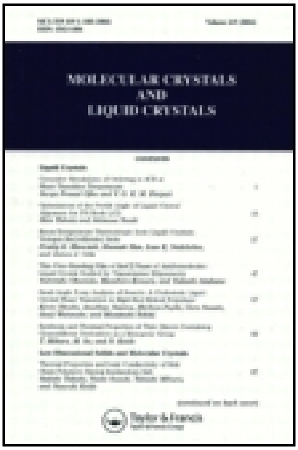

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Electron Emitting Nanostructures of Carbon+Pd System

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Electron Emitting Nanostructures of Carbon+Pd System

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A system of nanometer sized Pd crystals in fullerenes was grown by thermal deposition of fullerenes C_{60}/C_{70} mixture (C_{60}:C_{70}ratio was 8:2) and Pd organic compound from two separated sources. Films were deposited on the various substrate (fuse silica, copper band, molybdenum band and semiconducting Si). Obtained films were studied by TEM, ED, SEM and ESCA methods showing that films are composed of 2.5nm Pd clusters situated in fullerenes matrix. The bias voltage applied along the film caused the creation of electrical conductivity paths. After the formation of electrical conductivity path electron emission was observed for film (on fused silica) placed in diode system. These paths were formed of the nanometer sized Pd crystals. As a result of such structural changes we observed enhanced field emission from the film

Keywords: films; palladium; nanostructures; fullerenes; electron emission

INTRODUCTION

Field emission of electrons from various carbon films can occur at fields as low as few V/μm. For example for polycrystalline diamond film emission current of 10^{-10} A/cm^2 at the field of 6 V/μm was observed [1]. Some doped carbon materials can achieve emission at even 4 V/μm [2]. For example nitrogenation of carbon materials was investigated to show that nitrogen acts as n-type dopant [3,4]. In other technologies one searches for inhomogeneous and rough film to enhanced field emission.

We present the results of investigation of the influence of structural changes undergoing in consequence of the introducing electric field acting along the film on the intensity of electron emission current. We show that it is possible to obtain the emission current of 10^{-8} A/cm^2 at the field of 1V/μm.

EXPERIMENTAL

Investigated films were obtained by thermal deposition from two sources containing C_{60}/C_{70} mixture and Pd organic compound. C_{60}/C_{70} mixture (8:2 weight ratio) and Pd compound were placed into separated Ta boats. They were heated (up to 573K) and evacuated to 10^{-5}Torr for two hours before the deposition process. The substrates (Cu, Mo bands, n-Si and fused silica) were degreased before including them into the vacuum chamber. The deposition process was carried out under the pressure of 10^{-5}Torr and at the temperature of 330-340K (the temperature measured on the surface of the substrate).

Obtained films contained ~60wt% of Pd. Pd contents were determined by energy dispersive spectrometry (EDS) and chemical analysis. All results of chemical compound analysis were calculated by full standards method with ZAF (mass number, absorption and fluorescence coefficients) corrections. Scanning electron microscopy (SEM) was performed with scanning microscope operating at 20kV accelerating voltage and $3.x10^{-9}$ A probe current. The electron transmission microscopy (TEM) studies were performed with transmission electron microscope operating at 200kV incident beam energy. The samples were moved from the layer directly onto 400 or 1000 mesh copper microscope grids. X-ray photoelectron spectra (XPS) were acquired in ESCALAB 210 spectrometer (at pressure of 10^{-10} Torr). XPS measurements were performed for initial C_{60}/C_{70}+Pd film before and after cleaning it with Ar^+ ion beam.

The electron emission measurements were performed with the diode system presented in fig.1. The "point" electrode a spherical shape with active surface ~1mm^2. The anode-cathode distance was 100μm. The anode-cathode voltage (U_a) was changed within the limits 0-4kV DC and the bias voltage applied along the film (U_k) was changed within the limits 0-100V DC. During the measurements of U-I characteristics of electron emission the vacuum of ~ 10^{-5} – 10^{-6} Torr was maintained.

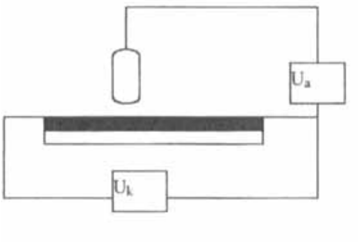

Fig.1 Schematic presentation of diode system used for electron emission measurements (film volume-marked with lines, electrodes – marked with dots)

RESULTS

TEM images of C_{60}/C_{70}+Pd film before electron emission measurements show 2.5 nm objects homogenously disperse in the observed volume (fig.2). The ED pattern of investigated area revealed diffuse rings, which can be correlated with fcc Pd with lattice constant slightly higher then for metallic Pd.

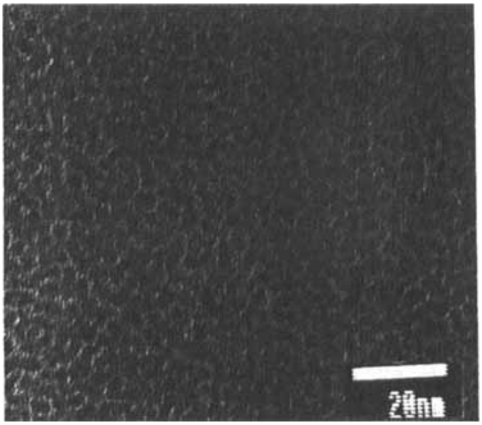

Fig.2 TEM picture of C_{60}/C_{70}+Pd film containing Pd nanonoobjects

In tab.1 XPS measurement results for binding energy region 250-400eV of C_{60}/C_{70}+Pd film before and after cleaning it with Ar^+ ion beam are presented. It appears from XPS spectra (O 1s photoelectron region) that Ar^+ removes most of oxygen atoms from film surface but it also degrades Pd cluster structure what is seen for Pd 3d doublet photoelectron region. The binding energy of the strongest Pd $3d_{5/2}$ peak (336.0eV) is higher then for metallic Pd (335.1eV [5]). The effect of changing of binding energy as the result of the formation of Pd clusters was noticed by other authors [6-7] for Pd nanoparticles of size of 1.4-80nm. The strongest C 1s peak (284.3eV) could be attributed to carbon in C_{60} [8]. Remaining peaks in the region of C 1s photoelectrons could be connected to the oxidation effect of carbon.

Tab.1 Energy of Pd 3d doublet and C 1s peaks for C_{60}/C_{70}+Pd film (before electron emission measurements) before and after Ar^+ ion beam cleaning

peak energy [eV]| integral intensity				photoelectrons	peak origin
before		after			
284.6	32910	284.3	47730	C 1s	C_{60} [8]
286.6	1530	285.8	16690		
288.1	1060	287.3	5940		
289.2	930	288.8	3090		
290.8	1100	290.3	1940		
336.7	32890	336.0	40020	Pd $3d_{5/2}$	Pd cluster of 1.4nm size [6]
338.4	7860	337.7	11320		
340.2	658	339.7	3520		
341.9	53880	341.2	27990		
343.7	8520	342.9	8300		
345.5	1080	344.9	2510		
				Pd $3d_{3/2}$	Pd cluster of 1.4nm size [6]

Electron emission of C_{60}/C_{70}+Pd film was measured in diode configuration (fig.1). When U_k bias voltage was applied and U_a bias voltage had exceeded 2kV the electron emission appeared and then, after such "break-down" it was observed as it is shown in fig.3. After the electron emission experiment we observed, by SEM as well as by TEM, formation of 10-20 nm Pd nanocrystals and creation of electrical conductivity paths composed of these Pd nanoparticles. In fig.4 TEM image of electrical conductivity path is presented. This image exhibits that the conductivity path is formed of Pd nanocrystals the size of 10-20 nm with the structure of fcc type as it could be deduced from electron diffraction pattern of such objects (see fig.4a). In fig.5

SEM image of the fragment of such "path» and the distribution of Pd in this area are shown. It could be seen that the maximum of palladium concentration takes place at the centre of the conductivity path what is consistent with TEM observation.

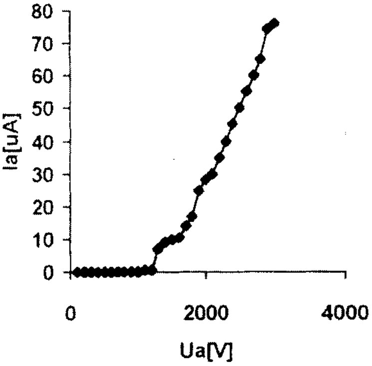

Fig.3 I-U characteristic of film after "break-down" (Ua - bias voltage anode-cathode, Ia – field emission current

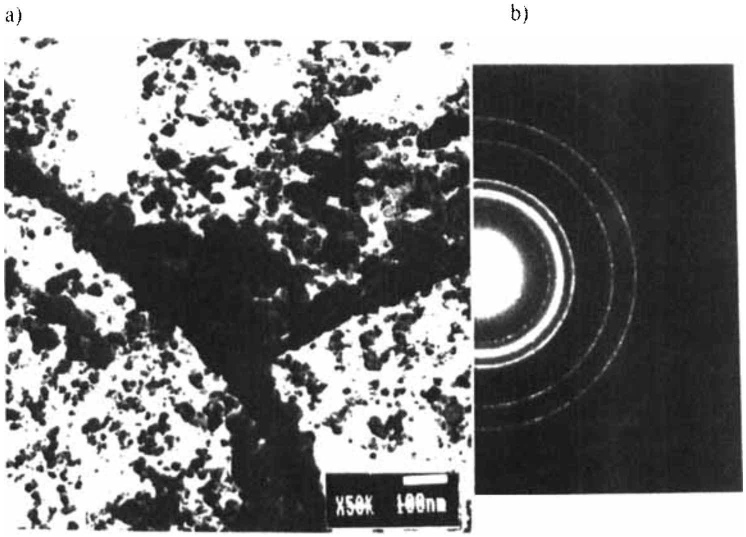

Fig.4 TEM image of electrical conductivity path a) and b) electron diffraction pattern from Pd nanocrystals

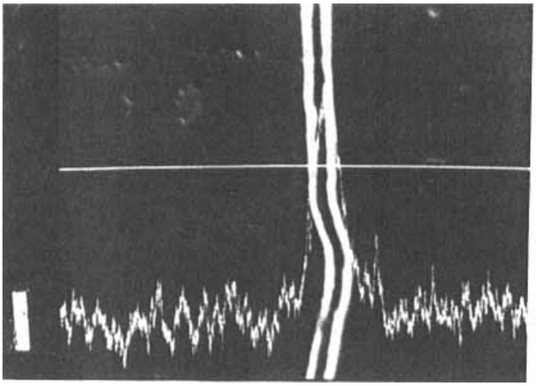

Fig.5 SEM image of electrical conductivity path with the Pd contribution analysis profile (white mark in left down corner = 1μm1)

CONCLUSIONS

We presented the method of preparation of cold electron emitting C_{60}/C_{70}+Pd films containing Pd clusters dispersed in fullerenes matrix. Structural information on cluster structure is contained in core-level binding energies and in electron diffraction patterns. We could suppose that the "break-down» is responsible for the formation of Pd nanoparticle paths. The existence of such paths enhanced electron emission.

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