MICROSTRUCTURE OF $Cu_2ZnSnSe_4$ FILMS ON FLEXIBLE SUBSTRATES FOR PHOTOVOLTAIC APPLICATIONS

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Kesterite $Cu_2ZnSnSe_4$ thin films were obtained by selenization of electrochemically deposited and preliminary annealed metallic precursors on flexible Mo and Ta foil substrates. The films and their precursors were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM).

Key words: kesterite, $Cu_2ZnSnSe_4$, selenization, annealing, microstructure.
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1. INTRODUCTION

In recent years kesterite $Cu_2ZnSn(S,Se)_4$ (CZT(S,Se)) thin films have been extensively studied as a potential earth abundant alternative material for thin film solar cell technologies such as ones based on $Cu(In,Ga)Se_2$. There is an increasing interest in the development of solar cells on the flexible metal substrates for the industrial and space power application due to their light weight, high specific power density, and radiation hardness [1].

A number of methods have been used to obtain CZT(S,Se) thin films for photovoltaic applications, including vacuum [2-7] and non-vacuum methods [5-7]. Latter are more preferable due to their low cost and technological simplicity. The prevalent way to obtain a CZT(S,Se) film includes two steps: 1) formation of metallic Cu-Zn-Sn (CZT) precursor, 2) heat treatment of the precursor in S and/or Se presents to obtain the desired CZT(S,Se) film. In some cases, preliminary annealing step before selenization/sulfirization is applied. Among the non-vacuum methods for CZT precursor formation, electrochemical deposition is the most commonly used due to precise control of the precursor composition and thickness. The Cu-Zn-Sn precursor metals can be deposited simultaneously or sequentially. However, the CZT(S,Se) solar cells based on successively deposited stack metal precursor showed the best solar energy conversion efficiency of 12.6% [7] among the whole CZT(S,Se) thin film solar cells obtained by both vacuum and non-vacuum deposition methods.

Normally, Mo-coated glass is used as the substrate for CZT(S,Se) thin films. Using this type of substrates raises a number of issues. Thus, it's difficult to obtain high-quality single-layered substrates with high adhesion and electrical conductivity of the molybdenum and, as the result, several layers of Mo deposited under different conditions are required, making the process difficult and expensive; 2) during electrochemical deposition of metals hydrogen evolution takes part, destroying the Mo layer and peeling off the precursor film. To solve the mentioned above problems we propose using flexible metal foils as the substrate and back contact material for CZT(S, Se) thin films and solar cells based on them.

The purpose of this work is preparation and characterization of the $Cu_2ZnSnSe_4$ thin films on flexible substrates (tantalum and molybdenum foils).

2. EXPERIMENTAL DETAILS

Flexible Mo and Ta foil substrates were mechanically polished and rinsed subsequently with 96% ethanol and deionized water. Electrochemical deposition of the metal layers in Cu/Sn/Zn and Cu/Sn/Cu/Zn sequences was performed in galvanostatic mode in a two-electrode cell with planar-arranged electrodes. The 99.999% pure metal plates were used as anodes. The Cu layers were deposited from aqueous solution containing 0.02M $CuSO_4$ and 0.25M sodium citrate with pH =6.3 at T=25°C and the cathodic current density of J_c=*1mA/cm*^{2}. The Sn layers were deposited from aqueous solution of 0.02 M $SnSO_4$ and 0.25 M sodium citrate with pH =6.3 at T= 65°C and J_c=*6 mA/cm*^{2}. The Zn layers were deposited from aqueous solution containing 0.75M $ZnSO_4$, 0.5M Na_2SO_4 and organic additives (pH =*3.7*) at *T=60°C* and J_c=*15mA/cm*^{2}.

The pre-annealing of CZT precursor layers was performed in a tube furnace in an Ar (N 6.0) 95 %+$H_2$5 % gas mixture. The *CZT* metallic films pre-annealed at a temperature of 350°C for 0.5*h* was selenized in a home-made quartz container (volume 12.5 cm^3) with 5

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mg of powdery Se under 1 bar of Ar gas pressure. Firstly, the tube was evacuated when filled with Ar gas, again evacuated, and afterwards filled with an Ar gas to 1 bar pressure. Selenization was performed at temperatures from 350 to 530°C. After the selenization samples were naturally cooled down inside the furnace [5,6].

The *XRD* studies were conducted using an x-ray diffractometer SmartLab (Rigaku) with a 9*kW* Cu rotating anode x-ray tube. The primary x-ray beam was conditioned by a multilayer Ni/graphite monochromator *CBO* (cross beam optics) in the case of grazing incidence (*GI*) *XRD* measurements. The *SEM* characterization of *CZT* and CZTSe film surface morphology were carried out in a dual beam system *FESEM-FIB* Helios Nanolab 650 (*FEI* Company).

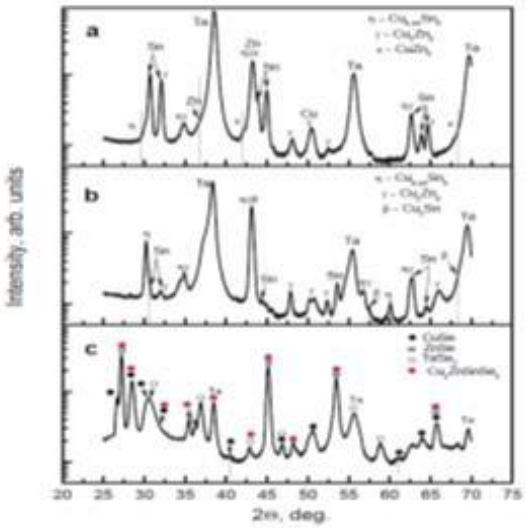

Fig. 1. Typical *XRD* patterns of *CZT* precursors (***a*** – as deposited, ***b*** –annealed) and CZTSe thin films (***c***) on Mo foil substrate.

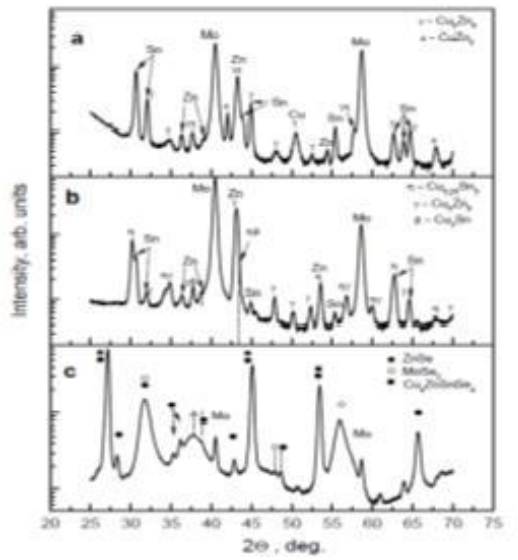

Fig. 2. Typical *XRD* patterns of *CZT* precursors (*a* – as deposited, *b* –annealed) and CZTSe thin films (**c**) on Ta foil substrate

3. RESULTS AND DISCUSSION

XRD measurements were performed to confirm the crystallinity and phase composition of the thin films. *XRD* measurements showed that phase formation in CZSSe films depends both on the composition ratio in the precursors and on the processing regimes. It has been determined that the as-deposited precursors besides the basic metals (Cu, Sn, Zn) contain a number of intermetallic metallic phases (Figures 1*a*, 2*a*).

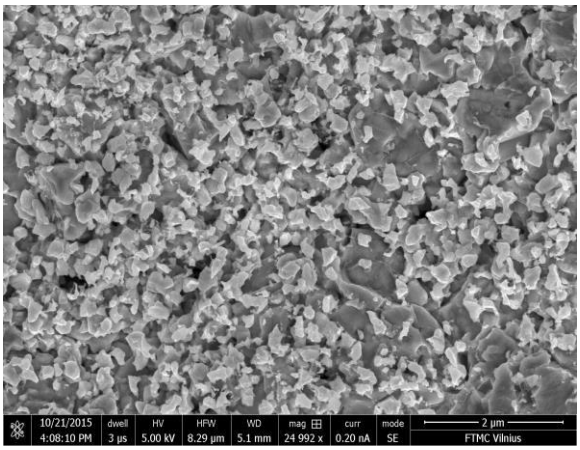

Fig. 3. A typical *SEM* image of the *CZT* thin film on Mo foil substrate

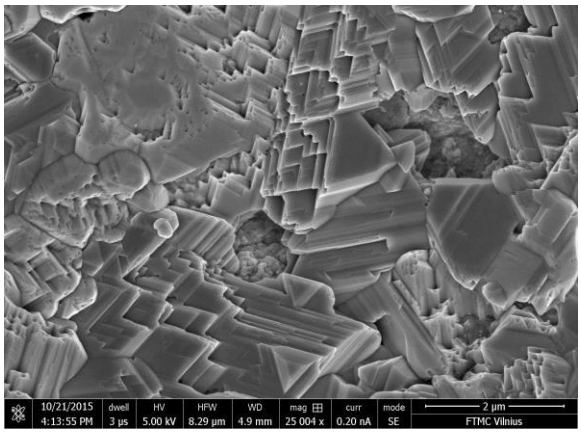

Fig. 4. A typical *SEM* image of the CZTSe thin film on Mo foil substrate

The pre-annealing of metallic films resulted in the formation of micro-meter size grains of the η-$Cu_{6.26}Sn_5$ and γ-Cu_5Zn_8 phases (Figures 1*b*, 2*b*). *XRD* studies of Cu-Sn-Zn and Cu-Sn-Cu-Zn precursor layers selenized at temperatures 500-550°C have shown the formation of crystalline CZTSe thin films. However, the selenized films contained additional ZnSe, CuSe and $MoSe_2$ (or $TaSe_2$) phases (Figures 1*c*, 2*c*) along with that of $Cu_2ZnSnSe_4$. The amount of ZnSe decreased with selenization temperature. The morphological analysis of as-deposited and annealed films has been done by *SEM*. The as-deposited metallic films showed non uniform distribution of agglomerated small particles with well-defined boundaries. The CZTSe thin films are densely packed with compact faceted grain

structure and without any voids on the surface (Figures 3, 4).

4. CONCLUSIONS

CZT metallic precursors were sequentially deposited on flexible Mo and Ta foil substrate, preliminary annealed and selenized leading to formation of CZTSe. Several intermetallic phases (Cu_6Sn_5, Cu_5Zn_8 etc.) where observed both in as-deposited and annealed precursors. The CZTSe films contain undesired ZnSe and CuSe phases. Morphologically, the resulting CZTSe thin films are densely packed with compact faceted grain structure and without any voids on the surface. The obtained results will be used to further improve the CZTSe-based thin-film solar cells technology.

5. ACKNOWLEDGMENTS

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