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DIAMOND-LIKE CARBON FILMS FOR ANTIREFLECTION COATINGS OF GERMANIUM INFRATED OPTICAL LENSES

Seong-young Kim*, Sang-hyun Lee, and Jai-sung Lee

** Advanced Consumer Products R&D Center, KITECH, Cheonan, Chungnam, 330-880 KOREA*
Depart. of Metallurgy and Materials Science, Hanyang University, Ansan, 425-791 KOREA

Abstract

Diamond-like carbon(DLC) films were directly deposited onto germanium(Ge) witness pieces and lenses by a capacitively coupled 13.56 MHz RF glow discharge plasma with CH_4 gas. The characterizations of DLC films were measured using a Raman and FTIR spectrometer. The configuration of Raman and FTIR spectra had a traditional shape. The IR transmittance was measured using an IR spectrophotometer. The maximum values of the IR transmission of Ge with the DLC/Ge/DLC, DLC/Ge/BBAR (broad band antireflection), DLC/Ge, and BBAR/Ge structures are 98%, 93%, 64%, and 63.5%, respectively, which come up to the theoretical values. The uniform DLC films were obtained by a rotation of the cathode at certain conditions.

Keywords : PECVD, Diamond like carbon, IR transmittance, antireflection, durability

1. INTRODUCTION

There is now widespread research activity in growing amorphous diamond-like carbon (DLC) films by a number of processes. DLC films are so named because their properties resemble, but do not duplicate, those of diamond. At least some of the carbon atoms in DLC are bonded in chemical structure similar to that of diamond, but without long-range crystal order. The potential of DLC films in technological applications has already been established. These films are characterized by their extreme hardness and low coefficients of friction, optical transparency over a wider spectral range, high electrical resistivity, chem inertness etc[1)-3)]. In general, the refractive index of the DLC films can change from 1.6 to 2.9 according to the deposition conditions[4),5)]. Besides, the micro-scopical surface of the DLC films is extremely smooth, which results in greatly reduced reflection. DLC films may therefore be considered suitable as protection and antireflection coatings for optical devices, which are to operate in hostile environments. Zhang and Cuo[6] used a non-uniform DLC film as the protction and antireflection films of Ge substrate. But, thin film structure (DLC/Ge/BBAR) to be used in a practical application (infrared optical lens) has not been reported in the open literature. DLC films directly deposited onto Ge substrate with one side BBAR coating have been used as protection[7), 8)] In the present study, excellent antireflection and protection effects by DLC films have been achieved.

2. EXPERIMENTAL DETAILS

2. 1 Substrate materials and pretreatments

Silicon (Si) wafer, germanium (Ge) pieces and germanium lenses with dimensions of $50 \times 50 \times 0.5mm^3$, ϕ $25.4 \times 1.5mm^2$, and ϕ $140 \times 12.7mm^2$ (curvature radius R1=158.91, R2=266.54) respectively were used as substrate. Both surfaces of Ge and one surface of Si were polished to a mirror finish. All samples were cleaned ultrasonically in acetone and then cleaned by high energy argon ion bombardment for 15 min prior to deposition. These surfaces cleaning were found to be an important role of improving the adhesion between the DLC films and substrates.

2. 2 Plasma deposition system

DLC films on Ge witness pieces and lenses were directly deposited by a capacitively coupled 13.56MHz RF plasma decomposition of methane gas. In this RF PECVD system the bottom electrode on which the substrate is placed is DC negative self-bias voltage driven and kept at room temperature by water cooling during the deposition. The flow rate of methane and argon gases was controlled by mass flow controllers. After in-situ cleaning of Ge substrate surface using argon plasma for 15min, methane gas was introduced into the reaction chamber with the pressure of the deposition system fixed at 60mTorr. The DC negative self-bias voltage was varied from 300 to 900 V. The RF power was adjusted between 100 and 500W. The deposition time varied from 20 to 140min as required.

2. 3 Characterization of DLC films

In general, the refractive index and the growth rate of the DLC films on Ge substrate linearly increase with increasing negative DC self-bias voltage[9),10)]. The refractive index of DLC films was not measured, because the spectral range for antireflection in the present study was varied from 7.5 to 12μm wavelength. But the evaluating optical characteristics of antireflection coatings had been reported in the other literature[11)]. The optimum IR antireflection film can also be prepared by using a trial and error methodology according to the relationship between the refractive index and growth rate, and deposition conditions. The thickness of the DLC films was measured by surface profilometer (Kosaka Lab. Ltd. Ay-41). The material characterization of the DLC films was measured by Raman (Jovin Yvon U1000 ; 514nm Ar^+ laser) spectrometer in the range 100-1700cm^{-1}. The C-H bond structures (sp^1, sp^2, sp^3) of DLC films was measured by employing a Fourier transform IR (FTIR) spectrometer (Shimadzu FTIR-8201PC). The IR transmittance in the range of 4000-600cm^{-1} (2.5-16.6μm wavelength) was measured by IR spectrophotometer (Perkin Elmer IR-781). The durability performance tests according to the MIL specification was performed.

3. RESULTS AND DISCUSSION

Fig. 1 shows the dependence of the growth rate of the DLC films deposited on Ge substrates on the DC negative self-bias voltage. The growth rate increases with increasing DC negative self-bias voltage. The growth rate in the higher DC negative self-bias voltage was saturated, and reduced. This reason that the net growth rate depends on two competing processes, i.e. deposition and sputtering, which occur during the whole process of preparing DLC films from beginning to end.

The FTIR spectroscopy provides information on the presence of CH, CH_2, and CH_3 groups. Furthermore the bonding type of these hydrogenated carbon atoms can be inferred[12]. The FTIR transmittance spectra in the wavenumber range 3600-2400cm^{-1} for the DLC films deposited onto Si wafer pieces are shown in Fig. 2. The peaks for sp^1, sp^2, and sp^3 were not clearly shown each other because of the high impact energy.

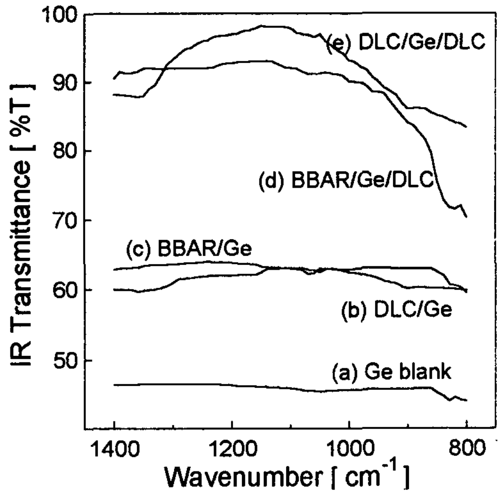


Fig. 2 FTIR spectra of DLC films deposited onto Si wafer pices at 60mTorr.
(a) Uncoated Ge blank, (b) DLC/Ge,
(c) BBAR/Ge , (d) BBAR/Ge/DLC , and
(e) DLC/Ge/DLC

The Raman spectra shown in Fig. 3 are for the DLC films deposited onto the Si wafer piec-

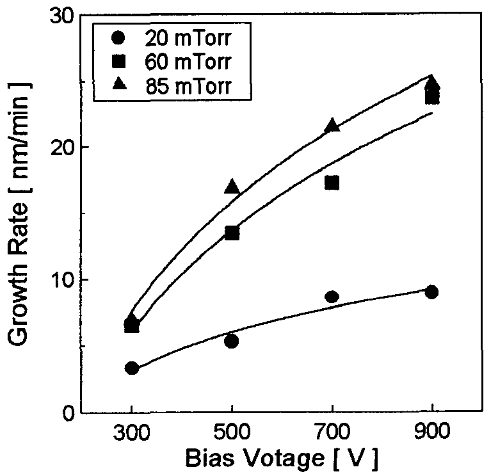


Fig. 1 Dependence of growth rates of DLC films on Ge substrates on DC negative self-bias.

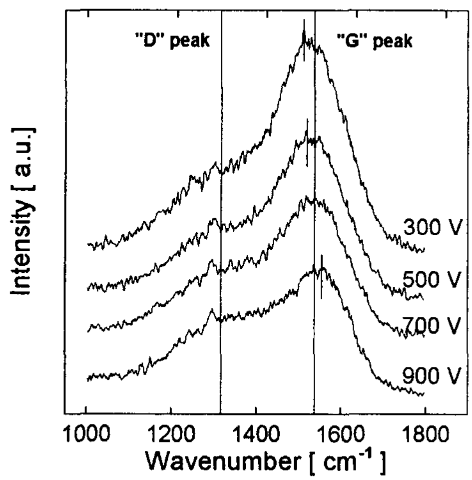


Fig. 3 Raman spectra of DLC films deposited onto Si wafer pieces at 60mTorr.

es at the various deposition parameters. The configuration of Raman and FTIR spectra had a traditional shape. The increase of I_D/I_G ratio is depended on the increase of negative DC self-bias voltage. The I_D/I_G ratio was shown in Table 1. The increase of I_D/I_G ratio is analogy to the sp^3/sp^2 ratio increase by the increase of the impact energy[13]. The peak position of I_G was shift to the lower wavenumber by the increase of negative DC self-bias voltage. This means that the local temperature increase of the DLC film surfaces by the increase of the ion impact energy is the increase of the graphite-like carbon contents by the thermal decomposition.

The transmittance curves shown in Fig. 4 are

Table 1. The I_D/I_G ratios of deposited DLC films at various conditions.

Self-bias	300V	500V	700V	900V
I_D/I_G	0.397 (20.7/52.2)	0.437 (15.6/35.7)	0.502 (16.5/32.9)	0.577 (14.6/25.3)

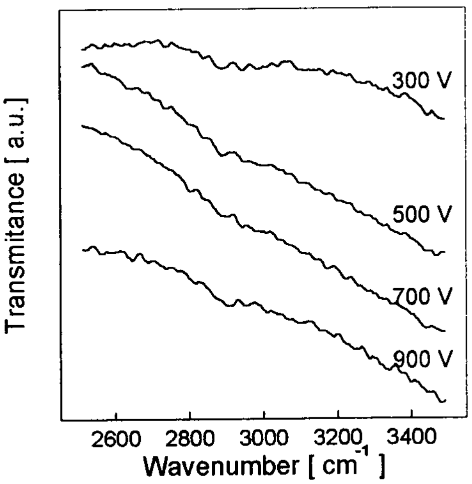
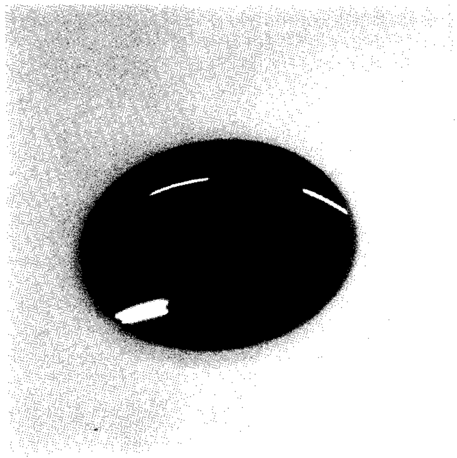


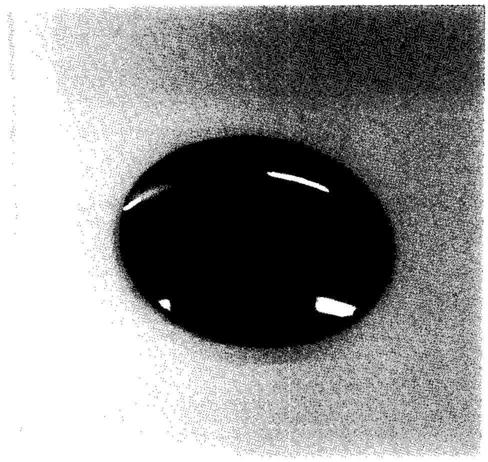
Fig. 4 The IR transmittance curves for the various structures.

for an uncoated Ge blank and for a Ge blank with one surface BBAR coating and for a Ge blank with BBAR coating with one surface and both surfaces coated with a $\lambda/4$ DLC film for $\lambda = 10\mu m$. Germanium has a refractive index of 4 with a reflectance of 36% for a single surface and a transmittance of 47% for a slab allowing for multiple reflections. To efficiently reduce reflection from the Ge the interference film index must be 2. The average IR transmittance ($\%T_{AVG}$) of BBAR/Ge, DLC/Ge, DLC/Ge/BBAR, and DLC/Ge/DLC structured samples was 62, 59.8, 92, and 96%, respectively, which comes up to the theoretical value taking into consideration the natural absorption of the DLC films.

The photograph in Fig. 5 shows the photograph for the uncoated Ge blank and DLC coated Ge objective lens. The size of these Ge objective lenses is Φ140㎜(curvature radius; R1=158.91, R2=266.54, center position thickness; 12.7㎜). It has been the goal of many investigations to apply DLC coatings to reduce abrasion and high speed rain erosion damage to Ge, ZnS and ZnSe infrared optical lenses. Especially, the goals of the Ge infrared optical lens application were to accomplish the following: (1) dramatically improve the abrasion resistance of Ge lenses; (2) increase durability to environmental conditions such as elevated temperature, humidity, salt, UV light, etc., compare with other commercial coatings. The environmental durability test(MIL-F-48616/101) results for the DLC coated Ge objective lenses are summarized in Table 2. These durability performance tests results for the DLC coated Ge objective lenses show very excellent protection.



(a) DLC coated Ge blank.



(b) Uncoated Ge lens.

Fig. 5 The photograph for uncoated Ge blank and DLC coated Ge objective lens.

Table 2 Durability performance tests for DLC coated Ge infrared lens.

Test description	Test condition	Result
Abrasion Eraser rub(MIL-C-675) Cheesecloth rub (MIL-C-675)	Severe (40 rubs) Moderate (50 rubs)	No visible damage No visible damage
Adhesion Tape(MIL-C-675)	Fast	No visible damage
Humidity(MIL-C-675) Temperature (℃) Relative humidity (%) Duration (h) Condition	 48.9 95-100 24 Constant	No visible damage
Salt fog-spray (STD-810) Temperature (℃) Duration (h)	 35 48	No visible damage
Saltwater immersion %NaCl Temperature (℃) Duration (h) %NaCl Temperature (℃) Duration (min)	 20 22 24 20 100 45	No visible damage No visible damage
Chemical resistance Methanol, acetone, gasoline Duration (min)	10	No visible damage
Accelerated aging(ASTM D756-71; D1501-71; D3359-78) Temperature (℃) Duration temperature (h) UV light Total duration (h)	 26-59 1.25 Cycled 336	No visible damage

4. CONCLUSIONS

1) The growth rate increases with increasing content of the hydrocarbon gas and DC negative self-bias voltage.

2) The deposition parameters that influence the optical and mechanical properties of DLC film are interrelated.

3) The high energy bombardment on the growing films caused by the DC negative self-bias voltage plays a very important role in the structure and properties of DLC films.

4) The average IR transmittance of BBAR/Ge, DLC/Ge, DLC/Ge/BBAR, and DLC/Ge/DLC structured samples was 62, 59.8, 92, and 96 %, respectively. These values come up to the theoretical value taking into consideration the

natural absorption of the DLC films.

5) These durability performance tests (MIL-F-48616/101) results for the DLC coated Ge objective lenses show very excellent protection.

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