SURFACE PHOTOVOLTAGE OF Au–C_{60}–Si STRUCTURES

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The methods of surface photovoltage, photoluminescence, AFM, and FTIR are applied to studying the Au–C_{60}–Si structure. The surface photovoltage kinetics was also investigated. It is shown that the photoluminescence and the surface photovoltage in the range 1.3–1.8 eV are caused by optical transitions with participation of singlet and triplet exciton states. It is established that the generation of surface photovoltage in the Au–C_{60}–Si structure is caused by the spatial separation of electron-hole pairs in the C_{60} film.

1. Introduction

Carbon modifications such as fullerenes of various kinds, carbon nanotubes, fullerites and other nanostructures are practically used in nanotechnology to develop new electronic and optical devices. Of special interest is the integration of these materials with the traditional silicon technology and their use as active elements of up-to-date nanoelectronic structures. For today, there already exist the successful practical applications of C_{60} films in MOS structures [1–3]. Electronic and optical properties of fullerenes were intensively investigated [4]. The band structure of C_{60} was studied using the methods of optical absorption spectroscopy [5, 6], photocurrent [7, 8], and photoluminescence [9, 10].

One of the photoelectric methods sensitive both to the electron structure and to peculiarities of the transport of charge carriers in thin films is the surface photovoltage technique. The formation of a surface photovoltage signal caused by a variation of the contact potential difference under illumination requires both the generation of electron-hole pairs and their space separation. This fact allows one to study the electron spectrum of films and peculiarities of the recombination of electron-hole pairs in them.

The aim of this work is to study the peculiarities of the recombination of electron-hole pairs in the Au–C_{60}–Si–Al structure.

2. Experimental Technique

The investigated Au–C_{60}–Si–Al structure was formed in the following way. An aluminum film 1 μm in thickness was deposited onto the back side of a crystal silicon (*c*-Si) substrate. The other polished side of the *c*-Si substrate was covered by a 350-nm-thick C_{60} layer. A semitransparent Au layer 35 nm in thickness was deposited over the C_{60} layer. The structure of the sample is presented in Fig. 1. The metal and fullerene films were deposited by the vacuum evaporation technique. The purity of metals used for the deposition amounted to 99.99% (Al or Au), whereas that of the fullerene powder was equal to 99.9% C_{60}. The pressure in the vacuum chamber approximated 10^{-5} Torr. The temperature of an evaporator containing the C_{60} powder was 450 °C, the temperature of the substrate during the evaporation was equal to 20 °C. The deposition rate of C_{60} amounted to 10 nm/s. The thickness of the deposited layer was found with the help of a calibrated optical sensor. The substrate was a passivated boron-doped plate of *p*-silicon with a specific conductivity of 7.5 Ohm·cm.

The photoluminescence of the C_{60} film deposited onto the silicon substrate was excited by an argon laser LGN-402 (λ = 488 nm). The power density of the exciting radiation amounted to 6 W/cm^2. The spectra were measured at room temperature. Their intensity was propor-

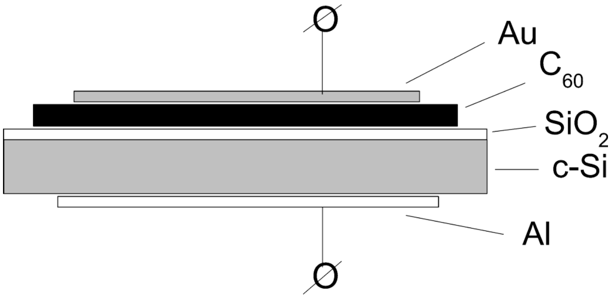

Fig. 1. Structure of the Au–C_{60}–Si–Al sample

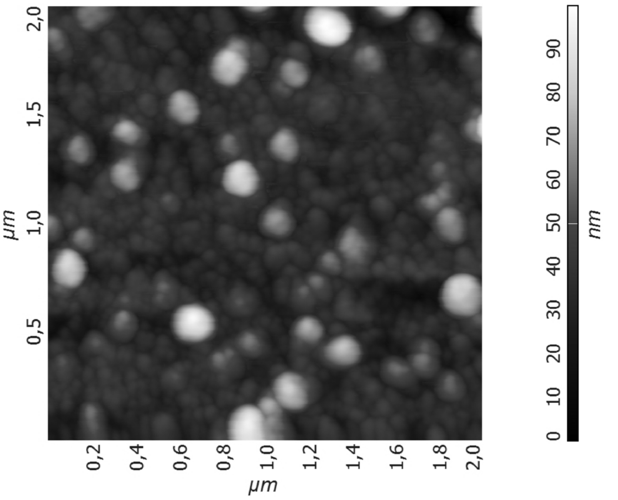

Fig. 2. Surface topology of the C_{60} film

tional to the number of quanta per unit spectral interval. The spectral width of the gap did not exceed 7 nm.

The infrared (FTIR) transmission spectra were obtained with the help of a PerkinElmer FT-IR System spectrum BX. The transmission spectra of the C_{60} film deposited onto *c*-Si were registered before the deposition of the Au and Al layers in the process of formation of the Au–C_{60}–Si–Al structure.

The surface topology of the C_{60} film was investigated with the help of an atomic force microscope (AFM) NT-MDT NTEGRA Prima Scanning Probe Microscope in the semicontact mode.

The photovoltage kinetics was studied by the example of the Au–C_{60}–Si–Al structure excited by semiconductor lasers with various wavelengths: $\lambda_1 = 540$ nm, $\lambda_2 = 650$ nm, and $\lambda_3 = 850$ nm. The laser radiation power was close to 100 mW. The lasers were supplied by the rectangular pulsed current generated by a GFG 8580 functional generator. The photovoltage signal was registered between the Au and Al layers with the help of a Bordo 221 digital oscilloscope.

3. Results and Their Discussion

As one can see from the AFM topogram shown in Fig. 2, the surface of the C_{60} film contains small grains with a mean diameter close to 70 nm. The mean-square roughness of the surface did not exceed 12 nm, which testifies to the fact that these grains must be clusters representing groups of nanocrystalline particles formed due to the compaction of fullerene molecules.

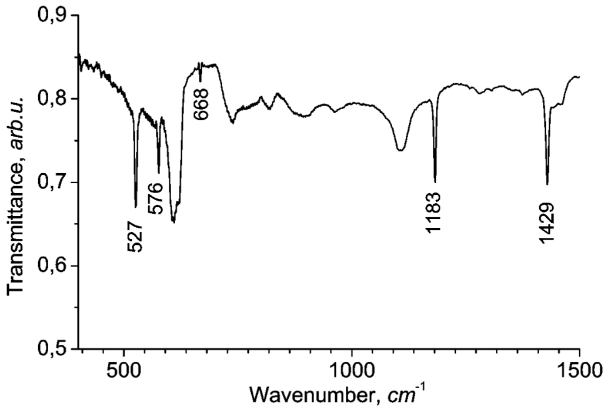

Fig. 3. Transmission spectra of the C_{60}–Si structure

Figure 3 presents the transmission spectrum of the C_{60} film deposited onto *c*-Si. The FTIR spectra demonstrate narrow absorption bands at the frequencies characteristic of C_{60}: 527, 576, 1183, and 1429 cm^{-1} caused by the F_{1u} vibrational mode.

Thus, the obtained thin films of C_{60} on the *c*-Si substrate demonstrate optical properties typical of fullerenes. The FTIR spectra also include a line at 668 cm^{-1} that is characteristic of graphite or amorphous carbon. This testifies to the presence of some number of molecules in the C_{60} films that were probably decayed in the deposition process.

The fullerene films excited by an argon laser with $\lambda =$ 488 nm manifested a typical photoluminescence in the range 1.3–1.9 eV at room temperature. The band had a width close to 0.32 eV and a complex asymmetric form, which was an evidence of the presence of at least several luminescence components, whose contribution could not be resolved at room temperature.

As is known, the luminescence of C_{60} films is mainly due to singlet and triplet excitons captured by crystal defects [11]. As a result, one observes a complex luminescence band with a maximum close to 1.69 eV corresponding to the emission from the bulk of the C_{60} film. The authors of work [12, 13] distinguished three bands with maxima at 1.52, 1.62, and 1.70 eV in the luminescence spectrum of C_{60} at 300 K. In practice, the broadening of these bands does not allow one to identify the electron spectrum of thin C_{60} films formed on *c*-Si based on the photoluminescence measurements.

The complex energy spectrum of C_{60} was studied by the technique of surface photovoltage spectroscopy that appeared to be more informative as compared to luminescence measurements and included the bands characteristic of C_{60} films. The spectrum of the Si structure without the C_{60} layer did not include such bands.

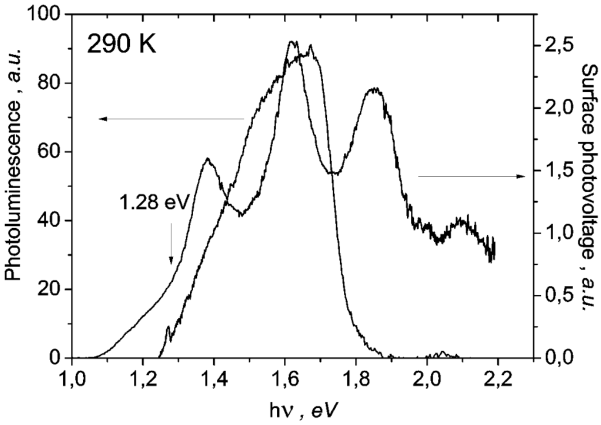

Fig. 4. Spectral dependences of the surface photovoltage and the photoluminescence of C_{60}–Si structures at 290 K

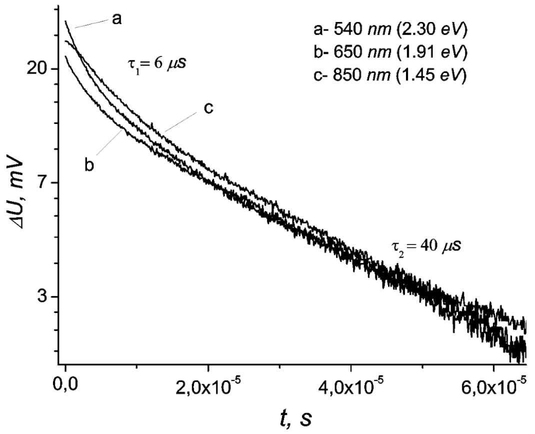

Fig. 5. Kinetics of photovoltage spectra excited by quanta with energies of 1.45, 1.91, and 2.30 eV

The generation of a photovoltage in this structure can be caused by the following processes. First, the optical transitions in C_{60} can result in the generation of bound electron-hole pairs (Frenkel excitons). They are destroyed at room temperature. Nonequilibrium holes can tunnel in the silicon SCR, whose field favors their shift in the direction from the illuminated surface. Nonequilibrium electrons are shifted in the opposite direction, i.e, accumulate. In this case, the surface potential decreases. A more probable reason for the observed photovoltage is the space separation of electron-hole pairs by the internal field of the Au–C_{60} contact. This fact is confirmed by the form of the photovoltage spectra, in particular, the photoresponse registered in the short-wave spectral region, where the major part of quanta is absorbed in the C_{60} film. In addition, this conclusion agrees with work [14] dealing with the study of the surface photovoltage kinetics in C_{60} films formed on the surfaces of Au and Pb metals.

Figure 4 presents the surface photovoltage spectra of the C_{60}–Si structures measured at room temperature. The signal in the region $h\nu < 1.28$ eV is mainly caused by nonequilibrium charge carriers generated in the Si substrate. Light absorption by the C_{60} film makes a noticeable contribution in the region $h\nu > 1.28$ eV. In particular, the peaks with maxima close to 1.38, 1.62, 1.9, and 2.1 eV are due to peculiarities of the electron spectrum of C_{60}, particularly due to the contribution of the forbidden $h_u \to t_{1u}$ optical transition and the influence of exciton effects. Moreover, it is worth taking into account that the electron-hole excitations without spin flip (singlet excitons) have a larger energy as compared to that of triplet ones having no exchange interaction.

4. Photovoltage Kinetics

The time dependences of the photovoltage signal excited by radiation with different quantum energies are demonstrated in Fig. 5. The photovoltage signal kinetics can be described by the dependence

$$U = U_1 \exp(-t/\tau_1) + U_2 \exp(-t/\tau_2), \qquad (1)$$

where $\tau_1 = 6 \pm 1\ \mu$s and $\tau_2 = 40 \pm 1\ \mu$s. The relative contribution of the short-wave component increases, as the exciting radiation wavelength decreases.

In all the cases, the photovoltage signal was mainly caused by the spatial separation of nonequilibrium charge carriers, while the lifetime of electron-hole pairs — by the recombination rate in the C_{60} film. The excitation with 1.45-eV light quanta mainly results in transitions with participation of triplet exciton states that are more long-lived as compared to singlet ones. The long-time component with $\tau = 40\ \mu$s results from the recombination of triplet excitons in the bulk of the C_{60} film. Its registration can also be caused by the disordering of the C_{60} film and the existence of deep traps.

The difference of the photovoltage kinetics for different wavelengths was observed in the region $\tau < 10\ \mu$s. As the wavelength decreases, a still larger part of radiation is absorbed in the near-surface layer of C_{60}. In this case, the singlet excitons with smaller lifetimes are mainly excited. The electron-hole pairs excited in such a way have a higher recombination rate. One of the reasons is that the near-surface layer contains a larger number of defects, which increases the probability of recombination of bound electron-hole pairs. The obtained data agree with the form of the photovoltage spectrum

(Fig. 4) indicating a decrease of the photovoltage signal in the region $h\nu > 2.1$ eV.

5. Conclusions

The electron spectrum of C_{60}–Si structures is determined, by using the methods of surface photovoltage spectroscopy and photoluminescence. It is shown that the photoluminescence and the surface photovoltage in the range 1.3–1.8 eV are caused by optical transitions with participation of singlet and triplet exciton states. The long-time component with $\tau = 40$ μs is due to triplet excitons and their recombination in the bulk of the C_{60} film, which results from a larger number of defects in its near-surface layer. With increase in the energy of light quanta, the transitions with participation of singlet exciton states that are more short-lived as compared to triplet ones are observed.

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ПОВЕРХНЕВА ФОТО-ЕРС СТРУКТУР Au–C_{60}–Si

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Резюме

У роботі методами спектроскопії поверхневої фото-ерс, фотолюмінесценції, AFM та FTIR досліджено структуру Au–C_{60}–Si. Досліджено також кінетику поверхневої фото-ерс. Показано, що фотолюмінесценція та поверхнева фото-ерс в інтервалі 1,3–1,8 еВ зумовлені оптичними переходами за участі синглетних та триплетних екситонних станів. Встановлено, що генерація поверхневої фото-ерс у структурі Au–C_{60}–Si зумовлена просторовим розділенням електронно-діркових пар в плівці C_{60}.