ZnO nanorods coating modified with AgInS$_2$ quantum dots

A A Ryabko, O A Korepanov, A A Bobkov, O A Aleksandrova, V A Moshnikov
Saint-Petersburg State Electrotechnical University «LETI», 5 Prof. Popova Street, Saint Petersburg, 197376, Russia

a.a.ryabko93@yandex.ru

Abstract. This paper presents the effect on the visible light photoresponse caused by the modification of ZnO nanorod coating with colloidal AgInS$_2$ quantum dots. The modification of ZnO nanorods by immersion in colloidal solution results in the enhancement of visible absorption and photoresponse. Obtained results indicate the possibility of local heterojunctions between ZnO and AgInS$_2$.

1. Introduction
Zinc oxide (ZnO) is an n-type semiconductor with a direct bandgap (3.37 eV at room temperature). ZnO nanorods could be applied in photovoltaic structures [1,2], resistive gas sensors [3], photocatalysis [4]. In the case of photocatalyst, modification of ZnO nanorods with QDs shifts the photoactivation region of the photocatalysis process from the ultraviolet to the visible region [5]. In the case of adsorption resistive gas sensors, ZnO nanorods sensitization with colloidal QDs could provide gas analysis response at room temperature (no high-temperature heating requirement) [6].

Zinc oxide particles and ternary metal chalcogenides QDs (AgInS$_2$ and CuInS$_2$) are thought to be biocompatible, non-toxic materials. Ternary metal chalcogenides QDs are usually compared with binary ones containing lead, cadmium, or tellurium [7]. The composition of ZnO and ternary metal chalcogenide QDs could be a convenient combination from the toxicology point of view. This work aims at the production and study of ZnO nanorods coating modified with AgInS$_2$ QDs.

2. Experiment
The ZnO nanorod arrays were formed in two stages [8]. At the first stage, a seed layer of ZnO was deposited by ultrasonic spray pyrolysis of a zinc acetate aqueous solution. At the second stage, ZnO nanorods were grown-up in an aqueous solution of zinc nitrate and hexamethylenetetramine by a low-temperature hydrothermal method. After synthesis, the coating of ZnO nanorods was annealed at a temperature of 500°C for 5 minutes to remove organic molecules from the surface. AgInS$_2$ QDs stabilized by 3-mercaptopropionic acid were synthesized in aqueous medium by the heating-up method [9]. 3-mercaptopropionic acid has a sufficiently short molecular chain to ensure the charge carriers’ transport between the AgInS$_2$ colloidal QD and the ZnO nanorod [10]. The modification of ZnO nanorods with AgInS$_2$ QDs was performed by substrate immersion in the colloidal solution.

The modified arrays of zinc oxide nanorods were studied by measuring the photocurrent under irradiation in the visible region. For this, nanorods were grown on ceramic substrates with interdigitated electrodes (Sensor Platform, Tesla Blatna, figure 1). The width of the interdigitated electrodes and the distance between them is about 25 μm, the electrode materials are NiCr/Ni/Au. Blue
LED ($\lambda = 460$ nm) was used as a visible light source (figure 1). The current through the sample was recorded using Keithley 6485 at the applied voltage of 5 V. Before measuring the photocurrent, the samples were preheated at 150 °C for 10 minutes to reduce the effect of adsorbed moisture.

Figure 1. Ceramic substrate with interdigitated electrodes (Sensor Platform, Tesla Blatna).

Figure 2. SEM image of ZnO nanorod arrays grown on a ceramic substrate with interdigitated electrodes.

ZnO nanorods cover the entire ceramic substrate with interdigitated electrodes. The area between the electrodes in the SEM image looks brighter due to the surface charging during the scan with an electron beam (figure 2).

Figure 3. LED emission spectra and AgInS$_2$ QDs absorption spectrum.

Figure 4. Sketch of the measurement of the short-circuit current of an FTO/ZnO/AgInS$_2$ structure.

Blue LED was chosen as a light source due to the high overlap between its emission spectrum and AgInS$_2$ QDs absorption spectrum.

The surface presence of QDs after immersion was controlled by absorption spectroscopy. For this, nanorods were grown on a quartz substrate.

Finally, the nanorods were grown on an FTO (fluorine-doped tin oxide) coated glass substrate. On which the layer of QDs from aqueous-alcoholic colloidal solution was deposited by the spin-coating method (2500 rpm, 30 sec, 20 cycles). Then, the short-circuit current was measured with gold pressure contact when irradiated with a lamp (figure 4).
3. Results and discussion

As it can be seen from figure 5, after modification the absorption increases due to additives of ZnO and QDs absorption. Photoresponse of a ZnO nanorods array on a ceramic substrate with interdigitated electrodes before and after AgInS₂ QDs modification are presented in figure 6. Nanorods without QDs modification show ~3.7 times conductivity change (I_{light}/I_{dark} ratio) under blue light irradiation (for ~5 min), which is due to the influence of intrinsic defects [11]. Modification of nanorods with AgInS₂ QDs leads to an increase in the photoresponse of the sample up to ~ 13.4 times (for ~ 5 minutes), which could point to the formation of local heterojunctions between ZnO and AgInS₂. ZnO nanorods resistivity after QDs modification could decrease due to the appearance of additional electrically conductive paths, which could arise with the embedding of colloidal QDs between the zinc oxide nanorods at their base.

![Absorption spectra of ZnO nanorods array on quartz substrate before and after modification with AgInS₂ QDs](image1)

![Photoresponse of a ZnO nanorods array on a ceramic substrate with interdigitated electrodes before and after AgInS₂ QDs modification. The radiation source is a blue LED (460 nm). The area without irradiation is highlighted with grey.](image2)

The photo of ZnO nanorods coating on an FTO coated glass substrate before and after modification with the AgInS₂ QDs, and corresponding absorption spectra are shown in Figure 7.

![The photo of the sample before and after modification with AgInS₂ QDs](image3)

![The corresponding absorption spectra](image4)

Figure 5. Absorption spectra of ZnO nanorods array on quartz substrate before and after modification with AgInS₂ QDs

Figure 6. Photoresponse of a ZnO nanorods array on a ceramic substrate with interdigitated electrodes before and after AgInS₂ QDs modification. The radiation source is a blue LED (460 nm). The area without irradiation is highlighted with grey.

Figure 7. The evolution of an FTO/ZnO/AgInS₂ absorption: a) the photo of the sample before and after modification with AgInS₂ QDs, b) the corresponding absorption spectra.
As can be seen from Figure 7, after 20 centrifugation cycles, a layer of AgInS$_2$ QDs is formed, which ensures the absorption of the sample in the visible region (more than 380 nm). In this case, the registration of the short-circuit current during irradiation of the structure indicates the formation of a ZnO/AgInS$_2$ heterojunction (Figure 8).

4. Conclusion
Modification of ZnO nanorod array with AgInS$_2$ QDs leads to an increase in the photoresponse to visible light irradiation. This may indicate the formation of local ZnO/AgInS$_2$ heterojunctions. Short-term annealing at 150 °C does not destroy the colloidal nanocrystals, but allows partial removal of moisture from the surface of the nanostructured coating. Obtained results indicate the possibility to create gas sensors, photocatalysts, and photovoltaic structures based on the ZnO nanorods with AgInS$_2$ colloidal QDs.

Acknowledgments
The reported study was funded by RFBR, project number 19-38-90088.

References
[1] Lashkova N A, Maximov A I, Ryabko A A, Bobkov A A, Moshnikov V A and Terukov E I 2016 Semiconductors 9 1254-1260
[2] Zang Sh, Wang Y, Su W, Zhu H, Li G, Chang X and Liu Y 2016 Phys. Status Solidi RRL 10 745–748
[3] Bobkov A, Varezhnikov A, Plugin I, Fedorov F, Trouillet V, Geckle U, Sommer M, Go V, Moshnikov V and Sysoev V 2019 Sensors 19 4265
[4] Yukhnovets O, Semenova A A, Levkevich E A, Maximov A I and Moshnikov V A 2018 IOP Conf. Ser. J. Phys. Conf. Ser. 993 012009
[5] Yang Y, Que W, Zhang X, Xing Y, Yin X and Du Y 2016 Journal of Hazardous Materials 317 430–439
[6] Nalimova S S, Maximov A I, Moshnikov V A, Bobkov A A, Mazing D S, Ryabko A A, Levkevich E A and Semenova A A 2019 IEEE International Conference on Electrical Engineering and Photonics (EExPolytech) 8906789 223-225
[7] Hong S P, Park h K, Oh J H, Yang H and Do Y R 2012 Journal of Materials Chemistry. 22 18939
[8] Ryabko A A, Maximov A I, Verbitskii, Levitskii V S, Moshnikov V A and Terukov E I 2020 Semiconductors 54 (11) 1257-1263
[9] Korepanov O A, Mazing D S, Aleksandrova O A and Moshnikov V A 2019 Journal of Physics: Conference Series 1410 (1) 012024
[10] Carey G H, Abdelhady A L, Ning Zh, Thon S M, Bakr O M and Sargent E H 2015 Chem. Rev. 115 12732
[11] Khokhra R, Bharti B, Lee H-N and Kumar R 2017 Scientific Reports 7 15032