Defect Characterization of CIS-related Compound Solar Cells by Admittance Spectroscopy and DLTS

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1. Introduction

Thin film solar cells based on Cu(In,Ga)(S,Se)₂ family compounds (CIS) have reached almost 20% efficiency in the lab [1] and full size PV-modules are being produced on an industrial scale by several companies [2]. In many respects, however, the excellent performance is much ahead of the understanding of electro-optical properties of CIS materials and still using try-and-error approach may slow down future progress. Like for most semiconductor devices, also for CIS-based solar cells defect related issues are of primary importance. This contribution gives an overview of defect investigations in CIS devices by means of space charge techniques: admittance spectroscopy (AS) and deep level transient spectroscopy (DLTS). Special attention is paid to defects with negative-U correlation energy since their presence markedly hinders the interpretation of electrical measurements.

2. Theoretical predictions

According to recent first principles calculations two intrinsic defects in CIS (In_{Cu} and V_{Se} as well as their complexes with V_{Cu}) exhibit metastable behaviour [3, 4]. In both cases the change of the charge state of the defect is accompanied by a large lattice relaxation which results in an inverted ordering of their energy levels. In consequence both defects give rise to large non-uniformities of charge distributions in the CIS absorber [5]: in the close-tointerface region there exists a thin absorber layer (so-called p^+ layer) with excess negative charge on the order of 10^{17} - $10^{18}\mbox{ cm}^{-3}$ accumulated at In_{Cu} and V_{Se} in their metastable configurations. At farther distances from the junction both defects act as compensating donors and the net acceptor concentration decreases by orders of magnitude to 10^{15} - 10^{16} cm⁻³. The charge distributions change metastably under voltage bias or illumination [5]. V_{Se} gives more persistent changes and after capturing of electrons the additional negative charge remains frozen below 250 K (see an example in Fig. 1) whereas In_{Cu} defects are able to adjust their charge state to the actual electron and hole concentrations even at low temperatures. The metastable defect distributions play an important role in the interpretation of AS and DLTS data.

3. Experimental results

Metastable defect conversions

Typically at temperatures above 250 K DLTS spectra are characterized by broad featureless response dominated by large non-exponential capacitance transients due to metastable defect conversions:

$$\begin{split} (V_{Se} - V_{Cu})^{-} + 2h &\rightarrow (V_{Se} - V_{Cu})^{+} : \Delta E \approx 0.3 \text{ eV} \\ (V_{Se} - V_{Cu})^{+} + e &\rightarrow (V_{Se} - V_{Cu})^{-} + h: \Delta E \approx 0.1 \text{ eV} \\ (V_{Se} - V_{Cu})^{+} - 2h &\rightarrow (V_{Se} - V_{Cu})^{-} : \Delta E \approx 0.8 \text{ eV} \end{split}$$

Thorough analysis conducted in [6,7] confirmed the predicted values of energy barriers associated with above transitions.



Fig. 1 Typical low temperature (T<200 K) space charge distributions revealed by capacitance-voltage or drive level capacitance profiling in CIS-based devices. Metastable states were induced by light- or -2 V reverse bias soaking for 1 h at 300 K.

Low temperature AS and DLTS

Below 250 K both techniques detect minority carrier (electron) signal, called in the literature N1 [8]. It is attributed to donor-like surface states which pin the Fermi level at the buffer/absorber interface close to conduction band and/or to compensating donors charged in the close-to-interface CIS region [8, 9]. The activation energy of N1

states ranges between 350 meV and 50 meV. The height of N1 admittance step corresponds to the width of the buffer layer, independent on applied bias [10, 5]. Hence the ZnO/buffer/CIS devices behave in capacitance measurements analogically to MIS-like structures with the buffer playing the role of an insulator. The analysis of the height of DLTS peaks reveals that CIS are highly compensated materials [11].



Fig. 2 Arrhenius plots of experimental emission rates (symbols) measured by Laplace-RDLTS for N1 compensating donors. Solid lines represent emission rates calculated in the TAT model. Inset graphs the close-to-interface region of CIS absorber. Non-uniform band banding is due to a negative charge accumulated at acceptor states.

The emission rates of N1 traps change metastably after prolonged illumination or reverse biasing the junction. It was found that they are strongly influenced by thermally assisted tunnelling (TAT) [9]. In consequence, the position of the peaks in the DLTS and AS spectra depends not only on activation energy and capture cross sections but also on electrical field and corresponding Arrhenius plots are nonlinear as illustrated in Fig. 2. Careful investigations using the TAT model have shown that (i) illumination induced metastable increase of the emission rates is caused by the simultaneous lowering of the barrier height and the decrease of the electrical field and (ii) reverse bias causes metastable increase of both activation energy and the electrical field [9]. These changes are in agreement with charge redistribution on negative-U centres observed in CVprofiles: the decrease or increase of the electric field is due to the passivation or accumulation of the negative charge at deep acceptor states in the p+ layer, respectively. The change of activation energy can be ascribed to a different contribution from bulk or interface defects to the N1 signal [9, 12]. The states which are involved are bulk compensating donors located 340 meV, 260 meV and 190 meV below the conduction band and crossed by E_F in the vicinity of the buffer/absorber interface and a continuous distribution of interface states ranging from 50 meV to 100 meV as indicated in the inset of Fig. 2. The contribution of the individual states to the capacitance response depends on a given deep defect distribution as well as Fermi level position at the buffer/CIS interface.

4. Conclusions

In CIS-based devices intrinsic deep defects with negative correlation energy significantly influence space charge profiles. Illumination or bias induced metastable structural reconfigurations can be monitored by capacitance transients at temperatures above 250 K. Resulting electrical field distributions affect low temperature DLTS and AS spectra of minority carrier traps which can be understood within the p^+ layer model involving thermally assisted tunnelling.

It will be demonstrated that this model can also serve for explanation of metastabilities observed around room temperature in light current-voltage characteristics which is important for device performance in working conditions.

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References

- M. A. Contreras, K. Ramanathan, J. AbuShama, F. Hasoon, D. L. Young, B. Egaas, and R. Noufi, Prog. Photovoltaics 13, 209 (2005).
- [2] H.S. Ullal, and B. von Roedern, Proceedings of 22nd European Photovoltaic Solar Energy Conference, 3-7 September 2007, Milan, Italy, (2007) 1926
- [3] S. Lany and A. Zunger, J. Appl. Phys. 100, 113725 (2006)
- [4] S. Lany and A. Zunger, Phys. Rev. Lett. 100, 016401 (2008)
- [5] M. Cwil, M. Igalson, P. Zabierowski, S. Siebentritt, J. Appl. Phys. 103, 063701 (2008)
- [6] A.Urbaniak, M. Igalson, S. Siebentritt, *Mater. Res. Soc. Symp. Proc.* Vol. 1012, Y12-14 (2007)
- [7] A.Urbaniak, M.Igalson, Thin Solid Films, 517, 2231 (2009)
- [8] R. Herberholz, M. Igalson, and H. W. Schock, J. Appl. Phys. 83, 318 (1998)
- [9] P. Zabierowski, M. Edoff, Thin Solid Films, 480-481, 301 (2005)
- [10] A. Niemegeers, M. Burgelman, R. Herberholz, U. Rau, D. Hariskos, and H. W. Schock, Prog. Photovoltaics 6, 407 (1998)
- [11] P. Zabierowski, Ćwil, M. Edoff, Mater. Res. Soc. Symp. Proc. 865, F12.3.1 (2005)
- [12] M. Igalson, A. Urbaniak, and M. Edoff, Thin Solid Films, 517, 2153 (2009)