SHORT COMMUNICATIONS

Stability of the C−C Covalent Bonds in Fullerenes in the Solid Body−Vapor Structure during the Thermodynamic Action by a Quasi-Pulsed Electron Beam

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Abstract—The explosive evaporation of a fullerene mixture in a vacuum of $\sim 10^{-2}$ Pa during the contraction of a 1-kW hollow electron beam into a spot on a substrate in a time of $0.1-1$ s is considered. A comparative analysis of the Raman spectra and the absorption electron spectra of a starting fullerene mixture powder and the vapor condensates shows that the evaporation of C_{60} and C_{70} fullerenes proceeds without breaking C−C covalent bonds.

INTRODUCTION

Close attention has recently been devoted to investigations in the field of spin nanoelectronics, and the processes that occur at the ferromagnetic metal−semiconductor play an important role in functional devices in this field. The authors of [1] found that the interfaces in the ferromagnet/gallium arsenide insulator ($[SiO_2]_{1-x}Co_x$/GaAs) nanomultilayer structure make it possible to substantially change the electrical resistance of the interface in a magnetic field (creation of storage medium with an ultrahigh information density). Since a fullerite is an intrinsic semiconductor with an energy gap of $1.5-2.2$ eV, it is reasonable to use fullerene coatings as a semiconductor phase to study the mechanisms of tunneling polarized electrons and the effect of a magnetic field on this process.

Among the well-known methods of deposition of fullerene coatings by thermal evaporation in vacuum [2−4], the evaporation of a fullerene powder by a beam of accelerated electrons seems to be poorly understood. Here, we can use the specific feature of a rapid action of an intense electron beam, which consists in explosive evaporation of a powder so that fullerene molecules can retain the C−C covalent bond during evaporation. This approach is also supported by the fact that the binding energy between molecules is ~ 1.86 eV [5], which is significantly lower than the binding energy between a carbon atom and a molecule (~ 6.978 eV). Moreover, electron evaporation simplifies the deposition of coatings on a surface area of

>1 m^2, since electron beams achieve extremely high specific power densities ($>10^9$ W/m^2), which are sufficient to evaporate large volume of a fullerene-containing powder.

Below, we consider the explosive evaporation of fullerenes in vacuum using a hollow electron beam, as applied to the deposition of fullerene coatings.

EXPERIMENTAL

A starting fullerene mixture was synthesized in a plasmachemical reactor at an arc discharge current frequency of 44 kHz and a pressure of 10^5 Pa [6, 7]. Fullerenes were extracted from the synthesized soot with benzene. The fullerene mixture contained (in fractions) $0.8 C_{60}$, $0.15 C_{70}$, 0.04 higher fullerenes, and 0.01 $C_{60}O$ and $C_{70}O$ oxides. A pellet (target) 20 mm in diameter and 3 mm in thickness was prepared from the fullerene mixture powder during compaction at a pressure of $32-34$ kg/cm^2.

The experimental facility for pulsed evaporation of the fullerene mixture powder contained a plasma electron source [8, 9]. Electrons were emitted by the plasma magnetron discharge with a hollow cathode. The electron current was 50 mA and the accelerating voltage was 20 kV. Accelerated electrons penetrated into an electromagnetic lens connected to an electron beam control unit [10]. A hollow electron beam was formed at the exit from the electromagnetic lens. The beam power was 10^3 W. The outside beam diameter

was 50 mm and the inside diameter was 48 mm. Electrons were projected in the form of a coaxial ring onto the target. When the beam was rapidly sharpened, its ring projection onto the surface of a graphite collector was contracted into a spot 3 mm in diameter. The target was explosively transformed into a vapor. A special-purpose gate was used to let the vapor to a substrate and to provide its condensation to form a coating. The substrate (amorphous glass) sizes were 30×30 cm.

The film thickness was measured with a MII-4 Linnik microinterferometer. Raman spectra were recorded on an RFS 100/S (Bruker) Fourier Raman spectrometer and were excited with a continuous Nd:YAG laser at a wavelength $\lambda = 1064$ nm and a power of 10 mW. The electronic absorption spectra of fullerene solutions were recorded using a two-beam spectrophotometer UVIKON 943. The coating surface morphology was studied with a SolverP47 scanning tunnel microscope, and X-ray diffraction (XRD) analysis was performed on a DRON-4 diffractometer.

Evaporation was carried out in a vacuum of 2×10^{-2} Pa. The ring imprint of an electron beam was first detected on a graphite collector and coaxially covered the periphery of an evaporated target. Although the carbon vapor pressure in the zone where accelerated electrons reached the graphite collector at a temperature of 1.7×10^3 K was low (10^{-8} Pa) [11], a gate protected the substrate from the incidence of the carbon particles evaporated from the collector. The hollow electron beam was radially compressed from the initial state at a rate of $2-20$ cm s^{-1} using a control unit. The fullerene mixture powder begins to evaporate intensely when electrons approach and touch the target along the entire perimeter. The gate is opened, and the vapor leaving the electron heating zone expands and condenses freely on the substrate to form a coating at a substrate temperature of 393 K. In a time of $0.1-1$ s, the hollow electron beam is moved to the center of the target and evaporates it intensely (explosively) [12]. When the hollow electron beam is transformed into a spot, the target evaporates fully and the gate is moved to the starting position.

RESULTS AND DISCUSSION

The coatings formed upon the explosive evaporation of a fullerene mixture powder by an electron beam have a thickness of $1-2$ μm and are brown. The coated substrate area is 0.1 m^2.

Figure 1 shows a micrograph of the coating surface: arranged spherical globules $80-100$ nm in size are visible. XRD analysis showed that the deposited films are crystalline. A crystalline structure appears in the coatings deposited onto a substrate heated to 393 K and subsequent holding at 373 K for 0.5 h in vacuum.

The resistance of the films deposited in the temperature range $80-200$ K was constant (10^{16} Ω), and this resistance decreased to 10^{14} Ω in the temperature range $210-260$ K. The deposited coatings dissolve in
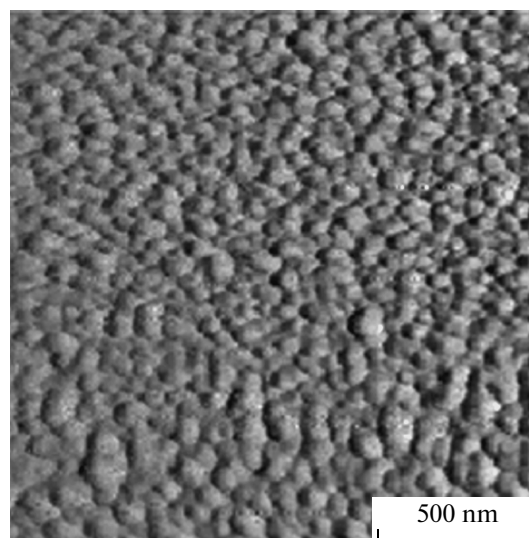

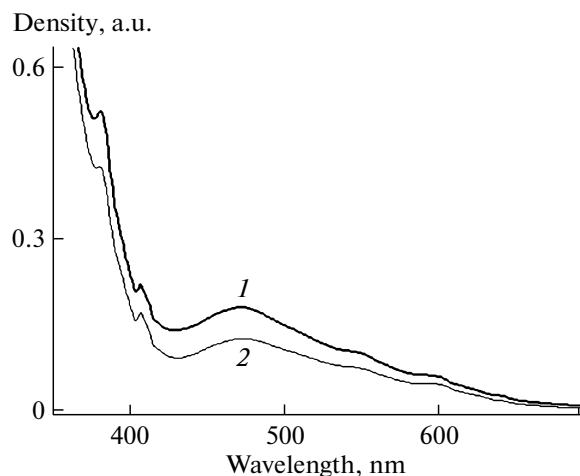**Fig. 1.** Micrograph of the coating surface relief.

Fig. 2. Electron absorption spectra of (*1*) coating and (*2*) starting fullerene mixture.

nonpolar solvents (Fig. 2), which supports the fact that the evaporation of C_{60} and C_{70} fullerenes occurs without breaking C–C covalent bonds. An analysis of Raman spectra shows that both the initial powder and the deposited films have all bands of fullerene molecule vibrations. The Raman spectrum shown in Fig. 3 has the most intense lines of C_{60} (495 cm^{-1}, 1468 cm^{-1}) and C_{70} (271 cm^{-1}) fullerenes, which demonstrates their presence in the coating. Assuming that the broad lines are related to the existence of higher fullerenes, we can conclude that the shift of these lines indicates the redistribution of the composition of higher fullerenes. This result suggests that the state of fullerenes in the coating differs from the state in the powder. The bonds between fullerene molecules and
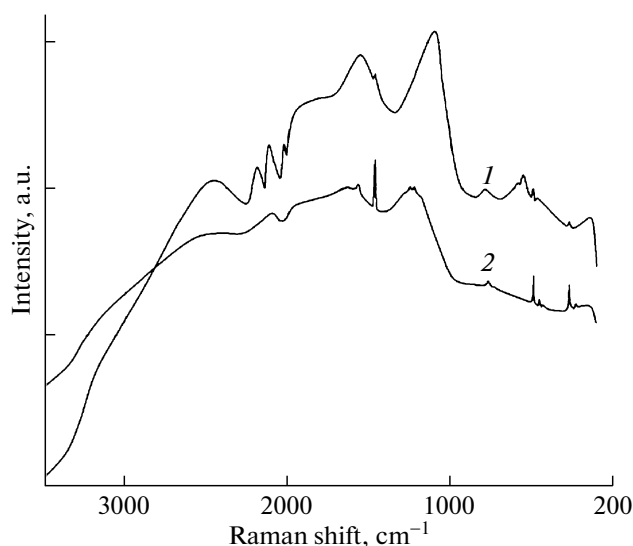
Fig. 3. Raman spectra of (*1*) coating and (*2*) starting fullerene mixture.

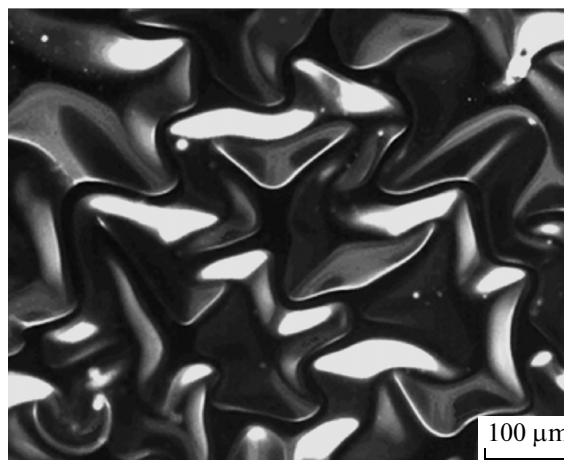**Fig. 4.** Micrograph of a coating exfoliated from the substrate.

the substrate make a significant contribution due to a small coating thickness.

It was found that the coatings are very active and sensitive to gaseous oxygen and nitrogen: they strongly change their properties in these gases and degrade. Electron-probe microanalysis showed that the films contain N and O. The presence of nitrogen and oxygen is likely to be explained by their adsorption on the film surface, which results from a high surface activity. The films exfoliate in time, which is also well explained by high sorption of chemically active gases. Figure 4 shows a micrograph of the surface of such a film. The process of destruction is completed in 24 h.

The "opening" of the carbon cages of fullerene molecules during the explosive evaporation of a fullerene mixture powder and the transfer of clusters (molecule fragments) onto the growth substrate surface with the formation of fullerene molecules via the "closure" (assembling) of carbon cages on the substrate seems not to be predominant, since no molecule fragments were detected in the coating. To support the appearance of molecule fragments and their growth (assembling) during fullerene synthesis onto a substrate, it is necessary to perform in situ experiments on the synthesis of fullerene mixtures during explosive evaporation by an electron beam using high-resolution mass spectrometry.

CONCLUSIONS

Fullerene coatings can be formed upon explosive evaporation of a fullerene mixture powder at an evaporation temperature of $>1.7 \times 10^3$ K, which is well above the fullerene sublimation temperature ($(7.23-7.73) \times 10^2$ K). The experiments performed under a

rapid action of an electron beam demonstrate that the evaporation of C_{60} and C_{70} fullerene molecules without breaking C−C covalent bonds is predominant. Such conditions of formation of fullerene coatings were achieved for the first time when a hollow electron beam was contracted into a spot on a substrate in 0.1−1 s.

Electron beams with a current of >1 A were generated at the output of an experimental plasma electron source, which opens up fresh opportunities for the deposition of fullerene coatings on a surface of >1 m^2 due to an increase in the beam power to >20 kW and, correspondingly, the quantity of an evaporated fullerene mixture powder.

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