Cathodoluminescence studies of C_{60} fullerene-based films and nanostructures

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The objects of investigation in this work are the submicron C_{60} fullerene-based films and fullerene nanostructures fabricated by electron beam lithography. The set of techniques for studying the fullerenes is extended due to attraction the spectral cathodoluminescence (CL) to either of initial fullerene films and submicron net structures with period about $0.9\,\mu$m, wall height $0.6\,\mu$m and width about $0.4\,\mu$m.

The maxima of CL spectrum of initial C_{60} films are in a good agreement with the energy-band structure of amorphous fullerene film. In turn, CL spectrum of the fullerene net structures possess both peculiarities of fullerene energy-band structure and it clearly exhibited the oscillations of spectrum with period as large as 0.08 eV. Such periodical fullerene net structures possess the properties of optical resonator on the system „fullerene net ($n = 2.3$)–air ($n = 1$)“.

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1. Infroduction

Progress in modern photonics may be achieved using new perspective materials and metods of their treatment. One of these materials are fullerenes, due to their non-linear optical properties [2]. Another advantage of fullerenes in solid state is possibility to be used as an electron resist that determines the relative technological simplicity of photonic structures based on fullerene films fabrication. Earlier it was obtained by using the *persistent* conductivity measurements the possibility of formation in fullerene C_{60} films the molecular chains, defining either of electrical and optical properties of C_{60} fullerenes [1]. In that work the direct correlation between this properties and the energy-band structure was also shown.

The equilibrium solid state of fullerene is a crystal with very weak van der Waals linkage between fullerene molecules [3,4]. An impact of electron or ultraviolet light beams cause the transitions of fullerenes to excited triplet states [2], in which molecules enter into chemical reactions between themselves. As a result, polymer complexes from fullerene molecules [5] are generated. The obtained fullerene-based material is characterized by high chemical and mechanical strength, new optical and electrical properties.

2. Samples

Fullerene films were obtained by depositing of 99.98% purity C_{60}-powder from a Knudsen-cell at 350°C on GaAs (100) monocrystaline substrates by vacuum thermal sublimation. During the deposition at a rate of 0.2 nm/s the substrates were held at room temperature and vacuum 10^{-6} Torr. The film thicknesses were varied from 200 to 600 nm. According to the results of electron-spectroscopic analysis, surface layer of films became 20 molar % oxygen saturated due to surrounding environment influence.

In our work a possibility of the photonic fullerene-based structures fabrication using electron beam impact on fullerene films were investigated. The research was performed using scanning electron microscope CamScan 4 DV100 with the acceleration voltage $E = 25-40$ kV and beam current $I = 10^{-10}-10^{-8}$ A. The time of single dot exposure by electron beam was less then 3 msec reasoning from the optimal exposure doze = 20 mC/cm^2 [6]. That corresponds to the reasonable time of the entire sample exposure. In the case of wires one should used two times shorter exposure time. To get the proper shape for the crossed wires exposure time should be varied with distance to the crossing point. The exposed films were developed with toluene during 5−30 s. The developing procedure follows immediately after the exposure to avoid depolymerization or oxidization effect. To achieve minimal geometrical size of structure elements for film thickness up to $0.6\,\mu$m the parameters of an electron beam were optimized. The best result was obtained at $E = 35$ kV and $I = 0.5 \cdot 10^{-9}$ A. When lower beam power was applied fullerene films were completely dissolved in toluene even for the very short developing time. While higher beam power leads to the formation of macro clusters in fullerene remains.

As a result the set of structures with fullerene-based wires and dots with typical sizes about 150−400 nm has been fabricated (Fig. 1, *a, b*). The shape of the obtained dots is explained by lateral function of charge distribution in C_{60}−GaAs system. This function has been found experimentally.

3. Results and discussion

The energy-band structure of amorphous fullerene film is presented in Fig. 2. The optical band gap forms for such films the value 1.6 eV.

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The cathodoluminescence spectra were measured both on initial fullerene films and on fullerene network structure with period as large as $0.9\,\mu$m, wall height as large as $0.6\,\mu$m and wall width $0.4\,\mu$m (Fig. 1, *b*). These spectra were measured under normal electron beam incidence to the plane of the structure.

On CL spectrum of initial C_{60} film one can see (Fig. 3, *a*) the maximums on energy levels 1.16 eV, the wide line around 1.5 eV and the peak on energy level 1.7 eV. These peculiarities are in a good agreement with electron transitions presented on the energy-band structure scheme (Fig. 2). In turn, CL spectrum of the fullerene net structures (Fig. 1, *b*) is also described by peculiarities of fullerene energy-band structure (Fig. 3, *b*), but at the same time it clearly exhibited the strongly enhanced multiple CL Fabry–Perot (FP) type oscillations with period about 0.08 eV.

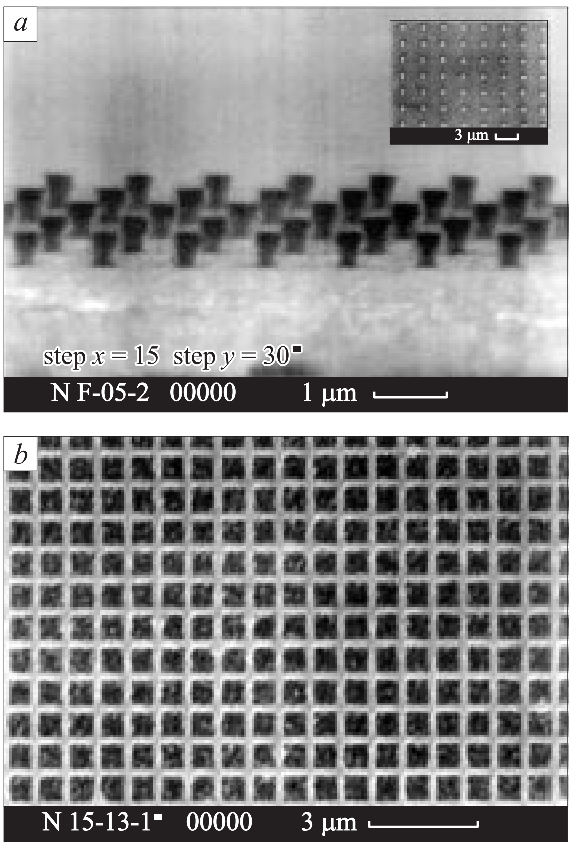

Figure 1. *a* — dots (pillars) array (inset — top view), *b* — fullerene net structure.

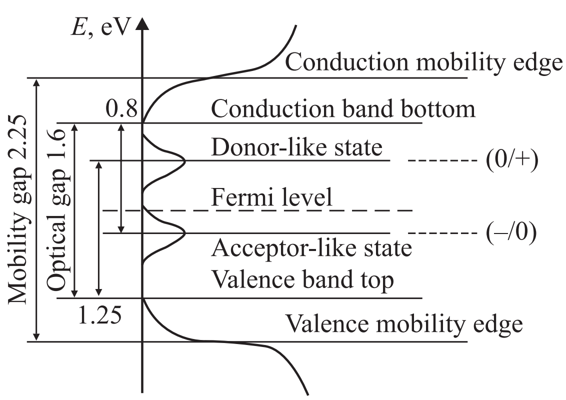

Figure 2. Energy-band structure of amorphous fullerene film [7].

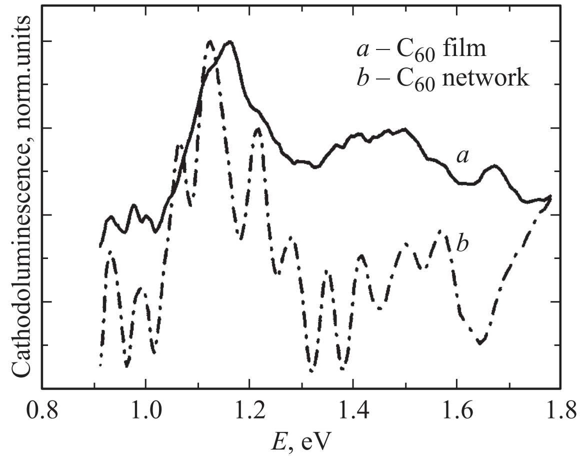

Figure 3. CL spectra: *a* — initial fullerene film, *b* — fullerene net structure.

Such periodical two-dimensional photonic crystal (PhC) structure in out-of-plane experimental configuration is known to possess with specific optical resonance properties but observation such the CL enhanced multiple oscillations of fullerene net structure (substrate–fullerene net ($n = 2.3$)–air ($n = 1$)) were made as we know at the first time. The period of CL multiple oscillations is determined by thickness of the fullerene net structure, but the intensity and FWHM ones by the ratio hole size to the lattice period. The optimal ratio selected here as about 0.3 ensures both high CL emittance and narrow line profile. Such fullerene net structure is supposed to have perspective for applications as infrared sensors of specific liquids.

4. Conclusions

Summary, it has been demonstrated the capability of the light intensity modulation near the fullerene photonic nanostructures surface.

We have shown the efficiency of the electron lithography method for successful manufacturing of the fullerene photonic nanostructures such as nanopillars and nanoholes type PhCs with high quality vertical walls. The CL enhanced multiple FP-type oscillations of fullerene net structure were observed at the first time for periodical two-dimensional PhC structure in out-of-plane configuration. Such fullerene net structures is supposed to have perspective for applications as infrared sensors of specific liquids.

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