Reverse-bias DLTS for investigation of the interface region in thin film solar cells

M. IGALSON[1]*, P. ZABIEROWSKI[1], A. ROMEO[2], and L. STOLT[3]

[1]Faculty of Physics, Warsaw University of Technology,
75 Koszykowa Str., 00-660 Warszawa, Poland
[2]Thin Film Group, Institute of Quantum Electronics,
ETH-Zurich, 1 Technopark Str., 8005 Zurich, Switzerland
[3]Ängström Solar Centre, Uppsala University,
P.O. Box 534, 751 21 Uppsala, Sweden

The interface states in TCO/CdS/CdTe and ZnO/CdS/Cu(In,Ga)Se_2 photovoltaic devices has been studied by use of reverse-bias transient capacitance spectroscopy. Laplace transform analysis has been used in order to enhance a spectral resolution of the technique. It is shown that the method yields useful information on the electronic characteristics of the heterointerface in the thin film solar cells. The conclusions include a degree of inversion of the heterointerface and a contribution of tunneling in the carrier transport. The influence of these factors on photovoltaic performance of the devices under study is discussed.

Keywords: DLTS, interface, solar cell, CdTe, Cu(In,Ga)Se_2.

1. Introduction

Solar cells based on CdTe and Cu(In,Ga)Se_2 are most promising thin film heterojunction devices, which have already reached the commercialisation phase [1]. However, much of their electronic properties are still not fully understood. In particular, the interface region and a relation of its characteristics to the device performance it is an issue that needs more thorough investigation.

DLTS and other junction techniques supply information on the interface states in the MIS-type structures, since a change of the Fermi-level position at the I/S interface is induced by use of a voltage pulse. Analysis of the transient capacitance following a pulse yields information on the concentration and electronic parameters of the interface levels [2].

Reverse-bias DLTS (RDLTS) is a modification of the standard DLTS technique, in which a voltage pulse in the reverse direction is superimposed on the quiescent bias. Therefore it is a capture process, not an emission as in the standard DLTS, which is analysed after removing a pulse. Since capture is most effective for the levels intersecting a Fermi-level, the emission rate is almost equal to the capture rate and the RDLTS signal gives basically the same information on the electronic parameters of states involved as DLTS but might have certain advantages over DLTS in the specific circumstances.

RDLTS has been first proposed for studying of the electric field influence on the capture cross section for the bulk traps in GaAs [3] and then used also to investigate the interface defects [4]. In Ref. 5 it has been noticed, that a capacitance signal due to charging of the interface states in the CIGS devices is much more pronounced and suitable for the investigation in the RDLTS mode. Further improvement in the accuracy and spectral resolution of the method has been achieved by replacing the standard DLTS processing based on the electronically set "emission rate window" by a computer analysis of the capacitance transients employing an inverse Laplace transform [6]. In this method, introduced by Dobaczewski *et al.* [7], a general relation between the capacitance transient and a density of deep states $g(E_T)$ is employed

$$\Delta C(t) \propto \int g(E_T)\exp\{-e_T(E_T)t\}dE_T . \qquad (1)$$

Here e_T is the emission rate from the trap of the depth E_T

$$e_T = \upsilon_0 \exp\{-E_T/kT\}. \qquad (2)$$

Laplace transformation of the experimental capacitance transient gives a spectrum of emission rates from one or more levels contributing to the transient at a given temperature, with much higher spectral resolution than the other junction spectroscopic methods.

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

In this paper we will present the results of the interface analysis obtained by the transient capacitance methods for two types of thin film photovoltaic devices: ZnO/CdS/Cu(In,Ga)Se_2 of efficiency about 14% and ITO/CdS/CdTe of efficiency 9%. The details of the preparation technique of these structures are given in Ref. 8 and 9 respectively. In both structures the CdS layer is depleted [10,11], which makes possible the observation of the response due to levels at the CdS/absorber interface.

The measurements have been performed in a closed cycle He refrigerator by use of DLS-E82 capacitance bridge. CONTIN numerical program [12] has been used for the calculations of the Laplace transforms.

2. Results

The spectra of DLTS and RDLTS for CdTe-based device are compared in Fig. 1. Similarly as for the Cu(In,Ga)Se_2 (CIGS) structures [5], we observe a positive signal, when the pulse superimposed on the quiescent voltage is in the forward direction. Thus, it is due to donor-type traps, which have to be situated at or close to CdS/absorber interface. In the reverse-bias mode the sign of the signal is reverted, but the emission rate is almost the same, as expected. A large difference of magnitude of the peaks is observed, which we attribute to the absence of effects related to the majority carriers capture in the bulk traps and interface states in the RDLTS mode. A position of RDLTS peaks does not change with quiescent bias as shown in Fig. 2, so a discrete single level or a continuous distribution of high density of interface states pinning the Fermi-level strongly at a fixed energy is here involved. In Refs. 10 and 11 it has been argued, that a continuous distribution of interface levels of order of 10^{13} $eV^{-1}cm^{-2}$, not a single level, is observed here, since the emission rates change under the influence of certain external factors as illumination or thermal annealing.

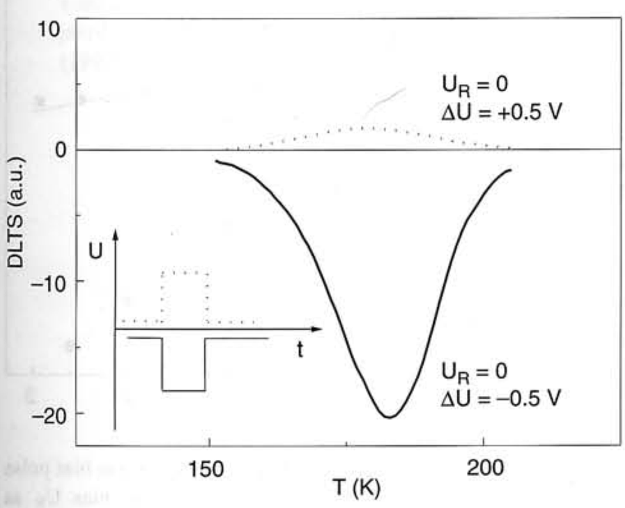

Fig. 1. The comparison of DLTS (dotted line) and RDLTS (continuous line) spectrum obtained for the CdTe device for the emission rate window $e_T = 5500$ s^{-1}.

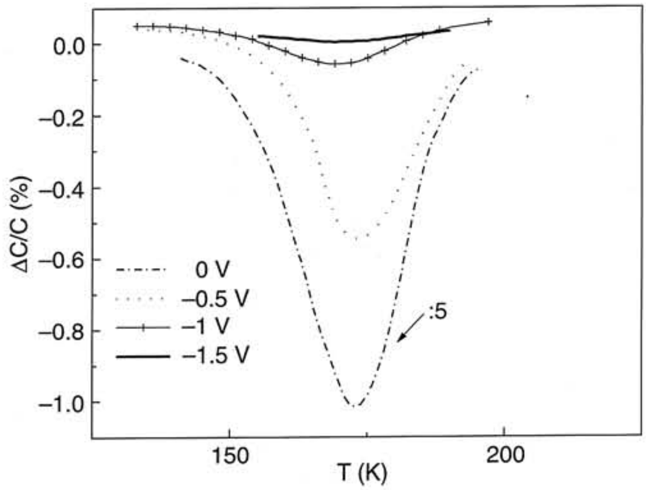

Fig. 2. RDLTS spectra obtained for the CdTe device by using of the same pulse height $\Delta U = -0.5$ V superimposed on the quiescent reverse biases indicated in the picture. The emission rate window has been set to 2200 s^{-1}.

The RDLTS signal is well suited for Laplace transform analysis, since it is high enough and not distorted by majority carrier contributions. For both types of devices the calculations give sharp, well-defined peaks and a very accurate determination of the emission rates as a function of temperature is possible. The examples of the results obtained for the CdTe- and CIGS-based devices are shown in Figs. 3 and 4, respectively. For the CIGS device apart of well developed peaks corresponding to the interface states, one might observe less pronounced signal, which has been attributed to a discrete donor level crossing the electron Fermi-level in the vicinity of the heterointerface [13].

The emission rates plotted against the inverse temperature for both types of devices are shown in Fig. 5. The activation energies calculated from these plots should corre-

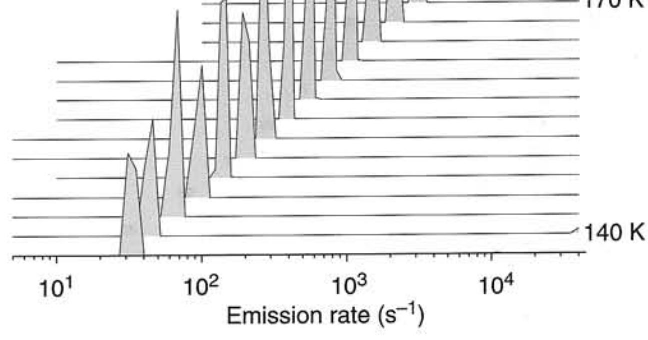

Fig. 3. The spectra of the emission rates calculated from the RDLTS capacitance transients by use of the inverse Laplace transform for the CdTe device in the temperature range 140–170 K.

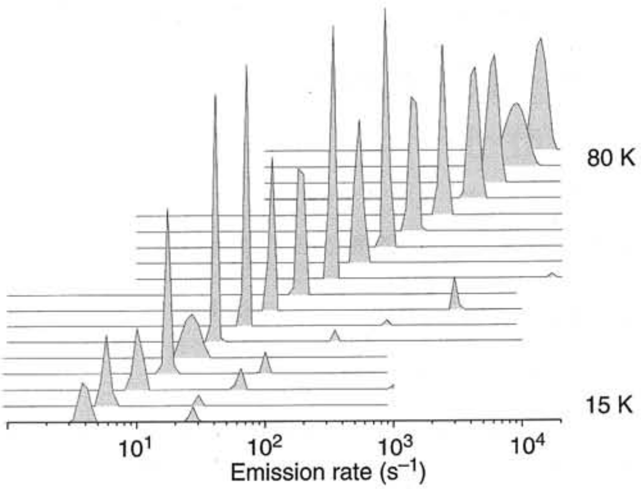

Fig. 4. The spectra of the emission rates calculated from the RDLTS capacitance transients by use of the inverse Laplace transform for CIGS device in the temperature range 15–80 K.

spond to the energetic distance between the Fermi-level position at the CdS/absorber interface and conduction band. For CdTe that activation energy is well-defined and equal to 0.32 eV. For the CIGS-based device the Arrhenius plots are strongly nonlinear. The activation energy of the emission rate is here equal to 0.07 eV at LN temperature and declines with decreasing temperature. This implies a presence of other mechanism, apart of thermal emission, which affects the emission/capture rate. A tunneling of electrons through a "spike" due to a negative conduction band offsets at the CdS/CIGS interface has been proposed to account for that [14].

The investigation of the dependence of the RDLTS signal amplitude on the quiescent voltage provides additional information on the transport properties of the junction. Following the analysis presented in Ref. 2 we obtain that a relative capacitance change after the voltage pulse ΔU superimposed on the total quiescent reverse bias $U_R + U_b$ might be expressed by

$$\Delta C/C = k\frac{\Delta U}{2(U_R + U_b)} \tag{3}$$

where k is the factor expressing relative potential distribution between the n- and p- side of the junction. The relation has been obtained under assumptions of a high interface states density and a small depleted region at the n side of the junction as compared to p (k<< 1). Expression (3) is valid if the hole transport to interface is neglected. As we see in Fig. 6, it is obeyed well enough in the case of the CIGS junctions with reasonable value of k = 1/5.

In CdTe devices however we observe much steeper dependence of the RDLTS amplitude on the reverse voltage bias. We also know, that tunneling prevails in the carrier transport in these structures [15]. Holes, recombining with electrons at the interface, will diminish a value of $\Delta C/C$ so it should decrease with increasing probability of tunneling. Electric field-enhanced tunneling depends exponentially on the inverse of electric field in the junction. As it can be seen in Fig. 6, the amplitude of RDLTS signal is indeed linear, when plotted against inverse voltage in the semilogarythmic scale. Therefore we conclude, that the observation of the deviation of RDLTS signal from Eq. (3) is a measure of the contribution of tunneling in the junction transport.

3. Conclusions

In the n^+-p photovoltaic devices the best performance is expected, when interface is as extrinsic as possible [16]. Comparing the results for the CIGS and CdTe devices we

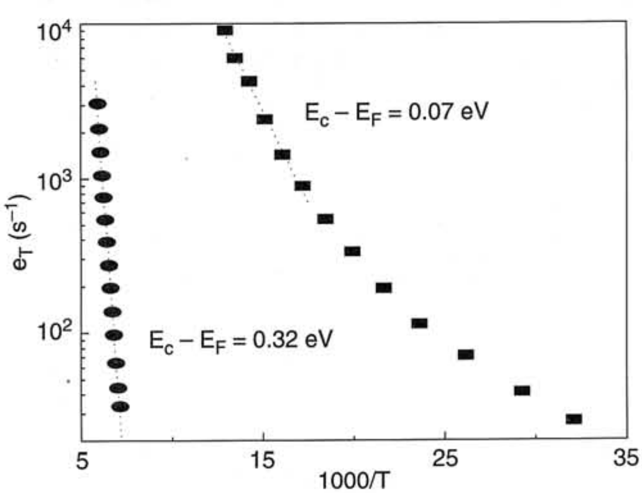

Fig. 5. The emission rates from the interface states as a function of the inverse temperature for the CdTe (circles) and CIGS (squares) devices.

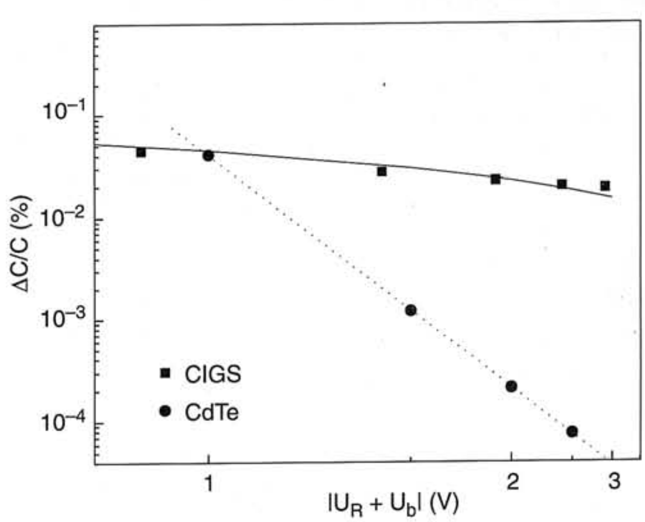

Fig. 6. The relative capacitance change after the reverse bias pulse of height 0.5 eV superimposed on the quiescent bias U_R as a function of the total voltage bias across the junction for CIGS and CdTe devices. The expression (3) for the CIGS junction is plotted as a continuous line.

conclude, that the first one is closer to optimal structure, with Fermi-level pinned very near to the conduction band at the heterointerface. Probably too wide (0.5 μm) and lightly doped CdS layer is responsible for relatively high value of (E_c–E_f) in the CdTe structures. Another source of efficiency losses is a high contribution of tunneling in the carrier transport, which might also be estimated by use of RDLTS. Availability of holes at the interface increased by electric-field enhanced tunneling enhances the recombination of photoelectrons via interface states.

Summing up we have shown, that the RDLTS method yields essential information on the interface region in thin film heterojunction structures, which helps to determine the factors significant for the efficiency loss in the thin film photovoltaic devices.

Acknowledgements

This work has been supported by the State Committee for Scientific Research (KBN) grant No 8T 11B 087 12 and by Swiss National Science Foundation under the program „Institute Partnership".

References

1. W. Fuhs and R. Klenk, "Thin-film solar cells – overview", *Proc. 2nd World Conf. on Photovoltaics Solar Energy Conversion*, Vienna, 381–386 (1998).
2. F. Murray, R. Carin, and P. Bogdanski, "Determination of high-density interface state parameters in metal-insulator--semiconductor structures by deep level transient spectroscopy", *J. Appl. Phys.* **60**, 3592–3598 (1986).
3. G.P. Li and K.L. Wang, "A novel technique for studying electric field effect of carrier emission from a deep level center", *Appl. Phys. Lett.* **42**, 838–840 (1983).
4. F. Lu, D. Gong, and X. Wang, "Detection of defects at homoepitaxial interface by deep level transient spectroscopy", *J. Appl. Phys.* 77, 213–217 (1995).
5. M. Igalson and L. Stolt, "DLTS spectra of thin film photovoltaic devices based on Cu(In,Ga)Se_2", *Proc. 14th European Photovoltaic Solar Energy*, Barcelona, 2153–2156 (1997).
6. M. Igalson and P. Zabierowski, "Laplace-DLTS of Cu(In,Ga)Se_2-based devices", *Proc. 11th Int. Conf. on Ternary & Multinary Compounds, Inst. Phys. Conf. Ser.* **152**, Salford, 931–934 (1997).
7. L Dobaczewski, P. Kaczor, I.D. Hawkins, and A.R. Peaker, "Laplace transform deep level transient spectroscopic studies of defects in semiconductors", *J. Appl. Phys.* **76**, 194–198 (1994).
8. J. Hedström, H. Olsen, M. Bodegard, A. Kylner, L. Stolt, D. Hariskos, M. Ruckh, and H. Schock, "ZnO/CdS/sCu(In,Ga)Se_2 thin film solar cells with improved performance", *Proc. 23rd IEEE Photovoltaic Specialists Conf.*, Luisville, 364–371 (1993).
9. A. Romeo, A. N. Tiwari, H. Zogg, M. Wagner, and J.R. Gnter, "Influence of transparent conducting oxides on the properties of CdTe/CdS", *2nd World Conf. on Photovoltaics Solar Energy Conversion*, Vienna, 1105–1108 (1998).
10. R. Herberholz, M. Igalson, and H.W. Schock, "Distinction between bulk and interface states in CuInSe_2/CdS/ZnO by space charge spectroscopy" *J. Appl. Phys.* **83**, 318–325 (1998).
11. M. Igalson, R. Stefanov, N. Stratieva, and G. Pchelarov, "DLTS study of bulk and interface traps in CdS/CdTe photovoltaic structures", *Proc. 2nd World Conf. on Photovoltaic Solar Energy Conf.*, Vienna, 1101–1104, 1998.
12. S. W. Provencher, "CONTIN – a general purpose constrained regularisation program for inverting noisy linear and integral equations", *Comput. Phys. Commun.* **27**, 213–227 (1982).
13. P. Zabierowski, M. Igalson, and H. W. Schock, „Light-induced metastabilities in the interface region of Cu(In,Ga)Se_2-based photovoltaic devices studied by Laplace transform junction spectroscopy"; Polycrystalline semiconductors V, *Proc. 5th Int. Conf., Schwabisch Gmünd* 1998, *Solid State Phenomena* **67-68**, 403–408 (1999).
14. P. Zabierowski and M. Igalson, E-MRS 1999 Spring Meeting, "Thermally assisted tunneling in Cu(In,Ga)Se_2-based photovoltaic devices", *Thin Solid Films*, in press.
15. M. Wimbor, A. Romeo, and M. Igalson, "Electrical characterisation of CdTe/CdS photovoltaic devices", *Opto-Electronics Review* **8**, 375–377 (2000).
16. H.J. Pauwels and G. Vanhoutte, "The influence of interface states and energy barriers on the efficiency of heterojunction solar cells", *J. Phys. D: Appl. Phys.* **11**, 649–667 (1978).