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Analysis of dielectric constants to determine sp^3/sp^2 ratio and effect of substrate bias on spectroscopic ellipsometric studies of tetrahedral amorphous carbon films grown using an S bend filtered cathodic vacuum arc process

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The carbon bonding ratio and optical properties have been studied by spectroscopic ellipsometry of as grown tetrahedral amorphous carbon (ta-C) films, deposited using an S bend filtered cathodic vacuum arc (FCVA) process. First, the carbon bonding ratio in ta-C films has been estimated from imaginary part of dielectric constant (ε_2) spectra obtained by spectroscopy ellipsometry. A method has been developed to find out the fractions of $sp^3$and sp^2 bonded carbon atoms from the Wemple-Didomenico plot. Second, the effect of varying negative substrate bias on the optical properties and sp^3/sp^2 ratio of as-grown ta-C films has been made. The values of the optical constants evaluated are found to increase with the increase of the negative substrate bias in the as-grown ta-C films but the values of sp^3/sp^2 ratio and the optical band gap (E_g) evaluated increase up to -200 V substrate bias and beyond -200 V substrate bias the values of sp^3/sp^2 ratio and E_g decrease. Application of substrate bias is, thus, found to increase the sp^3 bonding and E_g up to -200V substrate bias and beyond -200V substrate bias there is reversal of the trend.

Keywords: Spectroscopic ellipsometry, Optical constants, FCVA, sp^3/sp^2, ta-C, Substrate bias

1 Introduction

Tetrahedral amorphous carbon (ta-C) films are being studied with increasing interest for use in diverse areas which include electronics, opto electronics, vacuum micro electronics, micro electro mechanical systems and sensors besides its widespread use in tribological applications, especially as protective coatings for hard disc drives[1-6]. These ta-C films were grown using a wide variety of processes including filtered cathodic vacuum arc (FCVA) - direct and pulsed source, pulsed laser ablation, mass selected ion beam deposition and electron cyclotron wave resonance processes and there are many good reviews covering the same in the literature[2-4,7]. Among the successful methods for the preparation of ta-C films, the FCVA technique was particularly useful for industrial applications because it provided highly ionized plasma of energetic carbon ions, from which dense films of amorphous carbon could be grown at reasonable deposition rates[8]. The cathodic vacuum arc is a relatively low voltage process and high current density of discharge, in which the macroscopic fragments of the cathode material are also emitted. Electromagnetic deflection of the plasma through L bend (90°) using a curved solenoid was first used to remove the macro particles from the carbon plasma by Aksenov *et al.*[9]. The macro particle filter, on the other hand, has limited transport efficiency and tends to collimate the plasma leading to a restricted area of deposition. The efficiency of the removal of macro particles could also be improved using S bend magnetic filter, though it decreases the deposition rates due to the reduction in ion transport efficiency[10-15]. The pulsed mode of the plasma also allowed better filtering of the macro particle because the ions tended to be entrained in the plasma beam during the pulse but fall out of the plasma when the beam stops[16-20]. All the processes are highly energetic processes and the control of ion energy leads to the variation in the material properties. Further, the high rate of ionization and the option to vary the ion energy and ion density, under optimum conditions can lead to creation of momentary pseudo thermodynamic conditions of high temperature, on the surface of film, leading to nanostructured carbons[21,22]. Thus, very subtle variation in the process parameters leads to the variation in the material properties. There are reports of spectroscopic ellipsometry (SE) study on diamond-

like carbon[23,24], ta-C films[25-29] in the published literature. There is dearth of SE data available on the ta-C films deposited using an S bend FCVA process. The properties investigated were found to be system dependent[2]. We have recently reported the results of the systematic reflectance and photoluminescence[30], X-ray photoelectron spectroscopy, X-ray induced Auger spectroscopy (XAES) and Raman spectroscopy[31], plasma diagnostic[32] and other studies[33] on ta-C, ta-C: H and ta-C: N films deposited using an S bend FCVA process.

The detailed SE study on the influence of varying negative substrate bias on as grown ta-C films deposited using the S bend FCVA process has been reported here for the first time to the best of our knowledge. The characteristic of ta-C films is an average property of structurally ordered diamond, graphite and hydrocarbon polymers consistent with sp^3, sp^2 and sp^1 hybridization (bonding configuration) of carbon atoms, respectively. Several different techniques[34-42] have been employed for the estimation of sp^3/sp^2 in the diamond like carbon (DLC) films. Each of the methods mentioned in the literature above has certain limitations specially when applied to hydrogenated amorphous carbon (a-C: H) films. Thus, the accurate determination of sp^3/sp^2 ratio in DLC films is still a matter of debate. The determination of the relative amount of sp^3, sp^2, sp^1 bonded carbon atoms in a given film of ta-C is still investigative and various[34-43] methods proposed so far are only approximate, not applicable in general to all films prepared by different methods under different conditions. The amount of sp^1 sites in most of these films is negligibly small and is, generally, ignored. In our ta-C films, there is literally no hydrogen present and hence, it will eliminate the effect of hydrogen bond in carbon films and will, thus, produce more reliable and accurate values. The optical properties of the as-grown ta-C films grown using an S bend FCVA process using SE technique have been studied in this paper. The procedure for estimating the sp^3/sp^2 ratio in ta-C films from the spectral dependence of dielectric constants obtained from the SE measurements as proposed by Demichelis *et al.*[41] and then the effect of varying negative substrate bias on the optical properties of as grown ta-C films have been studied.

2 Experimental Details

The deposition of amorphous carbon films was carried out using an indigenously built double bend (S bend) FCVA process on cleaned, highly doped $< 100 > n^{++}$ silicon wafer of resistivity 0.001 – 0.005 ohm cm. The schematic of indigenously built S bend FCVA system has already been published[33]. The FCVA system consists of (a) water cooled cathode and anode, (b) S bend magnetic filter over 6 inch duct to remove the macro particles and neutrals and (c) 8 inch SS cross deposition chamber with a provision of biasing the substrate. Two turbo molecular pumps backed by two rotary pumps evacuate the system. Typically, a vacuum of better than 10^{-4} Pa can be achieved in the system. The magnetic filters are energized using three different dc power supplies and a magnetic field of ~350 G is achieved inside the duct. The arc was initiated using a mechanical striker (a retractable graphite rod of purity ~99.999% and diameter 7 mm) and a dc arc supply. The cathode target was made of ~99.999% pure graphite of 50 mm diameter.

The deposition was carried out at an applied arc voltage of 25V and an arc current of ~75 A. The temperature of the substrate was kept below 40°C during deposition. For a carbon cathode, the emitted material is primarily C^{++} ions with kinetic energy[44] broadly peaked at ~ 20-25 eV. The energy of the carbon bearing precursors could be further manipulated by applying an additional negative dc bias to the substrate in the range -20 V to -450 V. The sum of the bias voltage and the initial ion energy of the carbon ions gives the incident ion energy. The thickness of the films was in the range 500 ± 10 Å as measured by Talystep (Rank Taylor and Hobson) thickness profiler.

3 Results and Discussion

3.1 Methodology for the analysis of dielectric function using spectroscopic ellipsometry

Single wavelength nulling ellipsometry has been used for many years as a standard measurement technique to determine the film thickness and refractive index. However, it is difficult to obtain accurate and reliable results when the film extinction coefficient is not zero and there is an interface between the film and the silicon substrate. For certain thicknesses, the calculated parameters are significantly correlated making it very difficult to determine the thickness and refractive index accurately. The correlation problem is minimized through SE as the ellipsometry measurements are performed as a function of the wavelength.

SE is a very powerful, simple and totally non-destructive optical technique for determining optical constants, film thickness in multilayered system, surface and interfacial roughness and material microstructure. A Jobin Yvon Horiba UVISEL Phase modulated spectroscopic ellipsometer was used to obtain the ellipsometric spectra of as-grown ta-C films in the photon energy range 1.0-4.75 eV with 0.025 eV steps. In this technique, a beam of polarized light is incident on the sample and as a result the polarization state of the light gets modified after getting reflected from the sample. This change in the polarization state is recorded in terms of the ellipsometric angles Ψ and Δ, where $\tan \Psi e^{i\Delta} = r_p/r_s$, the ratio of the reflection coefficients of the parallel and perpendicular components of the electric field, respectively. The complex dielectric constant ($\varepsilon = \varepsilon_1 + i\ \varepsilon_2$) of these films is obtained using the following relation[45].

$$\varepsilon = \sin^2\phi\,[1+\tan^2\phi\,\{(1-\rho)^2/(1+\rho)^2\}] \quad \ldots (1)$$

where ϕ is the angle of incidence and ρ is the complex reflectance ratio r_p / r_s. The measured ellipsometric spectra are then fitted with the calculated spectra of an appropriate model, assuming a realistic sample structure, where the layer thickness and the optical constants are used as the fitting parameters. The optical constants of the substrates have been supplied and the trial dispersion relations have been used for the films. The angle of incidence was kept fixed at 70°. The ellipsometric spectra are interpreted by regression analysis using a multilayer model that assumes an ambient/roughness/film/interface/ substrate structure of the thin film[46-48]. The surface roughness is considered as an overlayer which is a mixture of 50% bulk material and 50% voids, whereas the interface is assumed to be a mixture of 50% amorphous silicon and 50% film material. Ellipsometry has been primarily used to measure the optical constants *n, k*, ε_1 and ε_2, where *n* is the refractive index of a thin film sample and gives the propagation speed of a light wave through the medium, *k* is the extinction coefficient which relates how much energy of the wave is absorbed in the material, ε_1 is related to the volume polarization for induced dipoles and ε_2 is related to the volume absorption due to carrier generation. The values of optical band gap (E_g) were evaluated by extrapolating $(\varepsilon_2 h\nu)^2$ versus $h\nu$ curve to zero abscissa.

3.2 Method for determination of sp^3/sp^2 ratio

Demichelis *et al.*[41] analyzed the real (ε_1) and imaginary (ε_2) parts of the dielectric constants of a-C: H film for obtaining more reliable information on the sp^3/sp^2 ratio. In this method, the contribution to $\varepsilon_1(E)$ of the $\pi \rightarrow \pi^*$ interband transition is taken into account through the Kramers-Kronig relationships and the contribution of the $\sigma \rightarrow \sigma^*$ interband transition to $\varepsilon_1(E)$ is analyzed within the framework of the Wemple-Didomenico model[49].

(1) Demichelis *et al.*[41] assumed the validity of the relation:

$$\varepsilon_2(E) = \frac{\pi}{2}\frac{E_P^{\,2}}{E}\delta(E-E_0) \quad \ldots (2)$$

whereas we have shown[50] how it follows from the basic relation:

$$\varepsilon(\omega) = 1+\frac{4\pi N e^2}{m}\sum_j f_j\left[\frac{1}{\omega_j^{\,2}-\omega^2} + i\,\frac{\pi}{2\omega}\delta(\omega-\omega_j)\right] \quad \ldots (3)$$

where ω is the frequency of radiation incident upon a solid having a fixed assembly of *N* independent neutral atoms and each atom has only one electron of mass *m* and charge *e* (single electron approximation) and f_j is the electric dipole oscillator strength associated with the transition at frequency ω_j. In the single oscillator approximation (j = 1) and $f_j = 1$, the energy dependence of the real and imaginary parts of the dielectric constant can therefore be written as

$$\varepsilon_1(E) = 1+\frac{E_P^{\,2}}{\left(E_0^{\,2}-E^2\right)}, \quad \varepsilon_2(E) = \frac{\pi}{2}\frac{E_P^{\,2}}{E}\delta(E-E_0) \quad \ldots (4)$$

where $E = h\omega/2\pi$, $h\omega_1/2\pi = \varepsilon_1 - \varepsilon_0 = E_0$ is the spacing between bands and the plasmon frequency ω_P and plasmon energy E_P are given by $\omega_P = 4\pi e^2/m$ and $E_P = h\omega/2\pi$, respectively.

(2) Demichelis *et al.*[41] analyzed the reflectance and transmittance data of the films in the UV region where the transmittance is very low. Low transmittance (reflectance) values have been found to

cause large errors in the dielectric constants of the films found using their data and thereby, rendering the final values of the sp^3/sp^2 ratio inaccurate and unreliable. In the present analysis, we have used the real and imaginary parts of the dielectric constant found using spectroscopic ellipsometric data of ta-C films, and hence the results for the sp^3/sp^2 ratio are expected to be more accurate and reliable.

The various steps involved in the calculation of the sp^3/sp^2 ratio of ta-C films are outlined below [50]:

(i) Measurement of ellipsometric angles Ψ and Δ as a function of the photon energy E, by SE, for a ta-C film of known thickness t, and thereby calculate the optical constants n (refractive index) and k (extinction coefficient) as a function of E.

(ii) The experimental values of n and k are converted to the values of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant at different photon energies (E), using the relations:

$$\varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk \qquad \ldots (5)$$

(iii) Dasgupta *et al*[51]. have proposed a Gaussian density-of-states model to calculate the contribution of the $\pi \rightarrow \pi^*$ interband transitions to $\varepsilon_2(E)$ according to the relation:

$$\varepsilon_{2\pi}(E) = \frac{A}{E^2} erf\left(\frac{E}{2\sigma_\pi}\right) \exp\left[-\left(\frac{2E_\pi - E}{2\sigma_\pi}\right)^2\right] \qquad \ldots (6)$$

where A denotes a scale factor and E_π and σ_π are Gaussian fit parameters. The low photon energy (2.0 – 4.0 eV) part of the experimental $\varepsilon_2(E)$ spectral data is fitted to this equation to calculate the values of A, E_π and σ_π.

(iv) The values of $\varepsilon_{1\pi}(E)$ are calculated using the Kramers-Kronig relation according to Demichelis *et al*.[41]:

$$\varepsilon_{1\pi}(E) = 1 + \frac{2}{\pi}\int_0^\infty \frac{E'\varepsilon_{2\pi}(E')}{(E')^2 - E^2} dE' \qquad \ldots (7)$$

and the values of $\varepsilon_{1\sigma}(E)$ are calculated using the experimental data for $\varepsilon_1(E)$ and the relation: $\varepsilon_1(E) = \varepsilon_{1\pi}(E) + \varepsilon_{1\sigma}(E)$.

(v) $M_{1\pi}$, known as the first moment of $\varepsilon_{2\pi}(E)$, which is evaluated using the relation given by Dasgupta *et al.*[51].

$$M_{1\pi} = \frac{2}{\pi}\int_0^\infty E'\varepsilon_{2\pi}(E')dE' \qquad \ldots (8)$$

(vi) The Wemple-Didomenico plot[49] is obtained by plotting $1/\left[\varepsilon_{1\sigma}(E) - 1\right]$ as a function of E^2 using the relation:

$$1/\left[\varepsilon_{1\sigma}(E) - 1\right] = \left({E_0}^2/{E_{P\sigma}}^2\right) - \left(E^2/{E_{P\sigma}}^2\right) \qquad \ldots (9)$$

the optimum linear fit to the experimental curve is obtained and hence the values of ${E_{P\sigma}}^2$ and ${E_0}^2$ are estimated where $E_{P\sigma}$ is the energy spacing of two delta function-like bands and E_0 is the energy spacing between bands. Then, the ratio of the number density of π ($n_{v\pi}$) and σ ($n_{v\sigma}$) electrons is estimated using the relation:

$$\alpha = n_{v\pi}/n_{v\sigma} = M_{1\pi}/{E_{P\sigma}}^2 \qquad \ldots (10)$$

(vii) Finally, the ratio sp^3/sp^2 can be calculated. Let X, Y and Z denote the number of sp^3, sp^2 and H atomic sites / unit volume, so that:

$$X + Y + Z = N, \text{ the atomic density} \qquad \ldots (11)$$

Now, each sp^3 site gives rise to four σ states, each sp^2 site gives rise to three σ states and one π state and each H atom to a single σ state. Thus, the total number of π states is Y, whereas the total number of σ states is $(3Y + 4X + Z)$ and so:

$$\alpha = n_{v\pi}/n_{v\sigma} = Y/(3Y + 4X + Z) \qquad \ldots (12)$$

Further, if $f_3 = X/N$ (the atomic fraction of sp^3 atoms), $f_2 = Y/N$ (the atomic fraction of sp^2 atoms) and $f_H = Z/N$ (the atomic fraction of H atoms), then Eqs (11) and (12) yield:

$$f_H + f_2 + f_3 = 1, \; f_2/(3f_2 + 4f_3 + f_H) = \alpha$$

and hence

$$f_2 = \frac{(4 - 3f_H)\alpha}{1 + \alpha}, \qquad f_3 = \frac{(1 - 3\alpha) - (1 - 2\alpha)f_H}{1 + \alpha}$$