

The affinity of Si–N and Si–C bonding in amorphous silicon carbon nitride (a-SiCN) thin film

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Abstract

The bonding sensitivities of Si–N and Si–C bonds in the a-SiCN thin films were investigated experimentally and theoretically. It was found that a sharp phase transition from the predominantly Si–C bonded structure to the Si–N bonded structure occurs during the deposition of SiCN thin films without and with N incorporation. The stronger affinity of silicon to bond with nitrogen than to bond with carbon results in the complete absence of Si–C bonds in a-SiCN thin films. These were further verified by the analyses of crystal structures and local bonding configurations, morphology, and optical properties. Finally, the relative stabilities of Si–C and Si–N bonds in the a-SiCN network were studied by the ab initio calculations for the simple SiCN clusters. The local atomic structure with Si–N–C (or Si–N=C) bonding exhibits a considerably lower total energy of 0.65 (0.52) eV than that with Si–C–N (Si–C=N) bonding, providing the explanation of the stronger affinity of Si–N bonds than Si–C bonds in a-SiCN thin films.

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1. Introduction

The syntheses of ternary Si–C–N materials have been attracting growing interest due to their excellent physical properties, such as high hardness [1], oxidation resistance [2] and high thermal diffusivity [3]. In addition, crystalline SiCN films exhibited a wide band gap of 3.8 eV, suitable for optoelectronic application in the blue–UV range [4]. Several techniques have been developed to produce various kinds of Si–C–N composite (SiCN) films. For example, amorphous SiCN films synthesized by thermal chemical vapor deposition (CVD) techniques showed a hardness in the range of 27–38 GPa and a stiffness of 224–289 GPa [1], whereas a-SiCN films deposited by electron cyclotron resonance plasma CVD

possessed a hardness of 22 GPa [5]. The physical properties depend, not only on the composition, but also on the chemical bonding and local atomic order of constituent elements in the films, which are strong functions of the process parameters. Compared to the hardness predicted for the hypothetical β -C₃N₄ [6], the values measured for the Si–C–N materials were much lower, although the addition of silicon was expected to promote the formation of sp³-hybridization of carbons bonds and also of the additional bonds with nitrogen [7]. Structural and local bonding analyses of SiCN films performed by X-ray diffraction (XRD) spectroscopy and X-ray-absorption near-edge structure (XANES) suggested that SiCN demonstrates similar local atomic structure to α -Si₃N₄ with the substitution of C atoms only for the Si sites [8]. High resolution X-ray photoelectron spectroscopy (XPS) scans of Si(2p), C(1s) and N(1s) peaks reveal Si–N peak as well as C–N and C=N peaks but undetectable Si–C signal for SiCN films prepared by different CVD techniques [9]. The origin of the complete

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absence of Si–C bond in the SiCN network is still not clear. To explore the knowledge of bonding sensitivity in the a-SiCN films becomes crucial to understand the basic physics for future applications.

In this study, various compositions of Si, C and N in the a-SiCN films were studied systematically to investigate the bonding sensitive properties in a-SiCN films. The physical properties of structural, chemical bonding, surface morphology, and optical properties were characterized by XRD, XPS, scanning electron microscopy (SEM) and the micro-reflectometry system respectively, were performed to characterize the structural and chemical bonding properties. In parallel, the ab initio total energy calculations were performed to study the stabilities of local bonding configurations in a-SiCN film using the cluster model approximation. The information is expected to improve the understanding of the mechanism governing the bonding sensitivity in a-SiCN films.

2. Experimental methods

Microwave CVD systems (MW-CVD, AsTex, 5 kW) were employed to grow the SiCN films on the Si(100) and fused silica substrates respectively. Details of the MW-CVD systems have been described elsewhere [9]. In brief, a 1.5 kW microwave source was employed to generate plasma as a mixture of semiconductor grade SiH₄, NH₃, CH₄ and H₂ gases in various proportions was used to deposit a-SiCN thin films. By adjusting the flow rate ratio of different gases, films with various compositions were obtained. A microwave power of 1000 W was set and the chamber pressure was kept about 3.73 kPa during deposition. In order to systematically investigate the bonding sensitivities of a-SiCN films, we performed the experiments by varying the NH₃ or CH₄ flow rates and by keeping other gas flow rates constant during deposition. Incorporation of hydrogen in the film is inevitable in most CVD process. It has been reported that the a-SiCN films with and without hydrogen incorporation prepared by CVD and ion-beam sputtering deposition (IBS), respectively, show similar chemical compositions and bonding states of C, N, and Si. Incorporation of hydrogen assists the formation of C–H, N–H and Si–H bonds in the films, resulting in the termination of dangling bonds of the a-SiCN network [5]. The chemical composition and bonding states of the a-SiCN films were determined by a Perkin-Elmer Phi 1600 XPS system with a (800- μ m)² sampling area and 11.75 eV pass energy. MgK α radiation of 1253.6 eV was used as the X-ray source, with a line width of 0.7 eV. To obtain information about the chemical bonding states, scans of Si(2p), C(1s), and N(1s) peaks of a-SiCN films were performed. Optical properties of refractive index, transmittance and film thickness were determined by the spectral micro-reflectometry (Mission peaks optics), which allows optical measurements in the UV–visible range of wavelength (250–1000 nm).

3. Structural simulation

This paper concerns the nature of the bonding sensitivity of Si, C, N in a-SiCN films. We have calculated the total energy of various Si, C, N configurations based on the simple cluster model with the bonds at the cluster surface terminated by hydrogen rather than use the periodic amorphous network as others [10]. This will mimic the local environment at the stage when the formation of chemical bonds from the dissociated gas during deposition is taking place. The total energy and electronic structure calculations were performed using the CASTEP code and the detailed simulation method has been described elsewhere [11].

4. Results and discussions

In order to investigate the bonding sensitivities of Si, C and N in a-SiCN films, we systematically varied the compositions of the films by controlling the flow rate ratio for different gases. Firstly, we varied the NH₃ flow rate gradually from 0 to 30 sccm and kept the flow rates of SiH₄ 3 sccm, CH₄ 30 sccm and H₂ 100 sccm unchanged during deposition. With the XPS scans of C(1s), N(1s), and Si(2p) peaks, information about the bonding behavior could be obtained. Fig. 1(a),(b) shows the XPS spectra of the deposited films without and with the addition of NH₃ gas. For Si(2p) spectra, the 99.2-, 100.3-, 102.7- and 104.6-eV peaks are attributed to the Si(2p)–Si, the Si(2p)–C, and Si(2p)–N and Si(2p)–O bonds, respectively. For the film without NH₃ addition, the XPS spectrum belonging to the Si(2p) with strong peak at 100.3 eV is the signature of the Si–C bonds and the spectra belonging to the C(1s) content with peaks centered at 282.8 and 284.6 eV are the signatures of C–Si and C–C, respectively, indicating the mixing phases of SiC and diamond-like carbon. As we slowly increased the NH₃ content, a significant phase transition was observed. Fig. 1(b) shows the XPS spectra of the a-SiCN sample with a composition of 20% C, 35% N, 41% Si and 4% O after the addition of NH₃ with a flow rate of 6 sccm (the minimum detectable flow rate for our nitrogen mass flow controller). The contribution at 102.0 eV in the Si(2p) peak is related to Si–N, suggesting that the major part of Si within the film was bonded to N with a complete vanish of the Si–C signal at the energy of 100.3 eV. For the C(1s) and N(1s) peaks, 285.9 and 287.7 eV as well as 397.8, 398.3 and 400.1 eV, are attributed to sp² trigonal C=N bonding, C–N bonds, N–Si bonds, N–C bonds, and N bonded to an sp²-hybridized C, respectively. There are no major peaks that match the C–Si bonding energy at 282.8 eV or the Si–C binding energy at 100.3 eV, suggesting the absence of Si–C bonds in the a-SiCN film after NH₃ gas was introduced during deposition. This result can be further verified by XRD spectra as shown in Fig. 2(a) and (b). The two pronounced diffraction peaks located at $2\theta \approx 33$ and 35.8° in Fig. 2(a) correspond to the

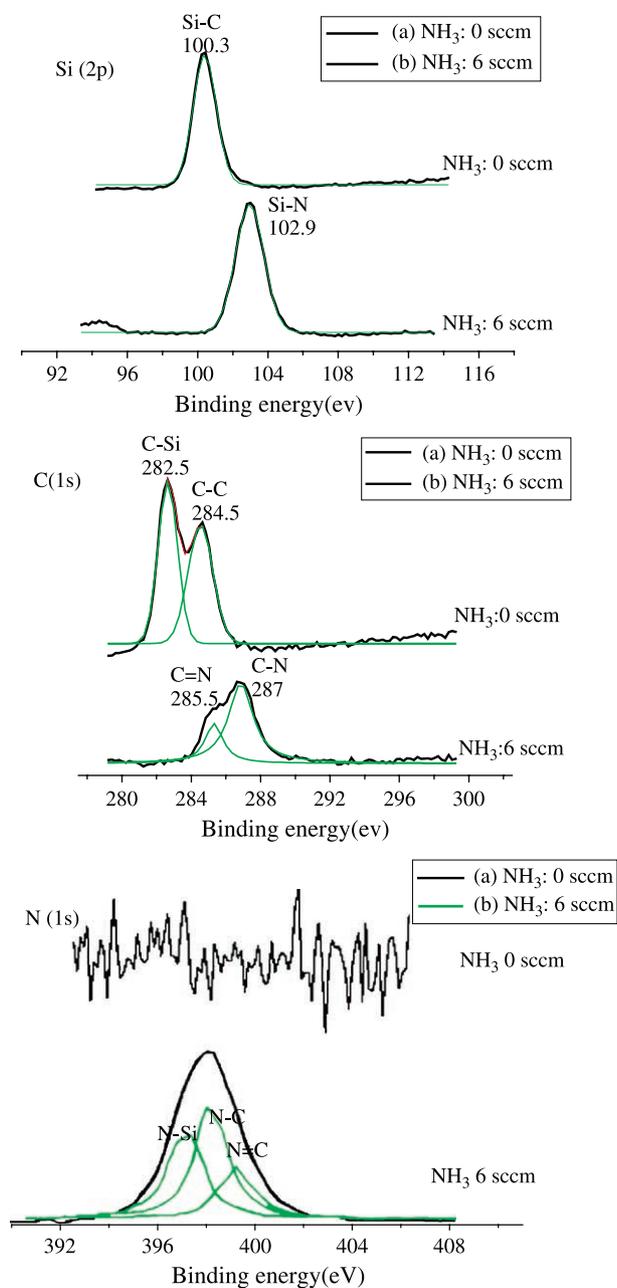


Fig. 1. High resolution XPS of the thin films deposited by us varying the NH_3 flow rate (a) 0 sccm and (b) 6 sccm and by keeping the constant flow rates of SiH_4 3 sccm, CH_4 30 sccm and H_2 100 sccm.

$\text{Si}(100)$ substrate background and the 3C-SiC crystal, respectively, indicating the formation of the SiC crystal under the condition without any addition of NH_3 . Fig. 2(b) shows the XRD spectrum of the a- SiCN film after the incorporation of NH_3 gas. In addition to the signal of the $\text{Si}(100)$ substrate background, no peak was observed, indicating the formation of amorphous phase. The SEM micrographs of the thin films in Fig. 3 show the transition from the SiC nanocrystalline phase to the amorphous SiCN phase after N incorporation. The stronger affinity of silicon to bond with nitrogen than to bond with carbon suggests the local bonding structure of SiCN is similar to Si_3N_4 with C

atoms substitution only for the Si sites. This result is further evident by the spectra of the refractive index for the films without and with N incorporation as shown in Fig. 4. The dispersion of the refractive index for the film without N incorporation exhibits a value from 2.5 to 2.65 close to that of SiC (~ 2.6). On the other hand, the refractive index of the film with N incorporation varies from 2.1–2.15 close to that of Si_3N_4 (~ 2.0).

Next, we carried out a series of experiments by varying the CH_4 flow rate from 0 to 30 sccm and keeping the flow rates of SiH_4 3 sccm, NH_3 20 sccm and H_2 100 sccm unchanged during deposition. The dependence of compositions of the SiCN films as a function of the CH_4 flow rate is shown in Fig. 5(a). It is shown that the C content in the SiCN films gradually increases with the increasing CH_4 flow rate up to 15 sccm and reaches to a value around 25% for the 30 sccm CH_4 flow rate. No significant variation of carbon content has been found in the a- SiCN thin films with further increasing the CH_4 flow rate under current experimental conditions. The XPS spectra (not shown here) for all these samples demonstrate similar signatures to those obtained in Fig. 1(b) but only with the variations of the area ratio of C-N/C=N (or N-C/N=C) in the $\text{C}(1\text{s})$ (or $\text{N}(1\text{s})$) spectra. All the Si atoms are found to bond to N with no detectable Si-C signal. The absence of the peaks that

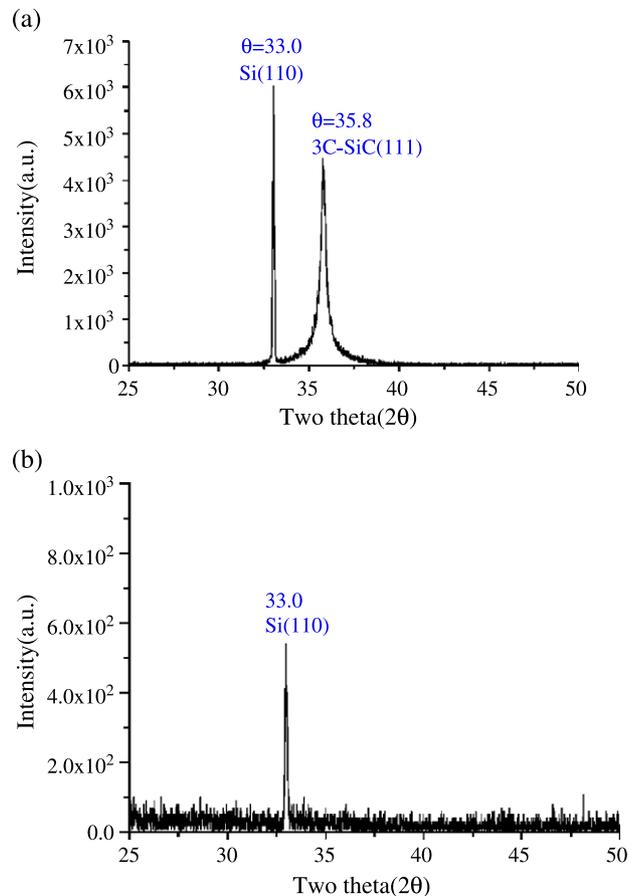


Fig. 2. X-ray diffraction spectra of (a) SiC nanocrystalline and (b) a- SiCN thin film.

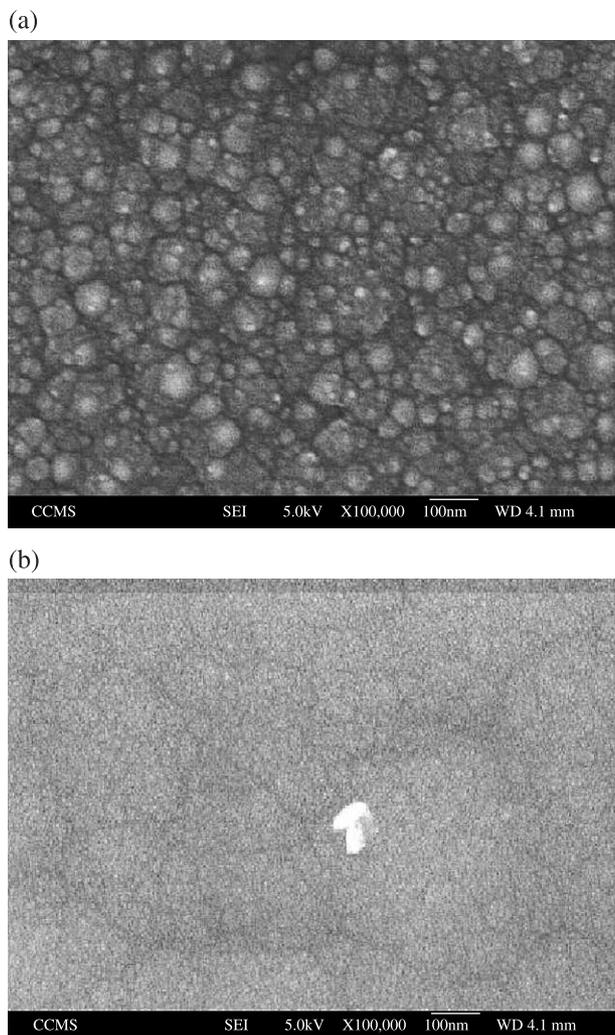


Fig. 3. SEM surface morphology of (a) SiC nanocrystalline and (b) a-SiCN thin film.

match the C–Si and Si–C binding energies again support the strong affinity of Si–N bonding compared to the Si–C bonding in the SiCN thin films during deposition. As the C content increases in the SiCN film, the intensities of C=N

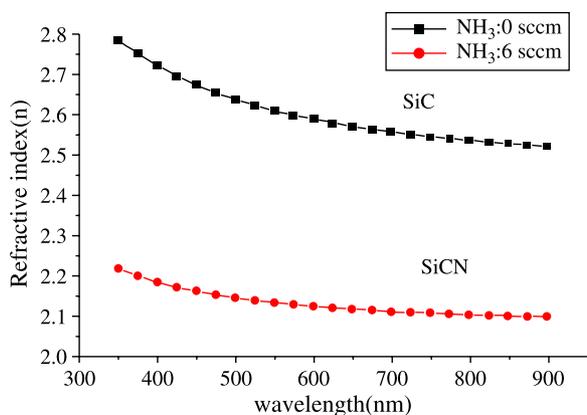


Fig. 4. The dispersion of optical refractive index of the thin films deposited without and with N incorporation.

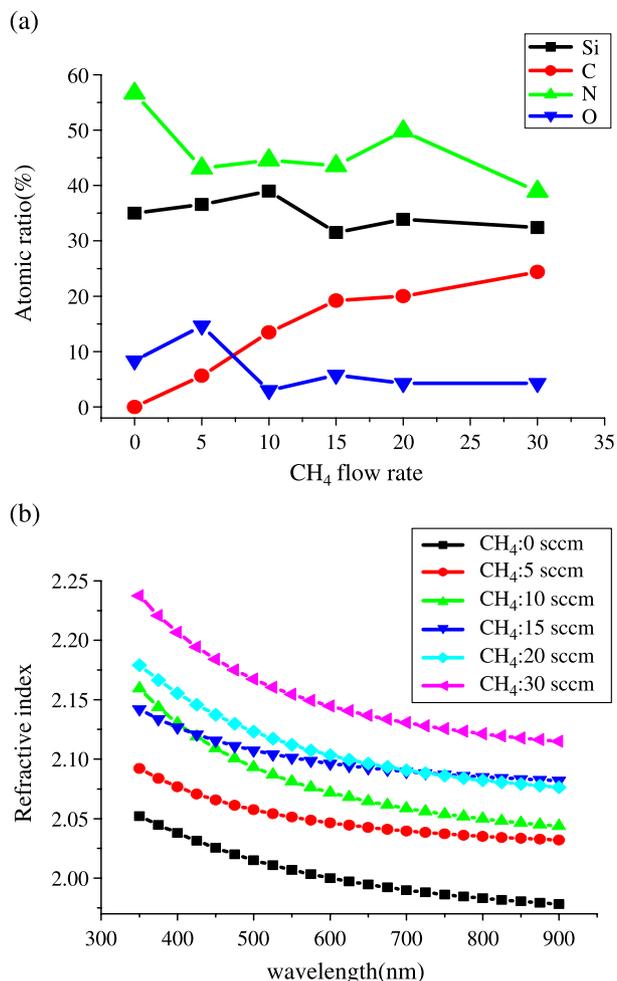


Fig. 5. (a) The dependence of compositions of the SiCN films as a function of the CH₄ flow rate. (b) The dispersion of refractive index for a-SiCN thin films with various carbon content.

bond signals in both C(1s) and N(1s) XPS spectra also enhance, indicating the difficulty to keep sp³-bonded C atoms in the a-SiCN network when the carbon content increases. This result is consistent with the physical properties of the thermal diffusivity, density and hardness of a-SiCN thin films decreased with increasing carbon content [3]. The dispersion of refractive index for a-SiCN thin films with various carbon content is shown in Fig. 5(b). The refractive index values $n(\lambda)$ of the a-SiCN thin films increase as the carbon content increases. The refractive index of the a-SiCN thin films varies from ~2.0 to ~2.2

Table 1

The relative stability of Si–C–N and Si–N–C clusters (or Si–C=N and Si–N=C) clusters by taking the total energy of Si–C–N (or Si–C=N) as zero

	Si–C–N	Si–N–C
Energy (eV)	0	–0.67
	Si–C=N	Si–N=C
Energy (eV)	0	–0.52

The unsaturated bonds are saturated by H atoms.

while the carbon content changes from 0% to 25%. These values are relatively closer to that of Si_3N_4 (~2.0) compared to that of SiC (~2.6) due to the similarities of local bonding configurations between SiCN and Si_3N_4 as mentioned above.

The total energies of the possible configurations for the SiCN clusters calculated by the ab initio method are shown in Table 1. The unsaturated bonds in all configurations were terminated by hydrogen atoms to avoid the boundary effects. It is clearly shown that the Si–N–C cluster has a much higher stability compared to the Si–C–N cluster with a lower energy about 0.65 eV. This value is considerably large in the small molecular cluster approximation. The Si–N exhibits a shorter bond length of 1.69 Å than that of Si–C of 1.86 Å. The energetics of local bonding configurations suggests that strong affinity to form Si–N rather than to form Si–C occurs for the dissociated gas radicals of Si, N, C, H during chemical vapor deposition. The Si–N=C cluster with the Si–N bond length of 1.71 Å also shows a lower energy of 0.52 eV than the Si–C=N cluster with the Si–C bond length of 1.87 Å.

5. Conclusion

The bonding sensitivities of Si–N and Si–C bonds in the a-SiCN thin films were investigated experimentally and theoretically. A sharp transition from the predominantly Si–C bonded structure to the Si–N bonded structure was found during the deposition of SiCN thin films without and with N incorporation. The stronger affinity of Si–N bonds over Si–C bonds in the SiCN thin films were further verified by the analyses of local bonding configurations and crystal structures characterized by XPS and XRD, surface morphology by SEM and optical properties

measured by micro-reflectometry. Finally, ab initio calculations for the simple SiCN cluster were performed to study the relative stabilities of Si–C and Si–N bonds in the a-SiCN network. The result indicates that the atomic structure with Si–N bonding shows a more stable configuration compared to that with Si–C bonding in terms of lower total energy and shorter bond length. From the experimental and theoretical studies, the origin of the complete absence of Si–C bond in the SiCN thin films during deposition can be explained.

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