OPTIMIZATION OF GROWTH OF TERNARY $CuInS_2$ BY SPRAY PYROLYSIS FOR PHOTOVOLTAIC APPLICATION

M. RAFI [a] *, Y. ARBA [a], B. HARTITI [a], A. RIDAH [a] and P.THEVENIN [b]

[a]Université Hassan II-Mohammédia, Laboratoire LPMAER.FSTM, Mohammedia, Morocco.
[b] Université de Lorraine, Laboratoire LMOPS, Metz, France.
*rafi3mhd@gmail.com

ABSTRACT: $CuInS_2$ ternary films is a promising absorber material for thin film solar cells. It has recently attracted considerable attention due to its high photovoltaic conversion efficiency, and the opportunity to be synthesized by low-cost techniques. In this work $CuInS_2$ thin films have been deposited by chemical Spray pyrolysis onto glass substrate at ambient atmosphere without sulfurization.

The effect of the [Cu]/[In] ration, substrate temperature and the time of spray, on the structural, chemical stoichiometry, topographical, and optical properties of CIS thin films were investigated. EDS result demonstrated that stoichiometric $CuInS_2$ film can be adjusted [Cu]/[In] ration. Chalcopyrite structure of this film was confirmed by XRD analysis. The near stoichiometric $CuInS_2$ film has the optical band gap Eg of 1.45eV.

Keywords: Thin films, $CuInS_2$, Spray pyrolysis, Solar cell absorber, Raman

I. Introduction

Among the group of chalcopyrite semiconductors, $CuInS_2$ (CIS) has attracted interest for use in photovoltaic solar cells. To date photovoltaic (PV) devices based on $CuInS_2$ now reach efficiencies of more than 19.9 % [1]. Depending on the deposition techniques and the process conditions, $CuInS_2$ can show a large variety in PV activity. CuInS2 (CIS) semiconductors crystallize on both, chalcopyrite or sphalerite structure. It is a promising material to be used as absorber layer in photovoltaic devices because of its direct band gap of 1.4–1.52 eV [2] and its high absorption coefficient value cited should be as high as ~10^5 cm^{-1} [3]. Further development of PV technology based on CuInS2 requires fundamental understanding of the physical and chemical nature of the defects in this material, which is the topic of the present investigation.

Various methods, have been used for the deposition of CIS films, such as three sources molecular beam epitaxy [4], sulphurisation of metallic precursor [5], co-evaporation from elemental sources [6], reactive sputtering [7], electrodeposition [8], chemical bath deposition[9], spray pyrolysis [10-11-12], etc. Among them, spray pyrolysis presents several advantages for instance its technical simplicity, its low cost in term of energy expends and consuming parts, and further it can easily upgraded to large scale production. Zouaghi et al. [10] and Krunks et al. [10–13] studied sprayed CIS films using nitrogen as carrier gas. In this paper, CIS films were deposited by spray pyrolysis in ambient atmosphere onto substrates maintained at temperatures between 375 and 400 °C for various spray duration, using solutions with different chemical compositions, and compressed air as carrier gas. In these conditions good CIS films, without oxide phases appearing in the XRD spectra, can be prepared. The structural, chemical composition and optical properties of these films are described in this paper.

II. Experimental details

Copper indium sulphide (CIS) deposited by spray pyrolysis onto glass substrates from aqueous solutions of copper chloride dehydrate, indium chloride and thiourea using compressed air as the carrier gas. The copper/indium molar ratio (Cu/In) in the solution was varied between 0.9 and 1.1 and the sulphur/copper ratio (S/Cu) was fixed at 3. The concentration of Indium was 20×10^{-3} mol/l. The solution was sprayed in air onto glass substrates (25×25×1 mm^3) heated at temperatures between 375 and 400 °C and using spray rates of 1 ml/min in various spray durations. The structural properties of these films were characterized by X-ray diffraction. XRD patterns in the 2θ range 10-60° configuration with a step size of 0.067° were performed using Cu-K_α radiation of a copper anticathode (0.154 nm) and the generator settings were 40 mA, 45 KV. Spectral transmittance and reflectance were recorded in the wavelength range 300-2000 nm. The microstructure and the surface morphology JEOL scanning electron microscope (SEM).The elemental composition of $CuInS_2$ thin films was determined by using an energy dispersive spectrometer (EDS) attached to JEOL SEM. For Raman spectroscopy, the LASER line used was 514.5 nm and the device was a Jobin-Yvon T64000.The optical set of the Raman spectrometer was an Olympus microscope equipped with a 100x magnification lens, it focused the

LASER beam down to a spot of 1 µm in diameter. The LASER penetration depth is estimated to be close to 500 nm.

III. Results and discussion

3.1. Composition

The elemental composition of $CuInS_2$ thin films determined from EDS analysis for films deposited at various substrate temperatures and at different duration substrate are shown in Table1. No traces of carbon were detected and chlorine appears in very little amounts, generally less than 1% which is the detection limit of EDS set up. There is a considerable deviation from stoichiometry for films prepared at high temperature (400°C), also for films are [Cu]/ [In] ratio equal 0.9.

Table 1: Composition analysis of CIS precursor thin film prepared for different conditions, (a) 375°C and 90 min, (b) 400°C (c) 0.9 and (d) 1.1 ratios

	Composition of elements in atomic			Composition ratio	
Sample film CIS	Cu	In	S	Cu/In	S/(Cu+In)
a	26.35	25.20	48.45	1.04	0.94
b	28.57	23.47	47.96	1.22	0.92
c	26.04	24.76	49.20	1.05	0.97
d	29.94	21.23	48.83	1.41	1.05

3.2. Structural and morphology properties

Sprayed films were extremely adherent to the glass substrates and homogeneous in appearance.

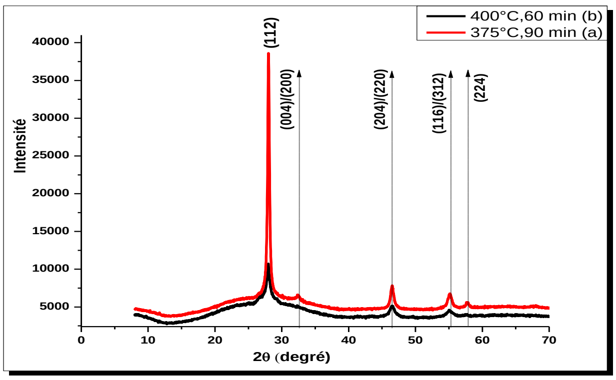

Fig.1. X-ray diffraction patterns of CIS precursor thin film prepared for different spray duration and at various substrate temperature, (a) 375°C and 90 min, (b) 400°C and 60 min with chemical composition of 1.1-1-3

Fig. 1 shows the effect of both the substrate temperature and spray duration of the starting solution on the XRD spectra of several CIS films deposited onto glass substrates. No XRD peaks corresponding to any phase of crystalline CIS were found when the films were sprayed onto substrates at temperatures lower than 350 °C. The XRD spectra reveals that all obtained films sprayed at substrate temperatures were equal to 375 °C and prepared during 90 min are polycrystalline with chalcopyrite structure (JCPDS File N°. 047–1372) with a preferred orientation along (112) direction. The intensity of the (112) diffraction peak decreases when the substrate temperature rises from 375 to 400 °C, a behavior which can be attributed to an increase of the crystallites size for films sprayed at higher temperature, in accordance with bibliography [13, 14]. The increase in grain size due to recrystallization processes is more effective in samples Fig.3.(b) than in sample Fig.3.(a)

The influence of the composition of the solutions on the films deposition in presented on Figure 2, with precursor ratio 0.9-1-3 and 1.1-1-3.

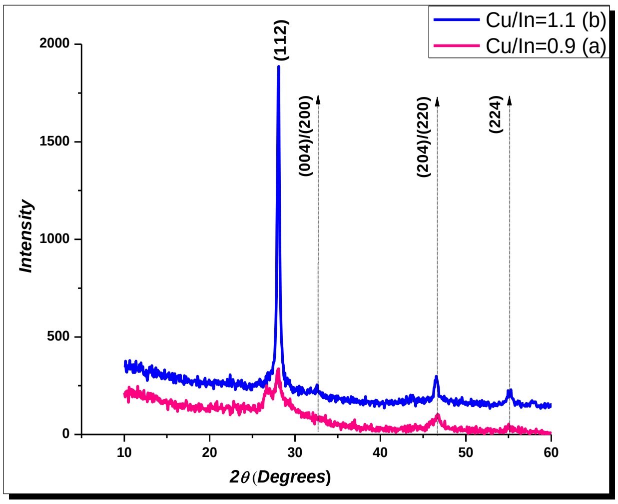

Fig.2: X-ray diffraction patterns of CIS precursor thin film prepared under different Cu/In ratios (a) 0.9, (b) 1.1 of spray duration 60 min and at substrate temperature 375°C

As can be seen, the CIS is deposited in the chalcopyrite structure, and a better degree of crystalline structure is achieved with the solution with the higher amount of copper. When [Cu]/[In] ratios departures from the value of 1.1, which seems to be close to the optimum, the crystallinity of the film decreases as a consequence of the crystal structure deformation. Although this phenomenon was observed in several samples sprayed under the same conditions, this work focuses on the conditions that make possible the synthesis of crystalline CIS films and the presence of other phases was not investigated in detail. SEM observation of the $CuInS_2$ thin films with different [Cu]/[In] ratios are shown in Fig.3 and Fig.4.

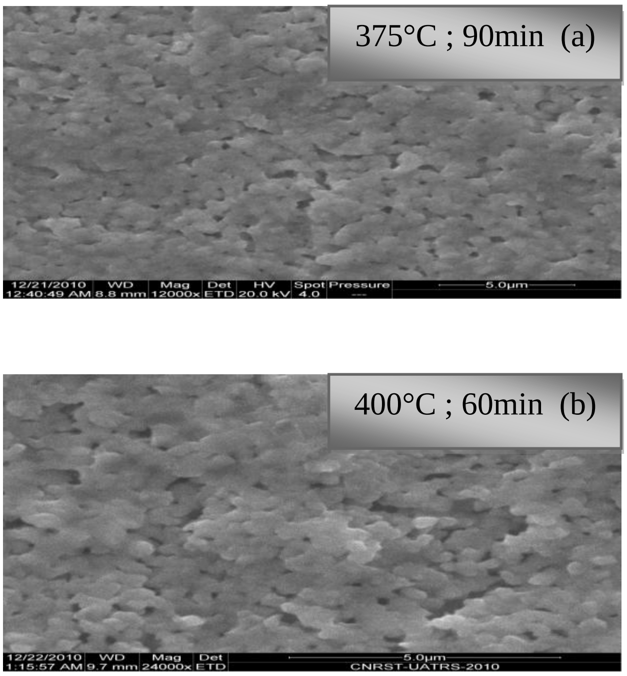

Fig. 3: SEM images of CIS precursor thin film prepared for different spray duration and at various substrate temperature, (a) 375°C and 90 min, (b) 400°C

As [Cu]/ [In] ratio 0.9, the films are comparatively smooth. The roughness of films increases in accordance with the increase of relative amounts of copper in the mixed precursor. Cu-rich films ([Cu]/[In] ratio more than 1) were rough due to the formation of bigger grains and large coherent agglomerates as shown in Fig. 4(b). This effect indicates that possible formation of the CuS segregated phase at the surface was caused by the higher Cu content and its mobility [15].

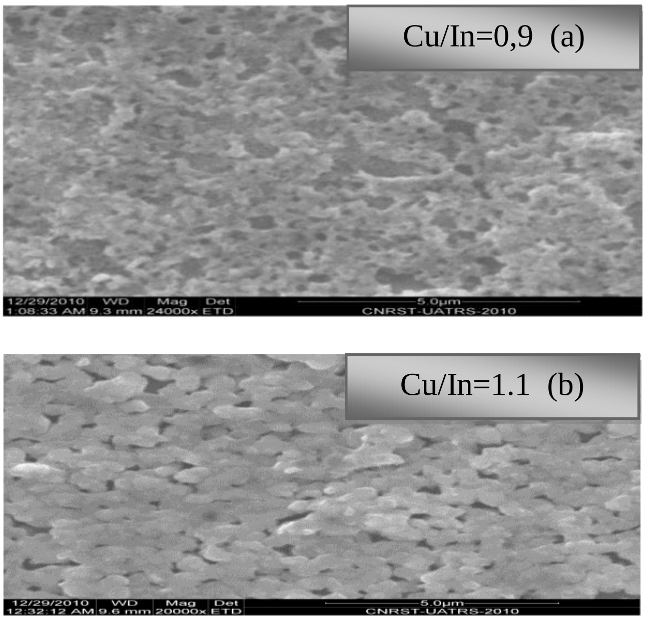

Fig. 4: SEM images of CIS precursor thin film prepared under different Cu/In ratios (a) 0.9, (b) 1.1 of spray duration 60 min and at substrate temperature 375°C

3.3. Optical properties

3.3.1. Transmission

Fig.8 shows optical absorption coefficient α as a function of photon energy hν for the thin films with [Cu]/[In] ratios 0.9 and 1.1. The absorption coefficient (α) was evaluated from the measurements of optical transmittance (T), Figure 5 and 6, and film thickness (t) using the formula [16 - 17]:

$$\alpha = \frac{1}{t} ln \frac{(1-R)^2}{T}$$

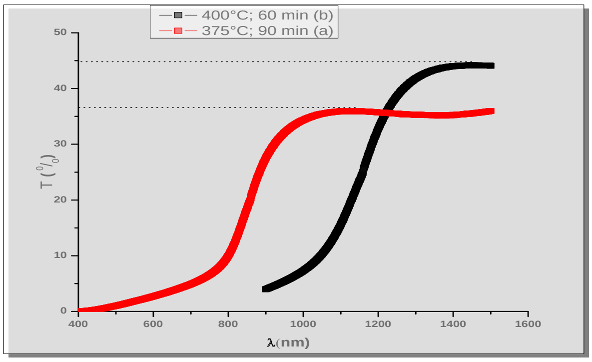

Fig. 5: Transmission T (%) as a function λ(nm) of CIS precursor thin film prepared for different spray duration and at various substrate temperature, (a) 375°C and 90 min, (b) 400°C and 60 min with chemical composition of 1.1-1-3

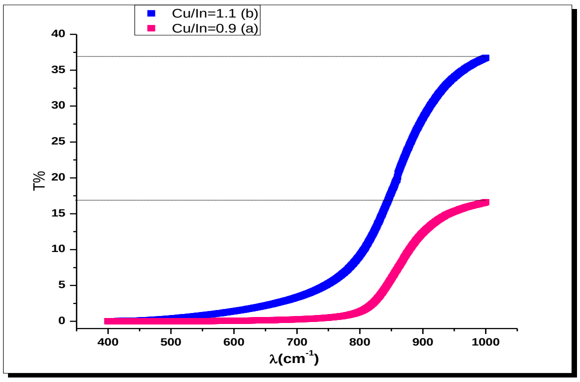

Fig. 6: Transmission T (%) as a function λ(nm) of CIS precursor thin film prepared under different Cu/In ratios (a) 0.9, (b) 1.1 of spray duration 60 min and at substrate temperature 375°C

The values of α are above 10^4 cm^{-1}. This rather high absorption coefficient is very important because its spectral dependence can drastically affect the solar conversion efficiency. For direct band gap materials, the absorption coefficient is related to the energy gap Eg according to the equation:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}}$$

Where A is a constant and h is the Planck constant. E_g can be obtained from the graph of $(h\nu)^2$ versus hν, which is illustrated in Fig. 7 and Fig. 8.

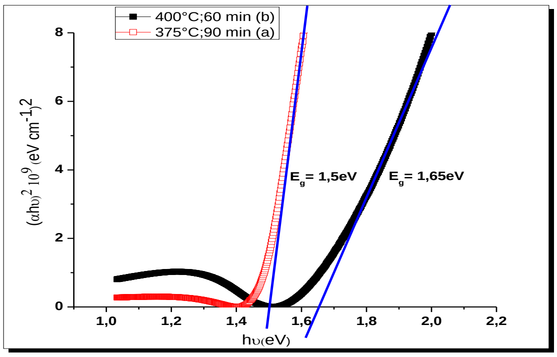

Fig. 7: Variation $(\alpha h\nu)^2$ as a function of photon energy (hν) of CIS precursor thin film prepared for different spray duration and at various substrate temperature, (a) 375°C and 90 min, (b) 400°C and 60 min with chemical composition of 1.1-1-3

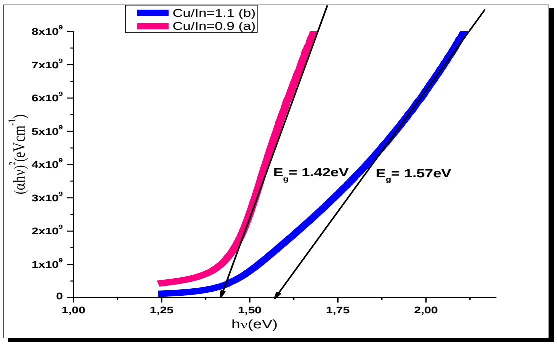

Fig. 8: Variation $(\alpha h\nu)^2$ as a function of photon energy (hν) of CIS precursor thin film prepared under different Cu/In ratios (a) 0.9, (b) 1.1 of spray duration 60 min and at substrate temperature 375°C

The straight line fits show that the films exhibit direct transitions corresponding of a band gap Eg in the range of 1.42–1.65 eV, which is in good agreement with the value of 1.55 and 1.57 eV for the CIS thin film prepared by spray pyrolysis [11]. However, these values are smaller than the reported values of 1.55 eV for single crystals. This can be interpreted by poor crystallinity or deviations from stoichiometry that give rise to defect states and thus induce smearing of absorption edge. On the other hand, it can be seen that E_g increases from 1.42 to 1.57 eV with increasing the [Cu]/[In] ratios from 0.9 to 1.1. A possible reason for this phenomenon is carrier degeneracy in $CuInS_2$ due to Continuous distribution of defect states.

Fig.7 shows that the films prepared at 400 °C about 60 min are of poor optical quality and have poor crystallinity, in contrary the films sprayed at 375°C which present good optical quality (E_g=1.5). It was found that the uniformity, growth rate and adhesion of the films depend strongly on the substrate temperature, spray rate and solution concentration. The chemical composition of films reveals that the use of a Cu/In ratio of 1.1 in the starting solution sprayed at 375 °C of 90 min produces good recrystallization of chalcopyrite CIS films. Our results are in agreement with those published in literature.

3.3.2. Raman spectroscopy

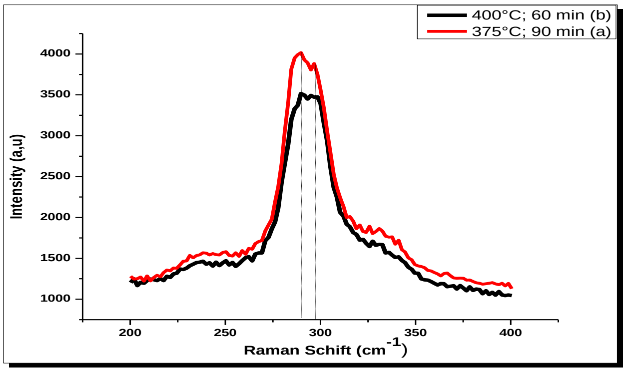

Fig. 9: Raman analysis of CIS precursor thin film prepared for different spray duration and at various substrate temperature, (a) 375°C and 90 min, (b) 400°C and 60 min with chemical composition of 1.1-1-3

Fig.9 shows Raman scattering results of same films of Fig.10. As previously mentioned, CIS film is observed to be grown with two different structures, CH- and CA ordering, respectively standing for chalcopyrite and for CuAu structures. A1 modes for CH- and CA-ordering are reported to be observed as the biggest peaks, which appear at 294 cm^{-1} and 305 cm^{-1}, respectively [18,19]. The broad peaks at 280–310 cm^{-1} indicate that sprayed-films are grown with CH ordering and CA-ordering mixed. Especially, for film fabricated with Cu/In of 1.1, on the other hand Raman spectroscopy results, the CIS film made with the precursor (Cu/In=0.9) shows lower intensity at 478 cm−1 compared to those made with other precursors (Cu/In=1.1). This leads us to be suspicious of some compositional inhomogeneities, which are observed near edge of sprayed film area. A1 mode of CA-ordering is pronounced, and this feature corresponds to the appearance of (100) peak in XRD result. The other peaks at 240 cm^{-1} and 340 cm^{-1} represent Raman modes for CH ordering [20,21]. It is reported that β–In_2S_3 shows peaks at 323 and 363 cm^{-1} [22].

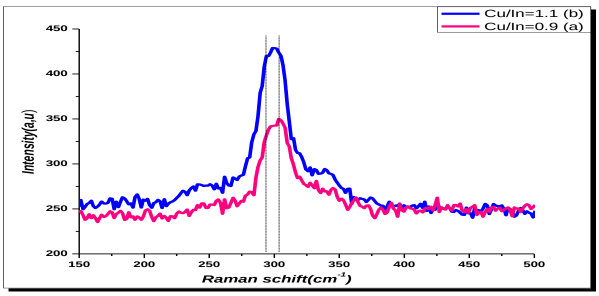

Fig.10: Raman analysis of CIS precursor thin film prepared under different Cu/In ratios (a) 0.9, (b) 1.1 of spray duration 60 min and at substrate temperature 375°C

Fig.10 shows Raman spectroscopy, the broad peak at 280–310 cm^{-1} is split into two peaks for all films, which are A1 modes of CH- and CA-ordering. In addition, the intensity of A1 mode for CH ordering is seen larger than that for CA-ordering. The peak intensity at ~295 cm−1 is observed to decreased, as substrate temperature is increased.

IV. Conclusion

The studies reported here show that it is possible to deposit CIS films using spray pyrolysis technique in ambient atmosphere using compressed air as carrier gas. Sprayed CIS films exhibit a chalcopyrite structure with a preferred orientation in the (112) direction. Structural, chemical composition and optical properties of sprayed films depend on the fabrication conditions, in particular on the substrate temperature spray duration and the Cu/In ratio in the starting solution. The chemical composition of films reveals that the use of Cu/In ratio 0.9 and in the starting solution sprayed at 375 °C produces good recrystallization of chalcopyrite CIS films. The band gap of about 1.57 eV is in good agreement with the 1.55 eV energy value of CIS single crystal.

References

[1] Ingrid Repinsl, Miguel A.Contreras, Brain Egaas, Clay De Hart, John Scharf, Craig L.Perkins, Bobby Toand Romenel Nou.,19.9% efficient ZnO/CdS/CuInGaSe2 solar cell

[2] K. Emst, A. Belaidi, R. Konenkamp, Semicond. Sci. Technol. 18 (2003) 475.

[3] K. Emst, A. Belaidi, R. Konenkamp, Semicond. Sci. Technol. 18 (2003) 475.

[4] H. Metzner, T. Hahn, J.H. Bremer, J. Conrad, Appl. Phys. Lett. 69 (1996) 1900.

[5] H.J. Muffer, C.H. Fischer, K. Diesner, Sol. Energy Mater. Sol. Cells 67 (2001) 121.

[6] R. Scheer, I. Luck, M. Kanis, M. Matsui, T.Watanabe, T. Yamamoto, Thin Solid Films 392 (2001) 1.

[7] T. Watanabe, M. Matsui, Jpn. J. Appl. Phys. 35 (1996) 1681.

[8] S. Kuranouchi, T. Nakazawa, Sol. Energy Mater. Sol. Cells 50 (1998) 31.

[9] H.M. Pathan, C.D. Lokhande, Appl. Surf. Sci. 239 (2004) 11.

[10] M.C. Zouaghi, T. Ben Nasrallah, S. Marsillac, J.C. Bernède, S. Belgacem, Thin Solid Films 382 (2001) 39.

[11]: M. Sahal ., B. Marí, M. Mollar ,Thin Solid Films 517 (2009) 2202–2204

[12] I. Oja, M. Nanu, A. Katerski, M. Krunks, A. Mere, J. Raudoja, A. Goossens, Thin Solid Films 480–481 (2005) 82.

[13] M. Krunks, O. Bijakina, T. Varema, V. Mikli, E. Mellikov, Thin Solid Films 338 (1999)125.

[14] M. Krunks, V. Mikli, O. Bijakina, E. Mellikov, Appl. Surf. Sci. 142 (1999) 356.

[15] M. Krunks, V. Milli, O. Bijakina, H. Rebane, Thin Solid Films 361 (2000) 61.

[16] W. Plaz, G. Cohen Solal, J. Vedel, J. Fermy, T.N. Duy, J. Volerio, Proc; 7th IEEE Photov.Spec. Conf. Pasadena, Nov 1968, p. 54.

[17] M. Abaab, M. Kanzari, B. Rezig, M. Brunel, Sol. Energy Mater. Sol. Cells 59 (1999) 299.

[18] E. Rudigier, B. Barcones, I. Luck, T. Jawhari-Colin, A. Pérez-Rodríguez, R. Scheer, J. Appl. Phys. 95 (2004) 5153.

[19] C. Camus, Ph.D. Thesis, Freien Universität Berlin, 2008.

[20] M. Krunks, O. Bijakina, V. Mikli, H. Rebane, T. Varema, M. Altosaar, E. Mellikov, Sol.Energy Mater. Sol. Cells 69 (2001) 93.

[21] M. Krunks, A. Mere, A. Katerski, V. Mikli, J. Krustok, Thin Solid Films 511–512 (2006) 434.

[22] J. A. Garcia, Ph.D. Thesis, Universitat de Barcelona, 2002.

