Determination of optical properties of nitrogen-doped hydrogenated amorphous carbon films by spectroscopic ellipsometry

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Nitrogen-doped hydrogenated amorphous carbon films have been deposited on silicon substrates by radio-frequency plasma-enhanced chemical vapor deposition using different N_2/CH_4 gas ratios from 0 to 3. The real and imaginary parts, *n* and *k*, of the complex index of refraction of these films have been determined for wavelengths between 300 and 830 nm by spectroscopic ellipsometry. Excellent agreement has been found between measured and modeled spectra, in which an empirical dielectric function based on classical Lorentz oscillator and Tauc joint density of states, and a linear void distribution along the thickness of the films have been assumed. Decrease in the optical energy gap and increase in the extinction coefficient, *k*, with increase in nitrogen concentration have been observed. Refractive index, *n*, increases rapidly with increase in nitrogen concentration up to 6.8 at. % ($\sim$7.0 at. %) and then increases slowly with further increase in nitrogen concentration. For all the samples, *n* is found to be highest at the film-substrate interface which gradually decreases towards the film surface. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1374501]

Considering the widespread application of hydrogenated amorphous carbon (*a*-C:H) such as solar cells,[1–3] the control of electronic doping, optical properties, residual defect, and chemical bonding must be achieved to realize high-performance electrical and optical devices. It has been reported that both optical and electrical properties, as well as their mechanical properties can be modified by nitrogen incorporation into amorphous carbon films without or with hydrogen (*a*-C or *a*-C:H).[4–6]

The material properties of nitrogen doped *a*-C:H grown by various deposition techniques have been studied by many workers.[7–9] However, there has been no simultaneous study of the optical constant and depth profile of the films in order to better understand their optical properties. Lee *et al.*[10] have analyzed ellipsometric data of *a*-C films from 1.5 to 5 eV by applying Bruggeman effective-medium theory with isotropic screening, assuming a model of the material as a composite with sp^2 and sp^3 carbon components. However, they did not investigate the degree of inhomogeneity of the films.

In this study, spectroscopic ellipsometry (SE), a nondestructive technique useful for the study of the optical properties of inhomogeneous films, has been employed to investigate the optical properties and depth profile of nitrogen doped *a*-C:H films deposited by rf plasma-enhanced chemical vapor deposition (PECVD). A four phase model (air/rough surface layer/inhomogeneous nitrogen doped *a*-C:H layer/Si substrate) has been used to fit the SE data taken in the wavelength range of 300–830 nm. Inhomogeneity of the film has been taken care of by assuming a volume fraction of void to vary along the thickness instead of the refractive index *n* and the unknown dielectric function of nitrogen doped *a*-C:H is described by the model developed by Jellison, Jr. and Modine.[11] A very good agreement between the calculated and the measured SE data in the 300–830 nm wavelength range has been obtained for all the films. A

parallel-plate rf PECVD reactor, using a capacitively coupled parallel plate, operating at 13.56 MHz was used to deposit *a*-C:H films on single crystal silicon (100) substrates at 300 K by water cooling of the sample holder. No bias voltage was intentionally applied between the substrate holder and the chamber wall. The rf power and the base pressure were 100 W (0.29 W/cm^2) and 10 Pa, respectively. The flow rate of CH_4 was held constant at 30 sccm while that of N_2 was varied from as 0, 10, 30, 60, and 90 sccm (N_2/CH_4 gas ratios between 0 and 3) for samples 1–5, respectively. The nitrogen concentration measured by x-ray photoelectron spectroscopy (XPS) in at.%, was found to be 0, 4.6, 6.8, 8.8, and 21.2 for samples 1–5, respectively.

The measurements of SE were carried out at an angle of incidence of 70° in the wavelength range of 300–830 nm. The SE used was of rotating analyzer type, fitted with a 75 W xenon lamp as a light source. The optical properties of thin films were fitted directly to measured SE (Δ, Ψ) data using empirical dielectric function. All the measurements were performed at room temperature. The details of the theoretical treatment for ellipsometric measurement of an inhomogeneous film have been discussed in our earlier publication.[12] In our SE data analysis, the unknown dielectric function of *a*-C:H is described by the model developed by Jellison, Jr. and Modine based on the classical Lorentz oscillator and Tauc joint density of states,[11] which is given by

$$\epsilon_{2TL}(E) = \begin{cases} \left[\dfrac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2}\dfrac{1}{E} \right] & \text{if } E > E_g, \\ 0 & \text{if } E \leq E_g, \end{cases} \quad (1)$$

where E_g is the optical band gap, E_0 is the peak transition energy, C is the broadening term, and A is the constant. The subscript TL indicates that the model is based on the Tauc joint density of states and the Lorentz oscillator; the four fitting parameters E_g, E_0, C, and A are all in units of energy. The real part of the dielectric function ϵ_1 is obtained by Kramers–Kronig integration. The independent unknown pa-

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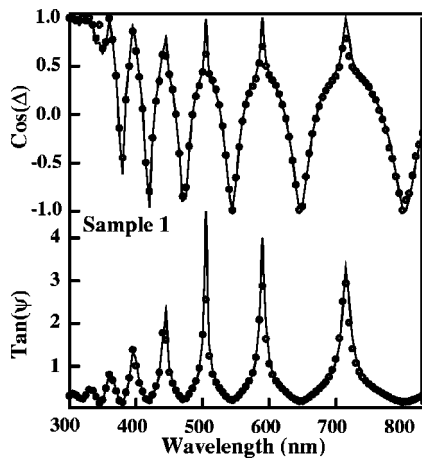[a]Electronic mail: yhayahi@theo.elcom.nitch.ac.jp

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FIG. 1. Measured (open circles) and fitted (solid lines) cos Δ (top) and tan Ψ (bottom) spectra of sample 1.

FIG. 2. Measured (open circles) and fitted (solid lines) cos Δ (top) and tan Ψ (bottom) spectra of sample 5.

rameters E_g, A, E_0, C, and $\epsilon_1(\infty)$ are numerically determined by minimizing the following mean squares deviation with a regression program. A four-phase structure (air/rough surface layer with thickness of d_1/inhomogeneous a-C:H film with thickness of d_2/substrate) has been used in the simultaneous fitting of measured parameters Δ and Ψ of SE. The rough layer on the surface was modeled as an effective mixture of 50% a-C:H and 50% void. Inhomogeneity of a film results from the nonuniform packing density of the film which is usually expressed by the volume fraction of void f_v. In our fitting analysis f_v is linearly varied from $f_{vo}=0$ at the film–substrate interface to f_{vi} at the outer surface of the film. This simplifies the calculation than considering the refractive index varying along the thickness of the film since f_v is a function of distance only while refractive index is a function of both distance and wavelength. However, it should be noted that our assumption of f_v varying from zero at the inner surface to f_{vi} at the outer surface is only for the sake of obtaining the distribution of dielectric function along the depth of the film by fitting to ellipsometric data and shows only relative variation in the void fraction along the thickness of the film.

Measured (open circles) and fitted (solid lines) cos Δ (top) and tan Ψ (bottom) spectra of undoped (sample 1) and most heavily nitrogen-doped (sample 5) carbon samples are shown in Figs. 1 and 2, respectively. An excellent agreement between the experimental and fitted cos Δ and tan Ψ spectra for both the samples has been obtained. From these figures, it can be clearly seen that there exists a strong interference in the spectra even below 400 nm wavelength for sample 1, while for sample 5 the interference almost disappears at the same wavelength range. The disappearance of interference for sample 5 below 400 nm wavelength suggests strong absorption by the film in that range, and a shift of the optical band gap towards longer wavelength compared to sample 1, may be due to nitrogen incorporation in a-C:H.

Table I shows the best fit model parameters used in the simulation of cos Δ and tan Ψ spectra. As shown in Table I, the optical band gap (E_g) gradually decreases from 2.28 eV for sample 1 to 1.80 eV for sample 5 as the nitrogen concentration increases from 0 to 21.2 at. %. It is reported that nitrogen incorporation in a-C:H leads to graphitization when deposited with standard PECVD system.[13,14] The decrease in
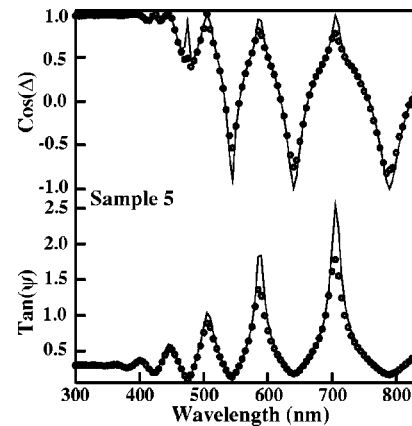
the optical gap, therefore, is presumably due to the increase in the sp^2 fraction induced by nitrogen incorporation. According to the cluster model proposed by Robertson and O'Reilly,[15,16] a-C:H contains both sp^2 and sp^3 sites, with sp^2 sites segregated into clusters embedded in an sp^3-bonded matrix. The difference between the $\pi-\pi^*$ gap of the sp^2 sites and the $\sigma-\sigma^*$ gap of the sp^3 sites creates very strong static disorder fluctuations. This model suggests that the size of sp^2 clusters (or the disorder in the film) increases with increasing nitrogen flow rate, thereby decreasing the optical band gap. The incorporated nitrogen acts as a bridge atom between the clusters leading to an increase in the sp^2 clusters size.[17,18] This also supports our earlier-mentioned interpretation of an increase in the sp^2 fraction induced by nitrogen incorporation. However, we did not observe the initial increase in the optical gap with nitrogen incorporation as observed by Silva and Schwan *et al.*[4,19] where they reported that sp^3 fraction increases at low nitrogen concentration and then decreases after a certain critical value. Amir and Kalish[13] reported similar gradual decrease in the optical gap with increase in the nitrogen concentration.

The values of Lorentz oscillator parameters, A, E_0, and C, are random in nature and do not provide much useful information. Since these parameters illustrate the peak of the dielectric function situated at a relatively shorter wavelength than the measurement range (300–830 nm), accurate determination of the parameter values by fitting in the longer

TABLE I. The important coefficients of the TL model [E_0, and $\epsilon_1(\infty)$], optical band gap (E_g), void fraction at the inner surface of a-C:H film (f_{vi}), and thicknesses of the rough layer (d_1) and a-C:H film (d_2) for all the samples, obtained by fitting the SE data. The 90% confidence limits are given with ($\pm$).

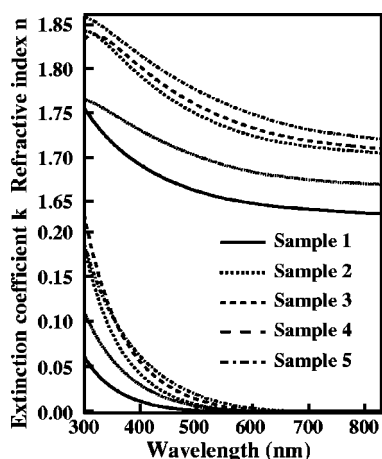| Sample No.	E_0 (eV)	E_g (eV)	$\epsilon_1(\infty)$	f_{vi}	d_1 (nm)	d_2 (nm)
1	6.64	2.28	2.09	0.12	6.6	1235.0
	±0.02	±0.01	±0.01	±0.02	±0.2	±0.1
2	5.97	2.04	2.27	0.18	5.38	1154.24
	±0.001	±0.01	±0.01	±0.001	±0.04	±0.02
3	5.21	2.02	2.33	0.25	3.93	1006.91
	±0.01	±0.02	$\pm.002$	±0.02	±0.09	±0.02
4	5.00	1.88	2.25	0.20	3.23	802.89
	±0.01	±0.01	±0.002	±0.009	±0.05	±0.02
5	6.02	1.80	2.10	0.22	1.0	1165.5
	±0.02	±0.07	±0.01	±0.05	±0.3	±0.2

FIG. 3. Variation of the refractive index n (top) and extinction coefficient k (bottom) at the surface of the samples over the wavelength range 300–830 nm.

wavelength region is not possible. However, though the individual values are not correct, the three parameters together do yield correct values of the dielectric function in the longer wavelength region as obtained by the fitting analysis.

Figure 3 shows the variation in the refractive index n (top) and extinction coefficient k (bottom) spectra at the surface of the samples, calculated using the film structure parameters as listed in Table I. Both k and n increase rapidly with increase in nitrogen concentration up to 6.8 at. % and then increase slowly with further increase in nitrogen concentration. We found that the optical constants (n, k) are significantly affected by nitrogen incorporation with nitrogen concentration less than ~7 at. %. The increase in k with increased nitrogen incorporation is due to the graphitization effect which decreases the optical gap resulting in higher k. The values of n obtained here are much lower than those reported in the literature for unhydrogenated a-C.[10] The existence of C–H bonds explains the lower indices of refraction for these films. Smith has reported n values of 1.75 ± 0.02 in the spectral range of 1.45–4.86 eV for the as deposited a-C film and observed a density of only 1.35 g/cm^3 for his film which is even lower than those of other disordered forms of carbon, such as, evaporated carbon films (1.35–2.4 g/cm^3), carbon chars (1.4–2.05 g/cm^3), and glassy carbon (1.47 g/cm^3).[20] The low density of the as deposited a-C:H film was attributed to the presence of hydrogen bonded to carbon in the form of polymeric component. Further lower values of n (<1.75) almost in the whole spectral region measured for our samples indicate still lower density which may be due to the presence of high voids along with the presence of hydrogen bonded to carbon. The increase in n with increased nitrogen incorporation is probably due to the removal of hydrogen and formation of C–N and C=N bonds in the film. For all the samples, the refractive index at the film–substrate interface is found to be the highest which gradually decreases towards the surface. Silicon is a crystalline substrate and it is likely that it will influence the formation of a dense carbon film with high sp^3/sp^2 ratio near its surface leading to higher value of n.[21] Therefore, we believe that the index gradient is partly due to the variation in the sp^3/sp^2 ratio and partly due to the variation in the void fraction along the thickness of the film.

In conclusion, a detailed optical characterization of nitrogen incorporated a-C:H thin films on Si substrates under different nitrogen concentration using rf PECVD, has been carried out by using SE. A four phase model has been used to fit the SE data taken in the wavelength range of 300–830 nm. Inhomogeneous a-C:H layer has been characterized by assuming a volume fraction of void to vary along the thickness instead of the refractive index n and the unknown dielectric function. Very good fitting has been obtained between the calculated and measured SE (Δ, Ψ) data. Increase in the extinction coefficient, k, and decrease in the optical gap are observed with increased amount of nitrogen incorporation which are probably due to the graphitization effect and decrease in sp^3/sp^2 ratio. The increase in refractive index, n, with increase in nitrogen concentration is related to the removal of hydrogen from the film and formation of carbon nitride species in the film. Furthermore, refractive index is found to be higher at the film-substrate interface than at the film surface for all the films. It is assumed that crystalline silicon substrate helps in the formation of a dense a-C film with higher sp^3/sp^2 ratio near the interface leading to a higher value of n.

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