

RF Power Effect On Structural Characteristics Of Amorphous Carbon Nitride Thin Films Deposited By Reactive Radiofrequency Sputtering

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Amorphous carbon nitride thin films were deposited, at room temperature, on silicon substrates by reactive radiofrequency (RF) sputtering from a graphite target in an atmosphere of nitrogen. The structural properties were investigated by Raman spectroscopy. This spectroscopy reveals the presence of C–C, C=C, C=N and C≡N bonding types. The Raman intensity (I_D/I_G) ratio of disorder and graphitic bands increased from 1.29 to 2.67 with increasing the RF power from 100 to 400W indicating an increase of structural disorder.

Keywords: amorphous carbon nitride, thin films, reactive radiofrequency sputtering, Raman spectroscopy, structural disorder

I. Introduction

In the last decade, many works have focused on the study of carbon nitride thin films. This material with a crystalline structure of β -C₃N₄, as described by Liu and Cohen [1], is characterized theoretically by hardness inclusively greater than diamond's. However, after several years, the structure of this material is still not well known and different groups have been trying to prepare it but unsuccessfully. The synthesis of the carbon nitride with a similar structure to that of β -Si₃N₄, remains at the moment an important goal for most laboratory research in the advanced materials scientists, however the investigation in this field needs much effort. Despite this intense work, in most cases the attempts have resulted in amorphous films with a nitrogen content deficient and not exceeding 50 at. %. It is known that the structure of the material depends strongly on both the deposition techniques and the parameters of preparation of the film [2-5]. This dependence is due principally to the fact that carbon atoms can be bonded to nitrogen and has one of the following configurations: C–N single bonds, C=N double bonds, and C≡N triple bonds. The obtaining of crystalline carbon nitride with C–N single bonds requires severe conditions to be grown. Amorphous carbon nitride (a-CN) thin films are in principle easy to be grown and can be used as potential candidates for eventual use in mechanical application as a protective coating [6-7], however, electrical and optical applications remain largely unexplored.

In order to contribute to the study of this material, we have investigated the influence of the radiofrequency (RF) power on the structural properties of a-CN thin films deposited by reactive RF sputtering from a

graphite target in an atmosphere of nitrogen. The characteristics of a-CN thin films were investigated by Raman spectroscopy.

II. Experimental Details

The a-CN thin films used in this study were prepared by RF sputtering in an ALCATEL SCM 451 deposition system equipped with an ALCATEL ARF 601 RF generator operating at 13.56 MHz. Prior to each deposition, the vacuum chamber was evacuated down to a base pressure of 10^{-4} Pa. The a-CN films were deposited, at room temperature onto polished silicon substrates, from a graphite target in an atmosphere of nitrogen. The total pressure of nitrogen, during the pulverization, was maintained at 1 Pa. The deposition time of the samples was fixed at 1 hour. The RF power was varied from 100 to 400 W. Before the deposition, the graphite target was pre-sputtered for 15 minutes in order to eliminate superficial layers resulting from exposure to ambient gases. Raman spectra were obtained using a Renishaw Raman 1000 spectrometer with an excitation wavelength of 514nm. The scanning resolution was 1 cm^{-1} and the scans were performed at room temperature and normal atmospheric conditions. The thickness (d) values of the a-CN films deposited at different RF powers, as deduced from X-ray reflectometry, are reported in Table 1.

RF power (W)	d (nm)
100	46
250	50
400	37

Table 1: Film thickness (d) for a-CN thin films deposited at different RF powers.

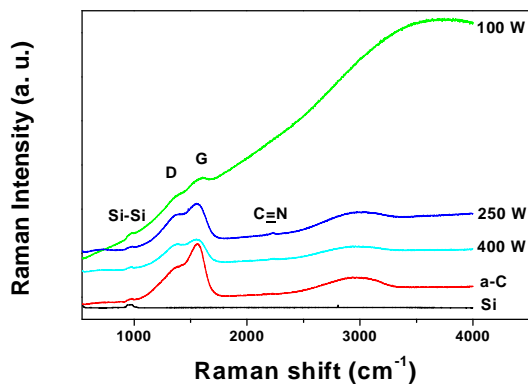


Figure 1: Raman spectra of a-CN thin films deposited at different RF powers. Raman spectra of a RF sputtered a-C film and of a silicon substrate are also included in the figure.

III. Results and discussion

Raman spectroscopy is a powerful technique that is widely used to study the structural properties of carbon and carbon related films. Fig.1 shows the Raman spectra of a-CN thin films deposited at different RF powers of 100, 250 and 400W. In the same figure we included, for comparison, the Raman spectra of a silicon substrate and of a RF sputtered amorphous carbon (a-C) thin film deposited at 250W with argon as sputtering gas. The peak at about 960cm⁻¹ is due to the second-order Raman mode of the silicon substrate. It can be observed that the Raman spectra are characterized by photoluminescent background that is more relevant in the a-CN film deposited at 100W. The principal characteristic of Raman spectra of the a-CN thin films is that they are almost similar to that of a RF sputtered a-C film but with an additional band centered at approximately 2232cm⁻¹ when the films were deposited with nitrogen as the sputtering gas. The later weak band is assigned to sp C≡N configurations [8], which are expected for terminators groups, and indicates that nitrogen is chemically bonded to carbon in the a-CN films. The presence of this less intense band in the a-CN film deposited at 100W is not clear; this can indicate that very few C≡N bonds were formed in this film. This result suggests that the formation of the C≡N bond in the a-CN thin films is strongly controlled by the applied RF power. As reported by Lejeune et al. [9], this type of bonding produces bond-terminating sites and induces the loss of connectiveness of the amorphous carbon network, which results in less densely packed structure. The similarity between Raman spectra of the a-CN with a-C films points out that the carbon network in the a-CN films is arranged in the same manner as in the a-C films. The broad band in the 1000-1800cm⁻¹ range is

characterized by two peaks: one broad peak centered at around 1580 cm⁻¹ corresponding to the graphite-like carbon bonds (G means graphitic) and the other one centered at about 1390 cm⁻¹ corresponding to the disordered sp² carbon (D means disordered) [10]. These spectra were deconvoluted, after subtracting the background, using two Gaussian components associated with D and G bands. The values of the positions (ω_D , ω_G) and the full widths at half maximum ($\Delta\omega_D$, $\Delta\omega_G$) of the D and G bands are reported in Table 2. It can be observed an increase of the width of D band and a decrease of the width of G band, with increasing the RF power. This result can be associated with the increase in structural disorder degree accompanied by a reduction of the bond angle distortions in the graphite plane [11].

RF power (W)	ω_D (cm ⁻¹)	$\Delta\omega_D$ (cm ⁻¹)	ω_G (cm ⁻¹)	$\Delta\omega_G$ (cm ⁻¹)	I_D/I_G
100	1370	251	1575.6	177.5	1.29
250	1394	311	1575.6	149.7	2.28
400	1392	312	1578.3	146.9	2.67

Table 2: The positions (ω_D , ω_G), the full width half-maximum ($\Delta\omega_D$, $\Delta\omega_G$) of the D and G bands, and the I_D/I_G ratio for the a-CN thin films deposited at different RF powers.

From the results of deconvolution, the I_D/I_G area ratio versus the RF power is calculated and is presented also in Table 2. With increasing the RF power from 100 to 400 W, the I_D/I_G ratio increases from 1.29 to 2.67. This behavior can indicate a structural modification by bombardment with more energetic particle and consequently the increase in structural disorder degree in the a-CN films with increasing the RF power. Jung et al. [4] reported, for a-CN films obtained by magnetron sputtering, that the incorporation of nitrogen atoms induces disorder in the carbon nitride films through the breaking of medium or long-range order of the sp² bonded carbon structure. The increase of disorder can be probably induced by both the increase of the temperature of the substrate and the presence of more energetic chemical species in the discharge during the growth of films. The increasing of the temperature of the substrate can be possibly the result of the higher kinetic energy of the species ejected from the sputtered target. An important increase in the RF power can produce a re-sputtering

of the films during the process of depositing giving rise to low film thickness and can be responsible for the formation of some defects and a change of composition in the final deposit. Jacobsohn et al. [12] observed for a-CN:H that the increase of I_D/I_G can be ascribed to the increase of the number or/and the size of sp^2 bonded carbon clusters in the film. Zheng et al. [13] reported that the graphite becomes more disordered after implantation by high-energy nitrogen ions.

In Fig. 1, a peak at around 692cm^{-1} can be observed in the a-C and a-CN films. It can be attributed to some form of disorder in the films deposited by sputtering [14]. The intensity of this broad band is more intense in the a-CN thin films than in the amorphous carbon film, which can indicate that the incorporation of nitrogen increases the disorder in the carbon network. This observation supports the result discussed previously. Finally, the broad and asymmetric band centered at around 2936cm^{-1} can be associated with second-order Raman scattering of the D and G bands.

IV. Conclusion

Amorphous carbon nitride thin films were obtained, at room temperature, by reactive RF sputtering using a graphite target under a pure nitrogen atmosphere. The influence of RF power on structural properties of a-CN films has been investigated. In addition to C–C, C=C bonds, the analysis by Raman spectroscopy reveals also that the nitrogen atoms are bonded essentially to the carbon atoms in two forms such as N=C and N≡C bonding types. The disorder in the a-CN films was found to increase with increasing the RF power.

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V. References

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