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Optical properties of PECVD deposited DLC films prepared with air addition

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Diamond-like carbon (DLC) films with addition of atmospheric air to benzene were prepared by DC discharge plasma enhanced chemical vapor deposition (PECVD). These films were compared with films made from benzene/argon mixture. Some properties of the films including their optical transmission, hydrogen content and Raman spectra were investigated. It was found that such films fabricated with air addition (even at low vacuum) exhibit properties suitable for optical applications.

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1. Introduction

In recent years diamond-like carbon (DLC) thin films are a subject of growing interest because of their unique properties [1]. These properties include mechanical hardness, electrical insulation, infrared transparency and chemical inertness. The most important industrial applications of DLC films now are wear-resistant coatings for computer hard-disks and optical coatings for the infrared and for the visible light ranges.

A variety of techniques have been used for preparation of DLC films. All of them are based on ion beam or plasma technique [2], because DLC films deposition requires their surfaces to be continuously bombarded by high energetic ions. During the ion bombardment the sp^2 (graphitic) bonds are more easily removed and this increases the ratio of sp^3 / sp^2. Main techniques for the deposition of diamond like carbon films are based on plasma enhanced chemical vapor deposition (PECVD). Today the most frequently used PECVD methods are rf excitation, microwave plasmas and electron cyclotron resonance (ECR) systems. DC discharge systems were the first systems to be applied for the deposition of DLC thin films. They are seldom used nowadays because in such systems the DC voltage is used to create the plasma, as well as to determine the energy of the bombarding ions and it is difficult to optimize such systems. However, the DC PECVD systems have the advantage that DLC films deposited by DC technique exhibit smaller stress values than the films deposited by RF PECVD technique [3]. Recently there is also a great interest in nitrogen doped DLC films not only for mechanical [4] but also for electronic and optical applications [5].

In the present paper we report our investigations of some optical properties of DLC films fabricated by the DC PECVD technique with high accelerating voltage and addition of atmospheric air. The DLC optical properties studied, were optical transmission, reflection, absorption and the Raman spectra. The hydrogen content of the films was determined by nuclear reaction analysis (NRA) and the depth profile of all other light elements was measured by elastic recoil detection analysis (ERDA).

2. Experimental

Hydrogenated DLC (a-C:H) films were deposited onto single-crystal (100) Si wafers and upon glass plates using a DC plasma reactor. The reactor was evacuated by a combination of a diffusion and a mechanical pump. Two sets of samples were made. The processing gas was always benzene (C_6H_6). In the first set argon was added to the benzene vapour and the reactor was continently pumped by the pumps. These films were used as reference. In the second set similar DLC films were deposited with air addition. In this case the chamber was evacuated only by a mechanical pump until the pressure of 10^{-4} Torr. Next the benzene was added in the chamber until the pressure of 8×10^{-3} Torr and during the film deposition the system was pumped only by the mechanical pump. The air was added because in many industrial applications it is desirable to deposit DLC coatings at low vacuum, where the residual air content is high. In the same time it is known [4-5] that small amounts of both nitrogen and oxygen have positive effect on the growth of DLC films. The oxygen is effective for etching sp^2-bonding fraction [6] whereas the nitrogen helps in reducing the stress of the growing films [7].

The substrates were placed upon the water-cooled cathode. The vacuum chamber acts as anode. Benzene vapours were obtained by boiling of benzene at a constant temperature and were introduced via a needle valve. After the stabilization of the plasma the DC voltage was set at 2 kV and deposition was carried out for (30 ÷ 150) min with ion beam power density of 1 W/cm^2. Before the film deposition substrates were degreased in acetone, methanol and de-ionized water in an ultrasonic bath and they were subjected to 10 min Ar sputter cleaning at 2 kV and about twice higher power.

The optical transmission and reflection of the films deposited on glass substrates were measured with a "Cary 5E" spectrophotometer at wavelengths between 350 and 3300 nm. Raman spectra of the deposited films were obtained at 532.14 nm and the spectra were taken accumulated 10 times in order to improve the signal/noise ratio of the measurements.

The H content of the films was measured by the nuclear reaction analysis (NRA) using a setup similar to that described in [8]. The energy scale can be converted in a depth scale using a mean density of the film. Depth profiles of other elements in the films were obtained by elastic recoil detection analysis (ERDA) using 35 MeV ^{35}Cl ions from a Rossendorf accelerator. The atomic concentration was calculated from the energy spectra on the basis of mean values of the atomic density of each element. This was possible because of the constant values over a wide region.

3. Results and discussion

The most important properties of DLC films for optical applications are their infrared and visible light transparency. Typically DLC films are transparent in the infrared range, weakly absorbing in the visible spectrum, and increasingly absorbing with decreasing the wavelength in the UV range [9]. Our results are in agreement with these observations. The curves of Figs. 1-2 represent the spectral transmittance and reflectance of both types of films on a glass substrate. The spectrum is very similar to those of DLC films produced by other methods. The films are found to have high transmission, about 80% in the whole IR range. In the UV range the films confirmed our expectations and manifested increase of absorption with the decrease of the wavelength.

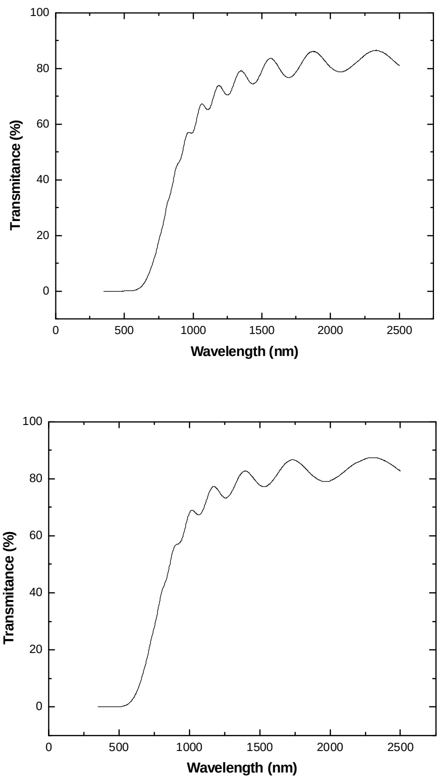

Fig. 1. Transmission spectrum of the DLC films deposited on glass substrate from Ar/benzene (a) and from Air/ benzene mixture (b).

The optical constants (refractive index, n and absorption coefficient, k) are very important parameters of the DLC films not only for optical applications. It was shown empirically [10] that the refractive index is also a reliable measure of film quality concerned to mechanical characteristics such as hardness, scratch resistance and wear resistance. Generally the film quality scales directly with the refractive index, therefore it can be used as the single parameter which has to be controlled for the film deposition optimization. From the interference effects the index of refraction n was determined to be 1.8-1.85 in the range 1000 –2000 nm, practically the same for both sets of films. This is in a good agreement with the typical values of DLC films fabricated by other methods and from other precursors different from benzene [11] and indicates high optical and mechanical properties. The only difference noticed between the two sets of films was in the deposition rate, which is lower (32 nm/min) for deposition in air/benzene mixture. In Ar/benzene this rate was about 43 nm/min. Our conclusion that both types of films are practically identical is supported by the calculated absorption coefficient (Fig. 3) of the DLC films deposited on glass substrate $\alpha=(1/d)\ln((1-R)/T)$, where R, T and d are measured reflectance, transmittance and film thickness respectively. Obviously these films can be used as protective and scratch-resistant coatings in infrared optical systems and as UV rejecting coatings in visible optics as well.

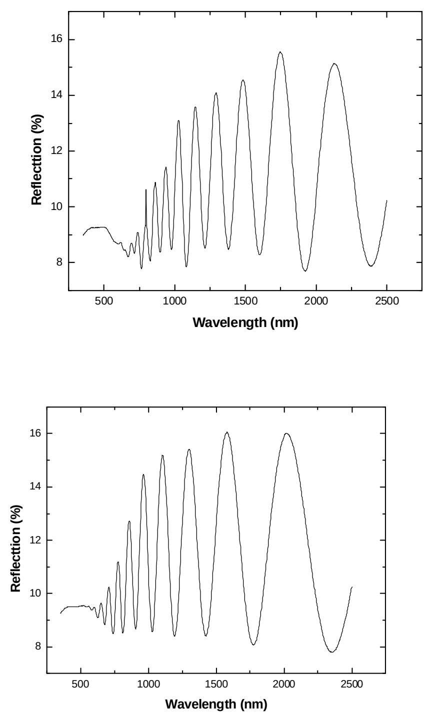

Fig. 2. Reflectance spectrum of the DLC films deposited on glass substrate from Ar/benzene (a) and from Air/ benzene mixture (b).

Based on our measurement, the optical energy gap E_g was evaluated to be 1.3 eV similar to the energy gaps of DLC films obtained by other methods. Because the optical gap in DLC films depend on the presence nanosize of graphitic clusters in the film [12], high E_g values indicate smaller size of the graphitic clusters in our films. This conclusion is confirmed below also from Raman measurements.

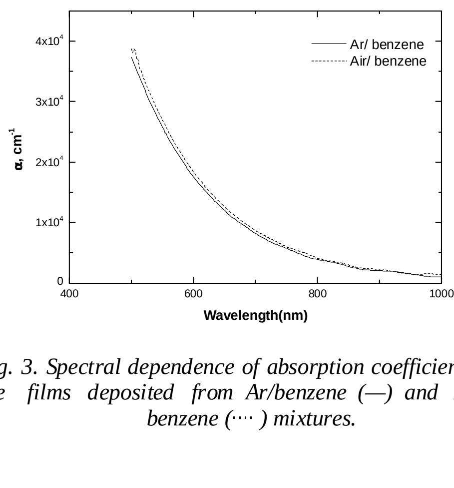

Fig. 3. Spectral dependence of absorption coefficient for the films deposited from Ar/benzene (—) and Air/ benzene (····) mixtures.

It is well known [13], that the hydrogen content of DLC films is an important factor for stabilization of DLC films and improving their optical properties. All our films deposited on different substrates, such as silicon, glass or metals, exhibit uniform distribution of hydrogen over the whole layer depth, the hydrogen concentration being from 21 % to 25%. Fig. 4 shows the hydrogen depth distribution obtained by NRA for the films deposited on Si substrate. The sample A is our reference film made as usual with Ar. Two other films were deposited by air addition.

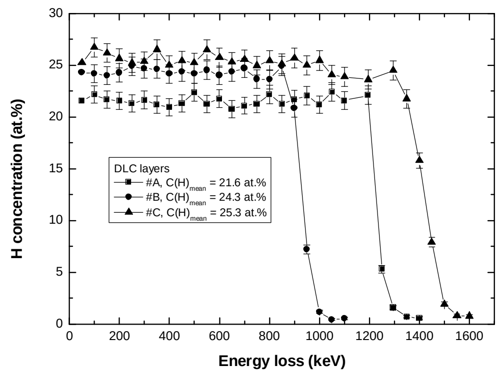

Fig. 4. Distribution of the hydrogen content in DLC films deposited on Si obtained by nuclear reaction analysis. Sample A is made from Ar/benzene and samples B and C are fabricated from Air/ benzene mixture.

ERDA results (Fig. 5) show distributions of all other elements. It is seen that it is nearly constant over the whole film depth for all samples. As expected in the films made with benzene/Ar mixture argon was detected, while in films prepared with air addition nitrogen and oxygen content was present.

To further understand the optical properties of our films, Raman scattering measurements were performed and some results are shown in Fig. 6. As shown in Fig. 6 the Raman spectra can be decomposed using Gaussian functions into two peaks at approximately 1350 and 1540 cm^{-1}, which is typical of amorphous carbon. The D peak, centered at 1350 cm^{-1} is the well-known “disordered” peak, which indicates presence of sp^2-bonded material. For films with very low sp^2 content this peak should disappear. Because for all our samples this peak is almost the same, this suggests that the sp^2 fraction is also the same. Unfortunately the Raman spectra are insensitive to the sp^3-bonded component of the films and the sp^2/sp^3 fraction of the films can not be determined accurately from Raman measurements. However, this relation can be estimated in the following manner. The second peak is the well-known G peak, which moves up with increasing sp^3 fraction [14]. In our films the G-peak position was observed near 1530 cm^{-1}, which indicate sp^2 content of less then 20% in our DLC films.

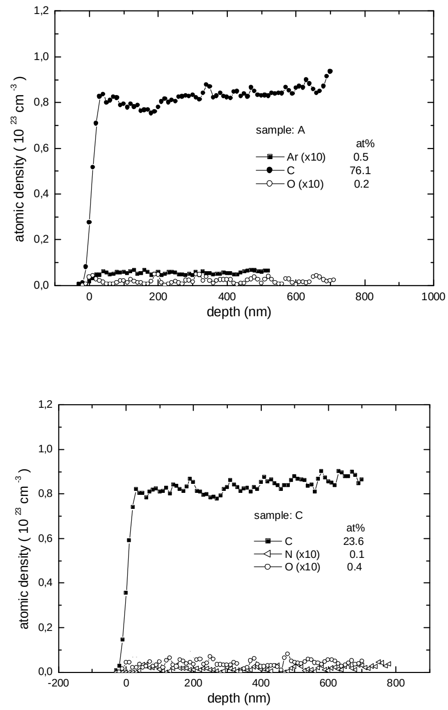

Fig. 5. ERDA results for sample A made from Ar/benzene (a) and sample C fabricated from Air/ benzene mixture (b).

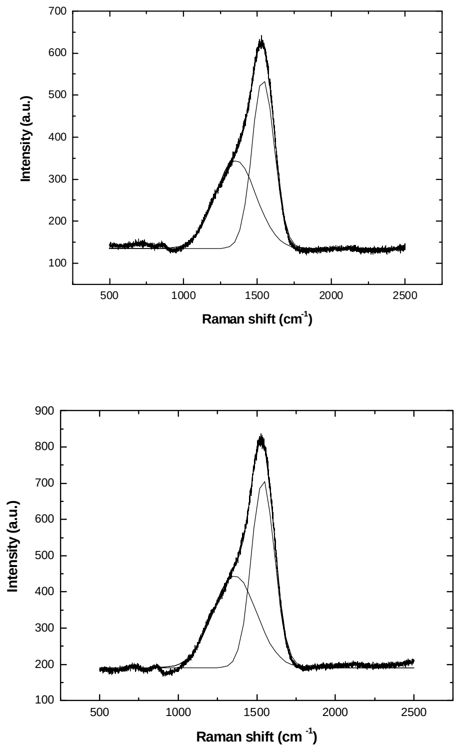

Fig. 6. Raman spectra of the DLC films prepared from Ar/benzene (a) and Air/benzene mixtures (b).

The ratio of the intensities of the D peak and G peak I_D/I_G, which is known to be inverse by proportional to crystallite size, is about 0.5 in all cases, suggesting small size of graphitic clusters in the samples.

4. Conclusions

DLC films deposited from benzene using DC PECVD system and atmospheric air additive have been investigated. The most important optical parameters of the material including optical transmission, index of refraction and Raman spectra were measured. It can be concluded that DLC films even prepared at low vacuum appear to be suitable for different optical applications in the visible and infrared ranges.

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