

Changes in screen-printed ZnO/CuInSe₂ p-n junction before and after laser ablation

A. Ogurcovs, Vj. Gerbrederis, E. Tamanis, A. Gerbrederis

G. Libert's Innovative Microscopy Centre, Daugavpils University,
1 Parades Str., Daugavpils, LV-5401, LATVIA

E-mail: max.kovac@gmail.com

Abstract. In the experiments, ZnO and CuInSe₂ semiconductor powders were used (the latter produced by the high-temperature synthesis method). Microstructural properties of the powders were analyzed using X-Ray diffraction and SEM. The experimental ZnO/CuInSe₂ samples were prepared by the screen printing technique. The V–I measurements of the samples indicated the presence of a p-n junction in the ZnO/CuInSe₂ contact zone. The samples were exposed to artificial solar radiation, during which an exponential decay of photo-emf was observed. It was shown that the starting conductive properties of the p-n junction restores in ~ 15 min after the exposition. Laser ablation technique was applied to ZnO/CuInSe₂ p-n junction with purpose to improve its performance and quality. After several attempts, significant changes in electrical properties of samples was observed. Improvement of p-n junction can be achieved only at single attempt at certain amount of delivered energy. Further ablation attempt leads to degradation of p-n junction of samples.

1. Introduction

Chalcopyrite CuInSe₂ (CISE)-based materials are most promising for thin-film photovoltaic devices owing to their high absorption coefficient ($\alpha \sim 10^5/\text{cm}$), tunable bandgap (1.7-1 eV) material that is dependent on the composition and higher efficiency than other thin-film solar cells [1]. Various technical methods aimed at improving the performance and decreasing the production cost of CISE solar cell with single-crystal and thin-films CISE have been reported [2]. CISE absorber layers can be prepared using several procedures, such as sputtering [3], electro-plating deposition [4], evaporation [5], and printing techniques [6]. Despite the advantages offered by above mentioned methods, thin film semiconductors are not useful in devices without thermal annealing to form the desired semiconductor phase, to improve crystallinity, and to minimize structural and electronic defects [7]. The main purpose of this work is to verify if laser ablation (LA) is compatible with a damage-free processing of CISE compound and improvement of quality of p-n junction formed by ZnO/CuInSe₂ contact. Laser ablation is quite different from conventional furnace annealing (FA) and or rapid thermal annealing (RTA). The main advantage that laser ablation offers is selective heating of the sample. Some works [8] reporting attempts in processing CuInSe₂ using laser ablation with little or no success, however more work needs to be done in order to understand laser ablation of CuInSe₂ [9].

2. Experiment

For the experiments, ZnO and CuInSe₂ powders were taken. Using a laboratory grinding machine Retsch PM100, the average size of ZnO particles was reduced to 300 nm, and CuInSe₂ particles – to 2.5 μm . After the milling process, ZnO powder was annealed in a muffle furnace at 500°C for 120 min. CuInSe₂ was obtained by high-temperature synthesis. Initial components (Cu, In, Se) were put in the evacuated (air-less) quartz jar. The jar was slowly heated (20°C/hour) till 1000°C. The homogenous melt was obtained within 48 hours at 1000 °C, then the jar was slowly cooled (7°C/hour). The total time of CuInSe₂ synthesis took 240 hours. After a preliminary mechanical grinding, the



average grain size was reduced to 7 microns. As a surface active agent, polyvinyl butyral ($C_8H_{14}O_2$)_n was used. The paint for screen printing was prepared by mixing ZnO and ($C_8H_{14}O_2$)_n in the proportion of 97:3; the same proportion was applied for the CuInSe₂ paint. The glass substrates with 180 nm DC magnetron sputtered ITO layer were coated with a 3 μ m thin ($C_8H_{14}O_2$)_n + ZnO layer using the screen printing method. After drying the first layer, a 10 μ m layer of the same composition ($C_8H_{14}O_2$)_n + CuInSe₂ was covered onto the first layer. The prepared samples were dried for 20 min in muffle furnace at 70 °C. A 300 nm magnetron-sputtered cobalt layer was used as a back-contact. Each layer was coated with a 1mm shift relative to each other (in a sandwich structure) to prevent short-circuiting of the CuInSe₂ layer on the ITO layer. Laser ablation was performed by the scanning laser system "TruMARK 6000" in CW mode with wavelength $\lambda = 1060$ nm. Laser focus diameter was 50 μ m, distance between each track – 50 μ m, scanning speed – 450 mm/s. Laser radiation were directed through the glass and from the CuInSe₂ side (Fig 1.). Chemical and surface analysis was performed using SEM "Vega Tescan LMU" with "INCA x-ray microanalysis" attachment. A solar simulator "Oriel Sol2A" with a 140W lamp and multimeter "Picotest M3500A" were used in photoelectric studies of the samples before and after laser ablation.

3. Results and Discussion

Samples were processed from CuInSe₂ side with 0.5W of laser power (1% of maximum power); this led to melting of separate grains to larger areas (Figure 1). Irradiated surface is rather heterogeneous, containing multiple cracks and cavities. Total thickness of the CuInSe₂ layer was ~ 15 μ m, thickness of meltdown area is ~ 8 μ m, which has almost no noticeable effect on photovoltaic properties of the sample. An increase of laser power didn't affected thickness of the melting layer and led to the destruction of working properties of CuInSe₂ compound.

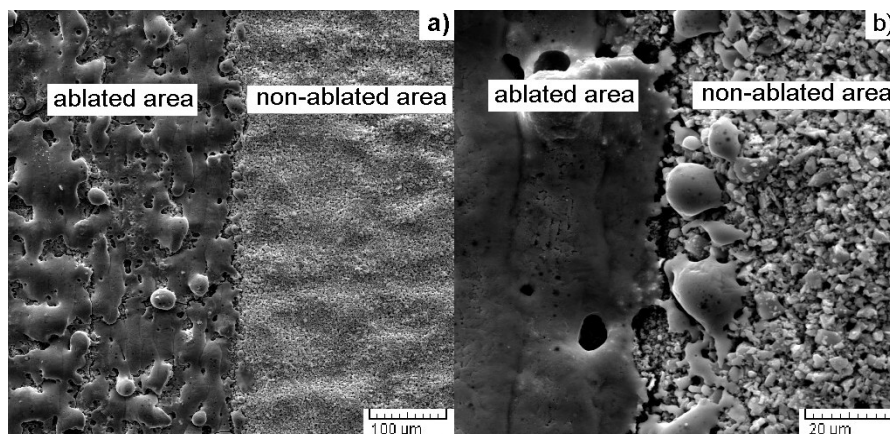


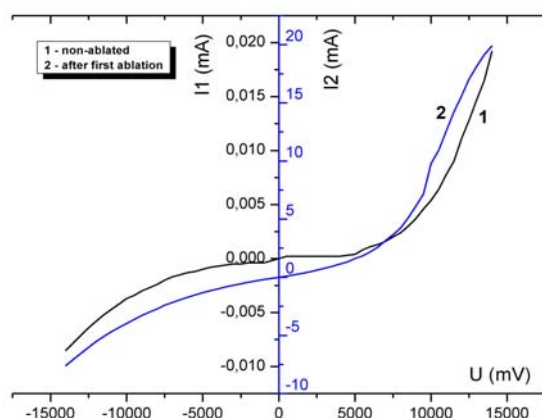
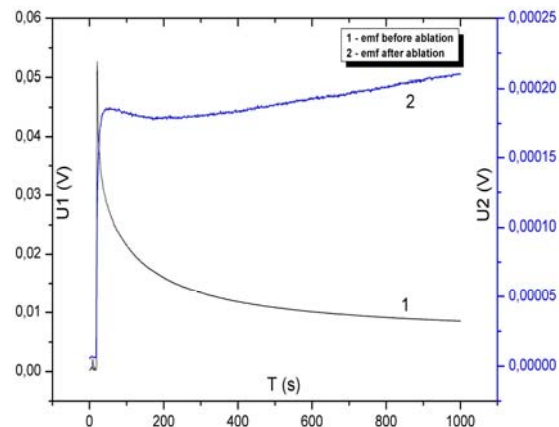
Figure 1. SEM images of the ablated and non-ablated CuInSe₂ areas.

Melting of CuInSe₂ grains without significant change in stoichiometry (Table 1), can be achieved by applying a certain amount of the laser radiation dose, going beyond these limits leads to irreversible changes in the structure of CuInSe₂, and loss of functional properties of the sample. Chemical analysis of an irradiated CuInSe₂ area indicates reduced level of Se, most likely, this is due to the evaporation of this substance as a result of the intense heat.

Table 1. Chemical analysis of the sample before and after irradiation

	Average atomic ratio %		
	Cu	Se	In
non-ablated area	26.644	48.651	24.705
ablated area	27.591	42.775	29.663

From above mentioned experiments, it can be concluded that irradiation from CuInSe₂ side is non-effective, therefore, an attempt of ablation of sample from ZnO side was made. During an irradiation of p-n junction from through ZnO layer, laser power was increased to 1W, due to insufficient transparency of ZnO layer. Sample treatment was carried out in one attempt with scanning laser beam on 2 cm² large surface area. Chemical analysis revealed no changes in the chemical composition and structure of ZnO, indicating the absence of absorption of laser radiation. Measurement results of the dark current-voltage characteristics of the sample before and after processing (through ZnO layer) are shown in Figure 2.

**Figure 2.** Dark voltage current curves of ZnO/CuInSe₂ p-n junction before and after ablation.**Figure 3.** Time base of the photo-emf level of the sample before ablation (curve 1) and after (curve 2).

After ablation, the quality of the current-voltage curve has improved significantly, but most importantly, the dark resistance of the p-n junction decreased by 2 orders of magnitude. This fact is apparently associated with improvement of contact between the layers of ZnO and CuInSe₂. Subsequent treatment of the same sample leads to irreversible degradation of the properties of the p-n junction. Destruction of p-n junction, presumably related to the formation of various phases based on the elements constituting CuInSe₂, such as CuSe₂, InSe₂, as well as Cu and In pure form, that shunts the p-n junction in the contact zone with ZnO. Comparative analysis of the photovoltaic properties of the sample before and after irradiation revealed significant changes in the dynamics of the photo-emf. Sample before ablation indicated an abrupt rise of photo-emf level to $V_{ph(max)} = 5.5E-3$ V, with followed exponential decay to $330E-6$ V within ~ 15 minutes (Fig.3. Curve 1). Completely different picture was observed after ablation of the sample. After sample illumination of an artificial solar spectrum, immediate rise of photo-emf level to $V_{ph} = 200E-6$ and subsequent slow rise to $V_{ph} = 330E-6$ was observed (Fig.3. Curve 2). Such dynamics of photo-emf before irradiation, presumably related to the large number of defects in the contact zone of ZnO/CuInSe₂, which negates the charge separation

in the potential barrier. An interesting fact is that the final value of the photo-emf reaches the same value $\sim 330\text{E-6 V}$. The observed decay of V_{ph} might be a result of a decrease in the height of the potential barrier under the influence of solar radiation or formation of the charge carrier recombination centers. The potential barrier's height can decrease with Fermi's level in CuInSe_2 changing due to generation of the electrically active point defects, with the donor and acceptor levels created. If the generated defects are the charge carrier recombination centers, this will lead to decrease in the photo-emf level because of a reduced (under direct sunlight during V_{ph} measurements) stationary stream of the excited charge carriers. In this case, most likely, changes in the properties of the potential barrier are caused by generation of defects in the area adjacent to ZnO/CuInSe_2 contact [10]. In turn, such generation might be due to flaws in the CuInSe_2 synthesis process, or in the mechanical milling of starting materials followed by residual stress in the crystalline lattice of experimental materials.

4. Conclusion

Properly chosen laser parameters can significantly improve properties of the p-n junction in the contact ZnO/CuInSe_2 zone. Quality improvement of p-n junction is possible only at a certain limits of laser radiation, irradiation beyond these limits leads to irreversible degradation of the p-n junction. Recrystallization of CuInSe_2 causes annealing of the large amount of defects that positively affects the photovoltaic properties of samples. This method has prospects of use in the production because of its cheapness and simplicity.

5. Acknowledgements

This study was supported by ESF project: Nr.2013/0029/1DP/1.1.1.2/13/APIA/VIAA/029.

6. References

- [1] Wyatt K Metzger Ingrid L Repins & Miguel A Contreras 2008 Long lifetimes in high efficiency Cu(In,Ga)Se_2 solar cells *Appl. Phys. Lett.* **93** 022110
- [2] Tatsuo Fukano Shin Tajima and Tadayoshi Ito 2013 Enhancement of Conversion Efficiency of $\text{Cu}_2\text{ZnSnS}_4$ Thin Film Solar Cells by Improvement of Sulfurization Conditions *Appl. Phys. Express* **6** 062301
- [3] J A Thornton T C Lommasson H Talieh B H Tseng 1988 Reactive sputtered CuInSe_2 *Solar Cells* **24** P 1-9
- [4] J F Guillenmoles A Lusson P Cowache S Massaccesi J Vedel D Lincot 1994 Recrystallization of electrodeposited copper indium diselenide thin films in an atmosphere of elemental selenium *Adv. Mater.* **6** 376
- [5] A M Gabor J R Tuttle D S Albin M A Contreras R Noufi A M Hermann 1994 High-efficiency $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ solar cells made from $(\text{In}_x\text{Ga}_{1-x})_2\text{Se}_3$ precursor films *Appl. Phys. Lett.* **65** 198
- [6] S A AL Kuhaimi S Bahammam 1990 All Screen-Printed CdS/CuInSe_2 Solar Cells *Jpn. J. Appl. Phys.* **29** 1499
- [7] Ashish Bhatia Phillip Dale Matt Nowell Michael Scarpulla 2010 Pulsed Laser Processing of Electrodeposited CuInSe_2 Photovoltaic Absorber Thin Films *MRS Proceedings* **1268**
- [8] Joliet M C Antoniadis C Andrew R and Laude L D 1985 Laser induced synthesis of thin CuInSe_2 films *Appl. Phys. Lett.* **46**(3) 266-267
- [9] Ashish Bhatia Helen Meadows Alexandre Crossay Phillip J Dale Michael A Scarpulla 2012 Pulsed and continuous wave solid phase laser annealing of electrodeposited CuInSe_2 thin films *SPIE Proceedings* **8473**
- [10] D Seghier, H P Gislason. Opto-electrical characterization of electrically active point defects in $\text{Al}_x\text{Ga}_{1-x}$, 2008 *J. Phys. D: Appl. Phys.* **41** 095109.