Lasers in Manufacturing Conference 2015

Picosecond laser modification of thin-film CIGS solar cell absorber layer for P2 micro-welding process

Paulius Gečys* , Andrius Žemaitis, Gediminas Račiukaitis

Center for Physical Sciences and Technology, Savanoriu Ave. 231, LT-02300, Vilnius, Lithuania

Abstract

The high efficiency of a large thin-film solar cell can be maintained if cells are divided into smaller segments interconnected in series in order to reduce photocurrent and resistance losses. Laser patterning is a promising tool for monolithic interconnect formation, although cell deposition processes have to be interrupted for the laser scribing to be applied. These issues are especially important when going to the mass role-to-role production. P2 micro-welding process can be made after the front-contact layer deposition replacing the standard P2 scribing process which interrupts absorber and window layers deposition. After being affected by laser radiation CIGS compound melts and recrystallizes becoming a metallic compound which makes the interconnection between two adjacent cells. The metallic compound can be made due to the formation of Cu-rich areas and diffusion of TCO to the CIGS layer in the laser affected zone. In this work, we used picosecond laser to form molten lines in CIGS layer. Energy dispersion spectroscopy analysis together with Raman spectroscopy was applied to investigate the composition of chemical elements and crystal structural changes along various laser scribes made in CIGS absorber layer. Electrical characterization of the CIGS mini-cells after laser modification revealed changes in the cell parallel resistance indicating changes of the CIGS conductivity in the laser modified areas. Our investigations showed the potential of the picosecond laser in local modification process of the CIGS material which could be applied to the P2 welding process.

Keywords: micro-welding, CIGS, solar cell, picosecond laser, EDS, Raman spectra

1. Introduction

Today the thin-film based CIGS solar cell technology became even more attractive for producers and end-users. CIGS is one of the best thin-film technologies that can compete with silicon-based solar cells today. At the moment, CIGS is one of the most promising technologies for its flexibility, excellent power to weight ratio, and high conversion efficiency. Usually, record-breaking efficiencies are set on small-scale devices in the laboratories, but, unfortunately, mass production of these devices is still facing serious challenges in maintaining the solar cell efficiency over large areas. Innovative technological solutions in the manufacturing process are required moving towards TW-scale production.

The high efficiency of a large thin-film solar cell can be maintained if cells are divided into smaller segments interconnected in series in order to reduce photocurrent and resistance losses. Laser patterning is a promising tool for monolithic interconnect formation, although cell deposition processes have to be interrupted for the laser scribing to by applied. These issues are especially important when going to the mass role-to-role production. P2 micro-welding process can be made after the front-contact layer deposition replacing the standard P2 scribing process which interrupts absorber and window layers deposition (see Fig. 1). After being affected by laser radiation CIGS compound melts and recrystallizes becoming a metallic compound which makes the interconnection between two adjacent cells. The metallic compound can be made due to partial evaporation of selenium and formation of Cu-rich areas and diffusion of TCO to the CIGS layer in the laser affected zone (Westin et al., 2008 ,Westin et al., 2011).

* Corresponding author. Tel.: +370-5-266-1640; fax: +370-5-260-2317.
E-mail address: p.gecys@ftmc.lt .

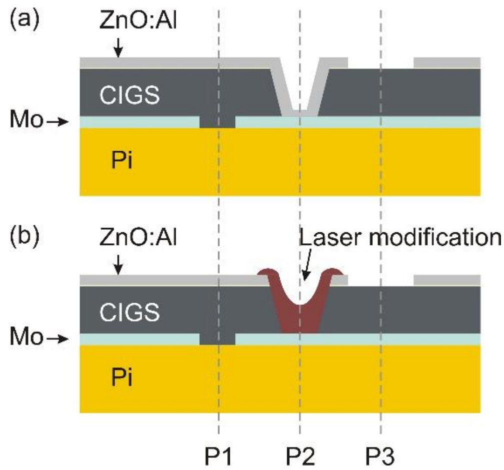


Fig. 1. (a) Conventional all laser scribed series interconnect in CIGS solar cell; (b) the series interconnect is formed via P2 micro-weld.

2. Experimental

In this work, we used Atlantic series picosecond laser from Ekspla to form molten lines in CIGS layer. Typical pulse duration was 13 ps at the 532 nm wavelength with a maximum pulse repetition rate of 1000 kHz. The experimental setup included the laser, beam expander and galvanometer scanner (ScanLab) with an 80 mm focusing objective for 532 nm wavelength. The minimum diffraction-limited spot size at the focus position was 10 µm. The spot size was varied during the experiments by shifting the samples out of the focal position. We were concentrating on the P2 micro-weld process to modify the complete stack of CIGS solar cell structure. Multilayer CIGS solar cell structure from Solarion AG with 350 nm Al:ZnO top-contact was used in scribing experiments. The cell consisted of 10-50 nm sputtered intrinsic ZnO and chemical-bath-deposited CdS buffer layers, 2 µm thermal co-evaporated $Cu(In,Ga)Se_2$ absorber layer, 0.5 µm sputtered molybdenum back-contact and 25 µm polyimide substrate. The P2 micro-weld conductivity testing included performing laser scribes on the sample between the mini-cell contact grid and measurement of the cell parallel conductivity. On-line parallel resistance monitoring during the scribing process was evaluated by applying the 4 point I-V measurements (see Fig. 2). Laser affected areas were investigated with SEM together with EDS spectrometer. Additional Raman spectroscopy measurements were also applied to investigate structural changes of the laser affected CGS material.

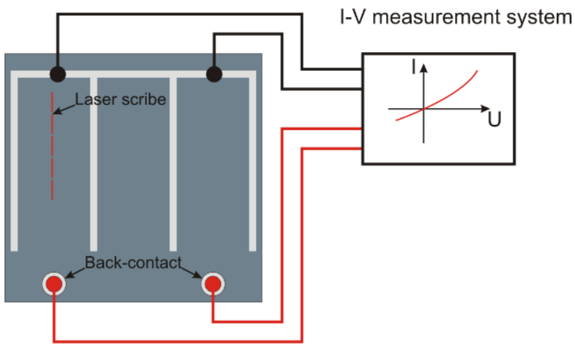
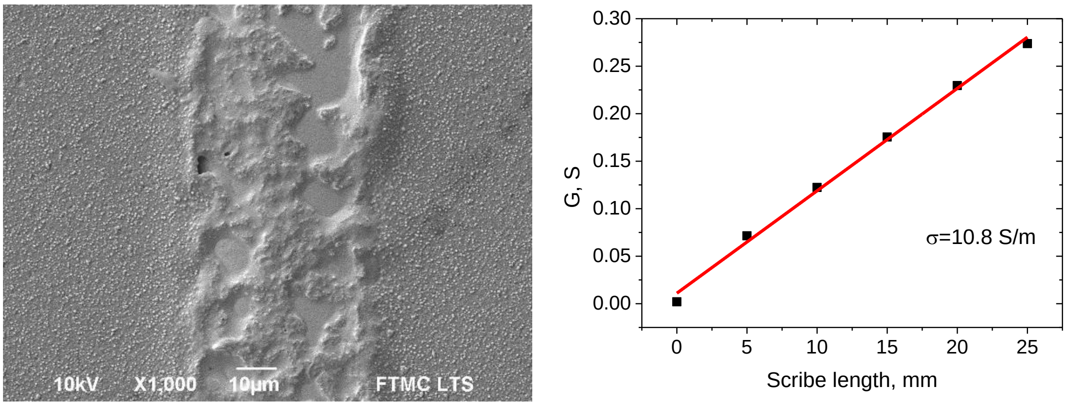


Fig. 2. Electrical measurement setup.

3. Results

3.1. P2 micro-weld formation

Series of tests were performed to modify the CIGS layer of complete solar cell structure. The laser power, pulse overlap and spot size were varied during the tests. The laser processing window was selected to obtain P2 weld without damaging the molybdenum back-contact. Scribe specific conductivity measurements were also applied to the selected laser welding regimes. Typical SEM image of the P2 micro-weld is shown in the Fig. 3.



(a) (b)

Fig. 3. (a) SEM image of P2 micro-weld in full CIGS structure, 0.1 J/cm^2, 100 mm/s; (b) scribe specific conductivity measurement.

Melting of CIGS layer was observed in the P2 welded channel, although the molybdenum back-contact was not damaged during the laser process. The scribe conductivity measurements were applied on the completely functional mini-cell (see Fig. 3 b). The typical P2 scribe conductivity reported in the literature is ranging from 15 to 0.1 Ω-cm (Westin et al., 2008 ,Pellegrino et al., 2010 ,Kessler et al., 1996 ,Schüle et al., 2013 ,Yoon et al., 2015 ,Ermer et al., 1993 ,Johansson et al., 2007). Our reported P2 micro-weld specific conductivity was in the range 10.8 S/m or 9.3 Ω-cm, which is acceptable for monolithic interconnection of the adjacent cells.

3.2. Raman analysis

CIGS is a complex multi-component compound, and laser-induced fast heating, melting and recrystallization of the material can lead to the secondary phase formation and structural disorders near the ablation area. These laser-induced modifications can result in significant changes of the absorber layer conductivity. Although, it is rather a positive effect in case of P2 welding. Raman spectroscopy is a useful tool to track material structural changes after the laser modification. Therefore, this technique was introduced to investigate the P2 micro-weld channels. Typical Raman spectra of the CIGS is shown in the Fig. 4. The main peak in the Raman spectra is the A_1 vibration line of $CuInSe_2$ at 174 cm^{-1}, with a shift to longer wavenumbers for CIGS (Chuan-Ming et al., 2004). A broad line in the range of 210-230 cm^{-1} is a combined intrinsic vibration B_2/E of CIGS (Wang et al., 2008). After laser processing, the decrease of the main CIGS peak at 174 cm^{-1} with the increasing intensity at 240 cm^{-1} was observed. This indicated the generation of $CuGaSe_2$ (CGSe) phase showing a peak at 240 cm^{-1} in Raman spectra (Rincón and Ramírez, 1992 ,Li et al., 2012). Electrical conductivity of $CuGaSe_2$ reported in literature was higher than CIGS (Kodigala, 2010). Therefore, the formation of CGSe phase could significantly increase the specific conductivity of the laser P2 micro-weld.

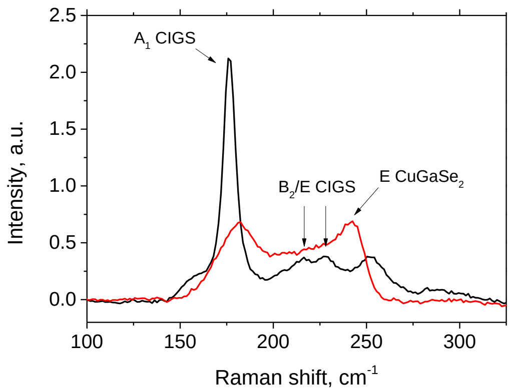
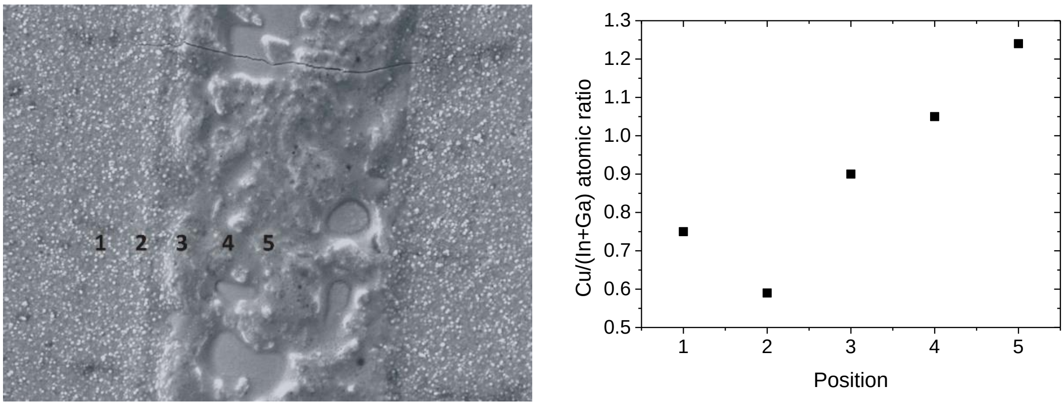


Fig. 4. Raman spectra of CIGS structure (black line) and laser modified P2 micro-weld area (red line).

3.3. EDS analysis

The electrical conductivity of CIGS absorber layer can be altered in the range of 10^6 Ω-cm by adjusting the Cu/(In+Ga) element atomic ratios from 0.7 to 1.2 (Kwon et al., 2001 ,Xue et al., 2008). Therefore, changes in material conductivity can be detected by tracking of Cu, In and Ga element distributions in laser modified areas. For this, EDS analysis of the

P2 micro-weld channels was performed. The average Cu/(In+Ga) ratio for laser unaffected CIGS was 0.75, which is typical for high-performance CIGS devices. The measurement area and Cu/(In+Ga) distribution is shown in the Fig. 5. The Cu/(In+Ga) ratio tends to increase starting from the edge of the scribe with a maximum value of 1.24 at the center of the channel. That confirms the formation of the Cu-rich metallic compound with significantly different electrical properties which contribute to increasing of the P2 micro-weld specific conductivity.



(a) (b)

Fig. 5 (a) EDS spectra measurement positions near the P2 micro-weld; (b) Cu/(In+Ga) ratios in the measured positions.

4. Conclusions

It was possible to control the picosecond laser energy deposition to the thin-film layer in order to modify the CIGS absorber material. The P2 micro-weld channel showed a specific conductivity of 9.3 Ω-cm which acceptable for the cell serial interconnection. Raman spectroscopy investigation of the laser affected area showed an increase of the CIGS material structural disorder and formation of the CGSe phase. The EDS analysis showed composition changes in laser modified P2 channel. The Cu/(In+Ga) ratio tends to increase in the center of the P2 micro-weld channel. Formation of Cu-rich CIGSe and CGSe phases in the laser processed P2 scribe channel resulted in significant changes of the material electric conductivity.

Acknowledgements

The research leading to these results was partially funded by the European Union FP7 Programme under grant agreement No 609355 (APPOLO). We acknowledge our thanks to Solarion AG, Germany, for kind support with the samples.

References

Westin, P. O., Zimmermann, U. and Edoff, M., 2008. Laser patterning of P2 interconnect via in thin-film CIGS PV modules, Solar Energy Materials & Solar Cells 92, p. 1230-1235.

Westin, P. O., Zimmermann, U., Ruth, M. and Edoff, M., 2011. Next generation interconnective laser patterning of CIGS thin film modules, Solar Energy Materials & Solar Cells 95, p. 1062-1068.

Pellegrino, S., Scorticati, D., Caldironi, M. and Acciarri, M., 2010, "New Procedure for P2 Laser Scribe Manufacturing in CIGS Solar Modules," 25th European Photovoltaic Solar Energy Conference and Exhibition. Valencia, Spain, paper #3654 - 3656.

Kessler, J., Wiedeman, S., Russell, L., Fogleboch, J., Skibo, S., Arya, R. and Carlson, D., 1996, "Cu(In,Ga)Se_2 based submodule process robustness," Photovoltaic Specialists Conference. Newtown, PA USA, paper #813-816.

Schüle, M., Schultz, C., Juzumas, V., Stelmaszczyk, K., Weizman, M., Wolf, C., Papathanasiou, N., Rau, B., Schlatmann, R., Quaschning, V., Stegemann, B. and Fink, F., 2013, "Laser patterning of CIGSe solar cells using nano- and picosecond pulses-possibilities and challenges " 28th European Photovoltaic Solar Energy Conference and Exhibition. Paris, France, paper #2302 - 2306.

Yoon, J.-H., Park, J.-K., Kim, W. M., Lee, J., Pak, H. and Jeong, J.-h., 2015. Characterization of efficiency-limiting resistance losses in monolithically integrated Cu(In,Ga)Se_2 solar modules, Scientific Reports 5, p. 7690.

Ermer, J., Gay, R., Pier, D. and Tarrant, D., 1993. Challenges and progress in the scale up of $CuInSe_2$ thin film photovoltaic technology, Journal of Vacuum Science & Technology A 11, p. 1888-1895.

Johansson, J., Zimmermann, U. and Edoff, M., 2007, "Modelling and optimization of cigs modules," 22nd European Photovoltaic Solar Energy Conference. Milan, Italy, paper #1922-1925.

Chuan-Ming, X., Xiao-Liang, X., Jun, X., Xiao-Jie, Y., Jian, Z., Ning, K., Wen-Hao, H. and Hong-Tu, L., 2004. Composition dependence of the Raman A 1 mode and additional mode in tetragonal Cu–In–Se thin films, Semiconductor Science and Technology 19, p. 1201.

Wang, D., Wan, L., Bai, Z. and Cao, Y., 2008. Mixed phases in p-type $CuInSe_2$ thin films detected by using micro-Raman scattering spectroscopy, Applied Physics Letters 92, p. 211912.

Rincón, C. and Ramírez, F. J., 1992. Lattice vibrations of $CuInSe_2$ and $CuGaSe_2$ by Raman microspectrometry, Journal of Applied Physics 72, p. 4321-4324.
Li, M., Zheng, M., Zhou, T., Li, C., Ma, L. and Shen, W., 2012. Fabrication and centeracterization of ordered $CuIn_{(1-x)}Ga_xSe_2$ nanopore films via template-based electrodeposition, Nanoscale Research Letters 7, p. 675.
Kodigala, S. R. 2010. Electrical Properties of I–III–VI2 Compounds, in "*Thin Films and Nanostructures"*, Kodigala S. R., Editor. Academic Press, Amsterdam, p. 319-391.
Kwon, S. H., Lee, D. Y. and Ahn, B. T., 2001. Characterization of $Cu(In_{1-x}Ga_x)Se_2$ Films Prepared by Three-Stage Coevaporation and Their Application to CIGS Solar Cells for a 14.48 % Effciency, Journal of the Korean Physical Society 39, p. 655-660.
Xue, Y.-m., Yang, B.-h., Qu, C.-q., Zhang, L., Xu, C.-m. and Sun, Y., 2008. Structural and electrical properties of co-evaporated In, Garich CIGS thin films, Optoelectronics letters 4, p. 437-439.