Fabrication Of Cu(In,Ga)Se$_2$ Solar Cells With In$_2$S$_3$ Buffer Layer By Two Stage Process

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Abstract: Cu(In,Ga)Se$_2$ thin films (CIGS) on metallic substrate (titanium, molybdenum, aluminum, stainless steel) were prepared by a two-step selenization of Co-evaporated metallic precursors in Se-containing environment under N$_2$ gas flow. Structural properties of prepared thin film were studied. To characterize the optical quality and intrinsic defect nature low-temperature photoluminescence, were performed. Results shows that the structural and optical properties of Cu(In,Ga)Se$_2$ thin films strongly depend on the growth condition, charactristics of substrate and chemical composition. In2S3 thin layer has been used as buffer layer in CIGS solar cells and physical properties of them investigated. Solar cells were completed by vacuum deposition of ZnO/ZnO:Al layers and Ni/Al contact fingers. The surface morphology and bulk composition of thin films were investigated by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The optical testing was carried out by recording transmittance spectra of the samples by spectrophotometers in the spectral range 190–3000 nm at a resolution of 1 nm. The better conversion efficiencies were around 12.0 %.

Keywords: buffer layer, Cu(In,Ga)Se$_2$, In$_2$S$_3$, morphology, optical property, solar cell.

1. Introduction

The use of flexible substrates instead of the commonly used rigid soda lime glasses offers new possibilities for the application of solar cells in space and

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terrestrial photovoltaic power system [1-4]. The chalcopyrite semiconductor $Cu(In,Ga)Se_2$ (CIGS) thin film cells have demonstrated the highest efficiency on the laboratory and industrial scale. The conversion efficiency approaching the theoretical value of over 20 % are already reached for CIGS thin film solar cells on glass substrates [5]. In addition, CIGS solar cells show good stability under and recovery from electron and proton irradiation, whereas, for example, high efficiency Si or GaAs solar cells are more prone to radiation damage. In the last years an increasing number of the studies have been performed on the CIGS thin films fabricated on ultralightweight flexible metallic foil and polymer substrates [5-6]. The conversion efficiencies up to 16 - 17.5 % have been achieved for the CIGS thin film solar cells on flexible foil substrates [6].

This work presents the results of investigation of $Cu(In,Ga)Se_2$ absorber films prepared by a two-step growth process in which metallic precursors were deposited onto different flexible metallic foils (titanium, molybdenum, aluminum, stainless steal) followed by an annealing under N_2 flow with solid Se source. With an aim to develop flexible CIGS solar cells with vacuum evaporated In_2S_3 buffer layer, an attempt has been made to investigate physical properties of films grown by thermal evaporation technique. The main thrust is towards development of fundamental understanding and baseline processes rather than attaining the highest efficiencies [7].

2. Experimental

Cu(In,Ga)Se2 films were deposited onto 7×2.5 cm2 flexible metallic foils with and without molybdenum layers, which were dc-sputtered. CIGS films with thicknesses from 0.8 to 2.8 μm were grown using a two-stage technological process: deposition of Cu, In and Ga layers and subsequent selenization. Metallic precursors were prepared by ion-plasma sputtering with a deposition rate of 10 nm/min. A specially designed target, which includes a base presenting an In-Ga alloy, was used to deposit films of required composition. The Ga content in the Cu-In-Ga film was controlled by choice of In/Ga ratio on the initial alloy. The substrate temperature during growth was maintained at 390 K and the base pressure of the system was 2×10-4 Torr.

The Cu-In-Ga precursors have been selenized by diffusion of elemental selenium from solid state sources into the alloy films in nitrogen flow using two-step annealing temperature profile. The selenization system consisted of a special container for precursors and pots to accommodate Se material. The first selenization stage was made at temperatures of 520 - 540 K for 10 to 30 min, the second one - at 730 to 790 K for 10 to 50 min [8,9]. The CIGS films with the same chemical composition were also prepared on soda lime glasses for the comparison.

High-transparent In2S3 films were thermally deposited at substrate temperatures of 490 - 515 K. Thickness of the films was defined by controlling the deposition time in the region 1–30 min.

The surface morphology and bulk composition of thin films were investigated by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The SEM system is a JEOL 6400 and EDS is an EDAX detector with ISIS software. The EDS is performed for acceleration voltages of 20 kV. The Cu, Ga and Se are measured by integration of the K lines whereas In is measured from L line. The EDS measurements are used to calibrate the sources and to confirm the various values of components in thin films. The depth profiling was done by Auger electron spectroscopy (AES) using a Perkin Elmer Physical Electronics model 590. An Ar ion beam was used for sputter etching. The crystal structure and crystalline phases of the materials were studied by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with CuKα (λ = 1.5418 Å) radiation. The 2θ - range for the diffractometer was set from 10 to 1000 with a step size of 0.02. The observed phases were determined by comparing the d - spacing with the Joint Committee on Powder Diffraction Standard (JCPDS) data files.

The optical testing was carried out by recording transmittance spectra of the samples, using Cary 500 Scan spectrophotometers in the spectral range 190–3000 nm at a resolution of 1 nm. The PL spectra were analyzed using a 0.6 m diffraction monochromator. A liquid nitrogen cooled InGaAs p-i-n detector (Hamamatsu, Japan) was used for the PL signal detection. Signal amplification was based on lock-in technique. For excitation, the 488 line of the Ar ion laser was used in the PL experiments. The samples were immersed into liquid nitrogen or helium during the measurements of the PL spectra at 78 and 4.2 K, respectively. Temperature dependent measurements from 4.2 to 300 K were carried out in an evaporation cryostat equipped with suitable heaters and temperature sensors. The PLE spectra were measured using a 400 W halogen tungsten lamp combined with a grating monochromator (600 groves/mm, focal length of 0.3 m) as an excitation source.

Thin film photovoltaic cells were prepared by deposition of Al-Ni/ZnO/In2S3/CIGS stacked layers on Mo-coated substrates by the standard process. The current-voltage (J-V) measurements of thin film solar cells were performed under AM1.5 condition to determine active-area efficiencies.

3. RESULTS AND DISCUSSION

The aim of these studies was to develop a reproducible deposition process of CIGS thin films on different metallic foils for solar cell technology. The XRD investigation of Cu-In-Ga precursor films with different Cu/(In+Ga) composition rations showed the presence of highly oriented Cu1IIn9 phase and very little elemental or alloy phases [9]. The formation of the stable Cu11In9

stable phase simplifies reaction during selenization and enables the improved incorporation of the precursor into high-quality Cu(In,Ga)Se2 thin films.

As expected, the structural features (morphological features and formation of crystalline phases) of the final compound films were critically influenced by post-growth annealing. XRD measurements showed that phase formation in Cu(In,Ga)Se2 films depends both on the composition ratio in the precursors and on the processing regimes [8,9]. The dominant effect of substrate temperature and the time of crystallization (at the second step of the process) on phase formation were revealed. The CIGS films of near stoichiometric composition grown at temperatures below of 570 K with selenization time of 15-20 min showed disordered sphalerite Cu(In,Ga)Se$_2$, Cu11In9, In$_2$Se$_3$ and CuSe extra phases (Fig. 1). At temperatures of 650 K and above, all the secondary phases appeared to have been completely reacted to form single phase CIGS layers. All films exhibited (112) preferred orientation and had chalcopyrite structure. XRD pattern of CIGS layer fabricated on molybdenum (Mo) indicates the formation of the two-phase material – MoSe$_2$ along with CIGS.
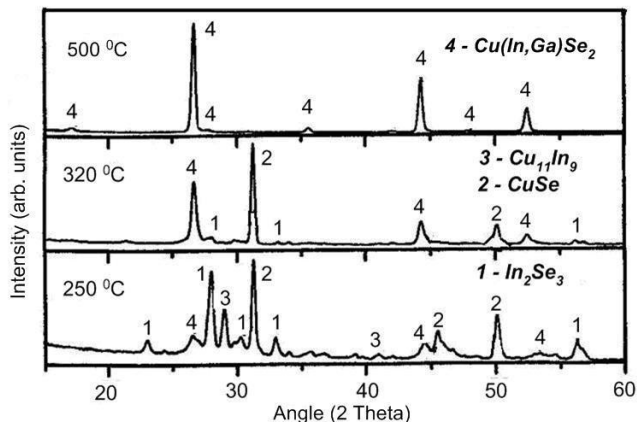

Fig. 1. XRD patterns of Cu(In,Ga)Se$_2$ film selenized at different temperatures

The AES depth profiling was used to study the elemental depth distributions by sputtering the analyzed areas by energetic argon ions. A typical depth profile for the thin film on Mo substrate obtained after the optimal selenization conditions is shown in Figure 2.
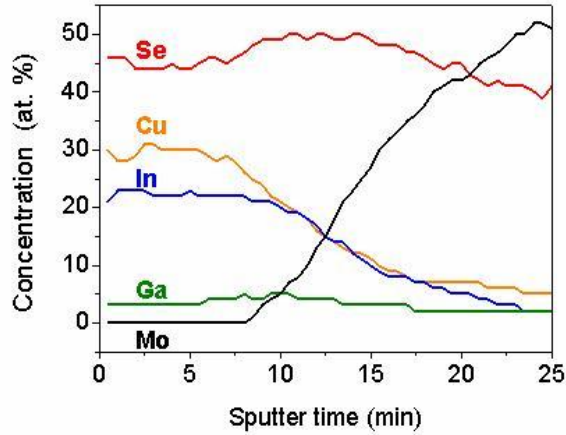
Fig. 2. Typical AES depth profile of Cu(In,Ga)Se$_2$ thin films on Mo substrate

As observed from our investigations, Cu, In, Ga and Se atomic concentrations remain fairly uniform through the depth of Cu(In,Ga)Se$_2$ thin films. The gradient of Cu, In and Mo near the interface between the CIGS layer and Mo foil suggests the formation of the additional phase MoSe2 along with CIGS, which was also confirmed by the XRD data. The AES measurements for CIGS thin films prepared on other metallic foils show uniform distributions of Cu, In, Ga and Se through the depth of the layers.

Figure 3 illustrates the typical surface morphologies of precursor films selenized at different temperatures for 30 min.
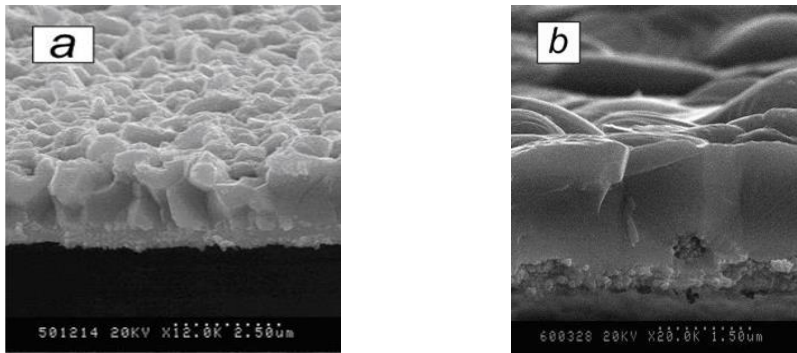

Fig. 3. SEM images of Cu(In,Ga)Se$_2$ films on stainless steel foil selenized at different temperatures: (a) - 620 K, (b) - 790 K

Thus, a clear evidence of the effect of recrystallization temperature on the film morphologies can be observed. The films selenized at 620 K show a rough surface structure which suggested that reaction process has not been fully concluded (Fig. 3a). It is important to note, that higher recrystallization temperature leads to the complete recrystallization of the film with the formation of uniform and densely packed faceted grains with sizes of 1.0 – 2.5 µm (Fig. 3b).

Typical PL spectra of Cu(In,Ga)Se$_2$ thin films at 4.2, 78 and 300 K on different substrates (glass, molybdenum, Ti with Mo layer and Al with Mo layer) are shown in Figure 4. The single broad band at 1.03 eV with full-width at half-maximum intensity (FWHM) of ~ 80 meV dominates the spectrum from 1MX sample at 4.2 K.
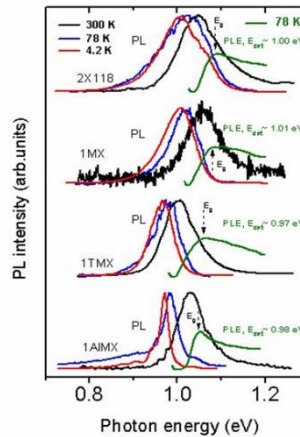

Fig. 4. PL spectra of Cu(In,Ga)Se$_2$ films taken at different temperatures (4.2, 78 and 300 K) and PLE spectra taken at 78 K

It can be seen that the band has an asymmetric spectral shape with a longer tail towards lower energies. This band shifts to a higher energy with increasing temperature. The FWHM and shape of the band also changes upon increasing the temperature. The PL band become more symmetrical and its FWHM slightly increases when temperature rises from 4.2 to 300 K. Similar single bands and temperature effects were also found in the PL spectra of other CIGS samples (Fig. 4). In order to identify the origin of the broad bands the excitation power dependence of the PL bands has been analyzed. It was found that increased excitation intensity generates a significant high-energy shift of the bands (blue j-shift). The experiments show that j-shift has different values strongly depended on the chemical composition and structural quality of the CIGS films. Our experimental results may be consistently explained in the

framework of the model of fluctuating potentials in highly doped and compensated semiconductors developed by Shklovskii and Efros [10]. The amplitude of the potential fluctuations strongly depends on the defect concentration and degree of compensation which are governed by the excess of (Ga+In) over Cu [11,12]. This ratio determines the energy position of the band in PL spectra and j-shift magnitude.

The PLE spectra of Cu(In,Ga)Se$_2$ films were detected near the maxima of the corresponding broad bands (Fig. 4). As seen from PLE spectra the emission slightly grows reaching a maximum near the gap energy Eg and than slowly decreases forming tails. The PL and PLE spectra are overlapped due to the absorption which extends to the energies that are lower that the apparent band gap Eg (impurities tails). These experimental facts indicates that PLE spectra, in the case of highly doped and compensated semiconductors can be used only for an approximate determination of the corresponding band gap Eg in the material.

All investigated In2S3 thin film samples with different thickness (35 – 1000 nm) are characterized by high transmittance (85-90 %) in the long wavelength region (500–3000 nm) and a clear absorption edge position. Moreover, the XRD spectra of all samples exhibited a broad hump in the 2θ range of around 20º–40º, and this indicated that the all samples deposited at slightly various but relatively low temperatures are amorphous in nature. Our result of amorphous nature of the indium sulfide films thermally deposited at 490 - 515 K is consistent with the literature data [13,14]. The AES data indicated that the deposited films are constituted upon the main elements, indium and sulfur. The analysis showed that the film becomes slightly rich in indium starting from half of thickness of the film. Although near substrate regions of the sample exhibited a S/In ratio of about 1, which is sulfur deficient, it is also certain that standard In2S3 composition ratio of S/In=1.5 are detected near the film surface. This could be due to the presence of more than one phases in the films. Hence it can be predicted that the oxygen in the films is not only the surface oxidation, but presents as an impurity element. Also, certain ratio of the indium is expected to be present in the form of In2O3 and/or In(OH)x (which cannot be determined by the AES technique) [13].

The relation between the absorption coefficient (α) and incident photon energy hν can be written as α×hν = A (hν – Eg)m, were A is constant and m=1/2, 2 for direct and indirect allowed transitions respectively. The graphs of (α×hν)2 versus hν are found to lead straight lines over any part of the optical absorption spectra, thus supporting the interpretation of direct rather than the indirect band gap for all samples. The direct band for the film were determined and were found to be 1.96, ~2.3, 2.4 and 3.4 eV for samples with defined thickness 800, 300, 170 and 35 nm.

Usually, InS single crystals have an indirect band gap of about 1.9 eV, whereas the In2S3 phase has a direct band gap in the range of 2.0–2.3 eV. In the present

study, the thin film samples of different thickness exhibited an optical band gap varied of about 1.96 up to 3.4 eV. The experimental data obtained by optical absorption and AFM measurements is simulated with a microstructure model considering the nano-granules of various phases.

The results indicate that the elaborated In2S3 thin films might be suggested as low-cost buffer materials for achieving high-efficient thin film solar cells with CIGS absorber layers.

Thin film $Cu(In,Ga)Se_2$-based solar cells were fabricated according to a standard CIGS technology. The different steps of this process were the vacuum evaporation of thin In2S3 buffer layer (50-60 nm) the CIGS film absorber followed by transparent conductivity RF-sputtered ZnO window layer, and vacuum deposition of (Ni-Al) grid as the front contact. The typical current voltage parameters for various CIGS single cells (S = 0.56 cm^2) are taken under standard AM1.5 conditions. The better conversion efficiencies for the best solar cells on stainless steel foil were around 10.0 %. Flexible metallic foils with high surface roughness showed a decrease in electrical properties and efficiency.

The incorporation of Na can result in an improvement of the efficiency and reliability of CIGS thin film solar cells [15,16]. Thus, further improvements in cell performance are expected by incorporation of Na.

4. Conclusion

Polycrystalline $Cu(In,Ga)Se_2$ thin films were prepared by the selenization of metallic precursors in a controlled N_2/Se environment. It is found that the structural and optical properties of CIGS absorber layers are strongly depend on the growth condition, type of substrate and chemical composition. X-ray patterns showed preferred (112) structural orientation for all investigated CIGS film on different metallic foils (titanium, molybdenum, aluminum, stainless steel). SEM studies showed uniform and dense CIGS films with grain sizes of $1.0 - 2.5$ μm. For the first time PLE measurements were employed to determine the band gap energy of CIGS film on nontransparent metallic substrates. Correlations between the optical properties and microstructure of the thermal evaporated In2S3 thin films of various thickness have been detected. The direct band for the film were determined and were found to be 1.96, ~2.3, 2.4 and 3.4 eV for samples with defined thickness 800, 300, 170 and 35 nm.

The better conversion efficiencies for the best solar cells on stainless steel foil were around 10.0 %. Optimization of the Cu/(In+Ga) content in $Cu(In,Ga)Se_2$ films and the incorporation of Na is expected to improve physical parameters and produce solar cell devices with conversion efficiencies well above 12 %.

References

[1] S. Bailey, D. Flood, *Space photovoltaics*, Progress in Photovoltaics, 6 (1998) 1-14.

[2] A. Romeo, M. Terheggen, *Development of Thin-film Cu(In,Ga)Se2 and CdTe Solar Cells,* Prog. Photovolt: Res. Appl. 12(2004) 93–111.

[3] T. M. Razykov, *Solar photovoltaic electricity: Current status and future prospects,* Solar Energy, 85 (2011) 1580-1608.

[4] M. A. Green, K. Emyry, Y. Hishikawa, W. Warta, *Solar cell efficiency tables*, Progress in Photovoltaics, 42 (2013) 827–837.

[5] F. Kessler, D. Rudmann, *Technological aspects of flexible CIGS solar cells and modules,* Solar Energy, 77 (2004) 685- 695.

[6] K. Otte, L. Makhova, A. Braun, I. Konovalov, *Flexible Cu(In,Ga)Se2 thin-film solar cells for space application*, Thin Solid Films, 511 (2006) 613-622.

[7] H. Izadneshan, V. F. Gremenok, *Influence of Annealing on the Optical Parameters of In2S3 Thin Films Produced by Thermal Evaporation*, Journal of Applied Spectroscopy, 81 (2014) 293–296.

[8] E. P. Zaretskaya, V. F. Gremenok, I. A. Victorov, *Properties of CuInSe$_2$ Polycrystalline Thin Films Prepared by Selenization of Co-Sputtered Cu-In Alloys.* Solid State Phenomena, 80 (2001) 287-292.

[9] M. V. Yakushev, A. V. Mudryi, V. F. Gremenok, E. P. Zaretskaya, V. B. Zalesski, Y. Feofanov, R. W. Martin, *Influence of growth conditions on the structural quality of Cu(InGa)Se2 and CuInSe2 thin films,* Thin Solid Films, 451 (2004) 133-136.

[10] B. I. Shklovskii, A. L. Efros, Electronic Properties of Doped Semiconductors, Springer Verlag, Berlin. (1984), 124.

[11] I. Dirnstorfer, M. Wagner, D. M. Hofmann, M. D. Lampert, F. Karg, B. K. Meyer, *Characterization of CuIn(Ga)Se2 Thin Films,* Physics Status Solidi (a), 168 (1998), 163-175.

[12] J. Krustok, H. Collan, M. Yakushev, K. Hjelt, *The role of spatial potential fluctuations in the shape of the PL bands of multinary semiconductor compounds,* Physica Scripta, T79 (1999) 179-182.

[13] P. Pistor, R. Caballero, D. Hariskos, V. Izquierdo-Roca Wächter, *Quality and stability of compound indium sulphide as source material for buffer layers in Cu(In,Ga)Se2 solar cells,* Solar Energy Materials and Solar Cells, 93(2009) 148-152.

[14] H. Dittrich, A. Bieniok, U. Brendel, M. Grodzicki, *A new class of compound semiconductors for photovoltaic applications,* Thin Solid Films, 515 (2007) 5745-5750.

[15] D. Rudmann, M. Kaelin, F. J. Haug, *Effects of NaF coevaporation on structural properties of Cu(In,Ga)Se2 thin film,* Thin Solid Films, 431 (2003) 37-40.

[16] D. Rudmann, A. F. Cunha, M. Kaelin, F. Kurdesau, *Efficiency Enhancement of Cu(In,Ga)Se2 Solar Cells Fabricated on Flexible Polyimide Substrates using Alkali-Silicate Glass Thin Layers,* Applied Physics Letter, 84 (2004) 1129-1131.