Optical properties of tetrahedral amorphous carbon films determined by spectroscopic ellipsometry


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Abstract

The optical and microstructural properties of tetrahedral amorphous carbon (ta-C) thin films prepared by filtered cathodic vacuum arc (FCVA) have been investigated as a function of the ion energy. The films were characterized by spectroscopic phase modulated ellipsometry (SPME) for the first time. The optical property of the ta-C layer was derived from the Forouhi and Bloomer amorphous semiconductor model. An effective medium approximation and a linear regression analysis have been used to determine the microstructure of thin ta-C films on silicon. The microstructure of these films deposited on silicon wafers was simulated by a four-layer model consisting of a roughness layer, a ta-C layer, a graded ta-C:Si layer and the silicon substrate. The graded layer consisting of the mixture of ta-C and silicon simulates the carbon ion impinging/diffusion into the surface of the silicon substrate. The complex refraction index, \( N = n - ik \), over the range of 250–900 nm, for ta-C had been determined. The Tauc (optical) band gap as a function of ion energy was also studied. © 1997 Elsevier Science S.A.

Keywords: Optical properties; Tetrahedral amorphous carbon films; Spectroscopic ellipsometry; Ion energy

1. Introduction

Tetrahedral amorphous carbon (ta-C) films deposited by filtered cathodic vacuum arc (FCVA) have a number of properties which make them suitable for optical and protective coatings. These properties include good IR transparency, high hardness, chemical inertness and impermeability to moisture penetration [1]. Ta-C films in general are amorphous with a mixture of sp² (graphitic) and sp³ (diamond) bonds, and the composition depends on the ion energy of the impinging carbon ions. It is, therefore, important to study the influence of the ion energy on the optical and microstructure of these films. Single-wavelength nulling ellipsometry has been used for many years as a standard measurement technique to determine the film thickness and refractive index. However, the method is not adequate as it assumed that the extinction coefficient of the film is zero and there is no interface between the film and the silicon substrate. For certain film thicknesses, the calculated parameters are significantly correlated making it very difficult to determine the film refractive index and thickness accurately. This correlation problem is minimized through spectroscopic ellipsometry as the ellipsometry measurements are performed as a function of the wavelength. In this paper, spectroscopic ellipsometry has been used to investigate the optical and microstructures of amorphous ta-C films. Using the dielectric functions, regression analysis was applied to characterize surface and interface structures of the films.

2. Experimental details

2.1. Spectroscopic ellipsometry

Ellipsometry is a powerful non-destructive optical technique which deals with the measurement and interpretation of changes in the polarization state of polarized light undergoing oblique reflection from a sample surface [2]. For a plane wave reaching a sample, the ratio of the Fresnel reflection coefficients for light polarized parallel (\( \rho \)) and perpendicular (\( \sigma \)) to the plane of the incident wave is given by

\[
\rho = \frac{r_{\rho}}{r_{\sigma}} = \tan \varphi \exp(i\Delta)
\]

where \( \tan \varphi \) is the amplitude ratio of reflectance and \( \cos \Delta \) the phase difference. Ellipsometric data are taken at multi-
ple wavelengths $\lambda$ at an angle of incidence $\phi$ and with each $\varphi$ and $\Delta$ measured pair, the corresponding complex pseudodielectric function $\langle \varepsilon \rangle$ of the film plus substrate is obtained directly assuming a two-phase ambient-substrate model where

$$\langle \varepsilon \rangle = (\varepsilon_1^y + i\varepsilon_2) = \sin^2 \phi [1 + \tan^2 \phi (1 + \rho)/(1 + \rho^2)]$$

(2)

In order to get information on the composition of a film, the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the pseudodielectric function of the film plus substrate, are compared to those of an optical model based on Bruggeman’s effective-medium theory (EMT) [3]. The EMT is expressed by

$$0 = \sum_{i=1}^{N_c} \frac{f_i}{\varepsilon_i - \varepsilon}$$

(3)

and allows one to calculate the effective complex dielectric function $\varepsilon$ of a microscopic composite from the dielectric function $\varepsilon$ and the volume fractions $f_i$ of its $N_c$ component materials. The EMT is also used to model the surface roughness layers on thin films. The differences between the measured and calculated data are minimized by a linear regression analysis [4]. A detailed description of the spectroscopic phase modulated ellipsometer and the ellipsometric equations can be found elsewhere [2,5].

2.2. Sample preparation

Two sets of experiments were carried out. In the first set, ta-C films were deposited at various bias voltages on (100) Si substrates. In the second set, $N_2$ gas was injected at different flow rates into the plasma stream within the filter region of the FCVA system via a leak valve. The details of the deposition system have been published elsewhere [6]. The film thicknesses were measured by laser spectral reflectometry to within ±50 Å. The ellipsometric angles were measured with a UVISEL spectroscopic phase modulated ellipsometer in the wide spectral range of 250–900 nm. The measurement of the optical indices, film thickness and film composition can be classified into three stages, i.e. the data acquisition, the structural modeling and simulation and the fitting. Careful selection of acquisition parameters, such as the spectrum increment (0.05 eV) and integration time (2000 ms) will produce good experimental data. The modeling and simulation can be considered as a qualitative analysis. The fitting process has to be performed once the user has obtained the correct layer-structure model from the modeling and simulation process and therefore can be considered as the quantitative analysis.

3. Results and discussion

The optical constants and thicknesses of the films were determined by fitting the ellipsometric measurements to a Forouhi and Bloomer model [7] shown to be appropriate for amorphous diamond-like carbon films [8]. In this model the mechanism for optical absorption is interband excitations between the bonding and antibonding $\pi$ bands [9]. This mechanism allows for the determination of the imaginary part of the refractive index ($\kappa$) over the range of interest and the determination of the real part ($n$) within an integral constant via the Kramer–Kronig relation. Four kinds of sample structures were considered for the thin film as shown in Fig. 1. The graded layer consisting of the mixture of ta-C and silicon simulates the carbon ion impingement (or bombardment) into the surface of the silicon substrate. Sample structure 1 which assumes a single layer did not fit well the measured values from its $\chi^2$ of 0.076. To account for surface roughness effect, sample structure 2 includes a void in the ta-C film and its $\chi^2$ value was found to improve slightly to 0.074. Next, sample structure 3 consisting of a graded layer and a ta-C layer was compared but is not good enough from its $\chi^2$ of 0.098. Lastly, sample structure 4 consisting of four layers was examined. The quality of the fit to the data becomes increasing better when the effect of surface roughness and grading are taken into consideration. Because of the smallest $\chi^2$ value of 0.043, sample structure 4 is good enough to simulate the microstructure of the ta-C film. The fit results also show that the confidence limits of all the parameters and the cross-correlation values determined by linear regression analysis are fairly low. It is found that the simulation of the ta-C/Si mixed layer is very important since this layer is relatively thick (~4–8 nm). The formation of this interface layer could be explained by the subplantation mechanism where ions with an energy ranging from 20 to 200 eV are capable of penetrating the surface layer of (100) oriented silicon and subsequently the carbon atoms could diffuse into the deeper region. However, the exact mechanism responsible for this relatively thick interface layer is not known at present and is currently under investigation. Fig. 2 shows the experimentally and simulated values of the variation of real and ima-

![Fig. 1. Four models of the regression analysis for a 70-nm thick ta-C film.](image-url)
ginary pseudodielectric functions with photon energy for one of the ta-C films deposited on a crystalline silicon substrate. As shown, the fit to the experimental data is good. The $\chi^2$ for all the films was of the range of 0.03–0.2. The modeled thickness of the film ranged from 540 to 940 Å and in all cases agreed with the measured results within ±10% error in the thickness.

The refractive index and extinction coefficient derived from the model simulation are shown in Figs. 3 and 4 respectively, for films deposited at different ion energy. Fig. 4 shows that as the ion energy increases from 35 to 105 eV, the extinction coefficient decreases and reaches a minimum value at 105 eV. Thereafter, the extinction coefficient increases when the ion energy increases further to 195 eV. The optical band gap, $E_g$ is one of the most important parameters which can provide an insight into the luminescent properties of the thin films. It can be determined using Tauc’s relation [10]:

$$a h \nu = m (h \nu - E_g)^2$$

(4)

where $a$ is the absorption coefficient of the ta-C film, $h$ is the Planck constant, $\nu$ is the frequency of radiation while $m$ is a constant proportional to the joint density of states. By constructing a plot of $(a h \nu)^{1/2}$ vs. photon energy $E = h \nu$, the optical band gap $E_g$ can be determined from the intercept of the extrapolated linear fit to the observed data. Fig. 5 shows the optical band gap as a function of ion energy. Fig. 5 shows that the band gap initially rose with increasing ion energy and then started to decrease as the ion energy was further increased. This is in accordance with theoretical and experimental observations that there is an optimum ion energy.
energy range for ta-C films [11]. It shows a curve with an optimum band gap value of 2.58 eV occurring at about 105 eV. Initially, when the ion energy varies from 25 to 105 eV, there is an increase in the optical band gap. However, as the ion energy increases from 105 eV onwards, the optical band gap starts to reduce. This behavior of the optical band gap can be explained by using the subplantation model proposed by Lifshitz [11]. The effect on optical band gap due to nitrogen incorporation is shown in Fig. 6. The optical band gap first increases slightly from 2.56 eV at 0 sccm nitrogen flow rate (undoped condition) to 2.62 eV at 0.5 sccm nitrogen flow rate. It then decreases from 2.62 to 1.34 eV with increasing nitrogen flow rate from 0.5 to 8 sccm. Fig. 7 shows the variation of extinction coefficient with nitrogen flow rate. The films exhibit a higher extinction coefficient with increasing nitrogen flow rate ranging from 0.08 to 0.15 at a wavelength of 370 nm and from 0.0033 to 0.05 at a wavelength of 620 nm, respectively. This shows that the optical absorption of ta-C films is increased by the addition of nitrogen gas to the plasma stream.

To obtain further information on possible sp$^3$-bond content in the film from the spectroscopic measurements, the effective number of valence electrons per carbon atoms taking part in interband transition, in the energy range 0–$E_n$ was determined by using a sum rule operation on the $e_2$ data

$$n_{opt} = 0.766 \frac{A}{d} \int \frac{E}{E_2} dE$$

where $A$ is the mean atomic weight, $E$ is the energy (eV) and $d$ is the density (kg m$^{-3}$). Fig. 8 shows plots of $n_{opt}$ as a function of photon energy. In carbon there are four valence electrons per carbon atoms and the integral eqn (5) should reach a plateau with $n_{opt} = 4$ as all optical transitions are exhausted at high energies. Diamond is essentially transparent below 7 eV so that $n_{opt} = 0$ at low energies but it rises to a value near 4 by about 25 eV [12]. For graphite, the integral saturates near 1 electron per atom at about 9 eV and again near 4 electrons per atom at about 25 eV. It is known that interband transitions in the energy range 0–9 eV involve only the $\pi$ bands which arise from 1 $\pi$ electron per atom. At about 9 eV transitions in $\pi$ bands are exhausted while transitions in $\sigma$ bands, involving 3 electrons per atoms, commence so that $n_{opt} = 4$ at high energies [13]. This clear energy separation between the $\pi$-electron
and $\sigma$-electron contribution to $n_{\text{eff}}$ in graphite can be used to determine the relative concentration of carbon atoms with sp$^3$ configuration. This is given by the ratio of $n_{\text{eff}}$ for films to $n_{\text{eff}}$ for graphite at energies ~9 eV. Using data at 7 eV, relative sp$^3$/sp$^2$ fraction were estimated for ta-C films deposited over a range of ion energies and are shown in Table 1. A relative high sp$^3$/sp$^2$ fraction, comparable to EELS measurement results determined in an previous study, [6] were obtained. The values also show that a wider bandgap is correlated with more localized $\pi$ bonding.

4. Conclusion

Spectroscopic ellipsometry has been employed successfully to study the optical properties of ta-C films. The graded ta-C/Si layer successfully simulated the carbon ion bombardment to the silicon surface. The optical band gap as a function of ion energy and nitrogen flow rate for ta-C films were obtained.

References


<table>
<thead>
<tr>
<th>Ion energy (eV)</th>
<th>Optical bandgap, $E_g$ (eV)</th>
<th>Relative sp$^3$ fraction (%)</th>
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