Raman and EPR spectroscopic studies of chromium-doped diamond-like carbon films

Dariya Savchenko[a,b,*], Vladimir Vorlíček[b], Andrey Prokhorov[b], Ekaterina Kalabukhova[c], Jan Lančok[b], Miroslav Jelínek[b]

[a] National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", pr. Peremohy 37, Kyiv 03056, Ukraine
[b] Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, Prague 182 21, Czech Republic
[c] V.E. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, pr. Nauky 41, Kyiv 03028, Ukraine

ARTICLE INFO

ABSTRACT

The diamond-like carbon (Cr-free DLC) and chromium-doped DLC (Cr doped-DLC) films prepared by a hybrid technology using a combination of pulsed laser deposition and magnetron sputtering were studied by Raman and electron paramagnetic resonance (EPR) spectroscopy. Raman spectra are dominated by the well-known carbon (D/G) band. The intensity ratio of the D/G bands was found to increase with the increase of the Cr content. Careful elimination of the substrate-related (SiO_2) peaks enabled us to identify new weak features attributable to the presence of the C−Cr bonds. Two EPR signals were observed in Cr-free and Cr-doped DLC films. The EPR signal at $g = 2.0025(3)$ was attributed to the sp^2 coordinated carbon-related defect (CRD) and the second EPR signal at $g = 2.0064$ was assigned to the P_{b0} interface defect which may appear due to the formation of the oxidized Si on the interface of the DLC film and SiO_2 substrate. The observed temperature behavior of the CRD EPR signal *g*-factor in Cr free DLC films was described by the model of exchange coupled two spin systems (localized defects and conduction electrons) in the bottleneck regime. From the temperature dependence of the linewidth and integral intensity of the CRD EPR signal it was concluded that ferromagnetic ordering occurs in the spin system with exchange constant of $J = 0.069$ meV. The spin density of the CRD was found to be significantly decreased in Cr-doped DLC films, possibly due to the formation of the C−Cr bonds. The observed change of the CRD lineshape from Lorentzian in Cr free DLC films to Gaussian in Cr-doped DLC films indicates that there is a superhyperfine coupling between unpaired spins of the CRD and surrounding Cr nuclei.

1. Introduction

The diamond-like carbon (DLC) films have recently attracted great interest owing to their excellent physical and chemical properties like extreme mechanical hardness, high wear resistance, high thermal conductivity, high chemical inertness, good biocompatibility and optical transparency in the infrared region [1–3]. DLC represents a metastable form of amorphous carbon (*a*-C) consisting of a network of sp^3 and sp^2 bonded carbon atoms. Properties of DLC layers are influenced by the sp^3/sp^2 bond ratio and by the concentration of dopants, such as silicon, fluorine, nitrogen, metal and metal carbides in the layers [4].

DLC thin films are frequently used for coating implants [5]. However, the practical applications of DLC films have been limited because they have poor layer adhesion to metal implants. One of the ways to overcome this problem and improve the mechanical and tribological properties of DLC is to use the doped DLC layers [6,7].

Dopants in DLC layers can change the hardness, the coefficient of friction, the surface roughness, the adhesion, and even the biocompatibility and medical properties. Especially metal-doped diamond-like carbon films have superior toughness, thermal stability, excellent tribological properties, as well as relatively lower residual stresses than that of pure DLC films [8]. When the concentration of the doped metal becomes high enough, the metal atoms incorporated into the DLC matrix can form nanoclusters or bond with carbon atoms, which significantly affect the microstructure and properties of the DLC films.

Usually, DLC layers are doped with metallic elements like Cr [9], Ti [10], W [11], Ag and Cu, which can improve the adhesion of DLC films and thus reducing the risk of layer cracking and separation from the substrate.

The metals can form either metallic clusters dissolved in DLC films or metal carbide phase embedding in the amorphous carbon matrix, which are able to stabilize the film structure and to relax the internal

stresses in the films [12]. The formation of the metal carbide phase depends on the doped metal solubility in the DLC matrix and deposition technique used [13].

Chromium (Cr) doping is often used for improving the performance of the layers because Cr possesses an attractive combination of such properties as corrosion and wear resistance [13]. In addition, DLC:Cr films are characterized by lower residual stress than pure DLC, which results in better adherence to the substrate [14].

The investigation of the Cr-DLC films obtained by a hybrid physical vapor deposition/plasma-enhanced chemical vapor deposition process was shown that Cr-DLC films with low Cr content had similar micro-structure characteristics with those of pure DLC films, while the films with high Cr content exhibited a composite structure with carbide phase embedding in the DLC phase [9].

In this work, we examine the DLC and Cr-DLC films using micro-Raman and electron paramagnetic resonance (EPR) spectroscopy with the aim to establish the influence of Cr doping on the carbon atom hybridization (sp^2 and or sp^3), on the structural arrangement of the atoms in the films and on the defects formed in DLC films. The Raman scattering results indicate that the carbon sp^3/sp^2 ratio decreased with the Cr concentration and the incorporation of Cr atoms results in the formation of chromium carbides. The paramagnetic defect, which was observed in DLC films, was attributed to the carbon-related defect (CRD). It was found that the spin density of the CRD significantly decreases in Cr-doped DLC films. The model of exchange-coupled two spin systems (localized defects and conduction electrons) in the bottleneck regime was applied to explain the observed temperature behavior of the CRD EPR signal in Cr free DLC films. Analysis of the CRD lineshape indicates that there is a superhyperfine coupling between CRD and surrounding Cr nuclei in Cr-doped DLC films.

2. Material and methods

The Cr-DLC films (~100 nm thickness) deposited on SiO_2 substrates were prepared by a hybrid technology using a combination of pulsed laser deposition and magnetron sputtering using graphite target [15–17]. The Cr content varied from 1 at.% to 12 at.% (measured by wavelength dispersive spectroscopy).

The micro-Raman measurements were performed with three different excitations: 633 nm (He-Ne laser), 514.5 nm and 488 nm (Ar laser), respectively. The Renishaw Ramascope, Model 1000 and Renishaw InVia Spectrometer equipped with the objectives with the 50× magnification were used. The measurements were performed at room temperature in the backscattering configuration. The polarization of the scattered light was not analyzed. It is well known that the *a*-C films are very sensitive to the exciting laser beam and may be readily annealed when the incident power density exceeds some limit (which depends on the type of the film) [18]. Therefore, care must be paid to the experimental conditions to avoid the unwanted distortion of the results, especially in such case, when the thermal conductivity of the substrate is low. Starting the measurement of each sample, its sensitivity to the illumination was tested and the intensity of the incident beam was then kept low enough to avoid the unwanted annealing.

For all the lasers used, the maximum power (100%) impinging the sample is between 2 and 3 mW; with the typical focus diameter (~3 μm) the corresponding power density was below 3.5×10^4 W·cm^{-2} for 100%. Our measurements were typically carried out with 10 or 5% (i.e. below 3.5×10^3 W·cm^{-2}). This is the "safe region" even for *a*-C:H films [18]. The Raman spectra were fitted using FITYK 0.9.8 software [19] after the baseline correction.

The continuous wave EPR experiments were carried out in the temperature range from 298 K to 5 K on Bruker ELEXSYS E580 spectrometer using the ER 4122 SHQE SuperX High-Q cavity at X-band ($\nu \approx 9.42$ GHz). The EPR spectra simulation was performed using EasySpin 5.0.1. software package [20].
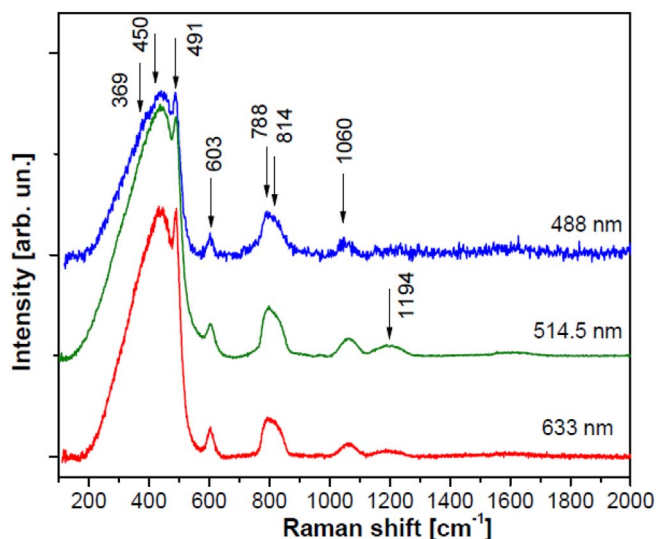

Fig. 1. The Raman spectra measured in the initial SiO_2 substrate under excitation with 488 nm, 514.5 nm and 633 nm.

3. Results and discussion

3.1. Raman spectroscopy results

With respect to the transparency of most of the films mentioned above, the knowledge of the spectrum of the bare SiO_2 substrate is very important. For all the exciting lasers, these Raman spectra are displayed in the Fig. 1. The key feature of the Raman spectrum of fused silica is a broad band centered at around 450 cm^{-1}, attributed to the Si−O−Si bond rocking and bending in SiO_4 tetrahedra. The two smaller bands at 491 cm^{-1} and 603 cm^{-1} should be attributed to three- and four-member siloxane rings, respectively, in the silica network. The bands at 788 cm^{-1} and 814 cm^{-1} can be related to Si−O stretching modes [21].

Fig. 2 shows the Raman spectra measured in the DLC and DLC + 12%Cr films under different laser excitation with 488 nm, 514.5 nm, and 633 nm. The simulated spectrum components are shown as well. Owing to the transparency of the film, also the features from the substrate were observed in Raman spectra measured on DLC film. They are marked by asterisks. Note that the transparency of the film decreases considerably when the exciting wavelength becomes shorter.

It can be seen from Fig. 2 that the Raman spectra are dominated by a broad band (between ~900 and 1800 cm^{-1}) typical of *a*-C films. We have found that a very good fit may be achieved by decomposing this band into three Gaussian components. In fact, the problem of the proper fitting has been widely discussed. The decomposition of the observed D/G band into two components (mainly Gaussians) was now and then both advocated [22] and questioned [23]. It is beyond any doubt that introducing properly more components results in better fits. However, a serious issue presents the interpretation of the additional components (cf., e.g., the recent detailed discussions in [24,25]). On the other hand, many useful empirical links relating the parameters from the two-Gaussian fits (mainly the I_D/I_G intensity ratio and the G-band width (FWHM) to various optical, bonding, and mechanical characteristics were developed (see, e.g., [22,26,27]).

The band in the range of 1365–1405 cm^{-1} is the so-called D band associated with the breathing vibrations of the (graphitic) rings, as well as with the finite dimensions of the graphite domain size, induced by grain boundaries and/or imperfections. The band in the range of 1525–1570 cm^{-1} is the G-band caused by the C(sp^2)-C vibrations. Contrary to the D feature reflecting just the vibrations in the rings, the G mode probes both the (sp^2) rings and chains [26]. A weak broad feature at 1070–1110 cm^{-1} can be identified rather with the density of states (DOS) related feature, which is observed also in graphite [28],