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Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ solar cells by sulfurization of evaporated precursors

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Abstract

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising material for the production of thin film photovoltaic modules. In this paper we report on the fabrication and characterization of $\text{ZnO}/\text{CdS}/\text{CZTS}/\text{Mo}$ solar cells. The CZTS absorber was grown by sulfurization of a precursor composed of a multilayer of ZnS, Sn and Cu. The CZTS structural, compositional and electronic properties were investigated by XRD, SEM-EDS, Raman spectroscopy and conductivity and mobility measurements. Solar cells with the structure $\text{ZnO}/\text{CdS}/\text{CZTS}/\text{Mo}$ were produced and fully characterized. The problems connected to the back contact are investigated and discussed.

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1. Introduction

Solar cells based on $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) have recently reached a conversion efficiency of 6.8% [1] and are considered a promising alternative to the $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells which contains materials with a limited availability. Currently the most important limiting factor for efficiency is the insufficient control of the material stoichiometry and quality [2]. Another important factor is the ohmic back contact formation. Even the record efficiency devices [1] have FF values limited by the back contact properties. If this limitation is described in term of a series resistance their better value is higher than $3.4 \Omega \text{cm}^2$ but the authors suggest that the CZTS/Mo back contact could be non-ohmic.

In this paper we report on the growth of CZTS using a two step process. A precursor composed of three evaporated layers (ZnS, Sn, Cu) is subsequently annealed in a sulfur atmosphere to obtain the CZTS film. This material is used to produce $\text{ZnO}/\text{CdS}/\text{CZTS}/\text{Mo}$ solar cells which are fully characterized by dark J - V and light J - V .

2. Growth and characterization of CZTS thin films

The first step in CZTS thin films growth is the evaporation by e-beam of a multilayer of ZnS, Cu and Sn on soda lime glass (SLG). These precursors were then placed into a small non-sealed glass reaction chamber with a small amount

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of sulfur. The sulfurization took place putting the reaction chamber in a tube oven in a N_2 flux for one hour at $550^\circ C$ reached after a temperature ramp at $10^\circ C/min$.

In most cases we used a precursor with the structure ZnS/Sn/Cu. These precursors exhibit a rough surface due to the fact that the Sn layer grows on the ZnS forming small drops with dimensions below $1 \mu m$. This roughness can be reduced by splitting the Cu layer and growing a four layer precursor ZnS/Cu/Sn/Cu which has a much smoother surface. This procedure was not adopted since it proved to be irrelevant for the final CZTS morphology which is therefore mainly determined by the grain growth process.

At the moment the optimized precursor structure is ZnS/Sn/Cu with nominal thicknesses of 220 nm, 115 nm and 100 nm respectively. With these values the stoichiometric proportions are $Cu/Zn/Sn = 2.00/1.31/1.02$ and EDS measurements did not show relevant variations after the sulfurization. A small loss of Zn and Sn is observed even if the variations are comparable with the experimental uncertainty. Therefore, considering that the sulfurization reaction is limited by copper, the final thickness of the kesterite layer should be about 700 nm. The Zn excess increases this value to the observed CZTS thickness of 750 nm. The spatial distribution of the ZnS is currently under investigation by SIMS measurements. The XRD spectra of the optimized films do not show any evidence of spurious phases (notice that ZnS XRD peaks are superimposed to those of CZTS).

The film properties are very different if the precursor sulfurization is not made inside the reaction chamber but directly in N_2 flux. In this latter case the samples are more conductive and show a strong absorption in the infrared suggesting the presence of copper sulfides spurious phases. The loss of Zn and Sn (via SnS evaporation or CZTS decomposition at high ($550^\circ C$) temperature) are often reported in the literature [3–5]. This loss is limited if the reaction is performed in a small volume.

The resistivity is an important quality indicator. Films with $\rho \approx 1 \Omega cm$ or less probably contain a Cu_2S spurious phases and typically give shunted cells. To obtain working devices the resistivity must be greater than about $10 \Omega cm$. TLM measurements have shown that the highest resistivity value measured in our samples is about $2 \times 10^4 \Omega cm$. Since Hall effect measurements show that $1 cm^2/(Vs)$ is an upper limit for the hole mobility in our samples, using a hole effective mass of 0.48 electron mass [6], we can estimate that in our samples the Fermi level distance from the valence band is less than 265 meV. The films with a low resistivity typically show a low transmittance without interference fringes even in the sub-bandgap energy region. We attribute this effect to the Cu_2S spurious phases which have a high infrared absorptance due to defects and free carrier. Etching the film with a KCN solution increases the transmittance but is not able to recover the high transmittance typical of the more stoichiometric films.

Raman spectroscopy proved effective at detecting copper and tin sulfides phases which are not easily revealed by XRD. On the other hand the ZnS Raman signals are quite weak and therefore difficult to detect. Micro-Raman measurements were performed using a He-Ne laser ($\lambda = 632.8 nm$) setup in backscattering configuration. The Raman spectrum of our optimized CZTS films is shown in Fig. 1 revealing only the CZTS peaks [7]. For the $CuInS_2$ -based

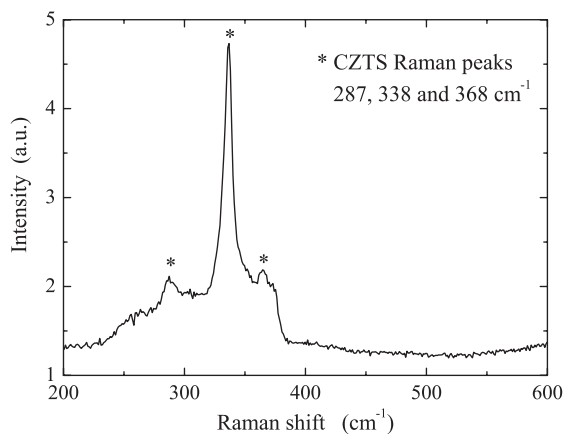


Figure 1: Raman spectrum of a CZTS film. Peaks of spurious phases such as $Cu_{2-x}S$ ($475 cm^{-1}$), ZnS ($355 cm^{-1}$), Cu_2SnS_3 ($318 cm^{-1}$) and Sn_2S_3 ($304 cm^{-1}$) are not observed.

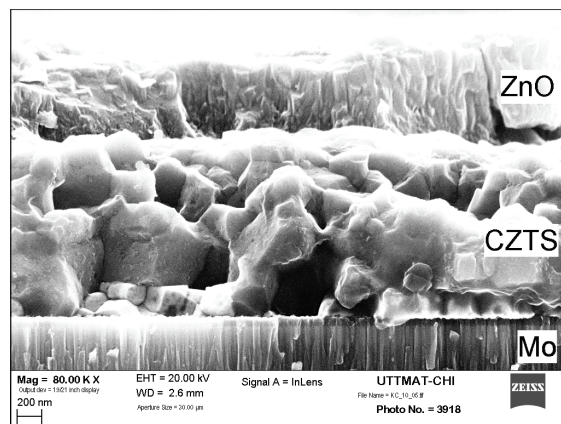


Figure 2: SEM image of a cross section of a CZTS based solar cell with the structure AZO/i-ZnO/CdS/CZTS/Mo.

solar cells it was found that when the FWHM of the main Raman peak at 292 cm^{-1} is larger than 3.8 cm^{-1} a clear degradation of V_{oc} and FF is observed [8]. In our CZTS films the main peak at 338 cm^{-1} has a FWHM of 7 cm^{-1} which is better than that reported for the IBM record solar cells. It is not clear if our longer annealing produces a material with a better crystallographic quality or if the larger FWHM in the IBM material is due to a limited resolution of their Raman measurements.

3. Solar cells fabrication and characterization

The solar cells were produced on two different substrates: SLG covered by a RF sputtered Mo or by a thermally evaporated bilayer Cr/Au. Cr is needed because of the poor adhesion of Au on glass. The CZTS growth is performed as described in the Sec. 2 but the film thickness was doubled using a precursor composed of two trilayers ZnS/Sn/Cu. After the CZTS growth we do not perform any KCN etching: this step does not seem to be able to improve the device performances but further investigation is necessary. The cell is completed by growing a CdS layer (50 nm) by chemical bath deposition, an intrinsic ZnO layer (100 nm) and an AZO layer (700 nm) deposited by RF sputtering (see Fig. 2). An Al grid is then evaporated to improve the carrier collection and the cell area is defined by mechanical scribing.

Fig. 3 (a) and 3 (b) show the comparison of the dark and light J - V curves of the best cells grown on Au and Mo. Their efficiencies are 1.95% and 1.05% respectively. It can be seen that the Mo back contact limits the dark current at high forward bias and the cell FF under light. If this limitation is described in terms of a series resistance, we obtain $R_s \approx 10\ \Omega\text{ cm}^2$ for the cell on Mo and $R_s \approx 2.5\ \Omega\text{ cm}^2$ for the cell on Au. It has to be noted that the series resistance value is not very reproducible from run to run and in many cells grown on molybdenum is much worse giving cells with FF values close to 25%. In many cases the fit of the dark J - V curves are quite bad, suggesting the presence of a blocking barrier at the Mo back contact [1]. To evaluate the fill factor which could be reached removing the back contact problems or any series resistance effect, we measured the Suns- V_{oc} curves using a Sinton Instruments tester [9]. The pseudo fill factor appears to be correlated with the cell V_{oc} and it reaches a value of 65% in our best solar cells on molybdenum which has $V_{oc} = 500\text{ mV}$. Together with a $J_{sc} = 8.5\text{ mA/cm}^2$ this would give for this cells an efficiency of about 2.75% if the back contact were ohmic.

4. Back contact investigation

Since the Cu(In,Ga)Se₂ solar cells have reached an efficiency of 20% using a Mo back contact, it is natural to make a comparison with CZTS. The comparison is facilitated by the fact that, according to *ab-initio* calculations [10], the CuInSe₂ has the valence band maximum (VBM) only 70 meV higher than CZTS. Therefore in both cases the VBM should lie around 5.5 eV below the vacuum level and this explains why a simple Mo contact with a work function of 4.6 eV is not able to give an ohmic contact while more noble metals (as platinum, gold and nickel) do [11]. It is also

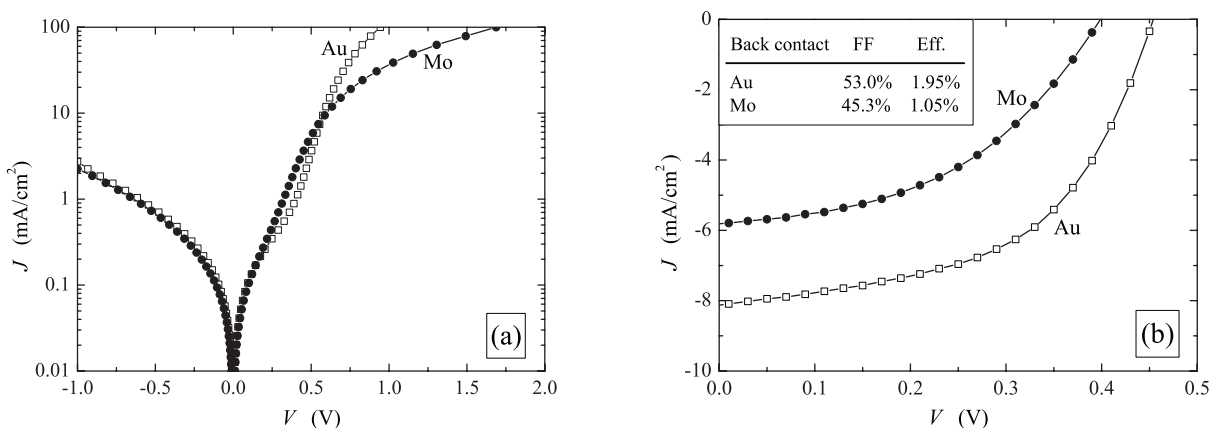


Figure 3: J - V characteristics of two cells with Mo and Au back contact: (a) J - V dark characteristic; (b) J - V light characteristic.

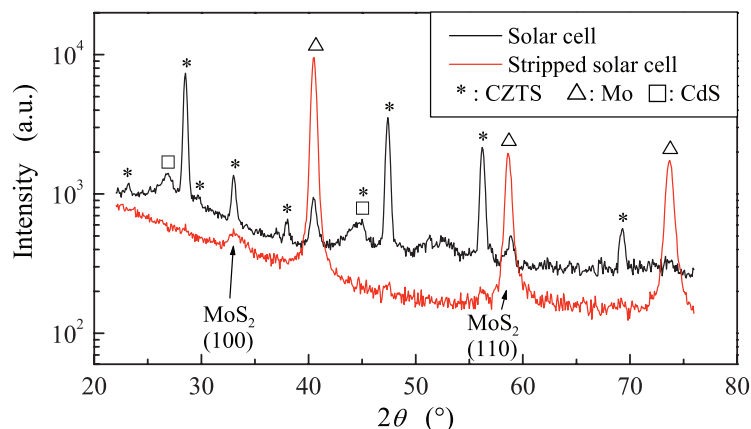


Figure 4: Grazing incidence XRD spectra of a CZTS solar cell and of its Mo substrate after the cell removal.

well known that, in the cells based on selenides, the Mo is able to give an ohmic contact due to the formation of a thin MoSe₂ layer [12]. Using UPS, IPES e XPS it has been shown [13] that the valence bands of CIGSe and MoSe₂ are well aligned: according to the authors this alignment explains the good properties of the contact.

MoS₂ and MoSe₂ have very similar band parameters. Both have an indirect gap of similar values: $E_g(\text{MoS}_2) = 1.17 \text{ eV}$ and $E_g(\text{MoSe}_2) = 1.06 \text{ eV}$ [14]. Their photo-threshold (i.e. the difference between the vacuum level and the VBM) are 5.6 eV and 5.5 eV for MoS₂ and MoSe₂ respectively [15], quite similar to that of CIGSe and CZTS. Using the simple electron affinity rule, only a small valence band offset of 0.1 eV should be present at the CZTS/MoS₂ interface, in good agreement with measurements performed on CIG(S,Se) solar cells [13]. It seems likely that a good ohmic back contact can be obtained if a MoS₂ layer with suitable properties forms at the interface. This is supported by the fact that the cells based on CuInS₂ have reached FF values up to 74%.

Therefore we see the importance of controlling the MoS₂ formation at the back contact of CZTS/Mo cells. A first evidence of MoS₂ formation was obtained by XPS measurements on Mo substrates after the removal of the deposited CZTS film [16] which showed a Mo/S ratio equal to 1/2 on the surface. We have instead performed some grazing incidence XRD (incidence angle $\theta = 1.6^\circ$) on completed cells and on the Mo substrate after stripping the cell using adhesive tape. The XRD spectra obtained before and after the cell removal are shown in Fig. 4. In the case of the cell the diffraction peaks of the MoS₂ are masked by the CZTS and CdS signals. After the cell removal the (1 0 0) of the MoS₂ can be clearly seen while the (1 1 0) peak cannot be easily observed since it is superimposed to the (2 0 0) peak of the Mo. The MoS₂ peaks corresponding to the planes perpendicular to c-axis are not detectable. This means that the MoS₂ layer grows with its c-axis parallel to the substrate surface. This is the orientation which gives the best results in CIGS cells and it is in agreement with previous work on the low temperature sulfurization of Mo [17].

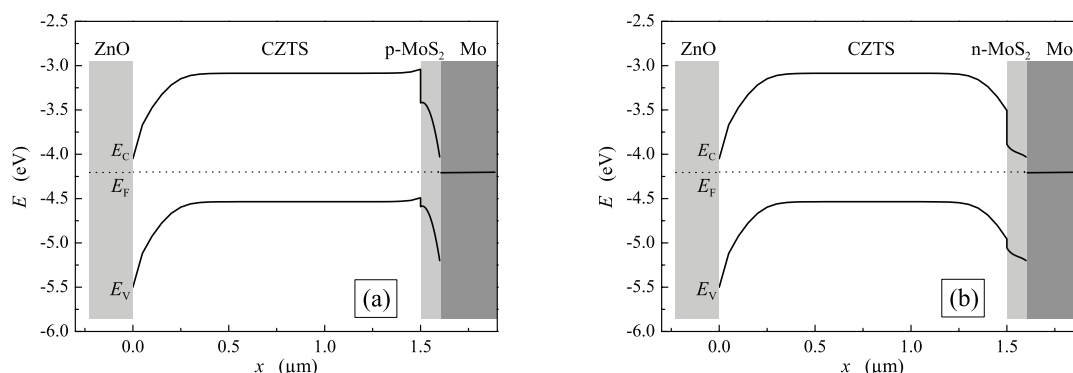


Figure 5: Simulated band profiles in a CZTS solar cell: (a) p-type MoS₂; (b) n-type MoS₂.

However we have to note that the mere formation of MoS₂ does not assure an ohmic contact. In our opinion the best situation is to have highly p-type MoS₂ which gives a band profile with a Schottky barrier at the Mo/MoS₂ interface as that shown in Fig. 5 (a) and in [1]. In the case of high doping the resulting narrow barrier can be crossed by tunneling. If instead the MoS₂ is n-type and considering that the work function of MoS₂ and Mo are in that case almost equal, the barrier is placed at the CZTS/MoS₂ interface as shown in Fig. 5 (b). This band profile was calculated assuming a uniform defect density in the CZTS and this gives a wide back contact barrier, detrimental for the cell performances. This band profile is quite different from the one proposed in [13] due to the fact that we have used a CZTS Fermi level of about 0.3 eV as previously discussed whereas in [13] the CZTS Fermi level is surprisingly far from the valence band (0.9 eV from E_V).

5. Conclusions

In this paper we have presented the fabrication of CZTS thin films by a two step process. We have shown that using a small reaction volume for the sulfurization we can avoid any substantial metal loss. In the resulting CZTS films no spurious phases can be detected by XRD and Raman spectroscopy. We have also investigated the properties of the back contact of the solar cells fabricated by using these CZTS substrates. In particular it has been found that MoS₂ with c-axis parallel to the substrate is formed at the CZTS/Mo interface. The influence of MoS₂ electronic properties on the band profile and on the solar cell performances has been discussed.

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