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Metastabilities in the electrical characteristics of CIGS devices: Experimental results vs theoretical predictions

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Abstract

Recent theoretical calculations have traced an origin of light- and voltage bias-induced metastabilities in Cu(In,Ga)Se_2-based solar cells to negative-U properties of the V_{Se}–V_{Cu} complex. In this paper we compare experimental findings with theoretically predicted properties of these defects and calculated values of parameters characteristic for transitions between their different states. Profiles of net acceptor concentrations in the relaxed and metastable states obtained by capacitance profiling have been studied, as well as annealing kinetics of the persistent defect distributions by thermally stimulated capacitance and conductivity. Good qualitative and quantitative agreement are found between theory of V_{Se}-related defects and experimental results. The consequences from the point of view of photovoltaic efficiency of the Cu(In,Ga)Se_2-based solar cells are discussed.

Keywords: Defects; Capacitance; CIGS; Solar cells; Relaxation

1. Introduction

Metastabilities in the electrical characteristics induced by illumination or voltage bias are typical features of photovoltaic devices based on Cu(In,Ga)Se_2 (CIGS) absorbers. All effects (changes of photovoltaic parameters of the cells, which are accompanied by changes of net doping of absorbers and thin films, admittance and deep level transient spectroscopy (DLTS) spectra [1–5]) indicate that persistent changes of the charge and defect distribution within the junction is involved.

Two explanations for these observations have been proposed: DX-like behavior of a defect center which undergoes a shallow-deep transition upon a change of the defect occupation [3,5] and copper migration in the junction electric field [6,7]. The first one was widely accepted as an origin of the optically-induced effects, while both models: mobile copper ions [6] and relaxing defects [8] have been proposed as a source of the reverse-bias-induced metastabilities.

A new support for the relaxing donors model has recently emerged thanks to the first principle calculations by Lany and Zunger on properties of selenium vacancy-related defects [9,10]. Two defects with negative-U behavior and large bond rearrangement following change of the charge state have been identified: the isolated V_{Se} and defect complex V_{Se}–V_{Cu}, i.e. the combination of V_{Se} with copper vacancy. Properties and energetical parameters calculated for both types of defects are very similar, so it would be difficult to distinguish between them experimentally, but according to Ref. [10], a complex V_{Se}–V_{Cu} is more probable due to abundance of copper vacancies in Cu-poor material. Thus we will refer further to this defect as to VV complex having in mind that in principle it can also be an isolated vacancy. The main results for V_{Se} or VV complex derived by Lany and Zunger might be summarised as follows:

i There are two configurations of the defect: in a donor configuration VV^+ and VV^0 the In–In bond is formed and the defect level is situated close to the conduction band minimum, while in the VV^- state the bond is broken, distance between two indium atoms becomes large and energy level moves close to the valence band maximum. The reactions involving this bond rearrangement and a change of defect energy level from shallow donor to shallow acceptor are

$$VV^+ + 2e \rightarrow VV^- \quad (1)$$

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or

$$VV^{+} \rightarrow VV^{-} + 2h \quad (2)$$

ii The reverse reaction bringing the defect back to the VV^{+} configuration involves the capture of two holes by the acceptor-like defect and, again, a lattice relaxation

$$VV^{-} + 2h \rightarrow VV^{+} \quad (3)$$

iii The energy barrier for transition (1) is about 0.1 eV in CIS, for transition (2) — 0.7 eV and for reaction (3) — about 0.3 eV, almost independently on gallium content in CIGS compouds.

iv The distribution of VV centers between two states depends on the position of the Fermi-level E_F. Thus, in the device a Fermi-level dependent defect distribution arises — closer to the interface the acceptor VV^{-} state prevails.

v The VV complex in the acceptor state introduces not only shallow level into the gap, but also an antibonding level situated at 0.85 eV above the valence band minimum. Two additional electrons might be trapped by that level if only E_F is close enough to the conduction band.

In the following sections we will examine the experimental data focusing on these predictions. Finally we will outline the consequences of the relaxing V_{Se}–V_{Cu} vacancies for the efficiency of CIGS devices.

2. Experiment

ZnO/CdS/Cu(In,Ga)Se_2 devices have been fabricated by the baseline process described e. g. in [11]. We present also conductivity measurements of thin CIGS films deposited on glass, supplied with molybdenum contacts in van der Pauw configuration.

The metastable changes have been produced at room temperature by 1 h of illumination with a halogen lamp of intensity corresponding to the 1.5 AM solar spectrum, by reverse bias of −2 V or by injection (about 5 mA/mm^2), followed by cooling under illumination or bias to 100 K. The relaxed state of the sample has been achieved by annealing at 330 K for 1 h.

Charge distributions have been measured by both capacitance voltage (CV) and drive level capacitance profiling DLCP [12], using HP 4284A admittance meter at low enough temperature (T<200 K), such that no hysteresis effects are observed. Only CV data will be presented here since our investigations show that for all samples and all metastable states the net acceptor distributions derived from both methods have exactly the same shape and differ only by a constant factor of 2 [13].

3. Results

3.1. Charge distributions

The metastable, shallow level distributions after light soaking and reverse bias, as well as the distribution for the relaxed state of the cell, both derived from C–V characteristics are depicted in Fig. 1. The typical feature is an apparent increase of the doping appearing for large distances from the junction, corresponding to high reverse bias applied to the junction. According to the analysis presented in [13], this is due to the increase of charge in the inversion region of the junction and does not represent real values of concentration in this region. Hence, the non-distorted value of the net acceptor concentration in the bulk of absorber corresponds to the middle part of the distribution. The interesting feature is that both factors — illumination and reverse bias applied at room temperature produce the increase of the apparent doping level. This shows two possible reactions of defect conversion, by capture of free electrons (1) and by hole emission (2). Illumination leads to more uniform increase of the net shallow doping, whereas reverse bias causes increase of defects in the acceptor configuration in the region, which becomes depleted under bias.

3.2. Creation of the metastable states

Characteristic feature of the transition (1) is that relaxation toward acceptor-like configuration follows overcoming of the energy barrier of about 0.1 eV. Thus we expect a difference between the results of light soaking at low temperature and at room temperature — this is documented by the data shown in Fig. 2a. Here the capacitance–temperature dependence measured after light soaking at 100 K and at 300 K for 1 h are shown. In Fig. 2b the results of the same procedure applied to the thin CIGS film are presented. We observe that persistent photoconductivity (PPC) behaves exactly in the same manner as the capacitance of the cell.

Reverse bias metastability might be produced only at temperatures around RT. This is easily explained, since according to Ref. [10] this effect can be created either by reaction (2) or by thermal excitation of free electrons while holes are (almost) absent and both processes need much higher activation energies.

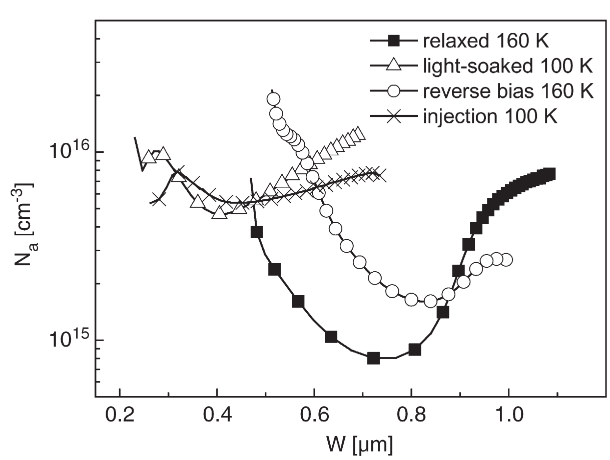

Fig. 1. C–V profiles measured at 100 kHz and at temperatures indicated in the picture fter light soaking, after injection, and after reverse bias, compared to the relaxed state.