM) and InSb(111) double crystal monochromator (DCM) beamlines, 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 for C and Si *K*-edge were measured using the sample drain current mode. The fluorescence measurements for N *K*-edge spectra were taken with a high-sensitivity seven-element Ge detector at room temperature. The *c*-Si–C–N sample was grown by a microwave plasma-enhanced chemical vapor deposition process on a crystalline Si(100) substrate. Details of the preparation procedure for similar compounds can be found elsewhere.[5]

Fig. 1. Normalized C *K*-edge absorption spectra of β -SiC, *c*-Si–C–N, and diamond/Si.

3. Results and discussion

Fig. 1 illustrates the C *K*-edge X-ray absorption near edge structure (XANES) spectra of β -SiC, *c*-Si–C–N, and CVD-grown diamond on Si substrate (abbreviated hereafter as diamond/Si) for comparison. According to this figure, the spectra of diamond/Si clearly display a sharp feature closely resembling that reported in earlier works [6]. The spike of the C 1s core exciton resonance at ~ 289.2 eV and a relatively broad sp^3 bonded carbon of σ^* features occur between 290 and 302 eV. The relatively small peak at ~ 285 eV of diamond/Si obviously appears due to nondiamond-like sp^2 bonded carbon of π^* states [7]. On the other hand, the C 1s core exciton resonance of β -SiC displays a relatively broader feature than that of the diamond/Si. We attribute the main broader feature of the near-edge region in β -SiC to dipole-allowed transitions of photoelectrons from C 1s states to unoccupied 2p states, which have been hybridized significantly with the Si 3sp states according to the calculated density of states for β -SiC [8]. Meanwhile, we infer, as for the case of diamond/Si, that the relatively broad resonance peak of the *c*-Si–C–N can also be attributed to the C 1s core excitonic state. Furthermore, based on results of the first-principles calculations using the pseudofunction method [9], the pre-edge π^* -like peak and the broad feature occurring in the energy range between ~ 290 and 300 eV on the C *K*-edge spectra of *c*-Si–C–N, can also be assigned to the antibonding C 2p–Si 3sp hybridized states and the C 2p–N 2sp hybridized states as well.

Fig. 2 displays the photon-flux-normalized N *K*-edge XANES spectra of the *c*-Si–C–N film and α -Si₃N₄ powders. This figure shows a splitting double-peak features near 406.0 and 403.8 eV in the α -Si₃N₄ spectrum. Based on the calculated density of states for N 2p symmetry [10], the double-peak at N *K*-edge spectra of α -Si₃N₄ can be attributed to antibonding N 2p–Si 3p and N 2p–Si 3s hybridized states. In addition, our experimental results indicate a nearly identical spectra between *c*-Si–C–N and α -Si₃N₄, implying that nitrogen atoms clearly have similar local environment in both *c*-Si–C–N and α -Si₃N₄. Consequently, the white line features at the N *K*-edge spectra of the *c*-Si–C–N can be assigned primarily to the antibonding N

Fig. 2. Normalized N *K*-edge absorption spectra of *c*-Si-C-N and α -Si₃N₄.

2*p*-Si 3*sp* hybridized states and the N 2*p*-C 2*sp* hybridized states.[9]

Fig. 3 displays the photon-flux-normalized Si *K*-edge XANES spectra for *c*-Si(100), *c*-Si-C-N, α -Si₃N₄, and β -SiC. In the case of *c*-Si(100), the Si *K*-edge XANES spectrum reflects transition from the Si 1*s* core level to unoccupied Si 3*p*-derived states. This figure also displays characteristic double-peak features (labeled as two vertical dashed lines) above the edge and its approximate 1.0 eV energy

Fig. 3. Normalized Si *K*-edge absorption spectra of *c*-Si(100), *c*-Si-C-N, α -Si₃N₄, and β -SiC.

separation. Fig. 3 also clearly exhibits the threshold in the Si *K*-edge XANES of *c*-Si-C-N film shifting toward higher binding energies, and the general line-shape of the spectra distinctly differing from that of *c*-Si(100). This observation reveals that the chemical states of the absorbing silicon atoms within *c*-Si-C-N are obviously altered in comparison with that of *c*-Si(100), and no segregation of silicon atoms or silicon atoms occurs for the local Si-Si bonds in the *c*-Si-C-N. Furthermore, as seen in Fig. 3, the Si *K*-edge XANES spectra for *c*-Si-C-N and α -Si₃N₄ are shown to be quite similar, both consisting of a main peak (labeled A) and accompanied by a shoulder (labeled B). However, the *c*-Si-C-N spectrum has a more prominent peak B and peaks A and B appear to be well resolved. We suggest that the prominent peak B in *c*-Si-C-N could be due to the existence of local Si-C bonds around silicon atoms so that the energy position of peak B is quite close to that of the maximum peak of β -SiC, which is supported by the result of C *K*-edge XANES which indicates the occurrence of local C-Si bonds in *c*-Si-C-N and our theoretical calculations [9]. In order to precisely determine the local environment around silicon atoms and to verify the conclusions deriving from the C, N and Si *K*-edge XANES spectra for the *c*-Si-C-N as discussed above, the Si *K*-edge EXAFS spectra were measured from *c*-Si-C-N using the sample drain current mode at room temperature [11]. We found that the Si atoms are bounded with three Si-N and Si-C bonds. Thus, the local atomic structure of *c*-Si-C-N, on average, is quite similar to that of the tetrahedral C-Si-N₃ arrangement and its crystal structure is probably α -Si₃N₄ phase, which further confirms the conclusions deriving from the C, N and Si *K*-edge XANES spectra for the *c*-Si-C-N.

4. Conclusions

In summary, combining the C and N *K*-edge XANES and Si *K*-edge XANES and EXAFS results for the *c*-Si-C-N film, we conclude that the silicon atoms in *c*-Si-C-N have similar local structure to that of α -Si₃N₄, showing the existence of a local tetrahedral C-Si-N₃ arrangement and having a long-range ordered atomic structure, rather than the Si

atoms randomly linked together through the C–N network.

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