12.6% efficient CdS/Cu(In,Ga)S$_2$-based solar cell with an open circuit voltage of 879 mV prepared by a rapid thermal process

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ABSTRACT

A Cu(In,Ga)S$_2$-based solar cell with a confirmed efficiency of 12.6% together with an open circuit voltage of 879 mV, prepared from sputtered metals subsequently sulfurized using rapid thermal processing in sulfur vapor, is reported. The performance of the new cell is superior to those obtained previously with multi-source evaporated absorbers. We show that by carefully adjusting the temperature profile, good absorber properties could be transferred from a long process to a rapid thermal process. The improved efficiency is due to an appropriate degree of gallium diffusion toward the surface, which could be achieved despite the short sulfurization time. Absorber and solar cell characteristics are presented.

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1. Introduction

Chalcopyrite semiconductors have proven to be promising materials for photovoltaic applications. Thin film solar cells based on Cu(In,Ga)Se$_2$ (CIGSe) have reached an efficiency of about 20% on the laboratory scale [1], which makes them competitive candidates for large-area application and commercialization. In addition to the low band gap Cu(In,Ga)Se$_2$ chalcopyrites, CuInS$_2$ has been the focus of attention due to its high gap of 1.5 eV, which is close to ideal. However, debates have been going on regarding the limited efficiency of wide band gap chalcopyrites, and open circuit voltages of the cells remained below the predicted theoretical values. An efficient transfer of the results from the laboratory to industrial production requires a straightforward and short processing time approach, which is more appropriate for the fabrication of low cost large scale modules. Although multi-source evaporation is used successfully by some companies such as Würth and Solibro, it is much more common in basic research. Chalcogenization of stacked metallic layers could be more appropriate for industrial applications and is widely used for the fabrication of Cu(In,Ga)Se$_2$ thin film based chalcopyrite absorbers [2–5].

CuInS$_2$ based solar cells, prepared from sputtered metals subsequently sulfurized using rapid thermal processing (RTP) in sulfur vapor, have reached 11.4% confirmed total area efficiency (area = 0.5 cm^2) [6]. However, significant improvement could not be achieved and open circuit voltage values did not typically exceed 730 mV. Incorporation of gallium has led to the most promising results where band gap widening was obtained, leading to higher open circuit voltages. Using different preparation methods, we could show that the open circuit voltage of the solar cells increases faster than the band gap at low gallium concentrations. Initially, the preparation was carried out using evaporated (rather than sputtered) precursors followed by conventional sulfurization or rapid thermal processing in H$_2$S [7]. We went back to multi-source evaporation in an attempt to investigate the efficiency limits on a laboratory scale and were able to demonstrate an efficiency of 12.3% (almost 1% absolutely higher than with our CuInS$_2$) and higher open circuit voltages of about 776 mV [8–10]. The best performance was obtained when there was a gallium content of about 5% in the upper part of the absorber layer, which is the active part of the heterojunction. However, the use of the sequential process for synthesis of gallium-containing CuInS$_2$ films turned out to be much more complicated. Unexpected problems were encountered while introducing gallium into our baseline process (sputtered precursors, RTP sulfurization). In addition to homogeneity and reproducibility problems, due to the difference in reaction rates between ternary sulfides, the sulfurization of sputtered metallic precursor layers usually results in either absorbers with a layered CuInS$_2$/CuGaS$_2$ structure, leaving the gallium on the backside of the sample, or slow and incomplete reaction that leads to samples where the unreacted metal phase remains at the back with the chalcopyrite on top of it [11]. Although an increase in

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efficiency to 12.9% was observed for solar cells prepared from the RTP process, process stability and repeatability could not be achieved [12]. The quantum efficiency measurement showed good current collection of the obtained solar cells; however, in many cases no band gap widening was observed compared to the gallium-free absorber reference.

In this paper, we show that the solar cell performance obtained by multi-source evaporation could be successfully transferred to a sequential process. Complete sulfurization of the precursors together with a reasonable amount of gallium in the active region of the junction could be achieved for a rapid thermal process leading to solar cells with increased open circuit voltage up to 890 mV. Process reproducibility and stability were finally achieved.

2. Experimental details

Stacked layers of In and (Cu,Ga) alloy precursors were deposited by DC magnetron sputtering onto 12.5×50 mm^2 Mo-coated float glass substrates. The samples were prepared under Cu-excess conditions to ensure that sulfurization occurred in the presence of a Cu$_x$S phase. Further details about sample preparation were described elsewhere [12,13]. For the in-situ X-ray diffraction (XRD) spectroscopy, sulfurization processes were carried out in an energy-dispersive X-ray diffractometry (EDXRD) vacuum chamber. The sulfur source and the sample could be heated separately. Sample temperature was varied between room temperature and 510 °C. White synchrotron radiation at the F3 beamline at HASYLAB (DESY) was used and the energy range for the spectra was between 28 and 60 keV. For rapid thermal processes, sulfurization was performed at the Helmholtz-Zentrum, Berlin. The obtained precursors were placed in a box together with elemental sulfur prior to processing and then transferred to a reaction chamber, where they were heated by radiation from halogen lamps. The sulfurization was carried out at nominal temperatures of 450–600 °C for 3–6 min.

A CuS layer forms at the top of the Cu(In,Ga)S$_2$ layer during the process. It was removed by etching in KCN solution prior to the completion of the heterojunction. The crystal structures of the precursor and Cu(In,Ga)S$_2$ thin film absorbers were examined by ex-situ X-ray diffraction and scanning electron microscope (SEM). Solar cells were completed by chemical bath deposition of a CdS buffer layer, sputtering of a transparent Zn(Mg)O/ZnO:Al window layer and evaporation of Ni–Al grids. The cells received a MgF$_2$ anti-reflection coating. Solar cells were characterized by current–voltage measurements under simulated standard AM1.5

conditions. The external quantum efficiency (EQE) was measured in the range 300–900 nm using xenon and halogen lamps.

3. Results and discussion

3.1. Precursor alloying

After sputtering, metal stacks were stored at room temperature and the phase composition was studied by X-ray diffraction. Alloying occurs immediately during or after the deposition due to interdiffusion of the layers. No intentional heating was carried out during sputtering; however, the possibility that the growth of the precursors occurred at a temperature higher than room temperature cannot be completely excluded. The XRD spectrum of an In/(Cu,Ga) standard precursor used for sulfurization is shown in Fig. 1. In the as-deposited conditions, it indicates the presence of the elemental unreacted In, Cu$_{1-x}$Ga$_x$ (solid solution of gallium in copper), CuIn$_2$ and Cu$_{16}$In$_9$. The broad width of the reflex at 43.4° stems from the Cu$_{1-x}$Ga$_x$ phase, which is characterized by small crystallites. This broadened peak is also observed when a single layer of Cu–Ga is sputtered. The peaks related to CuIn$_2$ and Cu$_{16}$In$_9$ are slightly shifted from the position expected for Cu–In binary alloys, suggesting a decrease in the unit cell by the substitution of indium by gallium. Therefore they are labeled as Cu(In,Ga)$_2$ and Cu$_{16}$(In,Ga)$_9$, respectively. The Cu(In,Ga)$_2$ reflexes show lower intensities compared to Cu$_{16}$(In,Ga)$_9$, which suggests that the latter phase is prominent. Marudachalam et al. [15] investigated sputtered In, Cu and evaporated Ga stacks behaviour. However, they reported no evidence of the existence of ternary Cu–In–Ga phases. Purwins et al. [16] also investigated phase relations in the ternary Cu–Ga–In system. Their as-deposited samples showed only binary Cu$_{16}$In$_9$ and Cu$_9$Ga$_4$ besides the elemental indium. They observed that ternary Cu$_{16}$(In,Ga)$_9$ is formed only when the samples are heated at 300 °C. The difference between our observations and other authors' could be explained by the different target compositions and layer sequences.

A SEM cross section image of the precursor is shown in Fig. 2. It is characterized by rough morphology. Due to the intermixing of metals, the layered structure is partly disturbed and big voids of about 300 nm height are clearly visible at the metals/Mo interface. We speculate that they are caused by out-diffusion of In into Cu–Ga and maybe partly responsible for the observed adhesion problems. The thin dark layer at the top is attributed to remains of the sputtered Cu–Ga layer (Cu$_{1-x}$Ga$_x$). The Cu$_{1-x}$Ga$_x$ phase did not completely react with In as the XRD measurement revealed.

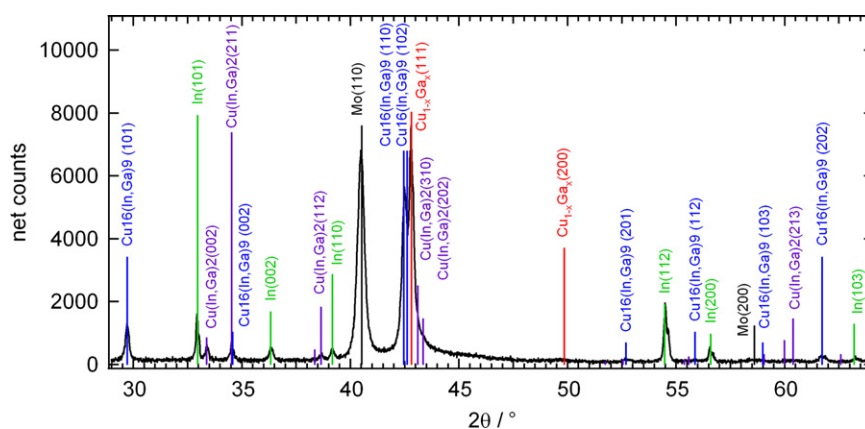**Fig. 1.** X-ray diffraction spectrum of a standard In/(Cu-Ga) precursor. Reflexes marked by Cu$_{16}$(In,Ga)$_9$ were calculated from JCPDS pattern 00-042-1475 for Cu$_2$In assuming lattice contraction by a factor of 0.99047. Reflexes marked by Cu(In,Ga)$_2$ were calculated from data from Keppner et al. [14] for CuIn$_2$ assuming lattice contraction by a factor of 0.998. Reflexes for the solid solution Cu$_{1-x}$Ga$_x$ were calculated from JCPDS pattern 00-004-0836 for Cu assuming lattice expansion by a factor of 1.00892. Mo and In references were taken from JCPDS patterns 00-042-1120 and 00-005-0642.