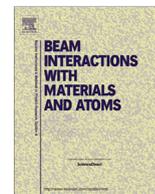




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## Interface defects in a-Si:H/c-Si heterojunction solar cells

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## ABSTRACT

The ability to incorporate a low concentration of defects at different near-surface or interface locations in a silicon heterojunction solar cell is reported here using argon ion implantation. Optical properties of the irradiated layers are addressed using spectroscopic ellipsometry while non-radiative recombinations through defects are addressed using photoconductance and photoluminescence measurements. Low energy ion irradiation at 1 keV under fluences up to  $7 \times 10^{13} \text{ cm}^{-2}$  induces no cell degradation while higher ion energies associated to larger penetration depths close to the amorphous/crystalline interface show increased degradation with ion fluence. This behavior allows to estimate some interface defect concentration threshold for cell degradation.

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## 1. Introduction

Combination of thin layers of hydrogenated amorphous silicon with a crystalline silicon substrate allows to obtain well passivated silicon surfaces which are mandatory for high efficiency silicon solar cells [1]. Silicon heterojunction solar cells have reached record conversion efficiencies of 24.7% [2], and even up to 25.6% in an interdigitated-back contact geometry [3]. They consist of a n-type crystalline silicon wafer on which both intrinsic (i) and p-type (p) hydrogenated amorphous silicon (a-Si:H) thin layers (~10 nm) are deposited by plasma enhanced CVD at low temperature (~200 °C). The electrical contact on the cell is usually made of a thin transparent conducting oxide (80 nm thick) achieved by sputtering. Both sputtering and plasma deposition processes may introduce defects at the c-Si/a-Si:H interface which in turn will determine the conversion efficiency of the cell [4,5].

The goal of this study is to understand the fundamental aspects of this interface modification via defect formation using a controlled introduction of point defects. Ion implantation of argon at low energy (between 1 keV and 17 keV) allows the modification of the a-Si:H thin layer and its interface with the crystalline silicon substrate. We control the depth and concentration of irradiation defects by varying the ion energy and fluence. The modification in the effective lifetime of minority carriers upon defect creation is characterized via photoconductance, while the generation of non-radiative recombination centers upon ion implantation is

evidenced through the decrease of the photoluminescence intensity. Understanding the degradation mechanisms of the cell under irradiation with controlled conditions will allow to improve the efficiency of future solar cells.

## 2. Experimental

High quality floated zone (FZ) phosphorus-doped (n type) c-Si(100) 4" wafers, about 250 μm thick, were first cleaned for 30 s in a solution of 5% diluted hydrofluoric (HF) acid, which allows for native oxide removal. The wafers were loaded into a plasma-enhanced chemical vapor deposition (PECVD) reactor operating at a RF frequency of 13.56 MHz. The samples were maintained at a temperature ~200 °C during deposition. Intrinsic hydrogenated amorphous silicon layers ((i) a-Si:H of about 21 nm) were coated symmetrically on both faces of the wafer. Top faces were coated with either n or p type doped hydrogenated amorphous layers ((p) or (n) a-Si:H 24 nm thick) while back faces were coated with n type hydrogenated amorphous silicon ((n) a-Si:H about 24 nm). Samples were then cut into four pieces and measured separately using the different characterization techniques. Top faces were then implanted at CSNSM using the IRMA implantor [6]. An argon ion beam energy between 1 keV and 17 keV was used with fluences spanning four orders of magnitude between  $10^{10} \text{ cm}^{-2}$  and  $10^{14} \text{ cm}^{-2}$ . Due to sample availability, at 1 keV, only (p) type top-layer a-Si:H samples were irradiated, whereas at 17 keV only (n) type samples and at 10 keV both (n) and (p) type samples were irradiated. The implantations were performed at room

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temperature with ion currents below  $2 \mu\text{A}/\text{cm}^2$  over a typical swept surface of  $28 \text{ cm}^2$  (homogeneous implantation of one fourth of wafer). Minority charge carrier lifetime has been measured before and after irradiation by using a Sinton Consulting WCT-120 tester in transient mode. The change of optical properties after irradiation is measured using a spectroscopic ellipsometer UVISEL from Horiba Jobin–Yvon. The measurements are performed in the spectral range from 1.5 eV to 4.5 eV at an incidence angle of  $70^\circ$ . Modeling of the experimental results is performed using the DeltaPsi2 software supplied with the ellipsometer. The photoluminescence (PL) was measured in reflection geometry at  $45^\circ$  from the sample at ambient temperature using an argon laser ( $\lambda = 488 \text{ nm}$ ) at a power of 20 mW and a spectrometer TRIAX320 from Horiba equipped with liquid nitrogen cooled InGaAs photodiode detector.

### 3. Results and discussion

According to the SRIM simulation program [7] (<http://www.srim.org>), the mean projected range for the argon ions is 3.5 nm, 15.5 nm and 23.2 nm respectively for 1 keV, 10 keV and 17 keV, while straggle also increases with energy from 1.5 nm to 10 nm. The depth distribution of displaced atoms was determined using the detailed calculation with full damage cascade in the SRIM program. As can be seen in Fig. 1, at 1 keV ion energy, damages are located in the top doped amorphous layer with a total number of Si atoms displaced of about 30/incident ion as obtained from the simulation. At the highest ion fluence used for this energy ( $7 \times 10^{13} \text{ cm}^{-2}$ ), the concentration of displaced atoms is about  $4 \times 10^{21} \text{ cm}^{-3}$  (about 10 at.%) at a depth of 3 nm. This estimation was obtained when multiplying the normalized concentration of vacancies as obtained from SRIM by the ion fluence: we have  $0.6 \text{ vacancy}/\text{\AA} \text{ ion} = 6 \times 10^7/\text{cm ion}$ . When multiplying this number by an ion fluence of  $7 \times 10^{13} \text{ cm}^{-2}$ , this gives a concentration of vacancies of  $4.2 \times 10^{21} \text{ cm}^{-3}$  at a depth of 3 nm. On another hand the estimated sputtering yield is about 0.57 atoms/ion, giving the sputtering of only 10th of a monolayer at the highest fluence. At 10 keV, as can be seen from Fig. 1, the damages are located in the amorphous layer up to a depth of about 35–40 nm. In this case, damages stop well before reaching the amorphous/crystalline interface situated at a depth of about 45 nm. The total number of displacements is about 250 atoms/ion. At the highest fluence of  $10^{14} \text{ cm}^{-2}$  the concentration of displaced atoms is about  $1.2 \times 10^{22} \text{ cm}^{-3}$  (about 25 at.%) at the profile maximum at a depth of about 10 nm. The highest energy of 17 keV was chosen in order

to reach the amorphous-crystalline interface, as can be seen from Fig. 1. In this case the total number of displacements is about 400/ion and the concentration of displaced atoms at the profile maximum (normalized to the ion fluence) is about  $1.35/\text{\AA} \text{ ion}$ , slightly higher than in the previous case, giving at the highest fluence of  $10^{13} \text{ cm}^{-2}$  a concentration of displaced atoms of about  $1.35 \times 10^{21} \text{ cm}^{-3}$  (about 3 at.%) at the profile maximum at a depth about 15 nm. The vacancy concentration at the amorphous-crystalline interface (about  $0.08/\text{\AA} \text{ ion}$ ), which corresponds to the argon ions end-of-range, is estimated from the simulation between about  $8 \times 10^{16} \text{ cm}^{-3}$  ( $10^{-4}$  at.%) and  $8 \times 10^{19} \text{ cm}^{-3}$  ( $10^{-1}$  at.%) for fluences in the range  $10^{10}$ – $10^{13} \text{ cm}^{-2}$ .

Strikingly, at 1 keV and  $7 \times 10^{13} \text{ cm}^{-2}$ , while the proportion of displaced atoms is rather low as well as the ion penetration depth, the observed effects as determined from spectroscopic ellipsometry are very pronounced. Indeed, as shown in Fig. 2, the real and imaginary parts of the pseudo-dielectric function are strongly modified with such an ion irradiation, shedding some light on the structural metastability of the amorphous silicon under ion irradiation. The adjustment of the results with the Tauc–Lorentz model [8] indicates some smoothing (roughness lowers from 4 nm to 2 nm), a lowering of the energy gap of the irradiated (p) doped layer from 1.79 eV to 1.77 eV, together with a lowering of the disorder level (parameter C in the model decreases from 2.8

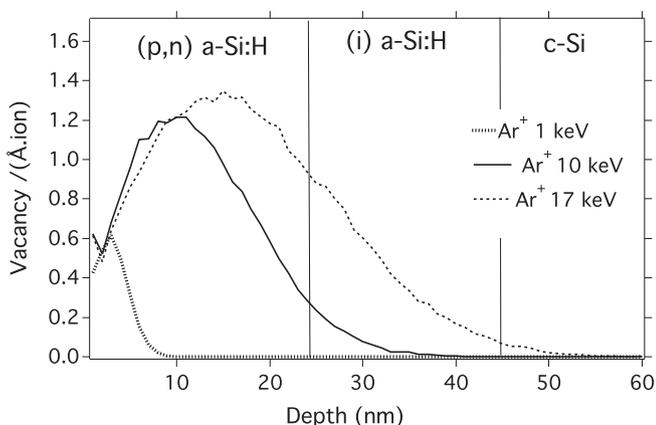


Fig. 1. Profile of vacancies, normalized by the ion fluence, created by the implantation of argon ions at 1 keV, 10 keV and 17 keV in a heterojunction solar cell, as deduced from SRIM simulations.

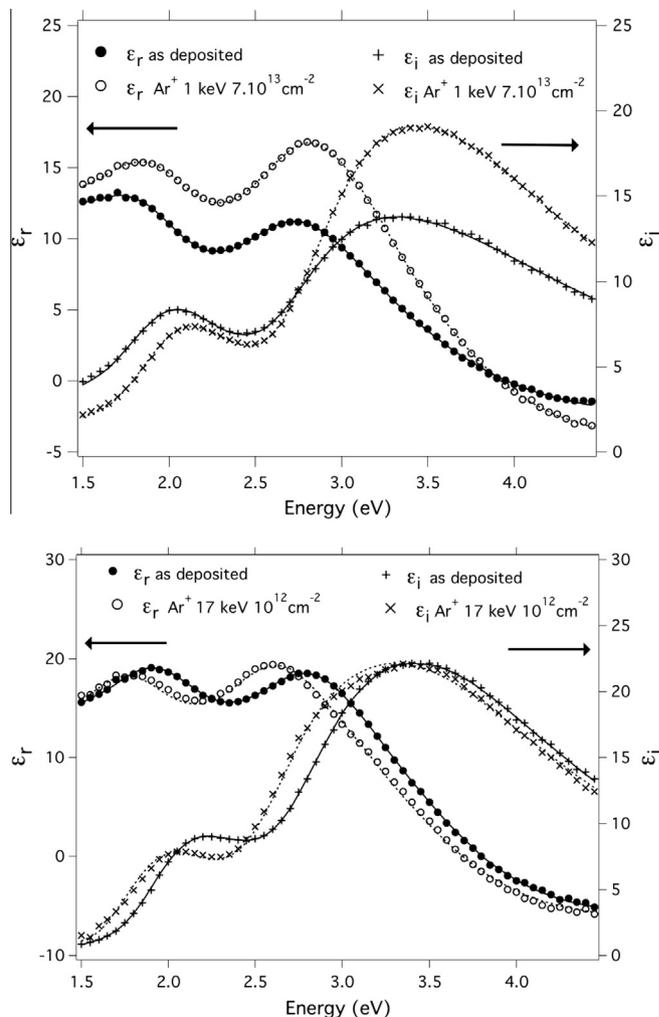


Fig. 2. Ellipsometry data (symbols) and fitting curves (lines), with Tauc–Lorentz model, of a-Si:H/c-Si heterojunction solar cell, before and after  $\text{Ar}^+$  implantation at 1 keV and 17 keV and a fluence respectively of  $7 \times 10^{13} \text{ cm}^{-2}$  and  $10^{12} \text{ cm}^{-2}$ .

to 2.4), with no significant densification of the material (parameter A almost constant at a value of 220), as the irradiated layer extends only to about 8 nm from the surface. The lowering of the energy gap after ion implantation is known to arise due to the increase in the density of localized states resulting from the introduction of point defects (dangling bonds) in the hydrogenated amorphous silicon network [9]. At 10 keV, for a similar fluence of  $10^{14} \text{ cm}^{-2}$ , the adjustment to the model gives rise to a density increase (parameter A changes from 253 to 287), associated with a thickness reduction of the (p) top layer (from about 25 nm to 20 nm) together with a disorder increase. At 17 keV, for a fluence of  $10^{12} \text{ cm}^{-2}$ , the trend is much different as can be seen from Fig. 2. In this case the values of the pseudo-dielectric functions are not much modified, but rather the position maxima indicating a quite important layer thickness modification. Indeed, an increase of the total amorphous layer thickness from about 40 nm to about 48 nm (intrinsic + (n) doped) was obtained from the data modeling. This is a very surprising result as the threshold for Si amorphization at room temperature is expected to be about 3 orders of magnitude higher in the range of  $10^{15} \text{ cm}^{-2}$  as was observed using P ion implantation for instance [10]. However, the presence of the interface with amorphous silicon together with an hydrogen reservoir in the material may lead to different diffusion mechanisms. It has been shown that hydrogen diffusion can play an important role in local Si–Si bonds restructuring [11] that may be of importance in our case. This unexpected result needs to be confirmed by other techniques, like direct observation using transmission electron microscopy.

The values of the effective minority carrier lifetimes in the c-Si wafer, after ion implantation, were measured in order to characterize the effect of amorphous silicon or interface degradation. After ion implantation at 1 keV, we did not observe any significant change in lifetimes as compared to the same samples measured in the same experiment without any ion irradiation. In any case, the lifetime values at an injection level of  $10^{15} \text{ cm}^{-3}$  only decreased by about 10–15%, for example from 3.6 ms to 3.2 ms after irradiation at the highest fluence of  $7 \times 10^{13} \text{ cm}^{-2}$ . The intrinsic limitation of ion flux at this energy on the implanter did not allow exploring higher fluences to check for possible long range effects in cell degradation [4]. At 10 keV, as can be seen from Fig. 1, damage generation stops 5–10 nm above the buried amorphous-crystalline interface, so we do not expect any direct influence of ion irradiation at this energy over lifetime of minority carriers created within bulk Si. Interestingly, for both (n) or (p) doped hydrogenated amorphous Si top layer, we observe at the highest irradiation fluence of  $10^{14} \text{ cm}^{-2}$  an important lifetime decrease, from 2.8 ms to 0.4 ms for the (p) type and from 2.9 ms to 0.1 ms for the (n) type. This result may be explained if point defects creation due to ion irradiation extends to longer distances than predicted from SRIM due for instance to defect diffusion as was also observed after ITO sputtering deposition [4,5]. At 17 keV and a low fluence of  $10^{10} \text{ cm}^{-2}$ , one can give a threshold for interface degradation as can be seen from Fig. 3 where the value at an injection level of  $10^{15} \text{ cm}^{-3}$  lowers from 4.2 ms to 3.3 ms. From SRIM simulation results shown in Fig. 1, the defect concentration created at a fluence of  $10^{10} \text{ cm}^{-2}$  at the interface region is about  $8 \times 10^{15} \text{ cm}^{-3}$ , which is consistent with an initial defect concentration about  $10^{15} \text{ cm}^{-3}$  in hydrogenated amorphous silicon. For comparison, the concentration of dangling bonds in high quality Si wafers is about  $10^{12} \text{ cm}^{-3}$  [12,13]. After irradiation at increasing fluences, one can observe lifetime reduction due to recombination of carriers on interface defects. At fluences of  $10^{11} \text{ cm}^{-2}$  and  $10^{12} \text{ cm}^{-2}$ , the measured lifetime values at an injection level of  $10^{15} \text{ cm}^{-3}$  are in the same range at respectively 0.4 ms and 0.2 ms, while the irradiation at a higher fluence of  $10^{13} \text{ cm}^{-2}$  shows a further step in the degradation with a lifetime value of only 30  $\mu\text{s}$ . This fall-off is comparable to what is

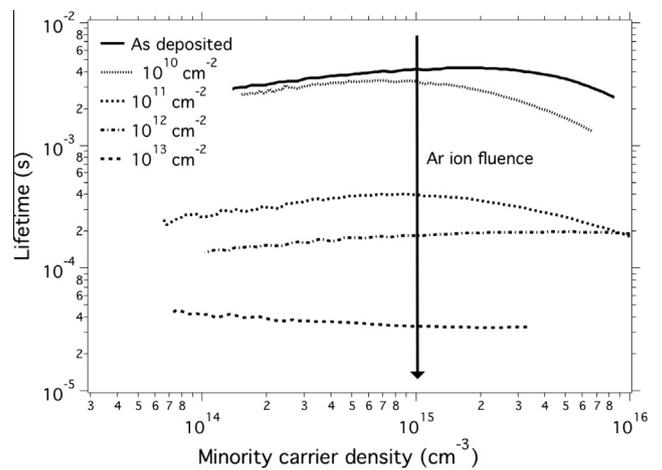


Fig. 3. Lifetime value for as deposited a-Si:H films on c-Si wafer, and after  $\text{Ar}^+$  ion implantation at an energy of 17 keV and various fluences.

observed after hydrogen plasma etching of the amorphous layers, when persistent defects are created at the crystalline silicon surface [14].

The results regarding the effects of recombination centers are consistent with photoluminescence spectroscopy results as can be observed in Fig. 4. It is generally very difficult to measure photoluminescence from bulk silicon samples due to the presence of a high number of surface defects acting as non-radiative recombination centers. In our case, the crystalline silicon is very well passivated through the deposition of hydrogenated amorphous silicon layers that allow to satisfy Si dangling bonds through hydrogen bonding. The dependence of photoluminescence yield upon different surface treatments has thus been shown to be a very sensitive probe of interface passivation [13,15,16]. Consistently, irradiations at 1 keV that did not have any effect on the lifetime values showed no influence on PL intensities. On the contrary, Fig. 4 shows a lowering by a factor about 10 of the PL intensity with an irradiation at 17 keV and a fluence of  $10^{11} \text{ cm}^{-2}$ . These conditions correspond to an interface defects concentration estimated at  $8 \times 10^{17} \text{ cm}^{-3}$ , ie about  $10^{11} \text{ cm}^{-2}$  if we assume an interface thickness of 1 nm. This value is somehow higher but consistent with the integrated defect density of  $5 \times 10^9 \text{ cm}^{-2}$  for (i) a-Si:H

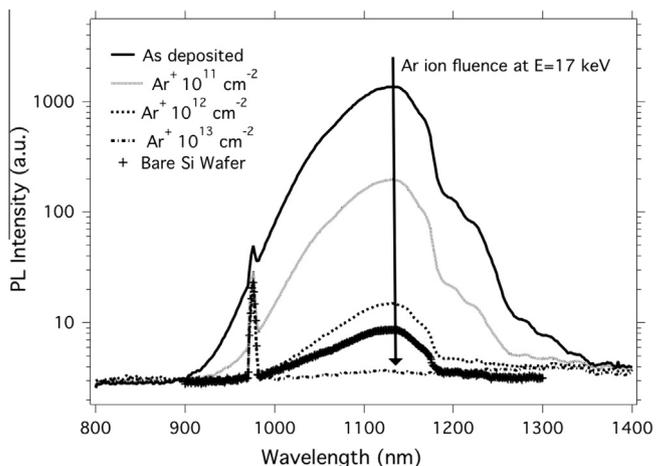


Fig. 4. Room temperature photoluminescence (PL) spectra from crystalline silicon passivated with hydrogenated amorphous silicon layers before and after  $\text{Ar}^+$  ion implantation at 17 keV and various fluences. The peak at 976 nm corresponds to an artefact at  $2 \times \lambda$ , where  $\lambda = 488 \text{ nm}$  is the laser excitation.

passivation of c-Si over an interface thickness of 5 nm that was used for numerical simulation of PL spectra in a previous study [15]. However, another study found from PL modeling about one order of magnitude higher defect densities ranging between  $10^{11} \text{ cm}^{-2}$  for well passivated interfaces with high PL yield to  $10^{13} \text{ cm}^{-2}$  for degraded interfaces with strongly quenched PL [13]. In any case, the low ion fluence threshold for PL intensity decrease illustrates the high sensitivity of the technique to a very low concentration of defects. At a fluence of  $10^{12} \text{ cm}^{-2}$ , ie an interface defect density also of about  $10^{12} \text{ cm}^{-2}$ , the PL intensity falls again by an order of magnitude, indicating a linear behavior of PL intensity with defect concentration. After irradiation at 10 keV and a fluence of  $10^{14} \text{ cm}^{-2}$ , we observed a PL intensity in the same order of magnitude (not shown here) whereas the damage range as obtained from SRIM do not extend to the interface. By comparison between these results after irradiation at different energies, given that the same level of PL intensity should be related to the same defect density, we can estimate an interface defect density of about  $10^{12} \text{ cm}^{-2}$  for the irradiation at 10 keV and a fluence of  $10^{14} \text{ cm}^{-2}$  (equivalent to the irradiation at 17 keV and a fluence of  $10^{12} \text{ cm}^{-2}$ ). At an energy of 17 keV and a higher fluence of  $10^{13} \text{ cm}^{-2}$ , the PL is too weak to be measured under our detection conditions, indicating that the passivation is worst than for a bare crystalline substrate without any treatment as shown in Fig. 4.

#### 4. Conclusion

We studied the incorporation and effects of low defect concentrations at different depths in silicon heterojunctions made of hydrogenated amorphous silicon thin layers deposited onto high quality crystalline silicon wafers. Argon ion irradiation has been shown to be a good tool for point defect introduction in near surface or interface layers. Irradiation at 1 keV up to a fluence of  $7 \times 10^{13} \text{ cm}^{-2}$  did not lead to any lifetime reduction while optical properties of the top amorphous layers are strongly affected, as observed using spectroscopic ellipsometry. An irradiation at 10 keV and a fluence of  $10^{14} \text{ cm}^{-2}$  leads to interface degradation while defect creation is supposed to be limited to a region about 5–10 nm away from the interface with crystalline silicon. In that case, defect diffusion has to be considered to explain lifetime reduction as well as PL intensity fall off. At 17 keV, an irradiation

at a fluence as low as  $10^{10} \text{ cm}^{-2}$  is responsible for lifetime reduction. At this energy, irradiation at a fluence of  $10^{12} \text{ cm}^{-2}$  leads to an increase of the amorphous layer thickness, as obtained from ellipsometry modeling. This result needs to be confirmed using TEM. Also, PL intensity evolution as a function of ion fluence at this energy gives an indication of the interface passivation quality. This degradation study of interface passivation in silicon heterojunction solar cells under ion irradiation gives some insights into the effects of recombination centers, using the possibility to localize a low concentration of defects in the surface cell layers.

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#### References

- [1] W.G.J.H.M. van Sark, L. Korte, F. Roca (Eds.), *Physics and Technology of Amorphous-Crystalline Heterostructure Silicon Solar Cells*, Springer-Verlag, 2012.
- [2] T. Mishima, M. Taguchi, H. Sakata, E. Maruyama, *Sol. Energy Mater. Sol. Cells* 95 (2011) 18.
- [3] K. Masuko, M. Shigematsu, T. Hashiguchi, D. Fujishima, M. Kai, N. Yoshimura, T. Yamaguchi, Y. Ichihashi, T. Yamanishi, T. Takahama, M. Taguchi, E. Maruyama, and S. Okamoto, presented at the 40th IEEE Photovoltaic Specialists Conference, Denver, Colorado, USA, 2014.
- [4] A. Illiberi, P. Kudlacek, A.H.M. Smets, M. Creatore, M.C.M. van de Sanden, *Appl. Phys. Lett.* 98 (2011) 242115.
- [5] B. Demaurex, S. De Wolf, A. Descoedres, Z. Charles Holman, C. Ballif, *Appl. Phys. Lett.* 101 (2012) 171604.
- [6] J. Chaumont, F. Lahu, M. Salomé, A.-M. Lamoise, H. Bernas, *Nucl. Instr. Meth. Phys. Res.* 189 (1981) 193.
- [7] J. Ziegler, J. Biersack, U. Littmark, *The Stopping of Ions in Matter*, Pergamon, New York, 1985.
- [8] A. Fontcuberta i Morral, P. Roca i Cabarrocas, C. Clerc, *Phys. Rev. B* 69 (2004) 125307.
- [9] R. Galloni, Y.S. Tsuo, F. Zignani, *Nucl. Instr. Meth. Phys. B* 39 (1989) 386.
- [10] L. Pelaz, L.A. Marqués, J. Barbolla, *J. Appl. Phys.* 96 (2004) 5947.
- [11] S. Sriraman, S. Agarwal, E.S. Aydil, D. Maroudas, *Nature* 418 (2002) 62.
- [12] R.C. Newman, *Rep. Prog. Phys.* 45 (1982) 1163.
- [13] A. Datta, M.-H. Song, J. Wang, M. Labrune, S. Chakroborty, P. Roca i Cabarrocas, P. Chatterjee, *J. Non-Cryst. Sol.* 358 (2012) 2241.
- [14] J. Geissbühler, S. De Wolf, B. Demaurex, J.P. Seif, D.T.L. Alexander, L. Barraud, C. Ballif, *Appl. Phys. Lett.* 102 (2013) 231604.
- [15] S. Tardon, M. Rösch, R. Brüggemann, T. Unold, G.H. Bauer, *J. Non-Cryst. Sol.* 338–340 (2004) 444.
- [16] S. Tardon, R. Brüggemann, *J. Phys. D Appl. Phys.* 43 (2010) 115102.