Development of Novel Target Materials for Cu(In,Ga)Se-Based Solar Cells

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At present, the market share of thin film photovoltaic (PV) within total PV production is approximately 10%, but it is expected to grow up to 20% by 2010 and beyond 30% in the long term. The availability of large area deposition equipment and process technologies, as well as the experience available from the architectural glass industry and the flat panel display industry, offer significant opportunities for high-volume and low-cost manufacturing of corresponding coating materials. A major challenge is to use materials which are easy to handle in large scale manufacturing and which offer cost advantages during PVD processing. GfE is developing CIGS target materials by different production procedures to meet future needs. This paper provides an overview concerning the status of development.

Introduction

Thin film solar cells have a high potential for cost-effective production and installation of electric power. The largest growth in the thin film photovoltaic (PV) market is estimated by cell configurations based on CIS or a-Si technology.

Such thin film solar cells have the advantage of less consumption of raw materials in comparison to crystalline silicon solar cells. Thin film solar cells are built up of several layers, which can be deposited by physical vapor deposition technologies (TCO, CuInSe2, a-Si, etc.) or by wet chemical deposition (CdTe, CdS). The technologies for these PVD layer depositions are state of the art in the flat glass or display industry.

CIS solar cells show the highest efficiency of up to 19.5% under laboratory conditions and about 14% in serial production, compared to other thin film configurations. The substitution of In by Ga offers the opportunity to define a specific band gap energy. Additionally, various intermediate band gap energy levels can be achieved by partial substitution of Se by S; thus, the efficiency of such PV cells can be adjusted to any specific local solar spectrum.

State-of-the-art production of CuInSe2 semiconductor layers is a sequential process. This process consists of the deposition of the elemental Cu-, In/Ga-, and Se layers on a conductive substrate (e.g., Mo-coated lime glass). In a following annealing step, the elemental layers react to the semiconductor at temperatures of approximately 550 °C in a reactive atmosphere (Se, H2Se). This relatively high annealing temperature requires substrates that withstand such temperatures. A consequence of this is that cost-efficient substrates, which would fulfill other operation requirements, cannot be used.

The availability of a multi-component sputtering target, including all elements in a defined ratio, offers the opportunity to reduce film formation temperatures and thereby also reduce manufacturing costs.

This aspect was GfEs motivation to evaluate the materials system CuInGa from the melt metallurgical point of view. Basically, the melt-metallurgical processing used for melting and alloying of elements, exhibiting significantly different melting points and equilibrium evaporation pressures, is very challenging. Furthermore, the formation of intermetallic phases may result in high melting compounds and cause segregation effects and other defects e.g., the so-called “sweating out” phases during the solidification.
If applying conventional melt-metallurgical processing technologies to the abovementioned materials system CuInGa in order to generate alloyed ternary and quaternary compositions, the results are very disappointing with regard to local deviations of the chemical composition, microstructural inhomogeneities, porous regions, and the formation of brittle phases.

Furthermore, the development of cast CIG alloys in more complex shapes, such as tube segments for rotatable targets suffers from a high thermal expansion coefficient in comparison to commonly used mold materials.

This paper presents the current status of metallurgical processing technologies of CuInGa alloys for sputtering targets and the resulting materials’ properties. As a following R&D-Projekt, the Selenium should be integrated in a suitable ratio in CuInGa-target material, for the “one-step” PV Deposition of the semiconductor layer.

**Experimental Part**

**Raw Materials**

Except Cu (standard ETP grade), the raw materials used for alloy manufacturing exhibited purities of 99.999 wt.-% or better.

**Alloy Manufacturing**

The casting tests were carried out in a vacuum induction melting furnace VIM 15 — Type M 6.1 (Pfeiffer Vacuum). The raw materials were positioned in a ceramic crucible, which was installed in the center of a water-cooled middle frequency coil. Experiments were carried out under inert atmosphere between \(2 \times 10^{-2}\)–800 mbar. The two-stage vacuum system consisting of a booster pump and a roots pump provided 10\(^{-3}\) mbar. The MF power was controlled in a range of 5–60 kW.

After melting and degassing of the molten material, the alloys were poured at temperatures of 20–30 °C above the melting points of the alloys.\(^2\) The liquid metal was cast in rectangular and cylindrical ceramic molds (Sital Cast 042). During the development of the casting mold it was modified by substituting the Sital Cast 042 by stainless steel 1.4301, glass fiber textile, and fiberfrax felt.

The detection of the temperature during the entire melting and pouring operation was done pyrometrically. The pyrometer was initially calibrated by a NiCr–Ni thermocouple and was then placed in the crucible.

**Alloy Characterization**

The microstructure of the samples was evaluated by optical metallography (Polyvar MET, Reichert-Jung) and SEM (LEO 1530VP Gemini, Zeiss). Metallographic cross sections were prepared using standard grinding, polishing, and etching techniques.

Metallographic phases were investigated by semiquantitative EDX analysis of prepared cross sections and XRD spectra of small polished disks and milled powders as well.

**Results and Discussion**

The objective is the development of a ternary CuInGa alloy, which can be used as a sputtering target for the deposition of an adjusted precursor layer for the formation of Cu(In,Ga)Se\(_2\) semiconductor thin films. Because of this, the material should be at least available as flat plates or cylindrical tubes.

The phase diagrams of the binary systems CuIn and CuGa show basically a comparable solidification behavior of both systems\(^2\). Solidification starts with the formation of high melting and brittle intermetallic phases, whereas the remaining liquid phase becomes increasingly enriched in In and Ga, during the cooling process. The microstructures of several binary CuIn and CuGa alloys with Cu contents between 40 and 68 at.-% show in the as-cast state, thus, serious materials segregation effects due to the extended solidification interval. At least, a small amount of In or Ga solidifies which sometimes causes the “sweat out” phases. Additionally, the binary intermetallic phases reduce the machining capability of the materials and show completely different evaporation behavior as compared to the matrix material. As a consequence of this, a suitable ternary CuInGa alloy should avoid any intermetallic phases in a low-melting matrix.

The binary InGa phase diagram is characterized by an eutectic composition at GaIn (80/20 wt.-%) at 16.5 °C\(^2\). The melting point of this composition is much too low for sputtering target applications and must be prevented.

First melting and pouring experiments were conducted with alloy compositions of 35–45 wt.-% Cu and In/Ga ratio of about 4:1 (wt.-%). Castings have been analyzed as described in chapter alloy characterization. Figure 1 shows the SEM image of the microstructure of the alloy Cu40-In46-Ga14, which is representative also for the microstructures of the alloys containing 35 and 45 wt.-% Cu. The microstructure consists of two major phases, the bright phase which consists of almost pure In with traces of Cu and Ga, and the dark phase which is a ternary composition of approximately 60Cu-20ln-20Ga (at.-%) but offering an extended homogeneous region with regard to the In/Ga ratio.

With variation of the Cu content, the volumetric fraction of the ternary phase changed too. The total amount of the relatively brittle ternary phase is limited in order to get reasonable machining capability of the material. (Figure 4, red area).

Any influence of the melting pressure on the formation of the microstructure could not be detected. The average
Grain size depended on cooling conditions, as could be expected. There is a minimum cooling rate, which should not be decreased further in order to realize a sufficient sputtering capability. The cooling rate is dependent upon the mold system, which should have a reasonable thermal conductivity to prevent extended grain growth during the solidification.

The ternary CuInGa phase has been further investigated. It could be demonstrated that the manufacturing of a single phase ternary alloy of the above-mentioned composition is possible using the techniques according to Section “alloy manufacturing”. According to the XRD spectrum of the single phase material shown in Figure 2, it is evident that the phase is of an intermetallic crystalline nature. At the time of writing, to the best of the authors’ knowledge no corresponding XRD files were available in the databases. The new phase is called $\pi$-phase$^{[3]}$ and describes ternary CuInGa

Figure 1. Microsection of a CuInGa 40:46:14 wt.-% alloy sample. The dark particles show the new undefined ternary phase, which incorporates gallium and indium in variable contents.

Figure 2. XRD-spectrum of the investigated particular phase in the micrograph of Figure 2. The lattice parameters of the wasn’t described before, but there is a similarity to the parameters of Cu$_2$Zn$_8$ phase.
compositions exhibiting 59–63 wt.-% Cu, 9–26 wt.-% In, and 19–28 wt.-% Ga. It is worth mentioning that the XRD peaks of the \( \pi \)-phase basically meet the XRD peaks of the intermetallic composition \( \text{Cu}_5\text{Zn}_8 \), which has a cubic body-centered structure. Thus, lattice parameters are estimated to be very close to those of the \( \text{Cu}_5\text{Zn}_8 \) phase. According to Ref.\[4\] the \( \text{CuInGa} \) phase is probably formed out of the binary \( \text{CuGa}_2 \) \( \gamma \)-phase by replacing Ga atoms by In, in case of a lack of Ga atoms. This would explain why all the Ga atoms participate in the formation of the ternary intermetallic phase and are not available for the formation of the low-melting eutectic InGa composition. This is of substantial advantage against the binary CuGa alloy containing at least elementary Ga, which melts at a very low temperature at 29.5 °C.

In case of manufacturing of real industrial components for rotatable targets exhibiting an indium-rich matrix phase, the very high coefficient of thermal expansion\[5\] causes problems during the solidification of the poured melt in a stiff and nonflexible casting mold. The introduction of a flexible mold system (e.g., stainless steel covered with fibre-based flexible ceramic sheets) overcomes this technical problem, as shown in Figure 3.

**Conclusion**

After months of development work, we defined a ternary \( \text{CuInGa} \) system as shown in Figure 4, which allows a forecast of suitable alloy compositions produced by the melting procedure in flat shapes and cylindrical tubes. The green area in the Cu-rich edge, contains CIG alloys that is similar to copper/zinc in the points of color and machinability. Red area alloys, which include the \( \pi \)-phase, are too brittle for machining. The large green area, describes mixtures with a balanced ratio of brittle intermetallic compounds and ductile In matrix. Alloy compositions, which are positioned in the yellow area are also suitable for casting. Machining becomes more difficult as the copper content decreases. Another issue is the existence of free gallium that sweats out at temperatures of above 29.5 °C while cooling down of molten metal, as well as during the sputtering process.

The existence of the \( \pi \)-phase in the larger green area causes, among other advantages, a higher temperature stability which is necessary during the sputtering process and the existence of free gallium, respectively; low melting indium and gallium eutectic alloys can be avoided.

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