



Structure, optical, electrical and electronic parameters of a new thin film composition for kesterite solar cell



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ABSTRACT

The work is devoted to the development of a new thin film composition for kesterite solar cell with the base $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) layer obtained by the combination of two low-cost liquid methods, namely electrodeposition and Successive Ionic Layer Adsorption and Reaction (SILAR). The *p*-CZTS absorber is fabricated by the creation of the main $\text{Cu}_2\text{ZnSnS}_4$ layer through sulfurization of a stack of the electrodeposited Cu/Sn/Zn metal films. The pores in this main $\text{Cu}_2\text{ZnSnS}_4$ layer were filled by SILAR-deposited nanocrystalline kesterite layer. For a creation of semiconductor heterojunction *n*-ZnS/*p*- $\text{Cu}_2\text{ZnSnS}_4$ we prepared ZnS thin films by SILAR method. The work shows the results of analysis of diode characteristics of the developed ZnS/ $\text{Cu}_2\text{ZnSnS}_4$ heterostructures (series resistance R_s , shunt resistance R_{sh} , ideality factor n_a and the saturation current densities J_0). Other investigated electrical and electronic parameters obtained from the current-voltage (*I*-*U*) and capacitance-voltage (*C*-*U*) characteristics are the electrical resistivities ρ_{CZTS} and ρ_{ZnS} , the ZnS/ $\text{Cu}_2\text{ZnSnS}_4$ rectifying barrier Φ , the height ϕ of symmetrical double Schottky barriers in the grain boundary regions in the polycrystalline kesterite layers, the width of the electron depletion regions ω , the concentration of the fully ionized donor impurity N_d in *n*-ZnS and acceptor impurity N_a in *p*- $\text{Cu}_2\text{ZnSnS}_4$, the density N_{SS} of the surface states in the kesterite layers. Structure and optical properties of the ZnS films as such as of the individual kesterite layers and of their combination have been also researched.

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1. Introduction

Currently, a quaternary compound kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has drawn much renewed interest as a potential candidate to meet a global energy demand on a terawatt scale (Suryawanshi et al., 2016). $\text{Cu}_2\text{ZnSnS}_4$ is a *p*-type semiconductor with a direct bandgap of 1.4–1.5 eV and an absorption coefficient $\sim 10^4 \text{ cm}^{-1}$ (Suryawanshi et al., 2014; Lim et al., 2015; Nam et al., 2016; Li et al., 2016). However, not only the ideal band gap energy and the high absorption coefficient make it a good candidate for high efficiency thin film solar cells. Besides it, CZTS contains only earth-abundant and non-toxic elements and its thin films can be fabricated by using relatively inexpensive processes. For all these reasons, kesterite has attracted much attention as a perspective material for next generation high-efficiency low-cost thin film

solar cells (Abermann, 2013). Despite all that, the world record of CZTS solar cell efficiency still stands at 9.66% (Chen et al., 2016). Several explanations for the poor performance of the available kesterite solar cells have been suggested. But generally accepted view is that the not high efficiencies of CZTS solar cells indicate that the current status of their fabrication is far from optimum, as the latter usually results in poor semiconductor characteristics. So, the preparation of the device quality $\text{Cu}_2\text{ZnSnS}_4$ films by a simple and low-cost technique is of great importance for photovoltaic applications (Rakhshani, 2016). Presently, there is no consensus on the best way to prepare CZTS thin films. In articles (Klochko et al., 2014; Momotenko et al., 2015) we presented CZTS films obtained by promising for large-scale production method consisting in the sulfurization of the electrodeposited metal stack precursors. Unfortunately, as shown by our further studies, such $\text{Cu}_2\text{ZnSnS}_4$ films produced by annealing of the electrodeposited precursors in sulfur vapor are fairly porous that prevents the creation of the inexpensive and efficient solar cells merely on their base. According to Chen et al. (2016), the high-density voids at

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the interface of the CZTS absorber and the Mo back contact is the major challenge for synthesis the high-efficiency CZTS solar cell. To overcome this problem, Chen et al. (2016) inserted the self-constituent CuS, SnS or ZnS buffer layers between the CZTS and Mo substrate. Our approach presented here is to close the pores in the main $\text{Cu}_2\text{ZnSnS}_4$ film via nanograin kesterite layers made by Successive Ionic Layer Adsorption and Reaction (SILAR) method. On the one hand, according to (Suryawanshi et al., 2014, 2016) SILAR method is among the sparsely studied nonvacuum, simple, inexpensive and green technologies with high throughput and material utilization, and SILAR-deposited thin films exhibit a good surface morphology without any voids or cracks. But at the same time, the best performance, which was obtained for photoelectrochemical solar cells based on SILAR-deposited $\text{Cu}_2\text{ZnSnS}_4$ films (Suryawanshi et al., 2016) was only 1.81%. The authors (Suryawanshi et al., 2016) note that the solar cell performance obtained in their work is still low in comparison with those in other studies, particularly because of unsuitable diode parameters of the CZTS solar cells with SILAR-deposited $\text{Cu}_2\text{ZnSnS}_4$ films. Namely, it has according to Suryawanshi et al. (2016) the higher series resistance R_s and lower shunt resistance R_{sh} . On the other hand, as it was shown by Klochko et al. (2016), by the combination of several methods suitable for the mass production we can obtain a balance of semiconductor layer properties, which together can give the device quality. In this manner we have successfully developed in (Klochko et al., 2016) a new thin film composition for SnS solar cell. The p -SnS absorber was fabricated by the creation of the main SnS film through sulfurization of the electrodeposited Sn thin film, and the shunt leakage was eliminated by SILAR deposition of SnS into pores of the main SnS. The work presented here is devoted to the development of a new thin film composition for kesterite solar cell with the base layer obtained in a similar manner. The structure, optical properties, electrical and electronic parameters of the individual kesterite layers and their combination are researched.

As kesterite thin film solar cell includes a heterojunction, a selection of the second layer with opposite charge carriers (n -type) to that of the semiconducting nature of the photo-active CZTS layer (p -type) also plays an important role. The selection is made in view of matching the conduction and valence energy levels of the two layers such that the separation of the generated charge carriers is encouraged. Some works are devoted to the fabrication of $\text{CdS}/\text{Cu}_2\text{ZnSnS}_4$ heterostructures for the photovoltaic applications (Abermann, 2013; Emrani et al., 2013; Lim et al., 2015; Nam et al., 2016; Rakhshani, 2016). However, in Inamdar et al. (2011) and Jafarov et al. (2015) CdS was replaced by zinc sulfide (ZnS) to avoid the use of environmentally hazardous cadmium as well as to increase the efficiency of the kesterite solar cells. In the present work for a creation of semiconductor heterojunction $\text{ZnS}/\text{Cu}_2\text{ZnSnS}_4$ we prepared n -ZnS thin films by SILAR method in accordance with technique described in (Klochko et al., 2016). Thus, when designing a new thin film composition for kesterite solar cell the p -CZTS absorber is fabricated by the creation of the main $\text{Cu}_2\text{ZnSnS}_4$ layer through sulfurization of a stack of the electrodeposited Cu/Sn/Zn metal films in accordance with (Momotenko et al., 2015). The pores in this main $\text{Cu}_2\text{ZnSnS}_4$ layer were filled by SILAR-deposited nanocrystalline kesterite layer. This work shows the results of analysis of diode characteristics of the obtained $\text{ZnS}/\text{Cu}_2\text{ZnSnS}_4$ heterostructures (series resistance R_s , shunt resistance R_{sh} , ideality factor n_d and the saturation current densities J_0). Other investigated electrical and electronic parameters obtained from the current-voltage (I - U) and capacitance-voltage (C - U) characteristics are the electrical resistivities ρ_{CZTS} and ρ_{ZnS} , the $\text{ZnS}/\text{Cu}_2\text{ZnSnS}_4$ rectifying barrier Φ , the height φ of symmetrical double Schottky barriers in grain boundary regions in the polycrystalline kesterite layers, the width of the electron

depletion regions ω , the concentration of the fully ionized donor impurity N_d in n -ZnS and acceptor impurity N_a in p - $\text{Cu}_2\text{ZnSnS}_4$, the density N_{SS} of the surface states in the kesterite layers.

2. Experimental procedures

Electrochemical deposition of kesterite precursors in the form of a stack of three metal films with the sequence Cu/Sn/Zn onto 400 μm thick molybdenum (Mo) plates was performed in a galvanostatic mode at room temperature in standard aqueous electrolytes. A chemical etching of the molybdenum substrates prior to copper plating was performed for 1 min at 55 $^\circ\text{C}$ in an alkaline solution containing $\text{K}_3[\text{Fe}(\text{CN})_6]$ 25 g/l and KOH 10 g/l. The next step was an improvement of the Mo surface microrelief by means of its anodic electrochemical polishing for 1 min in concentrated sulfuric acid with 3% CrO_3 . Electrochemical polishing of Mo was carried out at room temperature without solution stirring. The current density in the Mo electrochemical polishing was 1 A/cm^2 , the voltage was approximately 10–12 V. A stabilized DC power supply TES 5060-1 and two-electrode electrochemical cell were used for the electrochemical Mo polishing and for the electrodeposition of the metal films. The thicknesses of the individual metal films in the Cu/Sn/Zn precursor were determined by the coulometric method. Copper plating time was 23 s, the solution for copper plating contained $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 90 g/l and H_2SO_4 120 g/l. The 0.48 μm thick Cu films were obtained at 63 mA/cm^2 current density. For the deposition of 0.80 μm thick Sn film for 177 s at 8 mA/cm^2 cathode current density we used pyrophosphate electrolyte containing SnCl_2 80 g/l, $\text{Na}_4\text{P}_2\text{O}_7$ 180 g/l and NH_4Cl 50 g/l. Electrodeposition of 0.43 μm thick Zn film was performed in a solution which consisted of ZnO 12 g/l, NH_4Cl 240 g/l, H_3BO_3 20 g/l and wood glue 1 g/l. Zinc plating time was 169 s, the cathode current density was 8 mA/cm^2 .

Sulfurization of Cu/Sn/Zn film stack for its conversion into main $\text{Cu}_2\text{ZnSnS}_4$ layer was carried out in a sulfur vapor at 600 $^\circ\text{C}$ for 0.5 h using a reusable home-made quartz reactor represented in (Momotenko et al., 2015). Cooling of the sulfurized films was carried out simultaneously with the reactor for the protection of CZTS from the oxidation.

Deposition of nanograin CZTS film by SILAR method on the Mo/ $\text{Cu}_2\text{ZnSnS}_4$ surfaces as well as on K8 glass substrates was carried out at room temperature by sequential immersion of the surfaces to be coated into cation bath (i) contained aqueous solution 0.02 M CuSO_4 and 0.08 M SnSO_4 for 30 s, then into distilled water for 10 s, followed by dipping into 0.16 M Na_2S aqueous solution for 10 s and again into distilled water for 10 s. After that the sample was immersed for 30 s into aqueous cationic bath (ii), which contained 0.5 M ZnSO_4 , then washed with distilled water for 10 s, immersed for 5 s in the 0.16 M Na_2S anionic solution and again washed with distilled water for 10 s. All this procedure was 1 cycle SILAR ($n = 1$) of CZTS. The desired thickness of CZTS was obtained by repeating from $n = 15$ up to $n = 90$ SILAR cycles.

For the creation of ZnS films by SILAR the Mo/CZTS plates or K8 glass substrates were sequentially dipped into aqueous solution 0.01 M $\text{Zn}(\text{CH}_3\text{COO})_2$ at 70–80 $^\circ\text{C}$ for 20 s, then into distilled water for 10 s, then into 0.01 M Na_2S aqueous solution at 70–80 $^\circ\text{C}$ for 20 s and again into distilled water for 10 s. Temperature of the distilled water was 40–45 $^\circ\text{C}$. The zinc sulfide film thickness was regulated by multiple repeating this process. The number of cycles in the manufacture of ZnS by SILAR varied from $n = 30$ to $n = 150$.

Structure of the kesterite layers obtained by both through the sulfurization of the electrodeposited Cu/Sn/Zn metal stack and by SILAR methods as well as ZnS films deposited by SILAR were examined via analysis of X-ray diffraction patterns produced with a DRON-4 diffractometer in $\text{CoK}\alpha$ radiation ($\lambda = 1.78897 \text{ \AA}$) (XRD method). Scanning was performed with Bragg–Brentano focusing

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