Effect of nitrogen flow rate on the mechanical properties of CVD-deposited SiCN thin films

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Abstract. Silicon carbonitride (SiCN) thin films were deposited on p-Si (100) substrates with different N₂ flow rates using SiC and Si₃N₄ powder precursors by chemical vapour deposition. To investigate the structural, vibrational and mechanical properties, the SiCN thin films were characterized by atomic force microscopy, Raman spectroscopy, X-ray diffraction (XRD), Fourier transform infrared and nanoindentation techniques. The XRD results reveal nanocrystals embedded with amorphous networks in the SiCN thin films. An increase in the I_D/I_G ratio with an increase in the N₂ flow rate indicated the increase of sp³ bonds in the SiCN thin film. The hardness (H), Young's modulus (E), plasticity index (H/E) and (H^3/E^2) increase with an increase in the N₂ flow rate.

Keywords. SiCN; Raman; XRD; FTIR; nanoindentation.

1. Introduction

Silicon carbonitride (SiCN) is a potential material for a wide range of applications due to their chemical stability, excellent mechanical properties and interesting optical and electronic properties [1,2]. It is prepared mostly by using physical- or chemical-based vapour deposition techniques [3–5]. The major advantage offered by this material is the possibility to tailor its properties by varying its process parameters, appropriately, for wear resistance and high-temperature applications [6,7]. Ivashchenko *et al* [8] prepared SiCN coating by plasma-enhanced chemical vapour deposition (PECVD) using hexamethyldisilane, N₂ and H₂ as precursors at various nitrogen flow rates. With the increasing N₂ flow rate, the wear resistance of the film was found to be increasing. Sundaram *et al* [9] deposited α -SiC_xN_y by radio frequency magnetron sputtering and observed that the H and E of the films were sensitive to the ratios of N₂/Ar gas flow during sputtering. The H was found to be increase with the N₂/Ar ratio. Hong *et al* [10] and Porada *et al* [11] observed an increase in the value of H and E with an increase in the N₂ flow rate. Kozak *et al* [12] investigated the effect of the N₂ flow on the properties of Si–C–N amorphous thin films produced by magnetron sputtering. Rahmann *et al* [13] reported the effect of varying N₂ flow rates on the optical properties of amorphous-SiCN thin films.

Generally, SiCN thin films deposited using the sputtering technique are likely to have microscopic defects, for example, points defects, interstitial defects, vacancy, etc., which

can affect the symmetry of the grains. The defects or stresses produced during the deposition process affect the quality of the coating. The above-mentioned research group mostly deposited SiCN thin films by sputtering techniques. Present research work is an attempt to investigate: (a) the role of the N₂ flow rate on the mechanical properties and (b) the structural and chemical networks of SiCN thin films.

2. Experimental

The Si (100) substrate was used for the deposition of SiCN thin films by the CVD technique. SiC and Si₃N₄ nanopowder was used as the source and the N₂ and H₂ mixture as the precursor. The N₂ flow rate was varied from 40 sccm to 100 sccm and the H₂ flow rate was kept fixed at 80 sccm. Equal quantities of SiC and Si₃N₄ powder were taken in a ceramic boat and were placed at the centre of the furnace. The standard RCA cleaning procedure was used for cleaning the Si (100) substrate, after which it was placed in the ceramic boat. The CVD base pressure was fixed at 10^{−6} Torr and process pressure as atmospheric pressure throughout the deposition process. The experiment was performed at a processing temperature of 1000°C. The deposition was conducted for 3 h with a heating rate of 5°C min^{−1} in the furnace. After deposition, the furnace was cooled down gradually at a rate of 3°C min^{−1}. The morphology of the sample was characterized using a Nanoscope III scanning probe microscope fitted with a micro-fabricated Si₃N₄ cantilever (force constant of

0.5 Nm^{-1}) stylus assembly. A Dektak profilometer (model no. Dektak V300) was used for measuring the thickness of the SiCN coating which was found to be 4.6, 4.8, 4.9 and 5.1 μm for 40, 60, 80 and 100 sccm N_2 flow rates, respectively. The Raman spectrum was characterized in the range of 600–3000 cm^{-1} and is recorded with a Horiba Jobin Yvon instrument at room temperature while considering the 488 nm line of an Ar+ laser as an excitation source. The Fourier transform infrared (FTIR) spectra were obtained in the wavenumber range of 450–4000 cm^{-1} at a resolution of 2 cm^{-1} using a Perkin Elmer spectrometer (Model: Spectrum 2). X-ray diffraction (XRD) patterns were recorded with a Philips X-Pert (PAN-analytical) Model No. 3040/60 fitted with the RevakuUltima 3 software using the Cu $\text{K}(\alpha)$ anode. The H and E values were obtained by nanoindentation (Model no: Hysitron Triboindenter (TI 900)). The nanoindentation experiments were carried out at a load of 50 mN having a rate of loading and unloading as 1 mN s^{-1} .

3. Results and discussion

3.1 Atomic force microscopy (AFM)

Figure 1a–d represents the three-dimensional images of the SiCN thin films deposited at N_2 flow rates of 40–100 sccm. Unevenly shaped particles can be seen in the images which

are arbitrarily scattered over the surface of the SiCN thin film. AFM images are used for finding out the average roughness, R_a , of the surface of the thin film, which decreased with an increase in the N_2 flow rate. The minimum and maximum R_a values are 0.46 and 0.866 nm for the SiCN film deposited at N_2 flow rates of 100 and 40 sccm, respectively. The reason for the decrease in roughness can be the removal of voids and built-in compressive stress of the thin film which further caused the enhancement of the hardness in the thin film [9].

3.2 Raman analysis

Figure 2a shows the Raman spectra of SiCN thin films at a different N_2 flow rate from 40 to 100 sccm. The Raman signature appeared at $\sim 900 \text{ cm}^{-1}$ corresponds to the Si–N bond, and the intensity of the peak increased with an increase in the N_2 flow rate which may be due to an increase in N_2 at% in the SiCN thin film. A broad peak is observed at $\sim 1500 \text{ cm}^{-1}$ which indicates the existence of both disordered and graphitic carbon contents. The overtones of the D vibration, i.e., the 2D modes at $\sim 2200 \text{ cm}^{-1}$ are also visible in the SiCN thin film [14]. The Raman signature appearing at $\sim 2900 \text{ cm}^{-1}$ is due to the C–H bond present in the thin film [15]. For a detailed analysis of the broad peak appeared at $\sim 1500 \text{ cm}^{-1}$, it is deconvoluted into two different peaks, i.e., D peak and G peak, which is shown in figure 2b.

Figure 1. (a–d) AFM images of the SiCN thin films deposited at a N_2 flow rate of 40–100 sccm.

Figure 2. (a) The Raman spectra of SiCN thin films from 500 to 3000 cm^{-1} , (b) the deconvolution of D and G peaks in the region of 1100–1750 cm^{-1} , (c) the peak position and FWHM of D and G, and (d) I_D/I_G and L_a (nm) of carbon nanocluster of SiCN films with N_2 flow rate varied from 40 to 120 sccm.

Figure 2c shows the peak position and full-width at half maximum (FWHM) of the Raman spectra of both D and G peaks with the N_2 flow rate varied from 40 to 100 sccm. The Raman peak position is the indication of the bond strength of a thin film [16]. The D peak position of the film was found in the range of $1374.6\text{--}1397.3\text{ cm}^{-1}$, whereas the G peak position monotonically increased from 1567.8 to 1573.4 cm^{-1} . The degree of disorders of the carbon structure can be identified from the FWHM of D and G peaks. The bond angle and bond length in sp^2 clusters can be measured from the FWHM of the G peak [16]. The FWHM of the D peak decreased from 151.7 to 127.22 cm^{-1} , whereas the FWHM of the G peak increased from 236.27 to 248.76 cm^{-1} . The FWHM of a crystal includes the impurities present as well as the doping concentration in the crystal. The increase in the FWHM of Raman signature indicates a decrease in the short-range order which may occur due to the loss of crystallinity and ordering of the SiCN structure [4].

Figure 2d shows the variation of the I_D/I_G ratio and nanocrystallite size (L_a) with the N_2 flow rate varying from 40 to 100 sccm. The I_D/I_G is the ratio of the area of the individual D and G peaks, and it is directly related to the mechanical properties of the film. Also, it can be used to measure the defects present in the film [17]. The I_D/I_G ratio increased with an increase in the N_2 flow rate from 40 to 100 sccm. An increased I_D/I_G ratio signifies the increase in the sp^3 bond and is proportional to the H of the SiCN thin film [18]. The extent of the disorder can be defined in terms of nanocrystallite size (L_a) which can be calculated using the equation given below:

$$L_a \text{ (nm)} = \frac{560}{E_L^4} \left(\frac{I_D}{I_G} \right)^{-1}, \quad (1)$$

where E_L is the energy of the laser in eV [19]. From figure 2b, it is observed that the nanocrystallite size decreased from 8.4 to 6.15 nm with an increase in the N_2 flow rate. The value of L_a represents the amount of carbon clusters present in the thin film [20].

3.3 FTIR

Figure 3 shows the FTIR spectra of the SiCN films with varying N_2 flow rates from 40 to 120 sccm. Six main vibrational signatures can be observed from the FTIR spectra of the SiCN thin film. The vibrational bands at $530\text{--}563\text{ cm}^{-1}$ correspond to Si–Nn wagging vibrations [21]. The vibrational signature at $880\text{--}912\text{ cm}^{-1}$ corresponds to Si–C–Hn stretching [22]. The signature at $1106\text{--}1136\text{ cm}^{-1}$ appears from the vibrational signature of SiC–N bonds [23]. The Si–CH₃ bond can be observed at $\sim 1350\text{ cm}^{-1}$ [24]. The vibrational signature at $2984\text{--}3000\text{ cm}^{-1}$ corresponds to C–Hn. The peak at 3390 cm^{-1} appeared from the vibrational signature of the N–H stretching bond. The vibrational signatures of Si–N and SiC–N are shifting to a higher wavenumber with an increase in the N_2 flow rate from 40 to 100 sccm. With an increase

Figure 3. FTIR spectra of SiCN thin films in the range of $450\text{--}4000\text{ cm}^{-1}$ for different N_2 flow rates.

in the N_2 flow rate, the FTIR spectra moved to a higher wavenumber which may be because of: (a) high-electronegativity atom backing the chemical bonds and (b) nanocluster formation.

3.4 XRD

Figure 4a shows numerous crystal planes of SiCN thin films with changed N_2 flow rates from 40 to 100 sccm. The six-distinguishable diffraction planes are observed in the SiCN thin films. The diffraction planes are attributed to (200) ($\alpha\text{-Si}_3\text{N}_4$) at $2\theta = 26.45$, (201) ($\alpha\text{-Si}_3\text{N}_4$) at $2\theta = 30.29$, (102) ($\alpha\text{-Si}_3\text{N}_4$) at $2\theta = 35.63$, (302) ($\alpha\text{-Si}_3\text{N}_4$) at $2\theta = 50.25$, (220) ($\alpha\text{-SiC}$) at $2\theta = 61.47$ and Si (400) at $2\theta = 71.75$ [25–27]. Figure 4a shows that the peaks of (200) and (102) planes narrowed with an increase in the N_2 flow rate indicating an improvement in the intermediate range order of these two planes [28]. The Si (400) plane shifted from 72.94 to 71.92° with an increase in the N_2 flow rate from 40 to 120 sccm. According to National Bureau of standards, the diffraction angle of 69.13° represents the Si (400) plane and from figure 4a we can observe that with an increase in the N_2 flow rate Bragg's diffraction peak is moving towards the

Figure 4. (a) XRD plot of SiCN thin films and (b) variation of the crystal size with different N₂ flow rates from 40 to 100 sccm.

standard data which means that the increase in the N₂ flow rate has resulted in a decrease in the strain of the Si crystal in the SiCN thin film. Every peak of the film is corrected for instrumental broadening using the equation:

$$\beta_{hkl} = [(\beta_{hkl})_{\text{measured}}^2 - (\beta_{hkl})_{\text{instrumental}}^2]^{1/2}. \quad (2)$$

Figure 4b shows the crystallite size of the (102) plane in the SiCN thin films with varying N₂ flow rates from 40 to 100 sccm. Using Scherrer's formula the crystallite size has

been calculated as:

$$\text{Crystallite size} = \frac{k\lambda}{\beta_{hkl} \cos \theta}. \quad (3)$$

where $k = 0.9$ is the instrumental factor, λ is the wavelength of X-ray in nm, β is the FWHM in radians and θ is the peak in degrees. The crystallite size of the (102) plane increased from 3.84 to 10.66 nm with an increase in the N₂ flow rate from 40 to 100 sccm.

3.5 Nanoindentation

Figure 5a shows the load–depth curve at different N₂ flow rates in the SiCN thin film. For a fixed load of 50 mN, the depth of indentation is minimum for the film deposited at 100 sccm and a maximum at a N₂ flow rate of 40 sccm. From the above observation, it can be confirmed that the H of the SiCN film increased with an increase in the N₂ flow rate. In the present work, the Oliver and Pharr method [29] was used to determine the properties of the films. The H and E can be measured by analysing the unloading part of the load–displacement curve. The indentation H and E can be calculated by using equations (4 to 6).

$$H = \frac{P_{\text{max}}}{A}, \quad (4)$$

$$S = \frac{dp}{dh} = 2\beta \sqrt{\frac{A}{\pi}} E_r, \quad (5)$$

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_w^2}{E_w}, \quad (6)$$

where P_{max} is the highest load put on the specimen and A is the indenter tip's contact area. S is the contact stiffness measured from the upper portion of the load–displacement curve, and it gives a geometry independent equation (6) given by Oliver [29]. β is the constant whose value is 1.034 for the Berkovich indenter and E_r is the reduced elastic modulus. The subscripts i and w are used for indenter and workpiece, respectively. In the present case, the maximum H and E are found to be 65 and 375 GPa, respectively, for the SiCN thin film deposited at a N₂ flow rate of 100 sccm. Liao *et al* [30] deposited nanocrystalline silicon carbide films using thermal plasma CVD and found the H value of the film to be ~50 GPa. Kulikovskiy *et al* [31] prepared hydrogen-free α -C:Si films with a Si concentration between 3 and 50 at% using magnetron sputtering and the H of the film in the range of 45–55 GPa depending on the at% of Si. Vila *et al* [32] prepared silicon nitride thin films using reactive sputtering. The H and E values were found to be varying in the range of 8–23 and 100–210 GPa, respectively, which depended on the preparation parameter. Walsh *et al* [33] estimated the value of H for α -Si₃N₄ and α -Si₃N₄ using molecular dynamics calculations to be 50.3 and 31.5 GPa, respectively. The above references show that the SiCN

Figure 5. (a) Load–depth graph of the nano-indenter on the SiCN thin films and (b) variation of H/E and H^3/E^2 of SiCN thin films with N_2 flow rates varied from 40 to 100 sccm.

thin film has superior mechanical properties in comparison with SiC and Si₃N₄ thin films.

Also, the H and E of the SiCN thin films were observed to be increasing with an increase in the N_2 flow rate. This can be due to the following reasons: (a) incorporation of higher electronegativity nitrogen atom due to the N_2 flow rate, (b) Raman peak position increases to a higher wavenumber indicated an enhancement of crystallinity in SiCN due to an increase in the N_2 flow rate and (c) the increase in the I_D/I_G ratio. It is also observed from figure 5a that during unloading there is a characteristic event, known as pop-out, in the load–displacement curve which is marked by a circle in the figure is not purely elastic. It may be due to the phase transformation from Si-II to Si-III and Si-XII [34]. As silicon in a diamond anvil cell experiences a phase transformation from Si-II to less dense phases, Si-III and Si-XII [35], the pop-out phenomenon occurs due to the sudden volume expansion of the material beneath the indentation zone during unloading.

Figure 5b shows the plasticity index (H/E) and plastic deformation resistance (H^3/E^2) of SiCN thin films deposited

at N_2 flow rates of 40–100 sccm. The plasticity index indicates the toughness of the sample, whereas the plastic deformation resistance explains the creep resistance at the contact point. It has been proved that the wear of the material can be described better with the H/E ratio in addition to H and E than hardness alone [36]. Zhang *et al* [37] showed that in addition to the hardness a sufficient level of ductility is essential for practical applications and the correlation between the plasticity index and the tool life was proved by Beake *et al* [38] in their study. From figure 5b, it is observed that both H/E and H^3/E^2 ratios increase with an increase in the N_2 flow rate and the increase in these parameters confirmed that the film exhibits higher toughness and creep resistance with an increase in the N_2 flow rate.

4. Discussion

SiCN thin films were deposited on a Si (100) substrate using SiC and Si₃N₄ nanopowder by the CVD method. Raman spectra were used for finding the ratio of I_D/I_G . The I_D/I_G ratio was found to increase with an increase in the N_2 flow rate which indicates the increase in the sp^3 bond and further resulted in an increase in hardness. The FTIR results showed the shifting of vibrational signatures of Si–N and SiC–N bonds to a higher wavenumber indicating the nanocluster formation. Various planes of SiCN thin films were indicated by the diffraction patterns and the crystallite size varied from 3.84 to 10.66 nm. The H_{max} and E_{max} were found to be 65 and 375 GPa, respectively. The H and E increased with an increase in the N_2 flow rate. This may be explained as follows: (a) incorporation of higher electronegativity nitrogen atom due to the N_2 flow rate, (b) Raman peak position increases to a higher wavenumber indicated an enhancement of crystallinity in SiCN due to an increase in the N_2 flow rate and (c) the increase in the I_D/I_G ratio. Also, the plasticity index (H/E) and plastic deformation resistance (H^3/E^2) ratio increased with an increase in the N_2 flow rate which confirmed that the film exhibits higher toughness and creep resistance with an increase in the N_2 flow rate.

5. Conclusion

The morphological, structural and mechanical properties of CVD-deposited SiCN thin films with varying N_2 flow rates were studied. The AFM images reveal that an increase in the N_2 flow rate resulted in a decrease in the roughness of the SiCN thin film. The intensity ratio of D and G peaks was calculated by Raman spectroscopy, and it is observed that the ratio increases with an increase in the N_2 flow rate. The increase in the I_D/I_G ratio signifies the increase in sp^3 bonds in the film. From the nanoindentation results, the H_{max} and E_{max} are found to be 65 and 375 GPa, respectively, for SiCN thin films deposited at a N_2 flow rate of 100 sccm. Also, an increase in the N_2 flow rate resulted in an increase in SiC–N bonds and microstructural rearrangement of the SiCN thin

film which further resulted in an increase in hardness and Young's modulus.

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