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REARRANGEMENTS OF HYBRIDIZED BONDS IN NITROGEN INCORPORATED CAMPHORIC CARBON THIN FILMS DEPOSITED BY PULSED LASER ABLATION

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ABSTRACT

Thin 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. With increase of N content in the film, the reduction in Si Raman peak 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 Si Raman peak and are attributed to structural modifications through formation of some form of carbon nitrogen alloy (CN_x).

Keywords: Pulsed Laser Deposition, Carbon Nitride, Raman Spectroscopy, Optical Absorption

1. INTRODUCTION

Presently, research on diamond-like carbon (DLC) thin films has attracted much attention in the field of semiconductor technologies and tribology industries due to some of its extra ordinary properties, such as, extreme hardness, chemical inertness, high electrical resistivity, high dielectric strength and IR optical transparency. Interestingly, these properties can be tailored over an unusual wide range from that of semi-metallic graphite to that of insulating diamond which promotes its application in the field mechanical as well as semiconductor technologies. Nowadays, various methods are used for the preparation of carbon films [1]. In fact, the energy of the carbon species generated by various preparation methods is different and plays an important role in controlling the sp^3/sp^2 ratio. In the past decade, pulsed laser deposition (PLD) process has become popular for its ability to generate highly energetic carbon species which enhances the formation of high percentage of sp^3 bonded carbon atoms at low substrate temperatures, and therefore, deposition of high quality of DLC film can be realized. However, tunability of its characteristics is governed by the relative amount of trigonal (sp^2) and tetrahedral (sp^3) hybridizations. Furthermore, the population of these orbital states can be tailored by thin film deposition parameters, such as, method of deposition, precursor material, impurity content, etc. [1].

With the introduction of nitrogen (N) in the area of carbon research, the scope of carbon has increased manifold. Nitrogen incorporation in carbon is reported by many researchers [2-7]. 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 [2]. 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 [3]. Carbon nitride already has shown considerable interest in the field of protective coating for magnetic and optical materials [8-9].

Earlier we have reported effect of phosphorus in camphoric carbon film [10]. 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), Raman spectroscopy and optical absorption analyses.

2. EXPERIMENTAL

Camphor has been used as a source of carbonaceous thin film. Camphor was burnt in a 1-metre-long and 11-cm-diameter quartz tube. Details of the chemical structure of camphor molecule, camphor burning system and the target preparation method have been described elsewhere [11]. 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, λ = 308 nm, τ = 20 nsec, repetition rate = 2 Hz, spot size = 5.5 mm^2), 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. 1. 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 N_2 gas in the PLD chamber via leak valve. The pressure of the N_2 was varied between 0.1 to 500 mTorr. Prior to insert of N_2, the chamber was evacuated till about 10^{-6} Torr. The films are deposited on p-Si and quartz substrates. Structural properties of the films are studied by Raman and X-Ray Photoelectron spectroscopy (XPS), whereas, optical properties are investigated by spectral transmittance/ reflectance measurements.

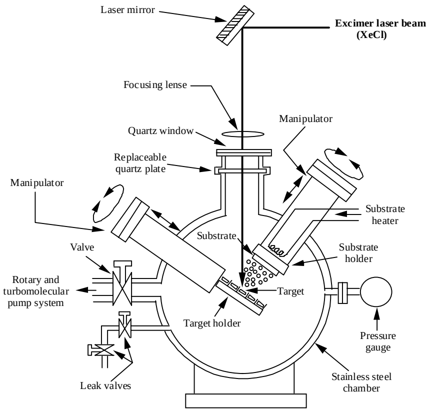

Fig. 1. Schematic of the pulsed laser deposition chamber

3. RESULTS AND DISCUSSIONS

3.1X-ray Photoelectron Spectroscopy

The presence of nitrogen in carbon films is detected by XPS spectra. Fig. 2 shows the XPS spectra for the undoped carbon film and the film deposited at 5×10^{-1} Torr 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 XPS spectral measurements in these two regions. Fig. 3 shows the variation of the atomic % of N in the carbon films as a function of nitrogen partial pressure (NPP) in the PLD chamber. N content in the film increased rapidly initially and gradually with NPP till 1×10^{-3} Torr. However, for higher NPP the N content is saturated. The N content is about 0.4% for the film deposited at 0.22mTorr 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.

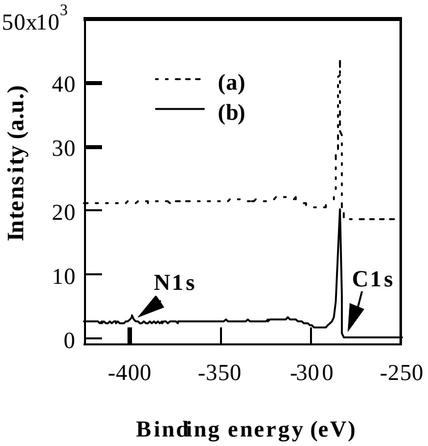

Fig. 2. Core level X-ray Photoelectron spectra of Carbon (C1s) and nitrogen (N1s) for the a) undoped carbon film and b) the film deposited at 500 mTorr.

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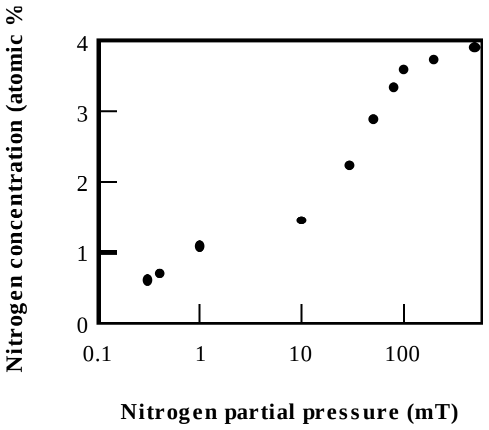

Fig. 3. Nitrogen content (at %) in the film as a function of nitrogen gas partial pressure in the PLD chamber.

3.2 Raman Spectroscopy

The first order Raman spectra (RS) consist of a single sharp line at about 1332 cm^{-1} for diamond and 1580 cm^{-1} (G line) for single crystal graphite. The G line results from the Raman allowed E_{2g} mode, while another line appears at about 1350 cm^{-1} (D line) for polycrystalline graphite due to grain boundary effect [12]. RS were obtained in the quasi-backscattering geometry using 488 nm line of Ar^+ ion laser. Figure 4 shows the RS of the undoped camphoric carbon (CC) and nitrogen incorporated carbon thin films. The spectra are vertically displaced for clarity. The RS of the CC film exhibits typical DLC structure. The downshift of G line from graphitic position (~1580 cm^{-1}) has confirmed the presence of both sp^3 and sp^2 hybridized bonds and disordered structure [1] in these laser deposited carbon films. Highly resonance-enhanced trihedral (sp^2 C-C) bonds tend to obscure any tetrahedral (sp^3 C-C) bonds, making it difficult to determine the actual sp^3 content in the films.

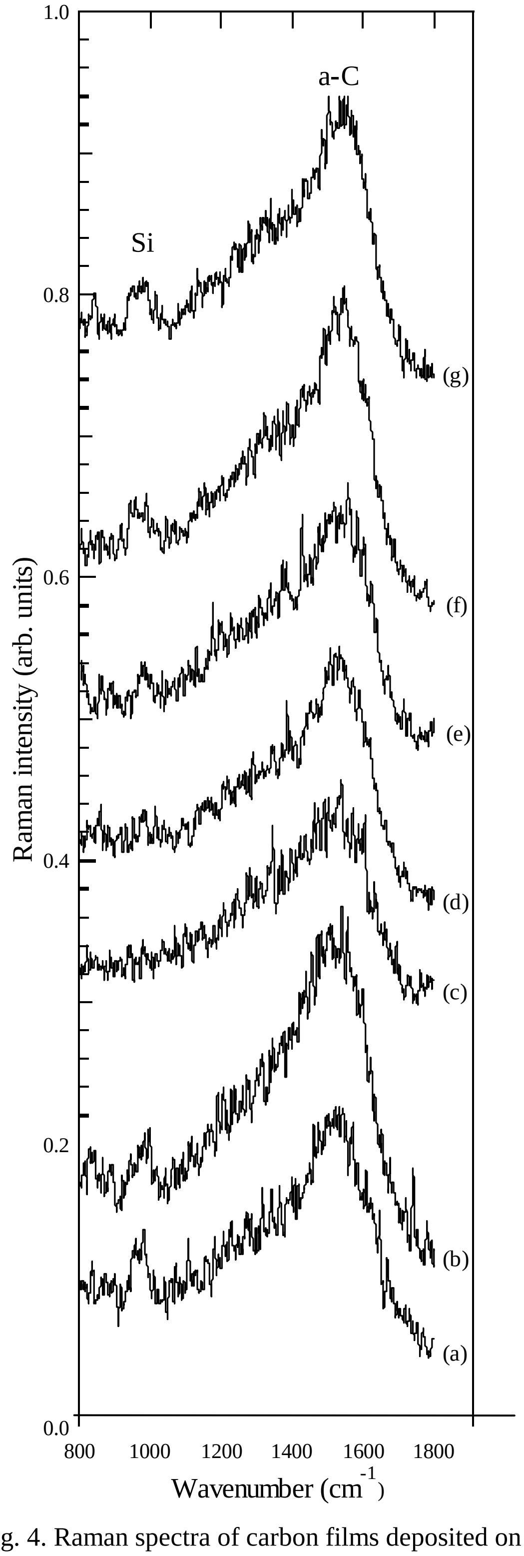

Fig. 4. Raman spectra of carbon films deposited on Si substrates at various nitrogen partial pressures in the PLD chamber: (a) undoped, (b) 10 mTorr, (c) 30 mTorr, (d) 50 mTorr, (e) 80 mTorr, (f) 100 mTorr, and (g) 200 mTorr.

However, appearance of the Raman peak at about 950 cm^{-1} from Si substrate reveals the ratio of trihedral and tetrahedral bonding information of the deposited carbon films [13]. Optical transmission through the films is assumed to improve as the sp^3 content increases. The Si Raman peak remain similar to undoped carbon films with low content of N due to unchanged bonded configurations, whereas, observed to decrease for more N content, indicating the films to be less transparent due to decrease of sp^3 fraction in these films, i.e, graphitization of the films. However, interestingly, with higher N incorporation, strong Si Raman peak is observed to appear indicates higher optical transmission. The more intense Si Raman peak could be related to the increase of sp^3 C-C bonding configurations in these films. The decrease of sp^3 to sp^2 fraction with N content and increase with further increase of N content reflects its strong influence on the properties of carbon films.

3.3 Optical Gap

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 $(\alpha h\nu)^{1/2}$ versus $h\nu$ using the Tauc relation[14] at the absorption coefficient α=0. 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 amount of nitrogen in this work is about 0.95 eV and is similar to that of the undoped film. Fig. 5 shows the variation of the optical gap as a function of the NPP.

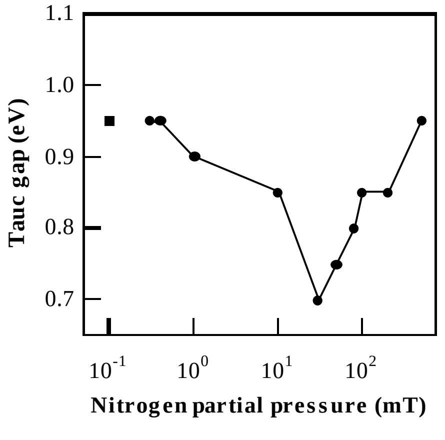

Fig. 5. Optical (Tauc) gap as a function of nitrogen partial pressure

The observations from Raman spectra are well in agreement with optical gap analyses. The intensity of Si Raman peak remains almost similar to undoped carbon for small content of N due to undisturbed hybridized sp^3/sp^2 bonds, i.e., optical gap also remain constant. The Si Raman peak observed to decrease for more N content, indicating the films to be less transparent due to decrease of sp^3 fraction in these films, i.e, graphitization of the films. The optical gap of this film is also observed to decrease to 0.7eV from about 0.95eV. With furtherer N incorporation, strong Si Raman peak is observed to appear indicates higher optical transmission. Raman spectral observation with increase of optical gap with more N content can be related to structural change with higher sp^3 content 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. Due to the incorporation of N in carbon films, the enhancement of tetrahedral bond formation is also observed, which might be suitable for optoelectronic as well as tribology applications.

4. 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 Si Raman peak intensity 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 Raman Si peak are attributed to structural modifications through formation of some form of carbon nitrogen alloy (CN_x). Furthermore, favorable environment to tetrahedral hybridized bond formation is observed. This film might be promising for optical as well as mechanical applications in tribology.

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