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Current instability in heterostructures based on thin layers of colloidal Ag_2Se quantum dots and fullerene C_{60}

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This paper presents studies of the electrical properties of thin-film layers of colloidal silver selenide quantum dots (Ag_2Se), as well as heterostructures based on fullerene C_{60} and Ag_2Se. The synthesis of materials, the technique for obtaining thin films and heterostructures are described. The study of conductive properties was carried out by analyzing the current-voltage characteristics. It is shown that thin films of Ag_2Se in the Al–C_{60}–Ag_2Se–ITO sandwich structure system have unique current-voltage characteristics, in particular, they have current instability with inversion of the sign of the flowing current. Implementation of the heterostructure in the Al–Ag_2Se–ITO system makes it possible to stabilize and enhance this effect.

Keywords: Ag_2Se, thin-film structures, voltage-current characteristics, current instability.

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Silver selenide Ag_2Se attracts research attention due to its potential applications in switching devices. Binary and ternary semiconductors are key materials for Schottky barriers, solar cells, and electronics [1–3]. However, the research into bulk Ag_2Se crystals was focused primarily on thermoelectronic devices, where Ag_2Se was used at room temperature [4–8]. Colloidal synthesis of Ag_2Se nanocrystals several nanometers in size, which are called quantum dots (QDs), opens up the opportunities for easy tuning of optical and electronic properties of Ag_2Se for devices operating in the near and middle [9,10] IR ranges, since the band gap of bulk Ag_2Se is 0.15 eV [11–14]. Colloidal Ag_2Se QDs absorb in the near and middle IR ranges, which is important for the production of compact, lightweight, low-power, and low-cost IR sensors [13,15,16]. The research into Ag_2Se QDs is aimed primarily at the development of procedures for fabrication of colloidal Ag_2Se QDs and the determination of trends in their absorption and luminescence properties [11,12]. However, experimental data on the application of colloidal Ag_2Se QDs as an active medium for optoelectronic components are scarce at the moment. The present study is focused on the examination of electrophysical characteristics of thin films of Ag_2Se QDs and the fabrication of a heterostructure based on fullerene C_{60} and Ag_2Se QDs.

The objects under examination were colloidal Ag_2Se QDs fabricated using the aqueous synthesis technique similar to the one developed earlier for Ag_2S QDs [17]. An aqueous solution of $AgNO_3$ (1 mmol, 10 ml) was the source of silver ions, an aqueous solution of Na_2SeSO_3 (0.1 mmol, 2 ml) was the source of selenium, and an aqueous solution of 2-mercaptopropionic acid (2-MPA) (2 mmol, 50 ml) was the stabilizing agent. The mentioned technique consists in mixing the aqueous solutions of $AgNO_3$, 2-MPA, and Na_2SeSO_3 at pH=10. The concentration ratio between $AgNO_3$ and Na_2SeSO_3 precursors was such that forming colloidal Ag_2Se QDs had an average size of 2.0 ± 0.5 nm. Fullerene C_{60} was produced by sputtering of graphite with a material purity of 99.5% [18].

Thin films of Ag_2Se QDs and fullerene C_{60} were formed by flow coating on dielectric and conducting substrates [19]. The initial fullerene C_{60} powder was dissolved in dichloromethane (CH_2Cl_2) with a material concentration of 0.5 mg/ml in the solution. The volume of the deposited fullerene C_{60} solution was 1 ml, while the volume of the aqueous solution of Ag_2Se QDs was 0.4 ml. The electrical parameters of Ag_2Se QDs were examined by fabricating an Al–Ag_2Se–ITO (ITO stands for indium tin oxide) sandwich structure (Fig. 1, *a*) [20]. A heterostructure was formed in the Al–C_{60}–Ag_2Se–ITO system (Fig. 2, *a*). Conducting aluminum and ITO substrates were fabricated by magnetron sputtering. The sheet resistance of conducting substrates did not exceed 20 Ω/sq. The geometric dimensions of conducting substrates were 10×10 mm.

Electrophysical parameters in the DC mode were examined using a Keysight B1500A (Keysight Tech., United States) semiconductor analyzer. The voltage sweep rate for the Al–Ag_2Se–ITO sandwich structure and the Al–C_{60}–Ag_2Se–ITO system was 50 and 12.5 mV/s, respectively. The surface morphology of thin films was studied via reflection and transmission microscopy with an MII-4M (LOMO, Russia) microinterferometer. The results of micrometric analysis of Ag_2Se QD films demonstrated that they were relatively uniform with the material spread

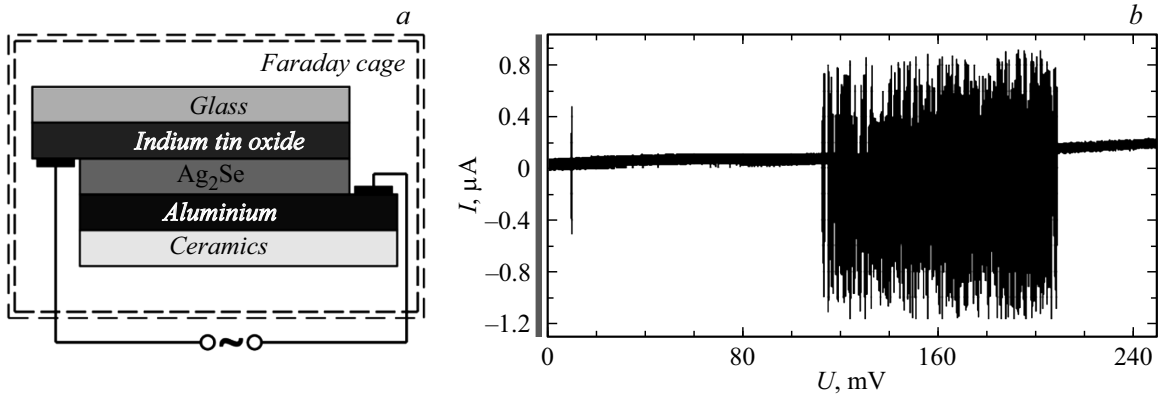

Figure 1. Sandwich structure (a) and current–voltage characteristics (b) of thin Ag_2Se films.

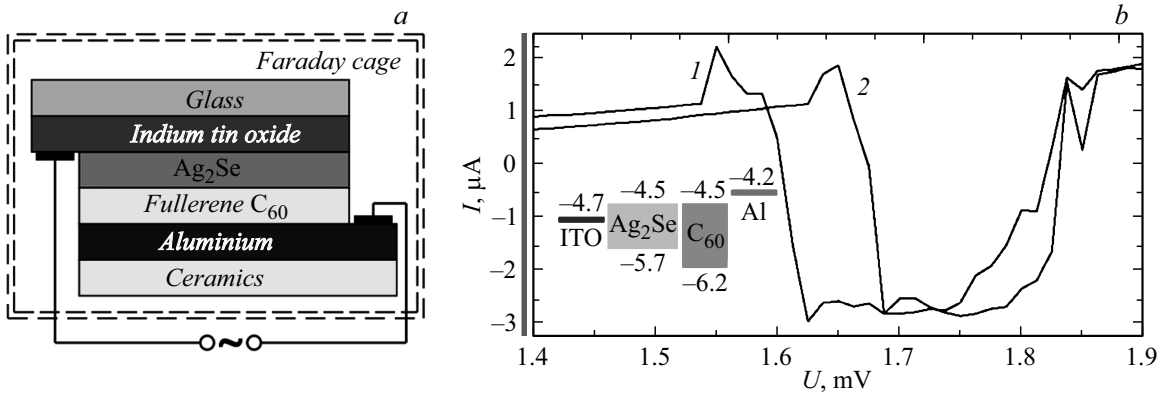

Figure 2. Sandwich structure (a) and current–voltage characteristics under forward (1) and backward (2) bias (b) of the $C_{60}-Ag_2Se$ heterostructure. The boundaries of the band gap of Ag_2Se QDs, highest occupied and lowest unoccupied molecular orbital levels for fullerene, and the work functions of electrodes are indicated (in eV) in the inset.

over the substrate surface in a layer with a thickness on the order of $1.5-2\,\mu$m (Fig. 3, a).

The analysis of morphology of fullerene C_{60} films prepared with the use of dichloromethane revealed that the surface was inhomogeneous and contained „star-like" structures (Fig. 3, b) [18]. The thickness of the film itself was approximately 750 nm, and the dimensions of „star-like" formations seen on its surface were as follows: a length of individual sides up to $40\,\mu$m and a height on the order of $2-3\,\mu$m. Thus, the formed heterostructure is a dimensional combination of the studied materials.

A screening chamber („Faraday cage") used in the measurements of electrical characteristics helped raise their sensitivity and minimize external influences. Current–voltage characteristics (CVCs) were analyzed in order to evaluate the conducting properties. The CVCs of Ag_2Se QDs have a distinctive feature in the $0.11-0.21$ V voltage range (Fig. 1, b). A significant current enhancement is seen in both positive and negative regions.

At a voltage of 90 mV, the current does not exceed 115 nA; when the voltage increases to 110 mV, the current grows abruptly to $0.4-0.9\,\mu$A with subsequent instantaneous switching to the negative region with currents ranging from -0.8 to $-1.2\,\mu$A. This CVC pattern is observed in experiments with Ag_2Se QDs through to a voltage of 210 mV. If the voltage increases further, the CVC reverts to its initial shape with currents of 190 nA.

This effect was both stabilized and enhanced after the introduction of fullerene C_{60} into the $Al-Ag_2Se-ITO$ structure (Fig. 2, b). The CVC in Fig. 2, b features a fixed region of current instability with sign inversion of the flowing current. It should be noted that the region of current instability was observed initially in the 0.5–0.6 V voltage range with a current of $-2.6\,\mu$A. The inversion region was shifted in voltage and expanded in current after repeated sequential CVC measurements. Figure 2, b shows the CVCs under forward and backward bias illustrating the maximum parameters of the observed effect. It is notable, in particular, that the characteristic switches from the region of positive currents to the negative region in the 1.60–1.85 V voltage range with currents ranging from -2.5 to $-3.0\,\mu$A. Note also that numerous repeated measurements of the electrical parameters of the $Al-Ag_2Se-ITO$ structure had no effect on the shift of the region of growth and switching of Ag_2Se QW CVCs.

The obtained results are indicative of the formation of a thin-film Ag_2Se-C_{60} sandwich structure that has fundamentally new electrophysical properties. It has been demonstrated for the first time that colloidal Ag_2Se QDs

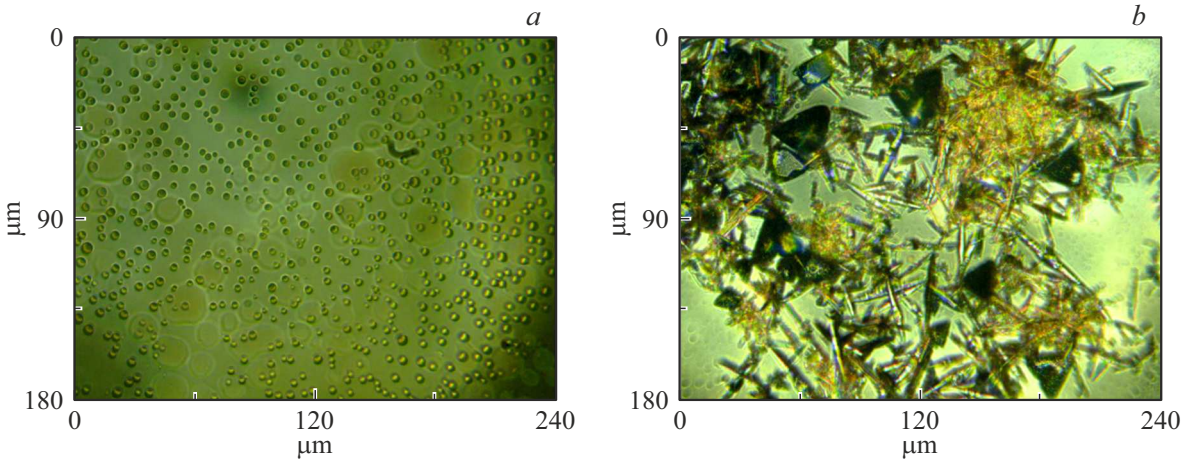

Figure 3. :layers with Ag_2Se QDs (*a*) and structures based on C_{60} molecules (*b*) imaged with an MII-4M optical interference microscope.

feature a current instability with sign inversion of the flowing current. This may eventually be used for primary signal generation. The obtained negative conductances in the Al−C_{60}−Ag_2Se−ITO heterostructure bode well for the development of advanced generators that support transistor-transistor logic voltage levels and may be integrated into conventional semiconductor electronics. The simplified fabrication cycle based on colloidal chemistry, which provides an opportunity to produce low-cost active elements, is an obvious advantage of the studied structures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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