

## Effect of $\text{CdCl}_2$ activation on the impurity distribution in CdTe/CdS solar cell structures

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### Abstract

CdTe/CdS/ $\text{In}_2\text{O}_3$ :F/glass solar cell structures made using 7N CdTe were investigated to determine the distribution of impurities. This study was carried out using quantitative secondary ion mass spectrometry (SIMS) profiling from the CdTe surface through the glass substrate. Particular emphasis was placed on the potential for electrically active impurities to originate from the cadmium chloride ( $\text{CdCl}_2$ ) processing step, since such impurities are likely to affect the CdTe/CdS device performance. The impurities: Cl, O, Cu, Na, In, Sb, Sn, Si, Zn, Pb and S were profiled for as-grown and  $\text{CdCl}_2$  treated structures. Ion implanted CdTe and CdS standards were used for SIMS quantification.

It has been shown that O and Cu do not originate from the  $\text{CdCl}_2$  activation process. Zn, Sn and Pb are also invariant on processing. Other impurities such as Cl, Na and Sb are definitely present in the activated structures due to their presence in the  $\text{CdCl}_2$  starting material used in the treatment. Si diffusion from the glass substrate as well as Te and S interdiffusion at the CdTe/CdS interface following the  $\text{CdCl}_2$  treatment were also highlighted.

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**Keywords:** Impurities; SIMS; CdTe; CdS; Solar cell structures

### 1. Introduction

In the drive towards low cost thin film solar cells, starting materials are used that are relatively impure by the usual standards of the semiconductor industry. In recent years, the effects of impurities like Cu and Cl on devices have been studied, and their concentrations through layers and at interfaces have also been studied. The electronically active layers in polycrystalline CdTe/CdS cells were identified in terms of their nature and thickness, and it was shown that the photovoltaic junction (i.e. p-CdTe/n-CdS) coincides with the metallurgical junction [1]. It was also found that the chemical and morphological properties of surfaces and interfaces were correlated to the solar cell efficiency [2].

Secondary ion mass spectrometry (SIMS) is a powerful analytical technique widely used in semiconductor device structures to profile intentional as well as unintentional

doping impurities that are paramount in terms of stability, lifetime and performance of the devices [3]. A review of SIMS for thin film photovoltaics was recently published [4]. Due to solar cell stability-related issues, qualitative SIMS analysis was mainly dedicated to Cu and/or Cl diffusion into the cell structure for cells back-contacted with Cu-containing material [5–7]. It was also used to determine residual Cl concentration in CdTe following a wet  $\text{CdCl}_2$  treatment [8] and to investigate the CdS/ $\text{SnO}_2$  interface in solar cells [9]. Furthermore, qualitative SIMS was used for studying the effect, on the efficiency of the solar cells, of the etching procedure [10,11] and different materials used as electrodes on the CdTe surface [12].

A survey of the literature available on CdTe-based solar cells shows a noticeable lack of quantitative SIMS analysis on entire device structures through to the glass substrate and a full study of impurity concentrations and distribution within device structures. Quantitative analysis on CdTe/CdS solar cells were reported by Durose et al. [13] for structures in their fresh, light-soaked and bake-tested states where

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several impurities were depth-profiled. They also reported quantitative SIMS data of the study of the diffusion from Sb-Te back contacts to CdTe, in which oxygen and antimony profiles were recorded for as-deposited as well as air annealed test structures [14]. More recently, Godines et al. [15] reported a quantitative SIMS investigation of CdTe/CdS/SnO<sub>2</sub>:F structures grown by pulsed laser ablation and ion sputtering deposition. This study used either HgCdTe relative sensitivity factors (RSFs) or a model for the quantification of the results, and was limited to light element impurities such as H, C and O—these were mainly introduced by adsorption from the residual gas atmosphere during the growth.

Cadmium chloride (CdCl<sub>2</sub>) is used in the annealing-induced activation of polycrystalline CdTe/CdS solar cells, and this step is crucial in the device fabrication process. It was established that CdCl<sub>2</sub> treatment leads to a grain growth and a passivation of the grain boundaries (GBs) in the CdTe active layer. It also promotes the formation, by interdiffusion, of CdTe<sub>1-x</sub>S<sub>x</sub> at the CdTe/CdS interface and reduces recombination in these devices [16–18]. Recent investigations showed that CdCl<sub>2</sub> treatment affects the interior of CdTe grains by the potential incorporation of electrically active impurities, in addition to its known effect on GBs [19]. These investigations also showed that the purity of the CdCl<sub>2</sub> used during the heat treatment may have an effect on the incorporation of Cu into the CdTe bulk. Surprisingly, these and other CdCl<sub>2</sub>-processing related effects have so far not been studied by SIMS.

In this study, we report on a systematic and quantitative impurity analysis in CdTe/CdS/In<sub>2</sub>O<sub>3</sub>:F/glass solar cell structures. Particular emphasis was made on potentially electrically active impurities likely to originate from the CdCl<sub>2</sub> processing step, and that may affect the stability, lifetime and performance of CdTe/CdS solar cell devices. This full depth investigation of the multilayered structures was quantitative in the CdTe and lead to the determination of the concentration, distribution and origin of many impurities as well as any interdiffusion. Impurities in the CdCl<sub>2</sub> starting material itself have been the subject of a separate study by a chemical analysis carried out using inductively coupled plasma mass spectrometry (ICPMS) [20].

## 2. Experimental

The cell structures investigated here were grown in the University of Parma (Italy). We used two samples of polycrystalline CdTe/CdS/In<sub>2</sub>O<sub>3</sub>:F/glass solar cell structures (without back contacts) that were fabricated separately using similar conditions as described below. Fluorine-doped indium oxide (In<sub>2</sub>O<sub>3</sub>:F) and CdS layers were grown by sputtering with a nominal thickness of 800 and 150 nm, respectively. The typical substrate temperatures and deposition rates were, respectively, 500 °C and 0.5–1 nm/s for

In<sub>2</sub>O<sub>3</sub>:F and 200 °C and 1 nm/s for CdS. A 8–10 µm thick CdTe layer was subsequently deposited using the close-space sublimation (CSS) technique at a substrate temperature of typically 500 °C, a source temperature of about 650 °C and a growth rate of 2 µm/min. In<sub>2</sub>O<sub>3</sub>:F (on soda lime glass) was used as transparent conducting oxide (TCO) since it gives the best efficiency for solar cells grown using this process [21]. The purity of the starting CdTe material was 7N for both structures. One of them was further treated with thermally evaporated CdCl<sub>2</sub> layer (150 nm thick, 99.9% purity) in order to distinguish the effect of this processing step on the impurity distribution in the whole structure. The treatment was carried out in air at 400 °C followed by a chemical etching in Br<sub>2</sub>-methanol solution for a few seconds.

The SIMS depth profiles were done at QinetiQ (UK) using a CAMECA system. The oxygen primary beam was used to determine the positive ion yield and cesium primary beam for the negative ions. Energies and analysed crater sizes were 8 keV and 150×150 µm<sup>2</sup> for O<sub>2</sub><sup>+</sup>, and 14.5 keV and 60×60 µm<sup>2</sup> for Cs<sup>+</sup>.

SIMS quantitative results were obtained using relative sensitivity factors (RSFs) extracted from SIMS standards. These calibration standards were undoped CdTe (Japan Energy) and CdS (Girmet) single crystals implanted at the University of Surrey Ion Beam Centre with <sup>208</sup>Pb, <sup>29</sup>Si, <sup>115</sup>In, <sup>35</sup>Cl, <sup>23</sup>Na, <sup>16</sup>O, <sup>63</sup>Cu, <sup>121</sup>Sb, <sup>64</sup>Zn, <sup>120</sup>Sn, <sup>32</sup>S (in CdTe only) and <sup>128</sup>Te (in CdS only). The implantation energy was 200 keV for all the species and the doses were in the range of 1.6×10<sup>12</sup> to 5×10<sup>13</sup> ions/cm<sup>2</sup>. For the purpose of accurate quantification, the samples were profiled under closely similar conditions to the standard implants to get the instrumental sensitivity in the same measurement sequence. Depth profiles of Cl, O, Cu, Na, In, Sb, Sn, Si, Zn, Pb, Te and S were recorded for each of the two structures from the uncontacted CdTe surface through the glass substrate and performed twice to confirm repeatability.

## 3. Results and discussion

Fig. 1 shows the quantitative SIMS depth profiles of O, Zn, Cu, Pb and Sn impurity atoms for the CdTe/CdS/In<sub>2</sub>O<sub>3</sub>:F/glass structures as-grown (a) and CdCl<sub>2</sub> treated (b).

For both structures, these impurities have a constant signal within the CdTe layers with a concentration ranging from about 4×10<sup>18</sup> atoms/cm<sup>3</sup> for O down to around 10<sup>14</sup> atoms/cm<sup>3</sup> for Sn. For each of these impurities, the profiles exhibit the same concentration and shape with and without CdCl<sub>2</sub> processing throughout the whole structures and show therefore that these impurities are clearly not originating from the CdCl<sub>2</sub> activation process.

An ICPMS study of the CdCl<sub>2</sub> starting material used in this work is published in Ref. [20]. The concentrations recorded in the powder were Na (5.26 ppm), In (0.94 ppm) and Sb (0.21 ppm). SIMS depth profiles of Cl, Na, In and

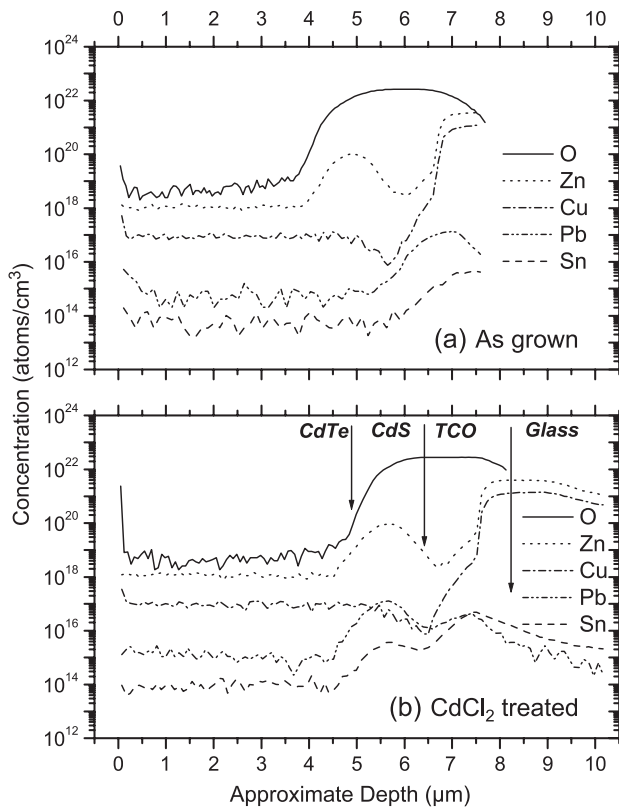


Fig. 1. Impurities in the CdTe that are invariant on  $\text{CdCl}_2$  treatment: quantitative SIMS depth profiles of O, Zn, Cu, Pb and Sn impurity atoms for the CdTe/CdS/ $\text{In}_2\text{O}_3$ :F/glass structures as-grown (a) and  $\text{CdCl}_2$  treated (b). The free surface of the CdTe is at depth zero and the approximate positions of the interfaces are shown in (b).

Sb impurity atoms are shown in Fig. 2 for these two structures as-grown (a) and  $\text{CdCl}_2$  treated (b). Following treatment, the Cl concentration in the whole structure is 100 times more than before treatment, while In has a concentration in CdTe 50% higher on average, and Na sees its concentration in CdTe increased by one to two orders of magnitude. Sb shows a noisy but constant concentration of about  $10^{16}$  atoms/ $\text{cm}^3$  in CdTe where the detection limit seems to be reached. These four impurities are likely to be present in the  $\text{CdCl}_2$ -activated structure due to their presence in the  $\text{CdCl}_2$  starting material used in the treatment as revealed by ICPMS [20]. However, In and Na may also originate from the TCO/glass.

Fig. 3 shows the quantitative SIMS depth profiles of Si, Te and S atoms for the CdTe/CdS/ $\text{In}_2\text{O}_3$ :F/glass structures as-grown (a) and  $\text{CdCl}_2$  treated (b) with a Te concentration in arbitrary units (a.u.). For the as-grown structure, Si shows a flat concentration of  $3 \times 10^{15}$  atoms/ $\text{cm}^3$  in CdTe (below the SIMS detection limit) that increases to about  $4 \times 10^{16}$  atoms/ $\text{cm}^3$  for the treated structure. This indicates that during the  $\text{CdCl}_2$  heat processing a migration of Si occurs from the glass substrate all the way across the structure as no trace of Si was detected in the  $\text{CdCl}_2$  starting material analysed [20].

For the  $\text{CdCl}_2$  treated structure, Te and S thermal interdiffusions across the CdTe/CdS interface were highlighted by the higher Te and S concentrations in, respectively, CdS and CdTe layers compared to their concentrations in the nontreated structure as shown in Fig. 3.

The depth scales shown in all the figures are approximate since they were calculated assuming a constant sputter rate. This rate is much higher in CdTe than in CdS, TCO and glass and thus the CdTe thickness is significantly underestimated. It appeared also that although the nominal thickness is the same in both structures, the actual thickness is different especially for CdTe layers (at least about  $1 \mu\text{m}$  difference) mainly due to the high growth rate ( $2 \mu\text{m}/\text{min}$ ) of CdTe, that is also not constant in the early stage of CSS growth. The CdTe surfaces appeared rough for both structures and the profiles of some elements such as Si, S, O, Pb, and Na show a surface tailing which mainly results from the CdTe surface roughness and probably also from an increase in crater bottom roughness while sputtering further in depth. The depth resolution is affected by these two factors but also by the CdTe layer thickness and crystallinity (as grains of different orientations may sputter at different rates), by the roughness of the interfaces as well as by the SIMS profiling conditions. In this work, we did not pre-polish the CdTe surfaces prior to SIMS in order to avoid contamination. Nevertheless, the CdS and TCO layers under

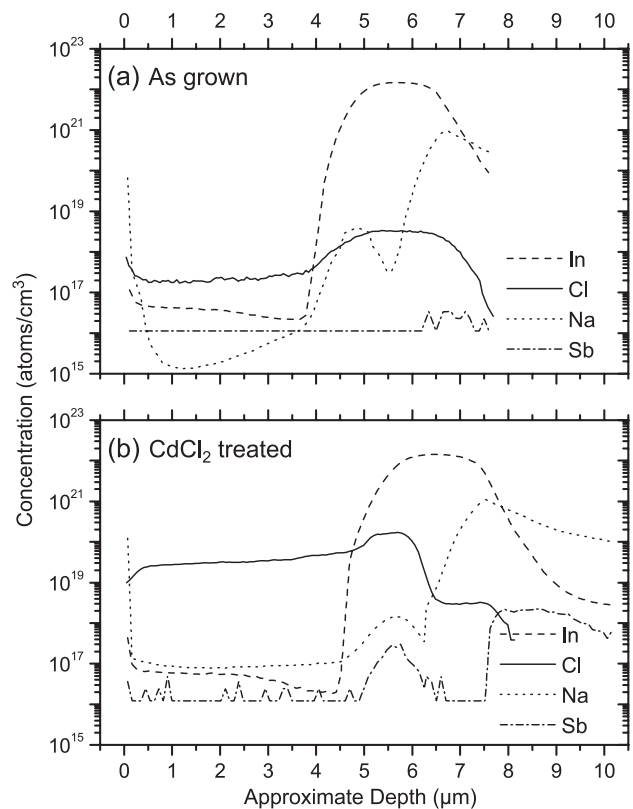


Fig. 2. Species that are present in the  $\text{CdCl}_2$  starting material: quantitative SIMS depth profiles of Cl, Na, Sb and In impurity atoms for the CdTe/CdS/ $\text{In}_2\text{O}_3$ :F/glass structures without (a) and with  $\text{CdCl}_2$  treatment (b).

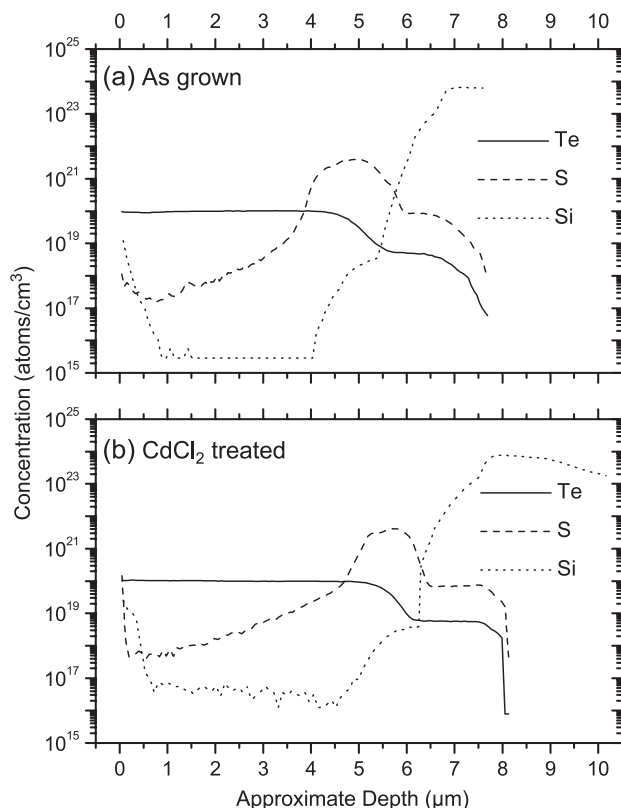


Fig. 3. Species from the cell layers: quantitative SIMS depth profiles of Te, S and Si impurity atoms for the CdTe/CdS/In<sub>2</sub>O<sub>3</sub>:F/glass structures as-grown (a) and CdCl<sub>2</sub>-treated (b). Note that for Te the concentration is in arbitrary units (a.u.) instead of atoms/cm<sup>3</sup>.

the CdTe appear reasonably well resolved and the approximate locations of the CdTe/CdS, CdS/In<sub>2</sub>O<sub>3</sub>:F and In<sub>2</sub>O<sub>3</sub>:F/glass interfaces are clearly apparent in the figures where the profiling goes further into the glass substrate for the sample treated with CdCl<sub>2</sub>, e.g. Fig. 1b.

The purpose of our study was to focus on the impurities that are relevant to CdTe-based solar cells and identify those that may originate from the CdCl<sub>2</sub>, i.e. the impurities that have an effect (as donors or acceptors) on the optical and/or electrical properties of the CdTe absorbing (and probably also on CdS window) thin layers and, ultimately, on the CdTe/CdS device performance. It has recently been shown that CdTe surface processing and composition have a strong effect on the device behaviour [22]. Since the heat treatment was carried out in air, the O concentration at the surface of the CdTe layer increases following this treatment (Fig. 1) but there is no indication of an increase in O concentration in the CdTe bulk. Conflicting reports were recently published concerning the behaviour of CdTe/CdS solar cells processed in oxygen-containing atmospheres. It was shown that CSS-grown CdTe/CdS solar cells heat-treated with CdCl<sub>2</sub> in He have very similar cell performance to those cells CdCl<sub>2</sub> heat-treated in oxygen [23]. Deep level transient spectroscopy (DLTS) results were also found to be similar for these two types of structures [23].

This has been attributed to the fact that either the presence of oxygen does not affect the electronic defects in CdTe solar cells, or the concentration of any oxygen related complexes is too low to be detected using DLTS [23]. On the other hand, a higher doping concentration was measured for air-activated samples compared to vacuum-activated ones and this was attributed to the fact that acceptor concentration increases when oxygen was present during the CdCl<sub>2</sub> treatment (Refs. [24], [6] and [7] therein). Finally, another recent study [25] postulates that oxygenation enhances concentrations of Cl<sub>Te</sub> and V<sub>Cd</sub> in CdTe, enhances diffusion of Te into CdS and can act to fill V<sub>s</sub> with O<sub>s</sub>.

It should also be emphasised that at least some of the Na present in the structure following treatment (Fig. 2) might be originating from the glass substrate and not due exclusively to the CdCl<sub>2</sub> activation. As for the distribution of impurities and their transport mechanism, SIMS does not indicate whether the diffusion of these impurities proceeds through the bulk or via GBs pathways. While faster diffusion is expected in the latter, conventional SIMS cannot distinguish whether the impurities are located in the grains, and therefore more likely to be active dopants, or at the GBs. Furthermore, SIMS does not elucidate whether the impurities detected in these structures, and particularly in the CdTe absorbing layer, are actually electrically active or forming active complexes or neutral or forming neutral complexes.

Assessment of interface sharpness by SIMS in these samples is limited by surface roughness. Nevertheless, in both structures the CdTe/CdS active interface appears to be graded over a greater width than the CdS/In<sub>2</sub>O<sub>3</sub>:F interface. Moreover, some of the depth profiles recorded (like Te, S, In and Na) seem to suggest that the CdTe/CdS interface becomes even more diffused following the CdCl<sub>2</sub> treatment. It has been shown elsewhere that high efficiency cells have graded interfaces while cells with low efficiency show abrupt interfaces [2].

#### 4. Conclusions

Quantitative and dynamic SIMS measurements were carried out to study the concentration and distribution of impurity elements all the way across CdTe/CdS/In<sub>2</sub>O<sub>3</sub>:F/glass solar cell structures in order to investigate the effect of the post-deposition CdCl<sub>2</sub> processing step. It was demonstrated that O, Cu, Z, Sn and Pb had the same concentration and distribution before and after treatment and did not originate from CdCl<sub>2</sub>. On the other hand, Na, In and Cl were present in the layers and also in the CdCl<sub>2</sub> starting material used in the treatment. This study also showed that migration of Si, and probably Na into the structure occurs from the glass substrate. Te and S interdiffusion at the CdTe/CdS interface following the CdCl<sub>2</sub> treatment was also indicated.



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## References

- [1] I. Visoly-Fisher, S.R. Cohen, D. Cahen, C.S. Ferekides, *Appl. Phys. Lett.* 83 (2003) 4924.
- [2] Z.C. Feng, H.C. Chou, A. Rohatgi, G.K. Lim, A.T.S. Wee, K.L. Tan, *J. Appl. Phys.* 79 (1996) 2151.
- [3] R.G. Wilson, *Solid-State Electron.* 39 (1996) 1113.
- [4] K. Durose, S.E. Asher, W. Jaegermann, D. Levi, B.E. McCandless, W. Metzger, H. Moutinho, P.D. Paulson, C.L. Perkins, J.E. Sites, G. Teeter, M. Terheggen, *Prog. Photovolt. Res. Appl.* 12 (2004) 177.
- [5] K.D. Dobson, I. Visoly-Fisher, G. Hodes, D. Cahen, *Adv. Mater.* 13 (2001) 1495.
- [6] K.D. Dobson, I. Visoly-Fisher, G. Hodes, D. Cahen, *Sol. Energy Mater. Sol. Cells* 62 (2000) 295.
- [7] C. Narayanswamy, T.A. Gessert, S.E. Asher, in: *AIP Conference Proceedings*, vol. 462, 1999, p. 248.
- [8] T.A. Gessert, M.J. Romeo, C.L. Perkins, S.E. Asher, R. Matson, H. Moutinho, D. Rose, *Mater. Res. Soc. Symp. Proc.* 668 (2001) H1.10.1.
- [9] M. Tsuji, T. Aramoto, H. Ohyama, T. Hibino, K. Omura, *J. Cryst. Growth* 214/215 (2000) 1142.
- [10] R.J. Rosenberg, R. Zilliacus, E.L. Lakomaa, A. Rautiainen, A. Makela, *Fresenius' J. Anal. Chem.* 54 (3) (1996) 6.
- [11] D. Kraft, A. Thissen, J. Broetz, S. Flege, M. Campo, A. Klein, W. Jaegermann, *J. Appl. Phys.* 94 (2003) 3589.
- [12] D.L. Batzner, A. Romeo, H. Zogg, R. Wendt, A.N. Tiwari, *Thin Solid Films* 387 (2001) 151.
- [13] K. Durose, M.A. Cousins, D.S. Boyle, J. Beier, D. Bonnet, *Thin Solid Films* 403–404 (2002) 396.
- [14] K. Durose, D. Boyle, A. Abken, C.J. Ottley, P. Nollet, S. Degrave, M. Burgelman, R. Wendt, J. Beier, D. Bonnet, *Phys. Status Solidi* 229 (2) (2002) 1055.
- [15] J.A. Godines, A. Villegas, Yu Kudriavtsev, R. Asomoza, A. Morales-Acevedo, A. Escamilla, G. Arriaga, H. Hernandez-Contreras, G. Contreras-Puente, J. Vidal, M. Chavarria, R. Fragoso-Soriano, *Semi-cond. Sci. Technol.* 19 (2004) 213.
- [16] M. Terheggen, H. Heinrich, G. Kostorz, A. Romeo, D. Baetzner, A.N. Tiwari, A. Bosio, N. Romeo, *Thin Solid Films* 431–432 (2003) 262, (and references therein).
- [17] J. Fritsche, T. Schulmeyer, A. Thissen, A. Klein, W. Jaegermann, *Thin Solid Films* 431–432 (2003) 267.
- [18] T. Schulmeyer, J. Fritsche, A. Thissen, A. Klein, W. Jaegermann, M. Campo, J. Beier, *Thin Solid Films* 431–432 (2003) 84.
- [19] K.J. Price, *Mater. Res. Soc. Symp. Proc.* 668 (2001) H1.7.1.
- [20] M. Emziane, C.J. Ottley, K. Durose, D.P. Halliday, *J. Phys. D: Appl. Phys.* 37 (2004) 2962.
- [21] N. Romeo, A. Bosio, V. Canevari, M. Terheggen, L. Vaillant Roca, *Thin Solid Films* 431–432 (2003) 364.
- [22] B.E. McCandless, S.S. Hegedus, R.W. Birkmire, D. Cunningham, *Thin Solid Films* 431–432 (2003) 249.
- [23] V. Komin, B. Tetali, V. Viswanathan, S. Yu, D.L. Morel, C.S. Ferekides, *Thin Solid Films* 431–432 (2003) 143.
- [24] J. Verslyus, P. Clauws, P. Nollet, S. Degrave, M. Burgelman, *Thin Solid Films* 431–432 (2003) 148.
- [25] M.A. Hernandez-Fenollosa, D.P. Halliday, K. Durose, M.D. Campo, J. Beier, *Thin Solid Films* 431–432 (2003) 176.