Raman analysis of Si-C-N films grown by reactive magnetron sputtering

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Abstract

Silicon carbon nitride thin films have been deposited by reactive magnetron sputtering of silicon and graphite targets in mixed Ar/N₂ atmosphere at substrate temperature of 300 °C. The substrate bias voltage varied from -50 up to +50 V and the nitrogen flow rate varied from 0 to 20 sccm. The as-deposited films were analyzed by Raman spectroscopy (RS) and X-ray photoelectron spectroscopy (XPS). The Raman analyses show that the film without nitrogen incorporation has mixed sp²-sp³ hybridized carbon structures while those with nitrogen introduction give rise to nitrogen-bound sp¹-, sp²- and sp³-coordinated carbon structures as well as Si-N phase. The change of the D band position (~1360 cm⁻¹), FWHM and its relative intensity with respect to the G band (~1595 cm⁻¹), I_D/I_G, seem to be correlated with the formation of these phases and therefore to the deposition conditions. XPS analyses not only confirm the bonding natures revealed by Raman spectroscopy, but also give quantitatively the relative importance of the phases. It was shown that the area ratio of the nitrogen-bound sp³- to sp²-coordinated carbon bonds is: 1.41:1.38:1.8:3.19 and that of Si-N bonds to (Si-N+Si-C) bonds is 0.4:0.5:0.9:1 for the Si-C-N films prepared with 5, 10, 15 and 20 sccm nitrogen flow rate, respectively.

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1. Introduction

Both silicon carbide and silicon nitride systems have been expected to offer great potential for mechanical, optical, electronic and other applications due to their attractive properties such as hardness, chemical stability and large band gap. Carbon nitride, another binary system has also attracted much attention in recent years owing to the theoretical prediction that this compound, preferably in the form of β-C₃N₄ which has the same structure as β-Si₃N₄, might have a bulk modulus comparable to that of diamond [1,2]. However, efficient methods for synthesizing pure crystalline β-C₃N₄ have not yet been found. It is expected that a Si-C-N ternary system may exhibit all the useful characteristics of these binary compounds. Recently, much attention has been drawn on the synthesis and characterization of Si-C-N films. It has been found that Si-C-N films have low friction coefficient [3], wide band

gap [4-6], high chemical inertness [7] and refractive index [3,6]. These features are strongly dependent on the composition and chemical environments of Si, C and N atoms, rather than integrity of pure Si₃N₄ and SiC. Si-C-N thin films are generally prepared by chemical vapor deposition (CVD) [8-11], reactive (N₂) magnetron sputtering [3,12,13] or ion-plasma sputtering of a SiC target [14], laser ablation of a SiC target in a nitrogen atmosphere [15,16], magnetron sputtering of SiC and graphite targets at room temperature [17] and rf reactive sputtering of a solid silicon target in Ar+H₂+N₂+CH₄ atmosphere [18]. In this work, we report the Raman and XPS analyses of Si-C-N films deposited by reactive (N₂) magnetron sputtering of silicon and graphite targets with different nitrogen flow rate and substrate bias voltage.

2. Experimental details

Si-C-N thin films were deposited on stainless-steel (AISI 316) substrates by reactive rf magnetron co-

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sputtering of pure silicon and carbon in a mixed Ar/N₂ atmosphere using Alcatel SCM 650 apparatus. A fixed silicon fraction on the carbon target erosion track with was used. The substrates were ultrasonically cleaned and sputter etched for 10 min in a 0.4 Pa Ar atmosphere (200 W rf power) prior to deposition. During deposition, the substrate temperature was kept at 300 °C and the target-substrate distance was 65 mm. Argon flow was set to 100 sccm. Three groups of samples were prepared. The first group was synthesized with different nitrogen flow rate (0, 5, 10, 15, 20 sccm) under fixed substrate bias voltage (0 V) and rf power (300 W), the second group with different bias (-50, 0, +25, +50 V) and fixed nitrogen flow (15 sccm, except the one at -50 V using 20 sccm) and rf power (300 W), and the third group with different rf power (100, 300, 500 W) and fixed nitrogen flow (20 sccm) and bias (-50 V). Only the first group of samples will be discussed in detail in this paper. Raman spectra were acquired with a Renishaw 2000 Raman spectrometer and a 633 nm excitation line. The X-ray photoelectron spectroscopy (XPS) analyses were performed using an Axis Ultra system with a monochromated Al K_α (1486.6 eV) X-ray source with an energy resolution of 0.48 eV. The binding energy values of the photoelectron peaks were measured with an accuracy of ±0.1 eV. The spectrometer was calibrated with photoelectron lines of clean pure Cu, Ag and Au foils at binding energies of 932.8 eV (Cu 2p_{3/2}), 368.1 eV (Ag 3d_{5/2}) and 84.1 eV (Au 4f_{7/2}).

3. Results and discussion

Fig. 1 shows the Raman spectra of the Si-C-N films deposited with different nitrogen flow. In the region from 1000 to 2000 cm⁻¹, the single Raman band situated at 1440 cm⁻¹ can be assigned to C-C bonds in the film

Fig. 1. Raman spectra of Si-C-N films with different nitrogen flow rate: (a) 0 sccm; (b) 5 sccm; (c) 10 sccm; (d) 15 sccm; (e) 20 sccm.

without nitrogen flow (Fig. 1a). This C-C signature, already observed in Si-C alloys with carbon excess, corresponds to a specific structure, which could be described like a random covalent network of tetrahedral-trigonal bonding carbons (mixed sp²-sp³ hybridization) with distorted bond angles and bond length. A weak band appears at about 2220 cm⁻¹ in Fig. 1c-e, which can be attributed to sp¹-coordinated C=N vibration. However, this band can hardly be seen in Fig. 1b, indicating that very few C=N bonds were formed in this film. Besides, the Raman band around 720 cm⁻¹ can hardly be seen in Fig. 1a, but it is pronounced in all the other spectra. Although this band was also observed in CN_x films and generally attributed to some form of disorder [19], some contribution from Si-N and Si-C vibrations can also be involved. While few C=N bonds were found in the film of Fig. 1b, plenty of Si-N bonds may be formed. Since this band becomes more obvious with the increases of nitrogen flow rate, more contribution from Si-N vibration is expected. The broad feature around 460 cm⁻¹ suggests the presence of amorphous silicon. These indicate that nitrogen is chemically coordinated in the films b-d. Two-band feature in the region between 1000 and 1800 cm⁻¹ is obvious in the films when nitrogen is introduced. The higher frequency band (~1595 cm⁻¹) and the lower frequency band (~1360 cm⁻¹) are generally recognized as G and D band, respectively, for carbon materials. The former originates from a Raman allowed Γ point vibration corresponding to the optical phonon modes of E_{2g} symmetry and the latter is disorder-induced and associated with optical phonons close to the K point of the Brillouin zone in graphite. The D band becomes Raman active due to the lack of long range order in amorphous carbon based materials. In Si-C-N films, the band at 1595 cm⁻¹ can be assigned to the sp²-coordinated C=N vibration and sp²-hybridized C=C vibration whereas the 1360 cm⁻¹ band arises from limitation in the graphite domain size, induced by grain boundaries or imperfections, such as substitutional N atoms, sp³-coordinated carbons and nitrogen-bound sp³-coordinated carbons. Compared to the film without nitrogen introduction, plenty of sp²-coordinated C=N and sp³-coordinated C-N bonds were formed besides the C-C bonds in the Si-C-N films. Several factors, second order Raman scattering of the D band, the combination of the D and G bands, and C-H_x vibrations may account for the broad feature around 2800 cm⁻¹.

In order to determine more precisely the D and G band parameters, some authors fitted the spectra of carbon or C-N films using Gaussians while others used Lorentzian or Breit-Wigner-Fano (BWF) line shape. In order to get some more insight into the D and G band nature with the film deposition conditions, the D band was fitted with a Lorentzian and the G band with a BWF line shapes. This choice was made since the asymmetric nature of the spectra suggests a BWF line shape and the spectra cannot be well

Fig. 2. Dependence of D band (ω_D) and G band (ω_G) positions with N_2 flow rate.

fitted with either Lorentzian or Gaussian line shape. The BWF line shape originates from the coupling between a discrete phonon to an electronic continuum based on collective excitations of the electrons [20].

The asymmetric BWF line shape is described by [21]

$$I(\omega) = I_0 \frac{1 + (\omega - \omega_{BWF}/q\Gamma)^2}{1 + [(\omega - \omega_{BWF})/\Gamma]^2}, \quad (1)$$

where $1/q$ is asymmetric parameter which is a measure of the interaction of the phonon with a continuum of states, ω_{BWF} is the BWF peak frequency, I_0 is the peak intensity and Γ is the full width at half maximum (FWHM). Figs. 2–5 give dependence of the D and G band position, FWHM, relative intensity (I_D/I_G) and the asymmetric parameter ($1/q$) on the nitrogen flow rate, respectively. The G band position remains almost stable (1592–1595 cm^{-1}), while the D band shifts obviously to lower frequencies (1419–1357 cm^{-1}) when nitrogen flow rate is increased from 0 to 20 sccm. It means that the D band

Fig. 3. Variation of the line width Γ (FWHM) of D and G bands with N_2 flow rate.

Fig. 4. Dependence of intensity ratio I_D/I_G Raman bands as function of nitrogen flow.

position is much more sensitive to nitrogen incorporation. The downshift of the D band may indicate the increase of the sp^3 fraction and the formation of more nitrogen-bound sp^3 -coordinated carbons. The FWHM of the D band decreases to a minimum and then increases with nitrogen flow rate while the G band changes inversely with the D band. The relative intensity of the D band with respect to that of the G band, I_D/I_G , decreases when the nitrogen flow rate is increased from 5 to 10 sccm and then increases with increasing of the nitrogen flow rate. The same behaviour is observed for the asymmetric parameter. I_D/I_G is generally a measure for the zone edges or border phonons of the carbon clusters, or a measure of the density of defects or the degree of disorder. It has also been used to derive the sp^3 fraction in the as-deposited tetrahedral amorphous carbon films [20]. The changes of I_D/I_G may reflect the fraction of nitrogen- or non-nitrogen-bound sp^3 -coordinated carbons as well as the fraction of Si–N or Si–C species in the films. The

Fig. 5. Variation of the asymmetric parameter ($1/q$) with N_2 flow rate.

Fig. 6. Variation of elemental composition with nitrogen flow.

composition of the films was measured with XPS and the dependence of the relative contents of Si, C and N elements on the nitrogen flow rate is given in Fig. 6. It can be seen from Fig. 6 that the Si content drops considerably (from 24.2% to 3.67%) while nitrogen contents increases from 0% to 27.3% when the nitrogen flow rate is increased from 0 to 20 sccm. However, the nitrogen content does not increase linearly with nitrogen flow rate, but it approaches saturation when the nitrogen flow is above 10 sccm. More and more Si and C atoms will be replaced by nitrogen in the SiCN network when more nitrogen is introduced.

How does the nitrogen content influence the micro-structure of the Si-C-N films? With the increase of nitrogen content, more Si-N bonds or SiN_x phase and more nitrogen-bound sp^1 , sp^2 and sp^3 carbon structures will be formed in the Si-C-N networks as indicated by the Raman

Fig. 7. Experimental XPS spectra of C 1s core-level spectra of Si-C-N films with different nitrogen flow rate: (a) 0 sccm; (b) 5 sccm; (c) 10 sccm; (d) 15 sccm; (e) 20 sccm.

Fig. 8. Experimental XPS spectra of N 1s core-level spectra of Si-C-N films with different nitrogen flow rate: (a) 0 sccm; (b) 5 sccm; (c) 10 sccm; (d) 15 sccm; (e) 20 sccm.

spectra in Fig. 1. The D band is mostly influenced by nitrogen-bound sp^3 -coordinated carbons and other defects, while the G band is related to sp^2 -hybridized carbons. Figs. 7-9 show the XPS of C 1s, N 1s and Si 2p, respectively. In order to see the bonding properties, we fitted all the XPS spectra with a XPSPEAK program and discuss Figs. 7d, 8d and 9d in more detail here. Fig. 7d can be well fitted with four peaks at 284.68, 285.73, 287.05 and 288.13 eV, respectively. The peak at 284.68 eV can be identified as polymeric C-C bonds and may be attributed to amorphous carbon phase while the two peaks at 285.73 and 287.05 eV are from nitrogen-bound sp^2 - and sp^3 -coordinated carbon, respectively [17,22-25]. The peak at 288.13 eV is recognized as C-O species. C-Si bonds are not detected in spectrum 7d but detected in spectrum 7a and c. In Fig. 8d, the spectrum can be fitted with three bands at 398.51 eV

Fig. 9. Experimental XPS spectra of Si 2p core-level spectra of Si-C-N films with different nitrogen flow rate: (a) 0 sccm; (b) 5 sccm; (c) 10 sccm; (d) 15 sccm; (e) 20 sccm.

(N-sp³ carbon and N-Si bonds), 399.73 eV (N-sp¹ carbon bonds) and 400.98 eV (N-sp² carbon bonds), respectively [17,22–25]. The Si 2p spectrum in Fig. 9d can be fitted with two bands corresponding respectively to the Si-C (101.81 eV) and Si-N (102.76 eV) bonds [25]. After fitting the spectra, it is possible for us to draw the relative importance of different bonds with their corresponding sub-band intensity, i.e., area under each sub-band. With this method, we get the area ratio of Si-N bonds to (Si-N+Si-C) bonds to be 0.4:0.5:0.9:1 for spectra 9b, c, d and e. This indicates that the number of Si-N bonds increases while that of Si-C bonds decreases with increasing the nitrogen flow rate. From the fitted data of Fig. 8, we obtained the area ratio of nitrogen-sp³ carbon bonds to nitrogen-sp² carbon bonds to be 1.41:1.38:1.8:3.19 for spectra 8b, c, d, and e, respectively. It suggests strongly that the nitrogen-bound sp³ carbon hybridization increases with increasing nitrogen flow rate. This is in accordance with the Raman observations. The decrease in Si-C bond content and increase in Si-N bond content are probably caused by the partial substitution of Si and C by N atoms and the formation of Si-N (possibly Si₃N₄ phase) and C-N (C-N, C=N and C≡N) bonds with introduction of nitrogen. With increasing nitrogen flow rate, more Si-N and C-N phases, particularly the nitrogen bound sp³ carbon, will be formed in Si-C-N films. Consequently, the formation of Si-C bonds will be inhibited.

The Raman spectra for the other two groups of samples are very similar to those shown in Fig. 1b–c and will not be shown here. For the samples prepared with different rf power, a minimum is observed for all the physical quantities as the D and G band position, FWHM, I_D/I_G and I_q at the rf power of 300 W, corresponding to an optimum rf power for Si-C-N film deposition so as the film quality is concerned. The dependence of the FWHM and I_D/I_G on

Fig. 10. Variation of the line width Γ of D and G bands with bias voltage. The samples were prepared with 15 sccm nitrogen flow except the one under -50 V bias voltage which was prepared under 20 sccm nitrogen flow.

Fig. 11. Dependence of intensity ratio I_D/I_G Raman bands as function of bias voltage. The samples are the same as in Fig. 10.

the substrate bias is given in Figs. 10 and 11, respectively. Notice that the sample prepared at -50V substrate bias corresponds to a nitrogen flow rate of 20 sccm, while all the other samples were prepared using a nitrogen flow rate of 15 sccm. We see a maximum for both FWHM of the D band and I_D/I_G at +25 V substrate bias. This corresponds to the maximum of nitrogen-bound sp³-coordinated carbons. The area ratio of N-sp³ C to N-sp² C calculated from the fitted XPS spectra are: 0.62:1.80:3.49:0.94.

4. Conclusions

A series of Si-C-N films were deposited on stainless substrates with different nitrogen flow rate. Raman analyses show that Si-N, C=N, nitrogen-bound sp²- and sp³-hybridized carbon bonds were formed in the films. The position of the D band decreases with increasing nitrogen flow rate while the FWHM and the relative intensity of the D band to G band first decrease and then increase with increasing nitrogen flow rate. This indicates that the D band is not only related to the nitrogen contents, but also to the chemical environments or bonding nature of the C and N atoms. It may be closely correlated with the formation of sp³ clusters. XPS measurements confirmed the presence of the bonds revealed by Raman spectroscopy (RS). They show also that the area ratio of N-sp³ C to N-sp² C is 1.4:1.38:1.80:3.19 for the films prepared under 5, 10, 15 and 20 sccm nitrogen flow rate, respectively. These imply that the physical features of Si-C-N films can be well controlled or tailored by changing the nitrogen flow rate.

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