

# Microcrystalline silicon n-i-p solar cells prepared with microcrystalline silicon oxide ( $\mu\text{-SiO}_x\text{:H}$ ) n-layer

Vladimir Smirnov<sup>\*</sup>, Wanjiao Böttler, Andreas Lambertz, Haiyan Wang<sup>1</sup>, Reinhard Carius and Friedhelm Finger

IEF-5 Photovoltaik, Forschungszentrum Jülich, D-52425, Jülich, Germany

<sup>1</sup> Permanent address: School of Physical Engineering, Zhengzhou University, PR China

PACS 84.60.Jt, 81.05.Gc, 81.07.Bc, 81.15.Gh

\* Corresponding author: e-mail v.smirnov@fz-juelich.de, Phone: + 49 (0)2461 61 8725, Fax: + 49 (0)2461 61 3735

N-type hydrogenated microcrystalline silicon oxide ( $\mu\text{-SiO}_x\text{:H}$ ) layers were used as window layers in n-side illuminated microcrystalline silicon n-i-p solar cells. Optical, electrical and structural properties of  $\mu\text{-SiO}_x\text{:H}$  films were investigated by Photothermal Deflection Spectroscopy, conductivity and Raman scattering measurements.  $\mu\text{-SiO}_x\text{:H}$  layers were prepared over a range of carbon dioxide ( $\text{CO}_2$ ) flow and film thickness, and the effects on the solar cell performance were investigated.

By optimising the  $\mu\text{-SiO}_x\text{:H}$  window layer properties, an improved short-circuit current density of  $23.4 \text{ mA/cm}^2$  is achieved, leading to an efficiency of 8.0% for  $1 \mu\text{m}$  thick absorber layer and Ag back contact. The correlation between cell performance and  $\mu\text{-SiO}_x\text{:H}$  layer properties is discussed. The results are compared to the performance of solar cells prepared with alternative optimised window layers.

**1 Introduction** Silicon oxide ( $\text{SiO}_x\text{:H}$ ), being a wide optical gap material, has been the subject of research as a material for photovoltaic applications [1-9]. Electrical, optical and structural properties of both amorphous (a- $\text{SiO}_x\text{:H}$ ) and microcrystalline ( $\mu\text{-SiO}_x\text{:H}$ ) silicon oxide films have been investigated. The properties of silicon oxide thin films are influenced by the doping and the oxygen content [2-4, 7]. Optical band gap ( $E_{04}$ ), refractive index ( $n$ ), and conductivity can be modified over a wide range by varying input gas ratios during material growth. Several reports concerned a preparation of silicon oxide thin films as p-type window layers [1-3]. An optical gap ( $E_{04}$ ) of 1.95-2.06 eV for p-type silicon oxide films was reported [2, 3]. More recently, n-type  $\mu\text{-SiO}_x\text{:H}$  has attracted attention as an intermediate reflector in tandem solar cells [6-9]. In that case, the  $\text{SiO}_x$  layer was incorporated between amorphous silicon (a-Si:H) and microcrystalline silicon ( $\mu\text{-Si}$ :H) sub-cells. This approach allows the current of the a-Si sub-cell to be increased, allowing the absorber layer to be kept reasonably thin to minimize the impact of light-induced degradation.

While optimal performance a-Si solar cells need to be illuminated through the p-side, solar cells utilising  $\mu\text{-Si}$ :H absorber layers may be illuminated from either p or n side, since the hole drift mobility in  $\mu\text{-Si}$  films is much higher than in a-Si films [10, 11]. It was recently shown [12], for example, that n-type microcrystalline silicon carbide ( $\mu\text{-SiC}$ ), having a wide optical gap of around 2.8eV and grown by Hot Wire Chemical Vapour Deposition (HWCVD), can be successfully used as a window layer in single junction microcrystalline silicon n-i-p solar cells.

The possibility to tune optical (such as  $E_{04}$  and  $n$ ) and electrical properties in n-type  $\mu\text{-SiO}_x\text{:H}$  offers potential for its application as a window layer in thin film solar cells. Here, we present the results of investigation of n-type  $\mu\text{-SiO}_x\text{:H}$  thin films and n-i-p solar cells prepared with  $\mu\text{-SiO}_x\text{:H}$  window layers.

**2 Experimental** n-type  $\mu\text{-SiO}_x\text{:H}$  layers were deposited by RF (13.56 MHz) plasma enhanced chemical vapour deposition (PECVD) technique at  $185 \text{ }^\circ\text{C}$  substrate temperature and a power of 50 W, using a mixture of phosphine ( $\text{PH}_3$ ), silane ( $\text{SiH}_4$ ), hydrogen ( $\text{H}_2$ ) and carbon

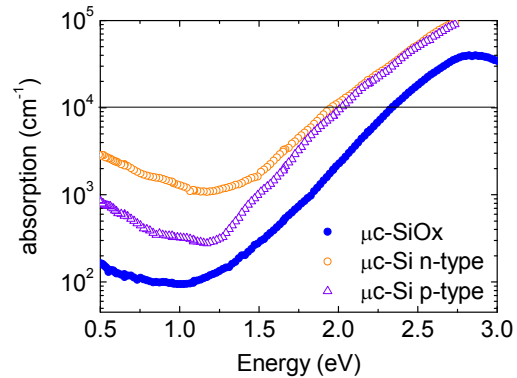
dioxide (CO<sub>2</sub>) gases. Additional details on the deposition conditions can be found elsewhere [7, 13]. The layers were deposited at varied CO<sub>2</sub> flows (up to 2 sccm) and thickness, and subsequently used as window layers in microcrystalline silicon solar cells. Silicon thin films were deposited by PECVD technique using either RF or VHF (94.7 MHz) excitation for different intrinsic and extrinsic layers. p-type and intrinsic  $\mu\text{c-Si}$  layers were prepared by VHF-PECVD; the deposition conditions of p-layer remained unaltered during this study. Intrinsic  $\mu\text{c-Si:H}$  layers (nominally 1  $\mu\text{m}$  thick) were prepared from a mixture of SiH<sub>4</sub> and H<sub>2</sub> gases, the silane concentration ratio SC = [SiH<sub>4</sub>] / ([SiH<sub>4</sub> + H<sub>2</sub>]) was varied between 4.2% and 5.5%.

Solar cells were prepared on textured glass/ZnO [14] substrates in the sequence: glass/ZnO/ $\mu\text{c-SiO}_x(\text{n})/\mu\text{c-Si}(\text{i})/\mu\text{c-Si}(\text{p})$ . Additionally, n-side illuminated n-i-p solar cells, employing  $\mu\text{c-Si:H}$  n-layer and p-side illuminated p-i-n cells were prepared to enable a comparison. The area of the individual devices was defined by the 1 cm<sup>2</sup> Ag back contacts. Solar cells were characterised by current-voltage (*J-V*) measurements under AM 1.5 illumination, and also under modified AM 1.5 illumination with red cut-on filter OG590 ( $\lambda > 590$  nm) and blue band filter OG7 ( $\lambda$  centred at around 480 nm). The total optical reflectance of the cells was measured on a Perkin-Elmer photospectrometer, type lambda 950, within a spectral range from 320 to 2000 nm.

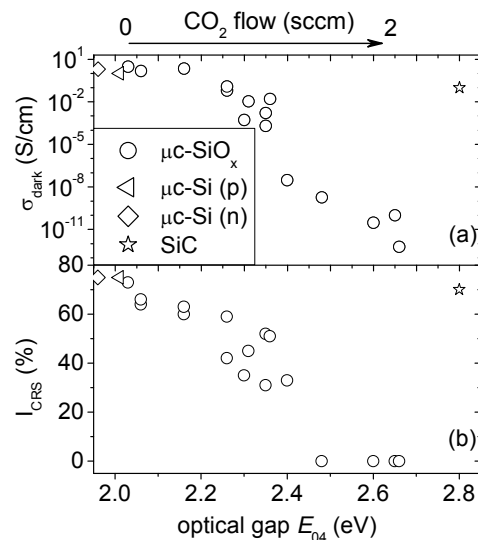
The window layers concerned in this work ( $\mu\text{c-SiO}_x\text{:H}$ ,  $\mu\text{c-Si:H}$  (n) and  $\mu\text{c-Si:H}$  (p)) were also prepared on Corning Eagle 2000 glass substrates. Optical and electrical properties of these layers were investigated by Photothermal Deflection Spectroscopy (PDS) and conductivity measurements, respectively. Conductivity measurements were performed on films equipped with coplanar electrodes 5 mm in length separated by a 0.5 mm gap. The structural properties of the layers were probed using Raman spectroscopy, with excitation at 647 nm supplied by an Ar-ion laser. The ratio of integrated intensities attributed to crystalline and amorphous regions,  $I_{\text{CRS}} = I_c / (I_c + I_a)$  was used as semi-quantitative value of the crystalline volume fraction [15].

**3 Results** Figure 1 shows an absorption spectrum of  $\mu\text{c-SiO}_x\text{:H}$  film, measured by PDS. For a comparison, absorption spectra of p-type and n-type microcrystalline silicon films are shown. One can see that in the case of  $\mu\text{c-SiO}_x\text{:H}$  material, the optical absorption edge is shifted towards higher photon energy, in comparison with both p-type and n-type  $\mu\text{c-Si}$  films. The optical band gap  $E_{04}$  in the case of this  $\mu\text{c-SiO}_x$  sample is found to be around 2.36 eV.

The variations in dark conductivity ( $\sigma_{\text{dark}}$ ), crystallinity ( $I_{\text{CRS}}$ ) and optical gap  $E_{04}$  of  $\mu\text{c-SiO}_x\text{:H}$  films, prepared at different CO<sub>2</sub> flows, are summarised in Fig. 2. The figure also includes additional data from ref. [13,16]. It is seen that  $E_{04}$  increases with an increase in CO<sub>2</sub> flow, while  $\sigma_{\text{dark}}$  and  $I_{\text{CRS}}$  decrease. For the  $\mu\text{c-SiO}_x\text{:H}$  film, prepared at CO<sub>2</sub> flow of 2 sccm, optical gap  $E_{04}$  is around 2.65 eV, but  $\sigma_{\text{dark}}$



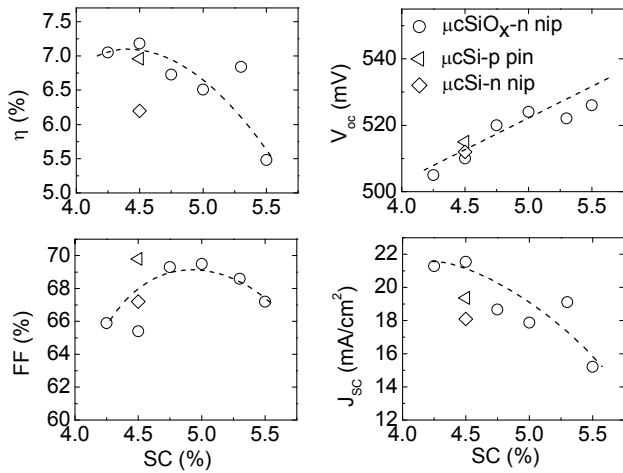
**Figure 1** PDS curve of  $\mu\text{c-SiO}_x\text{:H}$  film used as a window layer in n-i-p solar cells. The curves of n- and p-type  $\mu\text{c-Si}$  films are shown for comparison.



**Figure 2** Dark conductivity ( $\sigma_{\text{dark}}$ ) and crystallinity ( $I_{\text{CRS}}$ ) of  $\mu\text{c-SiO}_x\text{:H}$  films with varied optical gap ( $E_{04}$ ). The direction of an increase in CO<sub>2</sub> flow is indicated by the arrow. Data of p- and n-type  $\mu\text{c-Si:H}$  and  $\mu\text{c-SiC}$  are shown for comparison.

already drops significantly down to around  $10^{-11}$  S/cm and no crystalline content can be detected. At CO<sub>2</sub> flow of 1 sccm,  $E_{04} = 2.3$  eV,  $\sigma_{\text{dark}}$  is around  $5 \times 10^{-4}$  S/cm and  $I_{\text{CRS}}$  is around 35%. This flow was subsequently selected for the preparation of  $\mu\text{c-SiO}_x\text{:H}$  window layers, incorporated into solar cells. To enable a comparison, Fig. 2 also includes the data for n- and p-type  $\mu\text{c-Si}$  films and a  $\mu\text{c-SiC}$  layer, taken from ref. [12].

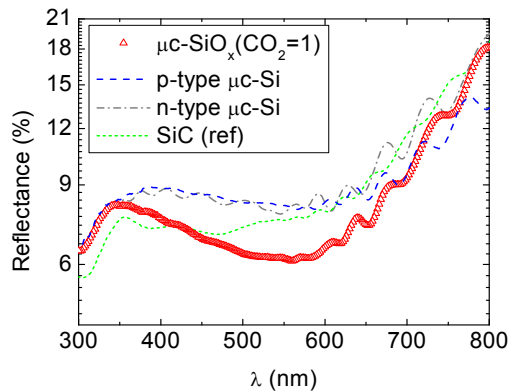
The performance of solar cells prepared with  $\mu\text{c-SiO}_x\text{:H}$  n-layer at varied i-layer SC is shown in Fig. 3. For this series of cells,  $\mu\text{c-SiO}_x\text{:H}$  window layer was deposited for 12 minutes. The best solar cell performance is obtained when the i-layer is prepared at SC = 4.5%. For the purpose of comparison, the figure also includes the performance of



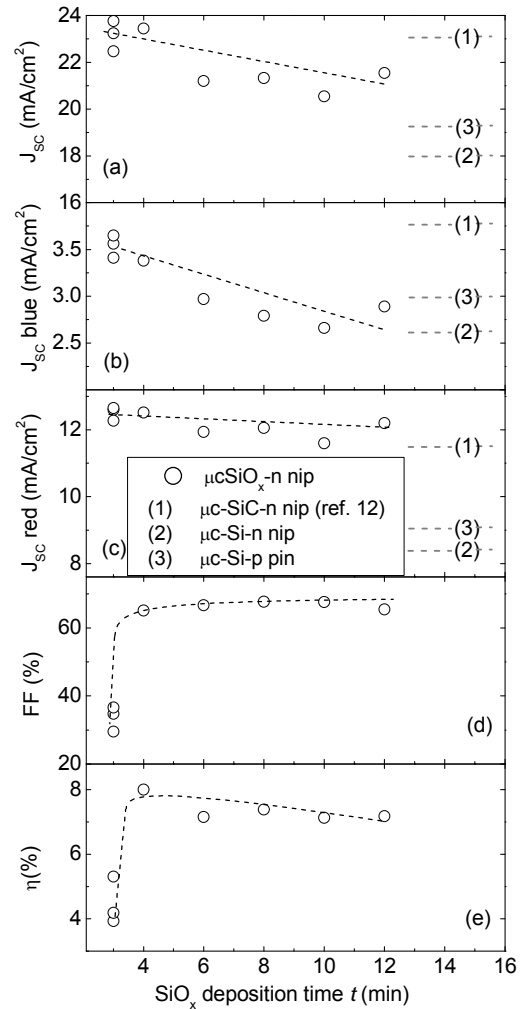
**Figure 3** Solar cell parameters ( $\eta$ , FF,  $J_{sc}$ , and  $V_{oc}$ ) of  $\mu\text{-SiO}_x\text{:H}$  n-i-p solar cells plotted as a function of SC. The data of cells using  $\mu\text{-Si}$ :H p- and n- type window layers are shown for comparison. The lines are to guide the eye.

cells prepared with p-type and n-type  $\mu\text{-Si}$  window layers at i-layer SC = 4.5%. One can see that the cells prepared with  $\mu\text{-SiO}_x\text{:H}$  window layers show an enhanced short circuit current density ( $J_{sc}$ ) and improved conversion efficiency.

Subsequently, solar cells prepared at i-layer SC = 4.5% were investigated in more detail. The results of total reflection measurements for the cells are displayed in Fig. 4. It can be seen that for the solar cells employing  $\mu\text{-SiO}_x\text{:H}$  window layers, the reflection in long wavelength region of the spectrum is significantly reduced. The effect of  $\mu\text{-SiO}_x\text{:H}$  layer thickness (growth time  $t$ ) on short circuit current density ( $J_{sc}$ ), fill factor (FF) and conversion efficiency ( $\eta$ ) is illustrated in Fig. 5. The  $V_{oc}$  values (not shown in Fig. 5) remain at nearly constant level of around 520 mV for  $t > 4$  mins and drop by around 15-20% for shorter deposition times. The  $\text{CO}_2$  flow of 1 sccm was maintained during the



**Figure 4** Total reflectance spectra of  $\mu\text{-Si}$  solar cells prepared with different window layers.



**Figure 5**  $J_{sc}$ , FF and  $\eta$  vs. the deposition time ( $t$ ) of  $\mu\text{-SiO}_x\text{:H}$  n-layer. The values are determined from the  $J$ - $V$  characteristics measured under: (a), (d) and (e) AM1.5 illumination without filters and filtered AM1.5 with (b) BG7 (blue) and (c) OG590 (red) filters.  $J_{sc}$  values of cells 1, 2 and 3 are shown by dotted lines for comparison. The lines are to guide the eye.

growth of  $\mu\text{-SiO}_x\text{:H}$  layers. Solar cells were also measured under the illuminations of a modified AM1.5 spectrum with OG590 or BG7 filters, to evaluate filtered short circuit current densities, red  $J_{sc}$  and blue  $J_{sc}$ , respectively. It is seen in Fig. 5b that the blue response of the cells ( $J_{sc}$  blue) tends to rise with reduction of  $\mu\text{-SiO}_x\text{:H}$  layer thickness, while the red- filtered  $J_{sc}$  remains at high level above 12  $\text{mA}/\text{cm}^2$ . The figure also includes the  $J_{sc}$  values of the cells prepared with alternative window layers (cells 1, 2 and 3). While the highest  $J_{sc}$  values are obtained for the cells prepared with 3 mins  $\mu\text{-SiO}_x\text{:H}$  layers, the performance of these cells is poor due to dramatic drop in FF values, as evident in Fig. 5d and Fig. 5e. The best cell in this series, fabricated with  $\mu\text{-SiO}_x\text{:H}$  window layer, is prepared at  $t = 4$  mins.

**4 Discussion** The correlation of dark conductivity ( $\sigma_{\text{dark}}$ ), crystallinity ( $I_{\text{CRS}}$ ) and optical gap ( $E_{04}$ ) with  $\text{CO}_2$  flow is evident in Fig. 2: the trend indicates that when  $\text{CO}_2$  flow increases,  $I_{\text{CRS}}$  decreases while  $E_{04}$  increases, resulting in a reduction of  $\sigma_{\text{dark}}$ . Such a trend has been previously observed for silicon oxide films and explained in terms of the effects of oxygen incorporation into silicon network [4, 5]. Additional information on the properties of  $\mu\text{-SiO}_x\text{:H}$  can be found in ref. [13, 16]. Considering the application of  $\mu\text{-SiO}_x\text{:H}$  as window layers in solar cells, there is the trade off between electrical ( $\sigma_{\text{dark}}$ ), structural ( $I_{\text{CRS}}$ ) and optical ( $E_{04}$ ) properties. While the optical band gap of  $\text{SiO}_x\text{:H}$  layer is highest for the  $\text{CO}_2$  flow of 2 sccm,  $\sigma_{\text{dark}}$  and  $I_{\text{CRS}}$  are rather low to employ this material as a doped and nucleation layer for subsequent intrinsic  $\mu\text{-Si}$  layer growth [14] in solar cells. When  $\text{CO}_2$  flow of 1 sccm is used to prepare  $\mu\text{-SiO}_x\text{:H}$  n-layer, good performance solar cells can be produced over investigated SC regime, as shown in Fig. 3. It is seen that  $V_{\text{oc}}$  increases and  $J_{\text{sc}}$  decreases with SC, while FF reaches a maximum value at certain SC. The reasons for the lower FF values of  $\mu\text{-SiO}_x\text{:H}$  n-i-p solar cells, in comparison with pin cell, are not fully understood at present and may be related to a stronger incorporation of defects during i-layer growth on  $\mu\text{-SiO}_x\text{:H}$  layer instead of p-type  $\mu\text{-Si}$ , as was suggested for the case of  $\mu\text{-SiC}$  n-i-p solar cells [12]. It is evident from Fig. 3 that  $\mu\text{-SiO}_x\text{:H}$  films can provide sufficient transparency, conductivity and crystallinity to function well as window, doped, and also nucleation layer for subsequent  $\mu\text{-Si}$  absorber layers growth at varied range of SC. A reduction of  $\mu\text{-SiO}_x\text{:H}$  layer thickness (see Fig. 5) results in slight (within 10%) improvement in red current (red  $J_{\text{sc}}$ ), while a substantial (around 30%) increase in blue response of the cell is observed, that would be consistent with reduced optical absorption in thinner films. Using  $\mu\text{-SiO}_x\text{:H}$  as a window layer, high  $J_{\text{sc}}$  values as compared to the solar cells utilising alternative window layers, namely n- and p-type  $\mu\text{-Si}$  and also  $\mu\text{-SiC}$  can be achieved, as evident in Fig. 5. Particularly, the observed high red response (red  $J_{\text{sc}}$  above  $12.5 \text{ mA/cm}^2$ ) is consistent with the high transparency due to wide optical gap (see Fig. 2) and low total reflection (see Fig. 4) for the wavelengths above 450nm. This is much above the current values obtained for cells with  $\mu\text{-Si}$  window layers (cells 2 and 3). We note slightly higher blue  $J_{\text{sc}}$  values obtained for the cell prepared with  $\mu\text{-SiC}$  window layer, that may be related to reduced total reflection (see Fig. 4) in short wavelength range and/or wider optical band gap in  $\text{SiC}$ .

The FF values drop dramatically (see Fig. 5d) nearly twice, down to around 30-35% when  $\mu\text{-SiO}_x\text{:H}$  layer is deposited for less than 4 mins, which is also accompanied by a drop in  $V_{\text{oc}}$ . In this case, the n-layer is possibly too thin to provide an appropriate built-in field in the device. Optimal  $\mu\text{-SiO}_x\text{:H}$  layer in this series of cells allows 8% conversion efficiency to be achieved ( $\text{FF} = 65.1\%$ ,  $V_{\text{oc}} = 523 \text{ mV}$ ,  $J_{\text{sc}} = 23.4 \text{ mA/cm}^2$ ) for  $1 \mu\text{m}$  thick absorber layer

and Ag back contact. Further improvement in device performance may be possible by utilising highly reflective  $\text{ZnO/Ag}$  back contact, which is currently under investigation.

**5 Conclusions** n-type  $\mu\text{-SiO}_x\text{:H}$  layers have been used as window layers in n side illuminated microcrystalline silicon n-i-p solar cells. The possibility to easily tune optical and electrical properties in n-type  $\mu\text{-SiO}_x\text{:H}$  suggests an advantage for its application as a window layer in n-side illuminated  $\mu\text{-Si}$  solar cells, particularly with respect to p-side illuminated p-i-n configuration. The results indicate that n-type  $\mu\text{-SiO}_x\text{:H}$  provides sufficient conductivity and crystallinity to function well as a doped and nucleation layer for microcrystalline i-layer growth. It also acts as a wide band gap window layer with a reduced light absorption and total reflection of solar cells, particularly in the long wavelength part of the spectrum. By optimizing the properties of  $\mu\text{-SiO}_x\text{:H}$  layers, a high short-circuit current of  $23.4 \text{ mA/cm}^2$  was achieved with an absorber layer thickness of  $1 \mu\text{m}$  and a simple Ag back reflector, which leads to a cell efficiency of 8.0%.

**Acknowledgements** The authors wish to thank T. Chen, T. Grundler and L.Xiao for a number of discussions.

## References

- [1] Y. Ichikawa, K. Tabuchi, A. Takano, S. Fujikake, T. Yoshida, H. Sakai, *J. Non-Cryst. Solids* **198–200**, 1081 (1996).
- [2] T. Jana, S. Ray, *Thin Solid Films*, **376**, 241 (2000).
- [3] Y. Matsumoto, V. Sanchez R., A. Avila G., *Thin Solid Films*, **516**, 593 (2008).
- [4] A. Janotta, R. Janssen, M. Schmidt, T. Graf, M. Stutzmann, L. Gögens, A. Bergmaier, G. Dollinger, C. Hammerl, S. Schreiber, B. Stritzker, *Phys. Rev. B* **69**, 115206 (2004).
- [5] D. Das, M. Jana, A. K. Barua, *Sol. Energy Mat. Sol. Cells* **63**, 285 (2000).
- [6] P. Buehlmann, J. Bailat, D. Domine, A. Billet, F. Meillaud, A. Feltrin, C. Ballif, *Appl. Phys. Lett* **91**, 143505 (2007).
- [7] A. Lambertz, A. Dasgupta, W. Reetz, A. Gordijn, R. Carius, F. Finger, in: *Proc. 22nd EUPVSEC*, Milan, Italy (2007) p. 1839.
- [8] C. Das, A. Lambertz, J. Hüpkes, W. Reetz, F. Finger, *Appl. Phys. Lett.* **92**, 053509 (2008).
- [9] D. Domine, P. Buehlmann, J. Bailat, A. Billet, A. Feltrin, C. Ballif, *Phys. Stat. Sol. (RRL)* **2**, **4**, 163 (2008).
- [10] T. Dylla, F. Finger, E. A. Schiff, *Appl. Phys. Lett.* **87**, 32103 (2005).
- [11] T. Dylla, S. Reynolds, R. Carius, F. Finger, *J. Non-Cryst. Solids* **352**, 1093 (2006).
- [12] Y. Huang, A. Dasgupta, A. Gordijn, F. Finger, R. Carius, *Appl. Phys. Lett.* **90**, 203502 (2007).
- [13] T. Grundler et al, these proceedings.
- [14] O. Kluth, G. Schoepe, J. Huepkes, C. Agashe, J. Mueller, and B. Rech, *Thin Solid Films* **442**, 80 (2003).
- [15] L. Houben, M. Luysberg, P. Hapke, R. Carius, F. Finger and H. Wagner, *Philos. Mag. A* **77**, 1447 (1998).
- [16] L. Xiao et al, these proceedings.