



Low voltage electrodeposition of CN_x films and study of the effect of the deposition voltage on bonding configurations

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Received 27 October 2004; accepted 14 December 2004

Available online 11 March 2005

Abstract

Carbon nitride (CN_x) films were deposited from acetonitrile at low voltage (150–450 V) through electrodeposition. The films were characterized by atomic force microscopy (AFM), Raman spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. AFM investigations revealed that the grain size was ~ 200 nm and roughness was ~ 10 nm. The films were found to be continuous and close packed. IR spectra revealed existence of strong sp^3 , sp^2 type bonding and weak sp type carbon nitrogen bonds and these bonds were found to increase with voltage. The fraction of sp^3 -bonded species in the sample increased in low voltage range and after reaching maximum at 350 V, decreased for higher voltages. However, the concentration of sp^2 CN ring structures in the film increased with increasing voltage. Also, the peak width decreased at low voltages reaching a minimum and increased thereafter. It was observed that the voltage dependent increase in the concentration of polymeric type sp^2 CN (chain) structures was much more pronounced than that of graphitic type sp^2 CN (ring) structures. Raman spectra showed the presence of both the D and G bands. The shift in the G band indicated the presence of nitrogen in the film. The I_D/I_G ratio was found to increase with the incorporation of nitrogen. Auger electron spectroscopy (AES) showed a clear increase in the nitrogen content with increase in the voltage. The formation of the film could be explained on the basis of dissociation of electrolyte under applied voltage.

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Keywords: Carbon nitride; Vibrational properties characterization; Scanning probe techniques

1. Introduction

Since Lin and Cohen [1] proposed the existence of hypothetical C_3N_4 having tribiological properties comparable to diamond, C_3N_4 has received consider-

able interest in materials science. Carbon nitrides have been previously synthesized by chemical vapor deposition (CVD) [2], laser ablation [3], magnetron sputtering [4] and filtered arc deposition [5]. Most of these methods are vapor deposition methods where controlling the stoichiometry is difficult. Recently electrodeposition technique for the deposition of CN_x [6,7] has received considerable attention as it offers a number of advantages over the other methods like

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large area deposition, simpler apparatus, milder reaction condition and lower deposition temperature. Electrodeposition of thin films of CN_x have been carried out in acetonitrile [6–9], saturated solution of melamine in acetonitrile [10], solution of urea in methanol [11], and dimethylformamide (DMF) [12]. In all these cases, deposition has been carried out in the potential range 400–4000 V and the high voltage used causes near-wall boiling of the electrolyte. This heating of the electrolyte near the electrode surface causes degradation in the film quality, poorer deposition rate and poor adhesion of the as-formed film to the substrate [13]. This problem can be overcome by using a lower potential. However, the current density decreases at lower potentials resulting in a lower deposition rate. We recently overcame this problem in the deposition of diamond-like carbon (DLC) by conducting the deposition at a lower potential at lesser electrode separation [14]. We also observed that under different deposition potentials, the bonding configuration of carbon with nitrogen varies with the applied voltage, as the increase in the voltage is known to cause a greater dissociation of the electrolyte. Since the bonding configurations in the film are known to affect the physical and chemical properties of the film, the study of voltage dependence of the concentration of different groups present in the film is of central importance. To the best of our knowledge there are no previous references on such a study for electrodeposition for carbon nitrides. In the present study, we have deposited carbon nitride from acetonitrile at deposition voltages of 150–450 V, which are much less than the potential used for acetonitrile electrolyte by previous authors [6–9]. The effect of the voltage on the incorporation of nitrogen and different bonding configurations in the film is also studied. The surface morphology of the films was studied by AFM. The bonding characteristics were studied by Raman and FT-IR spectroscopy. Nitrogen content in the film was measured by AES.

2. Experimental

Single crystal p-type Si(1 1 1) from Wacker-chemitronic GmbH with resistivity (ρ) 0.8–1.2 Ω cm was used as positive electrode and graphite was used as negative electrode. The interelectrode

separation in all the cases was 2 mm. Prior to deposition, Si(1 1 1) was degreased in trichloroethylene and rinsed with acetone and subsequently dipped in 40% HF for 2 min to remove the surface oxide layer. Four films were deposited at voltages of 150, 250, 350 and 450 V for a deposition time of two hours. Raman spectra were collected by LABRAM1, ISA make spectrometer in the back scattering geometry with 488 nm line of Ar^+ laser. Infrared spectra were collected with Bomem MB 102 spectrometer in the range 50–4000 cm^{-1} at a spectral resolution of 2 cm^{-1} in transmission mode. AFM studies were carried out using scanning probe microscope SPM-Solver P47, NT-MDT, Russia using rectangular silicon nitride tips (tip radius \sim 10 nm). AES analysis was conducted to identify the elemental ratio.

3. Results and discussion

3.1. Current density–time behavior

Fig. 1 gives the current density–time behavior for the potentials 150 and 250 V. The current density for the 250 V case is higher than the one prepared at 150 V, this is due to the fact that under a higher field, the dissociation of the electrolyte is higher. Also in both the cases the current density is found to decrease with time and gets saturated after 20 min. This observation could be explained by the fact that, as the

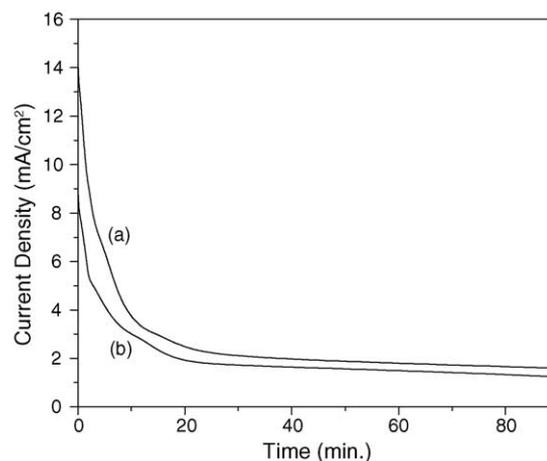


Fig. 1. The current density–time behavior of the samples deposited at (a) 250 V (b) 150 V.

deposition continues, more and more area of CN_x covers the silicon substrate, therefore the substrate changes from low resistive silicon to higher resistive carbon nitride for longer deposition time. Hence, the current density decreases as the surface is covered by CN_x and after complete coverage of silicon substrate surface, the current saturates. It is worth pointing out that the deposition rate is proportional to the current density and therefore, as the current density decreases the deposition rate also decreases.

3.2. Morphology

The AFM pattern of the film prepared at 250 V is given in Fig. 2. It is clear from the figure that the films were compact and the individual grains were of the order ~ 200 nm. The root mean square roughness of the film was ~ 10 nm. At higher voltages, the roughness of the film was found to be too high and therefore, could not be measured.

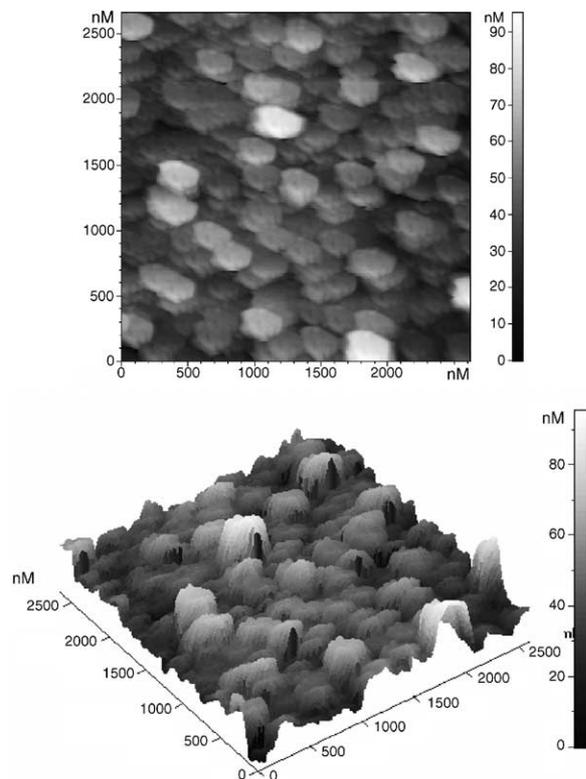


Fig. 2. AFM pattern of the sample prepared at 250 V.

3.3. Bonding characteristics

3.3.1. Infrared studies

In carbon nitrides, carbon and nitrogen are bonded in different configurations, depending on the hybridization of carbon (sp , sp^2 or sp^3) [15]. These bondings are known to have a major influence on the properties of the carbon nitride films. Therefore, study of the bonding in carbon nitrides prepared by electrochemical means is important. Infrared spectroscopy is a valuable tool in the characterization of bonding and therefore, is routinely used in the characterization of CN_x films. Each of the bonding configurations is known to give a different IR response. In the present case, we are interested in assessing the effects of the electric field on the nature of the bondings in the film. An increase in the electric field is known to increase the concentration and energy of the precursor ions formed from the dissociation of the electrolyte, thereby affecting the incorporation of nitrogen in the amorphous carbon network.

Fig. 3 gives the representative IR spectra of the samples. The assignment of the major peaks obtained in the samples is given in Table 1. The region 1000 – 1800 cm^{-1} consists of the peaks due to sp^2 and sp^3 bonded carbon–carbon and carbon–nitrogen bonds. The peaks at 1370 and 1560 cm^{-1} are the G and D bands of the sp^2 ring (hexagonal) structures. These bands are inactive in IR for graphite. However, in CN_x films, the symmetry breaking due to the incorporation of nitrogen and polarization of the sp^2 carbon attached to nitrogen causes the band to appear in the spectrum. The band at ~ 1650 cm^{-1} corresponds to the stretching mode of sp^2 C=N chain type bonding. The peak at 1250 and 1460 cm^{-1} corresponds to sp^3 C–N stretching and bending modes of C–H bond, respectively. The region between 2000 and 2300 cm^{-1} corresponds to stretching mode of sp^1 CN bonding. In the present case, the films were found to have very weak absorption in the region 2000 – 2300 cm^{-1} as shown in inset of Fig. 3. In carbon nitrides, $-C\equiv N$ is present as the terminal group, i.e. it truncates the network. A gaussian line shape was used for deconvolution of the spectrum in the region 1000 – 1800 cm^{-1} . The peak at 1100 cm^{-1} arises due to Si–O bonds. The spectra of the individual samples prepared under different voltages were deconvoluted and the influence of voltage on the concentration of different

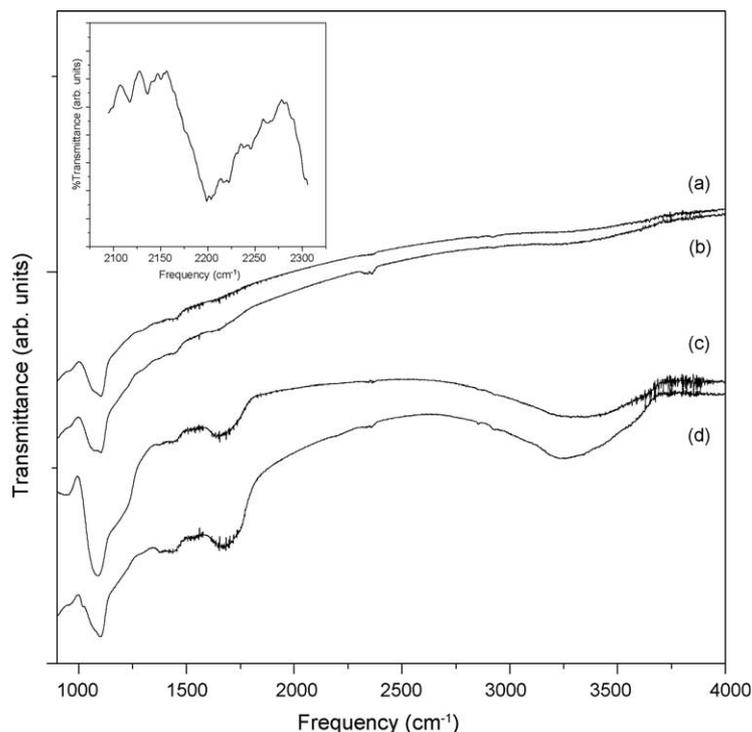


Fig. 3. Typical IR transmission spectrum of the samples: (a) 150 V (b) 250 V (c) 350 V (d) 450 V.

bonding configurations was carried out. The area of an individual group obtained from the deconvolution is normalized with the total area in the region to get the relative fraction of different bonds. It must be remembered that the normalized intensity is directly proportional to the concentration of the group responsible for the vibration. Moreover, the broadening of the individual peak denotes the disorder in the film. The study of the effect of the voltage on different bonding configuration present in the films is described below for different groups.

Table 1
Vibrational frequencies of different groups [16–19]

Group	Stretching vibrational frequency (cm^{-1})
C–N (tetrahedral)	~1212–1280 (stretch)
C=N (ring)	~1530 (stretch)
C=C (chain)	~1665–1680 (stretch)
C=N (chain)	1650–1680 (stretch)
–NH	~1720 (deformation)
–C≡N	~2200 (stretch)
–NH	~3353 (stretch)

3.3.1.1. sp^3 C–N bond. Fig. 4a indicates an increase in the bond fraction of sp^3 C–N bonds till 350 V and decrease for higher voltages. This clearly points to the fact that there is an optimum voltage for the growth of these structures in the film. The study of the effect of nitrogen on sp^3 to sp^2 transformation by Hu et al. [20] reveals that for high nitrogen (11–17%) sp^2 phase is energetically favored compared to sp^3 phase. As the voltage increases there is a greater presence of ions, hence more nitrogen is incorporated, thereby showing a decrease in the concentration of sp^3 phase in accordance with the present experimental observation. It is also observed from Fig. 4b that the peak position of this bond increases to higher frequencies for deposition potentials up to 350 V and decreases for higher voltages. Fig. 4c depicts an increase in the broadening of this sp^3 peak with an increase in the voltage indicating large distortions in these structures at higher voltages.

3.3.1.2. sp^2 C=C bond (rings). This peak is generally referred to as G peak and is inactive in IR spectrum for

graphite, however when carbon of the sp^2 ring system is bonded to nitrogen, there is an induction of static charge on the carbon bonded to nitrogen leading to an increase in the dynamic charge on the carbon thereby making the bond IR active. As more and more nitrogen is incorporated in the film, greater number of sp^2 ring structures becomes active, indirectly indicating the presence of nitrogen [21]. It is clear from Fig. 4a that the relative bond fraction of the G peak increases with respect to voltage while the peak position (Fig. 4b) decreases. Kaufman et al. [22] reported profound change in the IR spectra on incorporation of nitrogen for CN_x . Victoria et al. [23] reported that hydrogen also produces similar effects as nitrogen on the IR response. In the present case, both nitrogen and hydrogen are incorporated in the films as evidenced by IR spectra. Therefore, the shift in the peak position is a combined effect of both hydrogen and nitrogen present in the sample. Further studies are needed to understand the exact contribution from hydrogen and nitrogen. Moreover, we observed a decrease in the FWHM till 250 V (Fig. 4c) and an increase for higher voltages. This indicates a decrease in the disorder of the film for voltage till 250 V and an increase above this voltage. The nitrogen atom in graphitic ring type structures are present in the substitutional positions (i.e. in place of carbon), there being presumably only one nitrogen in a ring, for a low concentrations. This does not change the shape of the basal planes of graphite structure. The limit for the incorporation of the nitrogen without any distortion of basal planes is ~ 16 at.% of nitrogen and for higher concentrations, there could be large-scale distortions in the graphite structures [24]. The increase in the voltage can have two effects in the present case: (i) formation of higher concentration of precursor ions, leading to formation of more ordered domains [14], (ii) increase in nitrogen content owing to greater dissociation of the electrolyte. In the low voltage range, i.e. 0–250 V, presumably the nitrogen incorporation in the film is less than 16 at.% and, hence, the first effect is predominant, leading to the formation of a more ordered film. However, under high voltage the incorporation of nitrogen could be high enough, i.e. greater than 16 at.%, leading to large scale distortion of the lattice and hence, an increase in the FWHM with increase in voltage beyond 250 V.

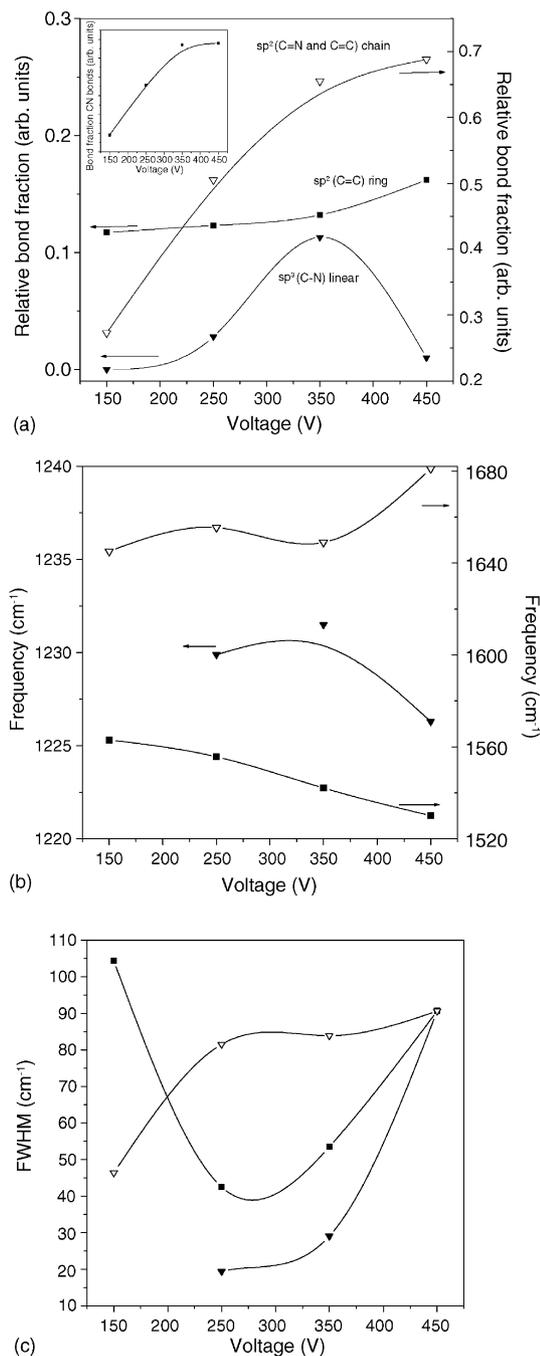


Fig. 4. The dependence of (a) relative bond fraction (b) peak position and (c) FWHM (broadening) of the peaks from the IR spectrum (open triangles: sp^3 C–N bond, filled triangles: sp^2 C=N and C=C bond (chains), Filled squares sp^2 C=N bond (rings)).

3.3.1.3. sp^2 C=N and C=C bond (chains). These peaks appear at position $\sim 1650\text{ cm}^{-1}$, since both of these peaks are situated very near the individual contribution, i.e. C=N and C=C could not be separated. An increase in the bond fraction of these linkages is clear from Fig. 4a. The increase in the bond fraction of these bonds with respect to voltage as compared to nitrogen incorporated C=C ring type linkage is much higher, indicating that at high voltages the film formed would be preferably of polymeric type. Furthermore, a gradual shift in the peak position (Fig. 4b) towards higher wave numbers with increasing voltage has been observed in our study. Also, the peak width (Fig. 4c) increases, implying a decrease in the long-range order of such bonding types with increasing voltage.

3.3.1.4. D peak and I_D/I_G . Fig. 5 gives the plots of peak position for D peak (Fig. 5a) and I_D/I_G (Fig. 5b) versus the voltage. It clearly illustrates a decrease in D peak position and I_D/I_G with voltage. Incorporation of nitrogen and hydrogen in the CN_x film is known to cause vast changes in the IR spectra as reported previously by Kaufman et al. [22] and Victoria et al. [23]. As mentioned earlier, the incorporation of nitrogen in the carbon network causes the symmetry breaking of the ring modes thereby making the D and G bands active [22]. Ferrari et al. [21] attributed the change to polarization of sp^2 carbon bonded to nitrogen. These authors also observed an increase in I_D/I_G with the incorporation of nitrogen in the film and they attributed this change to clustering of the sp^2 bonded carbon. Victoria et al. reported changes in IR even when the hydrogen content is changed and concluded that hydrogen produces similar effects as nitrogen in the IR spectrum of carbon nitrides [23] and they observed a decrease in I_D/I_G with increase in hydrogen. In the present case, we obtain a decrease in the I_D/I_G . Since the CN_x films prepared by us contain both hydrogen and nitrogen the reason for the observed behavior could be a combined effect of both hydrogen and nitrogen.

3.3.2. Raman study

Fig. 6 gives the Raman spectra of a typical film and the deconvolution to the respective components. The Raman spectra show two peaks, one at $\sim 1370\text{ cm}^{-1}$ and other at $\sim 1570\text{ cm}^{-1}$. The 1370 cm^{-1} peak is the

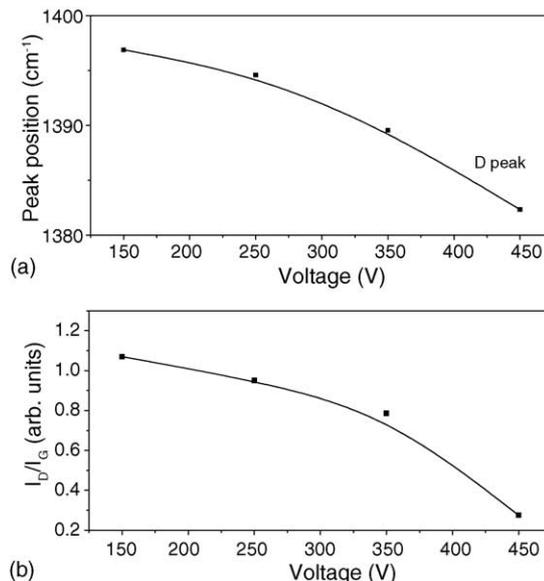


Fig. 5. The Dependence of (a) D peaks position (b) I_D/I_G with respect to voltage from the IR spectrum.

D band (breathing mode) of sp^2 ring (hexagonal or graphitic) structures [25,26], generally absent in the Raman spectra of crystalline graphite. However, this band is activated due to breakdown of the momentum selection rule caused by small domain size or impurities (substitutional nitrogen in the present case) [24]. The 1570 cm^{-1} band corresponds to the E_{2g} vibrational mode arising from the stretching of pairs of sp^2 atoms [25,26]. The shift in the G band from the ideal value of 1580 cm^{-1} for graphite is indicative of the formation of carbon nitride. As observed from the figure, the position of G band slightly decreases with the voltage (Fig. 7a). The peak width of the individual G band shows a small decrease till 250 V and thereafter an increase. This behavior is similar to that observed in the corresponding IR spectra. Fig. 7b shows the variation of I_D/I_G with voltage. It clearly indicates an increase in the I_D/I_G with respect to voltage; in CN_x films this ratio is found to increase with an increase in nitrogen. This is opposite of what is observed from the IR spectra as mentioned earlier. The incorporation of nitrogen and hydrogen influences the dynamic charge on carbon attached to the nitrogen thereby affecting the IR spectrum. However, this is not the case for Raman spectrum, which is affected only

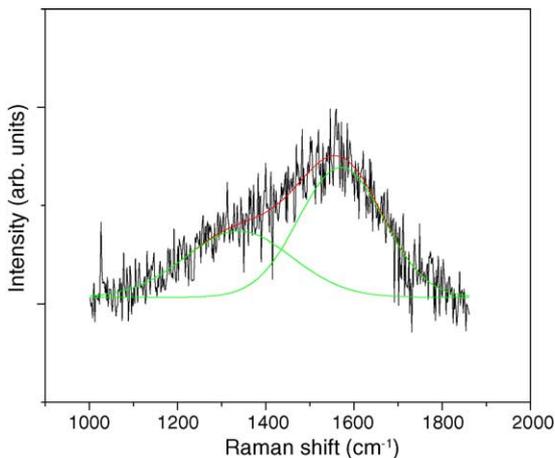


Fig. 6. Typical deconvolution of the Raman spectra of one of the samples.

by the presence of nitrogen [23]. Therefore, this observation further confirms that nitrogen content increases in the film with respect to voltage. It is noted that the variation of the ratio I_D/I_G is much more sensitive than the G band shift [21,23] to the nitrogen incorporation.

3.3.3. AES study

The nitrogen content in the films was analyzed by AES. Fig. 8 gives the AES patterns for the samples prepared at 350 and 450 V. The percentages of carbon and nitrogen in the films are also given in the figure. The samples prepared under a voltage of 350 and 450 V is found to have a nitrogen content of ~18% and ~31%, respectively. This shows clearly the evidence of higher nitrogen content at high voltages confirming the observation from the IR spectrum that the nitrogen content in the films increases with the increase in applied voltage.

3.4. Mechanism

Previous studies on the deposition of carbon nitrides by CVD, IBD and pulsed laser deposition revealed a major role of ionic species produced during the deposition [27,28]. We believe that in the present case also the presence of ions near the electrode surface during deposition plays a major role in the formation of the film. The ions are formed by the dissociation of the electrolytes. The applica-

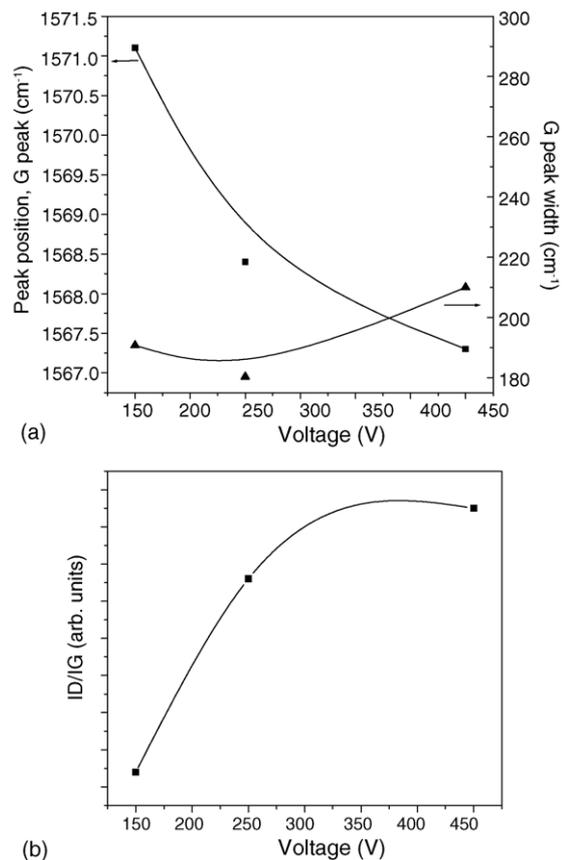
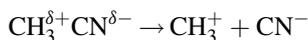
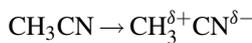


Fig. 7. The Raman spectrum of the films: (a) right Y-axis (filled triangles) G peak width, left Y-axis (filled squares) G peak position and (b) I_D/I_G with respect to voltage.

tion of high field causes the polarization of the electrolyte and subsequent ionization. These can be described as



The CN^- is added across the surface and this step continues further to form the film. In the present case, we found that the films were hydrogenated, indicating that H^+ and H^\bullet were present during the formation of these films. H^\bullet and H^+ are known to play a major role in the deposition of diamond and diamond-like carbon films [29]. We believe that in the present case too it may have a major role to play. Our IR studies revealed an increase in the CN related bonding with voltage.

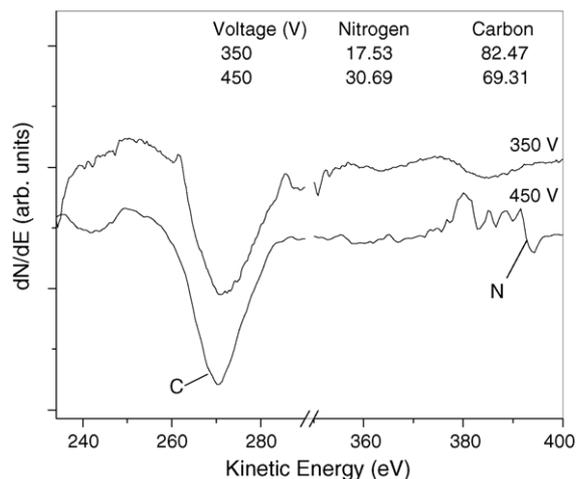


Fig. 8. AES spectra of the 350 and 450 V samples.

This could be explained by the fact that at higher field there was a greater dissociation of the electrolyte and hence, more precursor ions were available for growth. This is in accordance with the current density data as a function voltage.

4. Conclusion

CN_x films were synthesized by a low-voltage electrodeposition technique. The grain size and roughness in the film were found to be ~200 and ~10 nm, respectively. The IR patterns revealed the presence of a number of species with different bonding configurations between carbon and nitrogen, i.e. sp, sp², sp³. The sp bond was found to be very less in the present set of samples, revealing the larger grain size in the film. The extent of individual bonding configurations in the films were found to vary depending on the deposition voltage. The major effects of the voltage can be summarized as follows:

- i. The overall concentration of CN bonded species was found to increase with voltage. Optimum voltage was required for the formation of C–N bond. The concentration of this group was found to first increase and then decrease for higher voltages. This was reasoned out as due to sp³ to sp² conversion of the bond between C and N. Also, the peak position showed a shift to higher frequencies

and broadening with increasing voltage. The sp² CN ring structures were found to form under higher voltages. Furthermore, the broadening decreased with voltage initially for low voltages and increased for higher voltages revealing an increase in the order in the film due to distribution of nitrogen to large number of ring structures and formation of ring type (graphitic) species with larger domain size. Under higher voltages, the incorporation of larger concentration of nitrogen leads to distortion of the ring structure and, hence, destruction of long-range order in the film. The sp² CN (chain) type linkage had greater formation probability under higher potentials. The increase in the concentration of this type of linkage is found to be much more pronounced than that of ring type linkage, indicating that the films formed under higher fields would be of polymeric type.

- ii. The Raman results showed the presence of both the D and G bands. The shift in the G band indicated the presence of nitrogen in the film. Furthermore, the I_D/I_G was found to increase with the incorporation of nitrogen in accordance with previous studies.
- iii. The AES studies revealed an increase in the overall nitrogen content in the film with respect to voltage confirming the IR studies.
- iv. The importance of the role of ions after the dissociation of the electrolyte has been emphasized. Increase in nitrogen incorporation in the film with the voltage could be due to increased dissociation of the electrolyte under high fields.

Acknowledgements

We are thankful to Dr. S.K. Kulshreshtha, Head, Novel Materials & Structural Chemistry (NM&SC) Division for his constant encouragement and support. We thank Dr. (Smt.) Shilpa N. Sawant for the AFM measurements and Shri. Mainak Roy, NM&SC Division for his help in Raman measurements.

References

- [1] A.Y. Liu, M.L. Cohen, Science 245 (1989) 841.
- [2] H.K. Woo, Y. Zhang, S.T. Lee, C.S. Lee, Y.W. Lam, K.W. Wang, Diamond Relat. Mater. 6 (1997) 635.

- [3] J. Seth, R. Padiyath, S.V. Babu, *Diamond Relat. Mater.* 3 (1994) 1034.
- [4] S. Lopez, M.-S. Wang, W.D. Sproul, *J. Vac. Sci. Technol. A* 13 (1995) 1644.
- [5] Z.Y. Chen, Z.P. Zhao, Y.H. Yu, X. Wang, S.Q. Yang, T.S. Shi, X.H. Liu, *Mater. Lett.* 33 (1997) 85.
- [6] J.W. Wei, Y. Zhang, X. Hi, W. Liu, C.S. Lee, S.T. Lee, *Mater. Lett.* 38 (1999) 98.
- [7] Q. Fu, J.-T. Jiu, H. Wang, C.-B. Cao, H.-S. Zhu, *Chem. Phys. Lett.* 301 (1999) 87.
- [8] C. Cao, H. Wang, H. Zhu, *Diamond Relat. Mater.* 9 (2000) 1786.
- [9] Q. Fu, J.-T. Jiu, K. Cai, H. Wang, C.-B. Cao, H.-S. Zhu, *Phys. Rev. B* 59 (1998) 1693.
- [10] C. Li, C.-B. Cao, H.-S. Zhu, Q. Lv, J.T. Zhang, X. Xiang, *Mater. Sci. Eng. B* 106 (2004) 308.
- [11] S. Kundoo, A.N. Banerjee, P. Saha, K.K. Chattopadhyay, *Mater. Lett.* 57 (2003) 2193.
- [12] H. Wang, H. Kiyota, T. Miyo, K. Kitaguchi, T. Shiga, T. Kurosu, H.-S. Zhu, M. Iida, *Diamond Relat. Mater.* 9 (2000) 1307.
- [13] M.C. Tosin, A.C. Peterlevitz, G.I. Surdutovich, V. Baranaukas, *Appl. Surf. Sci.* 144–145 (1999) 260.
- [14] K. Sreejith, J. Nuwad, C.G.S. Pillai, *Appl. Surf. Sci.*, article in press.
- [15] A. Laskarakis, S. Logothetidis, M. Gioti, *Phys. Rev. B* 64 (2001) 125419.
- [16] N. Nakayama, Y. Tsuchiya, S. Tamada, K. Kosuge, S. Nagata, K. Takahiro, S. Yamaguchi, *Jpn. J. Appl. Phys.* 32 (1993) 1465.
- [17] M.R. Wixom, *J. Am. Ceram. Soc.* 73 (1990) 1973.
- [18] Y. Liu, C. Jiaa, H. Do, *Surf. Coating Technol.* 115 (1990) 95.
- [19] V.N. Khabashesku, J.L. Zimmerman, J.L. Margrave, *Chem. Mater.* 12 (2000) 3264.
- [20] J. Hu, P. Yang, C.M. Lieber, *Phys. Rev. B* 57 (1998) R3185.
- [21] A.C. Ferrari, S.E. Rodil, J. Robertson, *Phys. Rev. B* 67 (2003) 155306.
- [22] J.H. Kaufman, S. Metin, D.D. Saperstein, *Phys. Rev. B* 39 (1989) 13053.
- [23] N.M. Victoria, P. Hammer, M.C. dos Santos, F. Alvarez, *Phys. Rev. B* 61 (2000) 1083.
- [24] N. Hellgren, M.P. Johansson, E. Broitman, L. Hultman, J.-E. Sundgren, *Phys. Rev. B* 59 (1999) 5162.
- [25] F. Tunistra, J.L. Koenig, *J. Chem. Phys.* 53 (1970) 1126.
- [26] C. Castiglioni, F. Negri, M. Rigolo, G. Zerbi, *J. Chem. Phys.* 115 (2001) 3769.
- [27] G.M. Fuge, C.J. Rennick, S.R.J. Pearce, P.W. May, M.N.R. Ashfold, *Diamond Relat. Mater.* 12 (2003) 1049.
- [28] L. Nemes, M. Mohai, Z. Donko, I. Bertoli, *Spectrochim. Acta A* 56 (2000) 761.
- [29] W.A. Yarbrough, R. Messier, *Science* 247 (1990) 688.