Deposition of Diamond-Like Carbon Films on Polycarbonate by ECR-PECVD Method

Y-T. Hwang, J.C.S. Chu, Union Chemical Laboratories, ITRI, Taiwan; and B.S. Mercer, PlasmaQuest Inc., Richardson, TX

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ABSTRACT

Diamond-like Carbon (DLC) films had been prepared at 50°C by the plasma enhanced chemical vapor deposition method, using hydrocarbon CH_4 or C_2H_6 and H_2 as the precursors. It had been found that hard diamond-like carbon film can be prepared under the condition of rf induced negative self bias of the substrate holder. Data was shown to demonstrate the effects of hydrogen content, Ar content and rf bias on the film deposition rate and film properties. In addition, the effects of Electron Cyclotron Resonance (ECR) were also discussed. Raman spectra, optical band gap and mechanical properties of DLC on PC coupon, silicon wafer as well as glass were measured to characterize these deposited films.

INTRODUCTION

A lot of research activities have been generated in order to successfully deposit the diamond-like carbon (DLC) films and to gain some insight into its properties-structure relationship. Properties such as high hardness, high structure density, IR transparency, electrically insulating and wear resistance make it promising on various applications. Therefore, DLC is an ideal protective coating for the IR optics, medical transplants, magnetic recording devices, drilling tools as well as ophthalmic lenses. The polymer based ophthalmic lenses (PC, PMMA and CR-39) were superior in safety and inferior in wear resistance than its counterpart- glass. Therefore, to improve the abrasion resistance of polymers, especially PC, became a interesting topic.

The diamond-like carbon exhibits a wide range of characteristics due to the fact that DLC is not a single crystal material but a combination of amorphous carbon with hydrogen. This amorphous type hydrocarbon can be soft as polymer-like or as hard as the diamond, in which the hardness of DLC ranges from 5 to 20 GPa. The hydrogen contents on the DLC films can vary from several atom percent to as high as 60 atom %. The properties of DLC are largely determined by the energy that the hydrocarbon ions carry when arrive at the growing surface. Therefore, deposition methods will have a major influence on the film properties.

Aisenberg and Chabot were the first to use carbon ion beam to deposit the DLC in 1971 [1], where the carbon ions were generated by sputtering the carbon electrode in an argon environment. Besides the ion beam methods [1-3], the magnetron sputtering technique [4] has been used where the Ar plasma was utilized to sputter the graphite target producing desired ion species as well as to bombard the growing DLC film eliminating unwanted structures. Meanwhile, deposition of a single ion species was possible if a magnetic mass filter was applied, where the large size clusters were blocked out and only a pure ion beam of small size carbon ions reached the substrate surface [5,6]. However, the most popular deposition method was the plasma enhanced chemical vapor deposition method (PECVD) [7-11]. The common PECVD techniques utilized either a direct current (DC) or radio frequency (RF) power supply to generate plasma to ionize the hydrocarbon precursors, then deposited the ionized species onto a negatively self-biased substrates. A rf system was preferred than the DC system.

Most recently, Electron Cyclotron Resonance (ECR) PECVD method with characteristics of high ion density, low ion energy and low gas pressure has been explored to grow the DLC thin films [12-14]. The ion flux and ion energy can be controlled independently by adjusting the microwave (MW) power and rf self-biased power in this system. Besides, ECR-PECVD method gave the advantage of conducting the deposition process at a temperature less than 100°C, which is particularly suitable for handling polymeric substrates.

In this paper, we reported the results of DLC film prepared by the low temperature (50°C) ECR PECVD method. Raman spectra showed that the deposited films were Diamond-like carbon as characterized by the ~1547 cm^{-1} peak. The film properties were found to depend on deposition parameters, i.e., Ar/H_2 ratio, H_2 contents, MW power and rf power with the last two factors being the most significant. Scanning scratcher tests were used to compare the microhardness of DLC coated PC to the bare and polysiloxane coated PC. It appeared that the microhardness of DLC coated PC was substantially enhanced.

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EXPERIMENTAL

The DLC deposition experiments were carried out in a dual mode plasma system, which including an Electron Cyclotron Resonance (ECR) and a radio frequency (rf) power supply units. This two-electromagnet, low profile ECR PECVD system was customer designed and constructed by the PlasmaQuest Co. The water cooled stainless steel ECR chamber was 16 inches in diameter and 39 inches long. It was pumped by a turbo molecular pump (LH TMP1000C) with a base pressure of $1x10^{-7}$ torr.

The upper magnet of the ECR was used to create the resonance zone. The ECR plasma was generated by a 2.45 GHz microwave power supply (ASTeX AX4400) and the electron cyclotron resonance was taking place at a magnetic field of 875 G. The lower magnet was located below the chuck. The lower magnet was positioned so that it can collimate (magnetic field, B= constant value) or diverge (B= 0) the ion beam normal to the chuck. The 13.56 MHz rf power supply (ENI ACG5DC) with a matching unit was tunable from 0 to 500 W with a negative d.c. bias ranging from 0 to -600 V.

The upstream ion beam was generated by ionizing the Ar gas (UHP grade). Ar and the H_2 gases were both introduced into the plasma chamber through a spherical distribution ring. The hydrocarbon gases (CH_4 and C_2H_6) were introduced into the deposition chamber through another spherical distribution ring. The flow rate of the inlet gases were controlled by the mass flow controllers. The distance between the upper and lower rings was about 12 inches.

Substrates included the Si(100) wafers, sliding glasses and injection molded PC lenses. They were ultrasonic cleaned in isopropanol (IPA) before entering the ECR system. After the substrates were introduced into the system by the load luck mechanism, the substrates were cleaned by the O2 ashing reaction to eliminate any possible residuals on the substrate surface. Afterward, the DLC thin films were deposited onto the substrates.

The fourier transformed IR spectra were taken by a Bio-Rad FTS-60 spectrometer. The DLC Raman spectra on the Si(100) substrate was characterized with the 514.45 nm Ar laser. A variable angle ellipsometer (J.A. Woollam Co.) was used for the measurement of the film thickness and optical constants (n and k). The Refractive index reported here were the value observed at incident light of 550 nm. The optical band gap was determined by measuring the transmission and reflectance of the thin film on the sliding glasses, then calculated by the Tauc equation [16].

$$\alpha (E)^{1/2} = B(E-E_g)$$

where α is the absorption coefficient which can be calculated from transmission and reflectance, E is the energy of the incident light, B is a constant and E_g is the optical band gap. The microhardness of the polycarbonate lenses were measured by using a scanning scratcher Tester (Shimadzu SST 100). The stylus diameter was 50 um, the progressive loading were kept between 0 to 10 gf, the scanning speed were 5um per second.

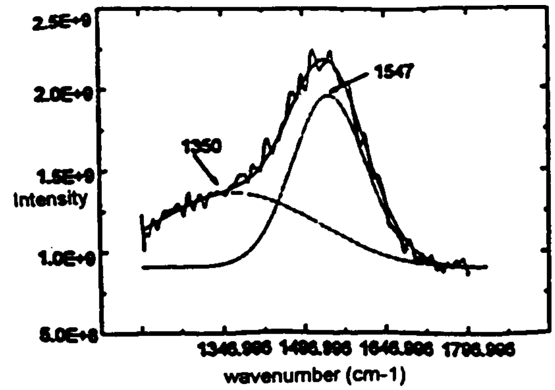

Figure 1. The raman spectrum of DLC film. The DLC was deposited at C_2H_6 flow rate= 50 sccm, H_2 flow rate=20 sccm, Ar= 10 sccm, rf power= 350 W and mw power= 100 W.

RESULTS AND DISCUSSION

a. Spectroscopic Studies of DLC films

Fig. 1 Showed the Raman spectrum of DLC thin film on Si(100) substrate deposited with microwave power of 100 W and rf power of 350 W. The film thickness was 870 nm. The broad DLC band can be deconvoluted by gaussian distribution into 2 bands centered at 1547 and 1350 cm^{-1}. Their positions agreed with the literature results [2,8]. Peak at 1547 cm^{-1} was assigned to be graphite optical zone center photons (G band) and the peak at 1350 cm^{-1} was due to disorder activated optical zone edge phonons of graphite (D band). The spectrum was dominated by the 1547 cm^{-1} band because the cross section of G mode was 30-60 times greater than the D mode.

The FTIR spectra (not shown here) also matched with the literature results reported by Dischler et al [8]. Three peaks located between 2800 and 3050 cm-1 were observed. According to Dischler's study, the 2855 cm-1 peak was due to sp^3 CH_3 symmetric stretching mode, the 2922 cm-1 peak was attributed to the sp^3 CH_2 stretching mode and a hump close to 2960 cm-1 was due to the sp^3 CH_3 asymmetric stretching mode.

b. Deposition processing studies of the DLC films

The effects of ionization gas were first explored. The percentage of Ar was varied between 83.3% to 16.7% while the total flow rate of Ár and H_2 was kept at a constant value. As shown in Fig. 2a, the deposition rate decreased from 1.0 A/sec to 0.43 A/sec as the Ar increased from 16.7% to 83.3%. The refractive

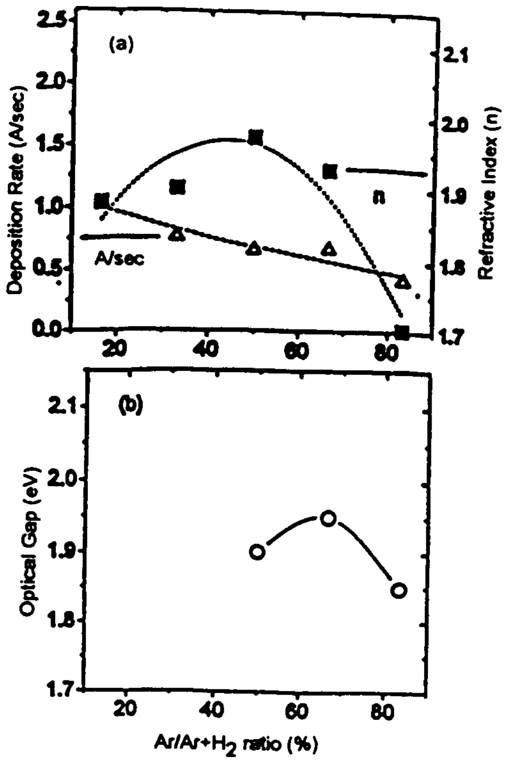

Figure 2. The Ar/Ar+ H_2 effects on (a) deposition rate and refractive index, (b) optical gap. The DLC films were deposited at C_2H_6 flow rate= 50 sccm, mw power= 200 W and rf power= 200 W. The total /Ar+ H_2 flow rate for each experiments was 120 sccm.

index of DLC films reached a maximum of 1.97 at 50 % Ar. According to Kobayashi et al. [16], the Ar plasma acted as an ion bombardment source which etched the amorphous carbon films. Raven et al. [14] had also observed that the deposition rate, density and microhardness of the DLC films increased then subsequently decreased as the Ar concentration raised. Our data suggested that , in the concentration range of 16 to 83%, the energetic particle of Ar ion bombarded the substrate surface transferring momentum to atom in DLC film and leading to a lower deposition rate together with a microstructure change which was then reflected on its properties such as refractive index and optical band gap (fig. 2b).

The effects of H_2 addition on the deposition rate and the refractive index were shown in Fig. 3. At constant Ar flow rate of 60 sccm, addition of up to 20 sccm H_2, the deposition rate had a negligible change. With higher H_2 flow rate, the changes in deposition rate became more dramatic. However, when H_2 content increased, the refractive index showed a significant drop then leveled off. This phenomena is not much different from what observed by Raven et al. [14] on their CH_4 and C_3H_6 systems. It was believed that the H_2 was capable of recombine with other active species in the reaction system and therefore reducing the probability of ionized precursors to reach the substrate surface.

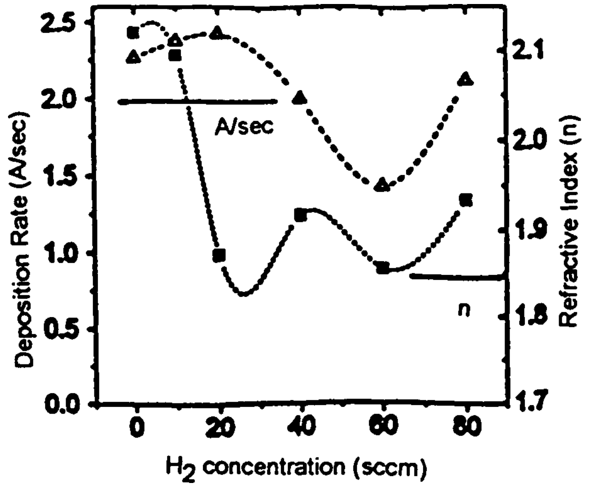

Figure 3. H_2 concentration effects on deposition rate and refractive index. The DLC films were deposited at C_2H_6= 50 sccm, Ar= 60 sccm, mw power= 100 W and rf power= 350 W.

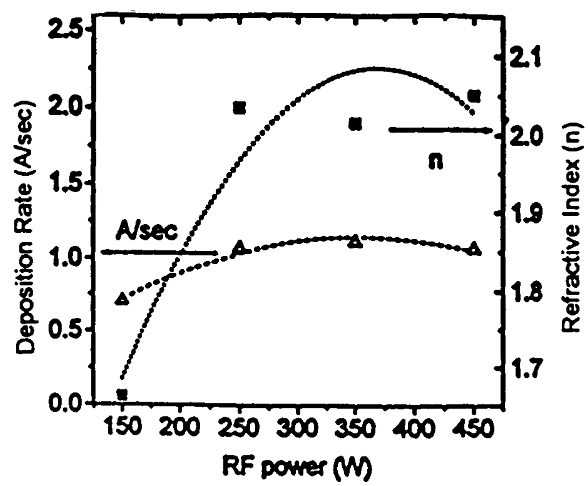

Figure 4. The rf effects on deposition rate and refractive index. The DLC films were deposited at CH_4= 70 sccm and H_2/Ar= 100 sccm. The H_2/Ar ratio was 10%.

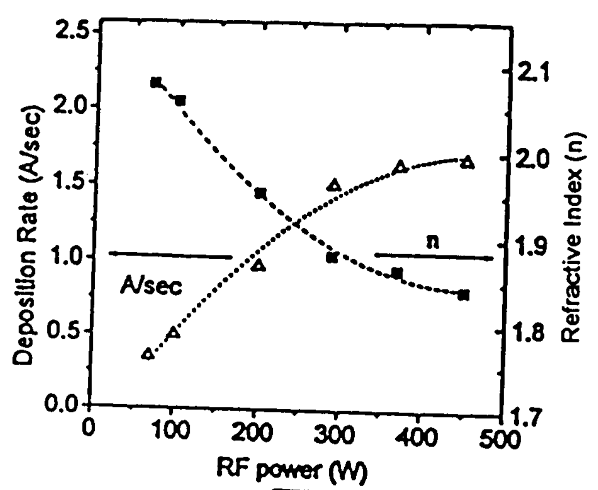

Figure 5. The rf power effects on deposition rate and refractive index. The DLC films were deposited at C_2H_6= 50 sccm, Ar= 60 sccm, H_2= 60 sccm and mw power= 100W.

The effects of rf power with or without microwave power were both studied. As shown in Fig. 4, deposition with only rf mode, the deposition rate and refractive index increased then leveled off as the rf power increased. However, with 100W microwave, a very different behavior was observed. The deposition rate was found to increase from 0.35 to 1.69 A/sec as the rf power increase from 70 W to 450 W. The refractive index decreased as the rf power increased. This result was different from what reported in the literature. Using rf discharge method, Koidl et al. [11] had observed that both the DLC film's n value and deposition rate changed according to the rf power. Our own rf discharge of CH_4 study (Fig. 5) indicated the same trend as Koidl's. The unusual behavior shown in Fig. 4 might attribute to the microwave influence. While the deposition rate was mainly determined by rf power as indicated by Koidl's work, the high energy Ar ion excited by microwave might bombard the DLC surface and change the optical properties of the DLC thin film.

The effects of microwave power were also investigated as the rf power fix at 200 W (Fig. 6). As the MW power increased, the deposition rate decreasing from 1.02 to 0.41 A/sec while the n value showed an inverse trend. This observation might be due to the unique etching nature of the microwave system. Work had also been carried out to deposit DLC film for a various length of time in order to vary the film thickness. When the refractive index of DLC film was plotted against film thickness, a very interesting result was observed: there was a correlation between refractive index and film thickness! As shown in Fig. 7, at MW power of 0, 100 W, there was a linear relationship between the film thickness and n. However, when the MW power was increased over 100 W, the relationship between thickness and n became non-linear. This result might suggest a non-equilibrium process where deposition and etching were proceed at different rate so that a continuous change of microstructure occurred during the period of deposition. A more detailed study is still underway to understand this discovery.

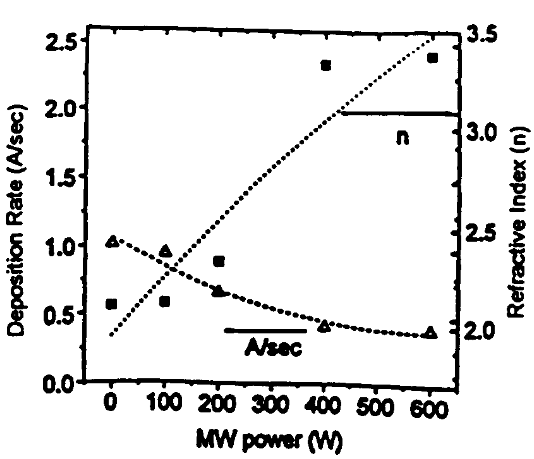

Figure 6. The mw effects on deposition rate and refractive index. The DLC films were deposited at C_2H_6= 50 sccm, Ar=60 sccm, H_2= 60 sccm and rf power= 200W.

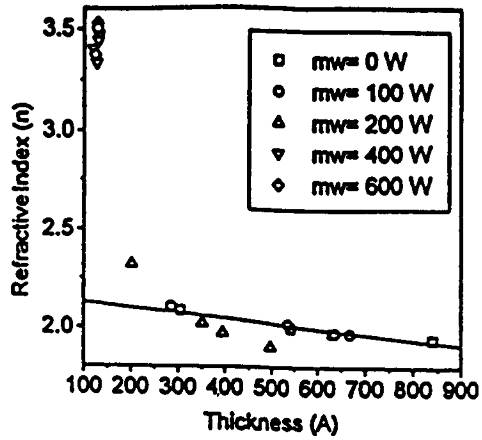

Figure 7. The refractive index vs thickness. The DLC films were deposited at C_2H_6= 50 sccm, Ar=60 sccm, H_2= 60 sccm and rf power= 200W.

The rf and MW power not only affected the deposition rate and refractive index substantially, they also affected the optical band gap of the DLC thin films and gave the films different color. Fig. 8a and b exhibited the plasma effects (rf and MW) on optical band gap. The optical band gap range from 1.6 to 2.1 eV.

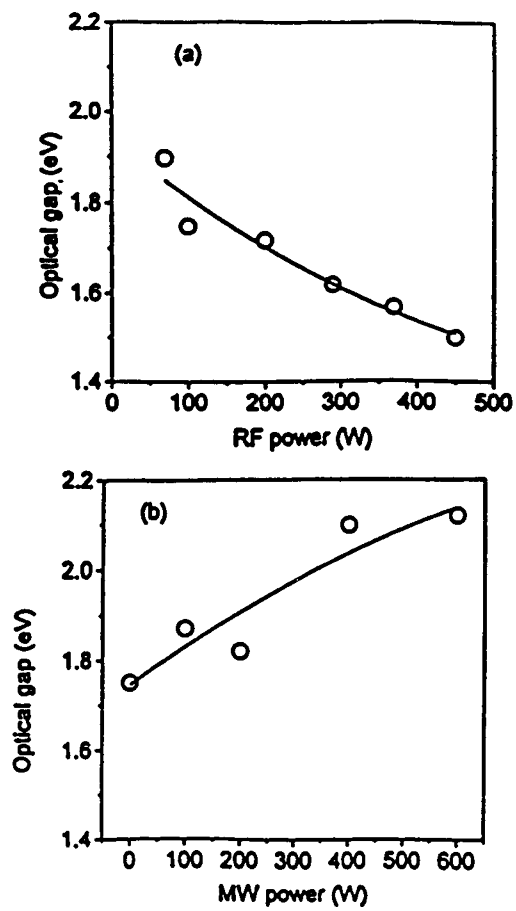

Figure 8. The (a) mw and (b) rf effects on the properties of optical gap. The DLC films were deposited at C_2H_6= 50 sccm, Ar=60 sccm and H_2= 60 sccm. The rf power= 200W for fig. 8a. The mw power= 200 W for fig. 8b.

c. Mechanical properties of the DLC films

A very important application for the DLC thin films was based on its hardness. The polycarbonate substrate was known for its transparency and mechanical toughness, which make it a suitable material for optical applications. However, its surface was soft and scratch-proned. Therefore, to improve scratch resistance of its surface became an important issue. The microhardness of DLC coated PC lenses compared with that of the polysiloxane dip coating were shown in Fig. 9. The microhardness of bare PC coupon and the polysiloxane treated PC were 4 and 7.3 kg/mm^2, respectively. Nevertheless, the DLC coated PC shown a substantial increase in the microhardness, which was about 12 Kg/mm^2

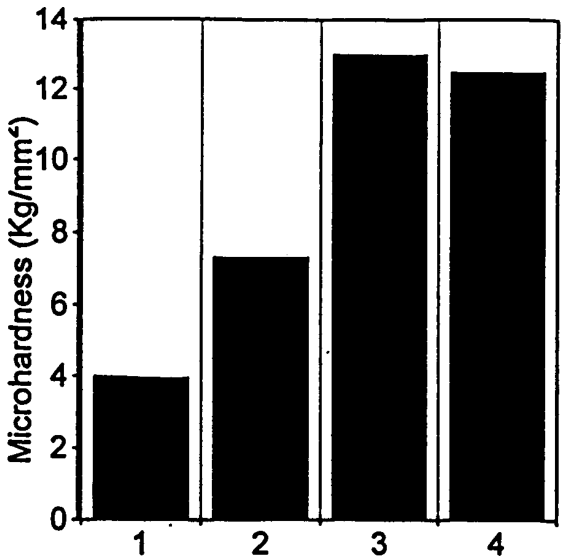

Figure 9. The microhardness of bare and treated PC.(1) Bare PC; (2) polysiloxane dip coated then cured PC, (c) DLC deposited PC1, mw power= 50 W and rf= 170 W; (4) DLC deposited PC2, mw power= 50 W and rf=250 W

CONCLUSIONS

The diamond-like carbon films were successfully deposited on the rf+ ECR mode PECVD system. The rf and ECR powers were found to be the most important factors to control the properties of the deposited DLC films. Meanwhile, test results shown that the microhardness of PC was enhanced substantially.

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