Arch. Metall. Mater., Vol. 61 (2016), No 4, p. 1953–1956

DOI: 10.1515/amm-2016-0314

A.M. ELNAGGAR*,** A. ALBASSAM*, K. OŹGA***,#, J. JĘDRYKA***, M. SZOTA****, G. MYRONCHUK*****

PHOTOINDUCED OPERATION BY ABSORPTION OF THE CHALCOGENIDE NANOCRYSTALLITE CONTAINING SOLAR CELLS

It is shown that for the solar cells containing chalcogenide nanocrystallites using external laser light, one can achieve some enhancement of the photovoltaic efficiency. Photoinduced treatment was carried out using two beams of splitted Er: glass laser operating at 1.54 μm. The light of the laser was incident at different angles and the angles between the beams also were varied. Also, the studies of nanocomposite effective structures have shown enhancement of effective nanocrystalline sizes during the laser treatment. Nanocrystallites of $CuInS_2$ and $CuZnSnS_4$ (CZTS) were used as chalcogenide materials. The optimization of the laser beam intensities and nanoparticle sizes were explored.

Keywords: photovoltaic cell materials, chalcogenide layers, photoinduced absorption, laser treatment, nanocrystlalline treatment.

1. Introduction

At the moment solar cells based ion chalcogenides present a huge interest for the further search of promising photovoltaic's devices [1, 2]. Among a couple of materials more interesting seem to be $CuInS_2$ [3, 4] and Cu_2ZnSnS_4 films [5, 6]. The maximally archived photovoltaic efficiency possessed magnitude up to 16 %. In order to enhance their photovoltaic (PV) efficiency there were applied different methods, i.e. light trapping in intra thin plasmonic cells [7], using of high efficient earth-abundant liquid-processed absorbers [8] and $CuInS_2$/polyaniline base heterojunction [9].

The use of the chalcogenides allows taking advantages of high electron-phonon anharmonicities which may favour enhanced photopolarization and related absorption. Additionally the existence of nanocrystallites with sizes within 20 nm…100 nm simulates formation of the local nanotraps enhancing the light absorption. The coexistence of disordered amorphous like and nanocrystallites is a crucial factor defining the efficiency of the light absorption. All the former efforts were prevailingly directed on sophisticated modifications of chemical content, using of different chemical deposition methods, first of all electrochemical ones, however possibility of external coherent laser light was almost absent.

At the same time the external laser light in the chalcogenide may cause additional polarization of the medium [10, 11]. The process of the formation of the internal dc-electric field is defined by its high polarizabilities and possible formation of the multi-wavelengths excitations which form enhanced ground state dipole moments. Additionally the nanocrystallites sizes favour enhanced two-photon absorption [12].

Particular interest presents a formation of the gratings which may induce dc-electric field favoring enhanced dipole moments. For the case of the nanocrystallites due to flattering of the bands [13] one can expect an occurrence of some additional reserves for the so desirable optical absorption.

All the mentioned approaches required a sophisticated technology and time consuming technology. In the present work it is proposed to use the possible treatment of active chalcogenide layers by external laser waves in order to enhance the effective absorption that plays principal role in the PV efficiency.

2. Materials and methods

The titled films were synthesized by electrodeposited methods similar to the described in the ref. [14, 15]. As a chalcogenide materials were used nanocrystallites of $CuInS_2$ and $CuZnSnS_4$ (CZTS) which possess promising optically induced properties [16, 17]. Their general architecture is presented in the Fig. 1. Using TEM methods performed by JEOL 2010 with resolution about 4 nm allows separating the films by the sizes within the 15 nm…80 nm. The different sizes were formed due to different times of electro-depositions. We have performed studies of photoinduced absorption under the external excitations by 25 ns Er: glass lasers at 1540 nm with time duration about 20 ns and frequency repetition about 10 Hz. The fundamental laser beam of diameter varying within the 0.5…4 mm was split by beam splitter and additionally

* RESEARCH CHAIR OF EXPLOITATION OF RENEWABLE ENERGY APPLICATIONS IN SAUDI ARABIA, PHYSICS AND ASTRONOMY, KING SAUD UNIVERSITY, P.O. BOX 2455, RIYADH 11451, SAUDI ARABIA

** PHYSICS DEPARTMENT, FACULTY OF SCIENCE, AIN SHAMS UNIVERSITY, 11566 ABASSIA, CAIRO, EGYPT

*** CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, INSTITUTE OF ELECTRONIC AND CONTROL SYSTEM, 17 ARMII KRAJOWEJ AV., 42-200 CZESTOCHOWA, POLAND

**** CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, INSTITUTE OF MATERIAL SCIENCE ENGINEERING, 19 ARMII KRAJOWEJ AV., 42-200 CZESTOCHOWA, POLAND

***** DEPARTMENT OF SOLID STATE PHYSICS, EASTERN EUROPEAN NATIONAL UNIVERSITY, 13 VOLI AVE., 43025 LUTSK, UKRAINE

Corresponding author: cate.ozga@wp.pl

the angle between the beams also was varied. The control of photoinduced absorption was performed using Ocean Optics fibber spectrometer with spectral resolution about 1 nm. The monitoring of the nanocrystallites sizes was performed by TEM JEOL 2010 with size resolution 0.4 nm. The detection of light scattering was performed by spherical quantum meter in the spectral range from 300 nm to 800 nm. The undesirable parasitic fluorescence was cut by spectrophotometer with spectral resolution about 1 nm.

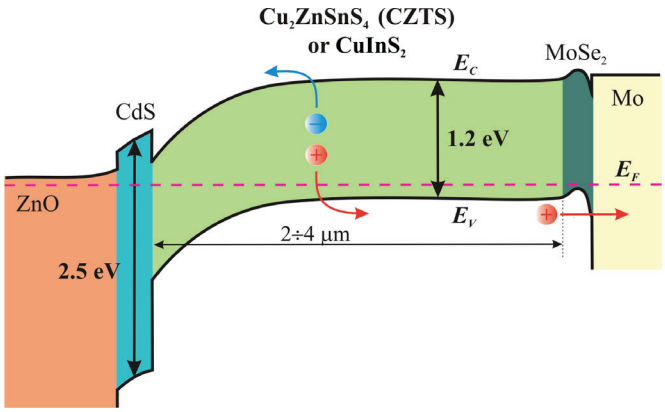

Fig. 1. General architecture of PV

3. Results and discussion

We will concentrate our attention on changes of absorption under influence of external laser light from Er: glass lasers at different incident angles with respect to surfaces as well as to the angle between the laser beams. The process of photoinduced absorption measurements was performed during the laser treatment due to frequency repetition 1 Hz. The pulsed laser beams with frequency repetition about 1 Hz allowed to gather a statistics in 30…50 points of the titled samples. Fig. 2 represents the kinetics features of the photoinduced (PI) absorption obtained during the long photo-treatment of the $CuInS_2$ and CZTS nanoparticle containing layers with thickness varying within 1…3 μm. From this figure one can see, that the PI absorption lines form the space quasi-grating which indicates a possible photoinduced polarization of the titled materials and internal coherent interference. Moreover, different colours indicate the different degree of the corresponding PI magnitudes. It is a substantial difference between the $CuInS_2$ and CZTS chalcogenide layers. For the $CuInS_2$ nanocomposites the process is slower and the absorption ranges are smoother. It may reflect different local ground state dipole moments for the titled compounds. For example in the case of the CSTZ nanocomposites the principal role plays Sn-S_4 clusters possessing a huge number of covalence bonds. For this reason we have performed DFT simulations of the principal structural clusters (see Fig. 3) using a method described in the ref. 18. Such covalence causes more quick reaction on the external polarized field. In the case of $CuInS_2$ film, the corresponding bonds are more ionic which cause some local polarizations.

Another important factor is a change in the effective sizes of the nanocrystallites. Fig. 4 there presents the effective transformation of the average diameters grains after using the coherent laser treatment. Due to effects of local electrostatic field stimulated by laser light, effects of electrostriction, and photothermal effects some higher clusters are occurred. They may favour additional absorption which is so desirable in the PV cells.

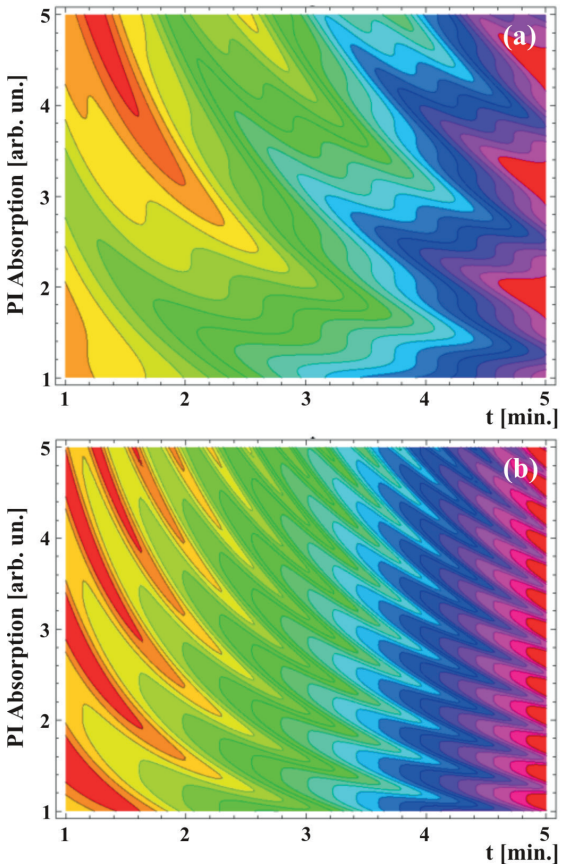

Fig. 2. Temporary kinetics of photoinduced absorption under the influence of laser illumination for the (a) $CuInS_2$ and (b) CZTS nanofilms

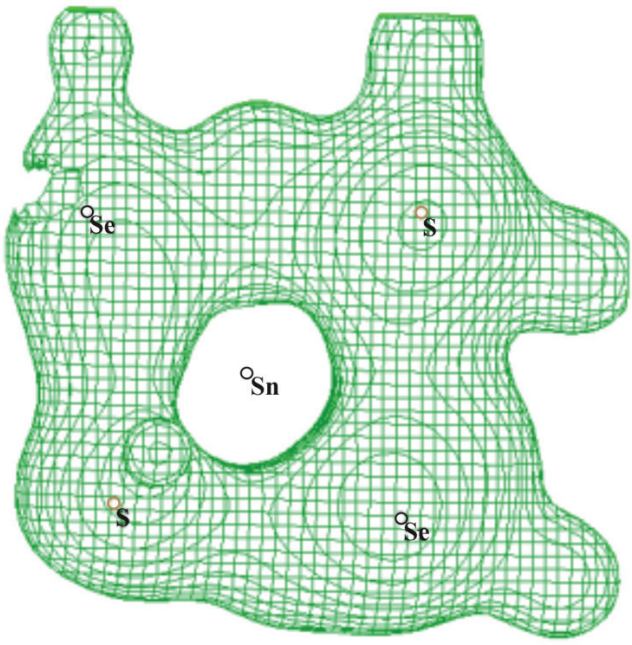

Fig. 3. Space charge density distribution for principal structural fragments during S-Se substitution

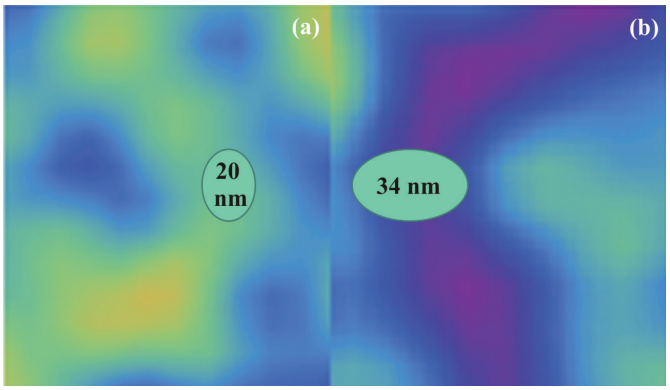

Fig. 4. TEM images of principal changes of effective nanocrystalline sizes before (a) and after (b) coherent laser treatment

The layers are very sensitive to the nanoparticles sizes and external laser beam power density. Therefore, we have performed measurements of PV efficiency versus different laser power densities and different particle sizes for the two titled chalcogenide nanolayers, their results are presented in the Figs. 5 and 6. From these figures one can clearly see that for the CZTS nanolayer, these values correspond to 45 nm nanoparticle sizes at photoinduced power density about 152 mJ/cm^2 and for the $CuInS_2$ nanofilms correspond to 65 nm at 125 mJ/cm^2. The mentioned dependences show substantially asymmetric behaviour which reflects substantial inclusion of trap levels. These results may explain different power densities of the propagating absorption as shown in the Fig. 2. Relative changes of the absorption achieved up to 7 %.

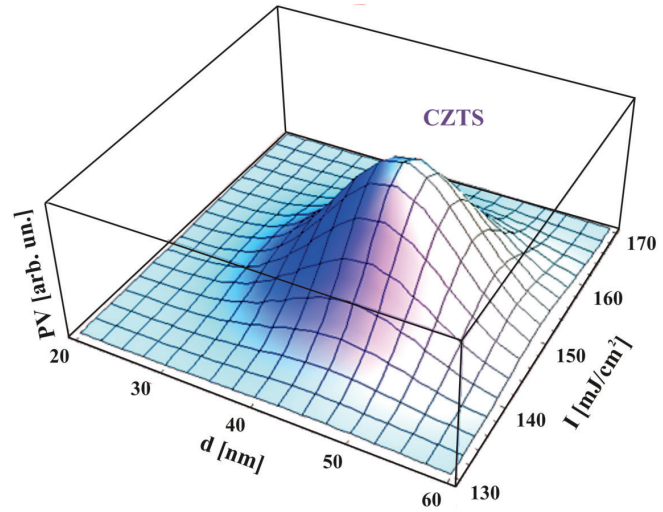

Fig. 5. Laser induced dependence for the PV efficiency for the CZTS nanofilms

The obtained results are very sensitive to the angle of the treatment with respect to the incident light. Fig. 7 shows angular dependences of PV efficiency for the CZTS compounds. These results obtained in the range from 20° to 50° for the angles between two beams of splitted Er: glass laser and for the three different angles of incident light of laser such as 30°, 33° and 40°. From Fig. 7, one can clearly see that the maximum of photovoltaic efficiency exists in the angular ranges 30-35°. The maximum PV efficiency was achieved for the optimal angle incident light of laser which is about 33 degree. Increase or decrease of incident angle laser beam value on the surfaces nanolayers leads to less PV magnitudes. One can conclude that the incident angle plays crucial role in the PV efficiencies. However also the angles between the beams show some influence.

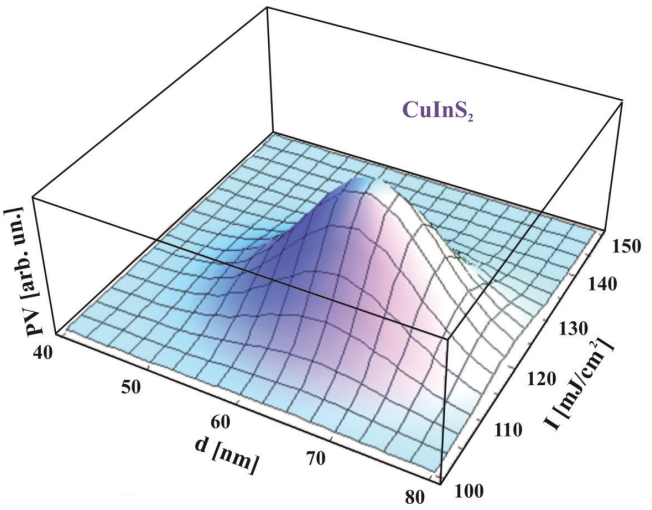

Fig. 6. Laser induced dependence for the PV efficiency for the $CuInS_2$ nanofilms

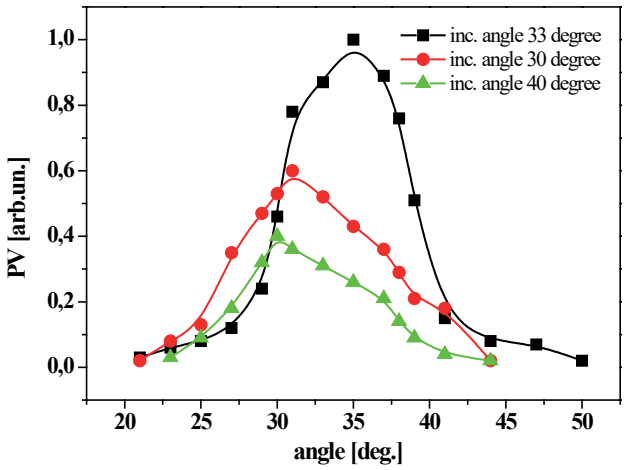

Fig. 7. Angular dependence of PV efficiency for CZTS nanocomposites

4. Conclusions

For two electrodeposited active layers of $CuInS_2$ and CuZnSnS4 (CZTS), we have demonstrated the possibility of the photovoltaic efficiency enhancement under influence of external laser light. The PV effect is caused by enhancement of effective absorption. This reflects the increase of photopolarization as well as effective changes of the grain sizes for the CZTS nanocomposites, these values correspond to 45 nm at photoinduced power density about 152 mJ/cm^2 and for the $CuInS_2$ nanolayer correspond to 65 nm at 125 mJ/cm^2. The maximally archived relative changes of absorption were up to 7 %. Principal role of the geometry of illumination may vary the observed parameters.

Acknowledgements

The project was financially supported by King Saud University, Vice Deanship of research chairs.

REFERENCES

[1] P.K. Sarswat, M.L. Free, Demonstration of a sol-gel synthesized bifacial CZTS photoelectrochemical cell, Phys. Status Solidi A **208** (2), 2861–2864 (2011).

[2] H. Cherfouh, T. Chari, A. Guermoune, M. Siaj, B. Marsan, Preparation and characterization of a new $CuInS_2$/graphene composite electrode, for application in electrochemical solar cells, in: Proceedings of the 219th Electrochemical Society (ECS) Meeting, 1870, Curran Associates, New Jersey 2011.

[3] N.A. Zeenath, P.K. V. Pillai, K. Bindu, M. Lakshmy, K.P. Vijayakumar, Study of trap levels by electrical techniques in p-type $CuInSe_2$ thin films prepared using chemical bath deposition, J. Mater. Sci.**35** (10), 2619–2624 (2000).

[4] S. Ebrahim, I. Morsi, M. Soliman, M. Elsharkawi, A. Elzaem, Preparation and characterization of chalcopyrite compound for thin film solar cells, Alexandria Engineering Journal **50** (1), 35–42 (2011).

[5] P.K. Sarswat, M.L. Free, An evaluation of depletion layer photoactivity in Cu_2ZnSnS_4 thin film, Thin Solid Films 520 (13), 4422–4426 (2012).

[6] N.M. Shinde, D.P. Dubal, D.S. Dhawale, C. D. Lokhande, J.H. Kim, J.H. Moon, Room temperature novel chemical synthesis of Cu_2ZnSnS_4 (CZTS) absorbing layer for photovoltaic application, Mater. Res. Bull. **47** (2), 302–307 (2012).

[7] V.E. Ferry, M.A. Verschuuren, H.B.T. Li et al., Light trapping in ultrathin plasmonic solar cells, Opt. Express **18** (13), A237–A245, (2010).

[8] T.K. Todorov, K.B. Reuter, D.B. Mitzi, High-efficiency solar cell with earth-abundant liquid-processed absorber, Adv. Mater. **22** (20), E156–E159 (2010).

[9] S. Ebrahim, I. Morsi, M.M. Soliman, A novel $CuInS_2$/polyaniline base heterojunction solar cell, in: Proceedings of the International Conference on Control Automation and Systems (ICCAS '10), 366–369, IEEE, Gyeonggi-Do 2010.

[10] I.V. Kityk. IR-stimulated second harmonic generation in Sb_2Te_2Se-BaF_2-$PbCl_2$ glasses, J. Mod. Optic 51, 1179–1189 (2004).

[11] I.V. Kityk. IR-induced second harmonic generation in Sb_2Te_3-BaF_2-$PbCl_2$ glasses, J. Phys. Chem. B **107**, 10083–10087 (2003).

[12] A. Majchrowski, I.V. Kityk, J. Ebothe, Influence of YAB: Cr^{3+} nanocrystallite sizes on two-photon absorption of YAB: Cr^{3+}, Phys. Status Solidi B **241**, 3047–3055 (2004).

[13] I.V. Kityk, A. Kassiba, K.J. Plucinski, J. Berdowski, Band structure of the large-sized SiC nanocomposites, Phys. Lett. A. **265**, 403–410 (2000).

[14] B. Asenjo, A.M. Chaparro, M.T. Gutiérrez, J. Herrero, Electrochemical growth and properties of CuInS2 thin films for solar energy conversion, Thin Solid Films **511–512**, 117–120 (2006).

[15] P.K. Sarswat, M.L. Free, A comparative study of Co-electrodeposited Cu_2ZnSnS_4 absorber material on fluorinated tin oxide and molybdenum substrates, J. Electron. Mater. **41** (8), 2210–2215 (2012).

[16] A.H. Reshak, K. Nouneh, IV. Kityk, Jiri Bila, S. Auluck, H. Kamarudin, Z. Sekkat, Structural, electronic and optical properties in earth-abundant photovoltaic absorber of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ from DFT calculations, Int. J. Electrochem. Sci. **9**, 955–974 (2014).

[17] K.J. Plucinski, A.M. El-Naggar, N.S. AlZayed, A.A. Albassam, A.O. Fedorchuk, D. Kulwas, I.V. Kityk, Laser stimulated changes of the effective energy gap in chalcogenide $CuInS_2$ photovoltaic films, Mat. Sci. Semicon. Proc. **38**, 184–187 (2015).

[18] M.G. Brik, I.V. Kityk, O.V. Parasyuk, G.L. Myronchuk, Photoinduced features of energy bandgap in quaternary Cu_2CdGeS_4 crystals. J. Phys.: Condens. Mat. **25**, 505802–1–11 (2013).