



# Effect of N<sub>2</sub> flow rate on the properties of CN<sub>x</sub> thin films prepared by radio frequency plasma enhanced chemical vapor deposition from ethane and nitrogen

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## ABSTRACT

Carbon nitride (CN<sub>x</sub>) thin films were deposited using radio frequency plasma enhanced chemical vapor deposition (rf PECVD) from a mixture of nitrogen (N<sub>2</sub>) gas and either methane (CH<sub>4</sub>) or ethane (C<sub>2</sub>H<sub>6</sub>) gases. The CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> flow rates were kept constant, while the N<sub>2</sub> flow rate was varied. The effects of nitrogen incorporation on the growth rate and structural properties of the films were studied. The use of these two hydrocarbon precursors was also compared. It was found that the effects of N incorporation are significant for films deposited from the CH<sub>4</sub> mixture and it greatly affects the bonding and optical properties of the films. In contrast, the effects of N incorporation on the films produced from C<sub>2</sub>H<sub>6</sub> are not as significant, though these films appear to be more uniform and show lower film porosity. Generally, the photoluminescence (PL) intensities increase with the increase in N incorporation for film deposited from both hydrocarbon mixtures. However, the PL properties of these CN<sub>x</sub> films are enhanced by the use of C<sub>2</sub>H<sub>6</sub> as compared to CH<sub>4</sub> since the films produced show lower defects.

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## 1. Introduction

Carbon nitride, CN<sub>x</sub> is an interesting material because of its desirable and unique properties suitable for various applications such as hard protective coatings, electroluminescence devices, sensors and electronics [1,2]. One of the most favored film growth technique used by researchers is the plasma enhanced chemical vapor deposition. This is due to the advantage of uniform large area deposition, easy handling, good adhesion, low pinhole density and good step coverage [3]. Research on carbon nitride has been carried out quite extensively since the theoretical prediction of Liu and Cohen in achieving crystalline super hard β-C<sub>3</sub>N<sub>4</sub> phase [4,5]. Lately, incorporation of nitrogen into carbon films has been studied intensively by many researchers since it promises an increase in the functionality of these carbon films. One of main motivations in these research works is to achieve high nitrogen incorporation. However, even low nitrogen incorporation enhanced the properties of these carbon films giving such characteristics as low friction [6], high photoconductivity [7] and low-k dielectric constant [8], which increases their potential in various applications.

A key point in the interest in nitrogen incorporation is that nitrogen would generate a two lone-pair e<sup>-</sup> per atom when incorporated as nitrile groups and/or as groups involving sp<sup>1</sup> carbon. This has

resulted in significant changes in the carbon films' photoluminescence (PL) properties. Studies have shown that PL intensities increase with the increase in N content in the films [9,10]. However, most of the CN<sub>x</sub> films with high PL intensity are made up of porous films which tend to degrade faster due to the absorption of OH. Thermal annealing has been used by many researchers to improve these films. Though this method manages to remove OH, the films' PL intensity also decreases [11]. Efforts to improve the CN<sub>x</sub> film quality while preserving or even enhancing its PL characteristic are of great importance.

A mixture of methane and nitrogen is normally used in the growth of CN<sub>x</sub> films by means of PECVD techniques. While methane is relatively safe to use as compared to volatile hydrocarbon gases such as acetylene and ethylene, the film produced is commonly found to exhibit high disorder and is porous in nature. There are very few comparative studies on the effects of using different hydrocarbon precursors on the properties of these CN<sub>x</sub> films. The use of ethane in the growth of CN<sub>x</sub> film is scarcely investigated. The higher ratio of C to H atoms in this gas compared to CH<sub>4</sub> is expected to produce an interesting effect on the film properties. Thus, this work embarks on the study of the different effects of using CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> on the growth, structural and optical properties of CN<sub>x</sub> films deposited by rf powered PECVD at low substrate temperature of approximately 100 °C.

## 2. Experimental method

Carbon nitride thin films were grown in a capacitively coupled rf PECVD system. The rf PECVD system is home-built and has been

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shown to produce good quality films [12–14]. The  $CN_x$  films were grown from the dissociation of a mixture of  $CH_4$  or  $C_2H_6$  and  $N_2$  gases onto p-type (111) crystal silicon (c-Si) and quartz substrates. The gas flow rate was fixed at 25 sccm for both  $CH_4$  and  $C_2H_6$  gases while the  $N_2$  gas was varied in the range of 0 to 100 sccm. The rf power density, electrode distance, deposition time and substrate temperature were fixed at 1.2 W/cm<sup>2</sup>, 5.0 cm, 90 min and 100 °C, respectively. The  $N_2$  dilution, that is  $N_2$  to total gas flow-rate ratio, was calculated as  $[N_2/(N_2 + C_nH_{2n+2})]$ , where  $CH_4$  or  $C_2H_6$  was represented by  $C_nH_{2n+2}$ . Prior to the film deposition, the substrates were exposed to hydrogen plasma treatment for 10 min at a  $H_2$  flow rate and rf power fixed at 50 sccm and 50 W, respectively. This was done to remove impurities on the substrate surface and improve the adhesion of films' layers onto the substrates [15].

Effects of the two hydrocarbon precursors on the growth rate, element composition, chemical bonding and photoluminescence of the films were studied. Film growth rate was calculated by dividing the film thickness by the deposition time. Film thickness was measured using a KKA TENCO P-6 profilometer. Elemental composition of the  $CN_x$  films was determined from Auger electron spectra (AES) within the energy range of 0–2000 eV using a JEOL JAMP-9500F field emission Auger microprobe system. Composition quantifications were carried out using the standard sensitivity factors of the instrument. The chemical bonding in the films was analyzed from Fourier transform infra-red (FTIR) spectra obtained in transmission mode within a scanning range from 1000 to 4000 cm<sup>-1</sup> using Perkin-Elmer System 2000 FTIR spectrometer. A Jasco V-570 Ultra-violet visible near infra-red (UV-vis-NIR) spectroscopy was used to measure the optical properties of the films. The optical energy gap ( $E_g$ ) was calculated from transmission and reflectance spectra in a wavenumber range of 190 to 2500 nm. Photoluminescence spectra of the films were measured using a Renishaw inVia Raman microscope at excitation wavelength of 325 nm, while the film surface roughness was analyzed using VEECO D3000 Atomic force microscope (AFM). The AFM was operated in contact mode using n-type Si tip with radius of <10 nm which was controlled by a Nanoscope IIIa scanning probe microscope controller and scanned over a film of 5  $\mu\text{m} \times 5 \mu\text{m}$ . Film thickness, AES, FTIR, AFM and PL measurements were carried out on films deposited on the Si substrates, while the optical properties were measured on those on quartz substrates.

### 3. Results and discussion

Fig. 1 shows the relationship between the deposition rate and gas flow rate ratio of the films produced by using  $CH_4$  or  $C_2H_6$  gases as a function of  $N_2$  to  $C_nH_{(2n+2)}$ . Note that the rf power density used in this work is relatively low as compared to those normally employed by other works [16,17]. High power density would result in complete dissociation of the precursor gases which voids the effects of using different gases. From Fig. 1, it is seen that films produced from  $CH_4$  generally exhibit higher growth rates than those produced from  $C_2H_6$ . This could be explained by the different reactions in two precursors. A detailed reaction mechanism is difficult to deliberate since the dissociation of these gases involves many active species in the reaction zone which can react through various processes. However it is believed that positive ions including  $CH_4^+$ ,  $CH_3^+$  and  $CH_2^+$  are directly incorporated into the film and contribute to its growth.  $CH_3^+$  is the dominant radical which exists through the dissociation process in the primary reaction in the plasma. The following reactions describe the production of  $CH_3^+$  radicals obtained from the  $CH_4$  and  $C_2H_6$  with  $N_2$  gases [18]:

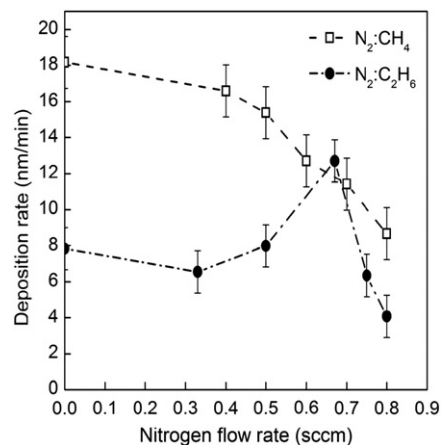
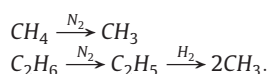


Fig. 1. Variation in growth rate as a function of  $N_2$  to  $C_nH_{2n+2}$  ratios. Lines are shown as guide to the eye.

The dissociation of  $CH_4$  permits a one step process to form the  $CH_3$  precursors in comparison  $C_2H_6$  have to undergo an additional step to form the  $CH_3$  radical. Thus, the growth rate of films prepared from the  $C_2H_6$  mixture is lower than  $CH_4$ . With respect to film growth rate,  $CH_4$  appears to be more favorable than  $C_2H_6$  if high growth rate is desired.

With respect to  $N_2$  dilution, the film growth rate for both sets of films remains almost the same up to a ratio of approximately ~0.4. Above the ratio of 0.40, both growth rates show remarkable changes. While the films deposited using  $CH_4$  show a linear decrease in growth rate with the increase in  $N_2/N_2 + CH_4$  ratio, those deposited using  $C_2H_6$  increase significantly up to the ratio of 0.75 and then decreases with further increase in the  $N_2/N_2 + C_2H_6$  ratio. We believe that the decrease in growth rate of the films deposited from the  $CH_4$  mixture is due to the decrease in the hydrocarbon partial pressure since for all films deposition the process pressure was maintained at a fixed value. This reduces the availability of  $CH_n$  radicals reaching the growth sites. On the other hand, the relative increase in N ions or energetic N atoms reaching the growth sites results in the increase in N incorporation in the film as shown by the increase in N/C ratio in Fig. 2.  $N_2$  dilution not only reduces the incorporation of C atoms in the sample but may also produce volatile radicals such as HCN which does not contribute to the growth of the films. The incorporation of N into the films produced from  $C_2H_6$  is much lower than those of  $CH_4$ . It appears that the N atoms or ions in the plasma are not easily

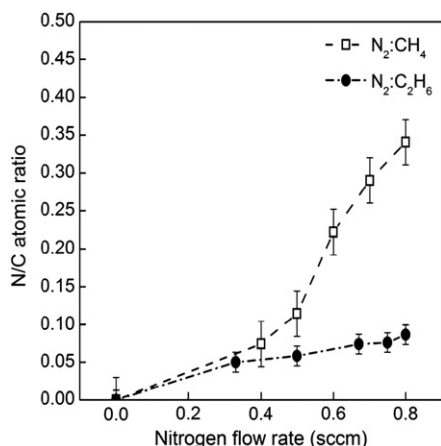


Fig. 2. Variation in nitrogen to carbon, N/C ratio for films deposited as a function of  $N_2$  to  $C_nH_{2n+2}$  ratios. Lines are shown as guide to the eye.

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