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A Comparative Study: Sequential and Single-Step-Electrodeposited CZTS Thin Films

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CZTS (Cu_2ZnSnS_4) is a relatively new and promising semiconductor material suitable for photovoltaic applications due to its favorable optoelectronic properties. Of the many techniques available for growing these films, a comparative study on sequential and single-step electrodeposition methods to grow CZTS films is carried out in this investigation to explore the possibility of improving the quality of the films using the inexpensive electrodeposition technique. Mainly in both methods, potentiostatic electrodeposition technique is adopted for growing CZTS thin films. In both methods, growth conditions of the CZTS films are optimized after measuring the photoresponses in a photoelectrochemical (PEC) cell of the films that resulted at the end of each deposition step. The observed structural and optoelectronic properties of the films reveal that, in general, structurally good and photoactive CZTS films can be prepared using both methods. Moreover, photoresponse and Mott–Schottky measurements on CZTS films in a PEC reveal that CZTS films prepared using the single-step electrodeposition have better photoactive properties and improved doping densities. This important finding shows that when developing CZTS-based solar cells using the inexpensive electrodeposition technique, single-step electrodeposition is more advantageous.

1. Introduction

Photovoltaic (PV) solar cells are among the most demanding electronic devices that are used in fast-growing alternative green energy technologies. Considering economic and environmental issues, it is very well understood that the development of solar energy converting devices using environmentally friendly and low-cost materials and techniques is extremely important. Especially, nontoxic semiconductor materials made with inexpensive Earth-abundant elements, such as, Cu, Zn, Sn, S, etc., are prominently considered for large-scale PV applications. In this respect, CZTS is one of the promising solar energy-converting materials due to its high absorption coefficient, greater than $10^4\,cm^{-1}$, and bandgap ($\approx$1.45 eV).[1] In fact, the bandgap of CZTS matches well with the theoretically predicted ideal bandgap of a semiconductor which can absorb a good part of the solar spectrum and produces good solar cell outputs.[2] On the other hand, CZTS material has an additional advantage because it can be prepared by several methods such as sputtering,[3,4] thermal evaporation,[5,6] spray pyrolysis,[7,8] sol–gel technique,[9,10] and electrodeposition.[11,12] In the literature, it has been reported that PV devices fabricated with CZTS films prepared with different techniques demonstrate the efficiency dependence on growth techniques. Although significant progress on this material has been achieved, the highest reported efficiency of CZTS-based solar cells is yet 12.6%.[5] This value is still low compared with the theoretically predicted efficiency value of 32.2%.[4] Therefore, with further research work, there is a very good possibility of developing a more efficient solar cell device using CZTS semiconductor material. Especially, a comparative study on different available techniques for the growth of CZTS films would be a promising approach in this regard.

Among different CZTS growth techniques, electrodeposition is very attractive due to many reasons, such as, its simplicity, low cost, and low-temperature process. In addition, another major advantage of electrodeposition technique is that it can be easily adopted for making large-area thin-film devices suitable for practical applications. Another major advantage of the electrodeposition technique is that the composition of films can be easily controlled to modify physical properties of the materials.[13] Importantly, electrodeposition technique can produce CZTS solar cells having efficiency comparable with other expensive growth techniques.[5,14–20] Therefore, investigations on developing CZTS films suitable for PV applications using the electrodeposition technique will be a promising and important research approach.

In this investigation, two different methods were studied for the growth of CZTS films on Mo substrates. One is the electrodeposition of constituent metal layers sequentially on the substrate using different baths containing different precursor ions.[21] In the other method, a single bath containing all the precursor ions is used and single-step electrodeposition is carried out.[21] Each deposition step is optimized by monitoring photoactive properties

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