Diamond-like Carbon Depositions and Characterization

D.E. Morton and I. Stevenson, Denton Vacuum, Moorestown NJ; R. Vernhes, B. Baloukas,
R. Snyders, and J.E. Klemberg-Sapieha, École Polytechnique, Montréal, Canada;
and S.J. Finke and J.E. Yehoda, Morgan Advanced Ceramics, Inc.,
Diamonex Products Division, Allentown PA

ABSTRACT

Diamond-like carbon (DLC) has been deposited by various means for 20-25 years with good results in many applications, including protective, antireflective (AR) coatings on infrared windows. It was heavily reported in the late 80's and early 90's by Ecole Polytechnique, Diamonex, Inc., and others for films deposited by radiofrequency plasma and ion beam deposition and other means. Deposition on Ge substrates required different parameters to achieve both good adherence and sufficient hardness of the DLC films. In this study we detail the deposition conditions needed to produce hard, adhering DLC films to the thickness needed for infrared AR coatings, using two complementary techniques: plasma-enhanced chemical vapor deposition (PECVD) and ion beam chemical vapor deposition (IBCVD). Environmental results are also reported for these films.

INTRODUCTION

Carbon-based thin films such as diamond like carbon (DLC) are being increasingly considered for numerous emerging technologies and applications. These range from coatings on cutting tools, shaving blades, wear resistance components, surgical knives, body implants, computer memory discs, infrared windows, optical devices, sunglasses and ophthalmic lenses, microelectromechanical systems (MEMS), sensors, flat panel displays, cold cathodes, sports equipment and specific functional or protective coatings with tailored surface characteristics.

DLC films can be prepared by various techniques, namely thermal evaporation, physical vapor deposition (sputtering and ion beam processes), and various chemical vapor deposition processes. In this paper, we will discuss the deposition of DLC films on germanium substrates as antireflective (AR) coatings in the infrared region, using two different processes:(i) radiofrequency (RF) plasma-enhanced chemical vapor deposition (PECVD) at Ecole Polytechnique and (ii) ion beam chemical vapor deposition (IBCVD), developed by Morgan Advanced Ceramics, Diamonex Products.

EXPERIMENT METHODOLOGY

Fabrication of DLC coatings by PECVD and IBCVD

In the PECVD process, the Si and Ge substrates were placed on the 8 inch diameter RF (13.56 MHz) powered electrode located at the center of the turbomolecular pumped vacuum chamber (Figure 1) [1]. DLC films were deposited at room temperature using a mixture of 10 sccm of Ar and 40 sccm of methane (CH_4) at the pressure *p* of 100 mTorr. The bias voltage (V_B) developing on the RF electrode was varied from 250 V to -500 V in order to find the fabrication conditions leading to films with low stress. The operating pressure was controlled by MKS Baratron and butterfly valve. Prior to the deposition, the substrates where pretreated using 1 minute Ar plasma at V_B=-500 V and *p*=100 mTorr.

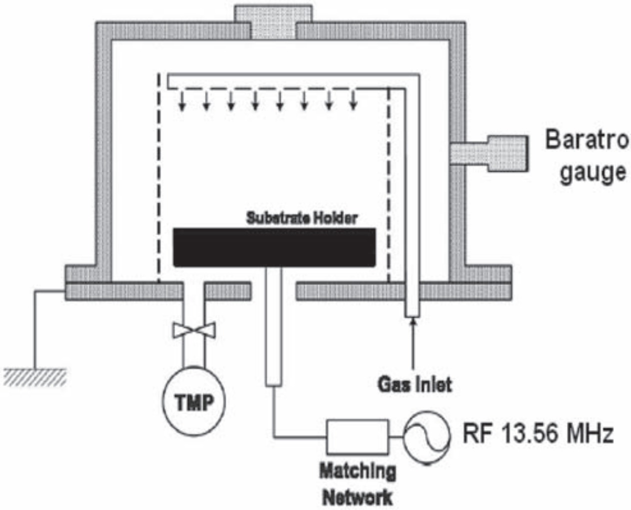

Figure 1: Schematic illustration of the PECVD deposition system.

The IBCVD of DLC films was carried out in a large box coating machine using a gridless closed-drift (CD) ion source manufactured by the Diamonex Products Division of Morgan Advanced Ceramics as shown in Figure 2 [2,3]. The ion source was located 7 inches below the samples which were mounted onto a 6-position carousel that could rotate samples sequentially into position for deposition above the source. The deposition position was located behind a shutter, which could be opened and closed in order to shield the samples when the deposition process was not required. The deposition process consists of flowing 60 sccm of ethylene (C_2H_4) 1-inch in front of the ion source, using a simple injector setup, while 50 and 20 sccm of Ar were flowed through the anode and hollow-cathode, respectively. The anode Ar sustains the discharge in the source channel, while the hollow-cathode provides a source of electrons for neutralization and discharge maintenance. For these depositions the ion source was operated at 80 V at 8 A of anode current. The deposition rate was nominally 68.7 nm/min.

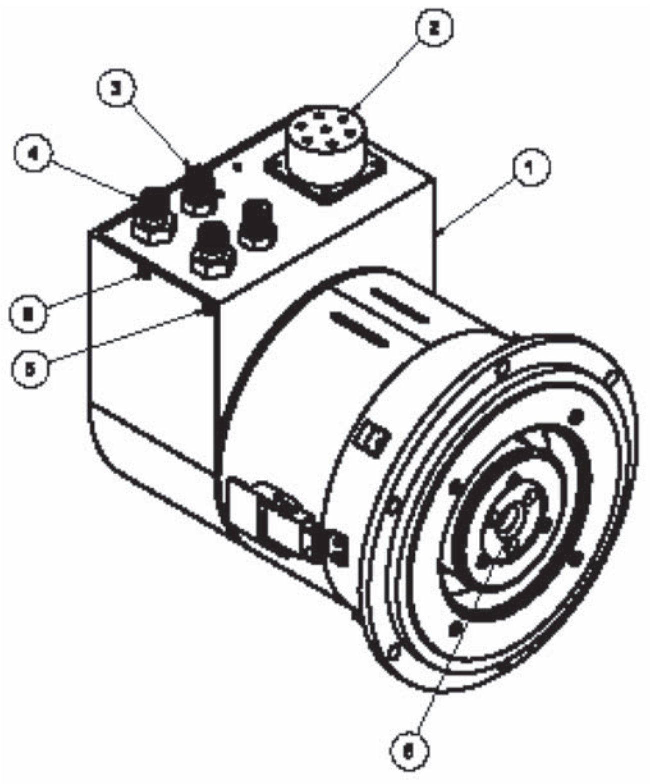

Figure 2: CD ion source used for IBCVD of DLC films.

Experimental conditions used for the deposition of DLC films studied in the present work are reported in Table 1. Deposition rates obtained with the IBCVD process were about five times greater than with the PECVD process.

Table 1: Deposition conditions, measured thicknesses and deposition rates for DLC films deposited by PECVD and IBCVD.

DLC#	Process	Time (min)	Bias (-V)	Ar/ CH4 (sccm)	Thick-ness (NM)	Rate (nm/ min)
1	PECVD	20	500	50/40	-	-
2	PECVD	15	300	10/40	210	14.00
3	PECVD	35	300	10/40	541	15.46
4	PECVD	70	300	10/40	1013	14.47
5	PECVD	65	250	10/40	800	12.31
1196	IBCVD	19	-	-	1347	70.9
1197	IBCVD	19	-	-	1342	70.6
1198	IBCVD	19	-	-	-	-

MECHANICAL CHARACTERIZATION

Nanohardness, H_N, and reduced Young's modulus, E_r, were determined by depth-sensing indentation using a Nano-triboindenter instrument (Hysitron Inc.) equipped with a Berkovich pyramidal indenter, in agreement with the International Standard [4,5]. The data were processed using the Hysitron software providing the load-displacement plots, F-h corrected for thermal drift and machine constants (frame compliance, transducer spring force and electrostatic force constants).

The F-h plots were analyzed according to the Oliver-Pharr method, by fitting a power law relationship to the unloading curve and determining the initial unloading stiffness, S. The contact depth, h_c, was found from the relationship for the Berkovitch indenter

$$h_c = h_{\max} - 0.75\frac{F_{\max}}{S}, \tag{1}$$

where h_{max} and F_{max} are the maximum displacement and load (Figure 3). The indentation hardness is a damage, and nanohardness can be obtained from

$$H_N = \frac{F_{\max}}{A_p}, \tag{2}$$

where A_p is the projected contact area at maximum load. E_r was found from

$$E_r = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_p}}. \tag{3}$$

E_r represents the reduced Young's modulus:

$$\frac{1}{E_r} = \frac{1-\nu'}{E'} + \frac{1-\nu_i}{E_i}, \tag{4}$$

where E' and E_i are the elastic moduli of the film and of the indenter, and ν' and ν_i are the Poisson's ratios of the film and of the indenter, respectively. For a diamond indenter, E_i=1140 GPa and ν_i=0.07. The applied loads range from 100 to 10000 μN.

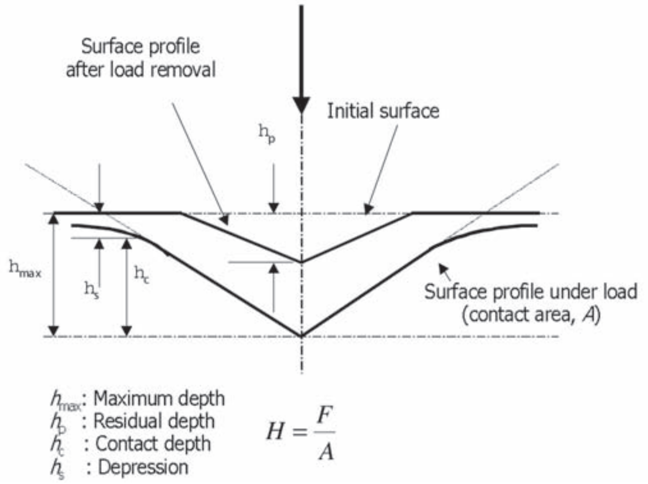

Figure 3: Schematic of the indentation trace.

OPTICAL CHARACTERIZATION

UV-VIS-NIR and FIR ellipsometric spectra ($\Psi\Delta$) were obtained by using two variable angle spectroscopic ellipsometers (VASE and IR-VASE), both from J.A. Woollam Co [6]. Measurements with VASE were performed for a wavelength range of 300 to 1700 nm, with a spectral resolution of 5 nm and an incidence angle of 65°. Acquisitions with IR-VASE were performed for a wavenumber range of 400-5000 cm^{-1}, an incidence angle of 65° and a spectral resolution of 16 cm^{-1}.

In this study, we modeled *n* and *k* dispersion curves of DLC films using Herzninger-Johs parameterized semiconductor oscillator. A top layer was inserted in the model in order to take into account surface roughness, which was modeled by the Bruggeman effective medium approximation (BEMA, 50% void-50% DLC). Lateral non-uniformity of the coatings was also considered, though it proved to be limited.

In the FIR range, the continuous decrease of *n* observed for DLC coatings was modeled using a pole oscillator defined by

$$\epsilon_1 = \frac{A}{E_0^2 - E^2},\ \epsilon_2 = 0, \qquad (5)$$

$$\text{with} \qquad \tilde{\epsilon} = \epsilon_1 + i\epsilon_2 = (n + ik)^2, \qquad (6)$$

where ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric function, *E* is the variable energy (eV), and *A* and E_0 are fitted parameters related to the amplitude and resonance energy of the oscillator. Two Gaussian oscillators were added to ϵ_2 in order to model absorption bands related to chemical bonds.

RESULTS

Hardness and Young's modulus obtained for PECVD and IBCVD DLC films are shown in Table 2 and examples of load-displacement curve are presented in Figure 4. H_N ranges from 13.9 to 19.4 GPa, which are typical values for DLC films [7]. H_N and E_r are systematically higher for samples prepared by PECVD than for IBCVD. The lower hardness for IBCVD samples is attributed to an increase of the hydrogen content in the films (see below).

Table 2: Hardness and Young's modulus for DLC coatings deposited by PECVD and IBCVD, as obtained from nanoindentation measurements.

DLC#	Process	E_r (GPa)	H_N (GPa)
1	PECVD	127	13.9
2	PECVD	_	_
3	PECVD	151	19.4
4	PECVD	148	19.2
5	PECVD	146	18.0
1196	IBCVD	128	14.8
1197	IBCVD	131	17.6
1198	IBCVD	129	17.0

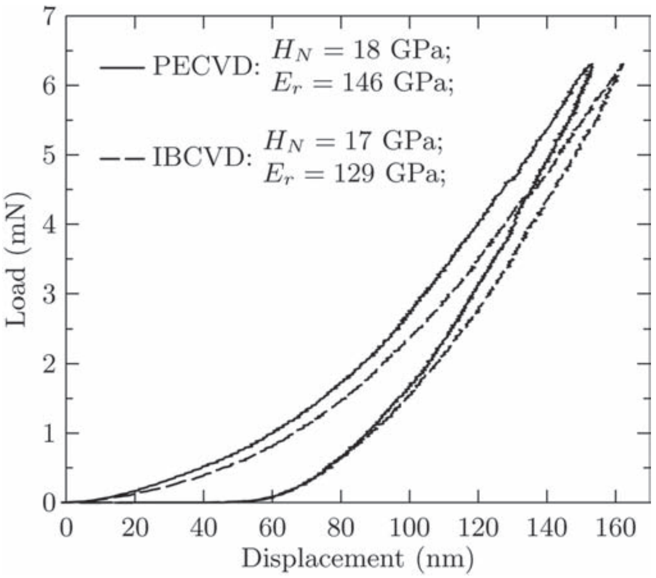

Figure 4: Load-displacement curves obtained for samples #4 (PECVD) and #1198 (IBCVD).

Figure 5 presents an example of Ψ and Δ ellipsometric spectra in both UV-VIS-NIR and FIR ranges, acquired on a DLC coating fabricated by PECVD. The curves calculated from the optical model match well the experimental data, proving the validity of the fitting procedure. The dispersion curves obtained from Ψ and Δ for two DLC coatings deposited by PECVD and IBCVD are shown in Figure 6. In the UV-VIS-NIR range, films are absorbing and k decreases with wavelength. The values of n and k, as well as the shape of dispersion curves are similar to those provided by literature [8,9]. In the FIR range, films are nearly transparent and n values are close to 2.0, which justifies the use of DLC films as AR coatings on Ge substrates (n=4.0). Additionally, n was systematically higher for DLC films prepared by PECVD rather than IBCVD, which is attributed to a lower hydrogen content. This is documented by the lower absorption band observed in the k dispersion of PECVD films at around 3.5 μm (see Figure 6), assigned to C--H bonds. Above 5 μm, DLC films show some absorption that cannot been explained at that time. This could be caused by an artifact in ellipsometric spectra. A deeper analysis should be performed in order to validate these preliminary results.

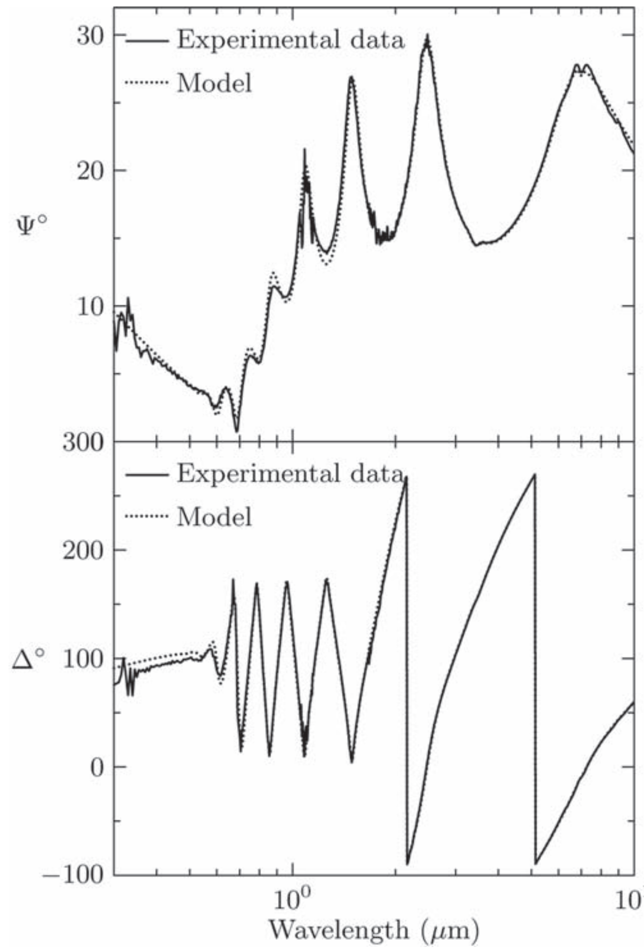

Figure 5: Example of ellipsometric spectra obtained from sample #4 (PECVD), compared to data calculated from the optical model.

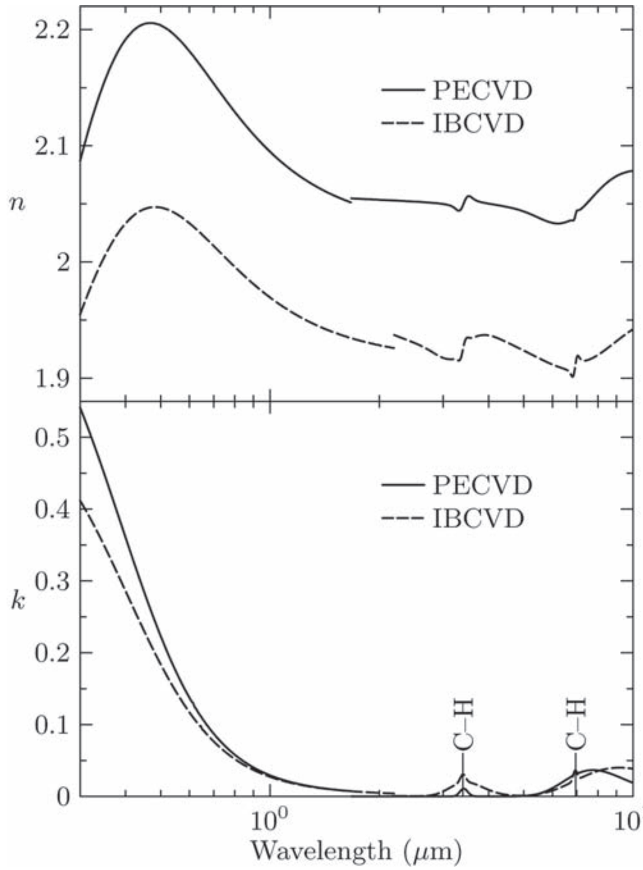

Figure 6: Comparison of refractive indices and extinction coefficients obtained for DLC coatings #4 (PECVD) and #5 1196 (IBCVD).

The transmission spectra of 1 mm thick Ge substrates coated on both sides with DLC films are presented in Figure 7. Deposition time for DLC films was adjusted in order to produce quarterwave AR coatings at 10 μm. Compared to the transmission of bare Ge, the transmission of DLC-coated Ge substrates displays a clear improvement: 47% for uncoated Ge, 90% for Ge with DLC films from PECVD and 89% for Ge with DLC films from IBCVD at 10 μm. The fact that the transmission is not 100% at 10 μm is attributed to several factors:

- The refractive indices of DLC coatings (n=2.08 and n=1.94) at 10 μm were not exactly the square root of that of the germanium substrate (n=4.0);
- DLC films seem to absorb at 10 μm (see Figure 6).

Finally, in the case of AR coatings deposited by PECVD, the blue shift of the peak position is due to film thicknesses slightly too thin.

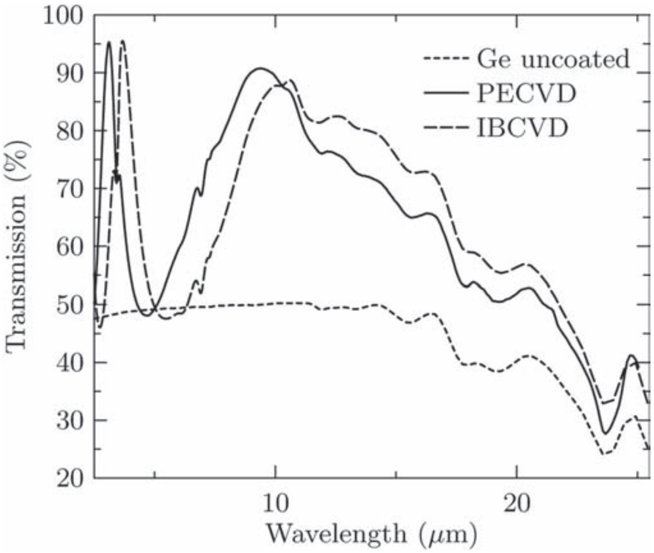

Figure 7: Transmission spectra for PECVD and IBCVD DLC coatings deposited on germanium substrates.

DLC coatings deposited by PECVD were submitted to 1-day and 5-day cyclic salt fog tests in order to evaluate their resistance to harsh environmental conditions. Samples #2 and #5 passed the test, while others were delaminating either before or after exposure, probably due to not effective enough surface treatment of the substrates, or because of the creation of excessive internal stress during deposition.

SUMMARY

DLC films were deposited by PECVD and IBCVD, presenting maximum hardness and Young's modulus values of 19.4 GPa and 151 GPa, respectively. DLC coatings fabricated by PECVD showed higher refractive index values (n=2.08 at 10 μm) compared to those prepared by IBCVD (n=1.94 at 10 μm), which was attributed to a lower hydrogen content. Ge substrates with DLC AR coatings on both sides displayed improved transmission at 10 μm (90%) compared to the bare substrate (47%). Environmental resistance measurements provided encouraging results, as two samples over five passed the test. These initial results warrant that, granted the optimization of the deposition processes, it is possible to deposit thick DLC coatings on Ge substrates with good optical properties and high mechanical resistance. This work is on-going and will be reported in the future.

REFERENCES

1. A. Raveh, J. E. Klemberg-Sapieha, L. Martinu and M. R. Wertheimer, "Deposition and Properties of Diamond-Like Carbon Films Produced in Microwave and Radio Frequency Plasma," *J. Vac. Sci. Technol.*, A10 (4), 1723, 1992.

2. L.J. Mahoney, B.K. Daniels, R.H. Petrmichl, F.J. Fodor and R.H. Venable, U. S. Pat. #5,973,447, "Hall-current ion source material processing apparatus - has power supply to form voltage between anode and cathode for breakdown of working gases injected into discharge region together with magnetic field," 26 Oct. 1999.

3. R.H. Petrmichl, D.W. Brown and L.J. Mahoney, U.S. Pat. #6,086,962, "Deposition of a diamond-like carbon or silicon-doped diamond-like carbon coating onto the surface of the substrate, involves depositing precursor gases at high beam current densities," Jul. 2000.

4. "Metallic materials - instrumented indentation test for hardness and materials parameters ñ Part 1: Test method," International Standard ISO, 14577-1, 2002.

5. W. C. Oliver, and G. M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments," *J. Mater. Res.*, 7, 1564, 1992.

6. H.G. Tompkins, *A User's Guide to Ellipsometry*, Academic Press, Boston, 1993.

7. G. Fedosenko, A. Schwabedissen, J. Engemann, E. Braca, L. Valentini and J.~M. Kenny, "Pulsed PECVD deposition of diamond-like carbon films," *Diam. Relat. Mater.*, 11 (3-6), 1047, 2002.

8. D. Franta, V. Burcikova, I. Ohlidal, L. Zajickova and P. Stahel, "Thermal stability of the optical properties of plasma deposited diamond-like carbon thin films," *Diam. Relat. Mater.*, 14 (11-12), 1795, 2005.

9. M. Pandey, D. Bhatacharyya, D.~S. Patil, K. Ramachandran, N. Venkatramani, A.~K.Dua, "Structural and optical properties of diamond like carbon films," *J. Alloys Compd.*, 386 (1-2), 296, 2005.