PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 2 (2017) P. 173-179
DOI: 10.15330/pcss.18.2.173-179

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 2 (2017) С. 173-179

UDK 621.382

ISSN 1729-4428

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Effect of Microwave Radiation on the Band Structure and Electronic Parameters of the Heterosystems with Fullerenes

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The results of a complex study of C_{60}/Si heterosystems are presented in this work: the crystal structure and composition of the films, internal mechanical stresses, electronic parameters of the film and the film-substrate interface, and the effect of external influences (ultraviolet irradiation, thermal annealing, gamma and microwave irradiation). The advantage of microwave treatment over others is established: the absence of fullerene decomposition, the removal of internal mechanical stresses in the heterosystem, and the improvement of its electronic parameters. Methods for remove the decomposition of C_{60} molecules under the influence of other treatments have been developed. To eliminate the interaction of fullerenes with oxygen, it was proposed to perform thermal annealing and UV irradiation in vacuum, and in the case of γ-irradiation, apply a protective coating on the surface of the film (GeO_x or SiO_x). In solar cells with C_6 films in the polymer matrix on Si, a significant advantage of titanium contacts in comparison with gold is established, especially after microwave treatment. Contact resistance decreased as a result of hybridization of 3***d***-orbitals of titanium and 2***p***-orbitals of fullerenes with the formation of Ti_xC_{60} carbides and radiation-stimulated diffusion of metals, which increases the contact area.

Key words: fullerenes C_{60}, heterosystems, crystalline and band structure of the films, internal mechanical stresses, electronic parameters, thermal and radiation treatments.

Article acted received 21.04.2017; accepted for publication 05.06.2017.

Introduction

The discovery of C_n molecules with an even number of carbon atoms (fullerenes) promoted the creation of new carbon materials and heterosystems based on them. Among the known fullerenes, the C_{60} molecules are the most symmetrical and stable [1]. They form molecular crystal with semiconductor properties. Heterosystems with C_{60} films and hybrid heterosystems with fullerenes in the polymer matrix are used in electronic engineering, sensorics and solar cells [2]. Their properties are determined by the conditions of manufacturing heterosystems and the influence of external influences on them [3]. The physical properties of the heterosystem are not a simple sum or averaging of the properties of the film and substrate. They acquire new properties due to the appearance of mechanical stresses and electronic states on the film-substrate interface, which substantially change the band structure of the semiconductor and its electronic properties.

The purpose of this work is the use of external factors (thermal annealing, ultraviolet, gamma and microwave irradiation) to determine their effectiveness in preserving the film composition, improving its electronic parameters and the film-substrate interface, as well as reducing internal mechanical stresses in the heterosystem without the decomposition of fullerenes.

I. Conditions for obtaining films and methods for studying heterosystems

C_{60} films were deposited on silicon substrates from a molecular beam of fullerenes in vacuum upon sublimation of C_{60} fulerite powder (99.9 % purity) from the Knudsen tantalum cell, heated resistively to 550 °C [4]. The method allows to obtain the films of different thickness in a single technological cycle, changing the distance between the fullerene source and the substrate. Substrates were not heated to eliminate thermal stresses in heterosystems. The surface of the films was investigated in an atom force microscope Nanoscope IIIa in the regime of periodic mode. Atom force microscopy provides information about the surface relief. The composition and crystalline structure of the film were

Fig. 1. Schematic representation of the structure under study: 1 – silicon substrate, 2 – lower metallization layer, 3 – polymer layer with C_{60}, 4 – upper ohmic contacts.

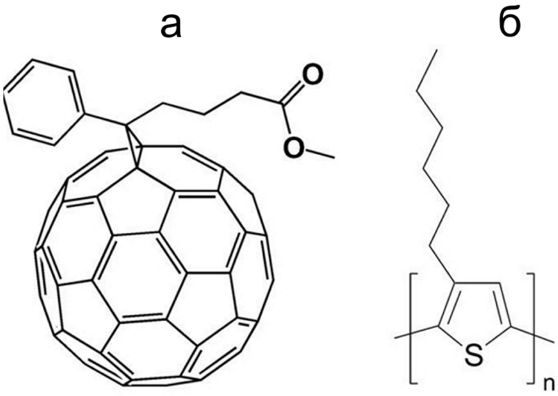

Fig. 2. Schematic representation of PCBM (a) and P3NT (b) molecules.

determined from the Raman spectra obtained on a DFS-24 monochromator at room temperature. The mechanical stresses σ in the films and their sign were determined from the bending profile of the heterosystem recorded on the P-104 profilograph, according to Stone's formula $s = \frac{Ed^2}{6Rt(1-n)}$ [5]. Here E is the substrate Young's modulus, d and n are its thickness and Poisson's ratio, R is the bending radius of the heterosystem. The mechanical stresses in the film and substrate were also determined from the electroreflectance spectra from change in their band gap in comparison with bulk samples. The spectra were measured by the electrolytic method [6] at room temperature on the double DMR-4 monochromator. Samples were in an electrolytic cell with a quartz window and 0.1 normal solution of potassium chloride in distilled water. This method makes it possible to investigate only semiconductors and only in the region of direct transitions. At a distance from them the signal disappears [7]. The spectra were analyzed by the three-point Aspnes method, taking into account the energy of the dominant peaks and the ratio of its intensities [8]. Transitions in the energy range of 1.6 eV and 2.1 eV were studied in the films, and in the substrates in the spectral region of 3.4 eV, which corresponds to the width of the band gap of silicon. In addition to the transition energy, we also determined the spectral broadening parameter Γ and the energy relaxation time of the charge carriers excited by light τ. They characterize the structural perfection of the surface under study.

The structure of the solar cell (Fig. 1) is a silicon substrate, a lower metallization layer (40 nm thickness of titanium film), and a film from the mixture of PCBM polymers with C_{60} fullerenes (6,6-phenyl-C_{60}-butylate methyl ether) and P3NT (poly-3 hexothiophene). Schematic imagine of these polymers is shown in Fig. 2, a and b, respectively. The mixture of polymers was dissolved in toluene and applied to the surface of the titanium layer in a centrifuge. When creating solar cells, much attention was paid to the selection of the type of metallization of ohmic contacts. Two pairs of gold and titanium contacts were applied through a mask to the surface of a hybrid polymer film. A four-probe method was used to measure the contact resistance. One pair of probes was stabilized by current, and the second pair measured the voltage.

II. Experimental results and their discussion

The atom-force image of the surface of a C_{60} film (thickness 2 μm) is shown on Fig. 3a. It is seen that the surface of the film is smooth, without asperities and cavities, with a uniform distribution of fullerenes over

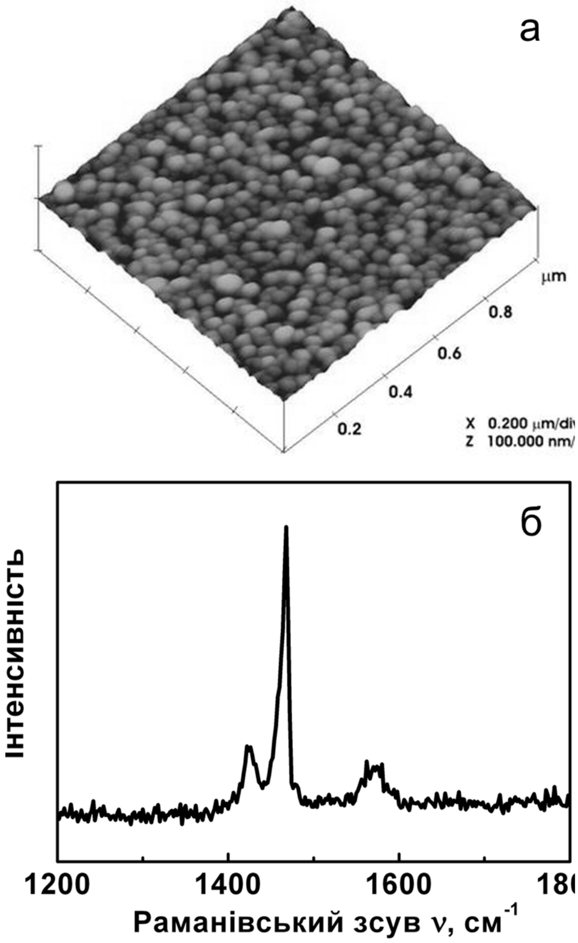

Fig. 3. AFM images of the surface (a) and Raman spectrum (b) of the C_{60} film.

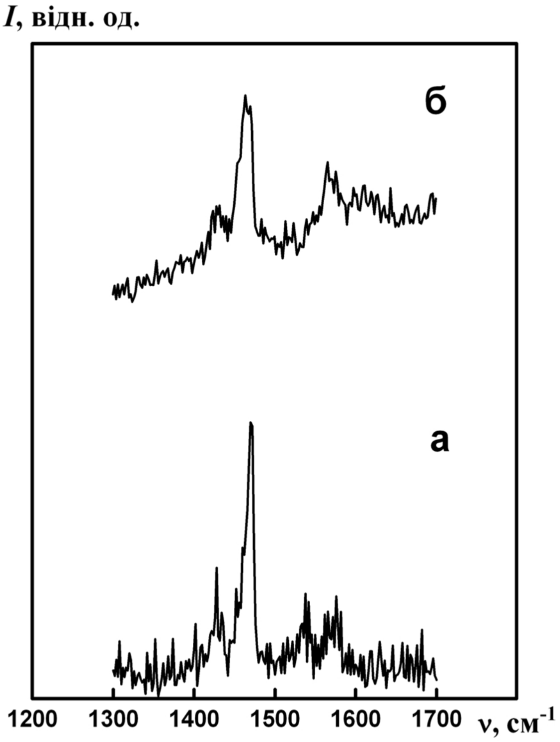

Fig. 4. Raman spectra of C_{60} films in C_{60}/Si heterosystem before (a) and after (b) isothermal annealing in vacuum (T_{ann} = 800ºC).

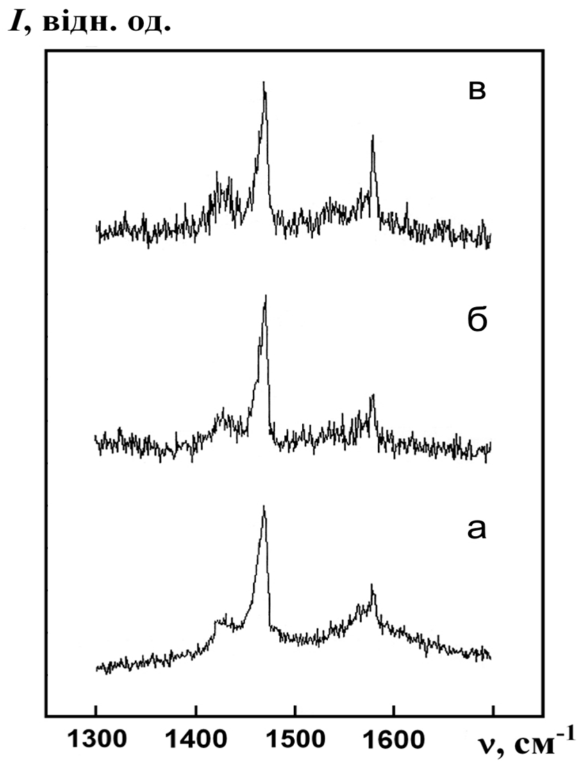

Fig. 5. Raman spectra of C_{60} films in the C_{60}/Si heterosystem before (a) and after UV irradiation for 1 hour (b) and 5 hour (c).

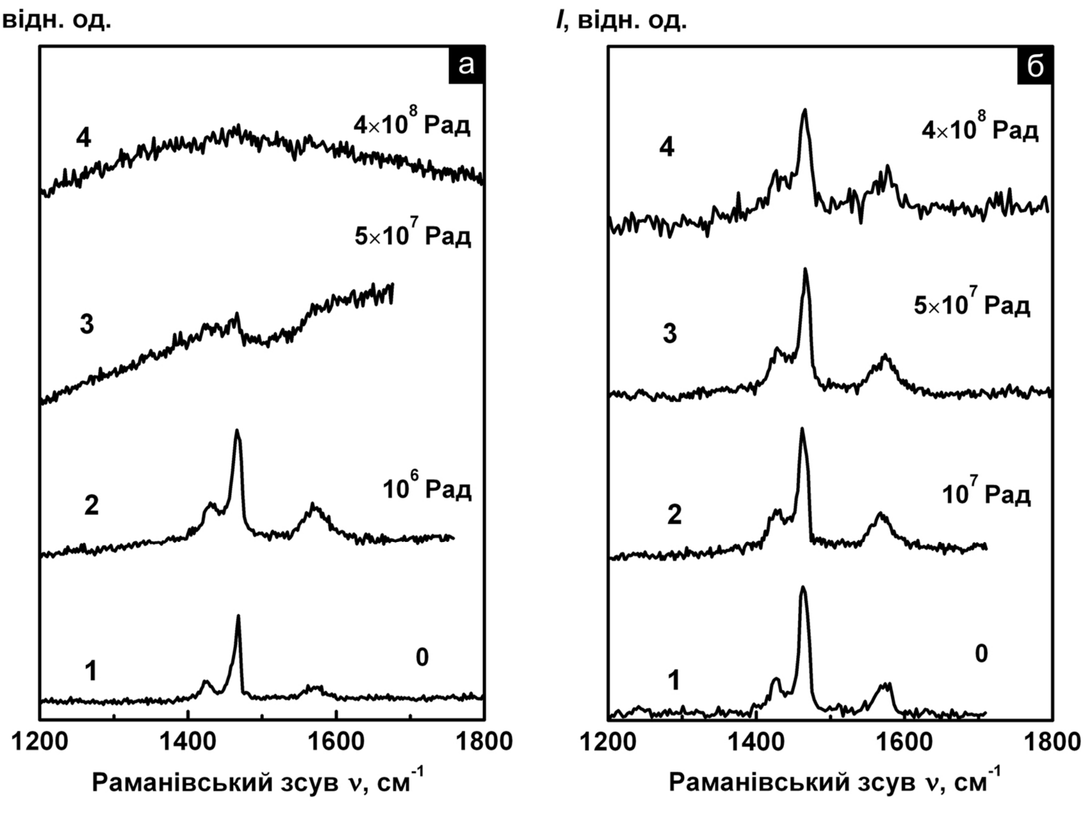

Fig. 6. Raman spectra of C_{60} films in the C_{60}/Si (a) and GeO_x/C_{60}/Si (b) heterosystems at different doses of irradiation with γ-quanta.

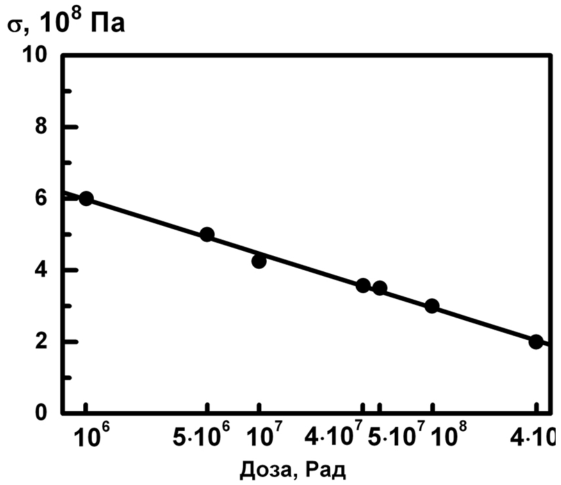

Fig. 7. Dependence of internal mechanical stresses in the C_{60} film on Si on the dose of γ-irradiation.

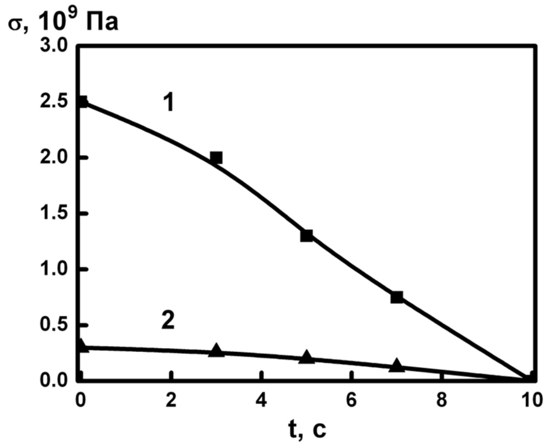

Fig. 9. Dependence of internal mechanical stresses in the C_{60} film on Si on the duration of the microwave treatment. The film thickness of C_{60} is 0.35 μm (1) and 2 μm (2).

the surface. On Fig. 3, b shows the Raman spectrum of this film. The intense band at 1470 cm^{-1} corresponds to the vibrations of the fullerene molecules in the crystal, and at 1425 and 1575 cm^{-1}, the less intense bands correspond to the vibrations of the carbon atoms in the molecule. The number of carbon atoms in the C_n molecule is always paired. It contains necessarily 12 hexagons and n–12 pentagons. Molecule C_{60} resembles a soccer ball, the tire of which consists of 12 hexagons and 48 pentagons. The bond between hexagons is short and double, and between hexagon and pentagon is longer and single. When molecules are excited, it is broken first, and a denser amorphous carbon phase at a frequency of 1600 cm^{-1} appears in the film [9]. Due to the destroy of the molecules both in the process of manufacturing the heterosystem [4] and under external influences, the surface of the film coarsens, the mounds and cavities appear on it, the intensity of the band at a frequency of 1470 cm^{-1} decreases [10].

It is known that under ultraviolet irradiation, as well as during thermal annealing at natural conditions, fullerenes decay [11, 12]. We showed that when these treatments are carried out in a vacuum they do not disintegrate. In Fig. 4 shows Raman spectra of C_{60} films on Si substrate after irradiation in vacuum for 1 hour (a) and 5 hours (b). In Fig. 5 shows Raman spectra of the

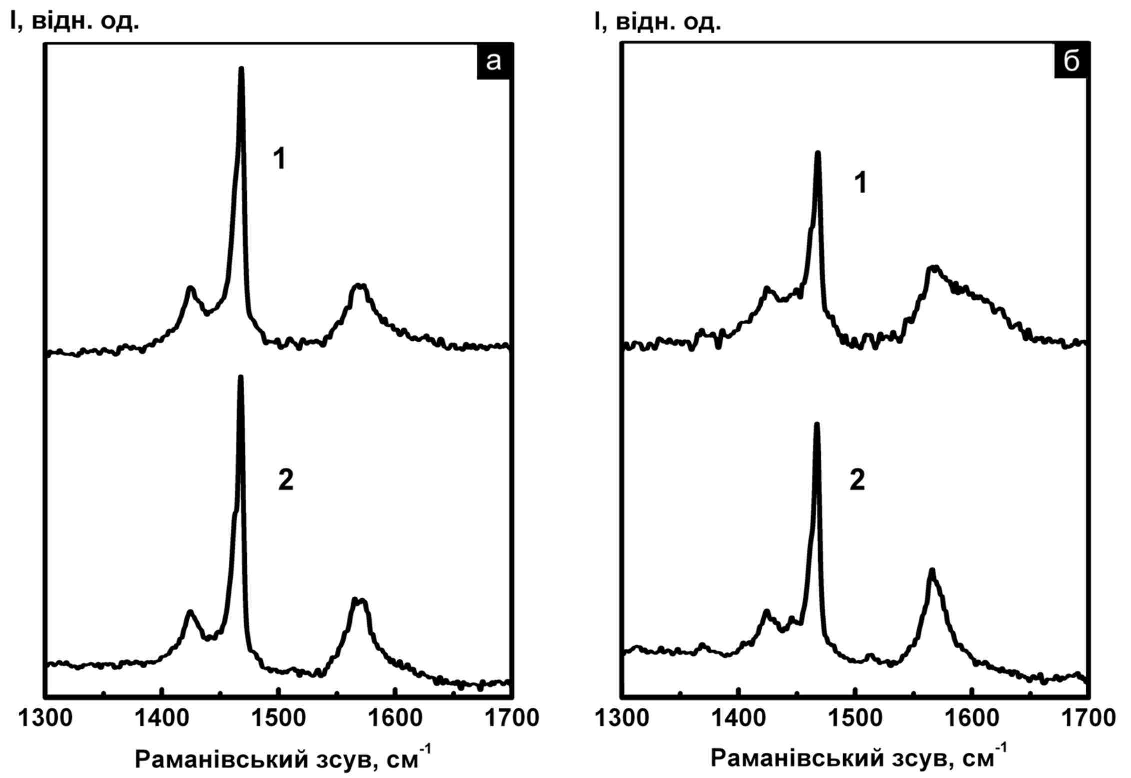

Fig. 8. Raman spectra of single-phase C_{60} films 0.35 μm thickness (a), 2 μm (b) up to (1) and after (2) 10 s microwave treatment.

films before (a) and after (b) annealing of the C_{60}/Si heterosystem in vacuum at 650 °C. This means that fullerenes do not decay in the Knudsen cell, but in interaction with the substrate surface. This conclusion was also confirmed in the preparation of C_{60} films from the powder, which remained in the cell after preliminary deposition of fullerenes. The decomposition of fullerenes with γ-irradiation (Fig. 6a) was eliminated (Fig. 6b) by applying a protective coating of GeO_x or SiO_2 to the surface of the C_{60} film to prevent its interaction with oxygen [13]. With γ-irradiation without protective film coating, the level of mechanical stress in the C_{60}/Si heterosystems decreased due to the appearance of the carbon phase after the decay of fullerenes (Fig. 7).

Microwave treatment of heterosystems (2.45 GHz, power density 1.5 W/cm^2 with an interval of 2...3 seconds with a total duration of 10 seconds) was carried out in the air without protective film coatings. During the irradiation the samples were not heated, the composition of the films did not change, the band at 1600 cm^{-1}, characteristic for Raman spectra of carbon amorphous films, did not appear (Fig. 8). It is known [5] that thin films have a higher level of mechanical stresses compared to thick ones. With an increase in the duration of microwave treatment, mechanical stresses in films of different thicknesses decreased (Fig. 9). After 10 seconds of irradiation, the heterosystems straightened, which indicates the complete relaxation of internal mechanical stresses in it.

Mechanical stresses and electroreflectance spectra of the film and C_{60}/Si interfaces were measured before and after microwave treatment. Relaxation of the stresses reduced the width of the band gap of the film for both transitions (Fig. 10, a), so the compressive stresses decreased, and increased the band gap of the substrate to 3.38 eV (Fig. 10b), which corresponds to silicon crystals. The table lists the electronic parameters (band gap E_g, spectral broadening Γ, energy relaxation time of light-excited charge carriers τ and internal mechanical stresses in the heterosystem) before and after 10 seconds of microwave treatment. By changing the transition energy and mechanical stresses, the dependences $dE_g/d\sigma = -2.8\cdot10^{-10}$ eV/Pa and $4.2\cdot10^{-10}$ eV/Pa for the first and subsequent transitions, respectively, were established in the films. Before our studies, these data were not available in the literature.

In the solar cells, the total resistance of the metal-polymer composite-metal structure for each type of metal contacts was determined. The resistance of the initial structures depended on the type of upper metallization. Before microwave irradiation, gold metallization had a

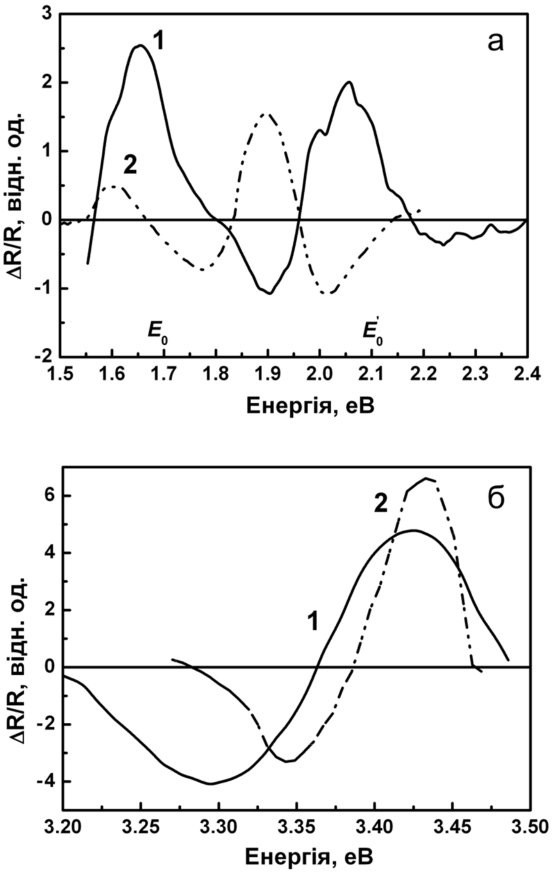

Fig. 10. Electroreflectance spectra of the C_{60} (a) film and the Si (b) substrate up to (1) and after (2) microwave treatment.

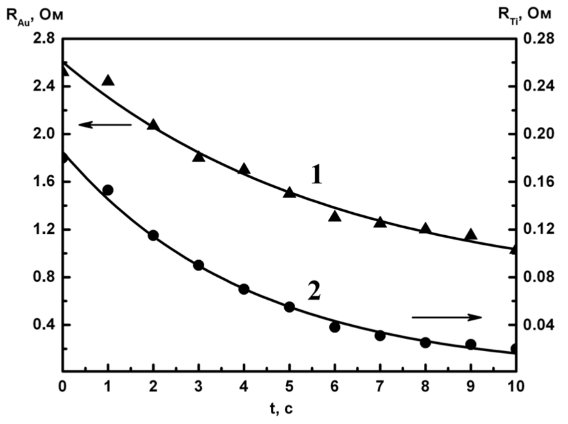

Fig. 11. Dependence of the structural impedance on the duration of microwave irradiation for gold (curve 1) and titanium (curve 2) upper metallization.

Table

Electronic parameters of the C_{60} film and internal mechanical stresses in the C_{60}/Si heterosystem before and after 10 seconds of γ-irradiation

Irradiation	E_g, eV	Γ, meV	τ, 10^{-15} s	σ, 10^8 Pa
before	1.700	235	2.8	2.5
after	1.628	63	10.8	0

resistance several times greater than that of titanium. This can be explained by the appearance of Ti-C chemical bond and the formation of Ti_xC_{60} compounds by hybridization of *d*-metal and *p*-fullerene orbitals, because carbon atoms interact only with titanium and lanthanum and do not interact with other metals [14].

In Fig. 11 shows the dependence of the contact resistance on the time of microwave treatment for gold (curve 1) and titanium (curve 2) metalizations. After 10 seconds of microwave irradiation, the R_{Ti}/R_{Au} resistance ratio decreased 50-times (Fig. 12). The result can be

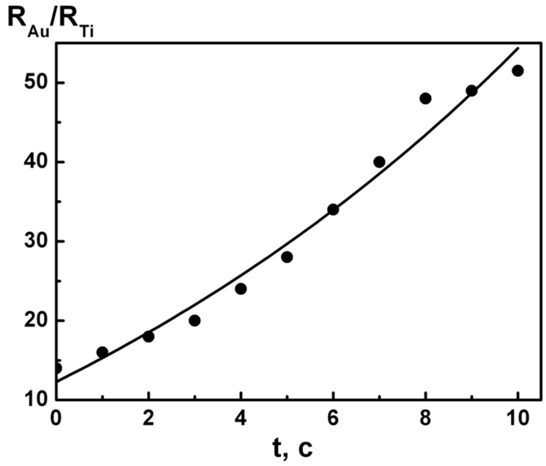

Fig. 12. Dependence of the resistance of the structure with gold metallization R_{Au} on the resistance of the structure with titanium metallization R_{Ti} on the duration of microwave treatment.

explained by the fact that radiation-stimulated diffusion in the contact regions of Ti-polymer and Au-polymer increases the contact area, and titanium carbide Ti_xC_{60} appeared both in the area of point upper titanium contacts and over the total surface of the lower titanium contact with the silicon substrate.

Conclusions

The paper presents the results of the complex study of heterosystems with C_{60} fullerenes on silicon substrates and the influence of external factors (thermal annealing, ultraviolet, gamma and microwave irradiation) on them. It was established the significant advantage before other used treatments of pulsed microwave treatment (2.45 GHz, power density 1.5 W/cm^2 with an interval of 2... 3 seconds with a total duration of 10 seconds). This is the absence of C_{60} fullerene decomposition in films, total removing of internal mechanical stresses in the heterosystem, improvement of the electronic parameters of the film and substrate, a decrease in contact resistance of metal contacts, a significant advantage of titanium contacts over gold due to the formation of Ti_xC_{60} carbides. It is also important that short-term microwave treatment of heterosystems with C_{60} fullerenes is the most effective in comparison with other treatments in terms of reducing internal mechanical stresses in the heterosystem without the decay of fullerenes. In addition, it is simple, fast, cheap and does not require much energy and expensive equipment.

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Вплив зовнішніх дій на механічні напруження і електронні параметри гетеросистем з C_{60} фулеренами

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В роботі приведені результати комплексного дослідження гетеросистем C_{60}/Si: кристалічної структури і складу плівок, внутрішніх механічних напружень, електронних параметрів плівки і межі поділу плівка-підкладка та впливу на них зовнішніх дій (ультрафіолетового опромінення, термічного відпалу, гамма та мікрохвильового опромінення). Встановлено перевагу мікрохвильової обробки перед іншими: відсутність розпаду фулеренів, повне усунення внутрішніх механічних напружень в гетеросистемі та покращення її електронних параметрів. Розроблені методи усунення розвалу молекул C_{60} під дією інших обробок. Термічний відпал і УФ-опромінення пропонується проводити у вакуумі, а для γ-опромінення наносити захисне покриття на поверхню плівки (GeO_x або SiO_x) для усунення взаємодії фулеренів з киснем. В сонячних комірках з плівками C_{60} в полімерній матриці на Si встановлена суттєва перевага титанових контактів перед золотими, особливо після мікрохвильової обробки. Контактний опір зменшувався в результаті гібридизації 3*d*-орбіталей титану і 2*p*-орбіталей фулеренів з утворенням карбідів Ti_xC_{60} та радіаційно-стимульованої дифузії металів, яка збільшує площу контакту.

Ключові слова: фулерени C_{60}, гетеросистеми, кристалічна і зонна структура плівок, внутрішні механічні напруження, електронні параметри, термічна і радіаційні обробки.