The Journal of Korean Vacuum Science & Technology
Vol. 2, No. 2, October 1998, pp. 101~106

Deposition of hard coatings on polycarbonate substrate by high frequency ion beam

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(Received August 29, 1998)

Abstract – The poor wear and scratch properties of polycarbonate have limited its application in many fields. In order to improve the wear and scratch properties of polycarbonate we have deposited diamond like carbon (DLC) coatings. The diamond like carbon coatings were made using a high frequency ion beam gun by introducing H_2 and CH_4 gases. The coatings were characterized with Raman spectroscopy, scanning electron microscope, ellipsometer, microscratch tester and hazemeter. Polymeric hard coating was applied onto the polycarbonate substrate before depositing a DLC coating to investigate the effect of interlayer on the system's failure mode.

I. Introduction

Polycarbonate has an unusual combination of high impact strength, transparency, and good electrical insulation properties. The properties of polycarbonate have led to many successful glazing applications, such as bus shelter, telephone booths, safety goggles, and lamp housings for automobiles. However, the poor wear and scratch properties of polycarbonate have limited its application in many fields.

There have been many studies on improving the scratch and wear properties of polymer by applying coatings [1-4]. The DLC coatings have numerous useful properties such as transparency for visible and infrared light, high hardness and chemical inertness. They can be applied as a scratch-resistant coating. DLC coatings on a polycarbonate substrate maintained the high-speed impact strength [1]. In a previous paper, the effect of precursor gases on the DLC coatings was investigated by the direct ion beam deposition method [5]. Depositing DLC coating using a high frequency ion gun made the polycarbonate surface wear-resistant and scratch-resistant.

In this study, the effects of gas compositions and interlayer coating on deposited DLC coatings were studied using Raman spectroscopy, scanning electron microscope, ellipsometer, microscratch tester and hazemeter.

II. Materials

A proprietary acrylic polymeric hard coating was applied to a Sam Yang TRIREX(r) polycarbonate substrate with thickness of 1/8". The pencil hardness of polycarbonate and polymeric hard coating were EE and 4H, respectively. The polymeric hard coating was applied by dipping method and the coating thickness was about 10 μm.

III. Experimental

The DLC coatings were deposited on a polycarbonate substrate and a polycarbonate substrate with a polymeric hard coating by a direct ion beam gun with a 60 MHz high-frequency ion beam source operated on a mixture of hydrogen and methane gases. The beam energy was 500 eV and ion current was 25 mA. The base pressure of vacuum chamber before deposition was

3×10^{-5} Torr and it became 2.5×10^{-4} Torr when reaction gases were introduced. The distance between ion gun source and the substrate was 22 cm. During deposition, the substrates were put on a rotating sample holder to have coating uniformity.

3.1 Microscratch Tests

The critical load for coating failure was measured by a scratch test. A CSEM micro-scratch tester under loading rate of 100 N/min and a scratch speed of 1 cm/min was used. A diamond indenter, ground to a 120° cone with a spherical apex of 80 μm radius, was used in all measurements. The acoustic signal and friction coefficient corresponding to coating failure were recorded. The coating failures could be cracking, delamination, spallation or the indenter plowing through the coating or substrate. The failure morphologies of coating or substrate layer were examined via scanning electron microscope.

3.2 Taber Abrasion Test

The Taber abrasion test (ASTM D1044) measures the percentage increase in haze after subjecting a DLC coated on polycarbonate or organic hard coating to an abrasive wheel that rotates under a 500 g load. A higher level of haze indicates a greater degree of abrasion.

IV. Results and Discussion

4.1 Characterization of DLC

In order to investigate the effect of gas composition on the deposited DLC coatings, we deposited DLC coatings with two gas compositions of $CH_4 : H_2$ ratio of 1 : 1 and CH_4 to H_2 ratio of 1 : 2 on a silicon wafer. The deposition rate was measured with a scanning electron microscope. It was 4.8 nm/min for $CH_4 : H_2$=1 : 1 and 4.0 nm/min for $CH_4 : H_2$=1 : 2.

The Raman spectrum of DLC coatings with

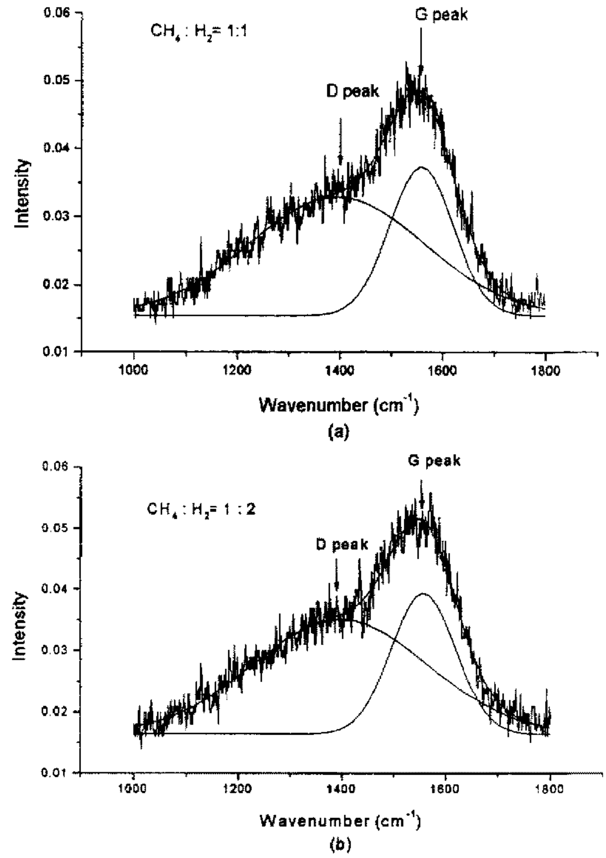

Fig. 1. Raman spectra of DLC coatings with two gas compostions of (a) CH_4:H_2 ratio of 1:1, and (b) CH_4:H_2 ratio of 1:2.

the two gas compositions were the same (Figure 1(a) and (b)). The Raman spectrum of crystalline diamond consists of a single sharp peak at 1332 cm^{-1}. The Raman spectrum of crystalline graphite consists of two peaks: The G peak centered on 1550 cm^{-1} is the zone center E_{2g} mode of the perfect crystal and the D peak centered on 1350 cm^{-1} is a zone edge A_{1g} mode activated by disorder in the graphite crystal [6, 7]. The D mode is a common feature of disordered graphite carbon. Its intensity relative to the G mode (as measured by the ration I_D/I_G) changes with the disorder. We have deconvoluted the Raman spectra with two Gaussian peaks which correspond to G peak with frequency at 1558 cm^{-1} and D peak with frequency at 1395 cm^{-1}. The I_D/I_G was 2.2 for the two gas compositions. The refractive index of 2.0 at 632 μm was the same for the two

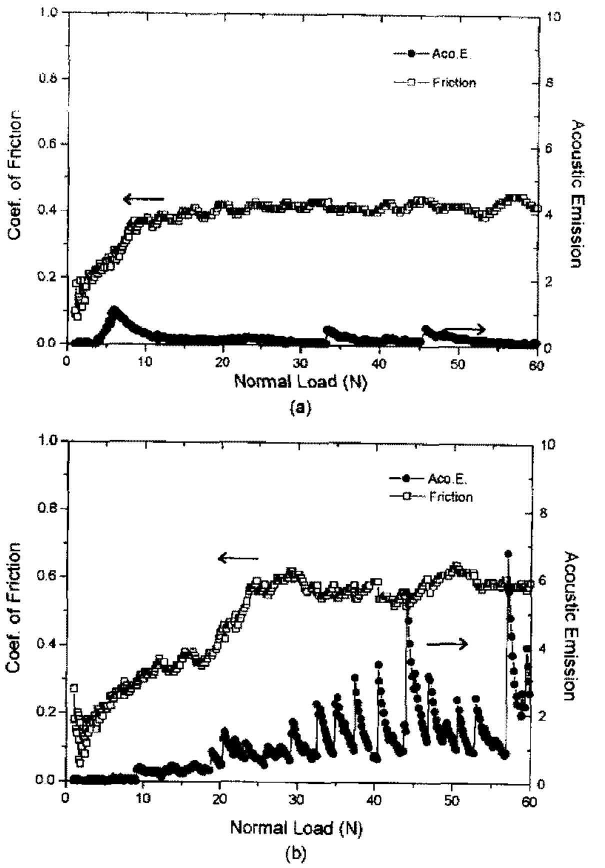

Fig. 2. Microscratch result of DLC (CH_4:H_2=1:1) on (a) polycarbonate, and (b) organic hard coating / polycarbonate.

DLC coatings.

4.2 Microscratch and Wear Results

The scratch properties of deposited DLC coatings were characterized using a microscratch tester. The microscratch results of DLC coating on polycarbonate are shown in Fig. 2(a) and its morphology is shown in Fig. 3. The scratch results and the fracture surface of DLC coating/organic hard coating/polycarbonate system are shown in Fig. 2(b) and Fig. 4, respectively. Figure 3 shows a scratched surface of DLC/polycarbonate system with increasing load to 60 N. The morphology of scratches on the DLC/polycarbonate showed good adhesion and the DLC coating remained fully adherent after the test. as in elsewhere [1]. Only slight scratches or tensile cracking in which the semicircular crack traces are parallel to the trailing edge of the sliding stylus were shown. These cracks form as a result of the tensile frictional stresses present behind the trailing edge of the stylus [8]. DLC/polycarbonate system showed a low coefficient of friction (approximately

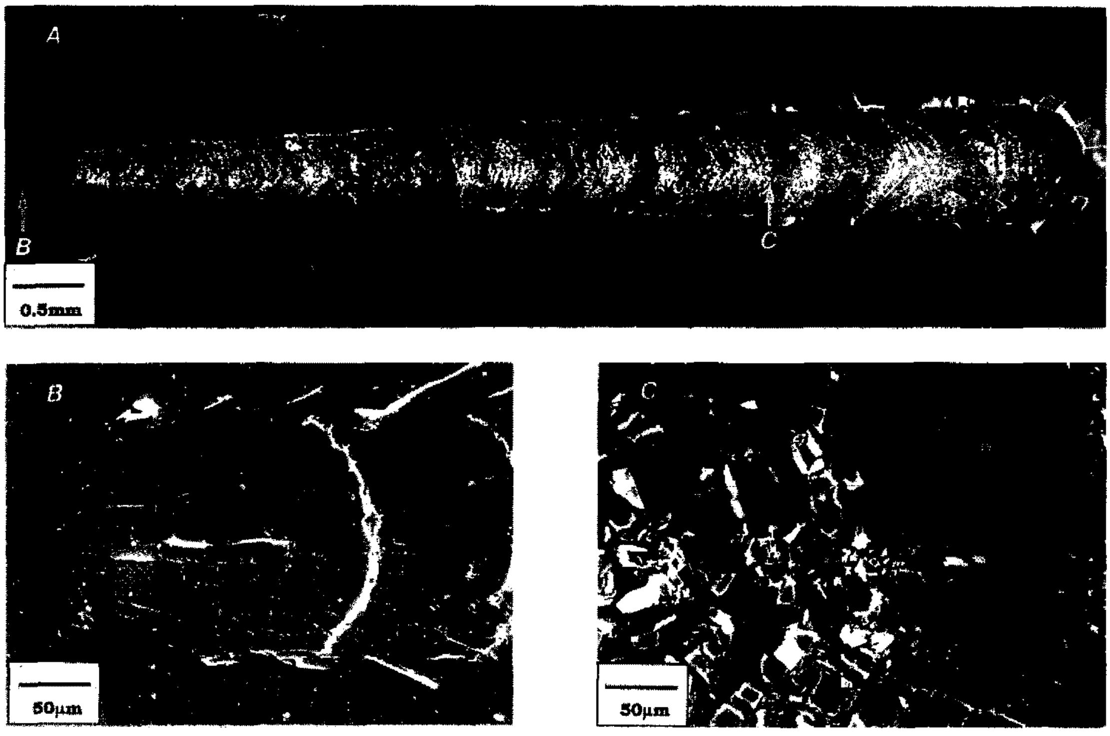

Fig. 3. SEM micrographs of scratch on a DLC/polycarbonate system by microscratch test. (a) Total view of a scratch (0 N~60 N), (b) Magnified view of scratched region at 5 N, (c) Magnified view of scratched region at 45 N.

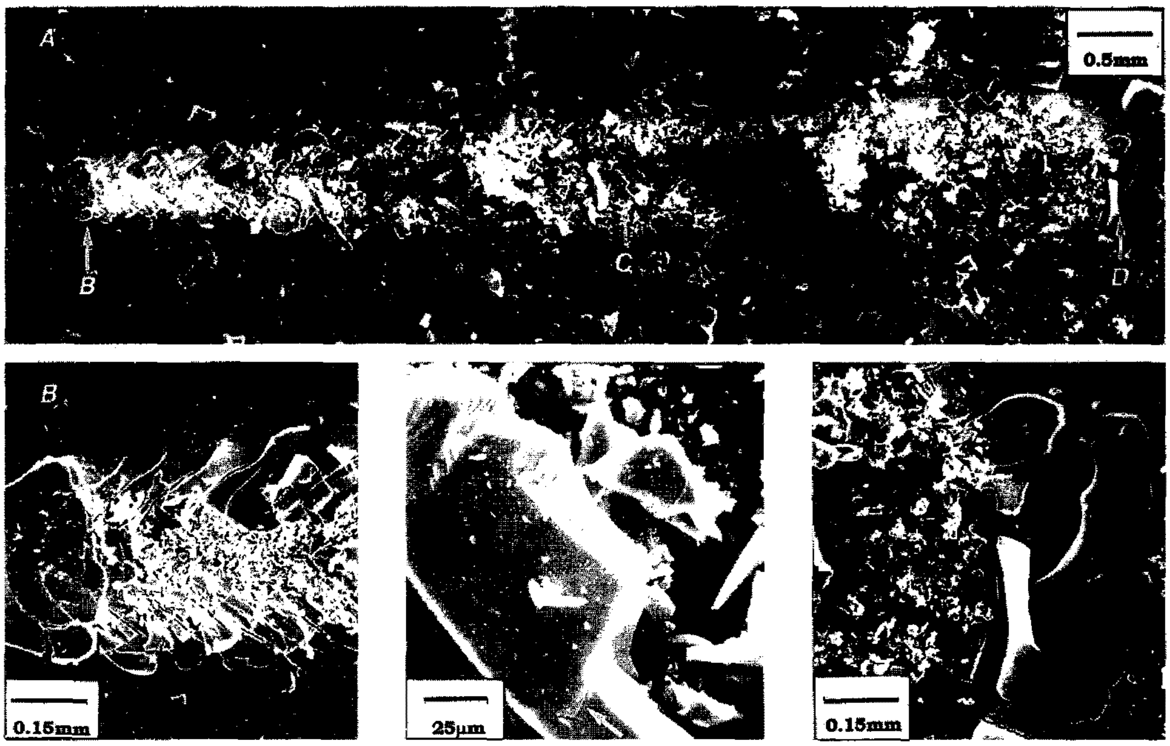

Fig. 4. SEM micrographs of scratch on a DLC/hard coating/polycarbonate system by microscratch test. (a) Total view of a scratch (0 N~60 N), (b) Magnified view of a crack at 5 N, (c) Magnified view of delaminated cracks at 40 N, (d) Magnified view of scratched region at 60 N.

0.4) at high load, while DLC/organic hard coating/polycarbonate system showed a higher value (approximately 0.6). The two systems showed different coefficient of friction. The low coefficient of friction of DLC/polycarbonate system may be result of stylus sliding on the DLC coating layer due to good adhesion between DLC coating and polycarbonate substrate. It is speculated that the higher coefficient of friction of DLC/hard coating/polycarbonate system are from the friction between hard coating and stylus rather than that of DLC coating and stylus. Figure 3(b) shows a magnified view of scratch at 4 N. The cracks by indentation were occurred in the direction of stylus movement without any noticeable spallation. The acoustic pattern showed a long base line that is the characteristic of smooth sliding without extensive coating failures. This coating did not show any distinctive acoustic events of the coating failure up to 60 N. The surface morphology at 34 N of applied load is shown in Fig. 3(c). Some cracked coating layer were delaminated but most of them were well adhered to the polycarbonate substrate. The similar surface morphology was retained up to 60 N. It is an example of good adhesion between DLC coating and polycarbonate. It is speculated that the DLC coating did not delaminate from the polycarbonate substrate because of its higher compliance and toughness. Hsieh *et al.* [1] tested DLC coated polycarbonate substrate. Delamination was not found with either the microscratch or the three-point bend tests.

A different failure mode was observed for a DLC/organic hard coating/polycarbonate system. DLC coating was deposited on a hard coated polycarbonate at a gas ratio of CH_4: H_2=1:1. When a DLC layer is deposited on organic hard coating the scratch property was rather poor. Figure 4(a) clearly shows substantial crackings and spallations of coatings. Figures 4(b), 4(c), and 4(d) are magnified view of three different regions in Fig. 4(a).

The rough surface of the scratched sample, and the debris of coating were observed. The coatings were started to spall at the loading of 10 N (Fig. 4(b)). Before spalling, it showed conformal cracking in which cracks follow semicircular trajectories parallel to the leading edge of the stylus. An arrow mark in Fig. 4(c) shows a delaminated coating piece with DLC coating remained attached to the hard coating. It implies better adhesion between DLC coating and hard coating than between hard coating and polycarbonate substrate. The poor adhesion properties can be detrimental to scratch properties [9]. A reproducible characteristic acoustic emission envelope was observed for this system.

The critical load at failure initiation on DLC coating deposited on polycarbonate or polymeric hard coating interlayer was investigated. However, it was difficult to define a critical load for DLC coatings from the acoustic signals compared to that of DLC coatings on a silicon wafer. A characteristic acoustic envelope and clearly distinguishable signal for critical load for failure initiation were developed for a DLC coating on a silicon wafer. The critical load of DLC coating was 15 N on a silicon wafer.

The wear experiments were also done in a hazemeter. In this case the wear of DLC coating and organic hard coating were determined. The result of haze increase before and after haze test with different number of rotation is shown in Table 1. The haze increase were 71% and 27% after 50 cycles for DLC/polycarbonate and DLC/organic hard coating/polycarbonate, respectively.

Table 1. The result of haze abrasion test

	Number of cycle	DLC on PC	DLC on hard coating/PC
ΔHAZE (%)	10	34	4.1
	20	63.6	8.0
	30	72.1	13.4
	50	71.8	27.1
	150		63.6

The small haze increase of DLC/organic hard coating can be explained by the presence of hard coating layer which makes the top DLC layer wear-resistant. The same result was obtained elsewhere [10].

V. Conclusions

DLC coatings on a polycarbonate and a hard-coated polycarbonate were studied. The interlayer effect on the failure properties of ion beam deposited DLC coatings was investigated using a scanning electron microscope, microscratch tester, and hazemeter. Two distinctive failure modes were observed by microscratch tests. The introduction of interlayer has led to different failure morphologies. The deposited DLC coating on polycarbonate did not show any delaminations after microscratch tests. However, the DLC coating deposited on the hard-coated polycarbonate substrate showed coating crackings and spallations. It was shown that the adhesion between the DLC coating and the organic hard coating was good. The delamination between hard coating and the polycarbonate substrate was observed instead of delamination between DLC coating and hard coating. The concentrated load by sliding stylus and the poor adhesion between organic hard coating and polycarbonate made the extensive spallation. The wear-resistance was improved with the introduction of organic hard coating layer. This could be explained by the fact that the interlayer of hard coating was effective to make the top DLC coating wear-resistant under the even load distribution such as in a hazemeter testing.

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