

# Preparation and characterization of electrochemically deposited carbon nitride films on silicon substrate

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## Abstract

Carbon nitride films (CN<sub>x</sub> films) were deposited on Si(100) substrates by the electrolysis of methanol–urea solution at high voltage, atmospheric pressure, and low temperature. The microstructure and morphology of the resulting CN<sub>x</sub> films were analysed by means of Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectrometry (FTIR), x-ray diffraction (XRD), and atomic force microscopy. The tribological properties of the CN<sub>x</sub> films were examined on an UMT-2MT friction and wear test rig. The Raman spectrum showed two characteristic bands: a graphite G band and a disordered D band of carbon, which suggested the presence of an amorphous carbon matrix. XPS and FTIR measurements suggested the existence of both single and double carbon-nitride bonds in the film and the hydrogenation of the carbon nitride phase. The XRD spectrum showed various peaks of different *d* values, which could confirm the existence of the polycrystalline carbon nitride phase. The hydrogenated CN<sub>x</sub> films were compact and uniform, with a root mean square roughness of about 18 nm. The films showed excellent friction-reduction and wear-resistance, with the friction coefficient in the stable phase being about 0.08. In addition, the growth mechanism of the CN<sub>x</sub> films in liquid phase electro-deposition was discussed as well. It was assumed that the molecules of CH<sub>3</sub>OH and CO(NH<sub>2</sub>)<sub>2</sub> were polarized under high electric field, and the CN<sub>x</sub> film was formed on the substrate through the reaction of the –CH<sub>3</sub> and –NH<sub>2</sub> groups on the cathode.

## 1. Introduction

Carbon nitride (CN<sub>x</sub>) films have been subjected to intense research since Cohen and Liu [1] theoretically predicted that the β-C<sub>3</sub>N<sub>4</sub> phase would be harder than diamond. Since then, various types of chemical and physical vapour deposition (CVD and PVD) techniques, such as sputtering [2–4], ion beam assisted deposition [5, 6], pulsed laser deposition [7–10], cathode vacuum arc [11–13], and microwave plasma CVD [14], have been tried to synthesize CN<sub>x</sub> films, and various CN<sub>x</sub> films with good mechanical properties such as high

elasticity and hardness, and good wear-resistance have been successfully prepared. The applications of these methods, however, have been limited, owing to the complex equipment, rigorous experimental conditions, including high vacuum and high temperature. Fortunately, the technique of depositing CN<sub>x</sub> films by the electrolysis of organic liquids has been showing great potential for the convenient preparation of these films [15–19]. When compared to CVD and PVD techniques, electrochemical deposition has advantages such as availability for large area deposition, low deposition temperature, low cost, and simple set-up. However, only Fu [15] and Kundoo [19] reported the synthesis of amorphous carbon matrices containing some mixed polycrystalline phases of α-C<sub>3</sub>N<sub>4</sub>

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and  $\beta$ - $C_3N_4$ . However, not much has been reported on the profound analysis of the microstructure of the liquid-phase-deposited  $CN_x$  films, the chemical analysis of their growth mechanism, and their tribological properties.

Accordingly, crystalline  $CN_x$  films were deposited on silicon substrates by electrolysis in methanol–urea solution. This paper deals with the microstructure, morphology, and tribological properties of the resulting  $CN_x$  films. The growth mechanism of the  $CN_x$  films is also discussed.

## 2. Experimental details

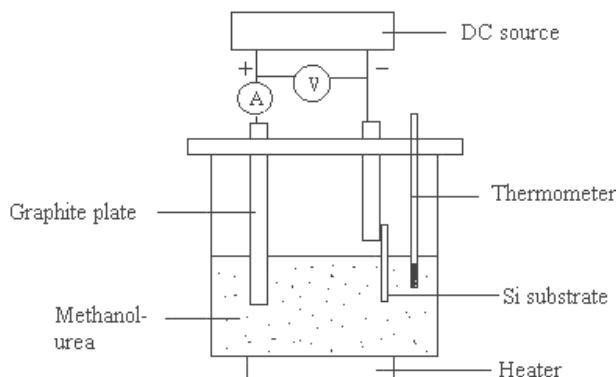
### 2.1. Preparation of $CN_x$ films

A simple electrolytic cell system was used to prepare the  $CN_x$  films. Figure 1 shows the schematic diagram of the system. The Si(100) substrate 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 and placed 6 mm away from the negative electrode. Urea ( $\text{CO}(\text{NH}_2)_2$ , purity above 99.9%) dissolved in analytically pure methanol ( $\text{CH}_3\text{OH}$ , purity above 99.5%) was used as the electrolyte. The electrolytic solution was prepared by mixing 0.15 g urea into 100 ml methanol (mole ratio of urea to methanol, 1 : 1000). The substrates were 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 dc power-supply voltage of 800 V, and for a duration of 10 h.

### 2.2. Microstructure and morphological characterization of $CN_x$ films

Raman spectroscopic measurements were carried out to investigate the surface structure of the  $CN_x$  films on a Renishaw2000 Raman spectrometer, operating with a 514.5 nm Ar laser and a laser power of less than 2 mW.

X-ray photoelectron spectroscopy (XPS) measurements of the  $CN_x$  films were performed on a PHI-5702 multifunctional x-ray photoelectron spectroscope, using  $\text{Al-K}\alpha$  radiation (photon energy 1476.6 eV) as the excitation source and the binding energy (BE) of Au ( $\text{Au}\ 4f_{7/2}$ : 84.00 eV) as the reference. The XPS spectra were collected in a constant



**Figure 1.** Schematic diagram of the apparatus for the electro-deposition of the  $CN_x$  film on Si substrate.

analyser energy mode, at a chamber pressure of  $10^{-8}$  Pa and pass energy of 29.4 eV at 0.125 eV/step. Au thin films of about 1 nm thickness were deposited on the tested surfaces of all the samples by thermal evaporation, so as to minimize the charging effect in the XPS analysis, because the charging effect would induce the change of the real BE.

Fourier-transform infrared spectrometry (FTIR) of the  $CN_x$  films were recorded on a Bruker IFS66V Fourier-transform IR spectrometer. By using the transmission mode, the spectrum was collected for 500 scans at a resolution of  $4\ \text{cm}^{-1}$ . The freshly cleaned single-crystal silicon wafer was used as the reference. In order to eliminate  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , the pressure in the sample and optical chambers was kept below  $3.0 \times 10^{-4}$  Pa.

The crystalline features of the  $CN_x$  films were determined on a D/Max 2400 Rigaku diffractometer, using  $\text{Cu-K}\alpha$  radiation operating at 40 kV and 30 mA.

Atomic force microscopy (AFM) (model SPM-9500; Shimadzu Corp., Kyoto, Japan) with a  $\text{Si}_3\text{N}_4$  probe was used to observe the morphology of the  $CN_x$  films, using the ‘constant force’ mode to obtain the morphology image.

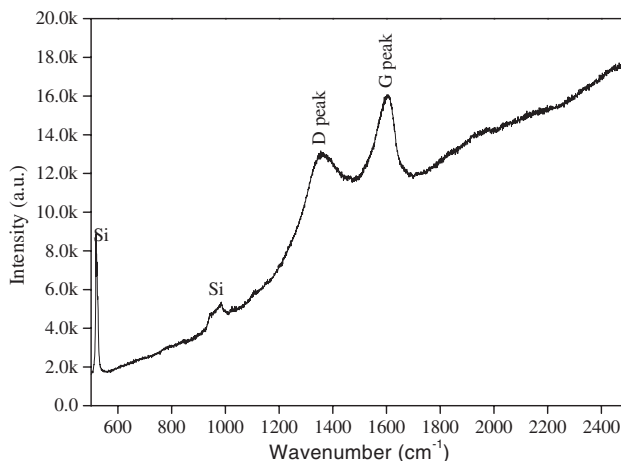
### 2.3. Tribological properties of $CN_x$ films

The friction and wear behaviours of the films were evaluated on a UMT-2MT test system, using a reciprocating-sliding mode. Thus the  $CN_x$  films on Si substrates were made to slide against an  $\text{Al}_2\text{O}_3$  ceramic ball (diameter 4 mm,  $HV\ 1500\text{--}1700\ \text{kg}\ \text{m}^{-2}$ , root mean square (RMS) 5.6 nm) at a frequency of 3 Hz and load of 0.2 N, for a sliding distance of 6 mm. All the tests were conducted at room temperature about  $20\text{--}26^\circ\text{C}$  and relative humidity of 40–45%. The friction coefficient and sliding time were recorded automatically during the test. The morphologies of the wear track of the films were observed on a JSM-5600LV scanning electron microscope (SEM).

## 3. Results

### 3.1. Microstructure and morphological characterization of $CN_x$ films

The films deposited from the methanol–urea solution are brown and have a thickness, measured with a profilometer, of about



**Figure 2.** Visible Raman spectrum of the  $CN_x$  film.