

06.1;07.2;08.3

Current instability in heterostructures based on thin layers of colloidal Ag₂Se quantum dots and fullerene C₆₀

© V.S. Gurchenko¹, A.S. Mazinov¹, A.S. Tyutyunik¹, I.G. Grevtseva², M.S. Smirnov²,
S.V. Aslanov², O.V. Ovchinnikov²

¹ Vernadsky Crimean Federal University, Simferopol, Russia

² Voronezh State University, Voronezh, Russia

E-mail: mazinovas@cfuv.ru

Received July 18, 2023

Revised September 4, 2023

Accepted September 19, 2023

This paper presents studies of the electrical properties of thin-film layers of colloidal silver selenide quantum dots (Ag₂Se), as well as heterostructures based on fullerene C₆₀ and Ag₂Se. 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 Ag₂Se in the Al–C₆₀–Ag₂Se–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–Ag₂Se–ITO system makes it possible to stabilize and enhance this effect.

Keywords: Ag₂Se, thin-film structures, voltage-current characteristics, current instability.

DOI: 10.21883/0000000000

Silver selenide Ag₂Se 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 Ag₂Se crystals was focused primarily on thermoelectric devices, where Ag₂Se was used at room temperature [4–8]. Colloidal synthesis of Ag₂Se nanocrystals several nanometers in size, which are called quantum dots (QDs), opens up the opportunities for easy tuning of optical and electronic properties of Ag₂Se for devices operating in the near and middle [9,10] IR ranges, since the band gap of bulk Ag₂Se is 0.15 eV [11–14]. Colloidal Ag₂Se 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 Ag₂Se QDs is aimed primarily at the development of procedures for fabrication of colloidal Ag₂Se QDs and the determination of trends in their absorption and luminescence properties [11,12]. However, experimental data on the application of colloidal Ag₂Se 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 Ag₂Se QDs and the fabrication of a heterostructure based on fullerene C₆₀ and Ag₂Se QDs.

The objects under examination were colloidal Ag₂Se QDs fabricated using the aqueous synthesis technique similar to the one developed earlier for Ag₂S QDs [17]. An aqueous solution of AgNO₃ (1 mmol, 10 ml) was the source of silver ions, an aqueous solution of Na₂SeSO₃ (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 AgNO₃, 2-MPA, and Na₂SeSO₃ at pH=10. The concentration ratio between AgNO₃ and Na₂SeSO₃ precursors was such that forming colloidal Ag₂Se QDs had an average size of 2.0 ± 0.5 nm. Fullerene C₆₀ was produced by sputtering of graphite with a material purity of 99.5% [18].

Thin films of Ag₂Se QDs and fullerene C₆₀ were formed by flow coating on dielectric and conducting substrates [19]. The initial fullerene C₆₀ powder was dissolved in dichloromethane (CH₂Cl₂) with a material concentration of 0.5 mg/ml in the solution. The volume of the deposited fullerene C₆₀ solution was 1 ml, while the volume of the aqueous solution of Ag₂Se QDs was 0.4 ml. The electrical parameters of Ag₂Se QDs were examined by fabricating an Al–Ag₂Se–ITO (ITO stands for indium tin oxide) sandwich structure (Fig. 1, a) [20]. A heterostructure was formed in the Al–C₆₀–Ag₂Se–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–Ag₂Se–ITO sandwich structure and the Al–C₆₀–Ag₂Se–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 Ag₂Se QD films demonstrated that they were relatively uniform with the material spread

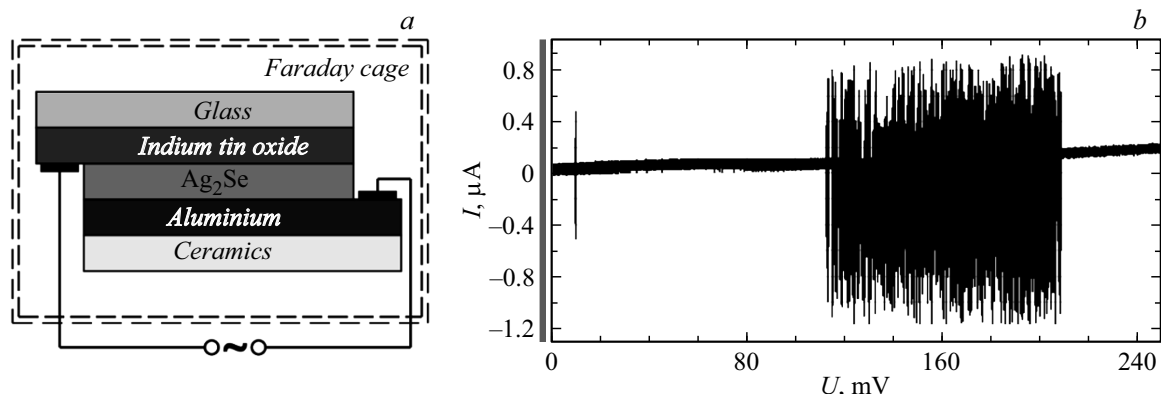


Figure 1. Sandwich structure (a) and current–voltage characteristics (b) of thin Ag_2Se films.

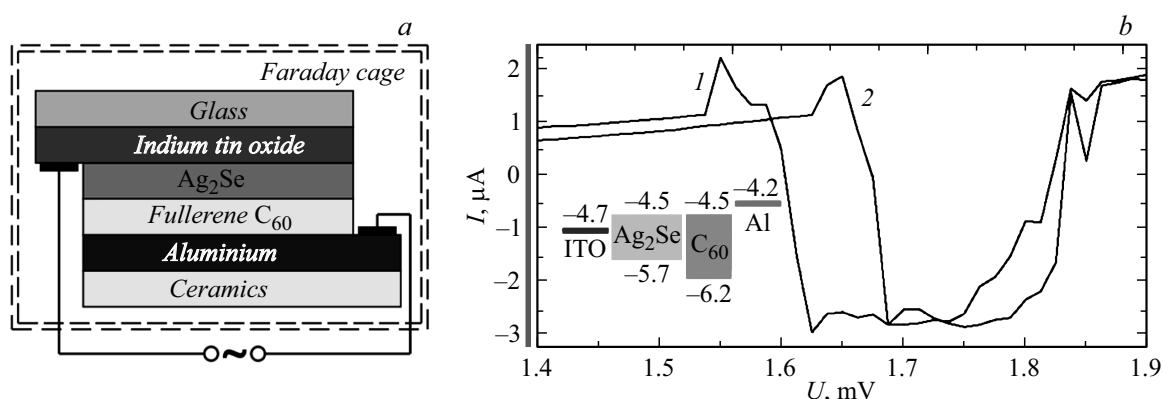


Figure 2. Sandwich structure (a) and current–voltage characteristics under forward (1) and backward (2) bias (b) of the C_{60} – Ag_2Se heterostructure. The boundaries of the band gap of Ag_2Se QDs, highest occupied and lowest unoccupied molecular orbital levels for fullerene, and the work functions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

over the substrate surface in a layer with a thickness on the order of $1.5\text{--}2\text{ }\mu\text{m}$ (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 $40\text{ }\mu\text{m}$ and a height on the order of $2\text{--}3\text{ }\mu\text{m}$. 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 $0.11\text{--}0.21\text{ V}$ 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 $0.4\text{--}0.9\text{ }\mu\text{A}$ with subsequent instantaneous switching to the negative region with currents ranging from -0.8 to $-1.2\text{ }\mu\text{A}$. 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 $\text{Al}\text{--}\text{Ag}_2\text{Se}\text{--ITO}$ 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 $0.5\text{--}0.6\text{ V}$ voltage range with a current of $-2.6\text{ }\mu\text{A}$. 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 $1.60\text{--}1.85\text{ V}$ voltage range with currents ranging from -2.5 to $-3.0\text{ }\mu\text{A}$. Note also that numerous repeated measurements of the electrical parameters of the $\text{Al}\text{--}\text{Ag}_2\text{Se}\text{--ITO}$ 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 $\text{Ag}_2\text{Se}\text{--}\text{C}_{60}$ sandwich structure that has fundamentally new electrophysical properties. It has been demonstrated for the first time that colloidal Ag_2Se QDs

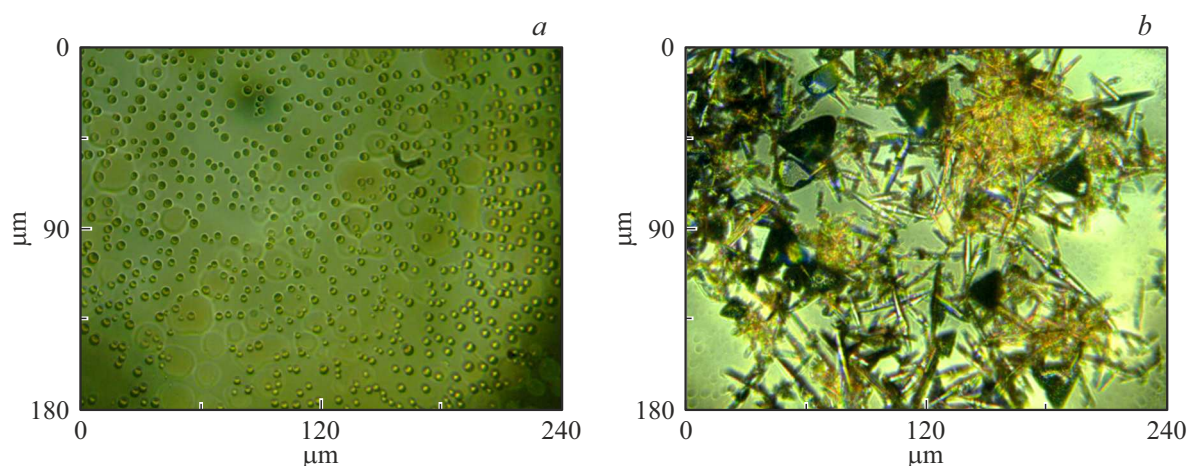


Figure 3. Layers with Ag₂Se QDs (a) and structures based on C₆₀ molecules (b) imaged with an MII-4M optical interference microscope.

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–C₆₀–Ag₂Se–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.

Funding

This study was supported by grant No. 23-22-10007 from the Russian Science Foundation and the Republic of Crimea.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] Z. Zhang, Y. Yang, J. Gao, S. Xiao, C. Zhou, D. Pan, G. Liu, X. Guo, *Mater. Today Energy*, **7**, 27 (2018). DOI: 10.1016/j.mtener.2017.11.005
- [2] Y. Yang, D. Pan, Z. Zhang, T. Chen, H. Xie, J. Gao, X. Guo, *J. Alloys Compd.*, **766**, 925 (2018). DOI: 10.1016/j.jallcom.2018.07.022
- [3] J. Ma, M. Chen, S. Qiao, J. Chang, G. Fu, S. Wang, *ACS Photon.*, **9** (6), 2160 (2022). DOI: 10.1021/acsphotonics.2c00474
- [4] J. Gao, L. Miao, H. Lai, S. Zhu, Y. Peng, X. Wang, K. Koumoto, H. Cai, *iScience*, **23** (1), 100753 (2019). DOI: 10.1016/j.isci.2019.100753
- [5] K.H. Lim, K.W. Wong, Y. Liu, Y. Zhang, D. Cadavid, A. Cabot, K.M. Ng, *J. Mater. Chem. C*, **7** (9), 2646 (2019). DOI: 10.1039/C9TC00163H
- [6] J. Niu, T. Chen, G. Liang, H. Ma, X. Zhang, P. Fan, Z. Zheng, *Mater. Lett.*, **312**, 131662 (2022). DOI: 10.1016/j.matlet.2022.131662
- [7] P. Jood, R. Chetty, M. Ohta, *J. Mater. Chem. A*, **8** (26), 13024 (2020). DOI: 10.1039/D0TA02614J
- [8] C. Jiang, Y. Ding, K. Cai, L. Tong, Y. Lu, W. Zhao, P. Wei, *ACS Appl. Mater. Interfaces*, **12** (8), 9646 (2020). DOI: 10.1021/acsami.9b21069
- [9] J.-J. Ma, M.-X. Yu, Z. Zhang, W.-G. Cai, Z.-L. Zhang, H.-L. Zhu, Q.-Y. Cheng, Z.-Q. Tian, D.-W. Pang, *Nanoscale*, **10** (22), 10699 (2018). DOI: 10.1039/C8NR02017E
- [10] M. Park, D. Choi, Y. Choi, H. Shin, K.S. Jeong, *ACS Photon.*, **5** (5), 1907 (2018). DOI: 10.1021/acsphotonics.8b00291
- [11] C.F. Pereira, I.M.A. Viegas, I.G. Souza Sobrinha, G. Pereira, G.A.L. Pereira, P. Krebs, B. Mizaikoff, *J. Mater. Chem. C*, **8** (30), 10448 (2020). DOI: 10.1039/D0TC02653K
- [12] R. Bera, D. Choi, Y.S. Jung, H. Song, K.S. Jeong, *J. Phys. Chem. Lett.*, **13** (26), 6138 (2022). DOI: 10.1021/acs.jpclett.2c01179
- [13] S.B. Hafiz, M. Scimeca, P. Zhao, I.J. Paredes, A. Sahu, D.-K. Ko, *ACS Appl. Nano Mater.*, **2** (3), 1631 (2019). DOI: 10.1021/acsanm.9b00069
- [14] Y. Ding, Y. Qiu, K. Cai, Q. Yao, S. Chen, L. Chen, J. He, *Nat. Commun.*, **10** (1), 841 (2019). DOI: 10.1038/s41467-019-08835-5
- [15] J. Qu, N. Goubet, C. Livache, B. Martinez, D. Amelot, C. Gréboval, A. Chu, J. Ramade, H. Cruguel, S. Ithurria, M.G. Silly, E. Lhuillier, *J. Phys. Chem. C*, **122** (31), 18161 (2018). DOI: 10.1021/acs.jpcc.8b05699
- [16] W.-Y. Lee, S. Ha, H. Lee, J.-H. Bae, B. Jang, H.-J. Kwon, Y. Yun, S. Lee, J. Jang, *Adv. Opt. Mater.*, **7** (22), 1900812 (2019). DOI: 10.1002/adom.201900812
- [17] O.V. Ovchinnikov, I.G. Grevtseva, M.S. Smirnov, T.S. Kondratenko, A.S. Perepelitsa, S.V. Aslanov, V.U. Khokhlov, E.P. Tatyana, A.S. Matsukovich, *Opt. Quantum Electron.*, **52** (4), 198 (2020). DOI: 10.1007/s11082-020-02314-8
- [18] A.S. Mazinov, A.S. Tyutyunik, V.S. Gurchenko, *Prikl. Fiz.*, No. 2, 64 (2020) (in Russian).
- [19] A.N. Gusev, A.S. Mazinov, A.S. Tyutyunik, I.Sh. Fitaev, V.S. Gurchenko, E.V. Braga, *Tech. Phys.*, **66**, 84 (2021). DOI: 10.1134/S1063784221010102
- [20] A.N. Gusev, A.S. Mazinov, V.S. Gurchenko, A.S. Tyutyunik, E.V. Braga, *Tech. Phys. Lett.*, **47**, 377 (2021). DOI: 10.1134/S1063785021040180

Translated by D.Safin