Preparation of CuGaSe₂ Thin Film Solar Cells Comprising an Electrochemical Gallium Deposition Step

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Dedicated to Prof. Dr. H. Schmidbaur on the occasion of his 60th birthday

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Thin film CuGaSe₂ solar cells were prepared from the elements using electrochemical deposition of Ga from an alkaline bath. Sputtered copper layers with a small gallium content (Cu_{0.86}Ga_{0.14}) on Mo/soda-lime glass served as a substrate. Subsequent reactive annealing of the thus created Cu/Ga precursor layer with selenium vapour yielded CuGaSe₂. Chalcopyrite phase formation was studied with XRD, micro-Raman spectroscopy, SEM-EDX and Auger electron spectroscopy. It was concluded from these measurements that the binary phases Cu₂Se and Ga₂Se₃ are generated prior to the formation of the favoured CuGaSe₂ phase. Complete solar cell structures were fabricated by chemical bath deposition of CdS and chemical vapour deposition of ZnO onto the CuGaSe₂ absorber layer. Promising 3.2% efficiency with U_{oc} = 542 mV, I_{sc} = 12.0 mA/cm² and FF = 0.49 were achieved, proving that electrochemical gallium deposition from an aqueous bath can contribute to the efficient thin film processing of chalcopyrite solar cells.

1 Introduction

Copper indium diselenide (CIS) has emerged as an important absorber material in low cost solar cells and modules for terrestrial applications [1]. The highest conversion efficiency reported so far for such cells is 16% [2]. In contrast to that, the photovoltaic efficiency of copper gallium diselenide with an energy band gap of 1.68 eV peaks at about 6% for solar cells containing monocrystals [3] as well as polycrystalline thin films obtained by coevaporation of the elements [2]. Nevertheless, CuGaSe₂ is an interesting material for solar cell devices, especially as a top layer in tandem systems, in graded band gap solar cells, or simply as an alloy with CuInSe₂ to form CuIn_{1-x}Ga_xSe₂. The addition of gallium increases the band gap starting with 1.0 eV of pure CuInSe₂ to values more suitably matched to the terrestrial AM 1.5 solar spectrum. Thus, the highest reported efficiencies for polycrystalline CuIn_{1-x}Ga_xSe₂ thin films have reached up to 17% [2], a level that had

so far only been achieved with solar cells based on crystal wafers such as Si, GaAs and InP.

In this paper we describe the preparation of CuGaSe₂ polycrystalline thin films comprising an electrochemical deposition step for gallium. The metallic Cu/Ga precursor films were reactively annealed in selenium vapour. Formation of CuGaSe₂ thin layers was studied with XRD, micro-Raman spectroscopy, SEM, EDX and Auger electron depth profiling. Mo/CuGaSe₂/CdS/ZnO heterojunctions have been prepared and first results are presented.

2 Experimental

2.1 Gallium deposition

Soda-lime glass sputter coated with molybdenum (0.7 µm) and copper containing gallium (Cu_{0.86}Ga_{0.14}, 0.2 µm) was used as substrate for the electrochemical gallium deposition. Gallium was cathodically electrodeposited onto about 10 cm² substrate sheets under potentiostatic control from an aqueous bath which contained 15 mM Ga₂(SO₄)₃·18H₂O and 5.0 M KOH in bidistilled water. Ga₂(SO₄)₃·18H₂O was prepared from gallium metal (99.999%, Heraeus) and H₂SO₄. The

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three electrode configuration in a 100 ml electrochemical cell under thermostatic control was completed by a mercurous sulphate reference electrode, MSE (+0.615 V vs. NHE) and a platinum auxiliary electrode (8 cm², sheet). All deposition potentials are given with respect to MSE. A Wenking LB 75 L potentiostat and a Wenking VSG 83 scan generator were coupled for potentiostatic deposition experiments. Continuous plating was performed with the above-mentioned electrolyte at a potential of -2.5 V and at 25 °C. For pulse plating, a Tacussel GSTP pulse generator was used. The applied rectangular pulse sequence was -2.5 V for 6 s and -1.9 V for 4 s at a temperature of 90 °C. All obtained gallium deposits were thoroughly rinsed with bidistilled water and dried in a nitrogen stream. The total amount of deposited gallium was determined by weighing the samples.

2.2 Selenization

For film formation experiments, 1 cm² sheets of the Cu/Ga precursor (Cu/Ga ratio = 0.85 and Cu+Ga = 6.2 μmol) on Mo/soda-lime glass were placed in a small chamber (volume *ca.* 0.5 cm³) made of stainless steel. Parallel to the Cu/Ga layer a sheet of glass with an evaporated selenium surface layer (3.2 cm², Se thickness: 1.4 μm, 24.6 μmol Se) was fixed at a distance of about 2 mm. A NiCrNi thermocouple which had been calibrated with a gallium thermometer was mounted to the reaction chamber, and the whole arrangement was repeatedly evacuated and purged with nitrogen in a Schlenk tube. The tube was then transferred to a preheated furnace whose temperature was kept constant with a two-point regulating unit. The temperature profiles were obtained by recording the voltage response of the thermocouple. The examination of different selenization stages was performed after rapidly cooling the samples in liquid nitrogen to the ambient within a few seconds.

To prepare CuGaSe₂ absorber layers for the fabrication of solar cells, Cu/Ga sheets of approximately 8 cm² were placed in a Schlenk tube and the above-mentioned Se/glass sheets were fixed at a distance of about 5 mm facing the metallic precursor.

2.3 Solar cell preparation

Solar cell test structures were completed by chemical bath deposition of a *ca.* 50 nm thick CdS buffer layer (see *e.g.* [4]) on the CuGaSe₂ film followed by a CVD-ZnO layer of about 1.0 μm thick-

ness as a transparent conductive oxide (TCO). Finally the plates were patterned mechanically into 0.09 cm² total area devices.

2.4 Instrumentation

Powder X-ray diffraction analyses of the thin films were carried out in steps of 0.05° 2θ at a rate of 1 s/step on a Siemens 5000D diffractometer with CuK_α radiation. Further characterization was performed with a Jeol JSM-35C scanning electron microscope (SEM) coupled with an energy dispersive X-ray detector (EDX, HNU X-Ray system 5000, standardless ZAF analysis) for film texture and composition analysis. Compositional depth profiles were derived from Auger electron spectroscopical investigations which were undertaken on a Physical Industries Inc. spectrometer. Micro-Raman scattering was performed with an Instruments S.A. (Riber, Jobin Yvon) setup including a BH-2 Olympus microscope and a Coherent+Innova 300/I-301 krypton laser using the 647.1 nm excitation line.

3 Characterization of Cu/Ga Precursors

Since gallium oxides and hydroxides show a minimum solubility at about pH 8, either acidic solutions at pH < 3 or basic solutions of pH > 12 are described for the cathodic gallium deposition from aqueous baths in the literature [5–8]. Gallium plating from aqueous solutions is always accompanied by hydrogen evolution, which is slightly less intense in the strongly basic electrolyte (5 M KOH) we have chosen, where gallium is present as gallate.

Continuous plating at -2.5 V led to lustrous gallium films of about 0.5 μm thickness in deposition times of a few minutes (current density: *ca.* 15 mA/cm²; deposition rate: 0.06 mgGa/cm²min). The macroscopic lateral gallium distribution on the whole deposit (10 cm²) was determined by analysing areas of about 1 mm² with EDX. A homogeneous macroscopic gallium distribution was observed, the measured standard deviation in the gallium amount was 1.4% which is very close to the relative statistical deviation of 0.9% characteristic for this EDX equipment. Large macroscopic inhomogeneities, *e.g.* a deviation of 5.3%, were found in gallium films obtained at higher deposition rates at -3.0 V. Hydrogen bubbles evolved at the vertical substrate and thus induced an electrolyte flow from the bottom to the top close to

the substrate. This led to a vertical decrease of the gallate concentration from bottom to top, and finally resulted in a simultaneous decrease of plated gallium.

Due to its low melting point and a high surface tension, however, gallium has the tendency to form little droplets, which under these conditions can grow up to 2 μm in diameter (Fig. 1). Thus only microscopically rough deposits were obtained with continuous Ga plating.

Fig. 1. SEM picture of gallium continuously deposited at -2.5 V vs. MSE and $25\text{ }^{\circ}\text{C}$ (sample tilted by 60°), magnification: $\times 3000$, 3 mm in the picture correspond to $1\text{ }\mu\text{m}$.

The Auger profile of an as-deposited Cu/Ga layer at $25\text{ }^{\circ}\text{C}$ is given in Fig. 2. Alloy formation to CuGa₂ occurred even at ambient temperature (cf. XRD investigation). Copper and gallium are partly mixed, but nevertheless a gallium rich surface is present, that becomes more enriched with copper towards the Mo back surface. The only contaminations are oxygen and carbon on the sur-

face due to air exposure, but the bulk oxygen concentration is close to the detection limit of the spectrometer ($<1\text{ at}\%$). Gallium could therefore be electrochemically deposited with a low oxygen content even from an aqueous electrolyte.

Further experiments were performed to smoothen the microscopic roughness of the gallium deposit. Lowering the deposition temperature to $-10\text{ }^{\circ}\text{C}$ had no effect, the same gallium morphology as in Fig. 1 was observed.

Diffractionmetry of gallium films on copper indicates the formation of a copper gallium alloy (CuGa₂ phase) even at $25\text{ }^{\circ}\text{C}$. Thus, no gallium droplets can form on the copper layer, provided the alloy formation is enhanced such that it takes place more quickly than the deposition of elemental gallium. This idea was realised by adjusting an electrolyte temperature of $90\text{ }^{\circ}\text{C}$ to speed alloy formation, and by pulse plating to reduce the gallium deposition rate. Upon applying a pulse sequence of -2.5 V for 6 s and -1.9 V for 4 s, gallium was incorporated into the sputtered copper layer and formed CuGa₂ crystallites. With this technique we obtained a microscopic more homogeneous Cu/Ga precursor (Fig. 3) in contrast to the continuous deposition method.

However, the pulse plating technique at elevated temperatures cannot be used to obtain areas free of defects of at least 1 cm^2 . Small holes in the copper led to enhanced hydrogen evolution at the molybdenum back contact, followed by hydrogen evolution in the Cu/Mo interface. Under these conditions this finally resulted in peeling off of Cu/

Fig. 2. Auger electron depth profile of a Cu/Ga layer on Mo/glass obtained by continuous Ga deposition at -2.5 V .

Fig. 3. SEM picture of pulse-plated gallium at 90 °C (sample tilted by 60°), magnification: $\times 3000$, 3 mm in the picture correspond to 1 μm .

Ga from Mo and formation of visible holes in the Cu/Ga film. The quality of the Cu/Mo substrate, especially the homogeneity of the copper layer is therefore essential for the adherence of the whole structure.

All experiments described furtheron were performed using Cu/Ga sheets on Mo obtained by the continuous gallium deposition technique at -2.5 V and 25 °C.

4 Selenization

To examine the selenization process, 1 cm² sheets of copper gallium layers on Mo/glass were heated with an excess of selenium in a stainless steel chamber. An annealing cycle shown in Fig. 4 with a slope of approximately 100 °C/min and a constant temperature of 550 °C for 10 min was applied. Different intermediate stages of the selenization were isolated by rapidly cooling the samples in liquid nitrogen (LN₂). The samples for diffractometry were A: as-deposited Cu/Ga layer, B: 250 °C/LN₂, C: 350 °C/LN₂, D: 450 °C/LN₂, E: 550 °C/LN₂, and F: 550 °C for 10 min and slow cooling to ambient temperature.

4.1 X-ray diffraction

The metallic precursor (sample A) shows a diffraction peak for copper (1) and several peaks for the CuGa₂ phase (2), see Fig. 5. No additional peaks for elemental gallium were observed, not even in the case of very thick gallium deposits. Gallium seem to be diffractometrically amorphous when measured at the ambient due to its low melting of *ca.* 30 °C. After annealing up to 250 °C (sample B) copper was totally dissolved in gallium,

Fig. 4. Temperature profile for the selenization of Cu/Ga layers: A–F: different stages of this process, B–E: rapid cooling with liquid nitrogen.

and only the CuGa₂ peaks were observed. At higher temperatures, *e.g.* 350 °C, the CuGa₂ alloy drastically changed its orientation and the <001> planes became dominant (2 a). The large amount of selenium of sample C (see EDX measurements) was amorphous. First reaction products with Se were observed at about 400 °C. At 450 °C (sample D) the binary phases Cu₂Se (3) and Ga₂Se₃ (4) occurred, as well as the chalcopyrite phase of CuGaSe₂ (5). Copper seemed to be selenized more easily than gallium. The copper selenides segregate to the upper portion of the film (see also SEM and EDX measurements). The CuGa₂ phase was completely selenized above 550 °C (sample E) where only the two binary phases (3 and 4) and the chalcopyrite modification (5) were present. Further annealing for 10 minutes at 550 °C led to single phase CuGaSe₂ thin films (sample F). The formation occurred *via* the binary compounds Cu₂Se (3) and Ga₂Se₃ (4).

4.2 SEM and EDX characterization

In addition to the studies mentioned above, the samples were subjected to EDX analysis to determine the change in the integral composition of the elements. In Fig. 6 the ratios of Cu/Ga and Se/(Cu+Ga) are shown versus the anneal temperature reached in the temperature profile.

Above 200 °C all the selenium has evaporated from the glass sheet into the gas phase, but at 250 °C only a small amount of Se was found on the substrate. From 300 to 350 °C, however, a thick

Fig. 5. XRD spectra of films annealed up to different temperatures (*cf.* Fig. 4) showing the transformation of the Cu/Ga precursor *via* the binary phases to the ternary CuGaSe₂ compound.

elemental selenium layer formed on the Cu/Ga precursor. But most of the selenium evaporated off again without reacting with the metals (400 °C). Selenization occurred mostly from the vapour phase above 400 °C. Thereby also the Cu/Ga ratio increased due to the segregation of copper(I)selenide to the surface and the higher X-ray efficiency for the upper layers. In Fig. 7 we show large Cu₂Se crystallites on top up to 2 µm in size (EDX [at%]: Cu/Ga/Se = 67.2/0.7/32.1, region a), and the gallium rich layer underneath (EDX [at%]: Cu/Ga/Se = 16.9/32.8/50.3, region b) for the anneal temperature of 450 °C.

Further annealing at 550 °C for 10 min led to a homogeneous surface with a composition Cu/Ga/Se = 24.7/25.1/50.2 [at%] as determined by EDX (Fig. 8). Integral measurements of fully annealed films always revealed a lower gallium content in comparison to the metallic precursor, possibly due to the formation of volatile gallium selenides, *e.g.* Ga₂Se.

Fig. 6. Integral EDX analyses of Cu–Ga–Se films annealed up to different temperatures (*cf.* Fig. 4).

Fig. 7. SEM picture of a Cu/Ga precursor annealed in selenium vapour up to a temperature of 450 °C and then rapidly cooled in liquid nitrogen; *region a*: Cu₂Se crystallite (EDX [at%]: Cu/Ga/Se = 67.2/0.7/32.1); *region b*: gallium rich layer (EDX [at%]: Cu/Ga/Se = 16.9/32.8/50.3), magnification: $\times 3000$, 3 mm in the picture correspond to 1 μm .

Fig. 8. SEM picture of a Cu/Ga precursor annealed in selenium vapour at a temperature of 550 °C for 10 min (EDX [at%]: Cu/Ga/Se = 24.7/25.1/50.2), magnification: $\times 3000$, 3 mm in the picture correspond to 1 μm .

Fig. 9. Raman spectra of a Cu/Ga thin film annealed in selenium vapour up to a temperature of 350 °C (lower curve), 550 °C (central curve) and 550 °C for 10 min (upper curve).

4.3 Micro-Raman analysis

The selenization process was also controlled by micro-Raman spectroscopy. The CuGa₂ alloy is Raman inactive, but the amorphous elemental selenium which could not be detected by X-ray diffraction, showed a very intense Raman signal at 233 cm⁻¹ (Fig. 9, lower curve) [9]. The CuGaSe₂ phase, with the A₁ mode at 183 cm⁻¹ [10] and an additional signal at 271 cm⁻¹ [11] evolved above 400 °C as mentioned before in the diffractometry section (Fig. 9, central curve).

Raman spectroscopy is also a very effective tool for the identification of the very intense gallium selenide scattering signals. The double peak (244 and 250 cm⁻¹) and a signal at 132 cm⁻¹ was assigned to gallium selenides, which have been further characterized. Ga₂Se₃ powder (Alpha, 99.999% metals basis) and a thin gallium film on

Fig. 10. Raman spectra of Ga₂Se₃ powder (upper curve) and a Ga₂Se₃ thin film prepared similar to the selenization of the Cu/Ga alloys (lower curve).

a glass sheet which was selenized for 10 min at 550 °C in the same way as the Cu/Ga samples on Mo were analysed (Fig. 10). EDX analysis of the obtained thin film yielded an approximate composition of Ga₂Se₃. Raman spectra of both samples roughly had the same signals (133, 208, 244, 250 cm⁻¹) and an additional peak at 155 cm⁻¹ for the powdered sample, but were totally different in the signal intensities. Therefore, we propose different gallium selenide phases which most probably originate from the laser beam irradiation of other species. To get a deeper insight of the gallium selenide Raman patterns, a low temperature experimental setup is currently developed. For the Cu₂Se phase commercially available powder (Cerac) as well as a thin film was analysed, but no intensive signals were found in both samples.

Supporting the diffractometric results, the very intensive gallium selenide signals decreased at

longer reaction times, and in a chalcopyrite thin film the peaks at 182 and 271 cm⁻¹ were dominant in the spectra besides a negligible amount of gallium selenide which was probably formed by the laser beam (Fig. 9, upper curve).

4.4 Auger electron spectroscopy

As reported by other groups before [12], we found a gallium-enriched back surface according to Auger depth profiling of films annealed for 10 min at 550 °C (Fig. 11). Compared to the metallic Cu/Ga precursor (see Auger depth profile Fig. 2) the Cu/Ga distribution gets inverted during reactive annealing. This element distribution might develop due to the preferred copper selenization, segregation of the Cu₂Se phase to the upper portions of the film and the additional gallium loss from the surface.

4.5 Film formation summary

Summarizing the results with all the above-mentioned measurement techniques a clear picture describing the formation of the ternary chalcopyrite phase can now be outlined as follows:

- 25 °C: Cu, Ga, and disordered CuGa₂
- 25–250 °C: Cu fully dissolved in CuGa₂
- 250–350 °C: CuGa₂ (becomes strongly <001> oriented) and Se (evaporated on the alloy from the vapour phase)
- 350–450 °C: Se evaporation into the gas phase
Selenization mostly *via* the gas phase
Preferred Cu selenization leads to Cu₂Se formation which segregates to the upper portion of the film, in parallel Ga selenizes to Ga₂Se₃ and CuGaSe₂ forms *via* the binary selenides
- 450–550 °C: Complete selenization of the metals leads to a Ga₂Se₃ enriched CuGaSe₂ bottom layer and a Cu₂Se enriched CuGaSe₂ surface layer, which becomes a more homogeneous CuGaSe₂ phase with increasing anneal time, but ends with a gallium enriched backsurface

5 Solar Cells

Dark and bright I–V characteristics of the Mo/CuGaSe₂/CdS/ZnO cells were measured under

Fig. 11. Auger depth profile of a Cu/Ga layer reactively annealed for 10 min at 550 °C in Se vapour.

simulated AM 1.5 illumination (100 mW/cm²) at 25 °C. The devices fabricated as described above, *e.g.* starting with a gallium excess in the metallic precursor, have shown rather poor performance. Although the integral composition of the obtained absorber layers, determined by EDX measurements, resulted in Cu/Ga ratios close to one, small amounts of binary copper selenides on the surface of the absorber layer cannot be avoided. These surface contaminations are one obvious reason for a low efficiency. Therefore we changed our strategy and started with Cu rich metallic precursors (Cu/Ga = 1.14). After reactive annealing we ended with a Cu/Ga ratio of 1.30. These films were then etched in a 10 wt% KCN solution [13] for 10 min to remove the copper selenides and yielded a Cu/Ga = 0.99. A cross-section of such a film, embedded in a complete solar cell structure is given in Fig. 12.

Fig. 12. SEM picture of the cross-section of a complete solar cell structure, magnification: $\times 10,000$, 10 mm in the picture correspond to 1 μm .

The best cell achieved so far reached a 3.2% efficiency with $U_{oc} = 542$ mV, $I_{sc} = 12.0$ mA/cm² and FF = 0.49 (Fig. 13). The efficiency demonstrated here may be limited by the still high Cu/Ga ratio of the absorber after the KCN etch.

6 Conclusion

We have demonstrated a simple electrochemical deposition step to introduce gallium into the Cu/Ga/Se system to form CuGaSe₂ solar cells. In a simple selenization setup we showed, that the metallic Cu/Ga precursor reacts with elemental Se to

Fig. 13. Bright and dark characteristics of a CuGaSe₂ solar cell under simulated AM 1.5 (100 mW/cm²) illumination.

the chalcopyrite *via* the binary phases Cu₂Se and Ga₂Se₃. Further investigations, especially to avoid copper selenides on the absorber surface and to enhance cell efficiencies without using a KCN etch are on their way. So far we proved, that an electrochemical deposition step for gallium can contribute to other deposition techniques for the chalcopyrite solar cell preparation.

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