Deposition of Diamond-like and Diamond Films by Electrooxidation of Lithium Acetylide - A. Kulak and T. Kulak (National Academy of Sciences of Belarus)

Introduction. In a parallel with the development of traditional CVD and PVD techniques for the deposition of carbon films, of considerable interest are the alternative approaches such as electrochemical deposition similar to the traditional methods of galvanic coating formation which are characterized by simple technical devices and the possibility to fabricate, using low deposition temperature, the films of large area at reasonable cost. Recently we have demonstrated the possibility of DLC film deposition by the anodic oxidation of lithium acetylide ($LiC\equiv CH$) in dimethylsulfoxide [1]. In the course of present work we have developed this approach for the deposition of DLC coatings which can be transformed to diamond films under thermal treatment.

Experimental. The solutions of lithium acetylide (1-3 mol/L) were prepared by the reaction of gaseous acetylene with lithium derivative of dimethylsulfoxide obtained by the dissolution of lithium hydride in DMSO. Stainless steel EN 1.4301 plates were used as the working electrodes. The electrodeposition was carried out at the potentiostatic regimes as well as at the constant current densities. Raman spectra were recorded in air using SPEX 1401 spectrometer (Ar^+ laser, diameter of laser beam 10 μ, beam power at sample surface P~100 mW).

Results and discussion. Under the potentiostatic regime, the values of current density during anodic oxidation of $LiC\equiv CH$ at the electrode potential ranged from 0.2 to 1.6 V (vs. sat. Ag/AgCl) were 0.2-5.0 mA/cm^2. As a result of anodic current passing, it was observed the formation of surface film with progressively changed color (from transparent light-blue to yellow, then red and dark-brown as the quantity of electricity passed through the electrode system increased). We have found the optimal conditions for obtaining perfect carbon films: current density of about 2 mA/cm^2 and deposition time equal to 30 min. From the AFM images of this film it was seen that a compact coating of a thickness 400-600 nm was deposited along with embedded spherical inclusions of a diameter 20-40 nm.

It should be mentioned that this technique allowed us to obtain very uniform high-quality coatings of fairly large area (40 cm^2).

Raman spectra of all samples obtained under varying deposition time and current density are relatively similar. A typical result of spectrum deconvolution is the emergence of two Gaussians – a narrow (FWHM 68 cm^{-1}) G-peak at 1572 cm^{-1} and a broad (FWHM 291 cm^{-1}) peak centered at 1438 cm^{-1}, which can be considered as a result of scattering from different carbon phases (amorphous sp^3 carbon and disordered sp^2 graphite clusters) and can be deconvoluted onto two additional Gaussian peaks at 1367 cm^{-1} and 1458 cm^{-1}. The first one can be considered as conventional for DLC films D-peak attributed to disorder activated mode of sp^2-bonded crystallites; the second corresponds to the scattering from amorphous sp^3 carbon. From the Raman shift of G-peak and the ratio of D- and G-peak intensities, taking into account previously reported data [2,3], it can be estimated that the films contain approximately 65-75% of sp^3 and 35-25% of sp^2 carbon. In this respect they are rather similar to those obtained by another ways (sputtering of Ar^+ ions, etc.) and can be considered as typical DLC films with somewhat higher content of amorphous carbon.

Thermal treatment of deposited DLC films at 600°C for 40 min under argon atmosphere with the specified oxygen content (about 3-5 vol. %) led to the transformation of their structure, which manifested itself in dramatic change of Raman spectra of annealed films. The initial peaks in the spectrum of deposited film completely disappeared after annealing; instead, one sharply defined peak with rather small FWHM (24 cm^{-1}) appeared at 1324 cm^{-1}. This Raman spectrum is attributable to the formation of diamond phase. The observed peak is slightly shifted to the low-frequency field as compared to that of natural diamond (1332 cm^{-1}). This is attributable to the nanocrystalline structure of obtained diamond films (in particular, it is known that Raman peak of diamond clusters being as small as 5 nm is shifted by approx. 10 cm^{-1} to the low-frequency field in comparison with the peak of natural diamond [4]).

Conclusion. In the course of this investigation we have demonstrated the possibility of electrochemical deposition of high-quality diamond-like carbon films at very mild conditions conventional for the classical electrochemical processes (rather low values of potentials and currents, room temperature, etc.). These films consist largely (by ~75%) of specific form of amorphous sp^3 carbon with the fragments of sp^2 phase, which provide the electric conductivity of the film sufficient for its electrochemical growth. Such carbon films can serve as diamond precursor and transforms after their thermal treatment into practically pure nanocrystalline diamond.

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