Paper

Investigations of electron emission from DLC thin films deposited by means of RF PCVD at various self-bias voltages

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Abstract— The aim of this paper is to report the results of field emission experiments on undoped, flat diamond-like carbon (DLC) thin films deposited at various self-bias voltages using radio frequency plasma chemical vapor deposition (RF PCVD) technique. It has been observed that the emission properties improve when the absolute value of self-bias voltage becomes higher, e.g., the turn-on field value decreases. The correlation between electron field emission and sp^2 content in these films showed improvement of electron emission properties of DLC films for higher amount of sp^2 phase.

Keywords— DLC, RF PCVD, Raman spectroscopy, turn-on field, electron emission, effective work function.

1. Introduction

Carbon-based materials grown by chemical vapor deposition (CVD) technique, which contain both diamond and non-diamond components, have been shown to have excellent field emission properties. It is supposed that the significant electron emission from diamond-like carbon (DLC) films may be caused by low positive or even negative electron affinity (NEA) [1–4]. Diamond-like carbon films are also known to have a high ratio of tetrahedral C-C sp^3 bonds to trigonal C-C sp^2 bonds. As a result, they have extreme physical hardness, high resistance and good adhesion to various substrates. The DLC coatings are also chemically inert. These properties make DLC a useful material for a wide variety of applications, especially as the material for field emitters.

In this paper, we present the results of investigation of electron emission properties of flat diamond-like carbon films synthesized by radio frequency plasma chemical vapor deposition (RF PCVD) method at various self-bias voltages. We estimated the influence of the structure of carbon films on the field emission. We also considered the role of the sp^2 bonds in electron emission effect.

In order to understand the role of the graphite content in diamond-like carbon films, the Raman spectroscopy (RS) was used. The scanning electron microscopy (SEM) was used to examine the surface microstructure of investigated carbon layers.

2. Experimental

Diamond-like carbon films were manufactured by RF PCVD, 13.56 MHz, process using methane as a carbon precursor. The coating deposition took place with the applied negative self-bias voltage of cathode from -60 V to -300 V. The gas pressure in the reactor chamber was about 26 Pa. As the substrate for DLC coatings, n-type flat silicon wafers ($< 0.002\ \Omega$cm) were used. The thickness of DLC films was less than 100 nm.

Figure 1 shows the image of typical surface morphology of examined carbon films. The amorphous DLC films had smooth, uniform surfaces which did not show any microcrystalline features. Both the SEM micrographs and Raman spectra proved that the investigated films were typical diamond-like layers of good quality having no detectable mechanical imperfections.

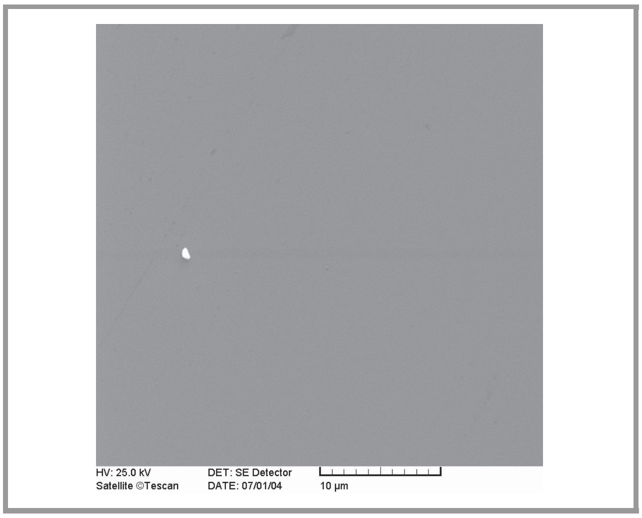

Fig. 1. The SEM micrograph of the smooth surface of a DLC film deposited on a flat silicon substrate by means of RF PCVD.

The structure of DLC films was evaluated using Raman spectroscopy. The Raman spectra were recorded at room temperature in back scattering geometry using Jobin-Yvon T64000 Raman micro-spectrometer. The instrument was equipped with a microscope whose focal spot diameter was $\sim 1.5\ \mu$m and 514.5 nm line from Argon laser was used for excitation. The spectral resolution was set below 2 cm^{-1}.

Scanning electron microscopy (SEM, Hitachi S 3000 N) examination was carried out before and after emission current measurements to bring out the state of surface morphology.

The emissive characteristics of the samples were measured in oil-free vacuum of the order of 10^{-5} Pa using diode configuration. The stainless-steel ball anode with the diameter of 5 mm was placed at a distance of $\sim 15\ \mu$m from the cathode surface. The voltage in the range from 50 V to 2500 V was applied between the electrodes during the emission measurements. The electron field emission properties were analyzed using the Fowler-Nordheim (F-N) theory [5].

3. Results and discussion

The electron emission characteristics were taken for DLC films deposited on flat n-type Si substrates. The dependence of the emission current (I) on the applied electrical field (E) for the DLC films deposited at voltages -60 V, -120 V and -300 V is shown in Fig. 2.

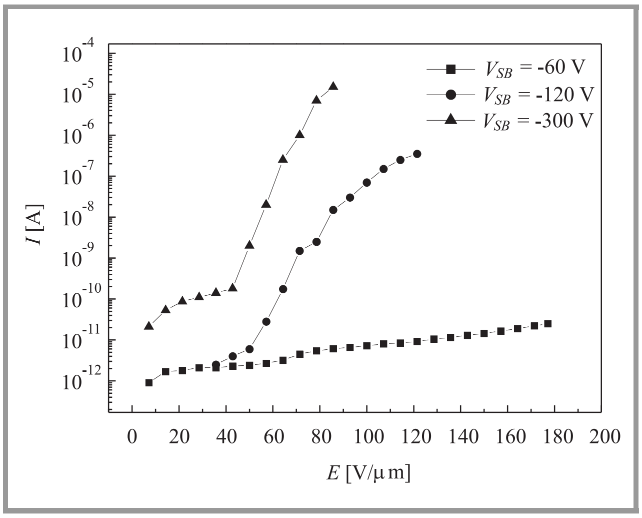

Fig. 2. Emission current I versus electric field E for DLC films deposited onto flat n-type Si substrates at various negative self-bias voltages (V_{SB}).

It can be seen that $DLC_{-60\,V}$ characteristics differ significantly from those of DLC films deposited at higher self-bias voltages. In the range about $50\ V/\mu m - 180\ V/\mu m$ the emission current for $DLC_{-60\,V}$ was very low in comparison with $DLC_{-120\,V}$ and $DLC_{-300\,V}$, for which the values of emission currents were several orders of magnitude higher. These results indicate that DLC films deposited at high self-bias voltages should have better field emission properties. The recorded *I-E* data of DLC specimens were used to generate F-N plots shown in Fig. 3.

The results of electron emission were analyzed using the F-N model. If the electron emission is controlled by the tunneling mechanism, the F-N plot: ln (I/E^2) versus $1/E$ presents almost straight line with negative slope giving reliable test of emission mechanism. Field emission properties were characterized by the parameters such as turn-on field and effective work function. The turn-on field indicates the beginning of the cold electron emission current, i.e., the state when the emission, with increasing electric field, begins to overwhelm the thermionic emission current and leakage currents. The turn-on field was defined by the intersection of two straight lines extrapolated from the low-voltage (thermionic and leakage currents) segment, and high-voltage (cold emission current) segment of the F-N plots (Fig. 3) [6].

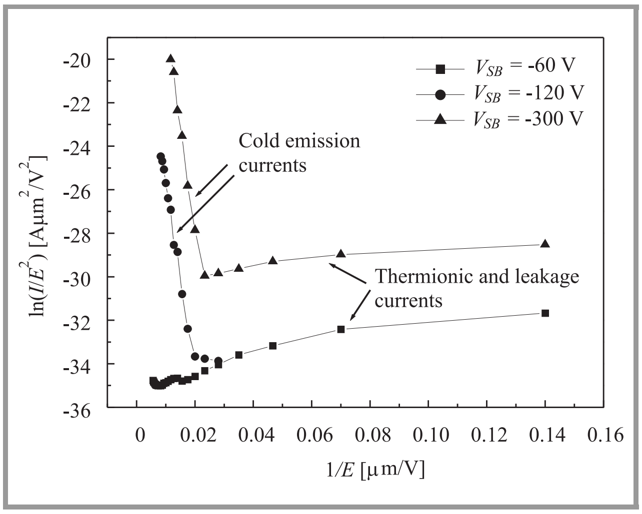

Fig. 3. The *I-E* data in the F-N system.

The effective work function φ_{ef} can be deduced from the F-N plots in cold emission region (Fig. 4) where its slope is in proportion to the ratio of the work function φ and field enhancement factor $\beta^{2/3} (\varphi_{ef} = \varphi/\beta^{2/3})$.

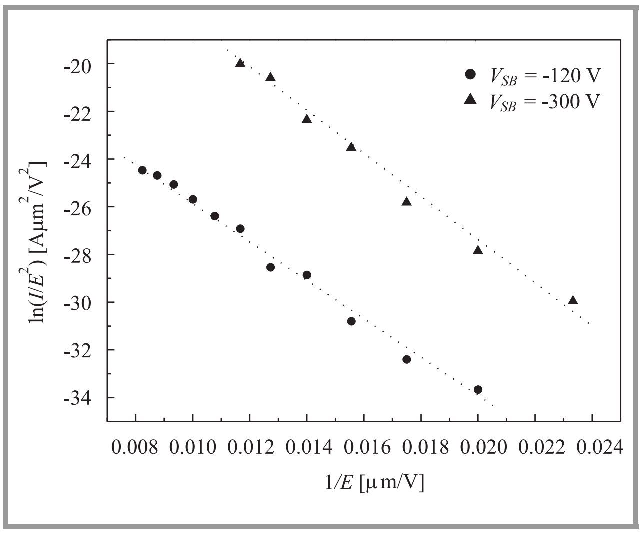

Fig. 4. The F-N plot of cold electron emission current for DLC films deposited with $V_{SB} = -120$ V and $V_{SB} = -300$ V.

We assume that for such flat and smooth surfaces as investigated DLC films the field enhancement factor β is equal to one. As it is seen in Fig. 3, the $DLC_{-60\,V}$ film does not show any field emission of electrons in the testing range of electric field. Table 1 collects the emissive parameters for the investigated samples. As we can see in Table 1 the values of emissive parameters for $DLC_{-120\,V}$ and $DLC_{-300\,V}$ coatings do not vary significantly.

Table 1
The turn-on field and the effective work function for the investigated films

Sample	Type of silicon substrate	Negative self-bias voltage V_{SB} [V]	Turn-on field E_{t-on} [V/μm]	Effective work function [eV]
$DLC_{-60\,V}$	n-type, flat substrate	−60	–	–
$DLC_{-120\,V}$		−120	50	0.246
$DLC_{-300\,V}$		−300	42	0.257

The values of the effective work function seem to be too low if we take into account the gap width of DLC films (between 1 eV and 3 eV usually). This may be due to the assumption $\beta = 1$, which may be unjustified for DLC films with non-homogeneous conduction. The emission turn-on field for the sample $DLC_{-300\,V}$ is slightly lowers than the value E_{t-on} for the sample $DLC_{-120\,V}$. Although the turn-on field values for those samples were close, the electron emission from $DLC_{-300\,V}$ sample was more efficient process, as it is shown in Fig. 2. The emission current ($6 \cdot 10^{-12}$ A) for $DLC_{-120\,V}$ film was three orders of magnitude smaller in comparison with $DLC_{-300\,V}$ sample one ($2 \cdot 10^{-9}$ A) for the same electric field 50 V/μm.

The mechanism of electron emission from DLC films is still not clear, but the obtained results may indicate that at higher self-bias voltages the increasing amount of sp^2 phase improves the electron emission properties.

As Cui *et al.* [7] reported the graphite phase is a necessary requirement for electron emission, because it provides the emission sites. One should remember that results of many previous investigations showed that the electrical conductivity of DLC films is much higher than the conductivity of polycrystalline diamond films [8, 9]. It may be suggested that cold field emission from various carbon structures can be enhanced by a system of better conducting micro-channels related to sp^2 phase [10]. The structural investigations of DLC samples prove that the amount of sp^2 phase increases with increasing value of the self-bias voltage [8], which confirms the influence of sp^2 phase on field emission properties of DLC films.

In order to identify diamond and graphite phases in the investigated carbon layers, Raman spectroscopy was used. The Raman spectra of diamond-like carbon films deposited at various bias voltages are shown in Fig. 5. An asymmetric Raman spectrum composed of the graphitic band (*G*) at about 1550 cm^{-1} and the disorder band (*D*) between 1200 cm^{-1} and 1360 cm^{-1} was obtained for each investigated DLC film. Those spectra are typical for this kind of material and confirm the amorphous structure of these layers.

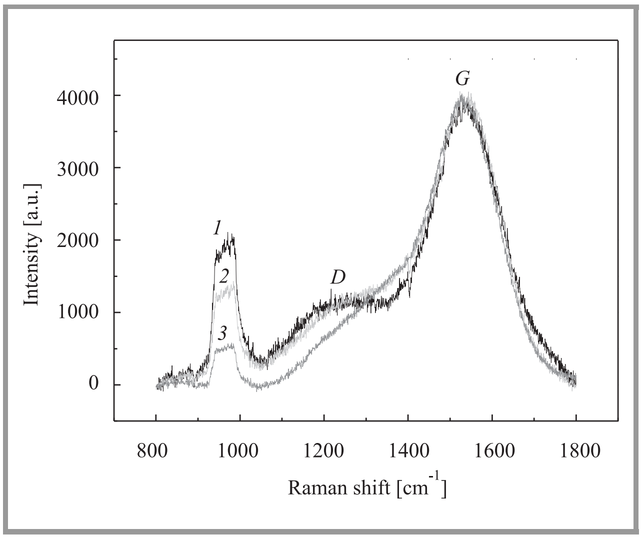

Fig. 5. Typical Raman spectra of DLC films obtained at $V_{SB} = -60$ V (curve *1*), $V_{SB} = -120$ V (curve *2*) and at $V_{SB} = -300$ V (curve *3*).

The Raman results indicated that the structure of DLC film deposited in high self-bias voltage (e.g., −300 V) differ slightly from the structure of the layer obtained at lower negative bias voltage (e.g., −60 V). The Raman spectra for those layers allowed us to assume that the disordered state (band *D*) was reduced with an increase of the absolute value of negative self-bias voltage during DLC films deposition. The decrease of the band *D* might indicate that the density of the sp^2 bonded carbon phase increases in the films.

The investigated carbon films are amorphous with the coexistence of graphite-like and diamond-like phase, the amount of which depends on the conditions of the RF PCVD process.

4. Conclusion

This work reports the results of a series of field emission experiments on amorphous DLC films deposited using RF PCVD. The investigations indicate that diamond-like carbon coatings on the silicon substrates show the ability to emit electrons from their surface. The deposition conditions of RF PCVD are of significant importance for the electron emission. The emission current-voltage characteristics show a good fit to the Fowler-Nordheim theory. The values of emission turn-on fields are between 40 V/μm and 50 V/μm for DLC films deposited at high negative self-bias voltages. There was no possibility to determine the turn-on field and the effective work function for the $DLC_{-60\,V}$ sample due to the domination of thermionic and leakage currents in the investigated range of the electric field. Samples $DLC_{-120\,V}$ and $DLC_{-300\,V}$ showed relatively low values of effective work function and were characterized by good emissive properties. The effect of sp^2 content on the *I-E* and F-N plots of DLC films was discussed. The electron emission was probably associated with the coexistence of graphite-like and diamond-like phases in DLC amorphous films. The results indicate that carbon-based films with good emissive properties can be obtained by suitable choice of the parameters of the RF PCVD process.

Acknowledgments

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