

CHARACTERIZATION OF NITROGEN INCORPORATED CARBON THIN FILMS BY PULSED LASER DEPOSITION

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Abstract in films of carbon have been deposited on single-crystal silicon and quartz substrates by pulsed XeCl excimer laser deposition of camphoric carbon, obtained from camphor ($C_{10}H_{16}O$), a natural source. The effect of nitrogen (N) incorporation in camphoric carbon thin film by pulsed laser deposition system is investigated. Optical gap for the undoped film is about 0.95 eV. The optical gap remains unchanged for low nitrogen content and decreases to about 0.7 eV. With higher nitrogen content the optical gap increases. The optical gap for the film having highest amount of nitrogen in this work is about 1 eV and is higher than that of the undoped film. The resistivity of the carbon film is observed to increase with N content initially and decreases with higher N content till for the film deposited at 30 mTorr. The increase of resistivity is observed for the films deposited at higher nitrogen partial pressure. With increase of N content in the film, the reduction in resistivity and optical gap is due to the graphitization of carbon film. With further nitrogen addition in carbon films results in increase of the optical gap and resistivity and are attributed to structural modifications through formation of some form of carbon nitrogen alloy (CN_x).

Keywords: Carbon Nitride, Pulsed Laser Deposition, X-ray Photoelectron Spectroscopy, Optical Absorption

INTRODUCTION

With the introduction of nitrogen (N) in the area of carbon research, the scope of carbon has increased manifold. N incorporation in carbon is reported by many researchers [Niu *et al.*, 1993]. The motivation behind this attempt can be divided into two broad categories; synthesis of crystalline carbon nitride alloy (C_3N_4) and doping of carbon in order to convert undoped p-type carbon to n-type. The properties of crystalline phase of carbon nitride (CN) alloy was reported [Liu and Cohen, 1989]. They have proposed β - C_3N_4 , a form of CN alloy analogous to β - Si_3N_4 , should have hardness closer to diamond, a super hard material reported [Liu and Cohen, 1990]. CN already has shown considerable interest in the field of protective coating [Prioli *et al.*, 1999]. for magnetic and optical materials [Nitta *et al.*, 1995].

However, undoped carbon is reported to be lightly p-type and doping is essential for the application of carbon in electronic devices. Veerasamy *et al.* reported n-type doping in carbon using phosphorus powder [Veerasamy and Amaratunga *et al.*, 1993] and nitrogen gas [Veerasamy and Yuan *et al.*, 1993]. Since nitrogen has smaller radius compared to phosphorus and is close

to that of carbon, the former would be preferred. Further, the nitrogen, being gas phase has the advantage of better control of dopant concentration over phosphorus in physical deposition systems. The ability to dope using nitrogen gas has shown a new direction for the application of the carbonaceous material in electronic devices. At present, there are numerous reports of attempts to use nitrogen gas and ion as a doping source [Silva and Amaratunga, 1995]. We have been working on carbon film obtained from camphoric carbon soot target which reveals better properties compared to carbon film obtained from conventional graphite target [Mominuzzaman *et al.*, 2000]. We have reported successful doping of phosphorus in camphoric carbon film [Mominuzzaman *et al.*, 2001]. Our objective of present work is to investigate the effect of nitrogen gas in camphoric carbon film by using PLD.

In the present work, we will present some structural and optoelectrical properties of the nitrogen incorporated carbon film as a function of nitrogen partial pressure (NPP) in the pulsed laser deposition (PLD) chamber. The deposited films are examined by X-ray photoelectron spectroscopy (XPS) optical absorption and electrical resistivity analyses.

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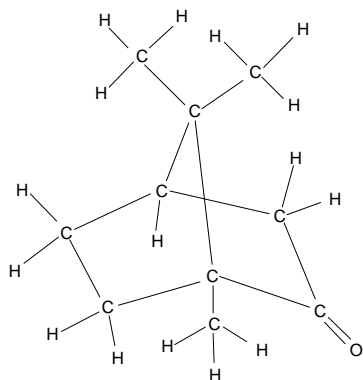


Fig. 1 Chemical structure of the starting material, camphor (C₁₀H₁₆O)

EXPERIMENTAL

Camphor has been used as a source of carbonaceous thin film. The chemical structure of camphor molecule is shown in Fig.1. Camphor was burnt in a 1-metre-long and 11-cm-diameter quartz tube. Details of the camphor burning system and the target preparation method have been described elsewhere [Mominuzzaman *et al.*, 1999]. In brief, the soot deposited along the walls of the tube was collected, dried in the oven for an hour and pressed into pellets. These pellets were used as targets for carbonaceous thin films. Films were deposited on silicon and quartz substrates by excimer laser (NISSIN 10X, XeCl, $\lambda = 308$ nm, $\tau = 20$ nsec, repetition rate = 2 Hz, spot size = 5.5 mm²), which is focused on the target at an incident angle of 45° to the target normal. The schematic of the deposition chamber is shown in Fig. 2. The substrate was mounted parallel to the target at a distance of 45 mm. The laser pulse energy was 150mJ on the window. To incorporate nitrogen in the film, we have introduced N₂ gas in the PLD chamber via leak valve. The pressure of the N₂ was varied between 0.1 to

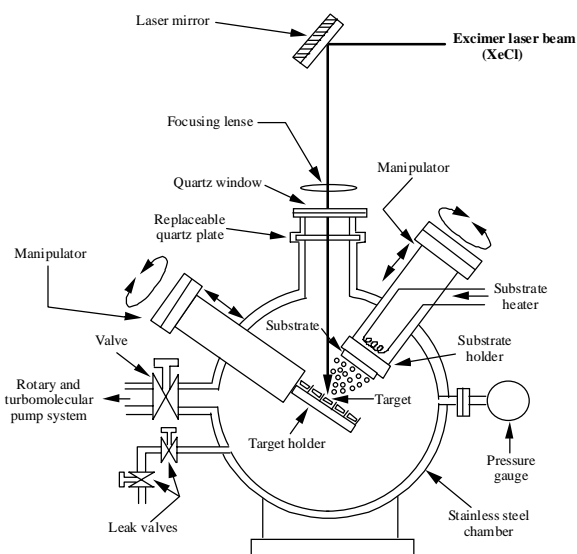


Fig. 2 Schematic of the pulsed laser deposition chamber

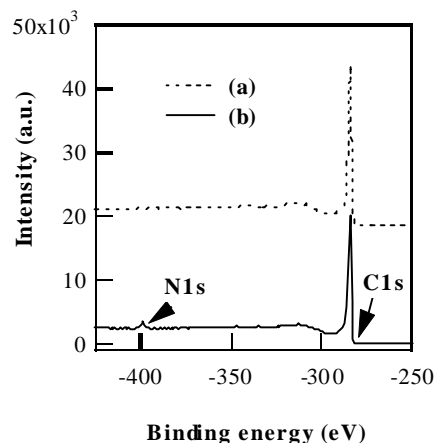


Fig. 3 Core level X-ray Photoelectron spectra of Carbon (C1s) and nitrogen (N1s) for the a) undoped carbon film and b) the film deposited at 500 mTorr.

500 mTorr. Prior to insert of N₂, the chamber was evacuated till about 10⁻⁶ Torr. The films are deposited on p-Si and quartz substrates. The presence of N and N content of the films are studied by X-Ray Photoelectron spectroscopy (XPS) while optical and electrical properties are investigated by spectral transmittance/reflectance and resistivity measurements.

RESULTS AND DISCUSSIONS

X-ray Photoelectron Spectroscopy

The presence of nitrogen in carbon films is detected by XPS spectra. Fig. 3 shows the XPS spectra for the undoped carbon film and the film deposited at 500 mTorr NPP (the spectrum of undoped film is vertically shifted for clarity). The peak at about 284 and 400 eV are due to photoelectrons excited from the carbon C1s and nitrogen N1s levels, respectively. Atomic % of N in the film is determined from analyses in these regions.

Nitrogen Content in the Film

Fig. 4 shows the variation of the atomic % of N in the carbon films as a function of NPP in the PLD chamber. N content in the film increased rapidly

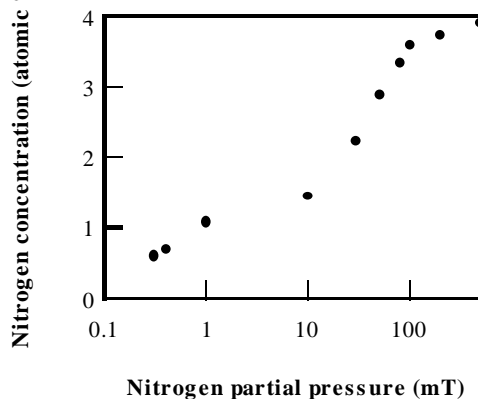


Fig. 4 Nitrogen content (at %) in the film as a function of nitrogen gas partial pressure in the PLD chamber

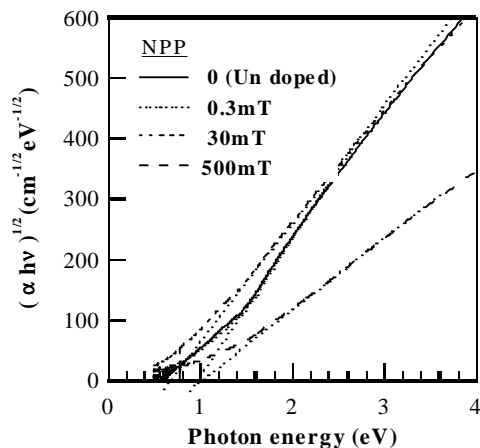


Fig. 5 $(\alpha hv)^{1/2}$ as a function of $h\nu$, for the N incorporated carbon films.

initially and gradually with NPP till 1mTorr. However, for higher NPP the N content is saturated. The N content is about 0.4% for the film deposited at .22mTorr and increases to about 1.4% for the film deposited at 1mTorr. With further increase of NPP, the N content increases to about 3.5 % for the film deposited at 10 mTorr and saturates thereupon at about 3.5% in the film.

Optical Absorption

From the measurements of optical reflectance and transmittance in the range of 300 to 2500nm wavelength, an optical absorption coefficient (α) is obtained. The optical gap (E_{opt}) is estimated from the extrapolation of the linear part of the plot of $(\alpha hv)^{1/2}$ versus $h\nu$ using the Tauc relation [Tauc, 1974] at the absorption coefficient $\alpha=0$. A plot of $(\alpha hv)^{1/2}$ versus $h\nu$ is shown in Fig. 5 for the films deposited without nitrogen and Nitrogen partial pressure at about 0.3, 30 and 500mTorr respectively. Optical gap for the undoped film is about .95 eV. The optical gap remains unchanged for low nitrogen content and decreases to about 0.7 eV. With higher nitrogen content the optical gap increases. The optical gap for the film having highest amount of nitrogen in this work is about 1 eV

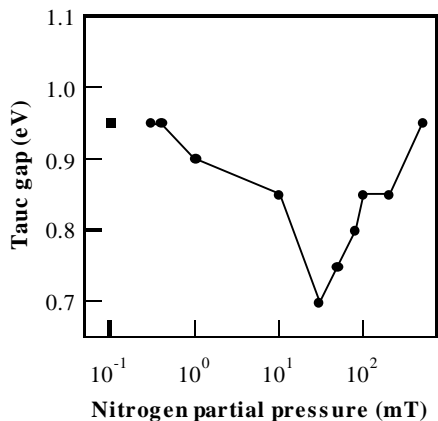


Fig. 6 Optical (Tauc) gap as a function of nitrogen partial pressure

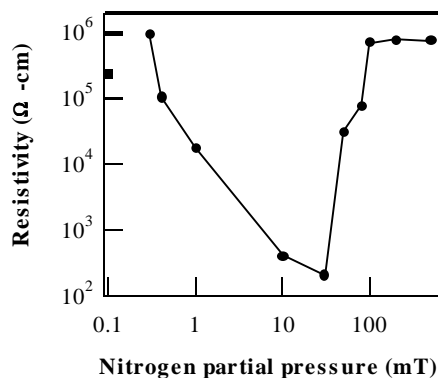


Fig. 7 Room temperature resistivity as a function of nitrogen partial pressure

and is higher than that of the undoped film. Fig. 6 shows the variation of the optical gap as a function of the NPP.

Electrical Resistivity

The resistivity of the carbon films are measured by 4-point probe technique -the usual way for high resistance measurement. The resistivity of the carbon film is observed to increase with N content initially and decreases with higher N content till for the film deposited at 30 mTorr. We have observed similar trend for our P-doped films [Mominuzzaman *et al.*, 2001]. Veerasamy *et al.* observed decrease of resistivity for their P and N doped films. However, the increase of resistivity is observed for the films deposited above 30mTorr nitrogen partial pressure. The variation of resistivity is shown in Fig. 7. We can relate this variation of resistivity to doping of nitrogen in our films for low content of nitrogen as the optical gap remain unchanged till for the film deposited at 10mTorr. Since both the optical gap and resistivity are decreased with higher N content, this phenomenaon can be related to graphitization as observed by other researchers [Silva and Amaratunga, 1995].

C-N Alloy

However, the increase of optical gap and resistivity with more N content can be related to structural change in carbon film. Usually this kind of behavior is observed for high content of N in the carbon film , i. e. for the CN alloy. This film might be promising for optical as well as mechanical applications in tribology. More information can be obtained for these N incorporated films from the analysis of Raman and temperature dependence conductivity measurements and is under progress.

CONCLUSIONS

The effect of nitrogen incorporation in camphoric carbon thin film by pulsed laser deposition system is investigated. With increase of N content in the film, the reduction in resistivity and optical gap is due to the graphitization of carbon film. With further nitrogen

addition in carbon films results in increase of the optical gap and resistivity and are attributed to structural modifications through formation of some form of carbon nitrogen alloy (CN_x), the material, that has great importance not only in optoelectronic applications but also in tribology

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