



High voltage electro deposition of carbon nitride film on aluminum surface



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ABSTRACT

Carbon nitride films, with good adhesion to surface, were deposited on aluminum surface plate by electrolysis of methanol–urea solution under high voltage condition for increasing the N content and sp^3 hybrid of C–N bonds. Carbon nitride electrodeposition was done in methanol and ethanol for various dielectric constants. The deposited films were characterized by X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). The results indicated that the main components of films contained sp^3 hybrid of C and N with single carbon–nitrogen bonds in the film with some oxygen impurities. The atomic weight percent of C, N, and O elements contained found to be 57.6%, 36.5% and 5.8%, respectively. The coatings had a uniform, flat and smooth morphology with an approximate N/C atomic ratio of 0.63.

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1. Introduction

The CN_x compound, namely β - C_3N_4 , with the structural and mechanical properties similar to diamond was predicted first through calculations of Liu and Cohen in 1989 [1]. The interesting properties such as superior hardness, high wear resistance, low friction coefficient and large energy gap make it attractive for industrial applications. Theoretical prediction efforts suggested five C_3N_4 structures, which are α - C_3N_4 , β - C_3N_4 , cubic (c - C_3N_4), pseudo cubic (p - C_3N_4) and graphite like (g - C_3N_4) [2]. Several attempts have been made to prepare this hypothetical material by various techniques, such as reactive sputtering, plasma deposition, laser ablation, electrodeposition and solvothermal deposition [3–12]. Electrodeposition from the liquid phase has a number of advantages over other methods, such as the simplicity of apparatus, the convenience control and the mildness of reaction conditions. Amorphous carbon films on aluminum by electrochemical deposition technique have prepared by Guo [13], Fu [14] and Yu [15], however, films easily warp upwards and peel off from the substrates. These films mainly had low N content.

In this work, we tried to cover carbon nitride thin films on aluminum plates by electrodeposition method, for increasing the N content and sp^3 hybrid of C–N bonds. To conduct this procedure, an organic solution containing methanol and urea as C and N source was chosen for depositing CN_x thin films.

2. Materials and methods

All chemicals including analytical grade of urea (99.9%), methanol (99.5%), ethanol (99.5%) and aluminum plate (99.99%) were used as received. The composition of the films was characterized by the X-ray photoelectron spectroscopy (XPS) on a KRATOS XSAM800 ESCA (electron spectrometer for chemical analysis), using $MgK\alpha$ X-ray as the excitation source. The Fourier transform infrared spectroscopy (FT-IR) a Perkin-Elmer (L-710) spectrophotometer was used. The scanning electron microscopy (SEM) studies were done on a JEOL JXA-840A electron probe microanalyzer.

2.1. Preparation of carbon nitride (CN_x) films

An electrolytic cell system was used to prepare the CN_x films. An aluminum plate with a dimension of $50 \times 10 \times 0.5 \text{ mm}^3$ was mounted as the negative electrode and a graphite plate was used as the counter-electrode. The space between the electrodes in all cases was 6 mm. Urea (3 g, 0.05 mol) was dissolved in methanol (50 ml) as the electrolyte. Prior to deposition, Al was immersed in an aqueous solution of 5% HF for a few minutes to remove the oxide layer, sequentially cleaned in an ultrasonic bath with deionized water, ethanol, and acetone.

The Al electrode placed in the electrolytic solution, with an area of $1.0 \times 3.0 \text{ cm}^2$, was immersed to allow the deposition of the CN_x film at boiling temperature. A direct current (DC) power-supply with a voltage of about 1300 V was used in this experiment.

For comparison, the ethanol was used instead of methanol in the same reactions. The results showed that ethanol had less reactivity than methanol because of its lower dielectric constant.

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Table 1
Film's deposition conditions.

Parameter	
Electrolyte	Methanol/urea
DC voltage (V)	1300 ± 20
Deposition temperature (K)	330–340
Electrode distance (mm)	6
Deposition time (h)	4
Maximum of current density (mA/cm ²)	50

3. Results and discussion

After 4 h of electrodeposition process, a gray thin film was obtained on Al plate. The deposited films were cleaned by water and ethanol to remove the adsorbed solutions. The carbon nitride films exhibits good adhesion to the Al substrate. The deposited films did not peel off from the substrate. Table 1 summarizes the deposition conditions of CN_x film.

3.1. XPS analysis

XPS is used to characterize the nature of chemical bonding of the film composition. The XPS spectra proved that the prepared films contain carbon and nitrogen; however, some oxygen impurity (about 5.8%) was also present.

The nitrogen and carbon content of the films is calculated from the integrated intensities of N_{1s} and C_{1s} lines corrected to their sensitivity factors. A typical XPS spectrum of deposited CN_x film on Al plate is given in Fig. 1. The peaks of C_{1s}, N_{1s} and O_{1s} were all detected. The detection of C_{1s} and N_{1s} confirms the formation of the CN_x thin film on the substrate. Some impurities of O_{1s} were also seen.

The atomic weight percent of C, N, and O elements was found to be 57.6%, 36.5% and 5.8%, respectively, as shown in Tables 2 and 3, and was determined from band intensity measurements. The atomic ratio of N/C (0.63) was calculated by dividing the number of N mole (36.5/14) to C mole (57.6/12) multiplied by 100. This corresponds to a stoichiometry of CN_{0.63}, less than the theoretical stoichiometric amount of C₃N₄ material (1.33). This lower value may be explained by the formation of some carbon–oxygen, nitrogen–oxygen functional groups among the carbon nitride thin film [16,17].

In order to analyze in detail the possible chemical bonds among C, N and O, the individual C_{1s}, N_{1s} and O_{1s} peaks can be deduced into Gaussian peaks after correcting the background. The best Gaussian fitting to the XPS lines resulted in four different peaks for the C_{1s} line, seven peaks for the N_{1s} and five peaks for O_{1s} lines (Fig. 2a, b and c).

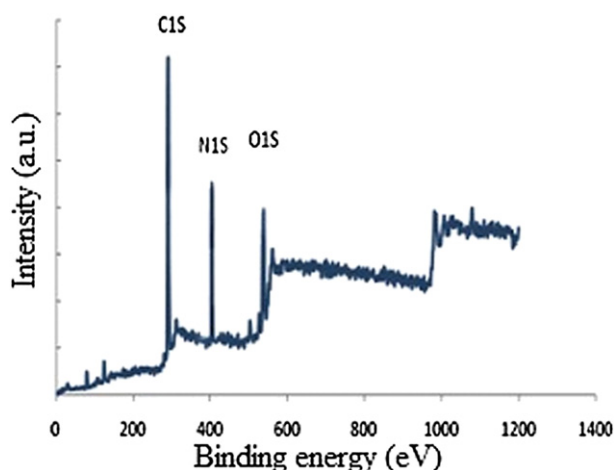


Fig. 1. XPS spectra of a typical sample deposited for 4 h on aluminum plate.

Table 2
XPS data of a carbon nitride film deposited on Al substrate.

Peak Label/ID	BE (eV)	Atomic %
C 1 s	284.724	57.6%
N 1 s	399.958	36.5%
O 1 s	531.824	5.8%

As shown in Fig. 2a, the C_{1s} spectrum can be deconvoluted into four lines peaked at 284.9 eV, 286.1 eV, 287.5 eV and 289.0 eV. The C_{1s} peak at 284.90 eV was attributed to the sp³-type C–N bonds, while there was no peak related to C in sp² coordination (C=C bond). The peak at 286.10 eV was ascribed to C atoms bounded to nitrogen neighbors in sp² coordination. The C_{1s} peaks at 287.5 and 289.0 eV were assigned to the O–C=O or C=O bonds, respectively [18,19].

The N_{1s} spectrum (Fig. 2b) can be deconvoluted into seven lines peaked at 402.82, 402.30, 401.40, 400.50, 399.80 and 398.90 and 398.00 eV. The N_{1s} peak at 399.80 eV was attributed to the sp³ type C–N bonds. The N_{1s} peak at 401.04 eV was related to the sp² type C–N bonds, which can be identified as originating from sp² C=N bonding [19–22].

No peaks corresponding to C≡N were observed in the spectra. The analysis of XPS revealed a significant amount of C–N and less C=N bonds for N and C atoms in the films.

The bands at 289.0 eV in the C_{1s} zone and the bands at 532.40 eV in O_{1s} zone (Fig. 2c) can be assigned to C=O bond, and the bands at 402.30 and 402.82 eV in N_{1s} zone and 531.80 in O_{1s} zone can be correlated to N–O bond, respectively.

3.2. FT-IR analysis

To confirm the analysis of CN_x thin film bonds, FT-IR spectroscopy analysis was also performed. The FT-IR spectrum of the sample deposited with the 3 g of urea solving in 50 mL methanol under 1300 V for 4 h is shown in Fig. 3. The assignment of the major peaks obtained in the samples is given in Table 4.

For the typical sample deposited for 4 h, the spectrum exhibits a strong C–H stretch peak at 1147 cm⁻¹ and two peaks at 1613 and 1741 cm⁻¹ corresponding to C=N and C=O stretching vibrations, respectively. There were no N–H and C≡N stretch peaks in IR spectrum region. The peak at 1461 cm⁻¹ is due to the overlapping of C–N single bond stretching vibration [23,24]. Vibrations at 3396, 2957, 2925 and 2855 cm⁻¹ likely indicate the presence of some OH, CH and CH₂ functional groups in the structure of carbon nitride film.

3.3. Scanning electron microscope (SEM)

Scanning electron micrograph of carbon nitride films deposited on aluminum plate illustrates a continuous and uniform morphology (Fig. 4). Part of the boundary of coated (bottom) and uncoated aluminum plate (top) is shown in Fig. 4.

Table 3
Individual C_{1s}, N_{1s} and O_{1s} peaks of a carbon nitride film deposited on Al substrate.

Individual peak	Deconvoluted peak	Binding energy (eV)
C _{1s} peaks	C=O	289.0
	O–C=O	287.5
	Sp ² C=N	286.10
N _{1s} peak	sp ³ C–N	284.9
	sp ³ N–C	399.80
	sp ² N=C	401.04
O _{1s} peak	N–O	402.30 and 402.82
	C=O	532.40
	N–O	531.80

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