Study for infrared spectroscopic ellipsometric properties of diamond films

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Spectroscopic ellipsometric measurements in infrared region (2.5 − 12.5 μm) are carried out to characterize the structure and quality of diamond films grown by microwave plasma chemical vapor deposition (MPCVD) and hot filament chemical vapor deposition (HFCVD), respectively. It is found that the establishment of appropriate models has the strongest influence on the fit of ellipsometric spectra. The best fit is achieved for MPCVD film with a 77.5-nm middle layer of SiO_2, and for HFCVD film with an 879-nm rough surface layer included by Bruggeman effective medium approtimation (EMA). Finally the refractive index and the extinction coefficient are calculated for both films, the results show that the film grown by MPCVD is optically much better than that grown by HFCVD at infrared wavelengths.

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Recently, diamond films, as promising materials, have attracted more and more interests and are being improved with each passing day. The excellent optical properties make diamond films excellent candidates for optical applications, such as protective optical coatings and anti-reflection films[1−4]. Natural diamonds are so valuable that artificial ones are developed for replacement. Among various preparation methods, microwave plasma chemical vapor deposition (MPCVD) and hot filament chemical vapor deposition (HFCVD) are two of prominence. As optical properties of diamond films highly depend on preparation steps and conditions and are obviously dispersing, how to measure them quickly and accurately seems very crucial.

Infrared spectroscopic ellipsometry (IRSE), with high precision and sensitivity, convenience and damage-free, is one of the most adopted measuring methods in analyzing the optical properties of diamond films. This optical method measures two independent parameters (ellipsometric angles ψ and Δ) at each wavelength and needs no numerical Kramers-Kronig inversion or reference samples for calibration. However, the data directly obtained from IRSE measurements are usually not very interesting. Usable parameters of the films such as film thickness, surface roughness, and optical constants must be obtained by model simulations[5].

In this work, infrared spectroscopic ellipsometer (2.5 − 12.5 μm) is used to measure and compare the optical parameters at infrared wavelengths of diamond films grown by MPCVD and HFCVD methods, respectively. Taking into consideration the influences that may be caused by microstructures, such as surface roughness and sublayer between the film and substrate, appropriate models are adopted to obtain validated results with the help of Levenberg-Marquardt arithmetic[6]. Finally the refractive index (n) and the extinctive coefficient (k) are calculated for both films.

The diamond films are deposited on polished [100]-oriented silicon by MPCVD and HFCVD. In MPCVD method detailed steps and optimized conditions are described in Ref. [7]. In our experiments, the growth time for diamond films is about 25 hours. HFCVD system has been described in detail elsewhere[8]. The system pressure is kept at 3.8 kPa, volume percentage of ethanol at 0.8%, and substrate temperature at 780 °C.

The ellipsometric measurements of ψ and Δ, in the range of 2.5 − 12.5 μm with 10-nm resolution, were performed by NS-IRSE-1 infrared spectroscopic ellipsometer with the incidence angle of 68°. The accuracies of the angles of the polarizer, analyzer, alignment and light incidence are all within ±0.001°. In order to achieve a higher mean resolution, we applied 10 integrations for each measurement and improved the signal-to-noise ratio.

It is well known that thin films deposited on solid surfaces have very complicated microstructures. Since there are many lattice dislocations, grain boundaries, and voids in the films, properties of these films are very different from their bulk counterparts. In ellipsometric analysis, a conventional method to simulate the optical variation of film with deposition conditions is to model the film with a stack of layers having different compositions.

Effective medium approximation (EMA)[9] is the most frequently used approach to model the optical properties of polycrystalline thin films, which includes the grain boundary effect, void, purity and surface roughness. The effective dielectric constant ε of the diamond film, consisting of i different phases, can be described by

$$\sum_{i=1}^{n}(\varepsilon_i-\varepsilon)(\varepsilon_i+2\varepsilon)f_i=0, \tag{1}$$

where ε_i and f_i are the dielectric constant and volume fraction of constituent i, respectively.

The root mean square error (RMSE) is defined as merit function

$$\mathrm{RMSE}=\{\sum_{j=1}^{n}[\left|Y_{\mathrm{exp}_j}-Y_{\mathrm{cal}_j}\right|^2\times\mathrm{weight}_j]\}^{\frac{1}{2}}. \tag{2}$$

In this equation, j is the number of measured points, n is the total number, Y_{exp_j} denotes the measured ellipsometric data, and Y_{cal_j} denotes the calculated data. The weight$_j$ gives the true statistical weight of each data point. The larger the weight, the more importance the target is given in the optimization process. The common variably damped least squares method (Levenberg-Marquardt)[6] is an efficient and stable gradient optimization method that varies smoothly between the extremes of the inverse Hessian method and the steepest descent method. This solution algorithm finds parameters such as film thickness and optical properties by minimizing the RMSE between measured and calculated data. It works very well in practice and has become the standard of nonlinear least-square routines. For this reason, the modified Levenmberg-Marquardt regression analysis is used as optimization method in this paper to get the model parameters.

Figure 1 shows the deviations between measured and calculated spectra using two different models to describe the structure of diamond films made by MPCVD. The fitting results and the RMSE are also summarized in Table 1. Model 1# assumes a homogeneous diamond thin layer deposited on a semi-infinite silicon substrate, namely Si|diamond|air. The resulting thickness of diamond film is about 24.099 μm, while the RMSE is 0.1202. The disagreements between calculated and experimental values clearly show the existence of other layers. Since silicon oxidization takes place inevitably, a native oxide layer is added in Model 2# on top of the substrate, that is, Si|SiO_2|diamond|air. Compared with the fit given by Model 1#, the fit calculated from Model 2# has remarkable improvement. With the RMSE down to 0.0015, best-fitted values of Model 2# show that the SiO_2 layer has a thickness of 77.5 nm, which has given good reference in optimizing substrate pretreatment and film growth conditions. For example, supersonic cleaning and surface corrupting process can be prolonged properly to thin the oxide and improve the quality. At the same time, such a low RMSE also shows that the results fit the experimental numbers very well.

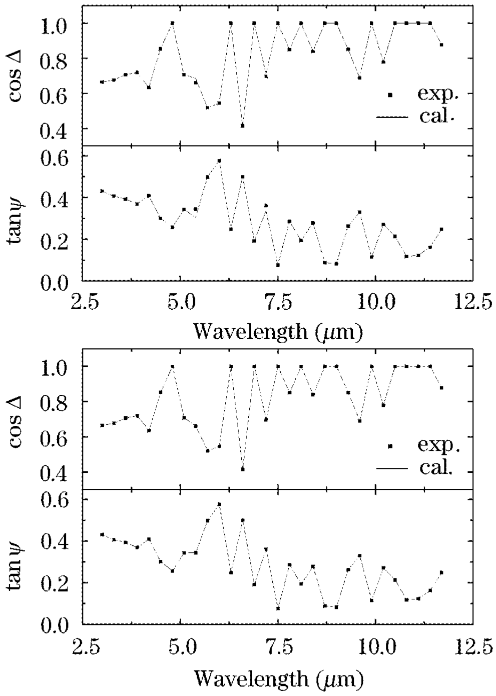

Fig. 1. Experimental and calculated IRSE data for the diamond film grown by MPCVD method on silicon substrate. (a) Model 1# (Si|diamond|air) and (b) Model 2# (Si|SiO_2|diamond|air).

Table 1. Results from Fitting of the Ellipsometric Spectra Applying Different Models to the MPCVD and HFCVD Films. The 90% Confidence Limits Are Given with (±)

	Model	d_{diamond} (nm)	D_{SiO_2} (nm)	d_{surface} (nm)	RMSE
MPCVD	1#	24099	—	—	0.1202
Film	2#	22388	77.5	—	0.0015
HFCVD	2#	12709	9.75	—	1.0197
Film	3#	12476	—	879	0.00207

As to the HFCVD films, we use model 2# first, namely, Si|SiO_2|diamond|air. Large RMSE (1.0197), also shown in Table 1, means that the model does not work in this case. Because of its extreme thickness (9.75 nm), the SiO_2 layer exists purely formal but scarcely affects the optical response of the system that is mainly given by diamond layer, and it cannot account for the difference between experimental and calculated data, but can be excluded from the model without expense of accuracy. Consequently, Model 3# assumes a two-layer model with a further Bruggeman EMA layer on the surface of film, but rejects the thin silicon oxide layer (Model 3# (Si|diamond|(diamond+void)|air)). Physically, the surface layer accounts for the effect of thick surface roughness or porosity that may be present in the upper surface of the HFCVD sample. The good fit between modeled and experimental spectra has been achieved (shown in Fig. 2, RMSE down to 0.00207), which confirms the presence of surface layer. It is found that the surface layer is as thick as 879 nm and the composition differs greatly from that of the bulk film, which means clearly that this thick layer cannot be omitted in the theoretical calculation, and also that the HFCVD film is far less smoother than the MPCVD sample. The fitting results and the RMSE are also summarized in Table 1.

Spectroscopic ellipsometry (SE) measures the complex ratio of the reflection coefficients R_P and R_S for light polarized parallel (P) and perpendicular (S) to the plane

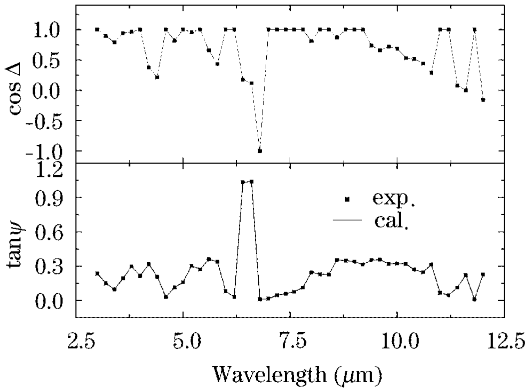

Fig. 2. Experimental and calculated IRSE data for the diamond film grown by HFCVD method on silicon substrate. Model 3# (Si|diamond|(diamond+void)|air).

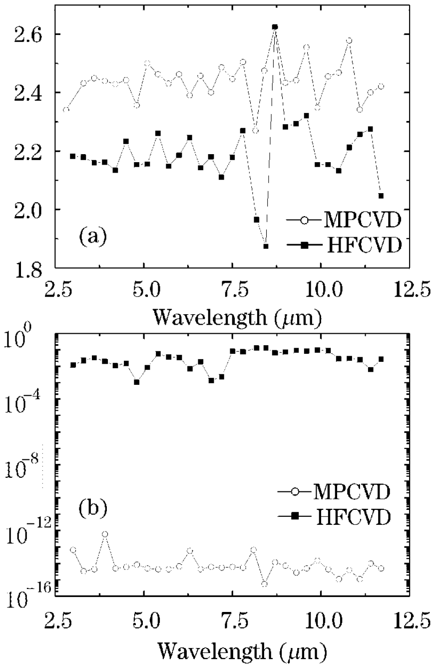

Fig. 3. Calculated n (a) and k (b) of MPCVD and HFCVD films.

of incidence, respectively, to determine two independent parameters: ψ and Δ. Together with the complex dielectric coefficient $\varepsilon = \varepsilon_1 + i\varepsilon_2$, the refractive index n and extinction coefficient k are

$$n = \frac{1}{\sqrt{2}}\sqrt{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}, \quad k = \frac{1}{\sqrt{2}}\sqrt{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}, \quad (3)$$

where ε_1 and ε_2 are the real and imaginary part of ε.

According to above formulas and Model 2# for the MPCVD film but Model 3# for the HFCVD film, n and k are calculated respectively as shown in Fig. 3. The reflection index of the MPCVD film with an average of 2.44 is very close to 2.42, n of natural diamond, while for the HFCVD film it is 2.19. Meanwhile, the extinction coefficients of the MPCVD film is in the range from 10^{-12} to 10^{-15}, which indicates the transparency of the film in infrared wavelengths (2.5–12.5 μm). However, the HFCVD film does not have so good performance as its extinction coefficients are at the scale between 1 and 10^{-3}. All these have proven that the chosen models work well, and the MPCVD film is optically much better than the HFCVD film.

In conclusion, the establishment of appropriate model has strong influence on the fit of ellipsometric spectra taken on chemical vapor deposition (CVD) diamond films. The best fit is achieved for MPCVD film with a 77.5-nm middle layer of SiO_2, and for HFCVD film with an 879-nm rough surface layer included by Bruggeman EMA. The calculation results indicate that the average n of the MPCVD film is very close to that of natural diamond and the k values are in the range of 10^{-12} to 10^{-15}, which show that the film grown by MPCVD method is transparent in infrared region, and is optically much better than the HFCVD film.

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References

1. F. Silva, A. Gicquel, A. Tardieu, P. Cledat, and Th. Chauveau, Diamond & Related Materials **5,** 338 (1996).
2. Z. Yin, Z. Akkerman, F. W. Smith, and B. X. Yang, Diamond & Related Materials **6,** 153 (1997).
3. K. M. McNamara, B. E. Scruggs, and K. K. Gleason, Thin Solid Films **253,** 157 (1994).
4. L. J. Wang, Y. B. Xia, J. H. Ju, Y. M. Fan, Y. W. Wu, and W. M. Shi, J. Phys.: Condensed Matter **12,** 257 (2000).
5. P. J. McMarr, K. Vedam, and J. Narayan, Appl. Phys. Lett. **59,** 694 (1986).
6. J. C. Comfort, *Annual Simulation Symposium* (Society for Computer Simulation, New York, 1987) p. 185.
7. Z. G. Ma, Y. B. Xia, L. J. Wang, Z. J. Fang, W. L. Zhang, and M. L. Zhang, Acta Opti. Sin. (in Chinese) **23,** 989 (2003).
8. Z. J. Fang, Y. B. Xia, L. J. Wang, Z. W. Wang, W. L. Zhang, and Y. M. Fan, J. Phys. D: Appl. Phys. **35,** L57 (2002).
9. D. A. G. Bruggeman, Ann. Phys. **5,** 636 (1935).