Properties of nitrogen doped tetrahedral amorphous carbon films prepared by filtered cathodic vacuum arc technique

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Abstract

The properties of nitrogen doped tetrahedral amorphous carbon films prepared by the filtered cathodic vacuum arc technique have been studied. The doping species, nitrogen ions, were produced by an ion beam source. The nitrogen flow rate was varied from 0.5 to 10 sccm while keeping other deposition conditions constant. The nitrogen content in deposited films was determined by Rutherford backscattering technique and ranged from 5 to 34 at.% depending on the nitrogen flow rate. The surface morphology, mechanical, optical, and electronic properties of the films were measured. The compressive stress, the hardness and the optical band gap all increased at low nitrogen content to a maximum at 5 at.% nitrogen and then decreased with increasing nitrogen content. The activation energy first increased and then decreased with increasing nitrogen content. We attribute these changes to the Fermi level moving up in the band gap, from below the midgap to near conduction band. We achieved continuously adjustable band gap and complex refractive index with nitrogen incorporation. Possible mechanisms of N ion in the ta-C:N films are discussed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The filtered cathodic vacuum arc (FCVA) technique was reported to be an efficient method for producing macroparticle free hard coatings [1-3]. Tetrahedral amorphous carbon (ta-C) film is an interesting material deposited by this technique. It has been shown, using electron energy-loss spectroscopy (EELS), that approximately 88% of the carbon atoms in the ta-C films form an amorphous tetrahedral ($sp^3$) structure [1,4,5]. This $sp^3$ content in the ta-C films results in properties that range from hardness of ~70 GPa and a Young’s modulus of ~700 GPa, chemical inertness, optical band gap of 2.7 eV and electrical resistivity of ~10$^9$Ωcm [1,6-10] such films could be useful for mechanical, optical and electronic applications [1,9,10]. Other important factors which make the ta-C an interesting material for coatings include, room temperature deposition, lack of necessity of gas except for doping, good adhesion [1] and transmittance in infra-red region [10].

Doping is an effective way of changing film properties. Several attempts were reported using nitrogen gas as the doping agent to change the electronic properties of ta-C and diamond-like
carbon (DLC) films [11]. When considering the ta-C film as an optical coating, the capability of achieving the continuously adjustable band gap and refractive index is useful. All these could be implemented by energetic particle bombardment of the growing ta-C film by an ionized nitrogen source. This method is called ion beam assisted deposition (IBAD), which refers to a family of film deposition techniques that involve the bombardment of the growing film with energetic particles in the energy range of a few electronvolts to tens of kiloelectronvolts. This technique can produce physical, structure changes, and changes in the chemical properties generally observed in most types of ion-beam-based film deposition technique, i.e. dual ion beam sputtering system and IBAD [12]. In this ion beam assisted FCVA technique, the film properties are affected by the plasma parameters which include the ion energy, density, and distribution, and the process parameters, such as the gas composition, pressure, flow rate, and substrate bias. Some of the parameters are inter-linked. Control of these parameters leads to the desired film properties.

In this paper, the doping of ta-C film by introducing the doping species, ionized nitrogen gas (100 eV), through a rf ion beam source is presented. The study is undertaken to determine the change of (i) surface topography, (ii) intrinsic stress, (iii) tribological properties, (iv) optical properties, and (v) electronic properties, with the change of the nitrogen flow rate. The successful control of an adjustable optical band gap, the complex index of refraction, electrical conductivity, and Fermi level is reported. Possible mechanisms of N ion in the ta-C:N films are discussed.

2. Experiment details

2.1. Samples preparation

The schematic diagram of the FCVA deposition system is shown in Fig. 1. The carbon plasma
is produced from the arc spot on a cathode 60 mm diameter, 99.999% pure graphite in vacuum. The base pressure was $2.0 \times 10^{-6}$ Torr. A radial electric field is introduced in our system via the torus duct wall bias and this field, coupled with the curvilinear axial magnetic field on a curved toroidal duct, forms the crossed electric-magnetic-field filtering assembly. The plasma steered by the field through the duct to the deposition chamber is deposited on the substrate without macroparticle and neutral atoms. The substrate in the deposition chamber was negatively biased at 80 V, which corresponds to 100 eV of impinging carbon ion energy in our experiment. The arc current was set to 60 A, the toroidal magnetic field fixed at 40 mT. The substrate used were cleaned (100) p-type silicon wafers of average thickness of 280 μm. The oxide layer on the silicon surface was removed by argon ions from a rf ion beam source before deposition.

During deposition, the nitrogen gas was introduced into the deposition chamber through the rf ion beam source with the ion energy of 100 eV and ion current density of ~2.8 mA cm$^{-2}$. The nitrogen partial pressure was varied between $2.6 \times 10^{-5}$ and $1.3 \times 10^{-4}$ Torr depending on the nitrogen flow rate monitored using a mass flow controller, and the nitrogen flow rate is directly related to the nitrogen partial pressure. To initialize the discharge in the rf ion beam source and obtain a reliable ion beam, the flow rate must be greater than 2 sccm. Therefore, argon was introduced together with nitrogen when the nitrogen flow rate was less than 2 sccm. In addition, a set of samples with purely ionized argon gas was prepared for the purposes of comparison.

2.2. Film properties

The nitrogen content was determined by the Rutherford backscattering (RBS) technique. The surface morphology of the film was measured by using an atomic force microscope (AFM) with tapping mode (Digital Instruments). A surface profilometer (Tencor P10) was used to determine the film stress. The mechanical properties of the films were investigated using an indenter (Nano Indenter® II). The optical properties were determined by a phase modulated spectral ellipsometer (Jobin Yvon UVISEL™)[10], the resistivity and activation energy were determined by temperature control system and an electrometer (Keithley 617).

3. Experiment results

3.1. Composition

The variation of nitrogen content of ta-C:N films as a function of nitrogen flow rate is shown in Fig. 2. The nitrogen content increases from 5 to 34 at.% as the nitrogen flow rate increases from 0.5 to 12 sccm.

3.2. Film surface roughness

Fig. 3 shows a typical AFM image of a silicon substrate cleaned with the ionized argon source (with Ar ion energy of 400 eV and ion current density of 5.66 mA cm$^{-2}$). The surface roughness was dependent on the impinging ionized argon energy, and this energy was kept constant at every deposition. The root mean square (RMS) surface roughness, over an area of $1 \times 1$ μm$^2$ for a silicon substrate was about 0.3 nm. The lateral dimension of the periodic ripple feature on the surface was determined by cross section analysis, and an average was about 40 nm.

![Graph showing nitrogen content as a function of nitrogen flow rate](image)
Large internal stress is known to develop in ta-C films during their growth [1]. The thermal stress developed during deposition due to the difference between the average coefficients of expansion for film and substrate was negligible since the temperature during deposition was always less than 60°C. The intrinsic stress has been determined by the radius of curvature technique which compares the curvatures of the bare silicon substrates and substrates coated with a film. The stress is given by Stoney’s equation [1]

$$\sigma_s = \frac{E_s}{6(1-\nu_s)} \frac{t_s}{R} \left( \frac{1}{R} - \frac{1}{R_0} \right),$$

where $E_s$, $\nu_s$, and $t_s$ are Young’s modulus, Poisson ratio, and thickness of the substrate. $R$ and $R_0$ are the radii of curvature of the film-substrate composite and bare substrate, respectively. For each film examined by the surface profilometer, the radius of curvature is average value measured at different locations. The intrinsic stress was found to be compressive under all deposition conditions and its magnitude was dependent upon the nitrogen flow rate. Fig. 5(b) shows the dependence of the compressive stress on the nitrogen flow rate. The stress decreases from 12 to 6 GPa when the nitrogen flow rate increases from 0.5 to 10 sccm.

### 3.3. Film stress measurement

The surface morphology for ta-C:N deposited on silicon substrate was dependent on the nitrogen flow rate. Fig. 4 shows the typical AFM images of ta-C:N surfaces grown on silicon surface cleaned with the ionized argon source. The ta-C:N films were deposited at various nitrogen flow rates (0.5 to 8 sccm) while keeping other parameters constant. The surface RMS roughness measured by AFM is shown in Fig. 5a and is observed to increase from $0.25 \pm 0.05$ to $0.47 \pm 0.05$ nm when the nitrogen flow rate increased from 0.5 to 8 sccm. In our experiment with the FCVA technique, which utilized the double bend filter, very few macroparticles and surface defects were observed with an optical microscope (200 times). In the AFM pictures of ta-C:N films periodic ripple structures were observed. The ripple structure was about 40 nm in width from the cross section analysis. The lateral size for the ripple structure for different nitrogen flow rate gave approximately the same width. Our experiment result is consistent with work of other researchers [13], who reported that the off-normal incidence ion bombardment often produces periodic height modulations on solid surfaces. This ripple or terraced topography has been observed on various amorphous solids such as glass and fused silica [13]. This terraced orientation is assumed to be dependent on the angle of ion beam incidence.

### 3.4. Hardness measurement

The indenter was operated in a constant-displacement-rate continuous stiffness mode. The continuous stiffness measurement measures the film stiffness continuously without the need for discrete unloading cycles. It therefore allows the measurement to be done at small penetration depths to obtain the hardness on film coated samples. As shown in Fig. 5(b), the true hardness decreases from 70 $\pm$ 5 to 26 $\pm$ 5 GPa when the nitrogen flow rate increases from 0.5 to 10 sccm nitrogen flow rate.

### 3.5. Optical measurement

In general, the Fourier transform infrared (FT-IR) spectra obtained for 50 nm thick ta-C:N thin
films deposited on quartz were featureless [10]. The two bands at 2920 and 2840 cm\(^{-1}\) (due to C-H stretch bonds) are absent in our ta-C:N films. This absence indicates that the ta-C:N is hydrogen free. These data agree with the results from Veerasamy et al. [14].

The optical band gap (Tauc band gap) is determined by [15]

\[
\varepsilon_2(E) = \text{const} \left[ \frac{(\hbar \omega - E_g)}{\hbar \omega} \right]^2, \tag{2}
\]
where $\varepsilon_2$ is the imaginary part of the dielectric constant, $E$ is the photo energy, $\hbar$ and $\omega$ have their usual meaning, and $E_g$ is the Tauc band gap proposed by Tauc[15] assuming density of states model as parabolic energy band edge. The film structure model used for the simulation in a spectroscopic ellipsometer is based on the four layer model developed by Shi et al. [10]. The Tauc gap was plotted as function of nitrogen flow rate, as shown in Fig. 6. It shows that the Tauc gap decreases from 2.7 to 1.1 eV with increasing in nitrogen flow rate from 0.5 to 10 sccm. The variation of the optical band edge is attributed to the removal or creation of band tail states [10], and the material is assumed to have less band tail states when the edge has an increase in slope. Fig. 7 illustrates the dependence of the optical absorption edge on the nitrogen flow rate. The slope increases from undoped to 0.5 sccm flow rate and decreases subsequently when the flow rate exceeds 0.5 sccm. The shape of the optical absorption edge in our experiment is similar to absorption edge found in the amorphous silicon by Cody [16]. In Fig. 8, the refractive index, n(E), and extinction coefficient, k(E), for the different conditions of ta-C and with photon energy varying from 0.75 to 4.5 eV are shown. The n(E) is in the range from 2.3 to 2.9. Apart from the shift of the magnitude, the position of the maximum is shifted towards smaller photon energy when the nitrogen dopant increased. For
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0.0
2.0 2.5 3.0 3.5 4.0 4.5 5.0
Photon Energy (eV)
Fig. 8. Refractive index (solids lines) and extinction coefficient (dash lines) of the ta-C:N films for different nitrogen flow rate.

k(E), the trend agrees with the absorption edge where it shifts towards the smaller photon energy region with increasing nitrogen flow rate indicating a reduction in transparency.

3.6. Electronic properties

The electrical measurements were obtained by sputtering 100 nm thick gold metal contacts to form gap cells (5 mm x 0.5 mm interelectrode spacing) on films deposited on quartz. The room temperature resistivity was measured. As shown in Fig. 5(c), the resistivity increases from 4 x 10^8 to 3 x 10^9 Ω cm when the nitrogen flow rate increases from null to 1 sccm. The resistivity then decreases to 9 Ω cm when the flow rate increases to 10 sccm. The variation in the resistivity due to the nitrogen doping agrees with the results from Veerasamy and McKenzie et al. [14,17].

The Davis and Mott model [18] for the band structure of amorphous semiconductors was used to obtain the information about the transport mechanism from the thermal activation energy data. The extended state conductivity for semiconductor can be expressed in the form [18]

\[ \sigma = \sigma_0 \exp \left[ - \frac{E_a}{kT} \right], \] (3)

where \( \sigma_0, E_a, k \) and \( T \) are the pre-exponential constant, activation energy, Boltzmann constant and temperature, respectively. The activation energy is determined from Eq. (3) and \( E_a = E_C - E_F \) for n-type semiconductor and \( E_F - E_V \) for p-type semiconductor. The measurement was taken with temperature ranging from 300 to 420 K. The linear function \( \ln(\sigma) = A(1000/T) + B \) was used to fit the data above and below 390 K separately (Fig. 9). The coefficient of determination \( (r^2) \) for all the fittings is greater than 0.99, which indicates a correlation between the \( \ln(\sigma) \) and the \( (1000/T) \). These curves present a linear relationship for temperature above 390 K, we interpret this data in terms of electrical conduction in extended states which are dominant at temperature \( >390 \) K [18,19]. At temperatures \( <390 \) K, the slope of the Arrhenius plot changes. We attribute the change to conduction in band tail states [19]. The slopes above 390 K correspond to the activation energies. Fig. 5(c) shows that the activation energy increases from 0.9 to 1.18 eV when nitrogen flow rate increases from null to 1 sccm and then decreases to 0.17 eV when the nitrogen flow rate increases further to 10 sccm.

4. Discussion

The largest content of nitrogen was 34 at.% for the film prepared with 12 sccm nitrogen flow rate. This content is much larger than 12 at.% of the film prepared with 16 sccm nitrogen flow rate in our previous work [19] in which nitrogen gas was
introduced into the cathode arc region and is also larger than that reported (less than 10%) by Veerasamy [14] in which the gas was fed into the torus. These data indicate that the ion beam assisted FCVA technique is an efficient method for introducing nitrogen into the ta-C films.

It was found in our previous work [19] that the compressive stress, the micro-hardness, and the optical band gap all increase linearly with the \( \text{sp}^3 \) fraction in the ta-C film [9,10]. So it is reasonable to assume that as the nitrogen content increases from null to 5 at.%, the incorporated N atoms compensate the dangling bands in the tetrahedral amorphous carbon structure and increase the \( \text{sp}^3 \) fraction of the film. Such a phenomenon was also found by Silva et al. [20] in hydrogenated amorphous carbon nitrogen films in which the \( \text{sp}^3 \) fraction of carbon atom and the \( \text{sp}^3 \) fraction of nitrogen atoms both reach a maximum at a critical composition of 7 at.% N. With the increase of \( \text{sp}^3 \) fraction, the increase of resistivity and the activation energy for the films at low nitrogen concentration can be understood.

Assuming that the optical band gap equals the electronic band gap and taking the midgap as datum, the shift of Fermi level from near the valence band to near the conduction band is plotted in Fig. 10. The undoped ta-C film is originally a p-type wide band gap semiconductor. With the nitrogen doping, the ta-C:N becomes intrinsic when the nitrogen flow rate was fixed to 1 sccm during deposition. A further increase of nitrogen flow rate to 10 sccm shifted the Fermi level from the midgap to near the conduction band. The shift of the Fermi level indicates that nitrogen from the ion beam source is a dopant for ta-C film which we interpret as showing that the N atom first compensates for the defect controlled p-type material, then subsequently dopes it to n-type. This result shows that ionized nitrogen dopes the ta-C during ion bombardment technique. This Fermi level shift is in agreement with that reported by Veerasamy et al., McKenzie et al. and Silva et al. [14,17,21].

It was proposed by Robertson [22] that incorporation of nitrogen as dopant can form both stable \( \text{sp}^2 \) and meta-stable \( \text{sp}^3 \). At nitrogen content less than 5 at.% nitrogen, the nitrogen atom is preferable for doping ta-C by ‘o-doping’, whereas at larger N content, N is incorporated ‘n-doping’. This proposal agrees with our optical band gap data in that the optical band gap first increases as the nitrogen flow rate increases from null to 0.5 sccm and then decreases to 1.1 eV with increasing nitrogen content. The ‘n-doping’ contributes to the decrease of optical band gap at larger nitrogen content. The optical absorption edge of the amorphous semiconductor has a wide variation in the slope of the edge for the same material when subjected to different preparation conditions [16]. In ta-C:N, the slope of the absorption edge can be directly related to the band tail for the valence and conduction band which are directly related to the n-bonding state and n*-antibonding state, respectively. It can be seen from the absorption edge in Fig. 7 that the slope of the absorption edge decreases when the nitrogen content increases, which corresponds to an increase in \( \text{sp}^2 \) fraction at larger nitrogen content. This phenomenon is evidence that nitrogen ion bombardment induces relaxation in the subsurface. The decrease of optical band gap, hardness, and compressive stress at larger nitrogen content is another important indication for an increase of \( \text{sp}^2 \) fraction, as shown in Fig. 5.

5. Conclusion

The ion beam assisted FCVA technique is an efficient method for incorporating nitrogen atoms into ta-C films. The nitrogen incorporation in the
ta-C films by nitrogen ion beam assisted doping is much larger than that by other means. The shift of the Fermi level indicates that nitrogen from ion beam source is a good dopant for ta-C film and we conclude that the N atom first compensates for the defect controlled p-type material, then subsequently dopes it to n-type. The increase in the compressive stress, the micro-hardness and the optical band gap at N content lower than 5 at.% results from the increase in the \( \text{sp}^3 \) fraction in the ta-C:N films, while the decrease of these physical properties at higher N content are caused by the increase in the \( \text{sp}^2 \) fraction. The change of the \( \text{sp}^3 \) fraction can also be used to explain the variation of the optical absorption edge with the nitrogen content.

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