

Chemical stability of the $\text{Cu}_2\text{SnS}_3/\text{Mo}$ interface

Jessica de Wild, Erika V.C Robert and Phillip J. Dale

University of Luxembourg, Physics & Material Sciences Research Unit, 41 rue du Brill, L-4422 Belvaux, Luxembourg

Abstract — Cu_2SnS_3 is an earth abundant semiconductor researched for photovoltaic applications. Due to the small energy difference in the $\text{Sn}^{2+}/4+$ oxidation states and low free energy of MoS_2 , the $\text{Cu}_2\text{SnS}_3/\text{Mo}$ interface is unstable and Cu_2SnS_3 decomposes. The interface is stabilized by growing Cu_2SnS_3 on a thin MoS_2 layer. Photoluminescence occurs only at the back of the Cu_2SnS_3 layers when grown on MoS_2 and no quantifiable amounts of Cu and Sn are measured at the MoS_2 substrate. The quenching of emission of Cu_2SnS_3 grown on Mo is due to binary sulfides formed in presence of Mo which are not formed when Cu_2SnS_3 is grown on MoS_2 .

Index terms — Semiconductor-metal interfaces, photoluminescence, semiconductor growth, tin compounds

I. INTRODUCTION

Cu_2SnS_3 is a new earth abundant semiconductor under investigation as a solar cell absorber layer [1]. It is known as a secondary phase in the kesterite system, $\text{Cu}_2\text{ZnSnS}_4$, but has by itself also suitable optical properties for solar cell application. Above all, it has the advantage over kesterite that less secondary phases can be formed, since it contains less elements. However, like kesterite, Cu_2SnS_3 does contain Sn and hence the same difficulties experienced for kesterite during high temperature growth can be expected. One problem is the reduction of Sn^{4+} to Sn^{2+} in the presence of Mo, which itself oxidizes to Mo^{4+} , that causes decomposition of the Cu_2SnS_3 into its binaries [2]. These binaries may have detrimental properties for solar cell performance [3]. Cu_2SnS_3 may decompose into Cu_2S and SnS at the back contact. SnS is harmful for the open circuit voltage of the device when it has a lower band gap than the absorber layer, however the band gap of Cu_2SnS_3 is lower than that of SnS and thus SnS does not have to be detrimental. Cu_2S is detrimental for solar cell performance due to its high conductivity and would be detrimental for Cu_2SnS_3 as well. Thermodynamic calculations show that Cu_2SnS_3 is highly unstable in the presence of Mo and that the binary sulfides will be formed at the Mo interface. To avoid this reaction Cu_2SnS_3 is grown on a thin layer of MoS_2 , and so removes the immediate driving force to decompose Cu_2SnS_3 . To investigate this hypothesis, Cu_2SnS_3 layers are grown on Mo and MoS_2 substrates after which the absorber layers are peeled off to investigate the Mo/absorber interfaces. SEM and EDX measurements show different morphologies and significant amount of Cu and Sn on the Mo

substrate, while the amount of Cu and Sn was too low to be quantified on the MoS_2 substrate. Photoluminescence measurements are done on the back of the peeled off absorber layers and it is shown that the luminescence is fully quenched when Cu_2SnS_3 is grown on Mo, while present when grown on MoS_2 . This quenching of emission is attributed to the presence of Cu_2S .

II. EXPERIMENTAL DETAILS

The MoS_2 layers are made by annealing a 600 nm Mo layer deposited on soda lime glass in the tube oven with only S (99.99995%, Alpha Aesar) for 2 hours, 1 mBar at 540 °C. Cu_2SnS_3 absorber layers are made by a metal precursor-sulfurization annealing route, which is described elsewhere [4]. The Cu/Sn precursors are coated on Mo and MoS_2 substrates. To analyze the interface, the Cu_2SnS_3 layer is peeled off as shown in figure 1. The resulting molybdenum substrate after peeling off the Cu_2SnS_3 layer is analyzed by SEM and EDX. Micrographs are recorded with a scanning electron microscope (Hitachi SEM (SU-70)) and elemental compositions are measured by EDX/WDX (Oxford instruments INCA X-MAX, 20 keV). Photoluminescence (PL) measurements were performed in a homebuilt set-up on all surfaces. The laser excitation wavelength is 514 nm and spot size is 1 μm . Several spots are measured and the results shown are representative.

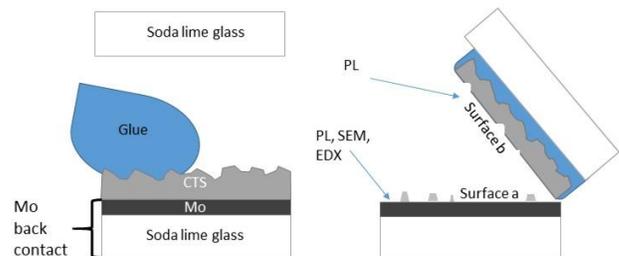


Fig. 1. Schematic view of the measurement done at the $\text{Cu}_2\text{SnS}_3/\text{Mo}$ interface.

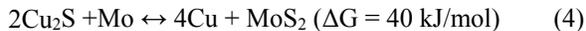
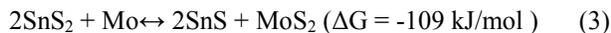
III. THERMODYNAMIC APPROACH

The thermodynamic approach allows a straightforward way to determine in which direction equilibrium reactions are expected to go. Details of this method are given in [2] and is summarized as follows. The free energy of formation of a

multinary compound is equal to the sum of its constituent binary compounds in the same oxidation state as the multinary compound, plus an additional term. The additional term is the difference of free energy between the multinary compound and an equivalent mixture of the binary compounds, estimated to be between 0 and 50 kJ/mol for chalcogenide compounds. The equilibrium reactions at the Mo/Cu₂SnS₃ interface are:



Reaction (2) is expected to be around 22 kJ/mol, which is the value estimated for CZTS [5]. The free energy change of reaction (1) can be determined from calculating the free energies of the reactions of the binary compounds given in (2) with Mo:



The free energies and methodology are taken from [2] and [5] and are calculated at 530 °C with the temperature dependencies found in [6]. The free energy of reaction (3) is much more negative than the free energy required to decompose Cu₂SnS₃ into its constituent binary compounds (2), which means that the Cu₂SnS₃ is not stable in the presence of Mo and will decompose. Note that reaction (4) is not expected since the free energy is positive, and thus SnS and Cu₂S are the expected secondary phases at the back contact. To avoid reaction (1) from happening, Cu₂SnS₃ layers should be grown on MoS₂. It is expected that when MoS₂ is present that reaction (1) is drastically reduced or even absent, since the equilibrium is already on the right hand side of the arrow.

IV. RESULTS

A. Interface morphology

Figure 2 shows SEM cross sections of the absorber layers grown on Mo and MoS₂ and figure 3 of the substrates after peeling off the absorber layer. The first thing that was noticed while making the cross sections and peeling off the absorber layers was the difference in adhesion of the absorber layer onto the substrates. It was much easier to peel off the Cu₂SnS₃ layer when grown on Mo than when grown on MoS₂. This is also visible in the cross section SEM images. Figure 2a shows the cross section of a Cu₂SnS₃ layer grown on MoS₂ and 2b Cu₂SnS₃ grown on Mo. In general more holes are visible in figure 2b. The MoS₂ layer was on average slightly thicker when the Mo was sulfurized before deposition of the precursor, 95 nm vs 70 nm. Larger difference are found when looking at the substrates from top after peeling of the absorber layers, see figure 3a and 3b. Figure 3a shows the MoS₂ substrate after peeling off Cu₂SnS₃ and figure 3b the Mo substrate after peeling off Cu₂SnS₃. It is assumed that the

shapes seen in figure 3b are Cu₂S flakes. EDX measurements are done to determine the composition of the Mo surfaces.

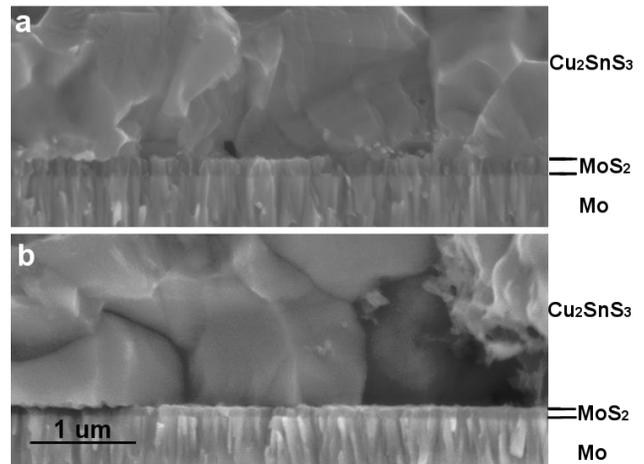


Fig. 2. SEM cross section images of Cu₂SnS₃ annealed on MoS₂ (a) and Mo substrates (b). The MoS₂ layer is slightly thinner in (b) and less holes are visible.

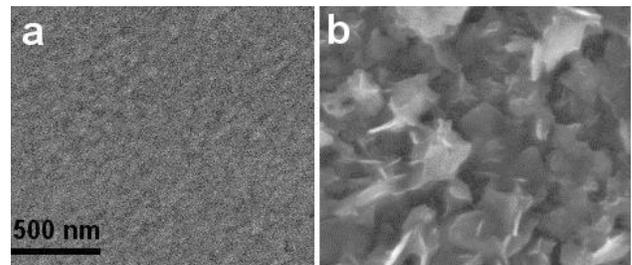


Fig. 3. SEM top view images of the substrates after peeling of the Cu₂SnS₃ layer. (a) MoS₂ substrate and (b) Mo. (b) shows a very different morphology to (a), likely Cu₂S flakes and SnS wires.

B. Composition

The composition of the two surfaces were measured by EDX maps and EDX/WDX. EDX maps show elements that are present and EDX/WDX measurement are performed for quantification. The SEM images in figure 3 are scaled to the size of the map for comparison. The MoS₂ substrate shows a rather homogeneously spread of Cu and Sn particles, while the Mo substrate has clear Cu and Sn agglomerations. EDX/WDX measurements show that MoS₂ surface contain 87 at% Mo and 13 at% S. Cu and Sn content, though visible in the raw scan, were both below the detection limit. The Mo substrate shows large variation in composition. Over 9 random points were measured. The Mo content varies between 50 and 98 % and S between 17 to 33%. The very low Mo value had a 20% Sn content. These variations indicate an inhomogeneous surface as was seen on the SEM already. For the exception of 1 point (the Sn particle), Cu and Sn was measured just above the detection limit i.e. 1 to 3%, and it is assumed that these Cu and Sn belong to the Cu₂S and SnS phases. Further investigation of

the phases separately was not possible due to the submicron size of the agglomerations and the Mo/MoS₂ background.

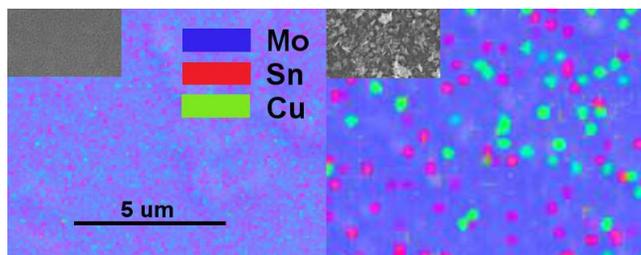


Fig. 4. EDX map of the top surface of the Mo substrates after peeling off the Cu₂SnS₃ layer. Left: MoS₂ right: Mo.

C. Photoluminescence

Photoluminescence (PL) spectra are measured on the Mo and MoS₂ substrates and at the back of the peeled off absorber layers. The penetration depth of the 514 nm laser light is approximately 100 nm in the Cu₂SnS₃, thus the emission come mostly from the surface. Also, when there is surface recombination, emission will be reduced. Hence differences in PL can be attributed to differences at the surface. Both Mo and MoS₂ substrates showed no luminescence peaks in the visible and NIR wavelength range (500 to 1500 nm). This could indicate that either the layer of SnS/Cu₂S particles are too thin and/or too defective to emit light. MoS₂ is an indirect semiconductor and no emission from this layer is expected. The back of the peeled off absorber layers shows a clear luminescence peak belonging to Cu₂SnS₃ for the layer grown on MoS₂, but no luminescence was measured from the layer grown on Mo, see figure 5. The absence of the PL signal can be explained by the presence of Cu₂S that quenches the emission since it has metallic properties and/or other highly recombinative active centers leading to non-radiative recombination paths.

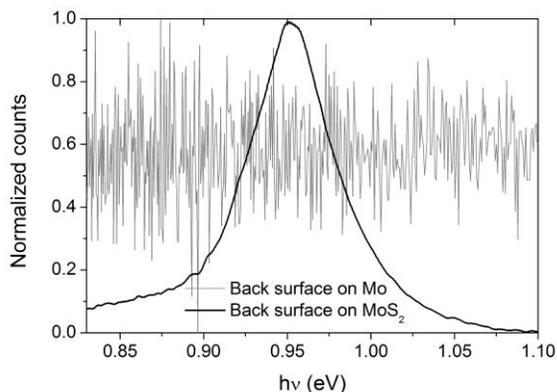


Fig. 5. Photoluminescence measured at the back of the absorber layer. Cu₂SnS₃ grown on Mo shows no PL at all, while Cu₂SnS₃ grown on MoS₂ show a clear sharp peak belonging to Cu₂SnS₃ [4].

V. DISCUSSION

Detrimental effects of secondary phases on device performance have varying root causes. Cu₂S is known to cause shunts in devices due to its high conductivity. Here we show that secondary phases, most likely Cu₂S, act as recombination centers. Adding a thin MoS₂ layer prior to annealing the absorber layer removed these recombination paths, which are detrimental for device performance. What exactly the effects are of stabilizing the interface on a Cu₂SnS₃ device is under investigation. Also, a recent study has shown that a too thick MoS₂ decreases device performance [7] and hence also the MoS₂ thickness requires a more detailed investigation.

V. SUMMARY

Thermodynamic calculations show that the Cu₂SnS₃/Mo interface is unstable due to the highly negative free energy of formation of MoS₂. This results in SnS and Cu₂S phases at the interface. Mo and MoS₂ substrates show different morphologies after annealing of the absorber layer. Mo shows a flowerlike shaped surface while the MoS₂ substrate is flat. The differences are attributed to the formation of Cu₂S and SnS in the presence of Mo. Photoluminescence measurements at the back of the absorber layer show a clear PL peak belonging to Cu₂SnS₃ when grown on MoS₂ but no emission when the absorber layer is grown on Mo. This quenching is attributed to the presence of recombination centers, most likely the highly conductive Cu₂S.

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