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OPTICAL PROPERTIES OF AMORPHOUS CN FILMS

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ABSTRACT

Carbon nitride (CN) films were synthesized on silicon substrates by a combined ion-beam and laser-ablation method under various conditions; ion-beam energy and ion-beam current were varied. Raman spectroscopy and spectroscopic ellipsometry (SE) were employed to characterize respectively the structural and the optical properties of the CN films. Raman spectra show that all the CN films are amorphous independent of the ion-beam current and the ion-beam energy. Refractive indices, extinction coefficients and optical band gaps which were determined from the measured SE spectra exhibit a significant dependence on the synthesis conditions. Especially, the decrease of the refractive indices and the shrinkage of the optical band gap is noticeable as the ion-beam current and/or the ion-beam energy increase.

INTRODUCTION

Recently, a great deal of attention has been paid to the study of carbon nitride films. Current interest in CN films originates mainly from the interesting prediction by Liu and Cohen¹⁾ that a covalently bonded C-N solid can have a hardness comparable with or greater than that of diamond. Even though numerous attempts to synthesize the predicted crystalline phase C-N solid have been largely unsuccessful but have produced only amorphous carbon nitride (a-CN) films, research activities concerning CN films are in still a higher gear, fueled by prominent characteristics of a-CN films from both scientific and technological point of views. Amorphous carbon nitride films are found to possess dia-

mond-like properties, namely, high hardness, wear resistance, chemical inertness, and high transparency. Hence, a-CN films are expected to be used as protective, tribological, and optical coatings. As for protective coatings, applications are found, for example, in magnetic recording disks, and in space and optical devices. Apart from the above applications, CN films also have the potential for device applications, for example, as a substitute for amorphous silicon nitride as gate insulators or as a variable gap material.

In carbon-based films, it is generally accepted that the excellent diamond-like properties are due to SP³ bonding. Hence, various synthesis schemes have been devised to pro-

mote the formation of SP^3 bonds in both hydrogenated and unhydrogenated amorphous carbon films. Nevertheless, the fraction of SP^3 carbon bonding varies considerably with the synthesis parameters. For example, the hydrogen content in the film influences the number of SP^3 bonding in hydrogenated amorphous carbon films²⁾, and the laser power density plays an important role in controlling the SP^3 bonding fraction in unhydrogenated amorphous carbon films³⁾. In the case of amorphous carbon nitride films, the role of nitrogen atoms in determining the degree of diamond-like character is even more complicated because a nitrogen can form either of a single, a double, or a triple bonding with a carbon (carbons)⁴⁾. Various synthesis methods have also been adopted to grow amorphous CN films. A partial list includes ion implantation in carbon films^{5, 6)}, ion and vapor deposition method⁷⁾, ECR plasma chemical vapor deposition^{8, 9)}, sputtering^{4, 10-14)}, ion-assisted arc deposition^{4, 10)}, and combined ion-beam and laser ablation method^{14, 15)}.

In this study, we deposited amorphous carbon nitride films on silicon substrates at room temperature in a high-vacuum environment by the combined ion-beam and laser ablation method under various deposition conditions, and investigated the variation of optical constants using the spectroscopic ellipsometry. Considering the potential application of amorphous CN films for optical coatings, it is very surprising to find few existing studies on optical properties as compared to an extensive documentation on the mechanical properties. Especially, optical properties of amorphous CN films deposited by the combined ion-beam and laser ablation method have not been re-

ported, yet. By virtue of the distinct differences in the the optical characteristics of the SP^3 and SP^2 bonded carbons, a study of the variation of the optical constants of amorphous CN films with deposition conditions can also lead us to understand how carbon bonding characteristics change with deposition condition.

EXPERIMENTAL

CN films were deposited on silicon substrates using the combined ion-beam and laser ablation method for a fixed deposition time. A pyrolyte graphite target of 99.9% purity was ablated with a Q-switched Nd-YAG pulsed laser of 1064 nm wavelength at the power density of 2×10^9 W/cm², and the nitrogen ions produced by the Kaufman type ion beam source were made to bombard the growing films. The ablation of carbon and the simultaneous ion-bombardment were performed in a high-vacuum chamber equipped with a substrate load-lock system. The vacuum system had a base pressure of 2.8×10^{-8} torr, and the working pressure was maintained at 2.5×10^{-5} torr. In order to remove contaminants from the substrate surfaces, silicon substrates were precleaned by the argon ion beam of 600 eV and 25 mA for 5 min before the film deposition. A series of CN films were deposited at fixed ion beam energy of 600 eV, while the nitrogen ion beam current was increased from 10 mA to 50 mA at the interval of 10 mA. Similarly, another series of CN films were deposited at a fixed ion beam current of 10 mA with the nitrogen ion beam energy ranging from 150 eV to 600 eV.

CN films were characterized by Raman

spectroscopy and spectroscopic ellipsometry (SE). Raman spectroscopy was employed for the structural characterization and SE was used for the investigation of the optical properties of the CN films. Raman spectroscopy was performed using a 5145 Å laser line over an effective frequency shift range of 1000 to 2000 cm^{-1} . A Rudolph model s2000 spectroscopic ellipsometer was used to measure ellipsometric spectra of the CN films from 1.5 to 4.0 eV in 0.01 eV increments. Refractive indices and extinction coefficients of the CN films were determined from analyses of the measured SE spectra.

RESULT AND DISCUSSION

The Raman spectra of CN films deposited at several nitrogen ion beam currents with the fixed ion beam energy of 600 eV are presented in Fig. 1. For the CN films deposited at lower nitrogen ion beam currents, the main features of the spectra are the broad D and G characteristic peaks of amorphous carbon which exhibit a downshift relative to the typical G and D peaks of the polycrystalline graphite. In our previous paper¹⁶⁾, we attributed this downshift to the presence of highly distorted four-fold coordination in the films. Also, there are discernible features in these spectra just below 1300 cm^{-1} in addition to the broad D and G peaks. It is very interesting to note that Bousetta and coworkers^{8, 9)} have reported a peak at 1275 or 1291 cm^{-1} from their CN materials with a high nitrogen content. They implied that this peak may stem from the carbon-nitrogen stretching mode. However, our observation of this feature even from the ablated amorphous carbon

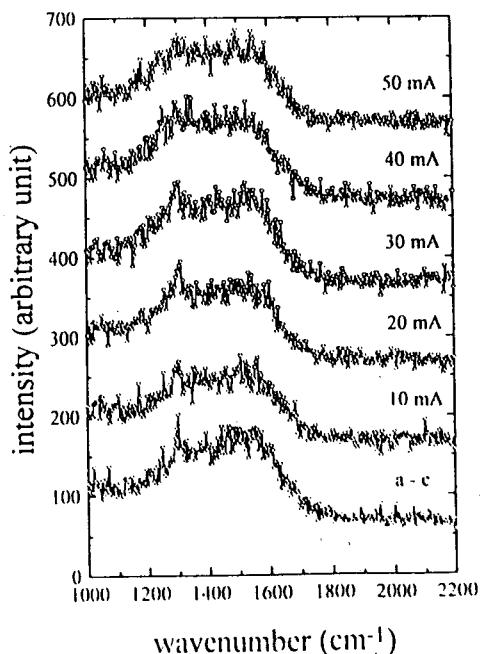


Fig. 1 Raman spectra of CN films deposited at the fixed ion beam energy of 600 eV. The nitrogen ion beam current were varied from 0 to 50 mA.

films without the nitrogen bombardment (a-c) excludes the possibility. But considering the excellent diamond-like properties of the a-C films, this feature can be still correlated with the formation of SP^3 bonding. As the nitrogen ion beam currents were increased, distinction between D and G peaks becomes less apparent. Bousetta and coworkers⁹⁾ have observed similar Raman spectra and compared them with the ones due to the diamond-like films. However, a general trend of the increasing D peak contribution and the peak broadening suggests that the films also suffer damage due to the ion beam bombardment at higher ion beam currents. In summary, Raman spectra lead us to conclude that our amorphous CN films have small grains of SP^3 bonded carbons embedded in amorphous SP^2

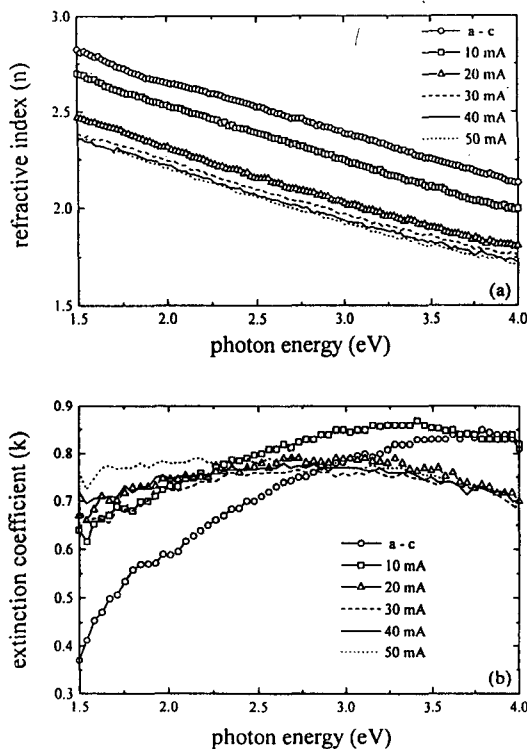


Fig. 2 The optical constants variation with nitrogen ion beam current; (a) Refractive indices, (b) Extinction coefficients. The nitrogen ion beam current were varied from 0 to 50 mA at the fixed ion energy of 600 eV.

bonded carbons, and the fraction of SP^2 bonded carbons increases at the expense of the SP^3 bonded carbons as we increase the ion beam currents. Also, even the SP^2 bonded carbons become more amorphous as the ion beam currents increase.

The refractive indices and the extinction coefficients of a-CN films were determined from the spectroscopic ellipsometry. The variation of the optical constants of the CN films which were deposited at the fixed ion energy of 600 eV with the nitrogen ion beam current from 0 to 50 mA are shown in Fig. 2. As shown in Fig. 2 (a), the refractive index n is

decreasing function of energy and is also found to decrease with no apparent change in the overall shape, as the nitrogen ion beam current is increased.

Fig. 2 The optical constants variation with nitrogen ion beam current were varied from 0 to 50 mA at the fixed ion energy of 600 eV.

The extinction coefficient k , as shown in Fig. 2 (b) exhibits a very different behavior. k of the a-C film is an increasing function of energy, but as we increase the nitrogen ion beam current, k in the low energy region, in particular, increases significantly, and eventually the variation in k over the whole measured energy range becomes small. A similar behavior in the variation of the optical constants has been reported by Wang and co-workers¹⁰ for their ion-assisted arc deposited a-CN films. It is also worth noting that the optical constants reported by Savides¹⁷) and Smith¹⁸) for their respective a-C and a-C:H films display a very different behavior with change in energy from that of our a-CN films. Savides reported that both the refractive indices and the extinction coefficients of a-C films decrease in the visible light region as the SP^3 bonding fraction increases. Smith also reported a similar trend in the energy region below 2 eV, but more prominent features in his data is that the refractive indices become more dispersive and the extinction coefficients become less dispersive as the SP^3 bonding fraction decreases. Especially, the extinction coefficients become almost nondispersive as the SP^2 bonding becomes dominant. The different behavior of our a-CN films strongly suggests that increase of the SP^3 bonding fraction cannot solely account for the observed variation, and also that the

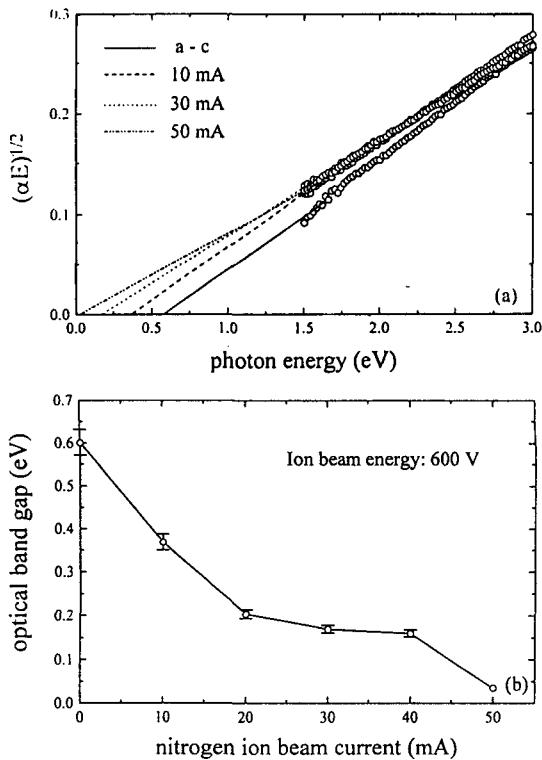


Fig. 3 Tauc's plot and the optical band gap variation with the nitrogen ion beam current; (a) Tauc's plot, (b) the variation of the optical band gap. The nitrogen ion current were varied from 0 to 50 mA at the fixed ion energy of 600 eV.

nitrogen must play an important role in determining the optical properties. In general, the decrease of the refractive indices can be also accounted for by the increase of the void fraction in the film, which, in this case, can be caused by nitrogen that acts as a kind of bond terminator, and induces the loss of connectiveness of the amorphous carbon network¹⁹. The increase of the extinction coefficients signals the loss of transparency, and especially the almost dispersionless extinction coefficients with values near 0.8 have been observed from the various SP² bonded carbon films¹². Hence, we propose that over a certain nitrogen

concentration, the SP² bonding fraction increases significantly in our a-CN films. The increase of the SP² bonded carbon is confirmed from the examination of the optical band gap. To estimate the optical band gap E_g we constructed a Tauc's plot in which the absorption coefficient α is plotted against the photon energy E as follows:

$$(\alpha E)^{1/2} = B(E - E_g)$$

where B is a proportional constant. The optical band gap E_g can be deduced from the intercept of the extrapolated straight lines with the E axis as shown in Fig. 3 (a). The variation of the deduced optical band gap of the a-CN films is presented in Fig. 3 (b): Here, we find that the optical band gap shrinks as the nitrogen ion beam current increases, which has been generally attributed to the growing SP² clusters^{4,18,20}.

In Fig. 4, the optical constants variation of the CN films which were deposited at various nitrogen ion beam energy values with the fixed ion beam current of 10 mA are shown. The most noticeable difference between Fig. 3 and Fig. 4 is the magnitude of the optical constant variation. As the nitrogen ion beam energy is increased, the whole refractive index n curve moves downward slightly as shown in Fig. 4 (a), and unlike in Fig. 2, the extinction coefficient k shifts up and down slightly while keeping the overall shape, as shown in Fig. 4 (b). This observation leads us to conclude that the optical constant variation is determined not only by the-ion bombardment damage, but more importantly by the nitrogen content. As already discussed above, the reduction of n can be attributed to the increase of the void fraction. Hence, Fig. 4 (a) suggests that the terminating CN triple bonding formation is promoted

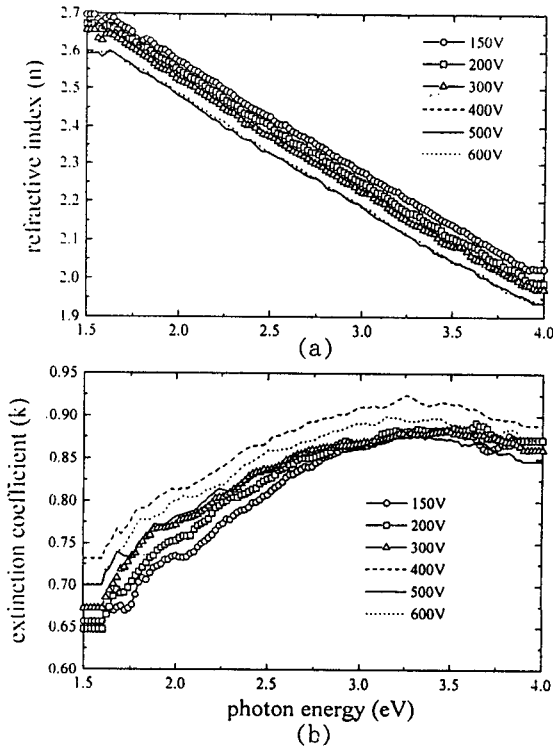


Fig. 4 The optical constants variation with nitrogen ion beam energy; (a) Refractive indices, (b) Extinction coefficients. The nitrogen ion beam energy were varied from 150 to 600 V at the fixed ion current of 10 mA.

by the higher ion energy. Also, based on Fig. 4 (b) we assess that at the lower ion beam current of 10 mA, the SP^2 bonding fraction does not increase over a certain level. Our asment is validated by the optical band gap variation shown in Fig. 5.

For the more detailed understanding of the a-CN film characteristics, it is required to quantify the nitrogen content, SP^2 and SP^3 bonding fractions, and the void fraction in the a-CN films. Also, the bonding character between the nitrogen and the carbon has to be examined. For these purposes, studies employing RBS, FT-IR, EELS, and a more advanced SE analysis using an effective medium theory are in progress.

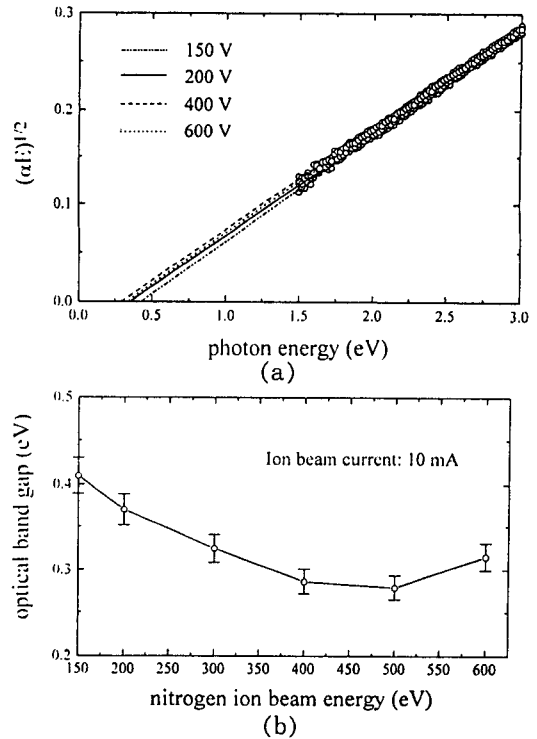


Fig. 5 Tauc's plot and the optical band gap variation with the nitrogen ion beam energy; (a) Tauc's plot, (b) the variation of the optical band gap. The nitrogen ion energy were varied from 150 to 600 V at the fixed ion current of 10 mA.

CONCLUSIONS

We used the combined ion-beam and laser ablation method to deposit amorphous carbon n itride films which seem to have very small grains of SP^3 bonded carbons embedded in amorphous SP^2 bonded carbons. We determined the optical constants of the a-CN films deposited under various conditions, and made an attempt to understand the observed optical constant variation in terms of the carbon and nitrogen bonding character change. We propose that the decrease in the refractive index is caused by the increase of the void fraction in the film due to the increased network terminat-

ing nitrogen-carbon triple bonding, the formation of which is promoted by the higher nitrogen ion current and/or energy. We also propose that as the nitrogen ion beam current and/or energy is increased, the SP^2 bonding fraction increases, which has been confirmed from the shrinkage of the optical energy gap.

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REFERENCES

1. A. Y. LIU and M. L. Cohen. *Science* **245**, (1989) 841.
2. B. Dishler, A. Bubenzer, and P. Koidl, *Appl. Phys. Lett.* **42**, (1983) 636.
3. F. Xiong, Y. Y. Wang, V. Leppert, and R. P. H. Chang, *J. Mater. Res.* **8**, (1993) 2265.
4. X. Wang and P. J. Martin, *Appl. Phys. Lett* **68**, (1996) 1177.
5. H. Xin, W. Xu, X. Shi, H. Zhu, C. Lin, and S. Zou, *Appl. Phys. Lett* **66**, (1995) 3290.
6. S. P. Withrow, J. M. Williams, S. Prawer, and D. Barbara, *J. Appl. Phys.* **78**, (1995) 3060.
7. K. Ogata, J. F. D. Chubaci, and F. Fujimoto, *J. Appl. Phys.* **76**, (1994) 3791.
8. A. Bousetta, M. Lu, A. Bensaoula, A. Schultz, *Appl. Phys. Lett.* **65**, (1994) 696.
9. A. Bousetta, M. Lu, and A. Bensaoula, *J. Vac. Sci. Technol. A* **13**, (1995) 1639.
10. X. Wang, P. J. Martin, and T. J. Kinder, *Thin Solid Films* **256**, (1995) 148.
11. J. Krieder, M. J. Tarlov, G. J. Gillen, G. E. Poirier, L. H. Robins, L. K. Ives, W. D. Bowers, R. B. Marinenko, and D. T. Smith, *J. Mater. Res.* **10**, (1995) 2265.
12. S. Kumar and T. L. Tansle, *J. Appl. Phys.* **76**, (1994) 4390.
13. A. Fernandez, P. Prieto, C. Quiros, J. M. Sanz, J. -M. Martin, and B. Vacher, *Appl. Phys. Lett.* **69**, (1996) 764.
14. Z. Ren, Y. Du, Z. Ying, Y. Qiu, X. Xiong, J. Wu, and F. Li, *Appl. Phys. Lett.* **65**, (1994) 1361.
15. Z. Ren, Y. Du, Y. Qiu, J. Wu, Z. Ying, X. Xiong, and F. Li, *Phys. Rev. B* **51**, (1995) 5274.
16. W. M. Kim, S. K. Lee, B. Cheong, S. G. Kim, O. S. Kim, and J. S. Ro, *Thin Solid Films* **270**, (1995) 237.
17. N. Savvides, *J. Appl. Phys.* **59**, (1986) 4133.
18. F. W. Smith, *J. Appl. Phys.* **55**, (1984) 764.
19. F. L. Frieire, Jr., C. A. Achete, G. Mariotto, and R. Canteri, *J. Vac. Sci. Technol. A* **12**, (1994) 3048.
20. J. Schwan, W. Dworschak, K. Jung, and H. Ehrhardt, *Diamond Relat. Mater.* **3**, (1994) 1034. n1