

Deposition of silicon carbon nitride films by ion beam sputtering

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Abstract

Silicon carbon nitride films have been successfully synthesized at a temperature below 100°C from an adenine(C₅N₅H₅)-silicon-mixed target sputtered by Ar ion beam. The effects of Ar ion sputtering voltage, area ratio of Si to adenine in the mixed target and nitrogen atom addition during deposition on the film growth are investigated. XPS, XRD, and ellipsometry were employed to characterize the composition, chemical bonding, structure, and optical property of the films. The growth characteristic and film properties of the silicon carbon nitride films are also compared with those of the carbon nitride films deposited from an adenine target to elucidate the effect of silicon incorporation. The silicon content of the resultant films increased significantly as the area ratio of Si to adenine increased, whereas a higher Ar ion voltage led to a lower level of silicon incorporation, presumably due to differential sputtering yield of Si and adenine. XPS chemical state analysis revealed multiple bonding structures for every element in the SiCN films, of which possible implications are given. XRD studies showed that only amorphous films for Si-rich SiCN were obtained, while the films with low Si incorporation and deposited at high Ar ion beam voltage contained nanocrystallites. Furthermore, the refractive index of the SiCN films increased with increasing silicon content. The appearance of the nanocrystalline structure in the films led to a reduction in the refractive index. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silicon carbon nitride film; Ion beam sputtering; Deposition; Film growth

1. Introduction

Since Liu and Cohen [1] predicted that carbon nitride with a structure similar to β -Si₃N₄ should have a bulk modulus superior to that of diamond, carbon nitride films have been the subject of great interest in recent years. Various methods have been employed to synthesize carbon nitride [2–11]. However, most of these efforts result in amorphous carbon nitride films or tiny crystals embedded in amorphous matrix. Only few reports of crystalline β -C₃N₄ growth have demonstrated to date. Among them, Hsu et al. [10] employed an inductively coupled plasma sputtering with a high degree of gas dissociation and achieved micro-crystalline β -C₃N₄ films. Xu et al. [11] demonstrated that polycrystalline β -C₃N₄ can be deposited at 70°C using r.f.-magnetron sputtering. In previous work [12,13], we reported that nanocrystalline carbon nitride has been successfully synthesized from bio-molecular compound targets, such as azaadenine and adenine, by ion beam sput-

tering method. Owing to the similarity in the ring structures of these C–N bio-molecular compounds and the hypothetical β -C₃N₄ phase, the use of these bio-molecular compounds as the targets is believed to reduce the energy barrier of carbon nitride growth. Without additional nitrogen source, a N/C composition ratio of 1:1 was achieved in this approach.

It has been demonstrated that the incorporation of silicon in the growth of carbon nitride can promote formation of large and well faceted SiCN crystallites in a microwave CVD process [14–17]. Silicon carbon nitride crystals up to several tens of microns, possessing hexagonal structure wherein the Si and C are substitutional elements in the network, with a wide range of composition can be deposited in this technique. Optical investigation of these crystals further indicates the potential of the ternary SiCN compound for blue and UV optoelectronic applications [17]. Our observation that silicon plays an important role in increasing the carbon nitride network connectivity is consistent with some recent molecular dynamics studies [18]. However, the detailed mechanism whereby Si is involved in the crystal growth is not yet clarified. Indeed,

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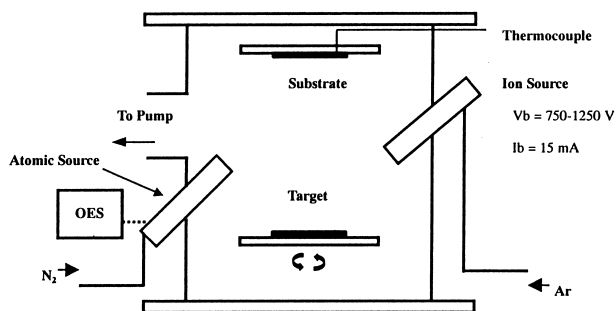


Fig. 1. A schematic diagram of a hybrid system combining the ion beam sputtering with an atomic source. The reactor is 35 cm in diameter and 25 cm high.

little is known about the effects of the silicon admixture on the structure and the property of the CN-based materials.

In this paper, we report the study on growth of SiCN films using Ar-ion beam sputtering from an adenine ($C_5N_5H_5$)-silicon-mixed target. By adjusting the area ratio of silicon to adenine in the target and by varying sputtering voltage in the process, various film growth phenomena were investigated. Furthermore, additional atomic nitrogen source is employed to enhance nitrogen incorporation in the growth. X-ray photoelectron spectroscopy (XPS) was used to determine the composition and chemical bonding of the films, while X-ray diffraction (XRD) was employed to characterize the structure of the films. Optical properties of the deposited films were characterized using a variable angle spectroscopic ellipsometer (VASE). The correlation between the refractive index and the silicon content in the films is investigated.

2. Experimental

The schematic of an ion beam sputtering system equipped with a nitrogen atomic source is shown in Fig. 1. A 3-cm Kaufman-type ion source under an incidence of 45° to the target provides the Ar ion for sputtering. A substrate parallel to the target holder was held at 20 cm from the target. An r.f.-atomic nitrogen source at 45° incidence angle to the substrate was employed to supply additional nitrogen atoms during the deposition. As shown in Fig. 2, adenine ($C_5N_5H_5$)-silicon-mixed target consists of interlaced adenine and silicon (111) disks on a target holder. The preparation of the adenine disks has been described in the earlier reports [12,13]. The composition of the mixed target was adjusted by varying the area ratio of adenine to silicon. To prevent overheating of the target and to ensure homogeneous film growth, the target holder was rotated at 40 rpm.

The base pressure of the deposition chamber was 0.1 mPa evacuated by a turbo molecular pump, while the pressure during deposition was about 40 mPa. The gas flow rates in the system were 1 sccm Ar for the Ar ion beam and 0.4 sccm N_2 for the N-atom source. The Ar ion beam current was held constant while the ion beam voltage was varied from 750 V

to 1250 V to study the sputtering voltage effect. The relationship between the N atom flux and the r.f. power of atomic source has been calibrated by the N/N_2 peak height ratio determined from optical emission spectroscopy (OES) measurement [13]. Si(100), Si(111), and quartz substrate were used to study the surface effect to the deposition. Except heating from ion beam bombardment during deposition, no external heating of the substrate or target was used. The deposition temperature was below 100°C as measured by a thermocouple from the backside of the substrate.

A Perkin-Elmer Phi 1600 ESCA system was employed to analyze the composition and the chemical bonding state of the films. Mg K_α radiation of 1253.6 eV was used as the X-ray source with a line width of 0.7 eV. The analyzing area for XPS measurement was 800 μm in diameter. The pass energy for chemical state analysis was 11.75 eV. The film thickness was measured from SEM cross section of the deposited sample. The spectroscopic ellipsometric characterization of the films was carried out using a variable angle spectroscopic ellipsometer (VASE) manufactured by J. Woolam Co., Inc.. The light source was comprised of a Xe lamp and a monochromator, which allows optical measurements in the UV-Vis range (300–1000 nm) of wavelength. The spectral dependence of the refractive index and the extinction coefficient of the deposited films were obtained assuming multi-layer plane-parallel structure (namely, rough surface layer/SiCN film/ SiO_2 interfacial layer/Si substrate).

3. Results and discussion

SiCN films were deposited at various sputtering voltages, adenine to Si area ratio in the target, and r.f. power of atomic

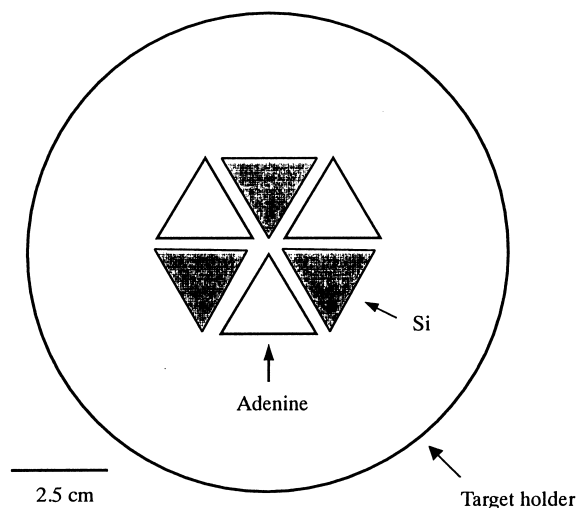


Fig. 2. A schematic of the adenine ($C_5N_5H_5$)-silicon-mixed target with an adjustable area ratio of the two sources. The white powders of adenine were commercially available from Aldrich Co. Adenine powders were first baked at 105°C for 24 h in a flowing nitrogen atmosphere to remove moisture, and were then compacted to form a disk target at a pressure of 1250 kg/cm^2 . The Si target is cut from a 4-inch Si(111) wafer.

Table 1
The composition and the growth rate of the films for some selective growth conditions

Target Si/adenine	Ar ion beam voltage (V)	R.F. power of atomic source (W)	Composition C/N/Si/O	Growth rate ($\mu\text{m/h}$)
0:1	750	0	48:52:0:0	0.28
	1000		53:47:0:0	0.51
	1250		47:53:0:0	1.12
1:1	750	0	58:17:18:7	0.11
	1000		60:24:13:3	0.30
	1250		53:41:4:2	0.87
	750	170	50:21:24:5	0.17
	1000		55:26:11:8	0.30
	1250		54:41:3:2	0.66
3:1	750	0	37:14:35:14	0.05
	1000		34:19:32:15	0.14

nitrogen source. Quantitative analyses of XPS data for the Si/C/N/O composition of the as-deposited films are listed in Table 1. The oxygen peak at 533 eV almost disappeared after sputtering with Ar^+ , indicating that oxygen was present mostly on the surface as the analyses were done. It is noted that the C/N ratio is around 1:1 without Si addition. Results of the CN films deposited using adenine alone are also compared. With a Si to adenine area ratio of 1:1, the Si/C/N ratio is around 1:3:1 for films deposited at a sputtering voltage of 750 V. As shown in Table 1, the growth rate increased with increasing sputtering voltage. Furthermore, the silicon content of the films decreased at higher sputtering voltages. Only 3.5% of silicon is incorporated within the film at a sputtering voltage of 1250 V, which is substantially lower than the 20% silicon content at 750 V sputtering voltage. This might be due to preferential sputtering of adenine over silicon at higher sputtering voltage. We also observed that the nitrogen content of the SiCN film was substantially increased to a level almost comparable to the carbon content at a sputtering voltage of 1250 V. It is somewhat surprising that the silicon incorporation appeared to suppress the nitrogen content in the films.

In order to enhance nitrogen incorporation in the films, an atomic nitrogen source was further employed during the process. As listed in Table 1, the compositions and growth rates of the films with the addition of nitrogen source did not experience significant enhancement as expected. To enhance the Si incorporation within the films, the Si to adenine area ratio of the mixed target was increased from 1:1 to 3:1. As shown in Table 1, at a sputtering voltage of 1000 V the silicon content of the films increased tenfold while the growth rate decreased by a factor of five. This indicates that the sputtering yield for silicon is much lower than that for adenine.

From the compositions and growth rates results, we suggest that the dependence of the sputtering yields of adenine and silicon on the sputtering voltage is very different. The sputtering yields of adenine is higher than that of silicon, and the difference is more pronounced at higher sputtering voltage. This explains why we observed lower silicon content of the films at higher sputtering voltage,

and lower growth rate when the ratio of silicon in the mixed target was increased.

The high-resolution XPS scans of the C(1s) and N(1s) peaks were employed to determine the chemical bonding states of the films. Three or two Gaussian peaks as shown in typical spectra in Fig. 3 could adequately fit the C(1s), N(1s), and Si(2p) spectra. According to the assignment by Marton et al. [19] and Stoner et al. [20], the carbon binding

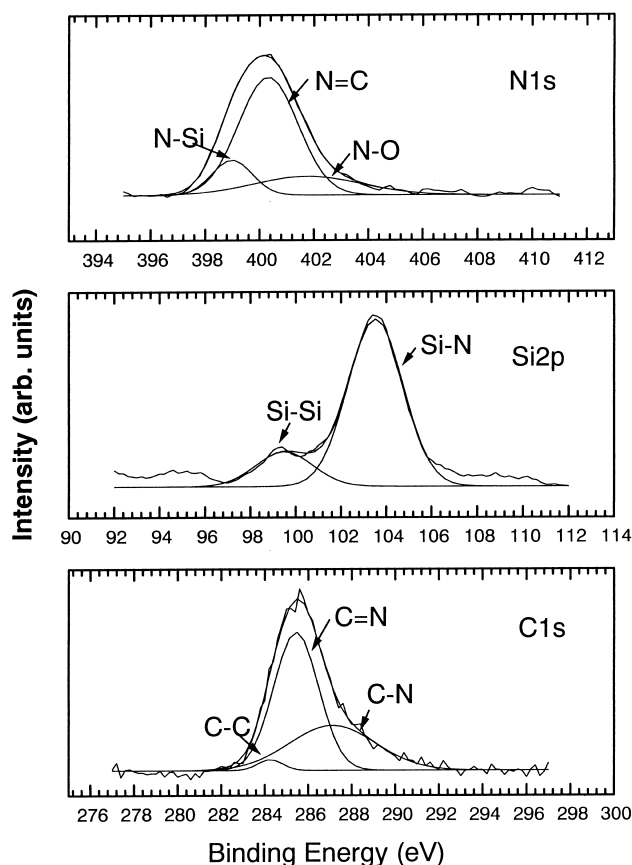


Fig. 3. Typical XPS spectra of C(1s), N(1s), and Si(2p) for a SiCN film deposited at a 3:1 Si to adenine area ratio and a sputtering voltage of 1000 V. Each spectrum is deconvoluted into Gaussian components to reveal the bonding states.

energies, as shown in Fig. 3, revealed C–C, C(1s)=N, and C(1s)–N bonding structures at 284.6 eV, 285.5 eV, and 287.2 eV, respectively. For N(1s), the 399.2 eV, 400.5 eV and 401.6 eV peaks were attributed to the N(1s)–C, the N(1s)=C, and the N(1s)–O, respectively. For Si(2p) [20], the 99.5 eV and 103.5 eV peaks were attributed to the Si(2p)–Si and the Si(2p)–N. Notably, there is no major separate peak that matches the C(1s)–Si bonding at 282.2 eV or Si(2p)–C bonding at 100.3 eV, thus excludes the existence of Si–C bonds in the deposited SiCN films. The area ratio of the Si(2p)–Si to the Si(2p)–N was around 1:6, as shown in Fig. 3, suggesting that the major part of Si within the SiCN films were bonded to nitrogen. Among the growth conditions listed in Table 1, a small fraction of Si(2p)–C at 100.3 eV appears in the Si(2p) spectra for films deposited at a 3:1 Si to adenine area ratio and a sputtering voltage of 750 V. This is also confirmed in the C(1s) spectra at 282.2 eV, which is attributed to C(1s)–Si peak. Nevertheless, it was not clear why Si–C bonds were formed only under such conditions. The results of XPS measurements showed that the nitrogen within the films was bonded with carbon and silicon, and the silicon was bonded with silicon and nitrogen under typical growth conditions. The presence of Si–Si peaks suggests that the films may contain some Si clusters embedded in the SiCN matrix.

From FTIR measurement, the peaks corresponding to the CH_n group in the regions 1400–1450 cm⁻¹ and 2800–3000 cm⁻¹ as well as N–H bonding at around 3000–3500 cm⁻¹ were observable. These peaks were also observed in the CN films deposited using adenine target [12,13]. Thus some hydrogen incorporation in the films cannot be excluded. Meanwhile, the broad XPS peaks may consist of unresolved multiple peaks resulted from minor peak position shifting by different chemical environment changes such as hydrogen bonding with C and N.

The XRD spectra of adenine and the silicon carbon nitride films deposited at various conditions are shown in Fig. 4. In contrast to the spectrum of adenine, which consisted of several distinguishable peaks, only a broad peak at 0.32 nm *d*-spacing ($2\theta = 27.5^\circ$) was observed in the XRD spectrum of the films deposited at sputtering voltages above 1000 V and the Si to adenine area ratio of 1:1 in the mixed target. The broad peak together with transmission electron microscopic investigation suggests that the film contained nanocrystalline grains [12,13]. Only amorphous SiCN films were obtained at lower Ar ion beam voltage and higher Si to adenine area ratio in the mixed target. As shown in Table 1, the Si content within the films increased as Ar ion beam voltage was lowered and the Si to adenine area ratio in the mixed target was

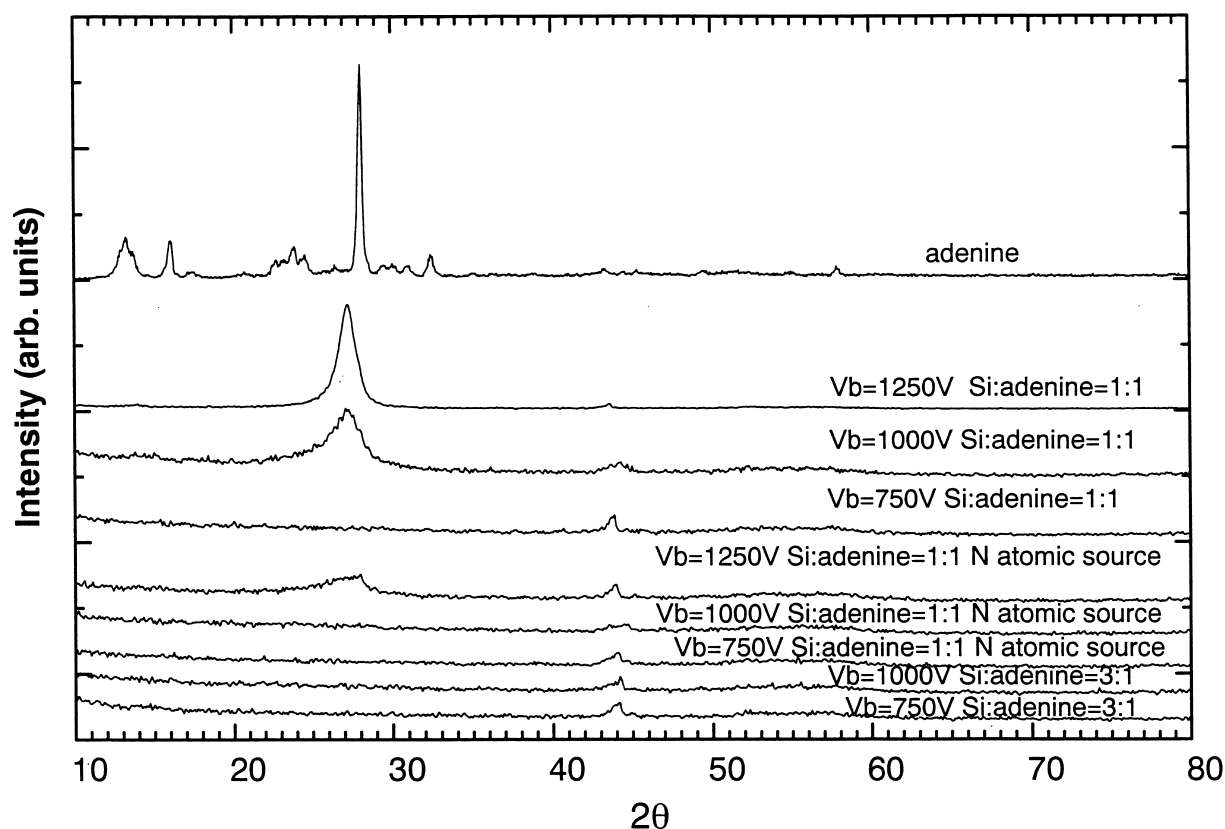


Fig. 4. XRD spectra of the films deposited at various conditions indicated. A broad peak at $2\theta = 27.5^\circ$ was observed in the XRD spectrum of the films deposited at sputtering voltages above 1000 V and the Si to adenine area ratio of 1:1 in the mixed target. The broad peak at around $2\theta = 43^\circ$ is a forbidden peak of Si(100) substrate from θ - 2θ scan.

increased. Thus, it appears that incorporation of Si within the films deposited by this PVD process could not promote the formation of large-sized crystallite SiCN, in contrary to the results by microwave CVD process [14–17].

The spectral dependence of the refractive index obtained from ellipsometry measurement is shown in Fig. 5 for films deposited at various conditions. The data for a film deposited with an adenine target without silicon incorporation is also shown as the solid line in Fig. 5. In general, the refractive index of the films with the silicon content below 25% was around 1.7, which is similar to that of the carbon nitride film deposited with adenine target alone. The spectral dependence of the refractive index changes dramatically at higher silicon content as shown in the top two curves in Fig. 5. For films deposited at 3:1 Si to adenine ratio and 1000 V sputtering voltage, which has 30% silicon content, the refractive index is around 2.0. The refractive index increases above 2.4 for films with a 35% silicon content. The fact that the silicon content in the films can tailor the refractive index is important in many practical applications.

Furthermore, as shown in the bottom curve in Fig. 5, the refractive index is lowered to around 1.3 for films deposited with a 1:1 Si to adenine area ratio in the mixed target and at 1250 V sputtering voltage. This is quite different from other films including the one deposited under the same conditions except with nitrogen atom addition during the growth. Meanwhile, the XRD data in Fig. 4 also showed the strongest peak at 0.32 nm *d*-spacing for films deposited in the

particular condition. This suggests a strong correlation between the crystallinity and low refractive index of the films.

4. Conclusion

Silicon carbon nitride films have been successfully synthesized at a temperature below 100°C from an adenine(C₅N₅H₅)-silicon-mixed target sputtered by Ar ion beam. The effects of the sputtering voltage, the area ratio of Si to adenine in the mixed target, and the nitrogen atom addition during growth have been examined in this study. We observed that Si incorporation has a strong effect on the structure and the property of the resultant films. The silicon content of the films was lowered as the sputtering voltage increased and was increased significantly as the area ratio of Si to adenine increased. XPS chemical state analyses show that while most of the Si atoms were bonded to the N atoms, the films may contain some Si clusters embedded in the SiCN matrix. Only amorphous SiCN films were obtained at lower sputtering voltage or higher Si to adenine area ratio in the mixed target, in which the Si content within the films is the highest, whereas nanocrystalline SiCN films can be deposited with low Si content. Furthermore, the refractive index of the SiCN films increases with increasing silicon content, while it decreases with the appearance of nanocrystalline structures in the films. In summary, adding CN

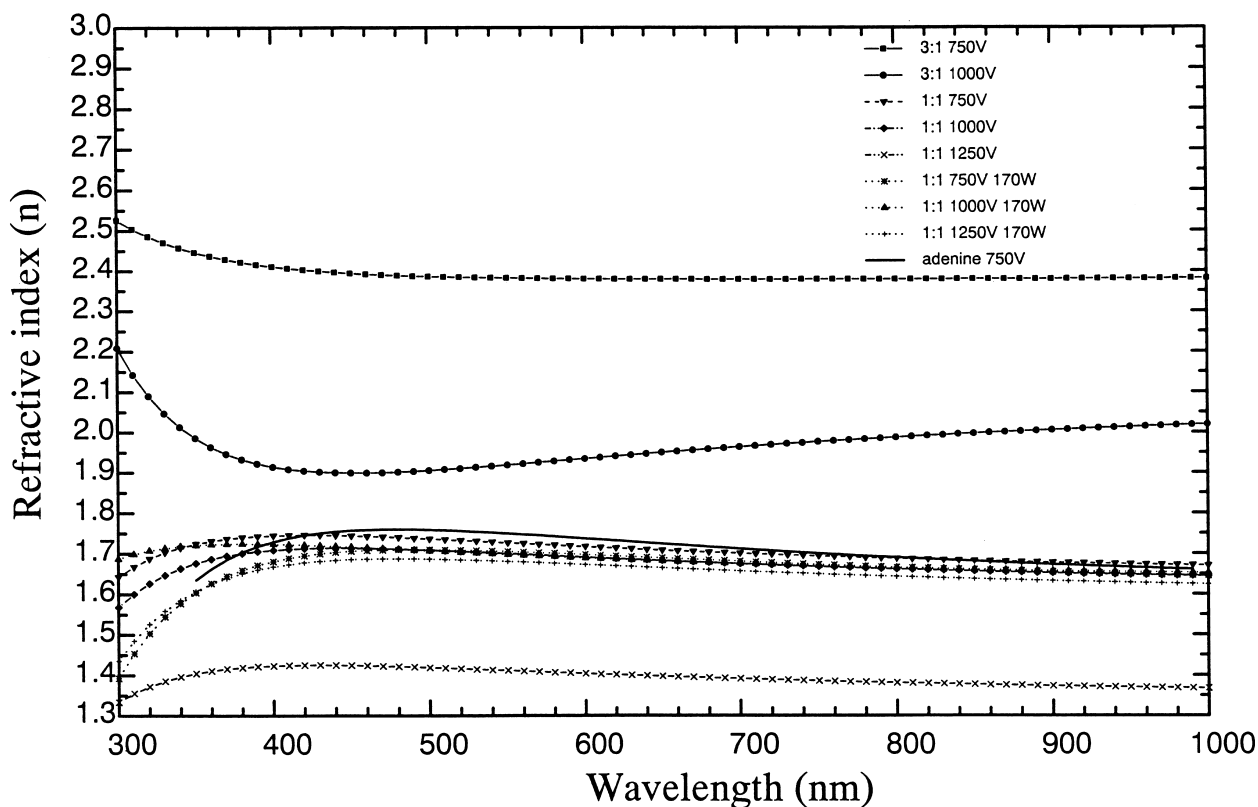


Fig. 5. The refractive index of the CN film and the SiCN films deposited at various conditions.

system with Si in the ion beam sputtering process induces amorphization of the nanocrystalline materials and provides a wide range of accessible optical constants for practical applications.

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