

THE SPECTRAL RESPONSE OF THE PHOTOVOLTAIC CELLS BASED ON CdS/CdTe HETEROJUNCTION WITH DIFFERENT TCO'S*

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Inorganic photovoltaic cells based on CdTe thin films were prepared by thermal vacuum evaporation technique. The samples were developed onto optical glass substrates covered with ITO and ITO/IGZO, as transparent conductive oxides (TCO). Indium Gallium Zinc Oxide (IGZO) thin films were prepared in situ by magnetron sputtering technique. After preparation, the structural, morphological and optical properties of the obtained thin films were investigated. The optical investigations showed a good transmittance, higher than 60% for the transparent conductive oxides in the 200 – 1100 nm range and the calculated band gaps values are similar with those that can be found in literature. Taking into account this, the photovoltaic structures based on CdS/CdTe heterojunctions, were prepared by thermal vacuum evaporation, using ITO and ITO/IGZO as TCO. The external quantum efficiency values were determined and compared for the prepared cells. Their study showed that the IGZO thin films could be used as TCO, replacing the conventional ITO films, but more that it behaves as photoactive layer shifting the action spectra toward the shorter wavelength too, and then improving the performances of the photovoltaic cells.

(Received January 6, 2014; Accepted February 5, 2014)

Keywords: ITO, IGZO, CdS, CdTe

1. Introduction

Finding new energy sources became nowadays one of the most important research directions, and the term "green energy" is being used more and more. In this field, the alternative of photovoltaic cells based on organic and/or inorganic materials attracted a lot of attention. Particularly, photovoltaic cells based on A^{II}B^{VI} compounds were intensively studied in the last years mainly due to their physical properties, like: direct bandgaps [1], high absorption coefficients and good mechanical and chemical stability [2]. Moreover, chalcogenides materials have the advantage of an easy deposition procedure by various methods, like: thermal vacuum evaporation (TVE) [3-13], magnetron sputtering [14], spray pyrolysis [15], etc. A special attention was given to cadmium sulfide/cadmium telluride (CdS/CdTe) heterojunction photovoltaic cells due to the fact that they are well suited for both terrestrial and space applications [1, 16]. To improve the photovoltaic performances for these kinds of devices a very simple way is to modify the architecture of the structures or to combine different materials and different deposition methods for the preparation of the thin films involved. One example is related with the nature and properties of the transparent conductive oxides that are frequently used in solar cell technologies.

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Most often indium tin oxide thin films (ITO) covering optical glass or flexible substrates like PET, are used as TCO, especially because they have the both requirements, high transparency in visible range and good electrical conductivity for optoelectronic applications, particularly for photovoltaic cells [17]. Frequently these layers are deposited by magnetron sputtering techniques [18-20], but also by electron beam deposition [21] or chemical vapor deposition [22].

On the other hand, recently, a lot of papers reports on the successfully replacement of ITO with other thin film oxides like fluoride tin oxide (FTO), un-doped zinc oxide (ZnO) or doped zinc oxide like: indium zinc oxide (IZO), aluminum zinc oxide (AZO), indium gallium zinc oxide (IGZO) [23-25].

Particularly, IGZO thin films have been paid attention due to a high transparency on the visible range, very good electrical conductivity and chemical and physical stability, properties required for electronic and optoelectronic applications. Taking into account all of this, in the present paper the spectral response is analyzed and compared for ITO/CdS/CdTe/CdCl₂/Cu/Au and ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au photovoltaic cells. In our case the IGZO thin films, deposited by magnetron sputtering onto optical glass substrates covered with 100 nm ITO, showed a good behavior as TCO but also photoactive component in the prepared ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au photovoltaic structures.

2. Experimental

Inorganic photovoltaic cells based on CdTe thin films were prepared by thermal vacuum evaporation technique onto optical glass substrates covered with indium tin oxide (ITO) commercially available and indium tin oxide/indium gallium zinc oxide (ITO/IGZO). The IGZO thin films were deposited onto ITO layers by magnetron sputtering, the work pressure in the deposition chamber was 4×10^{-3} mbar and the distance between target and samples was maintained constant at the value of 8 cm, during the deposition process. Further, as "window" layer a cadmium sulfide (CdS, 230 nm) thin film was deposited by thermal vacuum evaporation onto the optical glass substrates covered with ITO and ITO/IGZO, respectively. Before the CdS deposition a cleaning procedure was performed for the substrates consisting in 15 minutes washing in acetone and 15 minutes in isopropyl acid. The cadmium telluride (CdTe) thin film with the thickness of 2.4 μm , working as base absorber, was deposited onto CdS, also by thermal vacuum evaporation technique. After each deposition for CdS and CdTe thermal treatments were performed, for CdS 20 minutes at 250°C and for CdTe, 20 minutes at 350°C. To complete the photovoltaic cells a copper/gold back electrode was deposited by thermal vacuum evaporation, followed by a thermal treatment at 250°C for 20 minutes. A schematic representation of the obtained samples is presented in figure 1.

Before the Cu/Au back electrode deposition, a cadmium chloride (CdCl₂) thin film was also deposited onto CdTe and a thermal treatment at 150°C for 10 minutes was performed. In the previous papers we showed that a CdCl₂ treatment improves the photovoltaic performances for these kinds of structures representing so called "Golden Rule" for solar cells based on CdS/CdTe heterojunction [26-28].

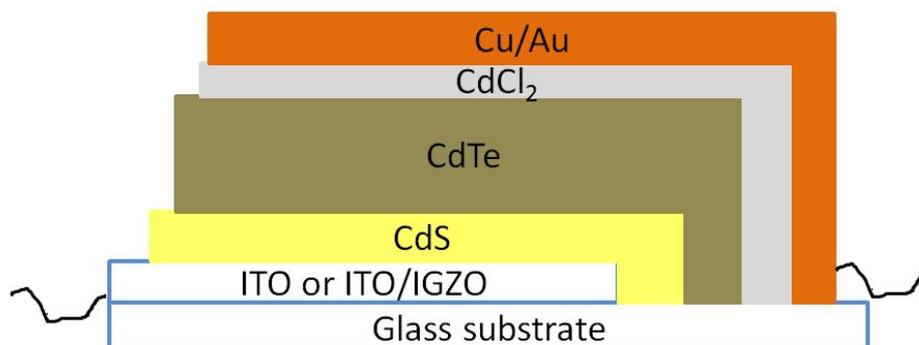


Fig. 1. Schematic representation of the prepared samples

Optical investigations of the involved thin films were performed using a Perkin-Elmer Lambda 35 spectrometer. The transmission and absorption spectra were drawn at room temperature in 190 – 1100 nm range. The structure of the samples was investigated by X-ray diffraction (XRD), using a Bruker D8 Discover high-resolution diffractometer and $\text{Cu}_{K\alpha 1}$ radiation ($\lambda=1.5406 \text{ \AA}$). The positions, widths and integrated intensities of the diffraction peaks were determined by fitting the experimental data in the peak range to Voigt profiles, after extracting the interpolated background; all numerical results were obtained by using the software package *fityk* [31].

The surface morphology was investigated using a Tescan Vega XMU-II microscope with secondary electrons as signal. The work parameters were described in detail in another paper [27]. The external quantum efficiency (EQE) spectra were registered using an experimental setup containing a Newport Oriel monochromator controlled by a computer, and compared for the prepared ITO or ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au structures. The sample's active area was 0.4 cm² and the investigated range was similar with that for optical investigations.

3. Results and discussion

The transmission spectra for ITO, IGZO and ITO/IGZO thin films deposited onto optical glass substrates are presented in figure 2.

As can be observed for all the analyzed transparent oxides the transmittance in the visible range is higher than 70%. The transmission peak that can be seen for IGZO individual film around 560 nm was found for ITO/IGZO two layers architecture having similar shape, with smaller value but not below 80%. Moreover, for ITO/IGZO thin films it was slightly shifted to higher wavelengths. On the other hand, taking into account the ITO thin film, the peak that can be found around 410 nm was shifted to shorter wavelength and was found around 360 nm for ITO/IGZO two layers structure.

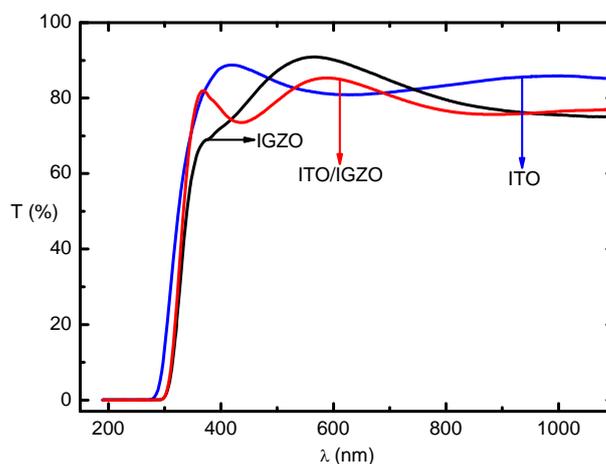


Fig. 2: Transmission spectra for ITO, IGZO and ITO/IGZO thin films

The absorption spectra for the transparent oxides and for "window" and absorber layers are presented in figure 3 a) and b), respectively.

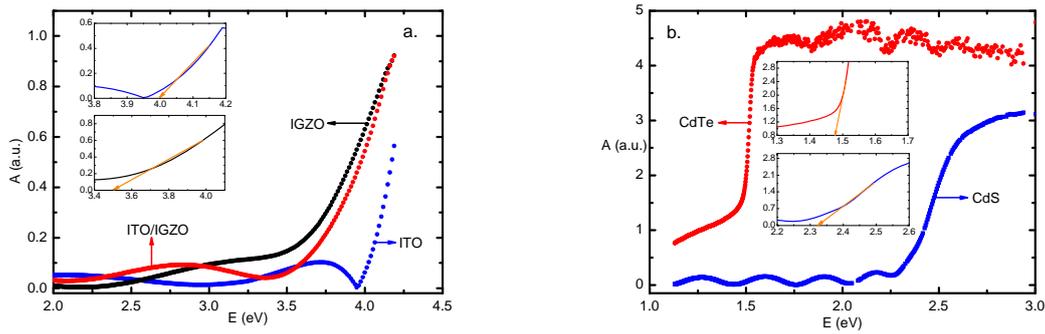


Fig. 3. a) Absorption spectra for ITO, IGZO, ITO/IGZO thin films; b) Absorption spectra for CdS and CdTe thin films

The band gap of ITO, IGZO, CdS and CdTe is a direct one, so the values can be easily determined from the absorption spectra. The absorption coefficient values can be directly

calculated using the next formula, $\alpha = \frac{(E - E_g)^{1/2}}{E}$, where $E = \frac{hc}{\lambda}$ is the photon energy.

Using the obtained experimental data the calculated values were 3.5 eV for IGZO thin film and 4 eV for ITO layer, respectively. Also, for cadmium sulfide and cadmium telluride the calculated values were 2.32 eV and 1.47 eV, respectively. These values are similar with those that can be found in literature [29, 30], even if the deposition method of these thin films is not always the same with that described in this paper.

The XRD patterns for CdS and CdTe are presented in figure 4 a) b), respectively. In the inset a detail of the experimental pattern in the region of CdTe (111) fcc + (002) hcp peaks, the results of fitting with two Voigt profiles and the residual of the fit are shown.

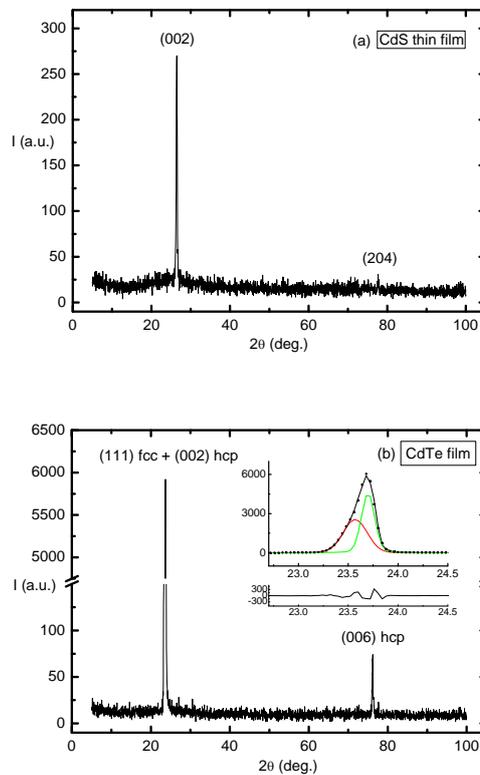


Fig. 4. a) XRD pattern for CdS thin film; b) XRD pattern for CdTe film

The CdS film consists of the normal hexagonal phase (space group $P6_3mc$, PDF2 41-1049) which is highly textured, with crystallites oriented with (001) planes parallel to the film surface (Fig.4.a). The measured lattice parameters, the size of coherent zones D_{eff} and local lattice distortions $\langle \varepsilon^2 \rangle^{1/2}$ (as determined from linewidths) are indicated in Table 1. In determining D_{eff} and $\langle \varepsilon^2 \rangle^{1/2}$ it was assumed that the Lorentzian component is entirely ascribed to size effects, while the Gaussian component is due to strain effects.

In the case of the CdTe film, the XRD pattern indicates a mixture of hexagonal (hcp, space group $P6_3mc$, PDF2 73-2871) and face-centered-cubic (fcc, PDF2 70-8041) phases, which is not unusual for the materials that present a normal hcp and/or fcc structure. The fcc structure is the normal one, while the hcp structure arises as a result of the segregation of the stacking-faults developing in the film during growth. This is supported by the relationship existing between the parameter a_c of the fcc structure and a_h and c_h parameters of the hcp phase (superstructure formed on the fcc phase with a stacking of the type ABAB... instead of the normal ABCABC...), which reads (see the data in Table I):

$$\begin{cases} a_h = \frac{a_c}{\sqrt{2}} = 4.594 \text{ \AA} \\ c_h = \frac{2a_c}{\sqrt{3}} = 7.503 \text{ \AA} \end{cases} \quad (1)$$

Table1. Structural data for CdS and CdTe phases present in the analyzed samples. D_{eff} and $\langle \varepsilon^2 \rangle^{1/2}$ correspond to (002) peak for hcp, respectively (111) peak for fcc phases.

Sample	Crystalline phase	Lattice parameters (Å)	c_h/a_h	D_{eff} (Å)	$\langle \varepsilon^2 \rangle^{1/2} \times 10^3$
CdS	hcp	$a_h=4.145$ $c_h=6.735$	1.625	481.0	4.5
CdTe	fcc	$a_c=6.497$	-	827.5	2.8
	hcp	$c_h=6.735$	-	271.5	5.2

The value of c_h in (1) is close to the experimentally determined value $c_h=7.523 \text{ \AA}$, which is increased by 0.57% as compared to the ideal value $c_h^{(0)} = 7.479 \text{ \AA}$ (PDF2 73-2871). The lattice parameter of the fcc phase is increased by 0.22% as compared to the ideal value ($a_c^{(0)} = 6.4827 \text{ \AA}$, see PDF2 70-8041) and D_{eff} and $\langle \varepsilon^2 \rangle^{1/2}$ values are larger and respectively lower for the CdTe fcc as compared to the hcp phase.

The morphology was analyzed using a Tescan Vega XMU-II microscope and the cross-section and sample surface images are presented in figures 5 (A) and 5 (B).

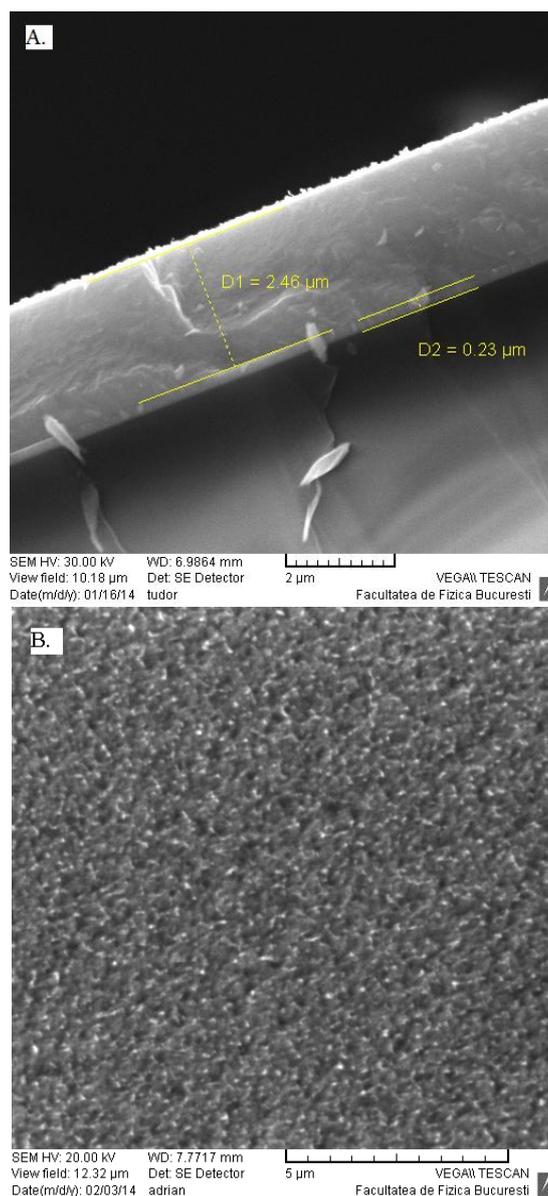


Fig. 5. Cross-section (A) and surface morphology (B) images for prepared ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au photovoltaic cells

Two distinct layers can be easily observed in the image above (figure 5(A)), the cadmium sulfide, 230 nm thick, and the cadmium telluride, 2.4 μm . Moreover, the cadmium telluride grains seem to be very large, giving the layer a patchy appearance, as can be seen in figure 5 (B).

The external quantum efficiency (EQE) spectra were drawn at room temperature using an experimental setup containing a Newport Oriel monochromator controlled by a computer. The obtained experimental data for ITO/CdS/CdTe/CdCl₂/Cu/Au and ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au structures are presented in figure 6.

The maximum value for external quantum efficiency for ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au samples was 25.5% at 450 nm, while for the same structures without IGZO thin film was obtained 3.5% at 520 nm. Analyzing also the EQE (see figure 6) the main conclusion is that the spectral response was significantly enlarged. Moreover, the IGZO thin film seems to behave like a photoactive layer, participating to charge carriers' photo-generation, in the range of wave lengths shorter than the threshold of CdS layer.

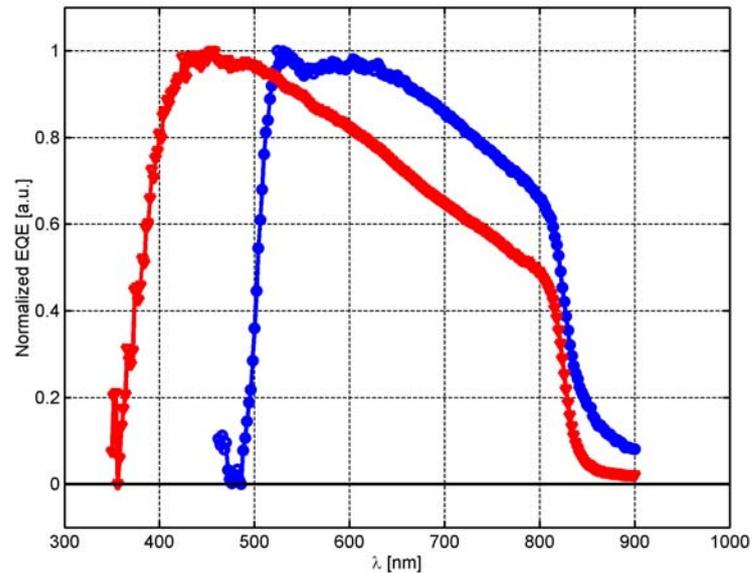


Fig. 6. Normalized EQE of the prepared ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au (red curve) and ITO/CdS/CdTe/CdCl₂/Cu/Au (blue curve) PVs.

To well understand the physical processes that occur a schematic diagram with calculated energy gaps for the layers involved is presented in figure 7.

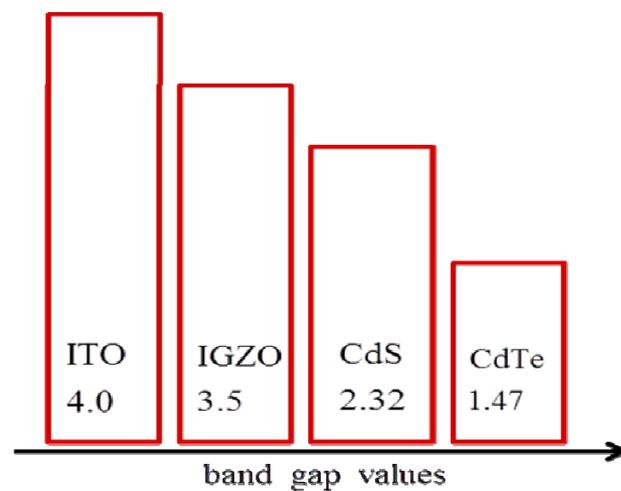


Fig. 7. Band gap energy values of the component thin films of the ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au PV structures

The calculated band gaps for ITO and IGZO can be correlated with the external quantum efficiency spectra that are presented in figure 6. It is clear that the shift of action spectrum of ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au cells, toward UV range until 350 nm, is strongly related with the measured optical gap of IGZO showed in Figure 7. Unfortunately the increasing of the thickness of this structure as a whole with respect with that of ITO/CdS/CdTe/CdCl₂/Cu/Au gives rise to an increased series resistance of the structure, decreasing a little bit the EQE in the range of wavelengths of the mainly absorber CdTe, see Figure 6. With a care design of the structures containing ITO/IGZO as TCO these could have improved performances as photovoltaic cells.

4. Conclusions

Photovoltaic cells based on CdS/CdTe heterojunction were prepared by thermal vacuum evaporation technique onto optical glass substrates covered with ITO and two layers architecture ITO/IGZO. IGZO thin films were deposited by magnetron sputtering onto ITO layers at 4×10^{-3} mbar work pressure. The calculated band gaps values, 4.0 eV for ITO, 3.5 eV for IGZO, 2.32 eV for CdS and 1.47 eV for CdTe, are similar with those that can be found in literature for these thin films. Moreover, for ITO, IGZO and ITO/IGZO layers the transmittance values are higher than 70% in the visible range. The SEM images showed well-organized structures, for both CdS and CdTe thin films, with large grains for cadmium telluride giving a rough aspect to the layer. The registered external quantum efficiency spectra showed that the spectral response was increased for ITO/IGZO/CdS/CdTe/CdCl₂/Cu/Au comparing with that of those samples having only ITO as transparent conductive oxide. Moreover, the IGZO thin films seem to behave like a photoactive layer participating to charge carriers' photo-generation, but new studies are required in order to improve the photovoltaic performances of these kinds of structures.

References

- [1] L. Ion, I. Enculescu, S. Iftimie, V. Ghenescu, C. Tazlaoanu, C. Besleaga, T.L. Mitran, V.A. Antohe, M.M. Gugiu, S. Antohe, *Chalcogenide Letters* **7**, 521 (2010)
- [2] S.N. Sahu, C. Chandra, *Solar Cells* **22**, 163 (1987)
- [3] V. Ruxandra, S. Antohe, *Journal of Applied Physics* **84**, 727 (1998)
- [4] S. Antohe, L. Ion, V. Ruxandra, *Journal of Applied Physics* **90**, 5928 (2001)
- [5] S. Antohe, L. Ion, V.A. Antohe, V.A., *J. Optoelectron. Adv. Mater.* **5**, 801 (2003)
- [6] L. Ion, S. Antohe, M. Popescu, F. Scarlat, F. Sava, F. Ionescu, *J. Optoelectron. Adv. Mater.* **6**, 113 (2004)
- [7] L. Ion, S. Antohe, *Journal of Applied Physics* **97**, 013513 (2005)
- [8] S. Antohe, L. Ion, V.A. Antohe, M. Ghenescu, H. Alexandru, *J. Optoelectron. Adv. Mater.* **9**, 1382 (2007)
- [9] L. Ion, I. Enculescu, S. Antohe, *J. Optoelectron. Adv. Mater.* **10**, 3241, (2008)
- [10] G. Socol, I. N. Mihailescu, A.-M. Albu, S. Antohe, F. Stanculescu, A. Stanculescu, L. Mihut, N. Preda, O. Rasoga, M. Socol, *Applied Surface Science* **255** 5611 (2009)
- [11] L. Ion, V. Ghenescu, S. Iftimie, V.A. Antohe, A. Radu, M.M Gugiu, G. Velisa, O. Porumb, S. Antohe, *Optoelectron. Adv. Mater. – Rapid Commun.* **4**, 1114 (2010)
- [12] O. Toma, R. Pascu, M. Dinescu, C. Besleaga, T.L. Mitran, N. Scarisoreanu, S. Antohe, *Chalcogenide Letters* **8**, 541 (2011)
- [13] O. Toma, S. Iftimie, C. Besleaga, T.L. Mitran, V. Ghenescu, O. Porumb, A. Toderas, M. Radu, L. Ion, S. Antohe, *Chalcogenide Letters* **12**, 747 (2011)
- [14] K. Subba Ramaiah, V. Sundara Raja, *Solar Energy Materials & Solar Cells* **32**, 1 (1994)
- [15] Kahee Shin, Sang il Seok, Sang Hyuk Im, Jong Hyeok Park, *Chemical Communications* **46**, 2385 (2010)
- [16] M. Radu, V. Ghenescu, I. Stan, L. Ion, C. Besleaga, A. Nicolaev, T.L. Mitran, C. Tazlaoanu, A. Radu, O. Porumb, M. Ghenescu, M. Gugiu, S. Antohe, *Chalcogenide Letters* **8**, 477 (2011),
- [17] Farhan S. Mansour, Erfan Zalnezhad, Abdul Razak Bushroa, Ahmed Aly Diaa Sarhan, *International Journal of Precision Engineering and Manufacturing* **14**, 1465 (2013)
- [18] O. Marcovitch, Z. Klein, I. Lubezky, *Applied Optics* **28**, 2792 (1989)
- [19] C. May, J. Strumpfel, *Thin Solid Films* **351**, 48 (1999)
- [20] S. Honda, A. Tsujimoto, M. Watamori, K. Oura, *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films* **13**, 1100 (1995)
- [21] S.A. Agnihotry, K.K. Sari, T.K. Saxena, K.C. Nagpal, S. Chandra, *Journal of Physics D: Applied Physics* **18**, 2087 (1985)
- [22] K.L. Chopra, S. Major, D.K. Pandya, *Thin Solid Films* **102**, 1 (1983)

- [23] C. Tazlaoanu, L. Ion, I. Enculescu, M. Sima, Elena Matei, R. Neumann, Rosemary Bazavan, D. Bazavan, S. Antohe, *Physica E-Low-dimensional Systems & Nanostructures* **40**, 2504 (2008)
- [24] C. Sima, Constantin. Grigoriu, S. Antohe, *Thin Solid Films* **519**, 595 (2010)
- [25] C. Besleaga, G. E. Stan, A. C. Galca, L. Ion, S. Antohe S, *Applied Surface Science* **258**, 8819 (2012)
- [26] S. Antohe, V. Ghenescu, S. Iftimie, A. Radu, O. Toma, L. Ion, *Digest Journal of Nanomaterials and Biostructures* **7**, 941 (2012)
- [27] S. Antohe, Sorina Iftimie, Veta Ghenescu, Raluca Constantineanu, M.M Gugiu, M. Ion, I. Stan, A. Radu, L. Ion, *Romanian Reports in Physics* **64**, 1153 (2012)
- [28] Elena Matei, L. Ion, S. Antohe and I. Enculescu, *Nanotechnology* **21** 105202 (2010)
- [29] L. Fang, J. Chen, L. Xu, W.N. Su, Y. Yu, J. Xu, Z.Y. Ma, *Chinese Physics B* **22**, DOI: 10.1088/1674-1056/22/9/098802 (2013)
- [30] S. Alam, M.A.K. Pathan, K.A.M.H. Siddiquee, A.B.M.O. Islam, M.A. Gafur, D.K. Saha, M. Mori, T. Tambo, *Optik* **124**, DOI: 10.1016/j.ijleo.2012.06.072 (2013)
- [31] M. Wojdyr, *Journal of Applied Crystallography* **43**, 1126 (2010)