BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES
Vol. 53, No. 2, 2005

Defect states in the CIGS solar cells by photocapacitance and deep level optical spectroscopy

M. IGALSON* and A. URBANIAK

Faculty of Physics, Warsaw University of Technology, 75 Koszykowa Str., 00-662 Warsaw, Poland

Abstract. Thin film solar cells based on multinary compound Cu(In,Ga)Se_2 show record photovoltaic conversion efficiency approaching 20%. Investigation on defect physics in this compound is crucial for making further progress in the technology. In this work we present the results on photocapacitance (PC) and deep level optical spectroscopy (DLOS) for two types of cells – high efficiency Cu(In,Ga)Se_2 cell with about 20% of gallium and pure gallium $CuGaSe_2$ device. We show that PC and DLOS, employed as the techniques complimentary to deep level transient spectroscopy DLTS and admittance spectroscopy, are useful methods in providing information on defect levels in solar cells. In particular they are helpful in differentiating between levels belonging to the bulk of absorber and to the interface states. We tentatively assign some of the observed deep levels to In_{Cu} or Ga_{Cu} antisites and Cu interstitials.

Key words: solar cells, CIGS, photocapacitance, deep levels.

1. Introduction

Solar cells with Cu(In,Ga)Se_2 (CIGS) chalcopyrite semiconducting compound as an absorber are among thin film devices of highest photovoltaic efficiency, which currently is close to 20% for laboratory cells and 12% for modules [1,2]. The successful development of this technology took place despite of relatively low level of knowledge about fundamental properties of CIGS compounds, especially about defects controlling photovoltaic performance of these devices. The lack of this knowledge appears now as more and more severe limitation in the pursuit of higher efficiencies and simpler, cheaper technology of CIGS-based solar cells.

CIGS compounds are well known for their ability to accommodate large deviations from stoichiometry without impediment of their photovoltaic properties. This makes possible to use relatively simple technology for preparation of the absorber layer, without the need of very strict control over its composition. Material used for photovoltaic application is fabricated with the excess of indium In/Cu > 1 (excess of copper results in separation of Cu_2Se phase in grain boundaries and short-cutting of the device). Thus the most probable defects are V_{Cu} and In_{Cu}. The first one gives shallow acceptors responsible for p-type conductivity. Antisites In_{Cu} are compensating donors, which make the compound a compensated material with a degree of compensation estimated as 1:100 [3].

The methods well known for their usefulness on providing information on defect states in semiconductors are capacitance techniques – DLTS and admittance spectroscopy. While the experiment itself and the interpretation of results are quite straightforward in simple structures and well known materials, it is not so for the complicated photovoltaic structure with many interfaces, nonideal diode behaviour and presence of non-thermal processes of carrier emission. Additional obstacle, making both experiments and their interpretation difficult, are metastable phenomena in the electrical characteristics of these devices, which are induced by illumination and/or biasing of a device at temperatures around 300 K. Our current understanding of these phenomena relates them to special defect states, with the electronic properties similar to DX centers or "dangling bonds" in amorphous compounds [3,4]. Changes of the occupation of these defects cause the metastable changes in the doping level of absorber, which persist for days. The consequences are persistent changes of the electric field strength in the absorber and of the potential distribution within the device. This in turn influences the spectra of levels revealed by capacitance spectroscopy. One example is the so called N1 level observed in most devices in the DLTS and admittance spectra at low temperature. Its apparent thermal activation energy depends on the state of the sample. Thus N1 has been interpreted initially as the response belonging to the continuous distribution of interface electron traps, depending on the position of the Fermi level in the vicinity of the heterointerface [5,6]. Illumination or voltage bias shifts the Fermi-level, hence the activation energy is different for various states of the sample.

However, the evidences have been accumulating recently that N1 (at least in the annealed cells) belongs rather to bulk single level [7–9]. The metastabilities in the activation energy are according to [8] caused by two factors: various contribution of the electric field-enhanced tunneling to the emission rates and the changes of the po-

*e-mail: igalson@if.pw.edu.pl

sition of the Fermi-level at the hetrointerface which cause that some levels situated in the upper half of the bandgap appear or disappear in the admittance and DLTS spectra.

In this contribution we will show the results obtained by photocapacitance (PC) and deep level optical spectroscopy (DLOS), which unambiguously show that the N1 levels in the baseline CIGS devices are situated in the bulk of absorber. The same methods also have been used for investigation of the cells based on the wide band-gap $CuGaSe_2$ compound and provided some new information on the spectrum of bulk levels in this material.

2. Samples

Historically first cells with chalcopyrite semiconductor as absorber have been based on ternary compound $CuInSe_2$. Addition of gallium widens the energy gap of this material, which should increase the efficiency of the cells. However, in contrary to the expectations, the highest photovoltaic efficiency has been obtained for relatively low gallium content: $Ga/(In + Ga) = 0.2$. Up to date there is no commonly accepted explanation why higher addition of gallium in the absorber leads to the lower efficiency of the cells – whether it is a question of a specific defect spectrum or heterointerface properties [10].

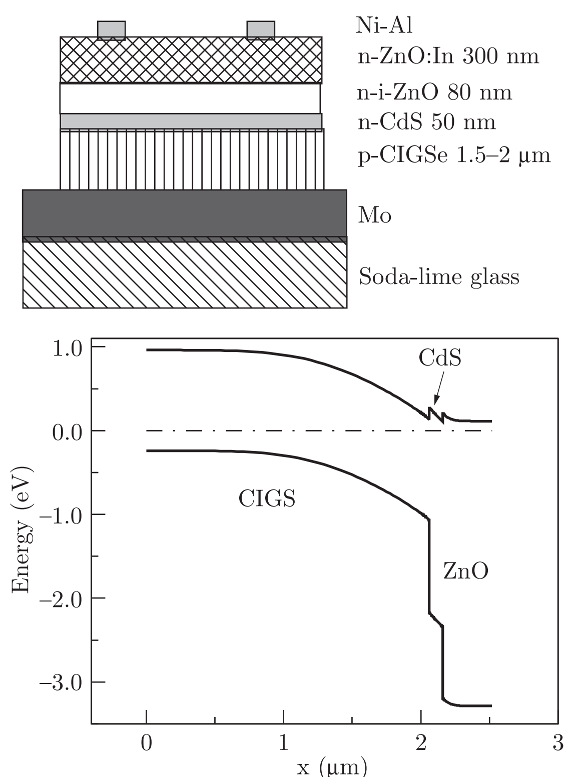

Fig. 1. Schematic of the ZnO/CdS/CIGS photovoltaic structure and its band diagram

In this contribution we present the results for high efficiency solar cells with absorbers of low gallium content ($Ga/(In + Ga) = 0.2$) prepared in Ångström Solar Center, Uppsala and cells with $CuGaSe_2$ wide band-gap absorbers fabricated in Hahn-Meitner Institute, Berlin. Comparison of the defect spectra for these two cells could perhaps provide some insight into the defect-related causes of efficiency losses in the wide band-gap cells.

Both types of cells have been prepared according to the similar recipe [11,12]. Absorbers have been deposited by co-evaporation of elements in so called three stage process on heated molybdenum-covered soda-lime glass. Then CdS buffer has been obtained by chemical bath deposition, followed by sputtered ZnO window (80 nm of i-ZnO and about 300 nm of ZnO:In). The structure has been completed by the evaporation of a Ni-Al grid (Fig. 1). Photovoltaic conversion efficiency of CIGS devices is about 14%, and of CGS cells – 8%.

3. Experimental details

In the DLTS measurements we used a DLTS-E82 apparatus in the frequency scan mode (emission rate window was swept quasi-continuously in the range 0.5–5000 s^{-1} while temperature was kept constant). We rather employed reverse-pulse DLTS (RDLTS) – a modification of the standard DLTS since RDLTS is particularly sensitive to traps in the interface region of the cell while providing essentially the same information on thermal emission rate as DLTS [13]. In the RDLTS measurement a voltage pulse is applied in the reverse direction (e.g. -1 V pulse to the junction kept at 0 V). In this mode a capture of carriers, not thermal emission is observed, so the sign of the signal should be opposite to that of the DLTS – negative for the minority carrier traps.

In the photocapacitance measurements (PC) a computer-controlled spectrometer with halogen lamp calibrated by use of a pyroelectric sensor has been used. Phase-sensitive detection by use of the SR810 lock-in amplifier has been employed to measure spectral distribution of the photocapacitance.

In the deep level optical spectroscopy (DLOS) experiments [14] we have registered a change of the DLTS signal corresponding to the specific DLTS peak induced by a weak sub-bandgap light. It has been recorded as a function of wavelength at the fixed emission rate widow. Similar method have been used for investigation of the CIGS cells by Heath *et al.* [15].

4. Experimental results

4.1. $Cu(In,Ga)Se_2$ cells. In Fig. 2 the typical Arrhenius plots of the emission rates characteristic for N1 level derived from admittance spectroscopy and RDLTS are presented. As reported already in [7–9] the emission rates depend on the state of the sample. Typical feature is also a decreasing activation energy from the trap level with decreasing temperature. This has been discussed in detail in [8] and attributed to the contribution of the electric-field assisted tunnelling to the emission process from levels crossing the Fermi-level close to the heterointerface. This contribution is most significant at low temperature and

low emission rates – in the region accessed by RDLTS. Thus the activation energies obtained from admittance spectroscopy are less distorted and should provide more reliable information on the level distance from the conduction band. The activation energy derived from the admittance data for the baseline CIGS cell is equal to about 0.24 eV after annealing at 330 K without voltage bias. After annealing with reverse bias, the energy increases to 0.32 eV [5].

Now we will check, how the sub-bandgap light affects the capacitance of the CIGS cell. Generally it might transfer carriers captured in the trap levels to the bands or fill empty trap states. At low temperature, when the thermal emission rates are slow, these processes will cause an increase or decrease of the junction capacitance, depending on the sign of the captured/released charge. Spectrum of the photocapacitance measured in the baseline device after annealing at 330 K and normalized by the photon flux is shown in Fig. 3. At low temperature two steps are observed, with energies about 0.86 and 1.0 eV (derived from the inflection points). They correspond to the increase of the negative charge in the absorber, so they belong to the transition of electrons into the empty trap states in the upper half of the band-gap. These transitions disappear from the spectrum at temperatures above 180 K, hence we conclude, that the thermal rates characteristic for the traps involved become too fast and electrons transferred by light are immediately emitted to the conduction band.

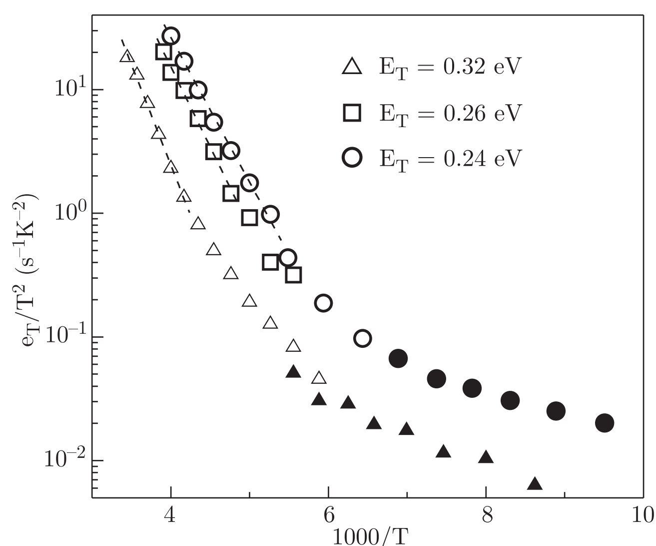

Fig. 2. Arrhenius plots of the emission rates from traps revealed in the admittance and RDLTS in the CIGS device (circles – measured after annealing at 0 V, triangles – after annealing at −2 V); and in the CGS cell (annealed at 0 V – squares). Full symbols are the data derived from RDLTS, open symbols – from admittance

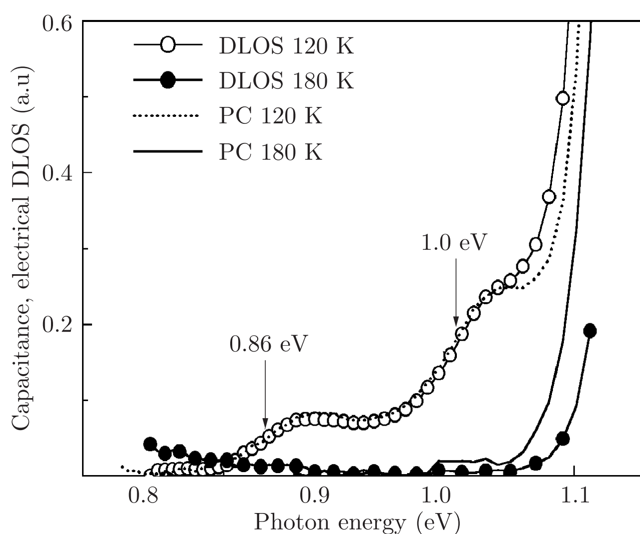

Fig. 3. Photocapacitance (continuous line) and DLOS spectra (circles) measured at 120 K and 180 K in the CIGS cell

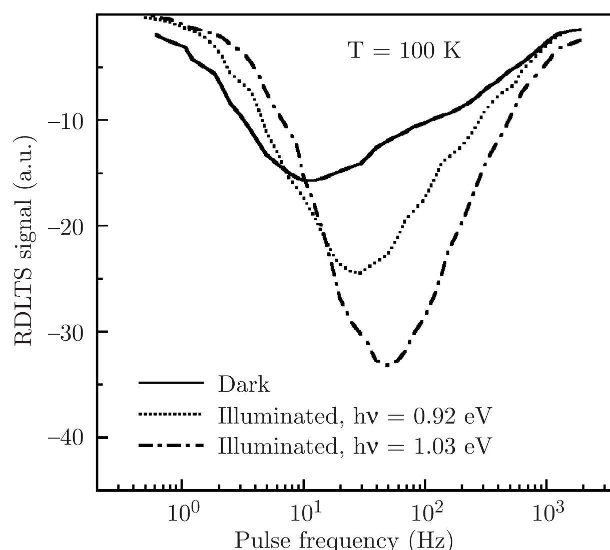

Fig. 4. RDLTS spectrum at 100 K in the frequency scan mode measured in the cell annealed under reverse bias prior to the experiment: measurement taken in the dark – continuous line, under illumination with photons of energy slightly above the first and second step – broken lines

By performing DLOS experiment we are able to check, whether sub-bandgap light influences a capture/emission process involving one specific level. In Fig. 4 the RDLTS spectrum of the sample annealed with reverse bias prior to the experiment is shown. It features the deep 0.34 eV peak with some shoulder belonging to the shallower 0.24 eV. Under sub-bandgap illumination we see an increase of the capture rate. We have to remember though that the capture rate is equal to the emission rate in our case, since only levels from the vicinity of the cross-point of the Fermi-level and trap level respond here [13]. The peak magnitude also increases, which is a natural consequence of the increasing capture rate for a fixed (and short) pulse length. Spectral distribution of the DLTS signal increment, measured at the fixed emission rate window

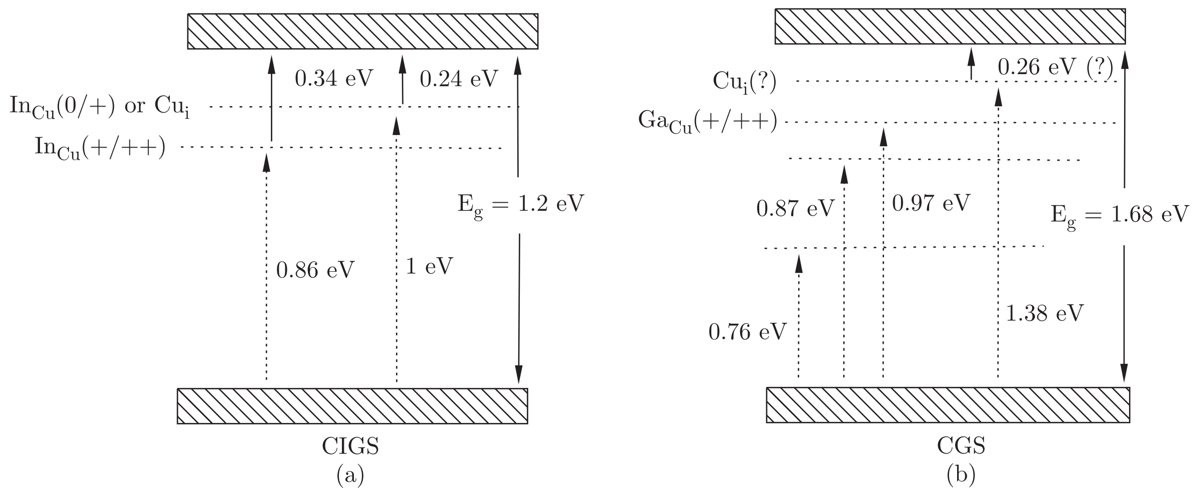

Fig. 5. Schematic of thermal (continuous lines) and optical (dotted lines) transitions observed in CIGS (a) and CGS (b) cells with tentative assignment of levels to intrinsic defects

(close to the RDLTS maximum) and normalized to the photon flux is exactly the same as the photocapacitance spectrum (see Fig. 3). Again the characteristic transition steps disappear at higher temperatures, when the thermal emission rates from both trap levels, 0.24 eV and 0.32 eV become faster than the emission rate window used in DLOS experiment.

The optical and thermal transitions observed in our measurements are illustrated in Fig. 5a. The sum of thermal and optical activation energies for both levels observed as N1 peak in the two analyzed states of the cell is close to the CIGS band-gap energy (1.2 eV) in our samples. All this findings lead us to the conclusion, that the optical transitions observed in PC and DLOS spectra involve the same N1 traps as revealed in admittance and DLTS spectroscopy. This result supports strongly the hypothesis that N1 levels in the annealed cells are discrete donor-type states in the bulk of absorber, and not the interface states at the CdS/CIGS heterointerface.

4.2. $CuGaSe_2$ cells. These cells exhibit much worse photovoltaic performance and, as it is usually the case, also worse diode behaviour – their I–V characteristics show large leakage currents and tunneling-like mechanism of current transport [16]. It is quite typical, that in these circumstances capacitance spectroscopy is not so efficient in revealing defect levels. Thus in the DLTS spectrum we observe only continuous distribution of the emission rates, and no peaks which could be attributed to the transitions to single levels. In the admittance spectrum a single level of energy 0.26 eV (see Fig. 2.) has been revealed, and two or three shallower and hardly discernible levels (not shown).

The photocapacitance spectrum of the CGS cell is relatively rich – at least four steps could be distinguished (Fig. 6). All revealed transitions originate from the transfer of electrons to the empty deep electron traps. The interpretation of these levels is here more difficult, since no DLOS experiment could be performed due to the absence of DLTS peaks in the spectrum up to 330 K. We may only notice that the sum of the energies of the PC step of 1.4 eV and thermal transition of 0.26 eV revealed by admittance is close to the bandgap energy of CGS (1.68 eV), so they might involve the same level (see Fig. 5b). The question arises why we do not observe in DLTS or admittance the other levels revealed by photocapacitance. Possible explanation is that they might be too deep (close to midgap) to be seen in the DLTS spectrum within the experimental range of temperatures (40–330 K) and emission rate windows (0.5–5000 s^{-1}).

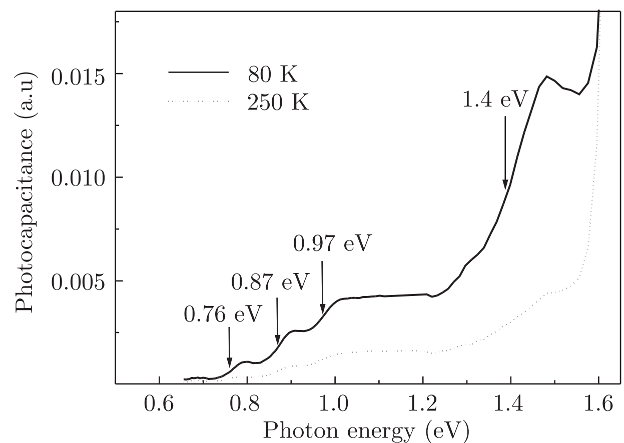

Fig. 6. Photocapacitance spectra in 80 K and 250 K measured in the CGS cell

5. Discussion and conclusions

In the CIGS samples we have observed the optical transitions of electrons from the valence band to trap levels and have been able to correlate them with the thermal transitions revealed by DLTS and admittance spectroscopies. We have concluded that these optical and thermal transitions involve the same bulk compensating donor states. The values of energies derived from our experiments match very closely the theoretical predictions for

In_{Cu} 0/+ and ++/+ level (0.25 eV and 0.34 eV below conduction band correspondingly [17]). Another bulk compensating donor, which may be taken under consideration as a candidate for the shallower of those two levels is Cu interstitial with its theoretical value of energy equal to 0.20 eV below the conduction band. This defect might be present in large concentration in the interface region of the absorber, since according to [18] its creation energy decreases in the regions, where the Fermi-level is situated close to the conduction band.

The experimental data on the levels in the CGS sample are collected in Fig. 5b. They are not so complete as for CIGS cells, since no DLTS peaks have been observed in the measurement temperature range and DLOS measurements could not be performed. In contrary to the findings of Heath *et al.* [15], we have not registered any change of the non-thermally activated DLTS signal by the sub-bandgap illumination. The optical transition of 1.4 eV and thermal of 0.26 eV, observed in admittance might involve the same level, but, as no confirmation by DLOS have not been obtained, this agreement could be only the circumstantial coincidence.

Comparing the spectrum of levels observed in CGS by photocapacitance with theoretical calculations of Zhang *et al.* [18] we notice that the step at the energy of 0.97 eV might involve a ++/+ level of Ga_{Cu} antisite (0.69 eV below the conduction band edge). Other levels with energies close to the midgap might be responsible for the reduced photovoltaic performance of this device. It is also worth noting, that Cu_i level according to [17] should be situated at the same energy below conduction band in CIS and CIGS compound. This is an argument in favour of assigning of the 0.24 eV level in CIGS and the 0.26 eV level in CGS to the copper interstitials as they feature very similar emission rates in the CIGS and CGS material.

Summing up, our experiments show that the investigation of the influence of sub-bandgap illumination on the cell capacitance can provide data helping to interpret the spectra of deep levels in the complicated photovoltaic structures. This is particularly true if the photocapacitance measurements are combined with deep level optical spectroscopy. That gives the possibility of observing at one time both types of transitions – thermal and optical – to a particular level. In the photocapacitance spectrum also the levels, which for some reasons are not observed in the admittance and DLTS measurements, might be revealed.

Acknowledgements. Authors are grateful to the colleagues from the Ångström Solar Center and the Hahn-Meitner Institute for providing samples used in that study.

References

[1] J. A.M. Abushama, S. Johnston, T. Moriarty, G. Teeter, K. Ramanathan, and R. Noufi, "Properties of ZnO/CdS/$CuInSe_2$ solar cells with improved performance", *Prog. Photov.: Res. Appl.* 12, 39–45 (2004).

[2] B. Dimmler, M. Powalla, and H.W. Schock, "CIS-based thin-film photovoltaic modules: potential and prospects", *Prog. Photov.: Res. Appl.* 10, 149–57 (2002).

[3] U. Rau and H.W. Schock, "Electronic properties of Cu(In,Ga)Se_2 heterojunction solar cells-recent achievements, current understanding, and future challenges", *Appl. Phys.* A69, 131–47 (1999).

[4] M. Igalson and H.W. Schock, "The metastable changes of hole and electron trap spectra of $CuInSe_2$-based photovoltaic devices", *J. Appl. Phys.* 80, 5765–9 (1996).

[5] A. Niemegeers, M. Burgelman, R. Herberholz, U. Rau, D. Hariskos, and H.W. Schock, "Model for electronic transport in Cu(In,Ga)Se_2 solar cell", *Prog. Photovolt.: Res. Appl.* 6, 407–21 (1998).

[6] P. Zabierowski, U. Rau and M. Igalson, "Classsification of the metastabilities in the electrical characteristics of ZnO/CdS/Cu(In,Ga)Se_2 devices", *Thin Solid Films* 387, 147–50 (2001).

[7] M. Igalson, M. Bodegård, L. Stolt, and A. Jasenek, "The defected layer" and the mechanism of the interface-related metastable behavior in the ZnO/CdS/Cu(In,Ga)Se_2 devices", *Thin Solid Films* 431–432C, 153–157 (2003).

[8] P. Zabierowski and M. Edoff, "Laplace-DLTS analysis of the minority carrier traps in the Cu(In,Gas)Se_2-based solar cells", *Thin Solid Films* 480–481C, 301–306 (2005).

[9] M. Igalson and P. Zabierowski, "Electron traps in Cu(In,Ga)Se_2 absorbers of thin film solar cells studied by junction capacitance techniques", *Opto-Electron. Rev.* 11, 261–267 (2003).

[10] S. Siebentritt, "Wide gap chalcopyrites: material properties and solar cells", *Thin Solid Films* 403–404, 1–8 (2002).

[11] J. Kessler, M. Bodegård, J. Hedström, and L. Stolt, "Baseline Cu(In,Ca)Se_2 device production: control and statistical significance", *Sol. Ener. Mat. Sol. Cells* 67, 67–76 (2001).

[12] S. Schuler, S. Nishiwaki, M. Dziedzina, R. Klenk, S. Siebentritt, and M.C. Lux-Steiner, "Solar cells based on PVD grown $CuGaSe_2$ absorber and device properties", *Mater. Res. Soc. Symp. Proc.* Warrendale, PA, USA 668, H5.14.1–6. (2001).

[13] M. Igalson and P. Zabierowski, "Transient capacitance spectroscopy of defect levels in CIGS devices", *Thin Solid Films* 361–362, 371–7 (2000).

[14] P. Blood and J.W. Orton, *The Electrical Characterization of Semiconductors*, pp. 698–704, Academic Press Ltd, London, 1992.

[15] J.T. Heath, J.D. Cohen, W.N. Shafarman, D.X. Liao, and A.A. Rockett, "Effect of Ga content on defect states in $CuIn_{1-x}Ga_xSe_2$ photovoltaic devices", *Appl. Phys. Lett.* 80, 4540–4542 (2002).

[16] J. Malmström, J. Wennerberg, and L. Stolt, "A study of the influence of the Ga content on the long-term stability of Cu(In,Ga)Se_2 thin film solar cells", *Thin Solid Films* 431–432, 436–442 (2003).

[17] S.B. Zhang, S.H. Wei, A. Zunger, and H. Katayama-Yoshida, "Defect physics of the $CuInSe_2$ chalcopyrite semiconductor", *Phys. Rev.* B57, 9642–9656 (1998).

[18] S.H. Wei, S.B. Zhang, and A. Zunger, "Effects of Ga addition to $CuInSe_2$ on its electronic, structural, and defect properties", *Appl. Phys. Lett.* 72, 3199–3201 (1998).