10-15-1988

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Published in *Journal of Applied Physics* **64**:8 (October 15, 1988), pp. 4175-4180

Submitted January 11, 1988; accepted July 5, 1988

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Abstract
The purpose of this paper is twofold. First, we report on the successful application of variable angle spectroscopic ellipsometry to quantitative thin-film hermeticity evaluation. Secondly, it is shown that under a variety of film preparations and moisture introduction conditions water penetrates only a very thin diamondlike carbon (DLC) top surface-roughness region. Thus DLC is an excellent candidate for use as protective coatings in adverse chemical and aqueous environments.

DOI: 10.1063/1.341331

Online at http://link.aip.org/link/?JAPIAU/64/4175/1

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I. INTRODUCTION

One of the most common uses of thin-film coatings is to prevent moisture penetration to an underlying surface. However (especially for very thin films), it is very difficult to quantitatively measure the penetration of a film by water. Common techniques for thin-film and near-surface evaluation such as electron spectroscopy for chemical analysis (ESCA), Auger, secondary ion mass spectroscopy (SIMS), and various ion beam analysis techniques cannot be used because moisture and high vacuum are incompatible.

In this paper we show that variable angle spectroscopic ellipsometry (VASE) can be used to detect the thickness of ultrathin layers of water both on a surface and penetrated into a surface. The technique has monolayer sensitivity, can be used at any ambient pressure (including atmospheric), and is fast and nondestructive.[1–4]

The material studied presently is diamondlike carbon (DLC), otherwise known as "hydrogenated amorphous carbon." DLC films are generally hard, semitransparent materials with properties that can be controlled by the deposition parameter settings, which in turn determine the amount of hydrogen contained in the films. DLC films are usually not affected by strong acids or by common organic solvents and are thus good candidates for use as protective coatings. They are totally amorphous so they lack grain boundaries through which moisture might otherwise penetrate. There has been frequent confusion recently because of a parallel development of *diamond* thin films.[5] The latter are films of polycrystalline diamonds containing very little hydrogen. Hard films of DLC, on the other hand, contain varying amounts of hydrogen and are amorphous.[6–8] Both DLC and diamond films are hard and transparent in much of the visible, thus the "DLC," terminology. DLC films have been, and are continuing to be, extensively studied.[9] The purpose of the present paper is to present results of quantitative analysis of hermeticity studies of DLC films using VASE.

II. EXPERIMENT

DLC films were prepared in a 30-kHz parallel-plate plasma deposition chamber using pure methane gas and a chamber pressure of ~20 mTorr (Ref. 10). Power levels from 100 to 300 W were used, and substrate temperatures from 23 to 250 °C. The plates were equal in area with 20 cm diam. and 2 cm separation. Deposition rates ranged up to 250 Å per min depending on power and temperature. Figure 1 shows deposition rate versus substrate temperature for three power levels and associated flow rates. Replots of the same data show that there is a linear relationship between deposition rate and flow rate. We find that there is no apparent relationship between power level and deposition rate. Thus the gas flow rate dominated over the power level in determining the deposition rate. All samples for these hermeticity studies were deposited on polished single-crystal silicon wafers.

Ellipsometry measurements were made with a rotating analyzer system combining a variable angle of incidence

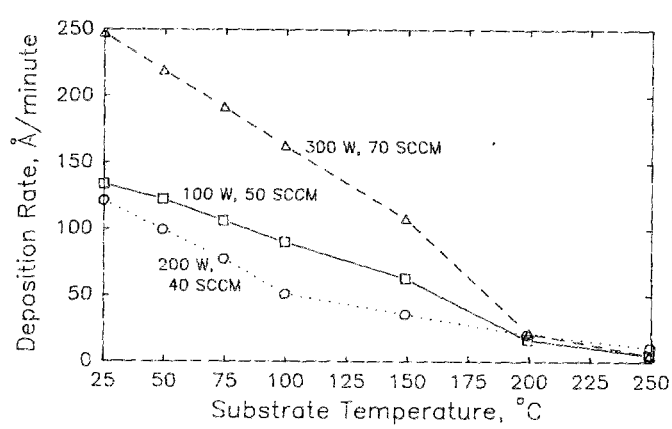

FIG. 1. Deposition rate vs substrate temperature for three different power level/flow-rate settings.

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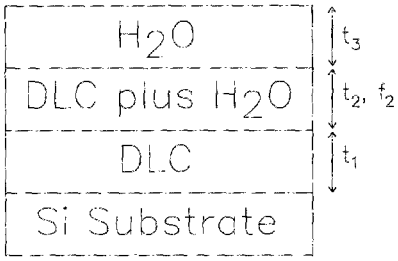

FIG. 2. Structure model assumed for analysis of DLC moisture studies.

with spectroscopic (3000 to 8500 Å) capabilities.[1–4] This system has linearly polarized light (at a controlled azimuthal angle) incident on a sample at an angle ϕ to the normal. The amplitude and phase (or equivalently, azimuthal angle and ellipticity) of the reflected wave is analyzed with a second linear polarizer rotating at 50 Hz. The signal detected by a photomultiplier tube is digitized, and a Fourier analysis of the amplitude and modulation is performed to determine the complex reflection ratio of ρ defined by

$$\rho = R_p/R_s \equiv \tan\psi \exp j\Delta, \tag{1}$$

where R_p and R_s are the complex Fresnel reflection coefficients for the components parallel and perpendicular to the plane of incidence, respectively, for the material system, and the measured ellipsometric parameters ψ and Δ are defined by Eq. (1).

Microstructural analysis is performed by making an assumption as to the nature of the sample under study. For the present samples the model is shown in Fig. 2. The t_i are the layer thicknesses, and f_2 is the fraction of DLC in a DLC plus H_2O Bruggeman effective medium approximation (EMA) mixture layer.[11] The procedure is to calculate ρ using Fresnel reflection coefficients for a multilayer parallel stack (and EMA mixed layers) for a given initial set of values for thicknesses and fractions. Next, a regression analysis is performed to minimize the error function (MSE) defined by

$$\mathrm{MSE} = \frac{1}{N}\sum_{i=1}^{N} (\psi_i^{\exp} - \psi_i^{\mathrm{calc}})^2 + (\Delta_i^{\exp} - \Delta_i^{\mathrm{calc}})^2, \tag{2}$$

where "exp" means experimentally measured, and "calc" means calculated. The psi and delta are functions of wavelength λ and angle of incidence ϕ. A large enough range of both λ and ϕ are chosen so that an "overdetermination" of the number of measurements with respect to the number of unknown parameters is made and correlation problems are avoided. In our analysis programs we can use Eq. (2) as formulated, or we can use psi alone or delta alone in the analysis. The final outcome of the analysis is a set of values for thicknesses, EMA fractions, and optical constants for any of the layers. The optical constant values can take several forms: (1) index of refraction n and extinction coefficient k, (2) real, $E1$, and imaginary, $E2$, parts of the optical dielectric function, or (3) the amplitude, position, and width of Lorentz oscillators representing the absorption and dispersion of the material.

Since the Lorentz oscillator model was used extensively in this analysis we will describe it further. When the wavelength-dependent n, k (or $E1$, $E2$) values are solved, the number of unknown parameters equals the number of wavelengths times two plus the number of layers plus the number of unknown fractions in an EMA. Thus if 20 wavelengths are used and there are two unknown thicknesses there will be $(2\times 20)+2=42$ unknowns to be solved. In the Lorentz oscillator model there are far fewer unknowns, since the following equation represents the spectral dependence of optical constants[12]:

$$E = 1 + \sum_{i=1}^{M} A_i\left(\frac{1}{\lambda + P_i + jW_i} - \frac{1}{\lambda - P_i + jW_i}\right), \tag{3}$$

where E is the complex dielectric function, and the sum is over the total number of oscillators M. For the presently reported work, the maximum number of oscillators we used was one. In Eq. (3), A_i, P_i, and W_i are the amplitude, position, and width of the ith oscillator, respectively, and λ is the photon wavelength. In the oscillator analysis A_i, P_i, and W_i thicknesses and EMA fractions are solved for in the regression analysis. Thus a typical one oscillator DLC analysis has five unknowns: three oscillator parameters and two layer thicknesses; or seven unknowns: three oscillator parameters, three layer thicknesses, and an EMA fraction (see the structural model shown in Fig. 2).

III. RESULTS

A. General

Figure 3 shows the dependence of the average (the index varies by less than 20% from 3000 to 8000 Å) index of refraction n on substrate temperature for three different plasma power levels. As shown, the index rises from a value near 1.75 to near 2.0 and then shows evidence of a decrease to 1.93 for the 250 °C sample. Similar results were reported by Alterovitz *et al.*[10] In Fig. 4 the percentage of hydrogen (as determined by proton recoil analysis) is plotted as a function of deposition temperature. Notice the gradual decline, with a slight increase at the highest temperature. The trends in Figs. 3 and 4 are in the opposite directions; lower hydrogen concentration results in a higher index of refraction and films with more hydrogen are optically less dense.

From analysis of optical absorption data we know that the optical band gap increases with increasing hydrogen con-

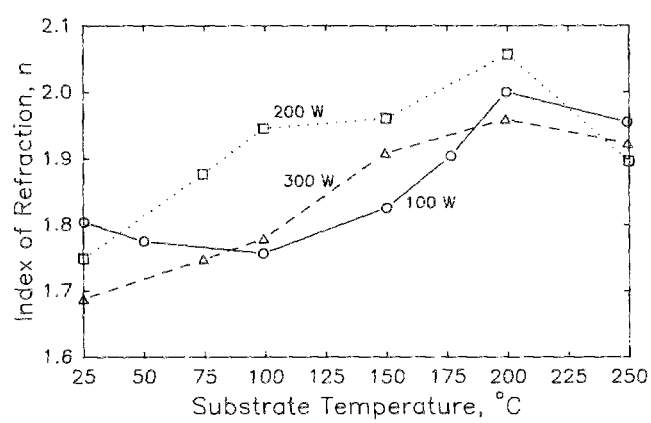

FIG. 3. Optical index of refraction vs substrate temperature for three different power levels.

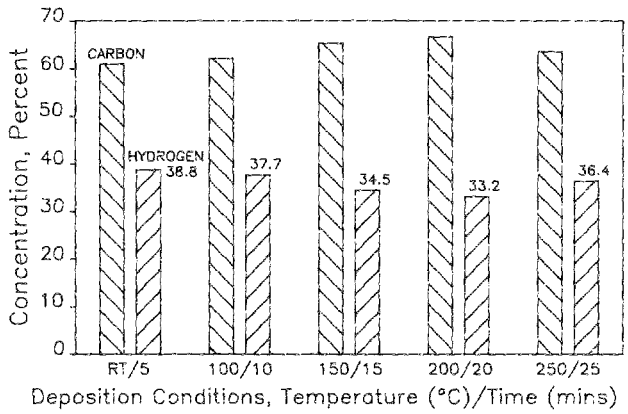

FIG. 4. Percent carbon and percent hydrogen for samples deposited at room temperature (RT) to 250 °C.

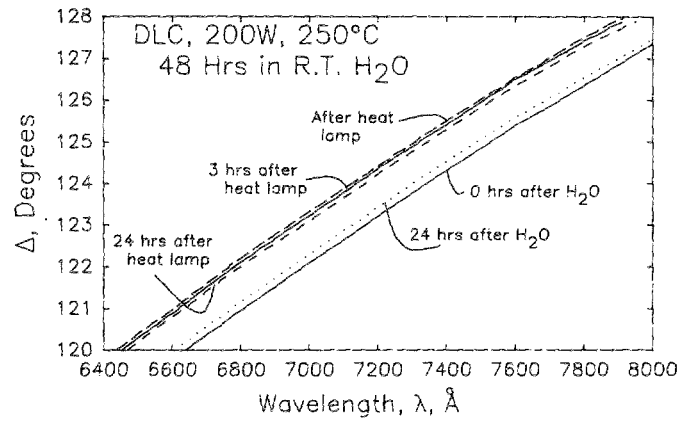

FIG. 5. Ellipsometric delta parameter vs wavelength at various times after removing the sample from water, as listed. Sample deposited at 200 W, 250 °C, soaked in room temperature water for 48 h. After removing from water, it was kept in a room atmosphere.

centration. Thus the index of refraction (for green and longer wavelengths, where k is zero) will decrease for films with greater band gap.

One final observation: we find that there is a slight decline in the index of refraction for films thicker than about 1000 Å. This suggests a "snow pile" effect; the latest DLC to deposit is less dense than the initial material deposited near the substrate interface.

To determine the environmental stability of DLC films we have deposited a large number of samples (at various power and temperature values) onto polished silicon single-crystal wafers and subjected them to immersions in trichlorethane, acetone, ethyl alcohol, sulfuric acid, nitric acid, hydrochloric acid, and hydrofluoric acid. After each immersion the samples were subjected to rubber eraser abrasion tests and "scotch tape" pull tests. Although barely qualitative, the latter tests served as a valuable comparative measurement. These tests had no effect on any sample deposited with 100 W. At 200- and 300-W depositions there was partial removal for samples deposited at room temperature, but there was no effect for substrate temperatures of 74 to 250 °C. Thus DLC samples prepared under all but a few conditions survived very stressing environmental tests.

B. Room-temperature moisture effects on (200 W, 250 °C deposited) DLC films: One Lorentz oscillator analysis

Moisture was introduced to the DLC films on silicon wafer substrates at two temperatures: room temperature and at 100 °C. In this section the following studies were made. The sample was prepared at 200 W in pure methane with a silicon substrate heated to 250 °C. The sample was then soaked in water at room temperature for 48 h. Ellipsometric data were taken after the following sequence of steps:

(1) Immediately after being taken out of water.
(2) 24 h after being taken out of water.
(3) After applying a heat lamp for 15 min.
(4) 3 h after applying the heat lamp.
(5) 24 h after applying the heat lamp.

The results were analyzed using both a two-layer ("DLC" plus water layer: $t_2 = 0$ in Fig. 2) and a three-layer model [DLC, water plus DLC, and water layer (nonzero t_1, t_2, and t_3 layers in Fig. 2)].

Plots of the ellipsometrically measured delta parameters as a function of wavelength are shown in Fig. 5 for steps (1)–(5) indicated above. Notice the sequence: delta increases as water leaves the surface. After 3 h (and then 24 h) in a laboratory environment moisture redeposits.

Using the "oscillator" regression analysis and a two-layer model we determined that the water layer was 66-Å thick on top of a 344-Å thick DLC film. The three-layer model analysis was consistent with this result: 330 Å of DLC, 29 Å of 50%-50% mixture of DLC and water, and 48 Å of pure water on top.

An interesting result was that the heat lamp removed only 12 Å of water and that 54 Å of water still remained! We propose that this thin water layer is being held to the surface by an ususually high surface tension associated with DLC surface micropores.

TABLE I. Ellipsometric analysis of room-temperature water penetration in DLC (200 W, 250 °C deposited).

	Two-layer analysis		Three-layer analysis		
Procedure step/number	DLC thickness	H_2O thickness	DLC thickness	Mixture (50–50) layer thickness	Water layer thickness
1	344 Å	66 Å	330 Å	29 Å	48 Å
2	344	62	330	30	44
3	341	54	330	24	40
4	342	54	330	25	39
5	342 Å	54 Å	330 Å	27 Å	37 Å

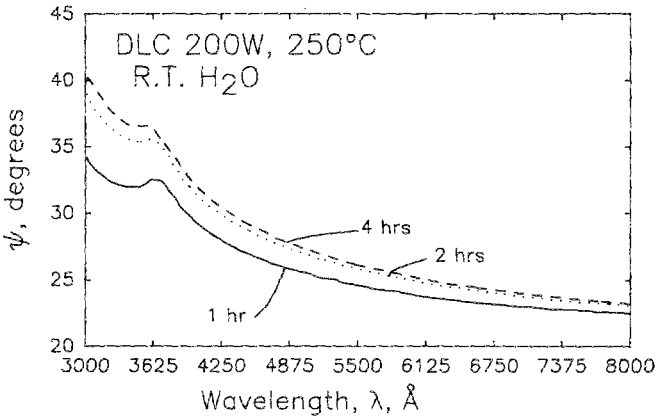

FIG. 6. Ellipsometric psi parameter vs wavelength for samples soaked for 1 to 4 h in room-temperature water.

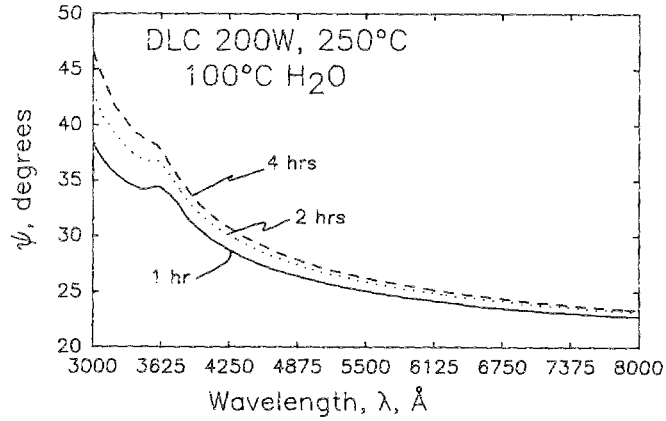

FIG. 8. Ellipsometric psi parameter vs wavelength for samples soaked in 100 °C water for 1 to 4 h.

Results of the present ellipsometric analysis are summarized in Table I.

We would like to propose that the "mixture" layer in the three-layer analysis is a *roughness layer* rather than a true material mixture. The water is just filling the spaces in the roughness region in this interpretation. A roughness layer of approximately 30 Å is entirely reasonable.

C. Moisture effects on (200 W, 250 °C deposited) DLC films: Room-temperature water and 100 °C water

In this section we present results of two-layer and three-layer analyses of both room-temperature water and 100 °C water for samples deposited at 200 W and 250 °C. Ellipsometric psi and delta data are shown in Figs. 6 and 7 for room-temperature water, and Figs. 8 and 9 for 100 °C water. The graphs show trends after 1, 2, and 4 h soaking before measurement.

The results of the analysis of the data shown in Figs. 6–9 are shown in Table II (for room-temperature water) and in Table III (for 100 °C water). In these tables "Mixture" indicates 50% water and 50% DLC. Several important points should be noticed: (1) For both room-temperature and 100 °C water the measured water layer thickness increases for longer time in water, a conclusion independent of

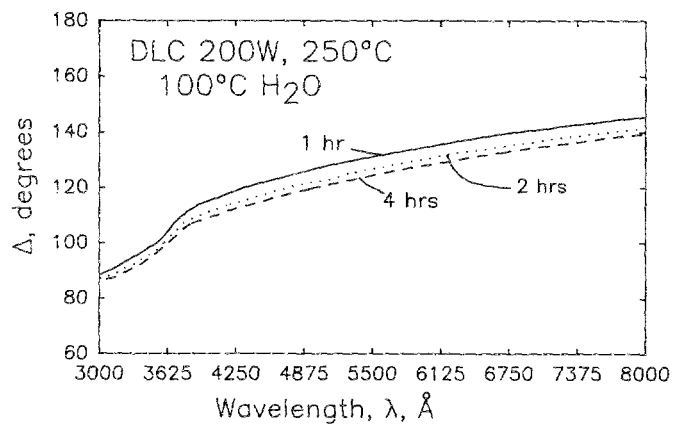

FIG. 9. Ellipsometric delta parameter vs wavelength for samples soaked in 100 °C water for 1–4 h.

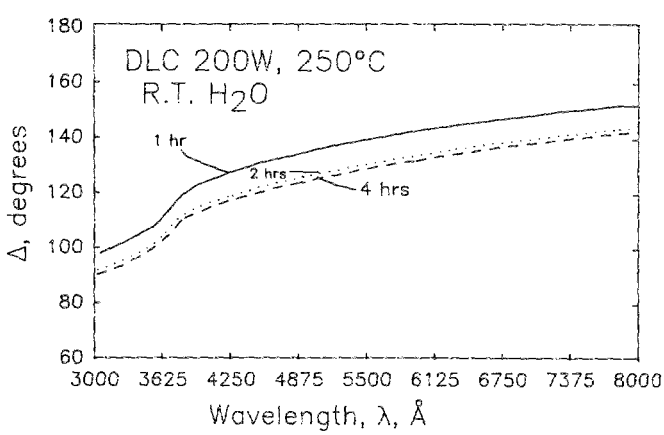

FIG. 7. Ellipsometric delta parameter, same conditions as in Fig. 6.

TABLE II. 200 W, 250 °C sample in room-temperature water.

	Two-layer analysis		Three-layer analysis		
Condition	DLC	Water layer	DLC	Mixture	Water layer
No water	328 Å	...	...	...	...
2 h in water	332 Å	57 Å	326 Å	24 Å	37 Å
4 h in water	336 Å	72 Å	328 Å	28 Å	51 Å

TABLE III. 200 W, 250 °C sample in 100 °C water.

	Two-layer analysis		Three-layer analysis		
Condition	DLC	Water layer	DLC	Mixture	Water layer
No water	328 Å	...	...	...	...
2 h in water	360 Å	63 Å	337 Å	46 Å	36 Å
4 h in water	361 Å	93 Å	339 Å	54 Å	56 Å

TABLE IV. Moisture penetration studies (water) of 200-W plasma deposited DLC, one-oscillator model: oscillator parameters [see Eq. (3)] are in the sequence A_i, P_i, W_i (measured in eV). For definition of t_1, t_2, and t_3, see Fig. 2. (If t_2 and/or t_3 do not appear, then they are assumed to be equal to zero).

RT	75 °C	100 °C	150 °C	200 °C	250 °C
		200-W DLC samples without H_2O			
$t_1 = 729$ Å oscillator parameters 9.6;7.8;3.8 MSE = 6.7	$t_1 = 915$ Å oscillator parameters 11.8;7.7;3.8 MSE = 10	$t_1 = 810$ Å oscillator parameters 13.2;7.9;3.8 MSE = 11.5	$t_1 = 840$ Å oscillator parameters 14.4;7.9;3.8 MSE = 7	$t_1 = 448$ Å oscillator parameters 14.8;7.9;3.8 MSE = 2.5	$t_1 = 252$ Å oscillator parameters 12.5;7.4;4.05 MSE = 0.18
		200-W DLC samples with H_2O, oscillator parameters (as given above) fixed			
$t_1 = 761$ Å $f_2 = 100\%$ MSE = 30	$t_1 = 943$ Å $f_2 = 97\%$ MSE = 5.1	$t_1 = 847$ Å $f_2 = 100\%$ MSE = 8.4			
$t_3 = 0$ $t_1 = 775$ Å MSE = 21	$t_3 = 4.5$ Å $t_1 = 936$ Å MSE = 2.8	$t_3 = 3$ Å $t_1 = 847$ Å MSE = 8.3	$t_3 = 74$ Å $t_1 = 904$ Å MSE = 13	$t_3 = 139$ Å $t_1 = 473$ Å MSE = 15.1	$t_3 = 123$ Å $t_1 = 271$ Å MSE = 0.21
$t_2 = 53$ Å $f_2 = 65\%$ $t_1 = 736$ Å MSE = 22	$t_2 = 31$ Å $f_2 = 99\%$ $t_1 = 906$ Å MSE = 2.6	$t_2 = 12$ Å $f_2 = 58\%$ $t_1 = 841$ Å MSE = 8.2			
$t_3 = 37$ Å $t_2 = 42$ Å $f_2 = 50\%$ $t_1 = 736$ Å MSE = 24	$t_3 = 3$ Å $t_2 = 33$ Å $f_2 = 98\%$ $t_1 = 904$ Å MSE = 2.7	$t_3 = 26$ Å $t_2 = 9$ Å $f_2 = 64\%$ $t_1 = 841$ Å MSE = 8.3	$t_3 = 73$ Å $t_2 = 20$ Å $f_2 = 90\%$ $t_1 = 885$ Å MSE = 13	$t_3 = 160$ Å $t_2 = 17$ Å $f_2 = 96\%$ $t_1 = 450$ Å MSE = 15.5	$t_3 = 122$ Å $t_2 = 1$ Å $f_2 = 0.2\%$ $t_1 = 271$ Å MSE = 0.21

whether a two-layer or a three-layer analysis is used. (2) The water layer is slightly thicker when soakings are in hot water as opposed to cold water.

D. Moisture effects on (200- and 300-W samples with deposition temperatures from room temperature to 250 °C) DLC films

As indicated in the title of this section, a series of 11 samples were prepared. For the 200-W series the depositions were at room temperature, 75, 100, 150, 200, and 250 °C. For the 300-W series the temperatures were at room temperature, 100, 200, and 250 °C. In this section we discuss the results of the one Lorentz oscillator model analysis when steam was directed at the surface of the sample.

Four structural models were considered, and these are combinations of finite values of t_1, t_2, t_3, and f_2 in Fig. 2.

The results are summarized in Tables IV (200 W) and V (300 W). If t_2 and/or t_3 don't appear in the *bracketed region* in the tables, then they are assumed to be zero. (For details of how the ellipsometric data analysis is carried out, see Refs. 1–4.) The mean square error (MSE) represents the quality (appropriateness) of the model fits to the experimental ellipsometric data; lower MSE means better fit. We suggest reading each table from top to bottom, one sample at a time. Taking the room-temperature 200-W sample first, note that the lowest MSE (for steamed sample) is for the model: water/DLC/substrate ($t_2 = f_2 = 0$ in Fig. 2).

The 75 °C 200-W sample has the best solution when the t_2 layer is 99% DLC. This is compatible with the nearly comparable water/DLC/substrate solution indicating the presence of only 4.5-Å water. Inspection of the solutions for the 100 °C 200-W sample are similar; there are only a few Angstroms of water on the surface with negligible penetration of the DLC.

For the 200 and 250 °C 200-W samples only two models were used (water/DLC/substrate and water/mixture/DLC/substrate). In all three of these samples there were much thicker water layers: from 74 to 160 Å. (This is still obviously very thin!)

Table V summarizes the results for the 300-W sample series. Note that, as in the case of 200-W sample (Table IV), the model with DLC and water mixed together (with no other layers) doesn't work at all. It has a much higher MSE compared to the other models, considered in the following rows in the same table. The three remaining models give similar results; the water resides mainly on the top of DLC, with negligible "mixing" between DLC and water.

It may appear to the reader that the original thickness has been swelled by the presence of water. We don't believe this to be the case, however. Rather, the results are consistent with "valleys" of roughness in the original structure being filled with water.

IV. SUMMARY AND CONCLUSIONS

We have shown that variable angle spectroscopic ellipsometry is an effective tool for moisture penetration studies on a monolayer resolution scale.

TABLE V. Moisture penetration studies (steam) of 300-W plasma deposited DLC one-oscillator model: oscillator parameters [see Eq. (3)] are in the sequence A_i, P_i, W_i (measured in eV). For definition of t_1, t_2, and t_3, see Fig. 2. (If t_2 and/or t_3 do not appear, then they are assumed to be equal to zero.)

RT	100 °C	200 °C	250 °C
	300-W DLC samples without H_2O		
$t_1 = 1322$ Å oscillator parameters 10.9;10.9;3.8 MSE = 39.3	$t_1 = 1341$ Å oscillator parameters 10.6;9.05;3.8 MSE = 39.1	$t_1 = 659$ Å oscillator parameters 13.02;7.4;3.8 MSE = 6.6	$t_1 = 136$ Å oscillator parameters 12.6;7.7;3.8 MSE = 0.16
	300-W DLC samples with H_2O (steam), oscillator parameters (as given above) fixed		
$t_1 = 1495$ Å $f_2 = 98\%$ MSE = 29.4	$t_1 = 1488$ Å $f_2 = 98\%$ MSE = 52		$t_1 = 236$ Å $f_2 = 60\%$ MSE = 0.25
$t_3 = 188$ Å $t_1 = 1384$ Å MSE = 11.4	$t_3 = 175$ Å $t_1 = 1380$ Å MSE = 12.5	$t_3 = 3$ Å $t_1 = 688$ Å MSE = 3.7	$t_3 = 102$ Å $t_1 = 156$ Å MSE = 0.07
$t_2 = 188$ Å $f_2 = -1\%$ $t_1 = 1386$ Å MSE = 11.4	$t_2 = 172$ Å $f_2 = 5\%$ $t_1 = 1377$ Å MSE = 13	$t_2 = 4.5$ Å $f_2 = 87\%$ $t_1 = 685$ Å MSE = 3.7	$t_2 = 113$ Å $f_2 = 14\%$ $t_1 = 138$ Å MSE = 0.08
		$t_3 = 1$ Å $t_2 = 9$ Å $f_2 = 96\%$ $t_1 = 680$ Å MSE = 3.7	$t_3 = 13$ Å $t_2 = 101$ Å $f_2 = 16\%$ $t_1 = 138$ Å MSE = 0.08

The main results on the DLC moisture studies are that: (1) Moisture resides mainly *on* the surface of DLC no matter if it was introduced as cold water, hot water, or steam jet. (2) In cases where there is an apparent penetration ($\leqslant 50$ Å) we feel it likely that water is merely filling the void regions of a "rough" surface. The substrates are highly polished oriented single-crystal (semiconductor grade) wafers. 50 Å of roughness layer is reasonable for polished silicon wafers used as substrate. (3) A heat lamp removes water but not all of it. This suggests that surface micropores provide a strong surface tension for these very thin water layers. (4) The amount of water on the surface after wetting (but without further treatment) does not depend on the parameters of deposition such as power or substrate temperature, nor does it depend on the first DLC film thickness in any systematic manner.

Thus, DLC is an effective protection against moisture penetration, and it can be prepared with a range of physical properties which depend on the deposition parameters. These properties are directly related to the amounts of hydrogen in the films.

ACKNOWLEDGMENTS

The research of S. Orzeszko, B. N. De, and J. A. Woollam was supported by Control Data Corporation and NASA Lewis Grant No. NAG-3-154. Research by D. C. Ingram and J. A. Woollam was supported by the U. S. Army Materials Technology Laboratory, Contract No. DAAL04-86-C-0030.

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