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$Cu_2ZnSnSe_4$ thin films grown by molecular beam epitaxy

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ABSTRACT

$Cu_2ZnSnSe_4$ has a potential for photovoltaic cells but the performances must be improved. Here, we report on CZTSe grown by molecular beam epitaxy. A smooth 2D growth mode was maintained during the deposition except for the early stage of the deposition where nanometer islands formed. This initial 3D growth is attributed to the formation of $CuGaSe_2$ and $CuGaZnSe_3$ detected by X-ray diffraction. Reflection of high energy diffraction oscillations, correlated to the growth rate, were obtained. The $Cu_2ZnSnSe_4$ film grew epitaxially on GaAs with its c-axis oriented along the GaAs[001] growth direction and $Cu_2ZnSnSe_4$(001)[110] parallel to GaAs(001)[110].

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) has a potential to be used as an efficient photon absorber in thin film photovoltaic (PV) cells. Its direct band gap can be tuned in the appropriate 1–1.5 eV range, depending on the Se/S ratio. In addition, CZTSSe is only composed of elements that are non toxic, abundant in the earth crust and low-cost [1]. Several technologies are used to fabricate CZTSSe solar cells, some being compatible with large scale fabrication, others less. A recent review of the major progresses in CZTSSe devices can be found in Ref. [2]. So far, the record PV conversion efficiency is 12.7% for CZTSSe PV cells fabricated by a non-vacuum process [3] and 11.8% by vacuum technologies [4]. These performances need to be significantly improved to become competitive against mature technologies like Silicon, CdTe and $C(In,Ga)(S,Se)_2$ solar cells; especially if one targets terawatt-scale production.

Fabricating single phase and stoichiometric CZTSSe is a serious challenge. It has been predicted [5,6] and evidenced experimentally [7,8], that the existence region of the compound is very narrow in the phase diagram. Thus, CZTSSe may coexist with secondary phases that can limit the performance of the cells. The data reported in literature concern usually polycrystalline CZTSSe PV cells, for which the role of the grain boundaries has to be clarified. The identification of the limiting factor(s) to the efficiency of polycrystalline CZTSSe PV cells is a difficult task. The possible fabrication of high efficient CZTSSe PV cells asks for more efforts to master the fabrication of high quality CZTSSe thin films, avoiding the formation of point defects that can degrade the efficiency of the cells [9,10].

In the particular case of CZTSe, 11.6% conversion efficiency could be obtained for a cell fabricated by annealing of co-evaporated elements in a Se rich atmosphere [11]. Co-evaporation of CZTSe has also been used in a single step process (i.e. without annealing) and lead to 9.8% efficiency [12]. This latter approach is of particular interest because it allows, in principle, real time control of the stoichiometry and formation path; what is much more difficult in the standard two-step approach.

While large-scale fabrication of CZTSSe PV cell is the main motivation in this field, one has to better understand the potential and limits of this material. Molecular beam epitaxy (MBE) is known to be a suited technology to fabricate high quality semiconducting thin films and heterostructures. It is therefore an appealing approach to develop CZTSSe thin films and investigate their properties in details. MBE is not suited for a large scale fabrication of CZTSSe PV cells but it will contribute to identify the fabrication path and the weak points of the material that have to be overcome in order to significantly improve the conversion efficiency of the CZTSSe cells. To date, few results can be found for the MBE growth of this class of material and restricted to either CZTS or CZTSe (no mixing of Se and S). Reported results on the growth of CZTS by MBE on Si highlights the difficulties to obtain defect free thin films [13–15]. The difficulty to form single phase CZTSe by MBE has also been evidenced [16]. The CZTSe layers reported in Ref. [16] exhibited either the presence of ZnSe or a significant amount of Cu_2SnSe_3, depending on the growth conditions. The authors pointed the need to grow the CZTSe at higher temperature,

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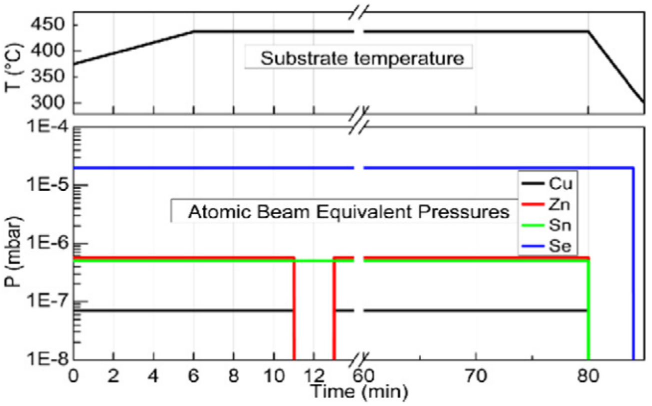

Fig. 1. MBE growth conditions of the CZTSe layer on GaAs(001): the layer is co-deposited with a 2-min growth break under Sn and Se fluxes to smoothen the surface.

compared to the two-step approach developed for the fabrication of polycrystalline films on Molybdenum coated soda lime glass, and the use of a SnSe effusion cell in addition to Sn and Se in order to reach supersaturation of Sn and Se during the growth.

Here, we focus on the MBE growth of CZTSe thin film using 4 elemental effusion cells (Cu, Zn, Sn, Se) without post treatment of the layer. An epitaxial layer of CZTSe was fabricated on GaAs(001). It was investigated, in situ, by reflection of high energy electron diffraction (RHEED) to check its morphology and measure its growth rate during the deposition of the elements. The layer was also probed by Raman spectroscopy to check for the possible presence secondary phases. Finally, the crystalline structure and orientation of the CZTSe layer was studied by high resolution X-ray diffraction (XRD).

The sample discussed here was grown in a MBE chamber equipped with 4 Knudsen cells used to evaporate Cu, Zn, Sn, and Se. The Beam Equivalent Pressures (BEP) of the 4 elements were measured by a gauge pressure meter positioned close to the location of the sample. The CZTSe layer was grown on a GaAs(001) substrate, glued on a Molybdenum sample holder with Indium. The temperature of the substrate was measured by a thermocouple in mechanical contact with the sample holder and remote controlled by a Eurotherm and the electric power sent through a Tantallum filament positioned a few mm behind the Mo holder. A calibration of the temperature was done to correct for a possible offset due to the change in the mechanical contact between the thermocouple and the Mo holder from one experiment to the other. For that, we visualized the melting of a Sn flake (melting point: 232 ° C) attached on the Mo holder when slowly ramping up the substrate temperature.

The native oxide was thermally removed from the GaAs in the growth chamber without any supply of arsenic. The RHEED pattern of the GaAs surface obtained after the removal of the oxide is shown in Fig. 2b. It is characteristic of a smooth 2D layer, with some shortening of the lines that is attributed to surface roughness caused by the thermal treatment. The growth conditions and chronology are illustrated in Fig. 1. CZTSe was co-evaporated with respective Cu, Zn, Sn and Se BEP of 7.10^{-8} mbar, 8.10^{-7} mbar, 5.10^{-7} mbar and 2.10^{-5} mbar. The substrate temperature was ramped up, during growth, from 375 ° C to 435 ° C in the first 6 min. After 5 min of growth at 435 ° C, the Cu and Zn shutters were closed during 2 min to smoothen the surface exposed to Sn and Se. The Cu and Zn shutters were then opened to continue the deposition of CZTSe. At the end of the co-deposition, the sample was cooled down to 300 ° C with the Se shutter open and further cooled down to 200 ° C in vacuum before taking the sample out of the MBE chamber. At the end of the growth, the surface of CZTSe layer is smooth, as revealed by the striky RHEED pattern shown in Fig. 2c.

The growth interruption under Sn and Se fluxes was done to smoothen the surface and indeed, RHEED oscillations were observed (Fig. 2a) when restarting the co-deposition. From the thickness of the CZTSe film, $h = 620$ nm, extracted from cross-section SEM image (inset of Fig. 2a), one can calculate a growth rate of $1.2\ \text{Å} \cdot s^{-1}$. As detailed later in this letter, CZTSe grew with its c-axis along the growth direction. In this case, a monolayer (ML) can be defined as one cation plane connected to a Se plane with a spacing corresponding to c/4, with c the lattice parameter. If one assumes the growth to occur layer by layer, one deduces a growth rate of about $0.4\ \text{ML} \cdot s^{-1}$. A systematic investigation of the change in the growth rate as a function of the atomic fluxes and substrate temperature could drive the optimization of the growth conditions and better understand the formation path of CZTSe.

One should stress that the RHEED pattern became spotty during about the first 30 s of the CZTSe growth. The RHEED spots elongated then progressively to become striky after some minutes of deposition. This reveals the presence of 3D islands in the early stage of the growth. This is confirmed by the cross-section SEM image (inset Fig. 2a), where holes can be seen at the CZTSe/GaAs interface. The appearance of the islands is attributed to the formation of $CuGaSe_2$ and $CuGaZnSe_3$ that are both detected by XRD (Fig. 4). We may assume that the growth mode is very similar to what has been observed in the case of the MBE growth of ZnSe on GaAs. It has

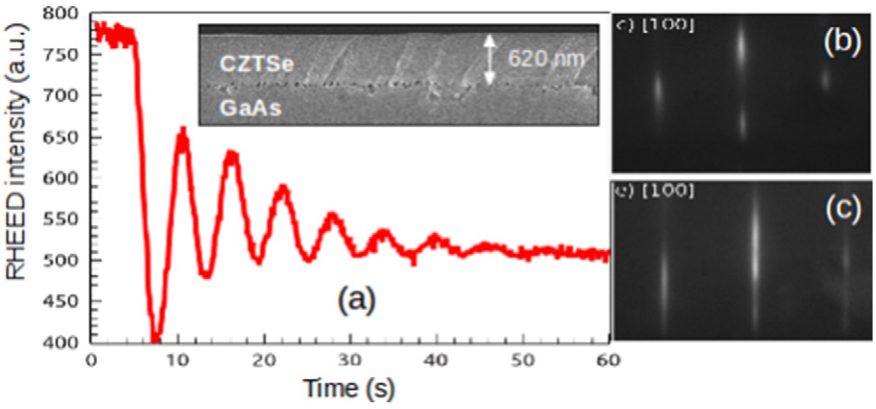

Fig. 2. (a) RHEED oscillations obtained after 11 min of growth and 2 min smoothing of the surface under Sn and Se. Inset of (a) represents a cross-section SEM image of the corresponding CZTSe layer MBE grown on GaAs. (b) RHEED pattern of the GaAs obtained at 375 °C, just before the deposition of the CZTSe layer. (c) RHEED pattern of the CZTSe layer at the end of the growth.