

Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

## Thin Solid Films

journal homepage: [www.elsevier.com/locate/tsf](http://www.elsevier.com/locate/tsf)Fabrication and characterisation of Cu(In,Ga)Se<sub>2</sub> solar cells on polyimideH. Zachmann<sup>a</sup>, S. Puttnins<sup>a</sup>, M.V. Yakushev<sup>b</sup>, F. Luckert<sup>b,\*</sup>, R.W. Martin<sup>b</sup>, A.V. Karotki<sup>c</sup>, V.F. Gremenok<sup>c</sup>, A.V. Mudryi<sup>c</sup><sup>a</sup> Solarion AG DE-04288, Leipzig, Germany<sup>b</sup> Department of Physics, SUPA, Strathclyde University, G4 0NG Glasgow, UK<sup>c</sup> Scientific-Practical Material Research Centre of the National Academy of Science of Belarus, P.Brovki 19, 220072 Minsk, Belarus

## ARTICLE INFO

Available online 13 January 2011

## Keywords:

Cu(In,Ga)Se<sub>2</sub>

Solar cells

Polyimide

Photoluminescence

## ABSTRACT

Solar cells with the structure ZnO:Al/i-ZnO/CdS/Cu(In,Ga)Se<sub>2</sub>/Mo/polyimide were examined using a range of techniques. The elemental composition of the Cu(In,Ga)Se<sub>2</sub> (CIGS) layers, their crystalline structure and optical properties were studied. Photoluminescence (PL) spectra of the CIGS absorber layers were studied as functions of temperature (4.2–240 K) and excitation power density. The band gap energy  $E_g$  of the CIGS layers was determined by employing photoluminescence excitation (PLE) spectroscopy. The influence of sodium incorporation on the PL properties of CIGS was analysed. Correlations of the optical properties of the CIGS absorber layers and the photovoltaic parameters of the solar cells were revealed.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The quaternary semiconductor compound Cu(In,Ga)Se<sub>2</sub> (CIGS), which has the chalcopyrite structure, is one of the most promising materials for solar cell absorber layers [1–8]. The achieved conversion efficiency of 19.9% [1] is the highest amongst thin film photovoltaic (PV) devices. Thin film solar cells, fabricated on thin flexible substrates made of polymer films or metal foils, have such advantages as small weight and volume. The record efficiency achieved to date for CIGS-based solar cells on flexible metal foils is ~17.5% [9] whereas on polyimide substrates it is ~14.1% [10] as measured at simulated AM 1.5 standard test conditions.

The growth temperature of CIGS absorber layers in fabrication processes on metal foils reaches ~520–600 °C, which is very close to the temperatures used for the growth of CIGS films on glass [11]. However, polyimide substrates require temperatures below 500 °C because of the danger of thermal decomposition of the polymer [7,12]. Therefore the temperature restriction requires the development of new technological processes for deposition of high structural quality CIGS thin films on polyimide at temperatures as low as ~400–480 °C. This problem requires new insights into the physical properties of CIGS grown on polyimide at lower temperatures and the study of the effects of Na incorporation during low temperature growth because such incorporation significantly increases the performance of solar cells [5,7,8]. In the current report we continue our previous study [12] of the optical properties of CIGS thin films deposited on polyimide

substrates and their correlation with the photovoltaic parameters of solar cells.

## 2. Experimental details

Three sets of polycrystalline 1.7 μm thick CIGS absorber layers were grown upon a Mo-coated polyimide (PI) web at temperatures below 480 °C by a vacuum co-evaporation of elemental Cu, In and Ga together with the incorporation of Se from a broad ion beam source. Details of this process were reported earlier [8,12]. Incorporation of Na into the first set of CIGS absorber layers was carried out by a vacuum co-evaporation of Na from NaF precursor in-situ with the CIGS deposition (Na-Co-VD, represented by solar cell 25-9I). Incorporation of Na into the second set of CIGS absorber layers was carried out in the same chamber using vacuum post-deposition treatment (Na-PDT, annealing at 450 °C during 10 min, represented by solar cell 29-9H). NaF was evaporated after the deposition of CIGS is completed. The third set of CIGS layers was prepared by using both the Na-Co-VD and Na-PDT methods (represented by solar cell 40-9I). The Na concentration was lower than 0.1 at.% (the detection limit of the XRF method) for all the studied solar cells. However, we expect more Na incorporated in the 40-9I sample. The CdS buffer layers were fabricated by chemical bath deposition on top of the CIGS absorber layers. Both a thin intrinsic i-ZnO and ZnO:Al layers were fabricated in a roll-to-roll web coating using a sputtering technique. Thus, the resulting solar cells have the ZnO:Al/i-ZnO/CdS/CIGS/Mo/polyimide structure. The crystalline phases and structural quality of the CIGS absorber layers were studied by X-ray diffraction (XRD). The elemental composition of the as-deposited CIGS films was measured in-situ with the deposition process by X-ray fluorescence spectroscopy (XRF). To

\* Corresponding author.

E-mail address: [franziska.luckert@strath.ac.uk](mailto:franziska.luckert@strath.ac.uk) (F. Luckert).

analyse the optical properties of the CIGS film photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy were used [12].

### 3. Results and discussion

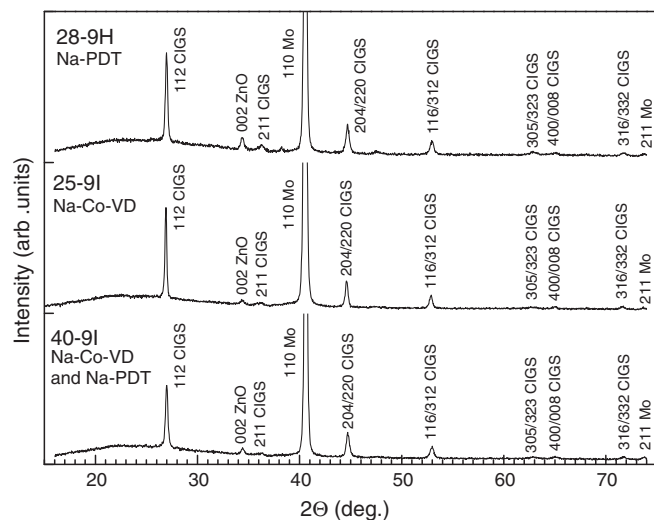
The elemental composition of the CIGS polycrystalline layers as well as the  $[Cu]/([In] + [Ga])$  and  $[Ga]/([In] + [Ga])$  ratios, defining the deviation from the ideal stoichiometry and band gap value of CIGS polycrystalline thin films, are shown in Table 1. These elemental compositions suggest that all the CIGS films are Cu-deficient with  $[Cu]/([In] + [Ga])$  varying from 0.79 to 0.87 and  $[Ga]/([In] + [Ga])$  varying from 0.21 to 0.26. These ratios suggest a band gap of about  $E_g \sim 1.2$  eV, which is in agreement with the earlier measurements of Cu-poor polycrystalline CIGS layers [13]. It is also necessary to note that the elemental ratios of the CIGS films fall within the limits  $0.69 \leq [Cu]/([In] + [Ga]) \leq 0.98$  and  $0.21 \leq [Ga]/([In] + [Ga]) \leq 0.38$ , which have recently been defined for CIGS solar cells with efficiencies from 19.0 to 19.5% [2].

Fig. 1 shows the XRD patterns for the three sets of solar cells fabricated using the CIGS thin films incorporated with Na using the described methods. The high intensity XRD peak at  $2\theta \sim 40.5^\circ$  is related to the  $\langle 110 \rangle$  oriented Mo layer. The other diffraction peaks (112, 211, 204/220, 116/312, 305/323, 400/008 and 316/332) are associated with the chalcopyrite structure of CIGS. The presence of the sharp and well defined diffraction peak 112 with a small full-width at half-maximum intensity (FWHM)  $\sim 0.2^\circ$  clearly indicates a good crystallinity of the CIGS layers. It is well known that in the case of a texture-free powder  $CuInSe_2$  sample (random orientation) the intensity ratio  $I_{112}/I_{204,220}$  should be  $\sim 1.6$  (Joint Committee on Powder Diffraction Standards, JSPDS, PDF-2, #65-2740) [14]. The intensity ratios of the 112 peak with respect to that of the 220/204 one in the 28-9H (Na-PDT), 25-9I (Na-Co-VD) and 40-9I (Na-PDT and Na-Co-VD) solar cells were measured to be 3.3, 3.6 and 2.8, respectively, indicating a predominantly  $\langle 112 \rangle$  orientation of the CIGS grains. The small differences between these intensity ratios (from 2.8 to 3.6) suggest relatively stable conditions of the CIGS film growth technology. This result also shows that different methods of Na incorporation have a little influence on the preferential crystallographic orientation and structural properties of the CIGS layers.

The PL and PLE spectra, taken at different excitation powers (4.2 K), for the three solar cells are shown in Fig. 2. For a better comparison of the shape the intensities of the bands were normalised to the maximum emission intensity. It is clear that the PL spectra strongly depend on the method of Na incorporation. All the spectra only contain broad bands without any narrow lines in the near-band gap excitonic region. The PL bands shift to higher energies and become slightly broader with increasing excitation power. The higher energy PL band (40-9I solar cell, Na-PDT and Na-Co-VD), whose maximum is at 1.058 eV, does not shift with increasing excitation power. The spectral position of all the observed PL bands, their widths and the rates of the high-energy shifts (j-shift) with increasing excitation power are collected in Table 2. The j-shifts are quite different and vary from 7.5 to 19.5 meV/decade. The excitation power dependencies of the maximum spectral positions for all the PL bands are shown in Fig. 3. The identification of the radiative recombination

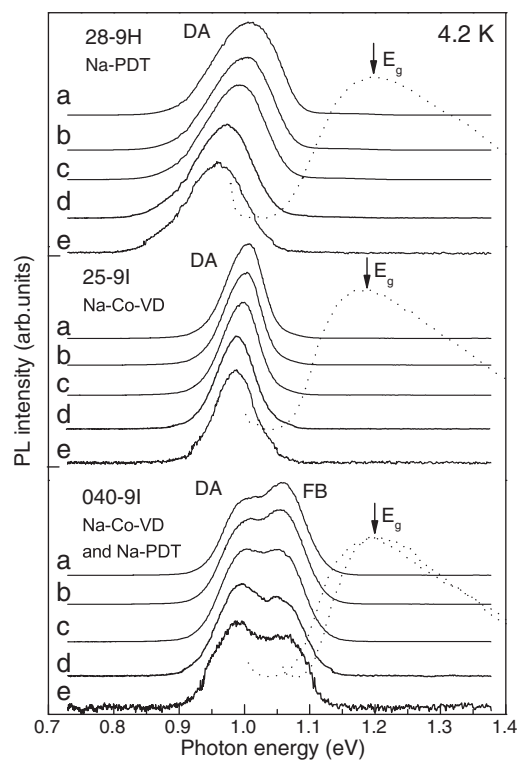
**Table 1**  
Chemical composition determined by XRF method and the method of Na incorporation for CIGS solar cells fabricated on Mo-coated polyimide substrates.

Solar cell and method of Na incorporation	Composition, at.%				Elemental ratio	
	Cu	In	Ga	Se	$[Cu]/([In] + [Ga])$	$[Ga]/([In] + [Ga])$
28-9H (Na-PDT)	23.4	22.4	7.2	47	0.79	0.24
25-9I (Na-Co-VD)	24.6	22.4	6	47	0.87	0.21
40-9I (Na-Co-VD and Na-PDT)	23.9	21.5	7.5	47	0.82	0.26



**Fig. 1.** X-ray diffraction patterns of solar cells on polyimide substrates fabricated using different methods of Na incorporation.

mechanisms of the PL bands was based on the excitation-power and temperature dependencies as well as on the value of the band gap energy  $E_g$ . The values of the band gap energy  $E_g$  for the three solar cells have been determined using PLE spectroscopy, with typical spectra for the three samples shown in Fig. 2. These spectra were recorded with detection at the energy near the maximum intensity of the corresponding PL band 0.973 eV (solar cell 28-9H), 0.991 eV (solar cell 25-9I), 0.996 eV, and 1.058 eV (solar cell 40-9I) and correspond to PL spectra (d) for each sample. It can be seen that in each spectrum the PLE emission intensity gradually increases up to the energy of



**Fig. 2.** PL spectra (solid lines, all PL spectra were normalised to unity) of CIGS solar cells on Mo/polyimide substrates taken at different excitation powers and temperature 4.2 K: (a)  $7.5 \text{ W cm}^{-2}$ , (b)  $2.92 \text{ W cm}^{-2}$ , (c)  $0.97 \text{ W cm}^{-2}$ , (d)  $0.11 \text{ W cm}^{-2}$ , and (e)  $0.02 \text{ W cm}^{-2}$ . PLE spectra (dashed lines) taken at excitation power  $\sim 0.11 \text{ W cm}^{-2}$ , correspond to (d) PL spectra.

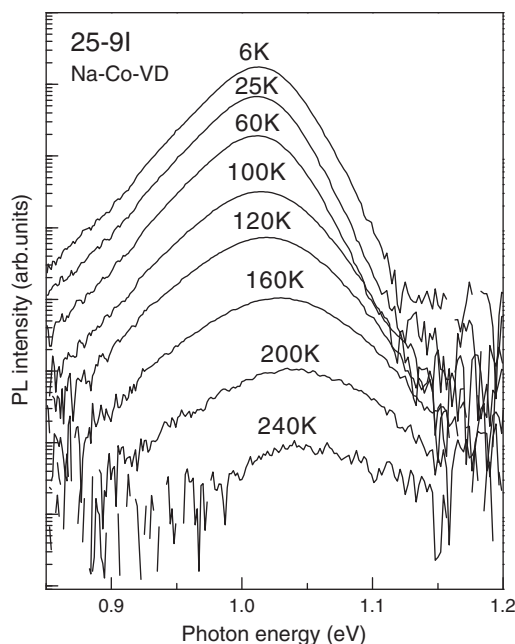
**Table 2**  
Optical parameters of the PL bands (j-shift, spectral position and FWHM for excitation power  $7.5 \text{ W cm}^{-2}$  measured at 4.2 K) and band gap energies in the CIGS layers incorporated with Na using different methods.

Solar cell and method of Na incorporation	Spectral position at 4.2 K (eV)	FWHM 4.2 K, (meV)	j-shift at 4.2 K, (meV/decade)	Band gap energy, (eV)
28-9H (Na-PDT)	1.008	109	19.5	1.195
25-9I (Na-Co-VD)	1.006	65	7.7	1.183
40-9I (Na-Co-VD and Na-PDT)	1.009	98	7.5	1.197
Na-PDT)	1.058	100	0	1.200

about  $\sim 1.2 \text{ eV}$  revealing a maximum near the  $E_g$  and then slowly decreases forming a tail. The band gaps determined from the PLE measurement are shown in Table 2 and marked in Fig. 2. The values of  $E_g$  are in a good agreement with those measured in CIGS films with similar chemical composition  $[\text{Ga}]/([\text{In}] + [\text{Ga}]) \sim 0.21\text{--}0.26$  using transmission measurements [12,13,15,16].

The energy differences between the band gap  $E_g$  and the energy position of the corresponding PL bands were found to be about 0.18–0.19 eV. All the PL bands increase their intensity with increasing excitation power although the one at 1.058 eV for the 40-9I solar cell increases its intensity at a slightly faster rate. The integrated intensity  $I$  of each band increased as  $I \sim P^k$ , where  $P$  is the excitation power. The  $k$  coefficient was found to be of about  $\sim 0.89$  (solar cell 28-9H),  $\sim 0.92$  (solar cell 25-9I),  $\sim 0.91$  (solar cell 40-9I) for the DA band (donor-to-acceptor recombination) and  $\sim 0.96$  (solar cell 40-9I) for the FB band (free-to-bound recombination). These values are smaller than unity, which is expected for donor-acceptor and free-to-bound optical transitions [15–18].

As an example, Fig. 4 shows the temperature dependence of the PL spectra of the 25-9I solar cell. A significant shift towards higher energies, reaching 35 meV at 240 K, can be seen. A similar temperature shift was observed for the PL band at 1.008 eV for the solar cell 28-9H. For the 40-9I solar cell a decrease of the intensity and a broadening of both bands (DA and FB) were observed at rising temperature. The experimental data above are consistent with the assignment of the recombination mechanism of the DA bands to a donor-acceptor recombination influenced by strong spatially fluctuating potentials (SFP). This interpretation of similar PL spectra measured in CIGS films and solar cells, fabricated on Mo coated polyimide substrates, was proposed earlier [12]. The effects of the influence of SFP on DA recombination in CIGS polycrystalline thin films were reported previously [15–18]. According to the literature

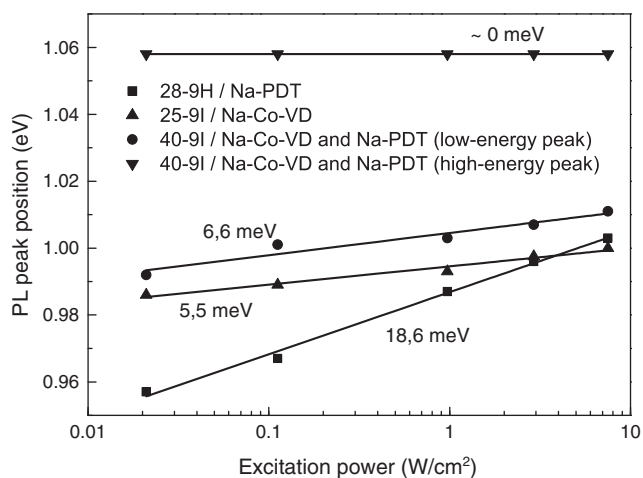


**Fig. 4.** Temperature dependence of the DA band for the 25-9I solar cell (Na-Co-VD), taken at an excitation power of  $10 \text{ W cm}^{-2}$ .

[18–21] the most likely defects, involved in the DA recombination, are the Cu vacancy ( $V_{\text{Cu}}$ ) as the acceptor and  $\text{In}_{\text{Cu}}$ , as the donor. The high-energy band at 1.058 eV (which does not shift with increasing excitation power) for the 40-9I solar cell can probably be assigned to a free-to-bound (FB) optical transition [22].

The effects of the Na incorporation on the PL properties of CIGS films can be seen in Fig. 2 and Table 2 whereas Table 3 shows the main parameters of the solar cells. Together they reflect the influence of sodium and the incorporation method. The use of the two Na-PDT and Na-Co-VD processes (as it is seen in Fig. 2) significantly changes the parameters of the DA band. The Na-Co-VD method leads to a significant reduction in both the DA band width and the j-shift (which is reduced by a factor of 3 in comparison with the Na-PDT process). This effect agrees with our earlier conclusion on the influence of the Na-Co-VD incorporation method on the j-shift [12]. For this method of incorporation the excess of Na diffuses to the grain boundaries, and passivates them, reducing the concentration of charged defects and the average amplitude of potential fluctuations as well as the level of compensation.

The influence of Na on the PL bands seems to be quite moderate when the Na-PDT process is employed. The large values of the j-shift and FWHM suggest a high value of the average amplitude of potential fluctuations. In the case of employing both the Na-PDT and Na-Co-VD processes (solar cell 40-9I) the PL spectra reveal an additional band FB suggesting the appearance of an additional radiative transition. There is no j-shift of this FB band for increasing excitation intensity. Also the j-shift of the DA band in this sample is small as shown in Table 2 whereas the widths of both FB and DA are very significant. The use of



**Fig. 3.** Excitation power dependence of the PL peak positions for different solar cells taken at 4.2 K. The straight lines are linear fits to the experimental data according to  $E_{\text{max}} = E_0 + B \log_{10}(P_{\text{exc}})$ .

**Table 3**  
Photovoltaic parameters of the CIGS solar cells fabricated on polyimide substrates.

Solar cell and method of Na incorporation	Fill-factor, FF	Short-circuit current, $J_{\text{sc}}$ ( $\text{mA/cm}^2$ )	Open-circuit voltage, $V_{\text{oc}}$ (V)	Efficiency, $\eta$ (%)
28-9H (Na-PDT)	0.57	27.2	0.54	8.3
25-9I (Na-Co-VD)	0.57	18.9	0.55	5.9
40-9I (Na-Co-VD and Na-PDT)	0.67	11.7	0.59	4.7

the different methods of Na incorporation affects the solar cell parameters as shown in Table 3. The highest performance solar cell 28-9H (Na-PDT) has the highest intensity DA band, whose intensity exceeds that of the nearest competitor (the 25-9I solar cell (Na-Co-VD)) by a factor of 1.5–2. The intensity of the DA band in the 40-9I solar cell (Na-PDT and Na-Co-VD) is smaller by another factor of 2. Thus the integral emission intensity of the DA band strongly correlates with the solar cell efficiency. Apparently the higher the intensity, the higher is the performance of the solar cell.

The lower current density  $J_{SC}$  of the 25-9I (Na-Co-VD) and 40-9I (Na-Co-VD and Na-PDT) solar cells is probably related to an excess of Na in the CIGS films. Such an excess can result in a higher carrier concentration, shorter space charge region and effective diffusion length of the carriers as well as in a poor carrier collection decreasing  $J_{SC}$  and increasing  $V_{OC}$  and FF. Similar results have recently been observed [23].

#### 4. Conclusion

Solar cells with the structure ZnO:Al/i-ZnO/CdS/Cu(In,Ga)Se<sub>2</sub>/Mo/polyimide were examined using a range of techniques. The elemental composition of the CIGS layers, crystalline structure and the effects of the Na incorporation method on the PL spectra of the CIGS absorber layers were studied. It was found that in all the solar cells the band gap, estimated by PLE measurements, is close to  $E_g \sim 1.2$  eV, corresponding to the ratio of  $[Ga]/([In] + [Ga]) \sim 0.21–0.26$ . The influence of the method of sodium incorporation on the PL properties of CIGS is quite dramatic. The Na-PDT (post-deposition) method results in the highest efficiency. However, the PL spectrum of the sample prepared using this method suggests the presence of a high concentration of charged defects resulting in a high amplitude of potential fluctuations although the PL intensity in this sample is the highest indicating a low level of non-radiative recombination. This study reveals correlations between the optical properties of the CIGS absorber layers and the photovoltaic characteristics of CIGS-based solar cells.

#### Acknowledgements

This work has been supported by the BRFFI (grant F09IC-003) and EPSRC (grant EP/E026451/1).

#### References

- [1] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, Res. Appl. 16 (2008) 235.
- [2] P. Jackson, R. Würz, U. Rau, J. Mattheis, M. Kurth, T. Schlötzer, G. Bilger, J.H. Werner, Res. Appl. 15 (2007) 507.
- [3] A. Goetzberger, C. Heblig, H.W. Schook, Mater. Sci. Eng. R 40 (2003) 1.
- [4] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, Res. Appl. 16 (2008) 61.
- [5] N.G. Dhere, V.S. Gade, A.K. Kadam, A.H. Jahagirdar, S.S. Kalkarni, S.M. Bet, Mater. Sci. Eng. B 116 (2005) 303.
- [6] F. Kessler, D. Herrmann, M. Powalla, Thin Solid Films 480–481 (2005) 491.
- [7] D. Bremann, D. Rudmann, G. Bilger, H. Zogg, A.N. Tiwari, in: C.R. Wronski (Ed.), Conference Record of the Thirty-First IEEE Photovoltaic Specialists Conference, Institute of Electrical and Electronics Engineering, Inc., Piscataway, NJ, USA, 2005, p. 223.
- [8] K. Otte, L. Makhova, A. Braun, I. Konovalov, Thin Solid Films 511–512 (2006) 613.
- [9] J.R. Tuttle, A. Szalaj, J. Keane, in: A. Rohatyi (Ed.), Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference, Institute of Electrical and Electronics Engineering, Inc., Piscataway, NJ, USA, 2000, p. 1042.
- [10] D. Rudmann, Appl. Phys. Lett. 84 (2004) 1129.
- [11] F. Kessler, D. Rudmann, Solar Energy 77 (2004) 685.
- [12] H. Zachmann, S. Heinker, A. Braun, A.V. Mudryi, V.F. Gremenok, A.V. Ivaniukovich, M.V. Yakushev, Thin Solid Films 517 (2009) 2209.
- [13] S.H. Han, F.S. Hasoon, J.W. Pankow, A.M. Hermann, D.H. Levi, Mater. Res. Soc. Symp. Proc. 865 (2005) F1.3.
- [14] H. Hahn, G. Frank, W. Klingler, A.D. Meyer, G. Storger, Z. Anorg. Allg. Chem. 271 (1953) 153.
- [15] N. Rega, S. Siebentritt, J. Albert, S. Nishiwaki, A. Zajogin, M.Ch. Lux-Steiner, R. Kniese, M.J. Romero, Thin Solid Films 480–481 (2005) 286.
- [16] S. Theodoropoulou, D. Papadimitriou, N. Rega, S. Siebentritt, M.Ch. Lux-Steiner, Thin Solid Films 511–512 (2006) 690.
- [17] S.A. Schumacher, J.R. Botha, V. Alberts, J. Appl. Phys. 99 (2006) 063508.
- [18] M.J. Romero, K. Ramanathan, M.A. Contreras, M.N. Al-Jassin, R. Noufi, P. Sheldon, Appl. Phys. Lett. 83 (2003) 4770.
- [19] V. Alberts, J.H. Schön, M.J. Witcomb, E. Bucher, U. Rühle, H.W. Shock, J. Phys. D Appl. Phys. 31 (1998) 2869.
- [20] S.B. Zang, S.H. Wei, A. Zunger, Phys. Rev. B 57 (1998) 9642.
- [21] C. Rincon, R. Marquez, J. Phys. Chem. Solids 60 (1999) 1865.
- [22] S. Shimakawa, K. Kitani, S. Hayashi, T. Satoh, Y. Hashimoto, Y. Takahashi, T. Negami, Stat. Sol. 203 (2006) 2630.
- [23] R. Caballero, C.A. Kaufmann, T. Eisenbarth, M. Cancela, R. Hesse, T. Unold, A. Eicke, R. Klenk, H.W. Schock, Thin Solid Films 517 (2009) 2187.