DIAMONDLIKE CARBON AS A MOISTURE BARRIER AND ANTIREFLECTING COATING ON OPTICAL MATERIALS†

JOHN A. WOOLLAM*, BHOLA N. DE*, AND L. Y. CHEN*
JOHN J. POUCH** AND SAMUEL A. ALTEROVITZ**
 *Department of Electrical Engineering, University of Nebraska, Lincoln, NE 68588-0511
**NASA Lewis Research Center, Cleveland, OH 44135

INTRODUCTION

Diamondlike carbon (DLC) is amorphous, hard, semitransparent, and is under consideration for use as a coating material for infrared optics [1] . DLC is also designated as a-C:H to indicate its amorphous nature as well as to indicate the presence of large (20 to 55 percent) amounts of hydrogen in the film.

Two important questions arise with respect to use of DLC in infrared optics. DLC is amorphous, and will the lack of grain boundaries help to keep moisture from penetrating the film? Secondly, application as an antireflecting coating places restrictions on the allowed values of the index of refraction of the film relative to the particular substrate material being used. Will DLC have the correct index range? These two questions are addressed in this paper.

MOISTURE PROTECTION STUDIES

It is very difficult to measure penetration of moisture into thin films. Common surface analysis techniques such as AUGER, and SIMS require ultrahigh vacuum, and therefore can't be used.

We have shown that variable angle spectroscopic ellipsometry (VASE) can be used to determine the thickness of ultrasmall amounts of water on, and in a thin film. This spectroscopy is not commonly known, so a brief description is given [2], [3].

Ellipsometry determines the complex reflection coefficient

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

where R_p and R_s are the complex Fresnel reflection coefficients for components of light parallel (p) and perpendicular (s) to the plane of incidence of the incident and reflected light. Our VASE data were taken from 300 to 850 nm with light incident at an angle ϕ to the normal to the sample. The reflected light polarization state was analyzed with a rotating polarizer. Light intensity was measured with a photomultiplier tube, and the signal digitized, and Fourier analyzed to determine the ψ and Δ parameters of equation 1.

The measured complex ratio $\tilde{\rho}$ is related to the optical index of refraction, n, and extinction coefficient, k, of the material under study. If complex materials structures are involved then n and k can be determined for individual layers, and layer thicknesses determined.

Microstructural analysis is performed assuming the nature of the sample under study. For the present samples the model shown is Fig. 1. The t_i are layer thicknesses, and f_2 is the fraction of DLC in a DLC plus H_2O Bruggeman effective medium approximation (EMA) mixture layer. The procedure is to calculate $\tilde{\rho}$ using the 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

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

The general set of materials parameters such as dielectric constants, layer thicknesses, and composition fractions giving the minimum MSE are then found. In the present experiments thicknesses and moisture fractions are found.

The films of DLC used for moisture penetration studies were prepared using a 30kHz parallel-plate plasma deposition system. Pure methane at a chamber pressure of 20 microns was used. Power levels of 100, 200, and 300 watts were used, but results for 200 watt are reported here.

Moisture was introduced to the films in two ways; from immersion in 23^{0}C water, and from a steam jet at 100^{0}C.

Example ellipsometric data are shown in Figure 2. The data at 0 hours after H_2O indicate that water was introduced, then the bulk of it allowed to run off a vertical surface. At this time the maximum amount of water remained, and the Δ parameter was lowest. Twenty four hours later some water had evaporated, and Δ increased. After exposure to a heat lamp much of the water on the surface was evaporated (but not all!). After exposure to the laboratory 23^{0}C atmosphere a small amount of moisture from the ambient air deposited, with an associated decrease in Δ .

Using regression analysis of ellipsometric data for this sample, and a two-layer (t_2 = 0 in Fig. 1) model in our ellipsometric analysis, we determined that the water layer was 66-$\overset{0}{A}$ thick on top of a 344-$\overset{0}{A}$ thick DLC film. The three-layer (t_1, t_2, t_3, in Fig. 1) analysis was consistent with this result: 330 $\overset{0}{A}$ of DLC, 29 $\overset{0}{A}$ of 50%-50% mixture of DLC and water, and 48 $\overset{0}{A}$ of pure water on top.

This type of analysis was performed on a large number of samples, with the same final result: DLC films were not penetrated by water [4] . The DLC surfaces had small amounts of roughness, and moisture was found to penetrate the valleys of this roughness but not further.

ANTIREFLECTION CONDITIONS USING DLC

Substrates on which we deposited DLC included: lexan, silicon, fused silica, KG-3 glass, BK-7 glass, ZnS, GaAs, Ge, and heavy metal fluoride glass. It was desired to know if DLC could be deposited to the proper thicknesses and with the correct indices of refraction for use as an antireflecting coating on each of these substrates.

Antireflecting coatings provide an important method of and enhancing transmission through optical window materials [5].

The reflectivity has a minimum when

$$n_1 d_1 = \lambda_0/4 \qquad (3)$$

where n_1 is the index of refraction of the coating, and d_1 its thickness. The

reflectivity minimum is at its lowest value (zero) when

$$n_1^2 = n_0 n_2$$

where n_0 is the index for the ambient, which is normally air, so

$$n_1 = \sqrt{n_2} \qquad (4)$$

is required, where n_2 is the index of the substrate at the wavelength of interest.

Table I lists infrared transmitting substrates, their indexes of refraction, the operating wavelengths of interest, and the required DLC thickness and optical index of refraction. The proper index came from use of Eq. 4, and the proper thickness from Eq. 3.

What is noticed immediately from Table I is that the required film index of refraction ranges from 1.2 to 2.85 for the examples listed.

The index of refraction of DLC can be controlled by choosing the proper deposition technique and parameters [1]. The range typically found is for

$$1.6 \leq n_1 \leq 2.3$$

which makes the optimum matching substrates have indices from

$$2.5 \leq n_2 \leq 5.3$$

These values are much higher than the indexes for the glasses under consideration (Table I), but results in a decent match for ZnS, diamond, $Ti O_2$, $As_2 S_3$ glass, Se glass, and results in good matches for Si, Ge, GaAs, and InSb. All are common infrared transmitting materials [6].

The effect of index match or missmatch on reflectance near the antireflecting condition is seen in Figs. 3 and 4 for the substrates indicated.

DISCUSSION AND CONCLUSIONS

We were able, with extreme care in surface preparation, to get DLC to adhere to lexan, silicon, fused silica, KG-3 glass, BK-7 glass, ZnS, GaAs, Ge, and heavy metal fluoride glass. The most difficult adherence problem was with ZnS, for which we were unable to deposit the required thicknes for antireflection (Table I).

Table I Candidate Substrates, and Conditions for Antireflection

Operating Substrate	Index at Wavelength	Operating Wavelength	Required DLC: Thickness	Index
ZnS	2.2	4 micron	676nm	1.48
Fused Silica	1.46	550nm	114nm	1.21
KG3 Glass	1.5	1.06 micron	217nm	1.22
BK7 Glass	1.52	550nm	90nm	1.23
Heavy Metal Fluoride	1.45	4 micron	833nm	1.20
Lexan	1.4	550nm	113nm	1.22
Silicon	3.42	10 micron	1351nm	1.85
GaAs	3.5	4 micron	535nm	1.87
Ge	4.0	4 micron	500nm	2.0
InSb	3.9	10 micron	1269nm	1.97
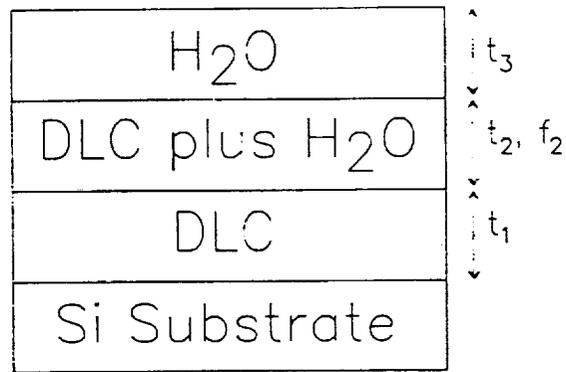
Fig. 1 Model structure assumed.
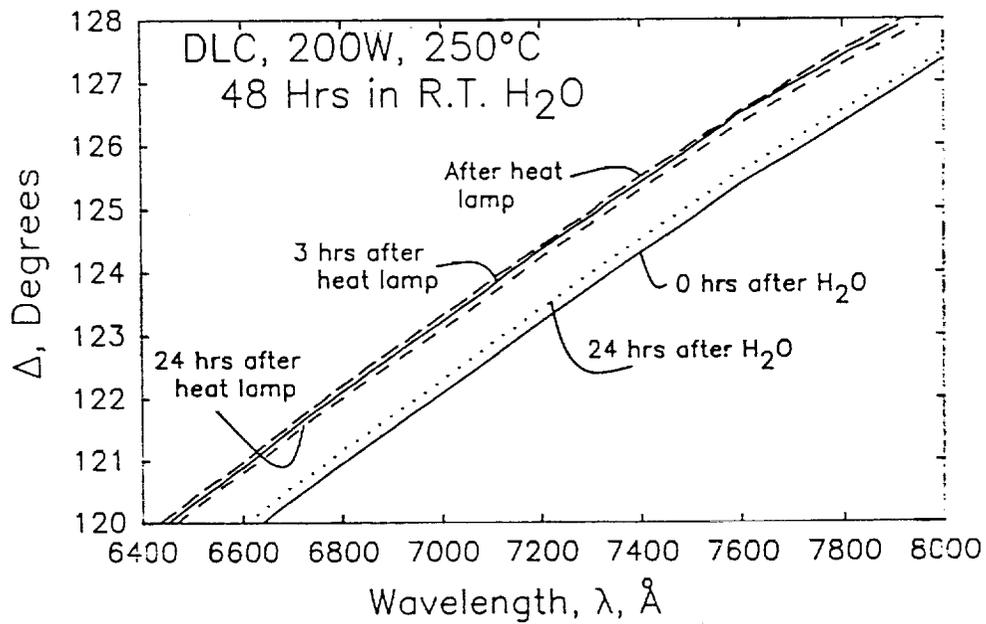
Fig. 2 Change in parameter Δ with moisture changes.

DLC film on Silicon
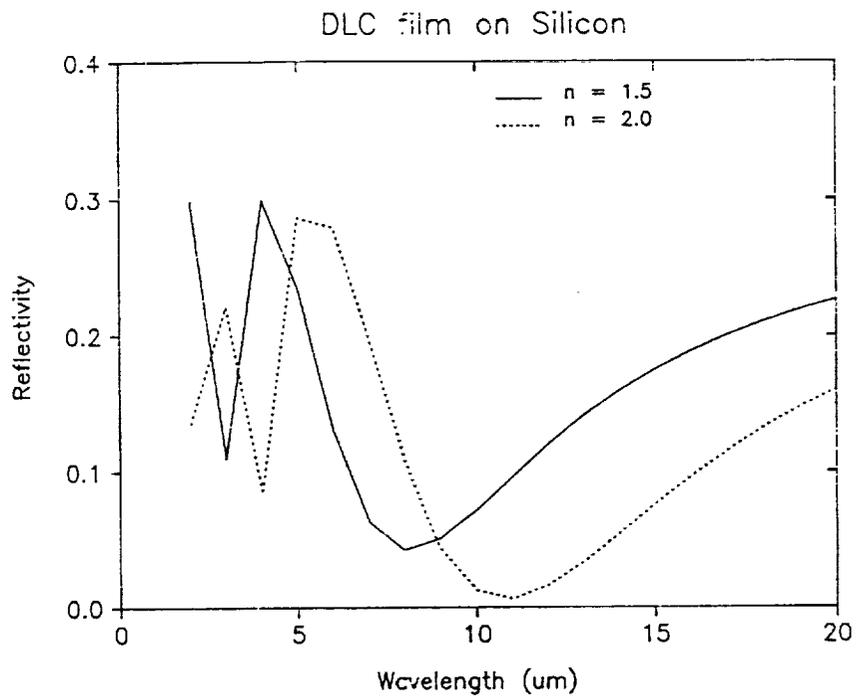
Fig. 3 DLC as an AR coating on Si.

DLC film on heavy metal fluoride
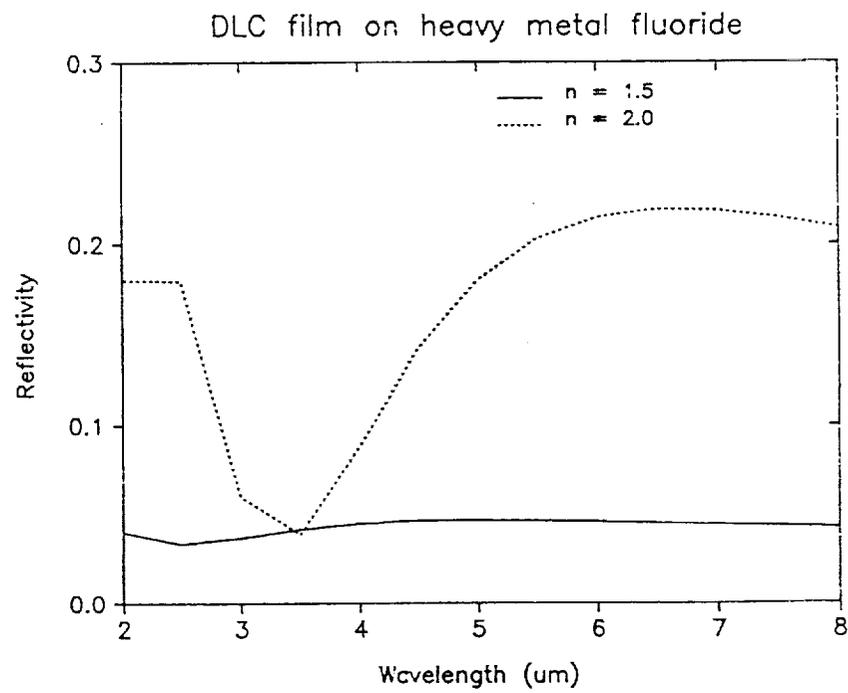
Fig. 4 DLC as an AR coating on heavy metal fluoride glass.

In conclusion, we find that DLC is an effective moisture barrier for use on infrared optics, and with the exception of ZnS we were able to directly deposit DLC on the chosen substrates to the desired thicknesses for antireflection. The indexes of refraction were measured from 300 nm to 10 microns, and found to be in the range from 1.6 to 2.0. Other workers have prepared DLC samples with indices up to 2.3. Thus, we have established a range of conditions for use of DLC as an antireflecting coating. Zero reflectance can be achieved on substrates of Si, Ge, GaAs, and InSb. Low reflectance can be achieved on ZnS, diamond, T_iO_2, As_2S_3 glass, Se glass; but DLC will not be a good antireflecting coating on the common glasses with index near 1.5.

References

[1] J. C. Angus, P. Koidl, and S. Domitz, in Plasma Deposited Thin Films, edited by J. Mort and F. Jansen (CRC, Boca Raton, FL, 1986), Chapter 4.
[2] J. A. Woollam, P. G. Snyder, and M. C. Rost, Thin Solid Films 166, 317 (1988).
[3] J. A. Woollam, P. G. Snyder, and M. C. Rost, Mat. Res. Soc. Symp. Proc. 93, 203 (1987).
[4] S. Orzeszko, B. N. De, J. A. Woollam, J. J. Pouch, S. A. Alterovitz, and D. C. Ingram, J. Appl. Phys. 64, 4175 (1988).
[5] H. J. Hovel, "Solar Cells", in Semiconductors and Semimetals, Vol. 11, edited by. R. K. Willardson, and A. C. Beer, Academic Press, New York, 1975, page 203.
[6] The Intrared Handbook, edited by W. L. Wolfe and G. J. Zissis, The Infrared Information and Analysis Center, Environmental Research Institute of Michigan, Ann Arbor, MI, 1978.