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HETEROJUNCTION p-Cu_2SnS_3/n-ZnO

A. V. BUDANOV[a], YU. N. VLASOV[a,*], G. I. KOTOV[a], YU. V. SYNOROV[a], S. YU. PANKOV[b], E. V. RUDNEV[c], V. E. TERNOVAYA[c], S. A. IVKOV[c]
[a]*Voronezh State University of Engineering Technologies, 19 Revolution Av., Voronezh, Russia*
[b]*Voronezh State Technical University, 14 Moskovsky Av., Voronezh, Russia*
[c]*Voronezh State University, 1 Universitetskaya pl., Voronezh, Russia*

Conditions for the formation of a Cu_2SnS_3 film uniform in phase composition upon annealing of a metal layer of copper and tin in sulfur vapor in a quasi-closed volume chamber using the methods of X-ray spectral microanalysis and X-ray phase analysis are presented. The rectifying heterojunction p-Cu_2SnS_3/n-ZnO was fabricated.
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1. Introduction

In recent years a significant progress in the technology of a thin-film solar cells has been achieved through the use of a perovskite-type light-absorbing layers such as Cu(In,Ga)Se_2. Efficiency of 25.2 % was obtained in the perovskite/silicon tandem solar cell [1]. However, the cost of such technology is too high due to the use of the rare-earth element indium. In addition, there is a significant decrease in efficiency after several hours of use of a perovskite films [2].

Structures using kesterite-type light-absorbing layers such as $Cu_2ZnSn(S,Se)_4$ is cheaper, but the maximum efficiency of 12.6% can be achieved on the basis of toxic and poorly reproducible liquid-phase epitaxy process based on hydrazine [3]. Cu_2SnS_3 (CTS) films with p-type conductivity are considered as an alternative to the layers described above. According to the Shockley-Queisser limit for a single-junction solar cell based on CTS with the band gap of 0.95 eV a theoretical estimate of the efficiency gives a value of 30% [4]. This is significantly higher than the current maximum value of 5.1%. for the experimental structure of ZnO:Al/ZnO/CdS/CTS/Mo/SLG, where SLG are substrates from a soda-lime glass [5]. In the work [5] CTS layers are formed in two stages. First, a Cu-SnS_2 precursor layer is sputtered to the substrate by the magnetron from copper and tin disulfide targets. Then the precursor is annealed in a glass tube at a substrate temperature of 550 °C in a stream of nitrogen with sources of sulfur and tin monosulfide SnS vapor. Unfortunately, the CTS film formed in this way is inhomogeneous in phase composition, in particular, contains the Sn_2S_3 phase.

2. Experimental

In the present work to form the basis of the solar cell the p-n heterojunction CTS/ZnO was created on a glass substrate with a 0.9 μm thick ZnO layer deposited by the ion-beam deposition in an argon atmosphere at a partial pressure of 0.1 Pa. We formed the CTS layer on the ZnO surface using technology that seems simpler than in [5]. At the first stage, a 0.3 μm layer of a metal precursor was formed by thermal spraying from an alloy of copper and tin with atomic ratio Cu:Sn = 1.8. Then, the substrate with the metal layer was annealed in sulfur vapor according to the "hot wall" method in a quasi-closed chamber made from graphite [6,7] at a substrate temperature of 420 °C during 60 minutes. The vapor pressure of sulfur was set by the temperature of the sulfur

* Corresponding author: youramail@mail.ru

source and was 20 Pa. According to X-ray spectral microanalysis in the CTS film obtained in this way, the copper content is 32%, tin – 17%, sulfur – 51% in atomic percentage. The ratio of elements in the CTS layer corresponds to the stoichiometry of the compound Cu_2SnS_3. Insignificant copper enrichment as a result of processing in sulfur vapor to the ratio Cu:Sn = 1.9 can be explained by the evaporation of volatile tin sulfides during annealing [8,9].

3. Results and discussion

On the diffraction pattern of the CTS sulfide film (Figure 1), obtained on the ZnO surface, the three most intense diffraction peaks corresponding to reflections from the (111), (220) and (311) planes of the cubic crystal lattice of the Cu_2SnS_3 phase of F-43m symmetry group (PDF 01-089-2877). A similar pattern is observed upon electron diffraction by reflection on a CTS film formed in the same technological conditions on a glass substrate: three most intense diffraction rings from a polycrystalline CTS film corresponds to the three most intense peaks of x-ray diffraction (insert in Figure 1). The absence of diffraction peaks from the secondary phases indicates CTS films phase uniformity.

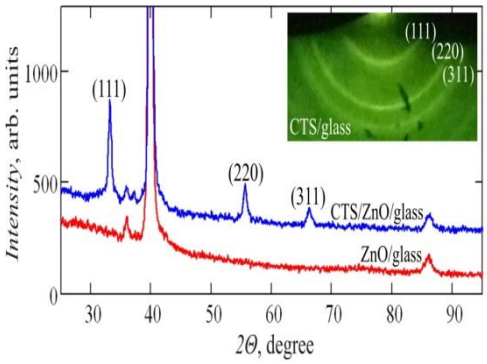

Fig. 1. X-ray diffractograms of ZnO film on glass substrate (bottom line) and of CTS/ZnO films (line above). Insert contain electron diffraction pattern of CTS film on glass substrate.

Ohmic contacts to the ZnO and CTS layers were obtained using graphite Kontactol paste. The current-voltage characteristic of the p-CTS/n-ZnO heterojunction is shown in Figure 2. The inset in Fig. 2 is a schematic representation of the p-CTS/n-ZnO heterostructure for electric investigations. The current-voltage characteristic in forward bias is a straight line with the Pearson correlation coefficient 0.99 in the coordinates ln(J) from U, where J is current density, and U is the bias voltage. An estimate of the height of the potential barrier gives a value of 0.9 eV. The barrier ideality coefficient is 5.1. A low breakdown voltage of 0.3 V can be explained by the high concentration of charge carriers in the CTS layer. Hole concentration determined by Hall method in the CTS layer is 10^{20} cm^{-3} with mobility 3 $cm^2V^{-1}s^{-1}$. Copper depletion and a decrease in the Cu:Sn ratio from 1.9 to 1.8 in the CTS film can lead to an increase in resistivity due to a decrease of hole concentration by two orders of magnitude, while hole mobility increases significantly [9]. Changing the composition of the initial metal precursor will allow controlling concentration of charge carriers of the CTS film and reaching a value of 10^{17}–10^{18} cm^{-3}, which is necessary to create a solar cell.

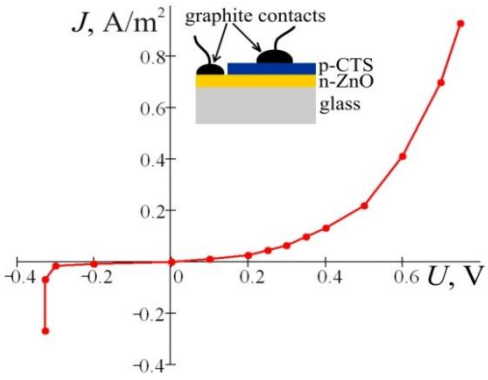

Fig. 2. Current-voltage characteristic of p-CTS/n-ZnO heterojunction.

4. Conclusions

The possibility of forming a p-n junction based on Cu_2SnS_3/ZnO heterostructures, which can be used to create thin film solar cell is shown. The advantage of this technology formation of a CTS film is the ability to create a sulfide layer homogeneous in phase composition at a sufficiently low temperature for the manufacture of photosensitive structures on flexible polymer substrates.

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