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SPECTRO-ELLIPSOMETRIC STUDIES OF STRUCTURE AND OPTICAL PROPERTIES OF PLASMA-GROWN DLC FILMS

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ABSTRACT

Diamond-like carbon (DLC) films were deposited on silicon substrates by the plasma decomposition of hydrocarbons under various conditions, and studied by the spectroscopic ellipsometry (SE). We used the effective medium approximation with the dispersion model developed by Forouhi and Bloomer to determine simultaneously both the structure and the optical constants of the DLC films from their ellipsometric spectra. Especially, we investigated the variation of the multilayer structure including the interface layer, of the refractive indices, and of the extinction coefficients as the deposition conditions were varied; substrate pretreatment procedure, hydrocarbon precursors, and the substrate bias voltage were varied.

INTRODUCTION

In the recent years, amorphous carbon films deposited by the decomposition of hydrocarbons have attracted a great deal of attention because of their interesting diamond-like properties; high hardness, high wear resistance, low friction coefficient, high thermal conductivity, chemical inertness, partial transparency in the visible, and low infrared absorption¹⁻³⁾ These films are known as diamond-like carbon(DLC) films. Due to the above outstanding properties, DLC films have been considered for the applications such as protective, tribological, and optical coatings. However, it is known that the DLC films can

exhibit very different physical properties in dependence on the deposition conditions. For example, in the hydrogenated DLC films the hydrogen content which influences the number of SP³ bonding that is considered responsible for the observed diamond-like properties is dependent on the choice of the hydrocarbon precursor for the typical plasma-enhanced chemical vapor deposition (PECVD) process. Also, there are some reports that the structure of these films, including the interface layer, depends on the deposition conditions, and plays a role in determining the physical properties.

In this study, we deposited DLC films on the silicon substrates by PECVD under vari-

ous deposition conditions, and employed the spectroscopic ellipsometry (SE) for the analysis. The ellipsometry which measures the polarization state of the reflected light from the sample surface has the advantage of being nondestructive and noninvasive^{4, 5}. Moreover, SE has the depth-profiling capability due to the energy-dependent penetration depth of light^{4, 5}. Hence, we were able to determine the optical constants of the DLC films, and simultaneously to depth-profile the DLC films. Considering the great potential of DLC films for use as optical elements in high-powered lasers⁶ or as antireflection coatings for solar cells⁹, it is very important to determine the optical properties of these films.

Usually, the analysis of the ellipsometric spectra is carried out by nonlinear least regression (NLR); the unknown parameters are determined by minimizing the difference between the measured and calculated spectra. Hence, it is essential to keep the number of unknown parameters as small as possible for the effective NLR analysis, which we accomplished by adopting the dispersion model developed by Forouhi and Bloomer⁷ to represent the optical constants of the DLC films. This approach allowed us to determine and to compare the multilayer-structure, the indices of refraction, and the extinction coefficient of the DLC films deposited under different conditions.

EXPERIMENTAL

DLC films were deposited on silicon substrates by the decomposition of hydrocarbons using either the HF + DC plasma or RF plasma. First, we prepared a series of DLC films

with the identical deposition conditions except the substrate surface pretreatment procedure. Second, we prepared another series of DLC films by varying the substrate bias voltage and the hydrocarbon precursor while keeping the substrate surface pretreatment procedure identical. For the first series (films #1, #2, #3, and #4), CH₄ was used as a precursor, and the HF + DC plasma condition was maintained at $V_{HF} = 700$ V, $I_{HF} = 270$ mA and $V_{DC} = -600$ V, $I_{HF} = 48$ mA. Except the film #2 for which the substrate was pre-cleaned by H₂ for 30 min., the silicon substrates for this series were pre-cleaned by the Ar sputtering for 10 min., and in addition the film #3 and #4 were heated up to 100°C. It has to be emphasized that film #4 is distinguished from the other films, because it went through the transition process in which the gas composition was changed from 100% Ar to 100% CH₄ in 7 steps. For the second series (films #5, #6, #7, and #8), 13.56 MHz RF plasma was used with either CH₄- or C₆H₆-precursor. The bias voltage was varied from -100 V to -800 V to cause the difference in energy of the activated species. All the silicon substrates for this series were pre-cleaned by the Ar sputtering for 15 min. at -400 V in the Ar pressure of 3 mTorr. The sample preparation conditions are presented in Table 1 together with the summary of the SE analysis results for all the DLC films.

Spectroscopic ellipsometry was employed for the investigation of the depth profile and the optical properties of the DLC films. A Jobin-Yvon model UVISSEL spectroscopic phase modulated ellipsometer was used to measure the ellipsometric spectra of the DLC films in 0.01 eV increments from 1.5 to 5.0

Table 1. Summary of the preparation conditions and SE analysis results of DLC films.

Sample ID	Precursor	Pretreatment	Plasma and Bias voltage (V)	σ	d1 (Å)	d2 (Å)	f2 (%)
# 1	CH ₄	Ar Sputtering (10 min.)	HF + DC plasma	0.007	2417	535	0.29
# 2	CH ₄	H ₂ cleaning (10 min.)	HF + DC plasma	0.005	2464	515	0.36
# 3	CH ₄	Ar Sputtering (10 min.) Heat-up to 100°C	HF + DC plasma	0.007	2221	423	3.07
# 4	CH ₄	Ar Sputtering (10 min.) Heat-up and transition	HF + DC plasma	0.005	2399	420	0.02
# 5	C ₆ H ₆	Ar Sputtering (15 min.)	RF plasma -100	0.005	2845	200	0.50
# 6	C ₆ H ₆	Ar Sputtering (15 min.)	RF plasma -300	0.022	5334	204	-0.50
# 7	CH ₄	Ar Sputtering (15 min.)	RF plasma -500	0.004	1500	328	0.50
# 8	CH ₄	Ar Sputtering (15 min.)	RF plasma -800	0.010	2147	252	0.40

where d1 and d2 represent the thicknesses of the first and the second layer, and f2 represents the void volume fraction of the second layer.

eV. To analyze the measured ellipsometric constants Δ and Ψ -spectra, we adopted multilayer model in which DLC films were considered to be composed of multilayers with different thickness and void fraction. The effective optical constants of each layer were calculated using effective medium theory, assuming that each layer can be optically represented by the physical mixture of DLC and void. To represent the optical constants of DLC, we employed Forouhi dispersion equation⁷⁾ which were originally developed to describe the spectral dependence of the optical constants of amorphous semiconductors and amorphous dielectrics. The actual determination of the multilayer structure and the opti-

cal constants of the DLC films were carried out by NLR analysis. Especially, we adopted Levenberg-Marquardt algorithm⁸⁾ to minimize a value of the unbiased estimator of the goodness of fit⁹⁾.

RESULT AND DISCUSSION

In Fig. 1, we show the measured spectra of the DLC films # 1-# 4 which were deposited under identical conditions except the substrate pretreatment. The spectra in Fig. 1 look similar, which suggest that these films have similar structure and also similar optical constants as expected. But the observed small discrepancies are the indication of the

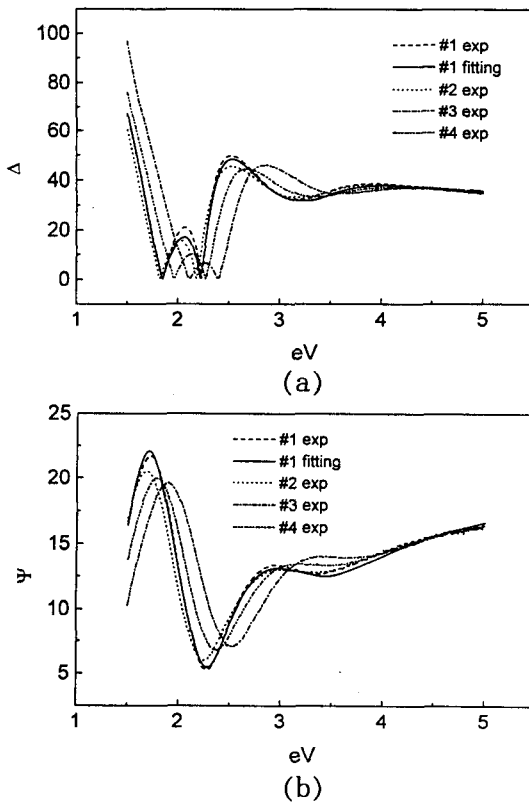


Fig. 1 SE spectra of the DLC films #1-#4. These films were deposited under identical deposition conditions (CH_4 precursor and HF+DC plasma) except the substrate pretreatment procedure. The typical best fit curve is shown by the solid line.

differences caused by the different substrate pretreatment.

To investigate these differences in detail, we employed the multilayer modeling as discussed in the previous section. The first attempt to fit the measured spectra with the single layer structure was unsuccessful. However, the second attempt with the two layer structure produced very good fits for all the films; the best fit curve for the film #1 is shown as a solid line. The structure used in the modeling is the 4 phase system of air/first layer/second layer/c-Si substrate, where

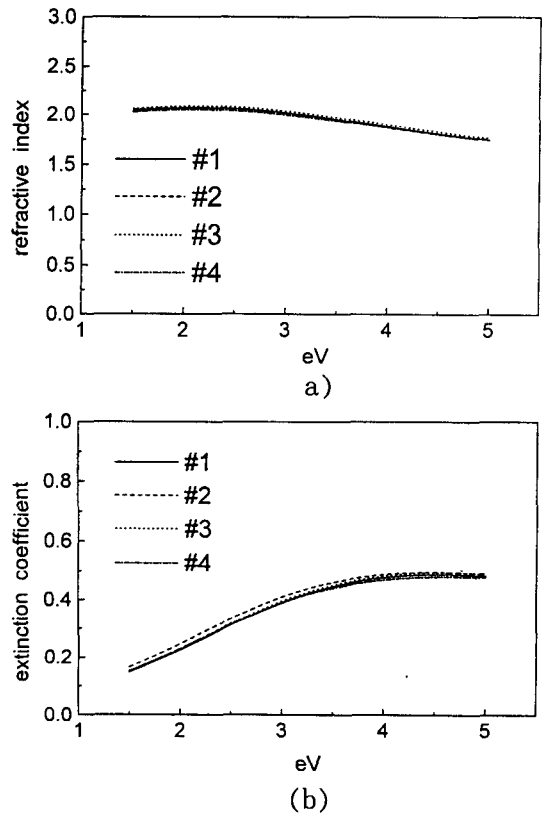


Fig. 2 The optical constants of the DLC films #1-#4; (a) Refractive indices, (b) Extinction coefficients. These optical constants were determined from the NRL analysis of the SE spectra shown in Fig. 1.

the first layer has no void fraction at all, but the second layer has the non-zero void fraction according to the NLR analysis result. The summary of the SE spectra analysis results are presented in Table 1. From this table, it is very interesting to note that all the films has the interface layers (second layers) which can be characterized to be less dense than the rest of the each films (first layers). Since we also treat the optical constants as fitting parameters, the comparison between the samples has to be made with caution. But still we can conclude that film #4 has the rel-

atively thinner and denser interface layers compared to other films. Based on this observation, we propose that the mixed plasma of Ar and CH₄ which were produced by stepwise gas composition change from 100% Ar to 100% CH₄ is the effective way to enhance the precursor surface diffusion and/or to promote the carbon atom cross-linking¹⁰.

In Fig. 2 the optical constants of the films #1-#4 which were determined from the SE spectra analysis are shown. In this Figure, we find that the films #1-#4 have the very similar optical constants as expected from their identical deposition conditions. We also find that the optical constant spectra exhibit the typical dispersion and magnitude of DLC films. Similar optical constant spectra have been reported for the hydrogenated and unhydrogenated amorphous carbon films by the Woollam group¹¹ and by Savvides³, respectively.

The similar characteristics and diamond-like nature of the films #1-#4 can be confirmed from the Raman spectra of these films shown in Fig. 3. First of all, it can be seen that the Raman spectra have asymmetric peaks near 1500cm⁻¹ which can be deconvoluted into two broad peaks that corresponds

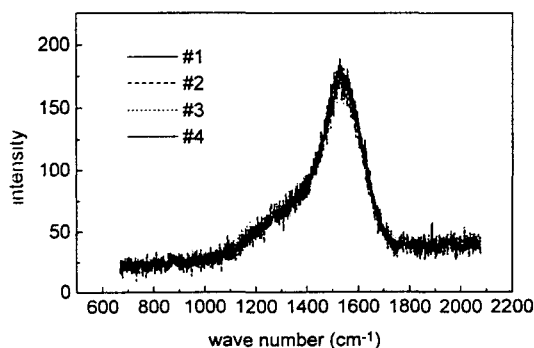


Fig. 3 Raman spectra of the DLC films #1-#4.

to the D (low energy component) and G (high energy component) characteristic peaks of the amorphous carbon^{12, 13}. These Raman spectra are the typical ones observed from the hydro generated amorphous carbon films. Usually, the wave number and the width of the G peak, and the integrated intensity ratio of the G peak to D peak are used as an indicator for the structural order of the graphitic component. Hence, the fact these films show identical Raman spectra implies that these films have the identical degrees of imperfections in SP² clusters.

The measured spectra of the DLC films #5-#8 were also analyzed using the same procedure and the results were summarized in Table 1, from which it can be seen that these films also have the interface layers. Interestingly, we find that films #5, #7, and #8 which were subjected to the identical substrate pretreatment have the similar interface structures. Due to the difference in the film deposition conditions, we cannot make the straightforward comparison between the interface structures of the films #1-#4 and those of the films #5-#8. But the relatively large void fraction in the films #5-#8 lead us to suspect over-etching of the substrate. Also, we attribute the relatively thin interface thickness in these films to the bias effects that can induce the earlier onset of the dense film growth than the case of the unbiased film growth. In the case of the film #6, the negative void volume fraction was obtained which can be interpreted as representing either the SP²-bonding-rich or denser interface. However, the more detailed analysis is required to confirm this conjecture. To show the effects that the bias voltage has on the

optical constants of the DLC films, we compared the optical constants of the DLC films deposited with the C_6H_6 precursor and the CH_4 precursor in Figs. 4 and 5, respectively.

In the case of the films deposited with the C_6H_6 precursor (#5, #6), we find that both the refractive index n and the extinction coefficient k decrease, and also the spectral dispersion of n is reduced as the bias voltage is increased, which we attribute to the SP^3 bonding fraction increase^{3, 14}. But in the case of the films deposited with the CH_4 precursor, we find very different variation of the optical

constants. As the bias voltage was increased, the refractive index n was decreased while the spectral dispersion of n is kept similar, and the extinction coefficient k was increased. The increase of the extinction coefficients represent the loss of transparency, which can be accounted only by the increase of the light absorbing SP^2 bonding fraction. Hence the observed decrease of n requires an explanation other than the one we presented above for the C_6H_6 -precursor films. We propose that the decrease of n in the CH_4 -precursor films stems from the increase of the

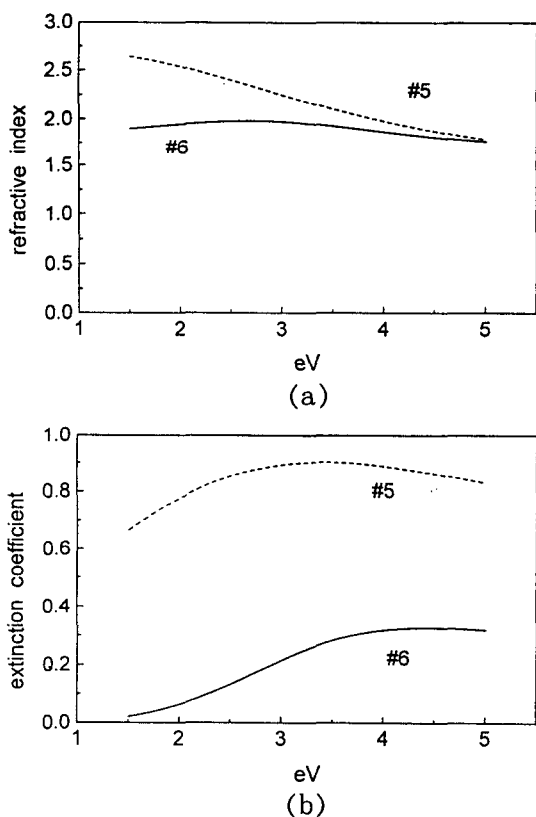


Fig. 4 The optical constants of the DLC films #5 and #6; (a) Refractive indices, (b) Extinction coefficients. These films were deposited under identical deposition conditions (Ar sputtering pretreatment, C_6H_6 precursor, and RF plasma) except the bias voltage.

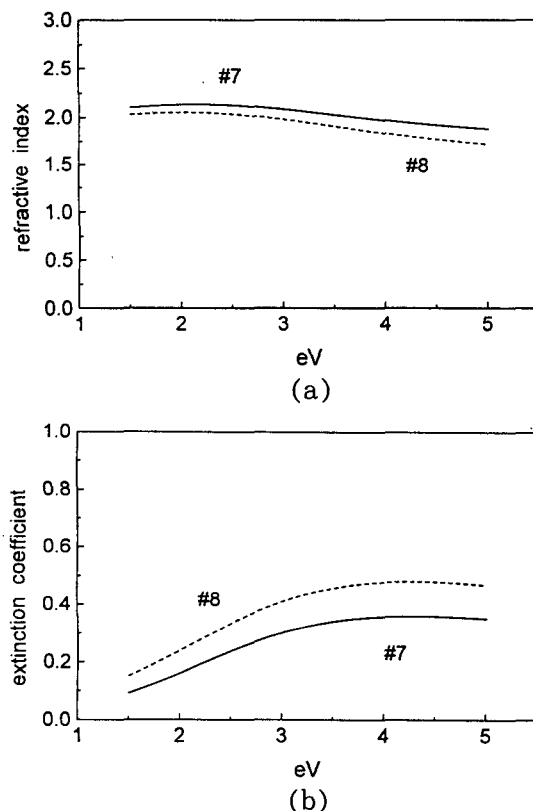


Fig. 5 The optical constants of the DLC films #7 and #8; (a) Refractive indices, (b) Extinction coefficients. These films were deposited under identical deposition conditions (Ar sputtering pretreatment, CH_4 precursor, and RF plasma) except the bias voltage.

void fraction in the film. The above discussions on the bias voltage effects can be summarized as follows; when the bias voltage is not too high the substrate bias can promote the SP^3 bonding due to the increased precursor energy, but when the bias voltage becomes excessively high the substrate bias cause the graphitization (similar to the heating effects¹⁴) and also the film becomes less dense. Finally, from the comparison of the optical constants of the films #6 and #7, we can see the effect that the choice of the precursor has on the DLC film characteristics. The films #6 and #7 were deposited under identical conditions (including the substrate pretreatment) except the bias voltage; the film #7 bias voltage is higher. Unlike the comparisons we made above, we find that the film #6 has more diamond-like optical constants, lower n and k , in spite of the lower bias voltage. To understand this precursor dependent effects, the plasma state of each precursor has to be studied.

CONCLUSIONS

We determined simultaneously both the structure and the optical constants of the DLC films by using the spectroscopic ellipsometry. First, it is found that the different pretreatment procedure induce the different interface structures. Especially, we find that the pretreatment with the gas composition transition produce the thinnest and the densest interface layer. We also find that the optical constants of the DLC films are deposition-condition dependent. Identical deposition conditions result in the similar optical constants, in spite of the different pretreatment

steps. When the applied bias voltage is adequate, the optical constants become more diamond-like, but when the bias voltage become excessive, the films become more graphitic and also less dense. Finally, we find that the different precursor makes the DLC films with different optical constants.

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