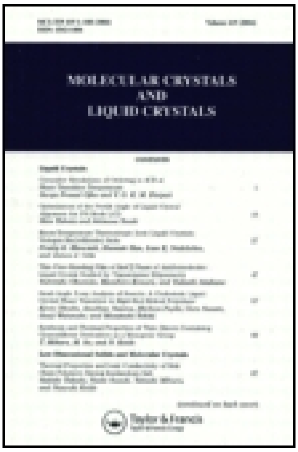

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Organic-Inorganic Nanosystem Based on Fullerene Embedded in Porous Silicon Matrix

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The structure and luminescent properties of a hybrid system based on fullerene C_{60} embedded in a porous silicon matrix have been studied. The investigation of the surface topology of a por-Si-C_{60} nanostructured layer by AFM shows clearly the incorporation of C_{60} nanocrystals inside pores of silicone. According to FTIR spectroscopy, a covalent interaction between the surface of a fullerene cluster and porous silicon takes place. This has influence on the luminescent properties of porous silicon, which is of a special interest for cathode luminescence spectra with the appearance of an additional band at $E = 3.2-3.4\,eV$. A possible mechanism of such an effect is discussed.

Keywords Cathode luminescence; fullerene; hybrid system; porous silicon; structure

Introduction

The development of silicon-based solid polymer fuel cells, light emitting diodes, sensors by means of the so-called silicon technology requires the creation of hybrid systems based on porous silicon (por-Si) and surface organic layers, among which the conjugated conducting polymers are intensively studied [1–3]. On the other hand, it was shown that the deposition of nanostructural carbon layers on the surface of porous silicon substantially (by several orders of magnitude) increases the specific surface area and significantly decreases the surface resistance of a porous material [4]. The subjects of a rising interest are the carbon clusters such as fullerenes, especially C_{60}, embedded in a porous silicon matrix [5–7].

The appearance of the luminescence of porous silicon in the visible range of the spectrum can be connected with the quantum size effects allowing the annihilation of excitons which are spatially limited (trapped) in the intermediate area [8]. On the

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other hand, the emission can be caused by the complexes of Si:O:H, H:Si:H, siloxen $Si_6H_3O_6$, and its modifications [9] formed during the etching process. The emission from porous silicon can be considered as a process of monomolecular recombination limited by the tunneling across a potential barrier or as the bimolecular process of recombination of an electron and a hole, being free or bound to an exciton [10]. The analysis of the photoluminescence (PL) excitation spectra indicates that the excitation process in embedded C_{60} molecules is completely similar to that in porous silicon [5–7]. The enhanced PL mainly arises from the radiative recombination of carriers which are formed in PS and then are transferred to C_{60} molecules. The mutual effect of two nanodimensional subsystems, porous silicon and fullerene C_{60}, on the course of the photoinduced processes in a por-Si-C_{60} composite was observed in [6]. It is demonstrated that the photoexcitation of this nanocomposite in the atmosphere of normal (triplet) molecular oxygen leads to the self-insulation of silicon nanocrystallites as a result of their oxidation by singlet oxygen species generated under the action of the excited fullerene subsystem. This repassivation of the por-Si surface leads to a significant recovery of the luminescent activity of por-Si. However, only few experimental results for the emission in por-Si-fullerene hybrid systems excited by an electron beam, namely the cathode luminescence (CL), have been obtained [1,11]. Simultaneously, the existence of CL is one of the tests for the possibility of electroluminescence in semiconductor heterostructures [12]. The excitation of the emission by an electron beam can be realized without making the special contacts on the semiconductor surface.

In the present work, the influence of fullerene embedded in a porous silicon matrix on the surface topology, molecular spectra, photo- and cathode luminescence of the por-Si – fullerene C_{60} nanostructure has been investigated.

Experimental

The porous silicon layers were formed by the etching of silicon wafers (100) with the *p*-type of conductivity in a 40% HF ethyl alcohol solution at a current density of $10\,mA \cdot cm^{-2}$ during 10–20 min. The fabrication of the por-Si-C_{60} hybrid structure was carried out by the coating of the por-Si surface by a fullerene (Aldrich, 98.5% grade) layer from a saturated fullerene solution in toluene. The molecular structure of the obtained hybrid layers was studied by FT-IR spectroscopy with an AVATAR 320N spectrophotometer in the spectral range $4000-400\,cm^{-1}$. The topology of the hybrid layer was studied by atom force microscopy (AFM) with a SZM SOLVER PRO-M microscope. Photoluminescence was excited by a pulse nitrogen laser LGI-21 ($\lambda = 337.1\,nm$), with the pulse duration $\tau_p = 20\,ns$, at a frequency of 60 Hz. Cathode luminescence was excited by a pulse electron beam with the energy $E_p = 9\,keV$, with the pulse frequency $f = 50\,Hz$, and $\tau_p = 3\,\mu s$. The current density in the electron beam $j = 150\,A/m^2$. The measurements were carried out both at room temperature and liquid nitrogen temperature.

Results and Discussion

The surface of porous silicon has the shape of vertical nanorods created due to the etching of separate places of the single silicon surface. The coating of porous silicon by fullerene not depending on the method of fullerene deposition [13] leads to forming a continuous organic layer on the silicon surface. As shown by AFM

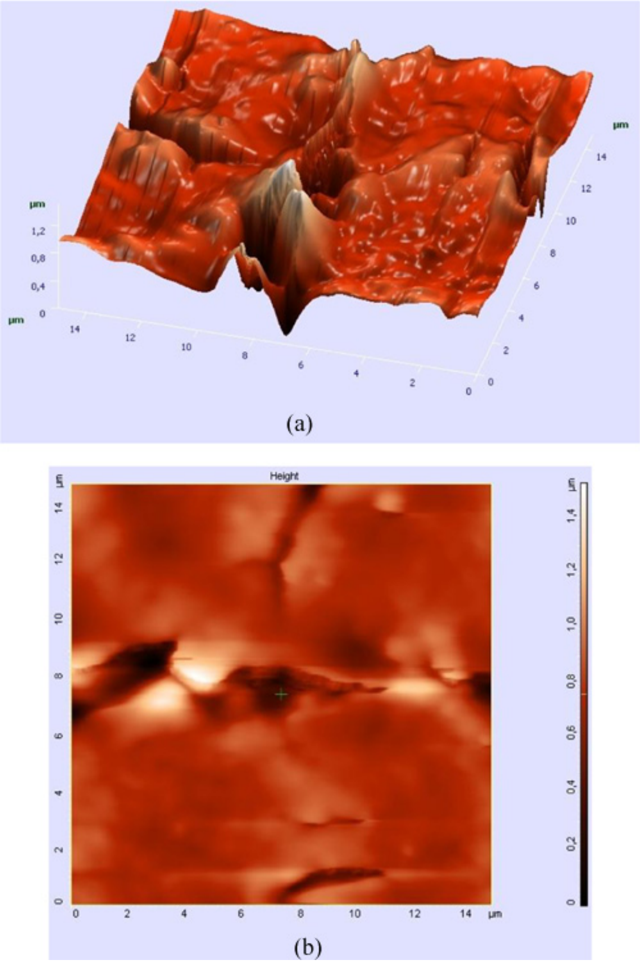


Figure 1. AFM images of (a) the surface topology of a por-Si-C_{60} hybrid layer; (b) incorporation of fullerene nanocrystals in silicon nanopores.

investigation in our experiments, the fullerene layer repeats, in overall, the relief of the porous silicon surface obtained after the electrochemical etching (Fig. 1a).

The more detailed consideration of the porous silicon surface allowed us to observe the fullerene nanocrystals incorporated into silicon nanopores (Fig. 1b).

This observation is in a good agreement with the suggestion made in [13] on the basis of Raman spectroscopy data and is the evidence of that a fullerene is in the form of nanocrystals.

A molecular structure of the por-Si – fullerene hybrid layer was studied by FT-IR spectroscopy, and its typical spectrum together with the spectrum of porous silicon is presented in Figure 2.

The surface of porous silicon obtained by the electrochemical etching of a silicon wafer in an HF alcohol solution contains various functional groups with characteristic absorption bands at 2850–3000 cm^{-1} (-OH), 2250–2100 (Si-H), 1100 cm^{-1} (Si-O-Si), 930, 620 cm^{-1} (Si-H_2, Si-F), and others (Fig. 2, curve 1).

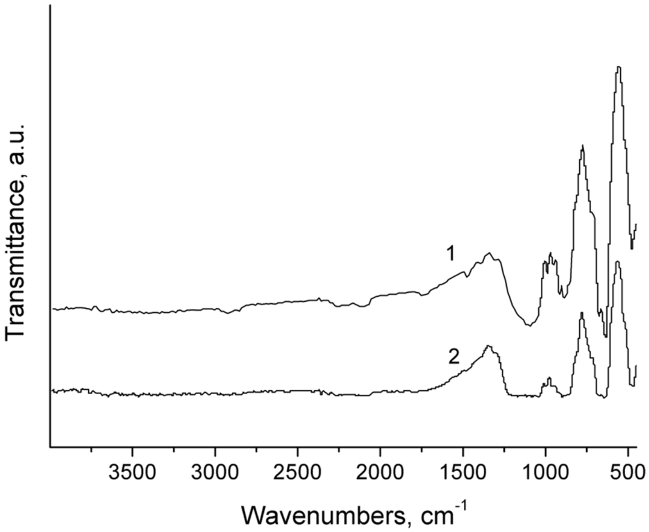


Figure 2. FTIR spectra of the porous silicon surface (1) and the hybrid nanostructure por-Si-C_{60} (2).

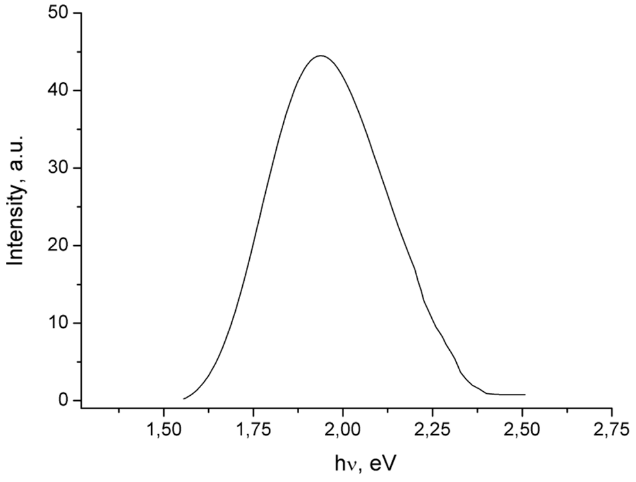
Like the FT-IR spectrum of porous silicon where the absorption bands at 1100 and 620 cm^{-1} are observed, we have found the absorption bands at 1050–1250 cm^{-1} and at 630 cm^{-1} for the por-Si-C_{60} hybrid layer (Fig. 2, curve 2). A shift of the absorption bands from 620 to 630 cm^{-1}, the redistribution of the band intensity in the range of 600−680 cm^{-1} and 850–900 cm^{-1}, and the overall decrease of the absorption in the whole spectral range indicate the possibility of an interaction between C_{60} molecules and the surface of porous silicon particles.

The existence of a covalent interaction between porous silicon and fullerene molecules can affect the luminescent properties of porous silicon [6,7]. In most investigations, such an effect is manifested only in the passivation action of a fullerene coating which become significant after the annealing of a hybrid layer in the hydrogen atmosphere [5,6]. As one can see from Figure 3, the PL spectrum of por-Si is in the spectral range of $E = 1.7$–2.3 eV with a maximum at 1.94 eV, while PL spectrum of por-Si-C_{60} is in the range of $E = 1.6$–2.9 eV with a maximum at 2.13 eV and has a complex shape.

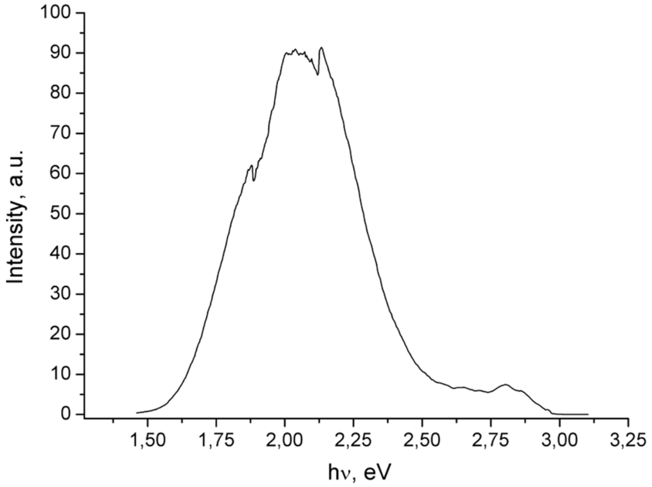
This spectrum also has a peak near $E = 2.8$ eV which is in a good agreement with PL spectra published in the literature [4]. So, in the hybrid structure, a widening of the PL spectrum and a shift of its maximum to high energies are observed.

A phenomenon of cathode luminescence (CL) in porous silicon and its heterostructure has currently a lack of study. Because a silicon single crystal does not develop any emission even at very high excitation energies and at low temperatures, the existence of a nanostructured porous layer makes it possible to excite the light emission under the action of a cathode beam [1]. We observed the cathode luminescence in porous silicon with a band maximum near 2.22 eV (Fig. 4) in a good agreement with the data described in [11].

The cathode luminescence was observed also at the electron excitation of heterostructures based on porous silicon and conducting polymers fabricated by different methods (electropolymerization, magnetron deposition, or dip coating) [1,14].



(a)



(b)

Figure 3. Spectra of photo luminescence for porous silicon (a) and the por-Si-C_{60} hybrid layer (b) at $T = 293$ K.

Furthermore, the shape of the spectrum and the character of its change in comparison with the CL spectrum of an initial por-Si sample depend on the electron and molecular structures of a polymer [1]. In the case of a por-Si-C_{60} nanostructure, the effect of fullerene embedded in a porous silicon matrix is significantly different (Fig. 4).

The magnitude of peak emission for the cathode luminescence at $E = 2.22$ eV in the presence of fullerene remains unchanged or decreases slightly (Fig. 4, insert), while an additional intense peak of “blue” emission appears at $E = 3.2$–3.4 eV. If some decrease of the peak intensity at $E = 2.22$ eV can be explained by the passivation action of fullerene molecules, the nature of the second peak is not clear.

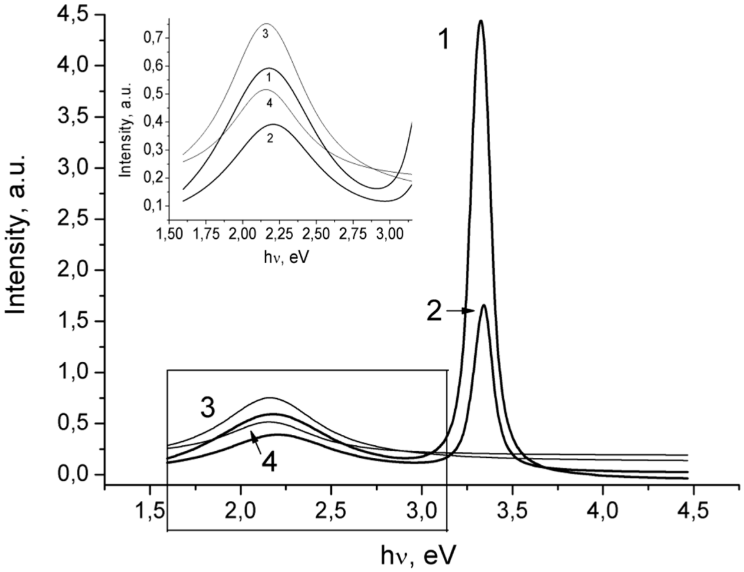


Figure 4. Spectra of cathode luminescence in the por-Si-C_{60} hybrid layer (1, 2) and in porous silicon (3, 4) at $T = 80$ K.

A "blue" emission near 420–480 nm ($E = 2.96-2.59$ eV) was observed in the process of photoexcitation of the higher fullerenes (C_{70}, C_{76}, C_{84}, C_{94}) which are covalently bound with porous Si and form fullerene-coupled por-Si systems. PL excitation spectral examinations reveal that photoexcited carriers are generated in the quantum confined nanocrystalline Si (nc-Si) cores, whereas the radiative recombination occurs at the coupled nc-Si surface [15]. The appearance of a high energetic band in the por-Si-C_{60} hybrid structure probably originates from a weakening of the action of the non-radiative recombination channels as a result of passivation of the dangling silicon bonds on por-Si surface at the deposition of fullerene clusters.

Conclusion

The fabricated porous silicon – fullerene hybrid nanostructures demonstrate a visible luminescence and the capability to a light emission under the electron beam excitation. Probably, this causes a change of the luminescent properties of porous silicon and the appearance of a long wavelength cathode emission at $E = 3.35$ eV, but its nature needs a further investigation.

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