

Structural and photoluminescence study of diamond-like layers grown by electrochemical method

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In this paper we describe the growth, optical and morphological properties of diamond like carbon layers (DLC) obtained by electrochemical deposition in ethanol solution. The structural and morphological properties of diamond like carbon samples were characterized by Raman scattering as well as scanning electron (SEM) and atomic force (AFM) microscopy. The SEM and Raman measurements indicated that obtained diamond films exhibit coexistence of two phases: amorphous and polycrystalline. The photoluminescence (PL) spectra of obtained layers were investigated at the temperature range from 13 K to 325 K. Spectral analysis suggest that the multi-peaks structure of photoluminescence spectra at low temperatures arise from sp^2 hybridized carbon clusters with different sizes.

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1. Introduction

Diamond-like carbon (DLC) is a name first introduced by Aisenberg and Chabot [1] to describe a group of carbon materials consists of a network of tetrahedral (sp^3) and trigonal (sp^2) bonds. These structures may also contain hydrogen, and hence it is reasonable to distinguish between hydrogenated-DLC (a-C:H - with up to 50 at. % of hydrogen) and tetrahedral amorphous carbon (ta-C - with less than 1 at. % of hydrogen but 85 % or more sp^3 bonds). DLC does not exhibit any specific structure; it is rather composed of a mixture of amorphous and crystalline carbon phases, properties of which strongly depends on deposition conditions. It is known that these layers have a wide range of exceptional properties such as: high hardness, chemical inertness, high thermal conductivity, high electrical resistivity and optical transparency [2, 3]. However, the knowledge of photoluminescence properties of such structures is still limited and further research is indispensable. It is known that structural properties, which are strongly affected by the deposition conditions, determine both optical and electrical features of thin films. Thin layers of emissive wide band gap materials can be applied in many optoelectronic devices such as electroluminescence diodes or lasers. Materials, which exhibit strong luminescence, especially at room temperature, are very desirable.

Since the first announcement of Aisenberg and Chabot [1], DLC films have been produced by a wide variety of vapor-deposition methods (chemical vapor deposition [4], physical vapor deposition [5], ion-sputtering [6] and others). Another possibility is the growth of DLC layers by electrolysis of liquid hydrocarbons. Some successful applications of this method have already been reported [7, 8, 9, 10]. Such

films have many advantages such as: the lack of carbide interfacial layer when are deposited on carbide-forming substrates (Si, Ti etc.), negligible thermal stresses due to low deposition temperature (less than 110 °C) and relatively inexpensive set-up.

In the present work, the DLC films deposited on Si substrates by electrolysis of ethanol are studied in terms of their structural and photoluminescent properties.

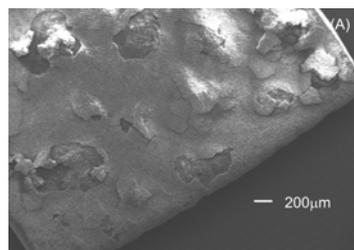
2. Experimental details

DLC films have been deposited from pure ethanol using graphite ($20 \times 20 \times 1 \text{ mm}^3$) and mirror-polished (110) silicon ($20 \times 11 \times 0.25 \text{ mm}^3$) plates as electrodes. The distance between the electrodes was equal 7 mm. The negative potential applied to the silicon substrate was equal 1600 V with respect to the anode (graphite plate). The self-heating of the electrolyte by flowing current increased the deposition temperature up to the boiling point of ethanol (78.3 °C) resulting in its bubbling in the substrate-liquid-air triple phase area. The deposition process was carried out for 148 h.

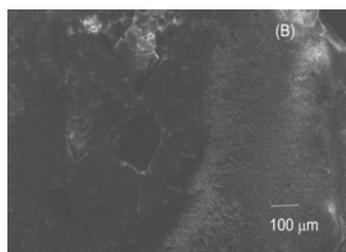
The sample morphology was observed using LEO 1430VP SEM microscope, and AFM NanoScope IIIa instrument (Veeco Inc.) working in a tapping mode. Jobin-Yvone U-1100 Raman spectrometer was used to measure Raman spectra of the films in the range from 1200 to 1800 cm^{-1} excited with 15 mW argon-ion laser line (488 nm). The spot diameter of argon-ion laser beam was about 0.5 mm. Optical properties were studied by photoluminescence measurements at temperatures ranging from 13 K up to 325 K. The 42 mW helium-cadmium laser (Omnichrom 75) line with 1 mm spot diameter and wavelength equal to 325 nm was used for excitation.

3. Results and discussion

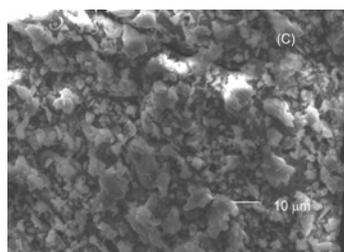
Previous observations proved that films grown by decomposition of ethanol are composed of mixed sp^2 - and sp^3 -hybridized carbon atoms [9]. The film presented in this work is also not homogeneous possibly due to current density variations. These irregularities are best seen in SEM images in Fig. 1.



a



b



c

Fig. 1. SEM images of the carbon films obtained by electrodeposition method: (A) film entirely immersed in liquid with hills and valleys onto its surface, (B) film deposited from the ethanol foam, (C) zoom-in view on the film deposited from the foam.

Fig. 1A presents a hilly deposit formed over the substrate immersed in the ethanol whereas Fig. 1B illustrates much smoother film grown from foam formed on the surface of the ethanol. Large-area views of the film shown in Fig. 1A and 1B both exhibit numerous cracks on the surface, rather poor contact to the substrate lying beneath, and the lack of structural continuity. The difference in thermal expansion coefficients between silicon and carbon layer cannot account for observed peeling off the substrate when the deposition temperature is low. In fact, films crack when are dried out under normal conditions in air, what might suggest that they

become rigid due to evaporation of alcohol molecules. Fig. 1C shows zoomed-in SEM image of the film seen in Fig. 1B which turns out to be sponge-like structure with rough and porous surface. It is composed of loosely packed irregular particles, size of which is less than $10 \mu\text{m}$. Similar compact granular films were obtained under comparable conditions by Sun et al [9] and Sreejith et al. [11] whereas corn-like structures were obtained by Wang et al. [12]. Surprisingly, further magnification of this area using AFM method allowed to evidence ordered substructure of irregular carbon particles (Fig. 2).

The AFM pattern shows that particles are made of grains of several hundreds of nanometers in size with rectangular, flat crystal planes and sharp edges. These results are consistent with Tosin et al. theory [10], according to which morphology and structural properties of immersed and non-immersed areas are different. This effect is caused by bubble formation, which inhibit film deposition on the immersed substrate but enhances the growth of carbon aggregates on the cathode above liquid level. The latter area is of particular interest in terms of its photoluminescence properties discussed in the following paragraphs.

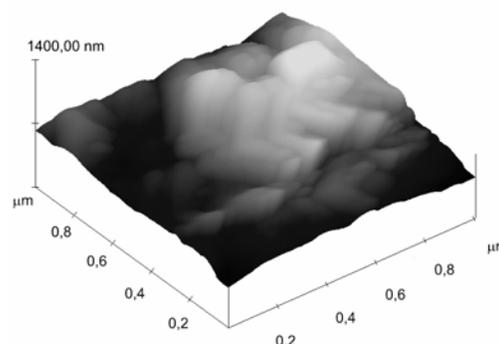


Fig. 2. AFM micrograph of the film deposited from the ethanol foam showing microcrystals with sharp edges and flat crystal planes.

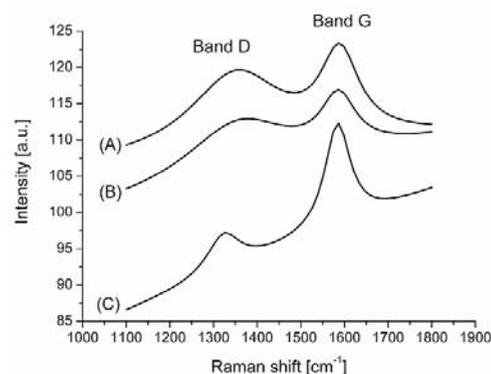


Fig. 3. Raman spectra of the films deposited from ethanol: (A) film in the bright dot (hill), (B) film in the valley area, (C) film deposited from the ethanol foam.

Fig. 3 presents Raman scattering spectra of different areas of investigated sample. Curves A and B of Fig. 3 show spectra taken from the area of film immersed in liquid during deposition process. The former corresponds to the bright dots (hills), whereas the latter comes from the valleys (see Fig. 1A). Curve C shows the spectrum of film deposited from the ethanol foam. Spectrum A exhibit two broad bands positioned at 1355 cm^{-1} (band D) and 1585 cm^{-1} (band G) whereas curve B has similar shape with the bands centered at 1375 cm^{-1} and 1585 cm^{-1} . The band G, which has the same position in both A and B spectra reveals the existence of graphite – like sp^2 micro-domains. However, it is known that DLC can contain high amount of sp^3 hybridized carbon atoms with various the sp^3/sp^2 ratio [12]. Thus, the second band (D) corresponds to the disordered graphite formed by linking sp^2 with sp^3 carbon atoms [9]. In case of hill area (curve A), the band D is downshifted with about 20 cm^{-1} relative to corresponding peak for valley region. Since the observed shift is toward diamond line (1332 cm^{-1}) [10], this effect can be explained by higher amounts of sp^3 hybridized carbon atoms in hill area. In contrast to the immersed region of layer, the cathode area above the liquid level exhibits the Raman line at 1330 cm^{-1} , which is typically assigned to sp^3 bonded carbon atoms (diamond line). Moreover, the G band is stronger and better resolved suggesting improved crystalline perfection of the graphite deposit. In addition, substantial linear background in C Raman spectrum is due to strong luminescence from carbon clusters. The influence of luminescence on the A and B Raman spectra is not as significant as in case of the layer deposited from foam formed on the surface of the ethanol.

Among various models proposed for the structures of DLC layers, commonly accepted is the model with sp^2 hybridized carbon atoms organized in clusters having different size and shape. Robertson [13] has shown that the energy gap of the clusters depends on both their shapes and the numbers atoms in the clusters. In general, when the size of cluster increases the emission shifts to lower energy. The existing of different sp^2 hybridized clusters in non-immersed part of layer is confirmed by photoluminescence study.

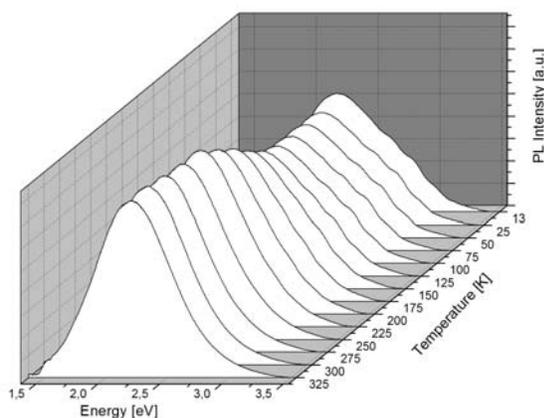


Fig. 4. Photoluminescence spectra of film deposited from the ethanol foam measured at different temperatures.

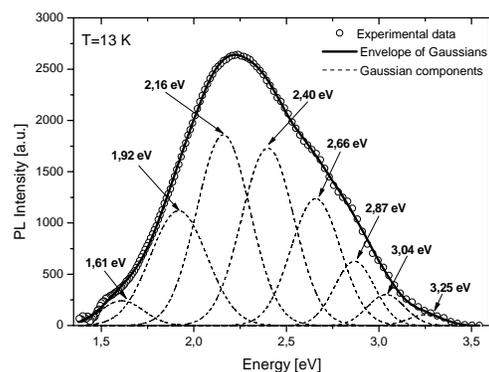


Fig. 5. Gaussian decomposition of PL spectrum at 13 K.

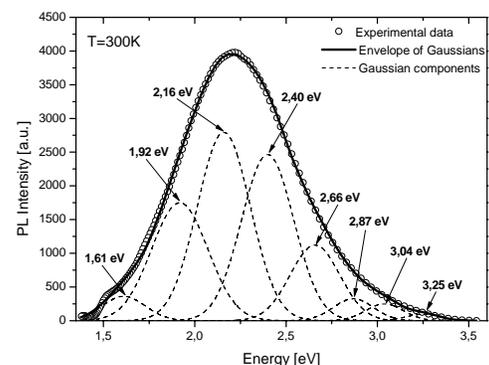


Fig. 6. Gaussian decomposition of PL spectrum at 300 K.

Fig. 4 shows the temperature dependence of photoluminescence spectra of this area. The spectra were taken under steady state excitation with the 325 nm line of a He-Cd laser at the temperature range 13 K – 325 K. The studied layer exhibit strong luminescence in the visible spectral range. We can see that the investigated film at low temperature shows a multi peaks PL spectrum with several bands, which can originate from band-to-band recombination in sp^2 hybridized carbon clusters with different sizes. The envelope of high energy part of low temperature spectrum can be reconstructed using Gaussians basing on positions of observed peaks. In order to fit whole spectrum additional Gaussians representing low energy transitions must be used. We assumed that line broadening is comparable for clusters with different sizes (or shapes). As a result we found that at least 8 components must be used for satisfactory fitting. Decomposition for Gaussian components, representing different recombination centers, is shown in Figs. 5 and 6 for temperature 13 K and 300 K, respectively. We found that the positions and broadening parameters of particular bands do not depend on temperature. The lowest energy peak centered at 1.61 eV descends from the largest clusters and other bands peaked at 1.92, 2.16, 2.40, 2.66, 2.87, 3.04 and 3.25 eV are connected with smaller and smaller aggregates. From Fig. 4 is evident that intensity of all

bands decreases from 13 K to 135 K. Next, the intensity of low energy bands (below 2.5 eV) increases up to 225 K and diminishes again with rising temperature. On the other hand, the higher energy bands (above 2.5 eV) decrease in whole measured temperature range. This behavior can be explained assuming participation of two processes. The decrease of intensity is connected with typical thermal quenching caused by enhancement non-radiative paths of recombination at higher temperatures. A second phenomenon is the transfer of energy from smaller clusters to the larger ones. It causes the rise of low energy bands intensities in the range 135 K – 225 K with simultaneous significant attenuation of higher energy bands. This feature is clearly visible in Fig. 5 and Fig. 6 where Gaussian decomposition at 13 K and 30 K, respectively, is presented.

4. Conclusions

The structural and optical properties of the DLC layers grown by electrolysis of ethanol deposition were investigated by SEM, AFM, Raman and photoluminescence spectroscopy. SEM and AFM results revealed morphological differences between immersed and non-immersed area of cathode, what is consistent with previous work [10]. Raman scattering measurements confirm structural heterogeneity of the films electrodeposited from ethanol. It was found that hilly region of immersed layer consists of higher amount of sp^3 hybridized carbon atoms than valley area. Moreover, in the non-immersed layer crystalline diamond and graphite microdomains exist. It was shown that layers deposited from ethanol foam exhibit strong photoluminescence in the visible spectral range whereas the emission from immersed part of layer is very weak. Low temperature PL spectra of non-immersed area are characterized by multi-peaks structure associated with emission from sp^2 hybridized carbon clusters with various shape and size. Moreover, the PL measurements at various temperatures revealed the mechanism of energy transfer between different carbon clusters.

To summarize, the strong luminescence in visible range at room temperature makes the investigated structures potentially applicable in various modern optoelectronic devices such as electroluminescence diodes or lasers.

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