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Factors controlling the structural properties of carbon nitride films deposited by electrochemical method

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Polycrystalline carbon nitride thin films were deposited on Si (100) substrates by electrolysis of methanol-urea solution at atmospheric pressure and low temperature. The effect of the process parameters, namely deposition time, concentration and applied voltage on growth and bonding state of carbon nitride (CN_x) thin films was studied using Fourier transform infrared (FTIR) spectroscopy, grazing incidence X-ray diffraction (GIXRD) and scanning electron microscope (SEM). The analysis of infrared (IR) spectra revealed that the nitrogen content in the film increased with increasing both urea concentration and the applied voltage. It found from GIXRD patterns that the crystalline structure of carbon nitride films at moderate nitrogen content changed from amorphous phase to polycrystalline α -C₃N₄, and β -C₃N₄ phases. At relatively higher nitrogen content, a new phase of CN_x appeared which increased gradually and became the more predominant phase. SEM images of the films indicated that the surface of the deposited films consists of homogeneous grains of ~0.2 μ m and these grains became more closely packed with increasing nitrogen content.

Key words: Carbon nitride, thin films, structure properties.

INTRODUCTION

Ever since the first-principle pseudopotential calculation of novel superhard crystalline α -C₃N₄ and β -C₃N₄ by Liu and Cohen (1989) and Cohen (1985), the synthesis of these phases has been a challenging research in modern science. So far, five different structures of C₃N₄ have been proposed (Teter and Hemley, 1996): the hexagonal α -C₃N₄ and β -C₃N₄, the cubic and pseudocubic C₃N₄ phases and the graphitic C₃N₄. The properties of their high hardness, high thermal conductivity, high atomic density and wide band gap make them have wide potential applications in various fields, such as good cutting tools, excellent resistance to corrosion and wear, heat-dissipative substrates for devices to be used in short wavelength photodiodes. Over the past few years, different kinds of amorphous carbon nitride films have been synthesized. However, the methods known for

depositing these films, such as particle-beam-assisted laser processing (Zocco et al., 1999), magnetron sputtering (Lopez et al., 1998) and ion-beam-assisted deposition (Hammer et al., 2000), were all vapor deposition. Compared to vapor deposition techniques, electrodeposition from a liquid phase has advantages such as the simplicity of the apparatus and the fact that this process can be performed at atmospheric pressure and near room temperature. Depositing the films at low temperatures also decreases the thermal stresses that can develop in the films and in the substrates as they are cooled. The electrodeposition process is also attractive because of its low production cost and easy scalability. Only in recent years have a few attempts been made to synthesis carbon nitride films by electrodeposition from various organic liquids under high voltages. Among these, Fu et al. (1999) reported the synthesis of an amorphous carbon matrix containing some mixed polycrystalline phases of α -C₃N₄ and β -C₃N₄. More recently, Kundoo et al. (2003) succeeded in depositing crystalline carbon nitride films by electrolysis of methanol-urea solution.

In carbon nitrides, carbon and nitrogen are bonded in different configurations, depending on the hybridization of

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Abbreviations: GIXRD, Grazing incidence X-ray diffraction; CN_x, carbon nitride; FTIR, fourier transform infrared; SEM, scanning electron microscope.

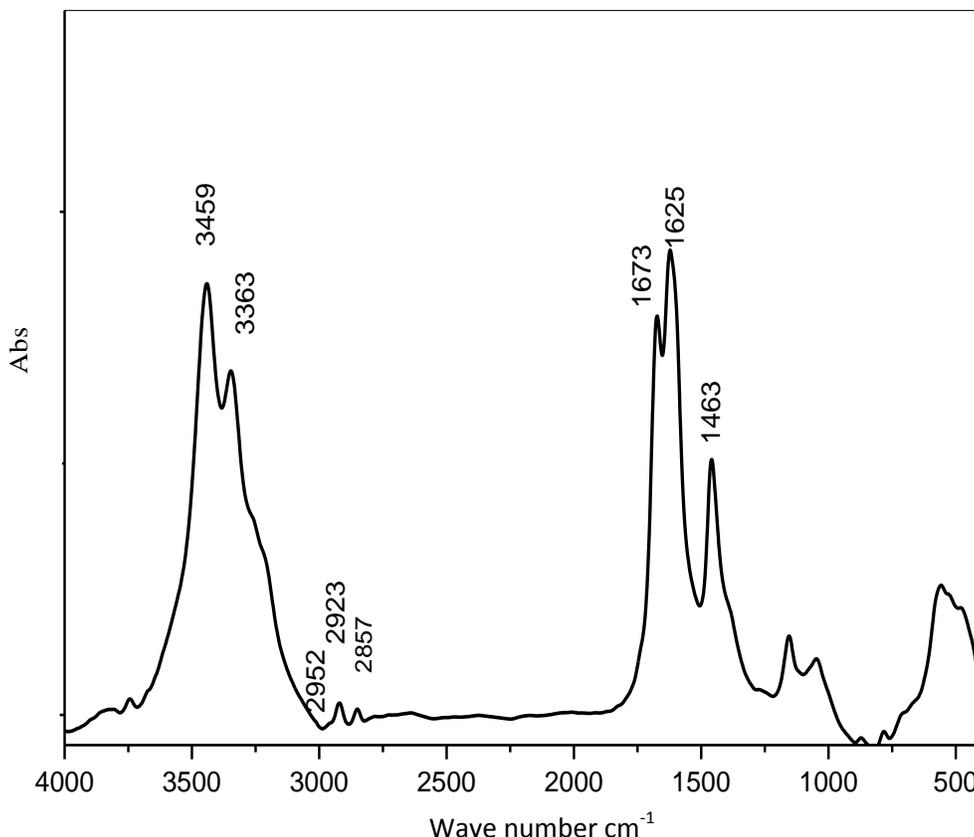


Figure 1. FTIR spectrum of sample deposited under concentration 2:1000 of urea to methanol at 800 V for 10 h.

carbon (sp , sp^2 or sp^3). 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.

In this paper, carbon nitride films were deposited on a silicon substrate by the electrolysis of methanol-urea solution under different conditions. Fourier transformation infrared (FTIR) spectrometry, grazing incidence X-ray diffraction (GIXRD), scanning electron microscope (SEM) with energy dispersive X-ray (EDX) were used in assessing the effects of the process parameters on the nature of the bonds in the film, and morphology of the deposited films.

Experimental

Preparation of carbon nitride (CN_x) films

A simple electrolytic cell system was used to prepare the CN_x films as used elsewhere (Kundoo et al., 2003; Yan et al., 2004). A substrate of Si (100) with a sheet resistance of about $7\text{--}13 \Omega\text{cm}^{-2}$ was mounted on the negative electrode. A graphite plate was used as the counter-electrode. The span between the electrodes in all cases was kept as 6 mm. Urea ($\text{CO}(\text{NH}_2)_2$, purity above 99.9%) dissolved in analytically pure methanol (CH_3OH , purity above 99.5%) was used as the electrolyte. The electrolytic solution was

prepared by mixing 0.075 (first), 0.15 (second) and 0.3 g (third) urea per 100 ml methanol. Prior to deposition, Si (100) was immersed in an aqueous solution of 5%HF for a few minutes to remove the native oxide layer, sequentially cleaned in an ultrasonic bath with deionized water, ethanol, and acetone, and then placed in the electrolytic solution, with an area of $1.0 \times 1.5 \text{ cm}^2$ submerged to allow the deposition of the CN_x film at a temperature of about $60 \pm 2^\circ\text{C}$, a direct current (dc) power-supply voltage of 0-1200V by applying three different voltages 800, 1000 and 1200 V.

Measurements

FTIR was used in the mid range $4000\text{--}400 \text{ cm}^{-1}$ on Jasco FT/IR-430. X Pert panalatical GIXRD was performed in the range $10\text{--}90^\circ$ using $\text{CuK}\alpha$ as X-ray source, operated at 40 kV/30 mA and an incidence angle of 0.5° . SEM of the model JEOL JXA-840A Electron probe micro analyzer was used to observe the morphology of the films.

RESULTS AND DISCUSSION

FTIR spectroscopy

The FTIR spectrum of the sample deposited with the concentration of mole ratio 2:1000 of urea to methanol under 800 V for 10 h is shown in Figure 1. The spectrum

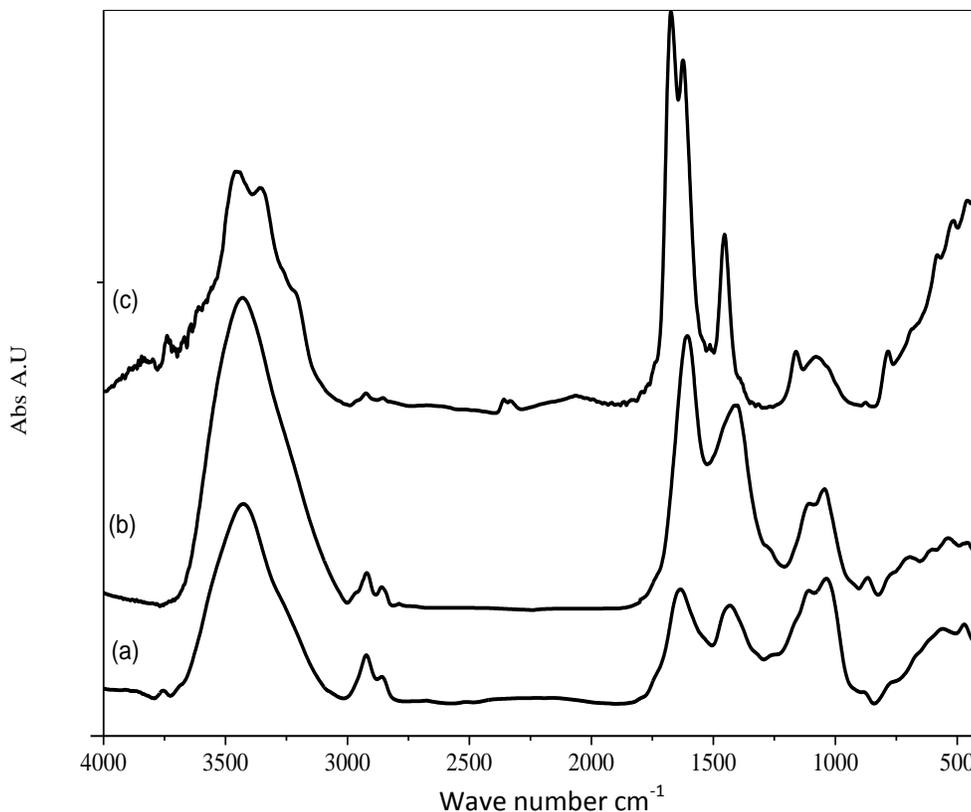


Figure 2. FTIR spectra of sample deposited with first (a) and third (c) concentrations under 800 V for 6 h.

exhibits absorption bands at 3459, 3363, 2952, 2923, 2857, 1673, 1625 and 1463 cm^{-1} . The assignments of these frequencies to their functional groups were carried out by comparison with the assignments reported in text books and literature. The peaks at 3459 and 3363 cm^{-1} are attributed to N-H stretching vibrations (Kundoo et al., 2003; Yan et al., 2004). The peaks at 2923 and 2857 cm^{-1} are assigned as CH_2 asymmetric stretching vibration and CH_3 symmetric stretching vibration respectively (Kundoo et al., 2003; Yan et al., 2004). It can also be observed that, there is weak shoulder at 2952 cm^{-1} which may be due to CH_3 asymmetric stretching vibration. The spectrum exhibits a peak at 1625 cm^{-1} ; this peak is due to the C=N stretching vibration (Majumdar et al., 2008). The presence of the peak at 1673 cm^{-1} indicates the existence of C=C bond. There is no significant peak attributed to $\text{C}\equiv\text{N}$. The peak at 1463 cm^{-1} is due to overlapping of C-H bending vibration and C-N single bond stretching vibration (Kundoo et al., 2006). The presence of these peaks proves that CN_x films were deposited on Si substrate.

FTIR spectra of carbon nitride films prepared at various concentrations of urea to methanol first, second and third concentrations at a constant voltage (800 V) for constant time (6 h) are shown in Figure 2. Visual examination of the spectra revealed the following:

- (1) In the region of the N-H stretching vibration, the spectrum of the sample deposited under the first concentration shows only a single broad band centered at 3436 cm^{-1} . The spectrum of the sample deposited under the second concentration displays the same features as before. On the other hand, the spectrum of the sample deposited under the third concentration exhibits two peaks in this region at 3436 and 3355 cm^{-1} .
- (2) In the region of the C-H stretching vibrations the spectra of the samples deposited under both the first and the second concentrations show two definite absorption bands at 2923 and 2858 cm^{-1} , while in the case of the third concentration the absorption in this region appears very weak.
- (3) In the region from 1700 to 1300 cm^{-1} the spectrum of the sample deposited under the first concentration shows two broad bands at 1634 and 1434 cm^{-1} , while in the case of the second concentration the spectrum displays these two peaks at 1604 and 1411 cm^{-1} . In case of the third concentration the recorded spectrum displays three bands at 1673, 1623 and 1454 cm^{-1} . The absence of both C-H stretching and C-H bending vibrations from the spectrum of the sample deposited at the third concentration resulted in the presence of a single stretching peak at 1454 cm^{-1} corresponding to the absorption of C-N stretching only.

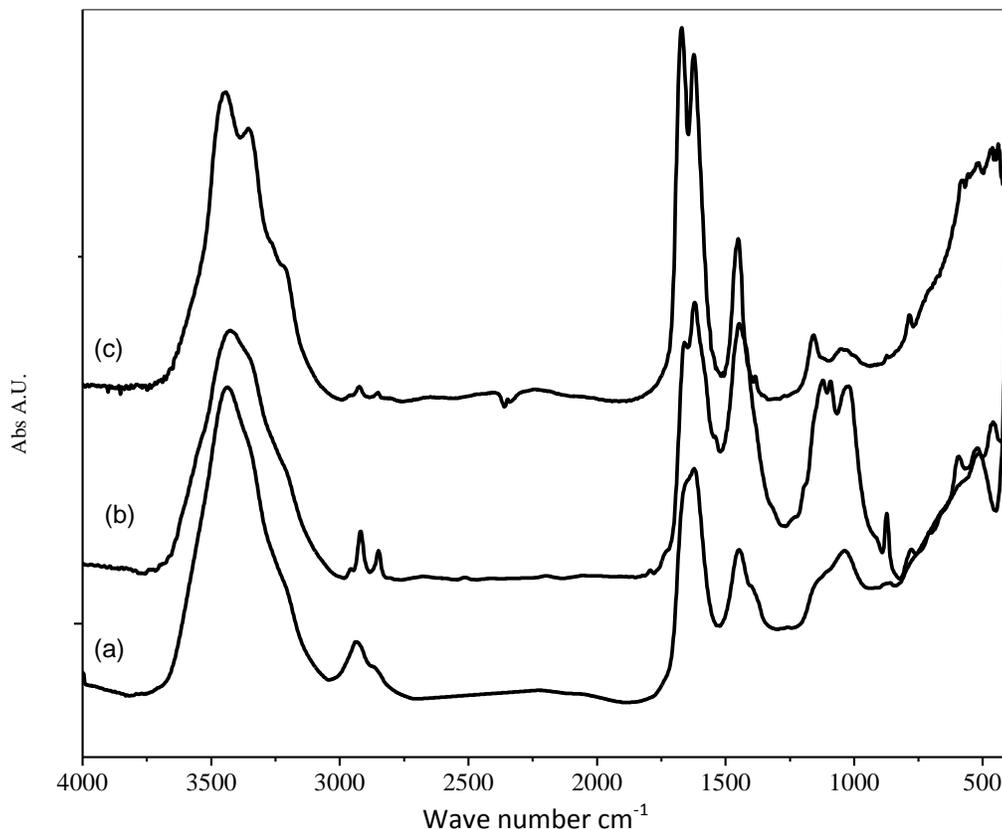


Figure 3. FTIR spectra of sample deposited with first (a) and third (c) concentrations under 1000 V for 6 h.

Based on the earlier mentioned observations, it could be concluded that increasing concentration from first to third concentration resulted in splitting the broad band of N-H stretching vibration into two peaks at 3450 and 3355 cm^{-1} , splitting the broad band at 1634 cm^{-1} into two sharp peaks at 1673 and 1625 cm^{-1} and shifting the peak appeared at 1431 cm^{-1} to 1454 cm^{-1} . It also appears that the latter peak became sharper. The decrease in the intensity of the C-H stretching vibrations and the increase in the number of N-H stretching vibrations may be caused by the increase in the nitrogen content in the film where NH_n group gradually replaces the CH_n group (Chengbing et al., 2008) and C=C becomes more active (Sreejith et al., 2005).

The appearance of the broad bands at 3436 and 1624 cm^{-1} in the spectra of the samples deposited under the first and the second concentrations suggests that the resulted carbon nitride material is in an amorphous state. While the splitting of these bands into doublets for the third concentration indicates that the amorphous state has been converted into crystalline state.

In this study the effect of the applied voltage has been taken into consideration. It is well known that increasing the electric field strength increases 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.

The applied voltage was raised to 1000 V then to 1200 V . Figures 3 and 4 show the spectra of the samples deposited under various concentrations and applied voltages of 1000 and 1200 V for 6 h respectively. In case of the first and second concentrations, increasing the voltage from 800 to 1000 V resulted in an appearance of a shoulder at the higher frequency side of the band at 1666 cm^{-1} . While in case of the third concentration increasing the voltage to 1000 V resulted in an increase in the intensity of the 1666 cm^{-1} band relative to that of the 1625 cm^{-1} band.

In case of the first and the second concentrations, raising the voltage to 1200 V , resulted in no significant changes in the spectral features of the sample deposited at the applied voltage 1000 V . Raising the voltage to 1200 V with the third concentration produces the height of the band due to C=C observes equal to the height of the band due to C=N.

Furthermore the time of deposition was taken into account as a factor affecting the bond structure. The FTIR spectra of the samples deposited under different concentrations and 800 V for 10 h are shown in Figure 5. It is apparent from Figure 5a that increasing the time to 10 h produces no significant effects on the spectrum of the sample deposited under the first concentration

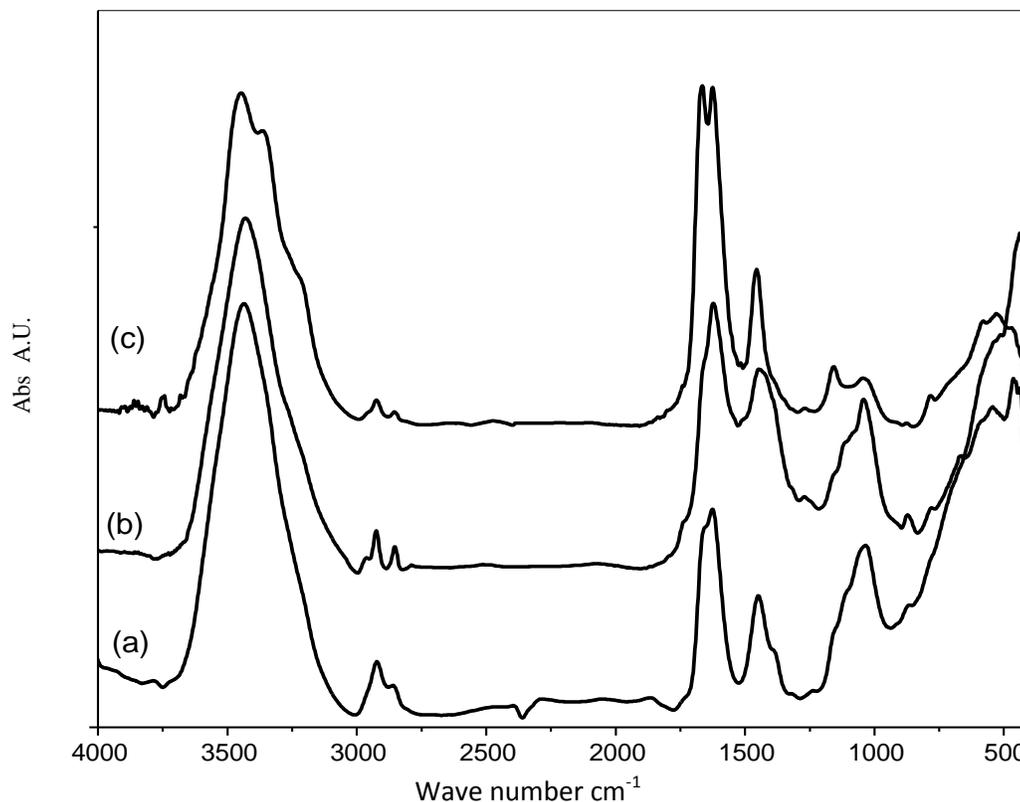


Figure 4. FTIR spectra of sample deposited with first (a), second (b) and third (c) concentrations under 1000 V for 6 h.

compared to that deposited for 6 h. For the case of the second concentration, Figure 5b shows that increasing the time to 10 h results in the appearance of two peaks at 3444 and 3336 cm^{-1} , and two bands at 1666 and 1623 cm^{-1} and a single sharp peak at 1450 cm^{-1} . In the case of the third concentration as shown in Figure 5c, the spectrum of the sample deposited for 10 h exhibits well defined peaks at 3443 and 3347 cm^{-1} , 1673 and 1625 cm^{-1} and sharp peak at 1463 cm^{-1} . It is evident from Figures 5b and 5c that the peak height of the band at 1625 cm^{-1} is lower than that of the band at 1666 cm^{-1} , in case of the second concentration; whereas in case of the third concentration, vice versa, that is, the peak height of the band at 1625 cm^{-1} is higher than that of the band at 1673 cm^{-1} . It is clear from the above mentioned observations that both time and concentration have significant effects on the concentration of C=C, C=N and C-N groups relative to each other. Thus increasing the time of deposition enhances the effect of the concentration; in addition, helps in the formation of crystalline phase.

Grazing incidence X-ray diffraction (GIXRD)

Figure 6 shows the GIXRD patterns of the films deposited by electrolysis of methanol urea organic solutions under

various concentrations at applied voltage 800 V for 10 h. In case of the first concentration the deposited sample is mainly amorphous as shown in Figure 6a. This result confirms what was suggested by FTIR measurements. It is clear from Figure 6b that the GIXRD pattern of the sample deposited under the second concentration contains a number of diffraction peaks of different intensities at $2\Theta = 31.64, 35.16, 38.08, 43.32, 48.04, 50.05, 52.56, 56.68, 62.96, 72.16, 74.24,$ and 79.48° . The pattern shows a number of diffraction peaks of different intensities at $2\Theta = 22.25, 31.64, 35.16, 38.08, 43.32, 48.04, 50.05, 52.56, 56.68, 62.96, 72.16, 74.24$ and 79.48° . The comparison between the experimentally measured lattice spacing of planes (d -values) and the theoretically predicted for the samples deposited under the second concentration assumes that, the peaks at $2\Theta = 35.16, 48.04, 52.56, 56.68, 72.16$ and 74.24° are matched to $\alpha\text{-C}_3\text{N}_4$ while the peaks at $31.64, 43.32, 50.05, 62.96$ and 79.48° are matched to $\beta\text{-C}_3\text{N}_4$ phase (Table 1). These peaks are similar to those reported in the literatures (GU et al., 1996; Zhang et al., 1999; 2000). The new additional peak at $2\Theta = 22.25^\circ$ which appeared in the GIXRD pattern of the sample deposited under the third concentration may be due to a new phase of CN_x (Kundoo et al., 2003; Yan et al., 2004; GU et al., 1996). These findings give strong evidence that increasing the

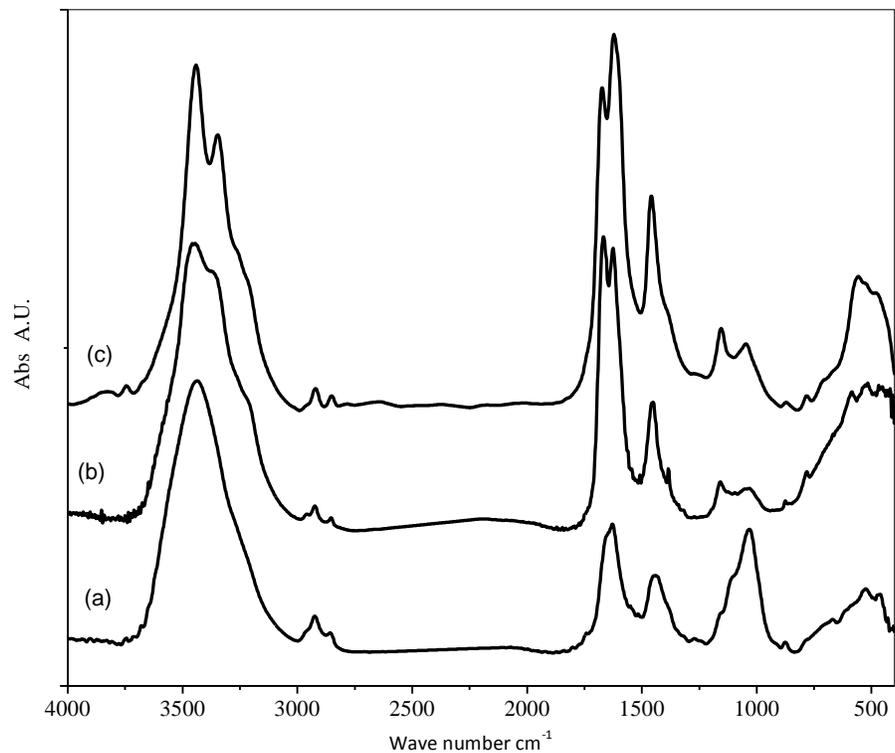


Figure 5. FTIR spectra of sample deposited with first (a), second (b) and third (c) concentrations under 800 V for 10 h.

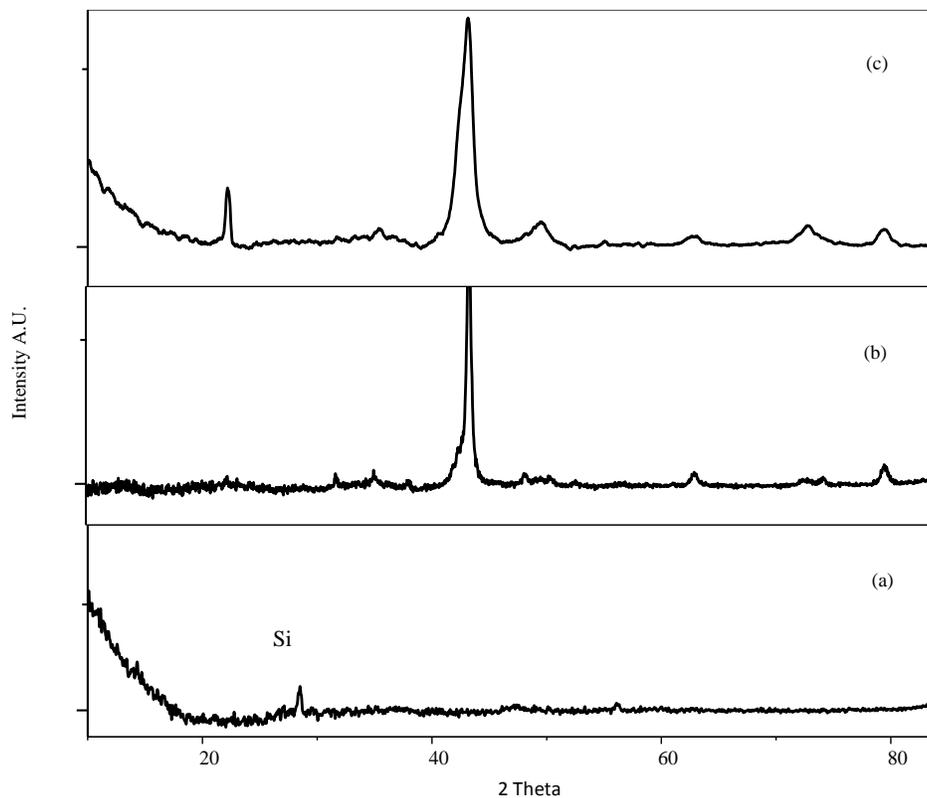


Figure 6. GIXRD of films deposited under first (a), second (b) and third (c) concentrations under applied voltage 800 V for 10 h.

Table 1. Theoretically predicted and experimentally measured d values for samples deposited under different concentrations and applied voltage 800 V for 10 h.

Experimental d (Å) concentration			Theoretical values phase		
First	Second	Third	α - C_3N_4	β - C_3N_4	CN_x
		3.99			4.09
	2.82	2.677		2.74	
	2.55	2.50	2.51		
	2.08	2.09		2.09	
	1.89		1.89		
	1.80	1.84		1.84	
	1.74		1.71		
	1.62		1.61		
	1.47	1.47		1.48	
	1.30	1.29	1.32		
	1.27		1.28		
	1.20	1.20		1.22	
		1.107			

concentration of urea from first to second concentration changes the structure from amorphous to crystalline one, that is, increasing the amount of urea in methanol results in an increase in the number of peaks belonging to some mixed polycrystalline phases of α - C_3N_4 , and β - C_3N_4 . Also, further increasing of the concentration of urea to the third concentration causes the appearance of a new phase of CN_x .

Figure 7a shows the pattern of the film deposited under the first concentration but at higher voltage (1000 V). Examination of the figure reveals that the deposited sample is mainly amorphous; while increasing urea concentration to the second and the third concentrations under the same applied voltage (1000 V) resulted in appearance of a number of diffraction peaks as is shown in Figures 7b and 7c respectively. For example increasing the voltage to 1000 V resulted in the formation of the new phase CN_x as well as the other two phases α - C_3N_4 and β - C_3N_4 . It was also noted that, in case of the third concentration, the amount of the new phase becomes more intense relative to the two other phases α - C_3N_4 , and β - C_3N_4 .

Figure 8 illustrates the GIXRD diffractograms of the samples deposited under various concentrations and applied voltage 1200 V for 10 h. In case of the first concentration (Figure 8a), the diffractogram displays two small peaks at $2\theta = 22.15^\circ$ and $2\theta = 35.48^\circ$. This result indicates that raising the applied voltage to 1200 V caused the appearance of tiny crystallite embedded with the amorphous phase of carbon nitride.

In case of the second concentration as is shown in Figure 8b, the recorded GIXRD shows a number of diffracted peaks at $2\theta = 22.13, 25.97, 29.22, 31.19, 33.21, 35.32, 43.29, 48.04, 49.38, 54.85, 62.99, 72.45$ and 79.39° . Raising the voltage from 1000 to 1200 V caused no appreciable change in the features of the

pattern apart from changes in the intensity of peaks belonging to the new phase of CN_x relative to the peaks of the two other phases.

In case of the third concentration as shown in Figure 8c, the recorded GIXRD pattern shows a number of diffraction peaks of different intensities at $2\theta = 22.25, 29.05, 31.69, 35.52, 40.60, 55.04, 67.4$ and 86.60° . It is clear that the peak at $2\theta = 22.25^\circ$ corresponds to the new phase becomes more predominant relative to those correspond to other phases.

Scanning electron microscope (SEM) and energy dispersive X-ray (EDX)

Figure 9 shows scanning electron micrograph of the carbon nitride films deposited on Si substrate under the second concentration at applied voltage of 800 V for 10 h. The figure shows the existence of the grains in the film, those are commonly observed in polycrystalline films. The average size of the spherical grains in the film can be measured, coming out at around $0.2 \mu\text{m}$. The chemical composition of the deposited carbon nitride film was examined by EDX analysis. The atomic concentration of N and C are 0.60 and 76.86 at% respectively. Also there are amounts of O, Ni, Cu and Zn of atomic percent 7.46, 0.21, 4.59 and 10.29 respectively. The presence of oxygen is common in many of publications and the presence of Ni, Cu and Zn impurities come from the contacts which we used in the electrolytic cell.

For higher urea concentration, the same applied voltage and time of deposition more closely packed crystal-like structures are observed in Figure 10. This may be attributed to the presence of more nitrogen in the film (Kundoo et al., 2006). The atomic concentration of

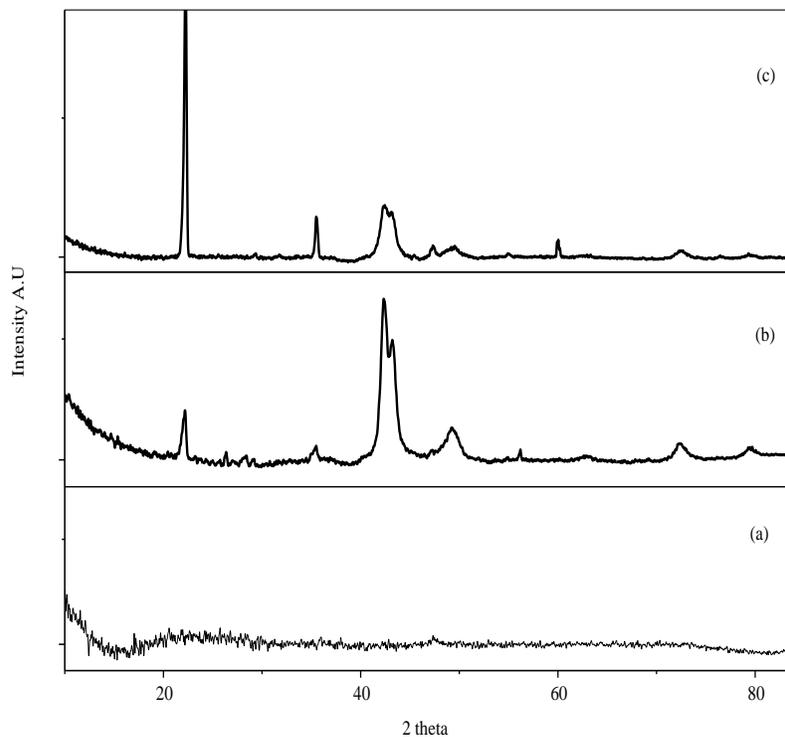


Figure 7. GIXRD of films deposited under first (a), second (b) and third (c) concentrations under applied voltage 1000 V for 10 h.

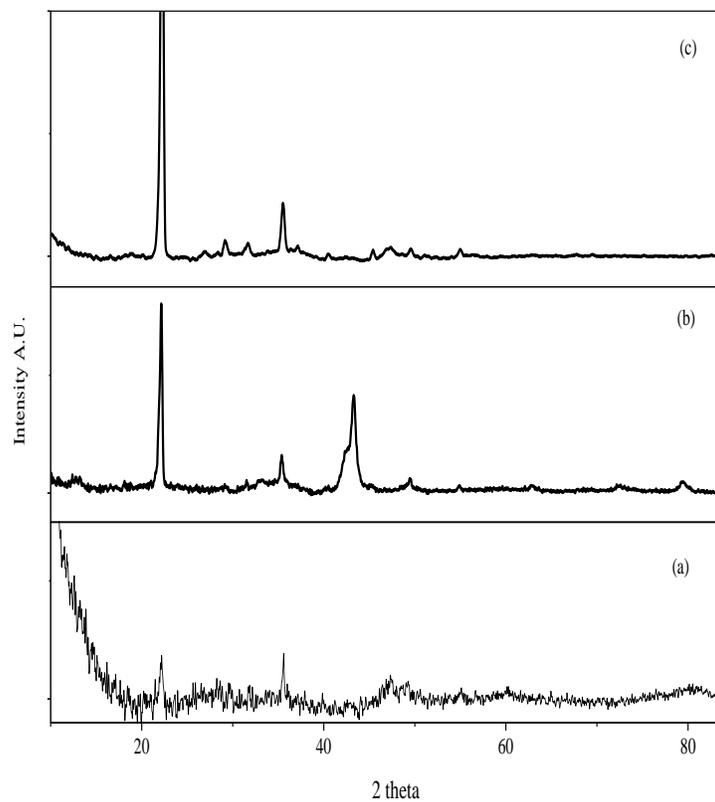


Figure 8. GIXRD of films deposited under first (a), second (b) and third (c) concentrations under applied voltage 1200 V for 10 h.

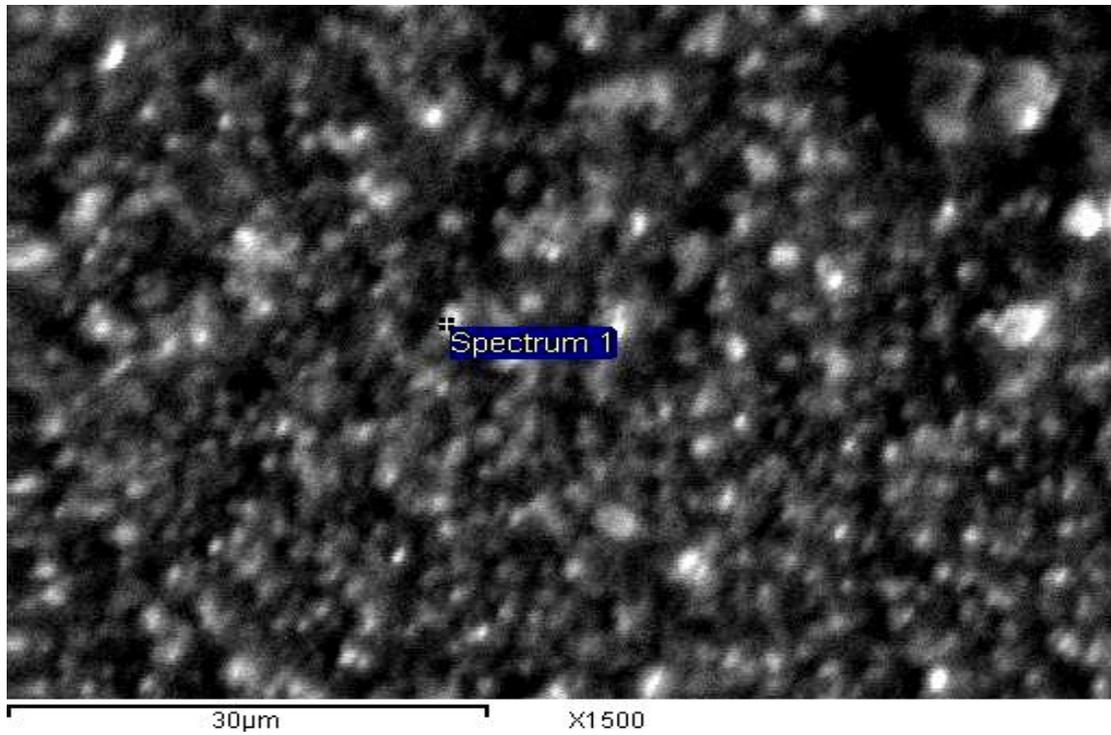


Figure 9. SEM micrograph of film deposited on Si substrate with second concentration and applied voltage of 800 V for 10 h.

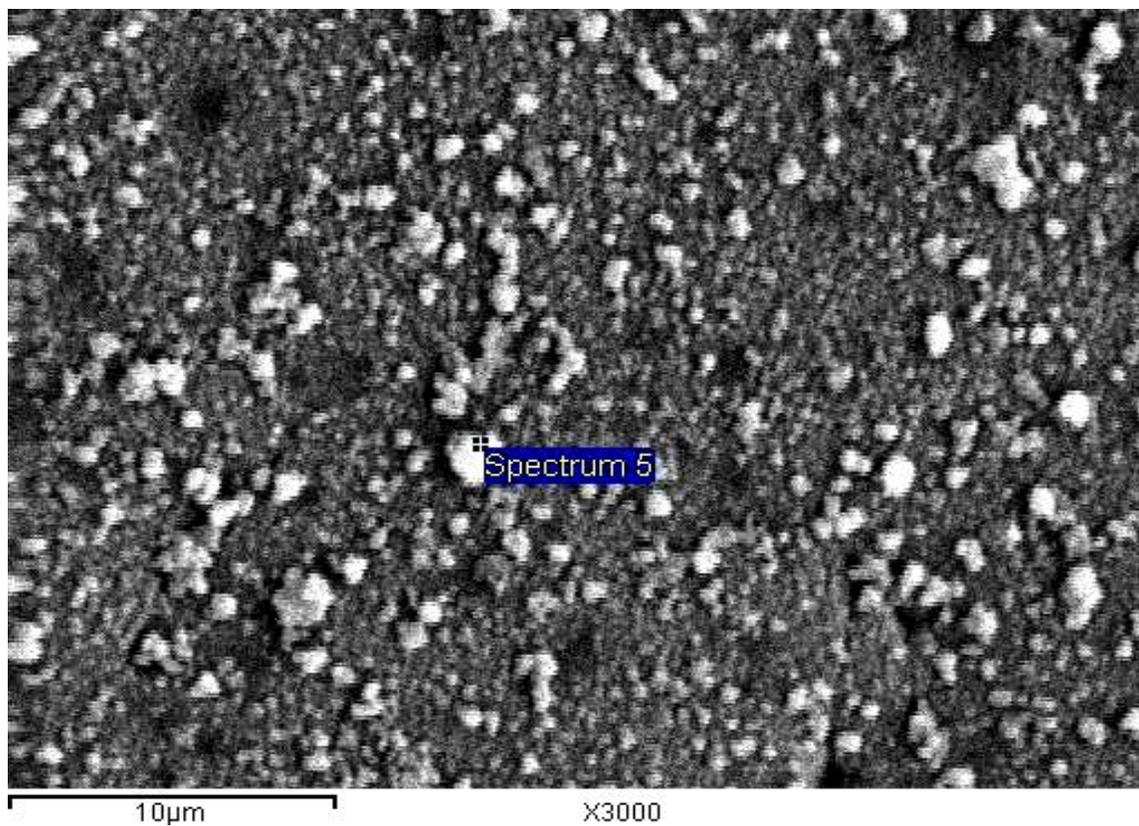


Figure 10. SEM micrograph of film deposited on Si substrate with the third concentration and applied voltage of 800 V for 10 h.

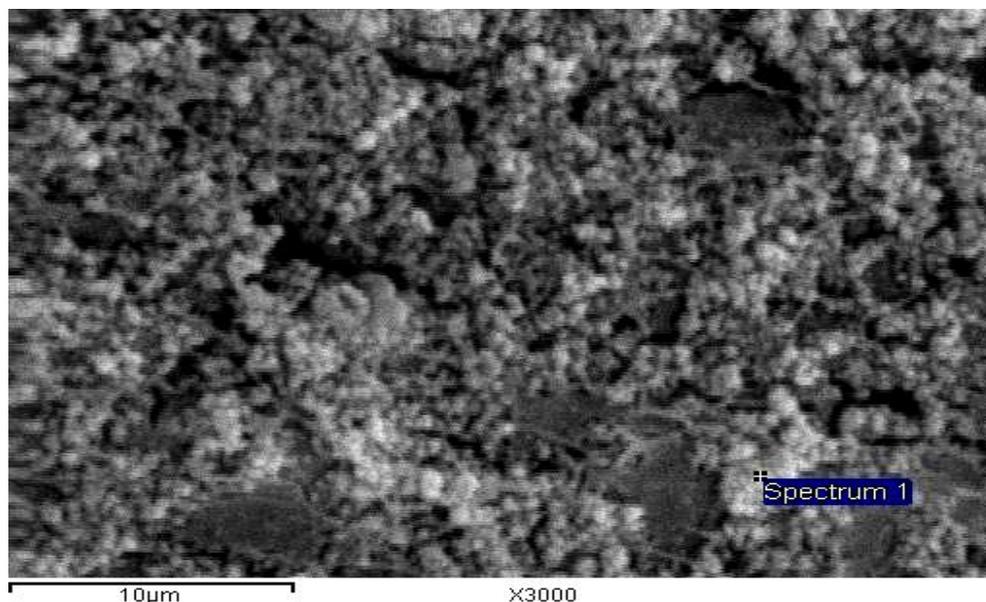


Figure 11. SEM micrograph of film deposited on Si substrate with the third concentration and applied voltage of 1200 V for 10 h.

N and C are 14.10 and 40.37% respectively. There are also O, Cu, and Zn of atomic percent which is 30.77, 8.04 and 6.73 respectively present in the film. It is noticed that the nitrogen concentration increased from 0.6 to 14.10% with increasing concentration of urea. Further, under the highest urea concentration (third) and highest applied voltage (1200 V) for 10 h the grains are observed more closely packed crystal-like structures (Figure 11). It means that nitrogen increased with increasing applied voltage. The atomic concentration of N and C are 29.54 and 29.90% respectively. There are also O and Cu of atomic percent of 33.12 and 4.45% respectively. It is noticed that under higher applied voltage (1200 V), the nitrogen and carbon concentrations are nearly equal.

Conclusions

It can be concluded that FTIR study of the deposited films revealed that carbon and nitrogen are bonded in C=N and C-N bonds as indicated by the existence of their absorption peaks at 1624 and 1450 cm^{-1} respectively. It is found that both the concentration and the applied voltage can influence the nitrogen fraction x incorporated in the CN_x films. When the applied voltage is increased, a unity of N/C ratio can be achieved with gradually increasing nitrogen content as verified by the FTIR results and confirmation by EDX data. Also it was found that the crystalline structure depends on the nitrogen content in the film where it changed from amorphous to polycrystalline of α - C_3N_4 , and β - C_3N_4 phases. With further increase in nitrogen content a new phase of CN_x appeared and at the highest nitrogen content, this phase

became more predominates relative to the other phases.

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