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Development of a new thin film composition for SnS solar cell

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Abstract

The work is devoted to the development of a new thin film composition for SnS solar cell based on semiconductor heterojunction *n*-Zn(O,S)/*p*-SnS by the combination of two low-cost liquid methods, namely electrodeposition and Successive Ionic Layer Adsorption and Reaction (SILAR). Structure and optical properties of the obtained layers have been investigated. The *p*-SnS absorber is fabricated by combining the two methods. The creation of the main SnS film was carried out by sulfurization of the electrodeposited Sn thin film. The elimination of the shunt leakage was made by SILAR deposition of nanocrystalline SnS into pores of the main SnS. All SnS films are single-phase and consisted of tin monosulfide with orthorhombic structure of Herzenbergite. Wide band gap and transparent buffer layer *n*-Zn(O,S) is created by air annealing of ZnS thin film prepared by SILAR. Series and shunt resistances as well as a height of the rectifying barrier of this *n*-Zn(O,S)/*p*-SnS heterostructure were investigated due dark current–voltage characteristics. The diode and electronic parameters of this new thin film composition is superior ones for the obtained by using tin sulfide absorber produced only by SILAR.

Keywords: Tin sulfide; SILAR; Electrodeposition; Photovoltaics; Heterostructure

1. Introduction

Thin film photovoltaics (PV) continue to attract interest and significant research activity. However, the economics of the PV market are shifting rapidly and developing commercially successful thin film PV has become a more challenging prospect. Manufacturing cost advantages over wafer-based technologies can no longer be taken for granted, and improvements in both efficiency and cost must be sought on an equal footing. In light of this reality, the development of tin sulfide (SnS) as an absorber material for thin film PV have been chosen by various research groups (Devika et al., 2008; Ghosh et al., 2011; Sinsermsuksakul et al., 2013; Xu and Yang, 2014; Jaramillo et al., 2015; Klochko et al., 2015a; Li et al., 2015). SnS is earth-abundant, non-toxic substance and it has intrinsic practical advantages that could translate into low manufacturing cost. Primarily, SnS offers easy phase control and it absorbs visible light strongly. Due to this SnS layers less than one micrometer thick can absorb most of the solar spectrum above the band-gap. Charge transport across such thin layers should be relatively immune to defects and impurities compared to silicon, which demands high purity and crystal perfection to make efficient, but expensive solar cells. Moreover, the available amounts of tin and sulfur are large enough to supply all

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of the world's energy. Also, SnS is stable in the presence of water and oxygen in the atmosphere, where it is found as a mineral Herzenbergite. Thus, SnS has better prospects for long-term stability than organic solar cells and lead iodide perovskites, which are destroyed by oxygen and water (Sinsermsuksakul et al., 2014). Although theory predicts that the maximum energy conversion efficiency of single-junction SnS-based solar cells is 32%, the best existing SnS solar cells has only reached efficiencies 4.36% (Jaramillo et al., 2015) and 4.63% (Sinsermsuksakul et al., 2014). These values far too low to compete with silicon solar cells with over 20% efficiency. Various research groups hence have focused on the factors that can improve performance of SnS solar cells. A lot of techniques for SnS deposition have been reported (Lindwall et al., 2016) including thermal evaporation, spray pyrolysis, sputtering from SnS and SnS_2 targets and metalorganic chemical vapor deposition. The attention of many investigators is focused on improving the absorption end electrical properties of the photo-active SnS layers prepared by inexpensive liquid methods suitable for mass production. For example, they used chemical bath deposition (He et al., 2014), galvanostatic electrodeposition (Ghosh et al., 2010), pulsed electrodeposition (Mathews et al., 2013). In Ghosh et al. (2011) low-cost liquid method Successive Ionic Layer Adsorption and Reaction (SILAR) has been employed for the growth of SnS films for photovoltaics. In the CdS/SnS heterostructured device CdS layer was obtained by Ghosh et al. (2011) through chemical bath deposition on indium tin oxide (ITO) layer on soda-lime glass substrate. The growth of SnS on CdS films was during 300 SILAR cycles, and after completion every 30 SILAR cycles the films were placed in ultrasonic bath for 10 min to remove the loosely bound particles. After the thickness of the SnS layer was found to be 525 nm, the resultant structure was subjected to heat treatment at 250 °C for 2 h in a vacuum furnace to reduce the internal stress between CdS and SILAR grown SnS and also to reduce the lattice mismatch between them. Despite the rather cumbersome procedure for obtaining this thin film composition, the series resistance value obtained on the base of dark current–voltage (I–U) characteristics presented in Ghosh et al. (2011) for CdS/SnS heterojunction was extremely high ($R_s = 98\ \Omega\ cm^2$). We believe that this is due to the nanograin structure of SILAR SnS and is the reason for the very low efficiency of PV presented in Ghosh et al. (2011), which equals 0.01%. In article (Klochko et al., 2015a) we presented tin sulfide films obtained by promising for large-scale production method consisting in sulfurization of electrodeposited tin precursors. These SnS films with thickness about 1–2 μm are characterized by indirect and direct allowed optical transitions, have high optical absorption coefficients $\alpha > 10^4\ cm^{-1}$, indirect band gap 1.1 eV and direct band gap 1.3 eV. Unfortunately, as shown by our further study such SnS films produced by annealing of the electrodeposited tin precursors in sulfur vapor are fairy porous that prevents the creation of the inexpensive and efficient solar cells merely on their base.

As SnS thin film solar cell includes a heterojunction, selection of the second layer with opposite charge carriers (n-type) to that of the semiconducting nature of the photo-active 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 CdS/SnS heterostructures for photovoltaic applications (Ghosh et al., 2010, 2011; Li et al., 2015). However, as it was shown by Xu and Yang (2014) during a research on the performances of CdS/SnS, ZnS/SnS and ZnO/SnS heterojunctions by numerical analysis, the calculated results have shown that the ZnS/SnS heterojunction among others has the highest conversion efficiency. According to Xu and Yang (2014) the less absorption in the window layer and the less photo-generated carrier barrier in the heterojunction interface the greater the improvement of the photovoltaic properties. Nevertheless, the record efficiencies of thin film SnS PV were experimentally obtained with buffer layer, which is a solid solution of ZnS and ZnO, viz. zinc oxysulfide (ZnO_xS_{1-x}, or Zn(O,S)), that is used in majority of research (Jaramillo et al., 2015; Sinsermsuksakul et al., 2013). According to these researchers, the enhancing efficiency of SnS solar cells was carried out via band-offset engineering.

This work is devoted to the development of a new thin film composition for SnS solar cell based on semiconductor heterojunction Zn(O,S)/SnS by the combination of several methods suitable for the mass production. The p-SnS absorber is fabricated by the use of two low-cost liquid methods, namely, by creation of the main SnS layer through sulfurization of the electrodeposited Sn thin film and by SILAR of nanocrystalline SnS layer into pores of the main SnS. n-Zn(O,S) buffer layer is obtained by air annealing of ZnS thin film prepared by SILAR. The paper studies structure and optical properties of the layers, as well as demonstrates diode characteristics of the n-Zn(O,S)/p-SnS heterojunction.

2. Experimental procedures

Electrochemical deposition of tin films as precursors of SnS main layers was performed in galvanostatic mode at room temperature in conventional aqueous pyrophosphate electrolyte containing 80 g/l $SnCl_2$, 180 g/l $Na_4P_2O_7$ and 50 g/l NH_4Cl. A stabilized DC power supply TES 5060-1 and two-electrode electrochemical cell were used for electrodeposition of Sn films. As a substrate for the Sn electrodeposition we used 400 μm molybdenum foils. Mo plates 1 × 3 cm in size were used as working electrodes (cathodes), stainless steel 5 × 6 cm plate was an anode. Before Sn electrodeposition a chemical etching of Mo allowing to clean the surface from contaminations was