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# Fabrication of ternary and quaternary chalcogenide compounds based on Cu, Zn, Sn and Si for thin film photovoltaic applications

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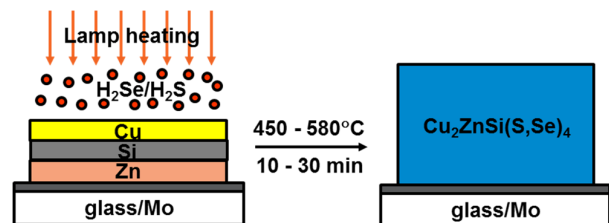
We investigated the use of ternary and quaternary chalcogenide compounds based on Cu, Zn, Sn and Si for use as high band gap absorber layers in thin film photovoltaics. We have investigated the fabrication of  $\text{Cu}_2\text{Zn}(\text{Sn},\text{Si})\text{Se}_4$ ,  $\text{Cu}_2\text{Si}(\text{S},\text{Se})_3$  and  $\text{Cu}_8\text{Si}(\text{S},\text{Se})_6$  thin film layers. Whereas  $\text{Cu}_2\text{Zn}(\text{Sn},\text{Si})\text{Se}_4$  and  $\text{Cu}_2\text{Si}(\text{S},\text{Se})_3$  appeared to be difficult to fabricate, because the Si did not intermix well with the rest of the elements at the typical process temperatures used for glass substrates,  $\text{Cu}_2\text{ZnSiSe}_4$  and  $\text{Cu}_8\text{Si}(\text{S},\text{Se})_6$

could be formed. The fabricated layers were polycrystalline with a typical thickness of about 1  $\mu\text{m}$ . We also fabricated solar cells with the different absorber materials, using a standard Mo back contact and CdS/ZnO buffer layer combination, but despite very bright photoluminescence response of the  $\text{Cu}_8\text{SiS}_6$  and  $\text{Cu}_8\text{SiSe}_6$  layers at an energy of about 1.84 eV and 1.3 eV respectively, the measured efficiencies remained below 0.1 % due to particularly low photocurrents.

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## 1 Introduction

In order to further improve current Si or  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  solar cell technology beyond their current efficiency limits, tandem cell geometries could be used with a top cell with a band gap in excess of 1.6 eV [1]. We have investigated in the present contribution high band gap chalcogenide compounds containing Cu, Zn, Sn and/or Si, namely the compounds  $\text{Cu}_2\text{Zn}(\text{Sn},\text{Si})\text{Se}_4$ ,  $\text{Cu}_2\text{Si}(\text{S},\text{Se})_3$  and  $\text{Cu}_8\text{Si}(\text{S},\text{Se})_6$  for their use as high band gap absorbers in a tandem solar cell geometry. All layers were fabricated as thin film layers on soda-lime glass substrates with a 400 nm thick Mo back contact layer. This sets a limitation on the maximum process temperature of about 580°C, as above that temperature the glass starts melting. The fabricated layers were then characterized using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Finally solar cell devices were fabricated with the successfully fabricated absorber layers using a CdS buffer layer and Al-doped ZnO top contact layer.



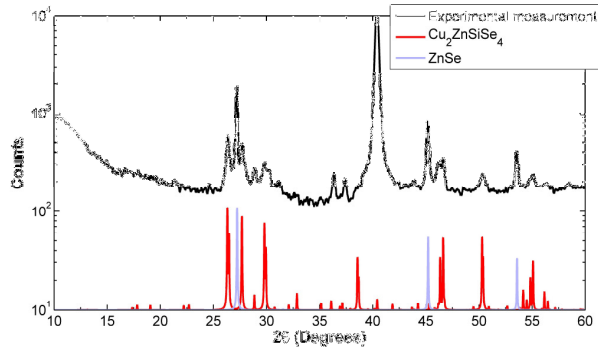
**Figure 1** Schematic representation of the fabrication process of the thin film  $\text{Cu}_2\text{ZnSi}(\text{S},\text{Se})_4$  layers.

## 2 Experimental details

For all fabricated absorber layers, the used process flow consists of two step selenization. First a multilayer stack of metals is deposited in a Pfeiffer PLS 580 evaporation chamber on 400 nm Mo on soda lime glass substrates. Then the metal stack is annealed for 10 to 30 minutes at temperatures of 450°C to 580°C in an Annealsys AS-150 rapid thermal anneal chamber in either an atmosphere of 100 %  $\text{H}_2\text{S}$  for

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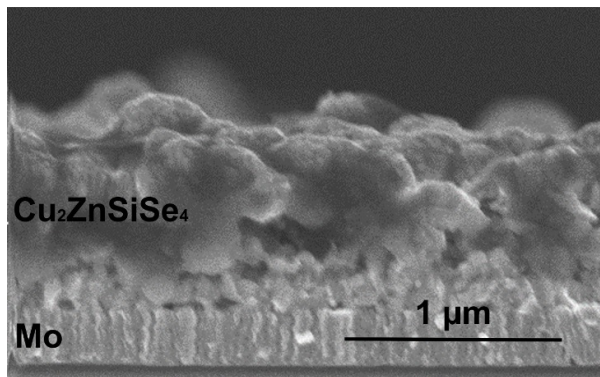
sulfurization or an atmosphere of 10% H<sub>2</sub>Se in N<sub>2</sub> for selenization. The process is schematically shown in figure 1 for the example of Cu<sub>2</sub>ZnSi(S,Se)<sub>4</sub>. The other materials are fabricated in a similar way, using a different metal stack [2].



**Figure 2** XRD spectrum of the best Cu<sub>2</sub>ZnSiSe<sub>4</sub> sample (black line) along with a simulation based on literature data for Cu<sub>2</sub>ZnSiSe<sub>4</sub> [2] (Dark red line) and ZnSe (powder diffraction file # 00-037-1463) (Light blue line).

### 3 Cu<sub>2</sub>ZnSiSe<sub>4</sub>

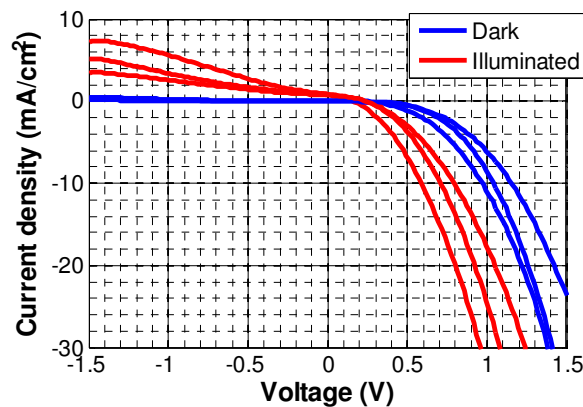
Cu<sub>2</sub>ZnSiSe<sub>4</sub> layers were fabricated using a stack of Zn(105nm)/Si(135nm)/Cu(165nm), where first the Zn layer was deposited, followed by the Si and Cu layers. The layers were selenized for times varying from 15 to 25 minutes and at a temperature varying from 450°C to 540°C. Best results were obtained for the 15 minute selenization at 480°C. The XRD spectrum of this sample is shown in figure 2. The peaks for Cu<sub>2</sub>ZnSiSe<sub>4</sub> can be clearly identified in the experimental spectrum, but also ZnSe seems to be present in larger quantities. The large peak at 40.5° corresponds to the Mo (110) reflection of the backside contact.



**Figure 3** Cross section SEM image of the Cu<sub>2</sub>ZnSiSe<sub>4</sub> sample.

Figure 3 shows a cross section SEM image of the sample, showing that the fabricated grains are relatively small and that element intermixing is not quite complete, with larger grains on the top and smaller grain layer in the bottom. The band gap of the Cu<sub>2</sub>ZnSiSe<sub>4</sub> material is expected to be around 2 eV [3]. Even though this band gap is a bit on the

high side for our application, solar cells were still fabricated with the material. A standard process flow for thin film solar cells was used, consisting of the chemical bath deposition of 50 nm of CdS, followed by reactive sputter deposition of 150 nm of intrinsic ZnO and 250 nm of Al-doped ZnO. The devices were laterally isolated using needle scribing. The current density – voltage (J-V) curves of the sample are shown in figure 4, showing both dark and AM1.5G illuminated curves for three different 0.5 cm<sup>2</sup> devices on the sample. Even though clear rectifying behaviour could be observed, the values for the short-circuit current J<sub>sc</sub> of 0.8 mA/cm<sup>2</sup>, open circuit voltage V<sub>oc</sub> of 238 mV and fill factor FF of 35 % were very low, yielding a power conversion efficiency of only about 0.07 %.

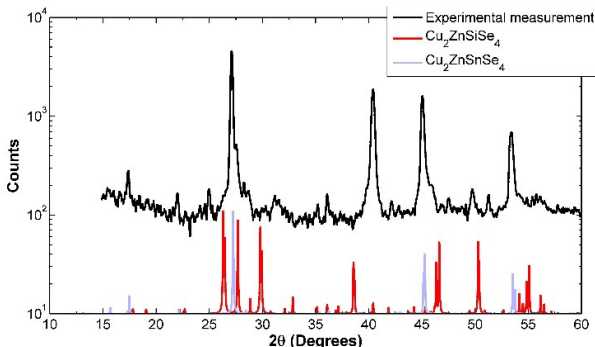


**Figure 4** Current density versus voltage curves for three different 0.5 cm<sup>2</sup> Cu<sub>2</sub>ZnSiSe<sub>4</sub> solar cell devices.

### 4 Cu<sub>2</sub>Zn(Sn,Si)Se<sub>4</sub>

As the band gap of the Cu<sub>2</sub>ZnSiSe<sub>4</sub> material is a bit on the high side, we tried to include some Sn in the material, in order to reduce the band gap to more acceptable values of about 1.8 eV. An extra layer of Sn was introduced between the Zn and the Cu in order to fabricate a Cu<sub>2</sub>Zn(Sn,Si)Se<sub>4</sub> layer with a 50/50 ratio between Si and Sn, yielding a band gap somewhere in between the band gap of Cu<sub>2</sub>ZnSnSe<sub>4</sub> and Cu<sub>2</sub>ZnSiSe<sub>4</sub>. The layers were then annealed in H<sub>2</sub>Se at temperatures varying from 450°C to 490°C. A typical XRD spectrum of a sample annealed at 480°C for 15 minutes is shown in figure 5 along with the expected spectra for Cu<sub>2</sub>ZnSiSe<sub>4</sub> and Cu<sub>2</sub>ZnSnSe<sub>4</sub>. In the XRD spectra Cu<sub>2</sub>ZnSnSe<sub>4</sub> can be clearly identified, but not Cu<sub>2</sub>ZnSiSe<sub>4</sub>. Also the lattice constant of the Cu<sub>2</sub>ZnSnSe<sub>4</sub> does not appear to be shifted compared to the reference data, such that it seems that not much Si was intermixed with the Cu<sub>2</sub>ZnSnSe<sub>4</sub>. In none of the fabricated samples we could actually identify an intermixing of the Si with Cu<sub>2</sub>ZnSnSe<sub>4</sub>, likely due to the fact that Cu<sub>2</sub>ZnSnSe<sub>4</sub> crystallizes in the Kesterite crystal structure, whereas Cu<sub>2</sub>ZnSiSe<sub>4</sub> crystallizes in the Wurtzite-Stannite crystal structure. In addition, photoluminescence measurements did not show any peaks in

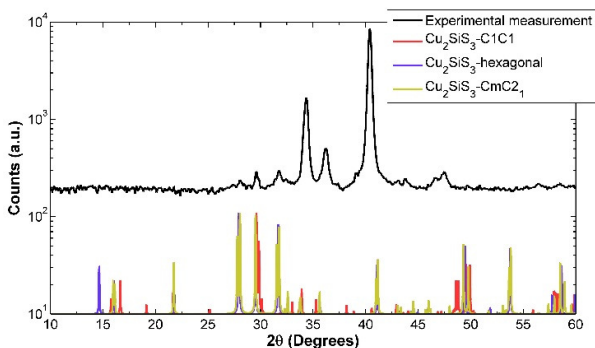
the 1 to 2 eV range. We have nevertheless tried to make solar cells with this material, but did not obtain any measurable efficiency.



**Figure 5** XRD spectrum of a  $\text{Cu}_2\text{Zn}(\text{Sn},\text{Si})\text{Se}_4$  sample annealed for 15 minutes at  $480^\circ\text{C}$  (black line) along with a simulation based on literature data for  $\text{Cu}_2\text{ZnSiSe}_4$  [4] (red line) and  $\text{Cu}_2\text{ZnSnSe}_4$  (powder diffraction file # 00-052-0868 - light blue line).

### 5 $\text{Cu}_2\text{Si}(\text{S},\text{Se})_3$

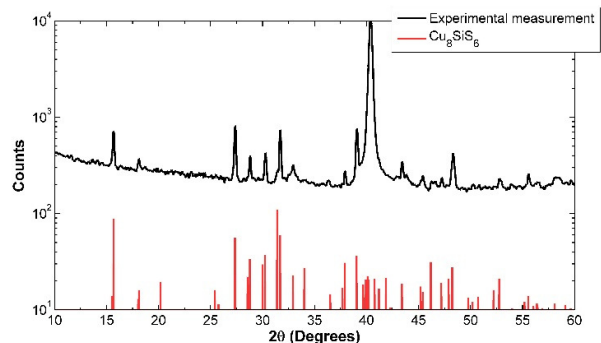
The ternary phases  $\text{Cu}_2\text{SiS}_3$  and  $\text{Cu}_2\text{SiSe}_3$  could also be interesting solar cell absorbers.



**Figure 6** XRD spectrum of a typical  $\text{Cu}(200\text{nm})/\text{Si}(170\text{nm})$  multilayer annealed for 15 minutes in  $\text{H}_2\text{S}$  at a temperature of  $560^\circ\text{C}$  along with the expected spectra for  $\text{Cu}_2\text{SiS}_3$  (powder diffraction files # 04-009-7132, 04-009-3320 and 04-001-6459).

We have deposited  $\text{Cu}(200\text{nm})/\text{Si}(170\text{nm})$  bilayer stacks on Mo on soda lime glass substrates and we have annealed them for 15 minutes in  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$  at temperatures varying from  $450^\circ\text{C}$  to  $560^\circ\text{C}$ . In the case of annealing in  $\text{H}_2\text{S}$ , no  $\text{Cu}_2\text{SiS}_3$  could be formed even for the highest temperatures. Figure 6 shows an XRD spectrum of a sample annealed for 15 minutes at  $560^\circ\text{C}$  in  $\text{H}_2\text{S}$ , but none of the known  $\text{Cu}_2\text{SiS}_3$  crystal phases could be clearly identified in the spectra, the Si does not seem to intermix sufficiently with the Cu at the used temperatures, as is also visible from cross section SEM images (not shown) where the Si layer seems to be more or less intact after the selenization. In the case of selenization in the presence of  $\text{H}_2\text{Se}$ , the correct crystal structure for  $\text{Cu}_2\text{SiSe}_3$  could be formed. The peaks of

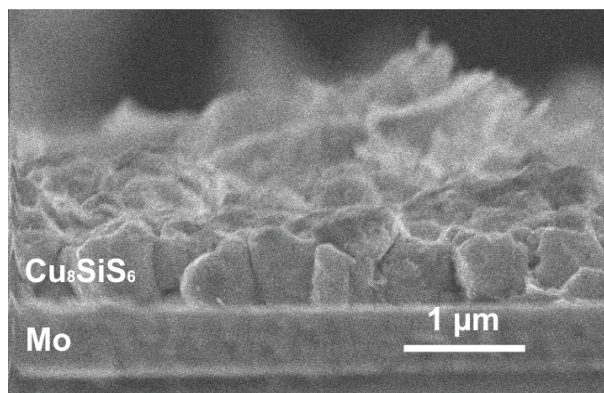
$\text{Cu}_2\text{SiSe}_3$  can be found back in the XRD spectrum (not shown), but also a large amount of a secondary phase, which was identified to be the  $\text{Cu}_8\text{SiS}_6$  phase. The sample was processed into a solar cell and even though rectifying behaviour could be observed, no photocurrents could be measured.



**Figure 7** XRD spectrum of a typical  $\text{Cu}(420\text{ nm})/\text{Si}(170\text{ nm})$  multilayer annealed for 25 minutes in  $\text{H}_2\text{S}$  at a temperature of  $490^\circ\text{C}$  along with the expected spectra for  $\text{Cu}_8\text{SiS}_6$  (powder diffraction file # 00-039-1200 – red line).

### 6 $\text{Cu}_8\text{Si}(\text{S},\text{Se})_6$

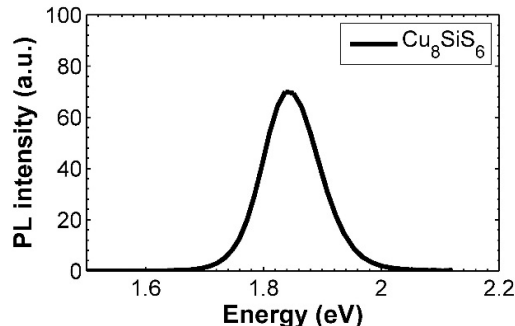
$\text{Cu}_8\text{SiS}_6$  is second stable phase in the Cu-Si-S phase diagram [5-8] and we found that this phase crystallizes easier as compared to the  $\text{Cu}_2\text{SiS}_3$  phase. By varying the thickness of the Cu layer in the Cu-Si bilayer stack, the correct stoichiometry was achieved. A large set of samples was fabricated and different process conditions were varied in order to find optimum process conditions.



**Figure 8** Cross section SEM image of the  $\text{Cu}_8\text{SiS}_6$  sample.

The varied process conditions for the  $\text{Cu}_8\text{SiS}_6$  fabrication were the thickness of the Cu layer, the  $\text{H}_2\text{S}$  partial pressure, the anneal temperature and the anneal time. The best process conditions were found to be a bilayer stack of  $\text{Cu}(420\text{ nm})/\text{Si}(170\text{ nm})$ , selenized for 25 minutes in 200 mbar of  $\text{H}_2\text{S}$  at a temperature of  $560^\circ\text{C}$ . The XRD spectrum of this layer grown on a Mo/glass substrate is shown in figure 7. The peaks of  $\text{Cu}_8\text{SiS}_6$  can be clearly observed and, besides

the Mo, no other peaks can be seen in the spectrum, indicating a relatively low amount of secondary phases. Figure 8 shows a cross section SEM image of the sample, showing the roughly 700 nm thick polycrystalline film with clearly identifiable grains with sizes of about 1  $\mu\text{m}$ . The photoluminescence response of this sample acquired with a Hamamatsu C12132 near-infrared time-resolved photoluminescence tool shows a relatively bright peak at an energy of about 1.84 eV with a full width at half maximum of about 110 meV (Figure 9). Time-resolved measurements with the same tool showed a photoluminescence decay time of about 0.8 ns (not shown). We have fabricated a solar cell with this absorber layer using the standard CdS and ZnO process flow. The measured current-voltage behaviour of these devices is very leaky and resistor-like, no rectifying behaviour or photocurrents could be observed (Figure 10). The measured resistance was of the order of 4 Ohm  $\text{cm}^2$  for all devices.



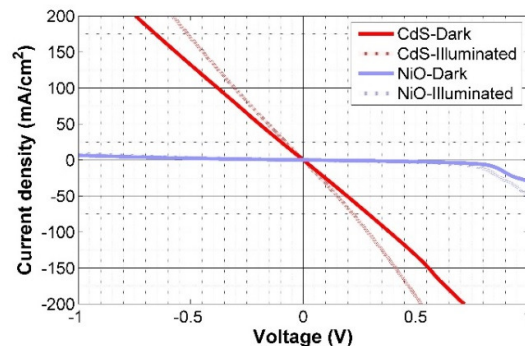
**Figure 9** Photoluminescence response of  $\text{Cu}_8\text{SiS}_6$ .

Such a large leakage current could possibly be explained by an n-type doping of the  $\text{Cu}_8\text{SiS}_6$  layer, so we also proceeded in the reactive sputter deposition of a 300 nm thick p-type NiO buffer layer on the  $\text{Cu}_8\text{SiS}_6$  layer. The current-voltage characteristics of this device can be seen in figure 10, this time not showing such a high leakage current but rather a rectifying behaviour. But still no photocurrent could be observed under illumination, such that the measured efficiency is still zero. Similar layers selenized in an  $\text{H}_2\text{Se}$  atmosphere showed an intense photoluminescence response at 1.3 eV, but also no photocurrents.

## 7 Conclusions

Using a two step selenization process, we have fabricated ternary and quaternary chalcogenide materials based on Cu, Zn, Sn and/or Si.  $\text{Cu}_2\text{Zn}(\text{Sn},\text{Si})\text{Se}_4$  and  $\text{Cu}_2\text{Si}(\text{S},\text{Se})_3$  appear to be difficult to fabricate at the used process temperatures, because of bad intermixing of the Si with the other materials.  $\text{Cu}_8\text{Si}(\text{S},\text{Se})_6$  layers on the other hand could be fabricated as polycrystalline thin film layers on Mo/glass substrates with relatively little secondary phases and grain sizes of the order of 1  $\mu\text{m}$ . The  $\text{Cu}_8\text{SiS}_6$  and  $\text{Cu}_8\text{SiSe}_6$  layers show intense photoluminescence peaks at respectively 1.84 and 1.3 eV

with a full width at half maximum of about 110 meV. Solar cells were fabricated with the  $\text{Cu}_8\text{SiS}_6$  layers using both n-type CdS and p-type NiO buffer layers, but under illumination no photocurrents could be measured on the finished devices.



**Figure 10** Dark (solid lines) and illuminated (dashed lines) current density versus voltage curves for 0.5  $\text{cm}^2$   $\text{Cu}_8\text{SiS}_6$  solar cell devices with an n-type CdS buffer layer (red curves) and a p-type NiO buffer layer (light blue curves).

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