Sub-bandgap photoconductivity and photocapacitance in CIGS thin films and devices

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A B S T R A C T

Photoconductivity and photocapacitance of Cu(In,Ga)Se\textsubscript{2} and CuGaSe\textsubscript{2} thin films and devices induced by sub-bandgap illumination are investigated. Both effects have been attributed to the optical transition from valence band to the same empty levels situated around 0.8–0.9 eV above the valence band. The influence of the metastable states created by illumination and voltage bias on the sub-bandgap response has been studied. The experimental results are discussed in the framework of a model based on negative-U property of a native defect in chalcopyrites, i.e. V\textsubscript{Se}–V\textsubscript{Cu} divacancy. The arguments are presented that the levels involved in the optical transition observed in photoconductivity and photocapacitance might be antibonding levels of the acceptor configuration of this defect.

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1. Introduction

Metastable phenomena in the electrical characteristics of Cu(In, Ga)Se\textsubscript{2} (CIGS) cells induced by illumination or voltage bias and among them persistent photoconductivity and persistent changes of doping profiles are a subject of continuing discussion in the scientific community \cite{1}. One of the explanations is based on \textit{ab initio} calculations of Lany and Zunger which show a negative-U property of the selenium vacancy and V\textsubscript{Se}–V\textsubscript{Cu} complex \cite{2,3}. These defects can assume acceptor or donor configuration depending on their charge state. In the acceptor configuration two levels, not only a shallow level above the valence band but also a deep level around 1 eV above the valence band is introduced into the gap. We show evidences which provide an experimental support for this theoretically predicted property.

A band of deep levels in the bandgap of CIGS absorbers corresponding to the optical transition induced by sub-bandgap photons has been observed previously in photocapacitance spectrum \cite{4} and in transient photocapacitance (TPC) measurements \cite{5,6}. Their characteristic feature first observed by Heath et.al. \cite{5} is that their energetic distance from the valence band centered around 0.8 eV does not depend on the bandgap width of CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2} solid solutions. The sign of the capacitance change induced by sub-bandgap light is positive, therefore a transition of electrons from the valence band to empty defect levels situated in the upper half of the bandgap has to be responsible.

In this work we present the results for baseline polycrystalline CIGS and also CuGaSe\textsubscript{2} (CGS) absorbers, thin films and devices, and demonstrate the metastable changes induced in the photocapacitance and photoconductivity sub-bandgap spectra. These results will be discussed in terms of the Lany–Zunger model explaining persistent photoconductivity in chalcopyrites.

2. Experiment

Baseline Cu(In,Ga)Se\textsubscript{2} layers on glass (gallium to indium ratio around 0.2) were prepared at HZB, Berlin, and polycrystalline CIGS films on glass were prepared at the University of Luxembourg, both by three-stage co-evaporation. Baseline CIGS and CGS cells in standard configuration were prepared at Uppsala University. Photoconductivity and photocapacitance measurements were performed at Warsaw University of Technology.

Photocapacitance has been monitored by measuring capacitance signal modulated by chopped light at a frequency around 30 Hz. Capacitance bridge (Boonton 7200) operating at 1 MHz ac frequency has been used and a lock-in amplifier SR810. An SP1 spectrometer together with a halogen lamp provided illumination in the wavelength range of 500–2000 nm. The spectral distribution of photon flux has been determined by using a pyroelectric detector.

Photoconductivity has been measured in thin films supplied with gold contacts in planar geometry. Essentially the same experimental set-up has been used as in case of photocapacitance measurements, only capacitance meter has been replaced by 428 Keithley current amplifier. Both photocapacitance and photoconductivity spectra have been measured in the relaxed state of the samples and after light soaking (LS) by white light corresponding to about AM1.5. In case of...
devices, also reverse bias treatment REV (−2 V at room temperature followed by cooling under bias) has been applied. The measurements have been conducted at temperature below 200 K when all metastable changes are persistent.

3. Results

The examples of the photocapacitance spectra measured at 80 K in the devices based on CIGS and CGS are shown in Fig. 1. Characteristic feature of these spectra, namely their similar cut-off energy not depending on the bandgap, as found in Ref. [5] by TPC, is observed. In Fig. 2 a set of spectra measured in various metastable states in the baseline CIGS device is shown. A slight decrease after REV treatment and a decrease beyond detection limit after light soaking have been observed. The same effect is typical also for CGS-based devices. In order to check how the width of the depletion layer influences the magnitude of sub-bandgap photocapacitance we have measured its dependence on the voltage bias applied to the cell. This time a total change of capacitance produced by sub-bandgap illumination (λ = 1400 nm in case of CIGS and 1000 nm for CGS) has been measured. In Fig. 3 a relative value of the capacitance change ∆C/C with corresponding to the quiescent capacitance at applied bias, as a function of depletion width, is shown for two states of the baseline CIGS sample: relaxed and after reverse bias. The decrease of the signal, both in absolute and relative values, with increasing reverse bias was observed. This is contrary to expectations similarly as in the case of traps filled by a voltage pulse during DLTS experiment total charge contained in deep levels filled with electrons excited by sub-bandgap photons in the depletion layer should increase with depletion layer width while a relative value ∆C/C should remain almost constant [7].

We will return to that point in the next section.

In CIGS and CGS thin films we have observed a sub-bandgap photoconductivity in the similar photon energy range as sub-bandgap photocapacitance: above 0.7–0.8 eV. The examples measured in the polycrystalline baseline CIGS and polycrystalline CGS films are shown in Fig. 4a and b. This signal should also correspond to the transition of electrons to the empty levels situated around 0.8 eV above the valence band which leads to the creation of additional free holes contributing to conductivity. On the basis of similar energetical distribution in the bandgap it seems only natural to conclude that the same deep levels are responsible for both phenomena, photoconductivity and photocapacitance in the sub-bandgap wavelength range. However here we observe an opposite metastable change: the sub-bandgap photocurrent signal increases after light soaking. How important is the exposure to illumination preceding the measurement for the results is best demonstrated in a “one shot” experiment. In Fig. 5 the photocurrent kinetics after switching on the sub-bandgap light pulse measured in the polycrystalline CIGS thin film at 80 K is shown. When the sample in the relaxed state (annealed at 330 K and not exposed to any illumination before cooling down to low temperature) is illuminated by photons belonging to the sub-bandgap PC range (here λ = 1 μm), no photocurrent was observed. After short illumination at the same temperature with photons of energy above the band-gap, the experiment was repeated and this time a photocurrent transient appeared. Magnitude of this transient increases more after longer exposure to white illumination.

4. Discussion

First we will discuss features of the sub-bandgap photoconductivity. Here only after exposure to illumination with hν > E_F the sub-bandgap photocurrent appears. Hence there is a relation between persistent photoconductivity (PPC) and levels involved in the sub-bandgap signal. The excitation of both PPC (as shown e.g. in Ref. [8]) and sub-bandgap signal does not require high temperature. The second important feature of both photoconductivity and photocapacitance is that the energetic distance of levels involved in both phenomena from the valence band does not depend on the gallium content in CIGS solid solutions. These experimental findings are in agreement with the predictions of the theoretical calculations of Lany and Zunger [3] on the negative-U property of V_{Cu}–V_{Cu} defect. In thermal equilibrium this defect assumes donor configuration if only the Fermi-level position is closer than 0.3 eV from the valence band, hence this configuration prevails in p-type thin films. Presence of free electrons created by illumination induces a change to the acceptor configuration and results in persistent photoconductivity. Defect conversion from the donor to acceptor state by the electron capture does not require overcoming any
meaningful potential barrier, thus it is possible also at low temperature. Most important for the interpretation of the data presented in this report is the theoretical prediction that an antibonding level coinciding with the conduction band in the donor configuration is brought down and appears in the bandgap as a very deep level around 1 eV above the valence band in both CIS and CGS. Exact values calculated for \((-\frac{1}{2} - \frac{1}{2})\) optical transition given in [3] are 1.05 (0.83) eV and 1.19 (0.90) eV for CIS and CGS correspondingly, with the values in parentheses obtained without the image charge correction. These levels might be responsible for the optical transition observed in photoconductivity and photocurrent.

Interpretation of the metastable changes of the photocapacitance spectrum is more complicated. First let us notice that the sub-bandgap photocapacitance both in CGS and CIGS devices decays after switching off the light pulse with time constant of order of tens of milliseconds even at 100 K. Time constants corresponding to the thermal emission from a level situated about 400 meV below CB as in case of baseline CIGS, and much deeper in case of CGS should be longer than \(10^4\) s at 100 K for reasonable values of capture cross sections. Hence we conclude that the magnitude and time constant of sub-bandgap photocapacitance signal is governed not by thermal emission rate of electrons to the conduction band, but by capture rate of holes diffusing from the bulk. It should be added here, that we have not observed any persistent signal induced by sub-bandgap light (within 0.2% accuracy relative to the quiescent capacitance value) i.e. such capacitance change which would persistently remain after switching off the light. Thus the observed signal corresponds to a change of occupation in the narrow region of the cell to which holes have an access. With this in mind we explain a dependence of the photocapacitance signal on the voltage bias applied to the sample as due, among other things, to the availability of holes for capture. In order to explain a steep decrease of the relative signal with the reverse bias applied during measurement (Fig. 3), the states have to be distributed in the limited region of the cell. Only then an increase of the depletion width under reverse bias leads to a decrease of the relative value of the capacitance change. This again is in agreement with Lany–Zunger model of \(V_{\text{se}} - V_{\text{Cu}}\). In the device the acceptor configuration of the defect prevails in the relaxed state up to a distance from the interface, at which the Fermi-level coincides with the energy characteristic for defect conversion \(\varepsilon \approx 0.3\) eV (see Fig. 6a).

Much higher decrease of the signal after light soaking cannot be explained by only an increase of the free hole density in the bulk after LS. In the example shown here, the net doping of the absorber increased after LS, as found by capacitance profiling, by a factor of 3, while sub-bandgap capacitance decreased by two orders of magnitude. We propose here as an explanation two factors acting together: a difference of the availability of holes deeper in the depletion layer due to a different voltage distribution in the relaxed and in the light-soaked state and a reduced concentration of defects in the acceptor state close to the interface. As discussed previously [9,10], in the relaxed state a p+ layer in the device makes voltage

![Fig. 4. Sub-bandgap photoconductivity spectrum measured in the relaxed state of the sample and after light soaking: a) CIGS polycrystalline layer; b) CGS polycrystalline layer.](image)

![Fig. 5. Photocurrent at 80 K after switching on the sub-bandgap light pulse (\(\lambda = 1000\) nm) measured in the sample in the relaxed state and after subsequent illumination with high energy photons (\(h\nu = E_g\)) for periods of time indicated in the picture.](image)

![Fig. 6. Band diagram of the cell: (a) in the relaxed state; (b) after light soaking, showing theoretically predicted distributions of \(V_{\text{se}} - V_{\text{Cu}}\) levels in the donor and acceptor states.](image)
distribution highly non-uniform as shown schematically in Fig. 6a. After light soaking, due to hole capture in the inversion region of the device, the p+ layer is reduced and the distribution of V_{Se}–V_{Cu} defects in the acceptor configuration becomes more uniform (Fig. 6b). The first effect reduces a number of deep levels involved in the process, and second decreases probability of the hole capture necessary for observation of the ac photocapacitance signal.

5. Summary

Investigations of the sub-bandgap photocurrent and photocapacitance show that the same process of optical excitation of electrons to empty levels in the upper half of the bandgap in the case of CIGS, and close to midgap in case of CGS, is responsible for both effects. Additionally we observe the opposite metastable behaviour after light soaking characterizing those two phenomena—an increase of the sub-bandgap photoconductivity and a decrease of the sub-bandgap photocapacitance. These observations we explain as related to the illumination-induced metastable changes of the configurational state of the V_{Se}–V_{Cu} defect: increased concentration of the acceptor configuration in the thin films and decreased in the inverted region of the device. In this model sub-bandgap signal is related to the antibonding levels of V_{Se}–V_{Cu} predicted by Lany and Zunger calculations. Albeit our experimental findings are not a direct proof themselves, subbandgap signal belongs to the antibonding levels of the double vacancy we think that the relations between the metastable state and subbandgap signals justify proposing this explanation as a plausible possibility.

Detailed discussion of the photocapacitance spectrum dependence on the reverse bias points towards specific doping distribution of these defects in the acceptor and donor configuration in the relaxed and metastable states as possible cause.

Finally we would like to emphasize that these results document the existence of large concentration of deep levels with energies close to midgap in case of CGS. Their contribution to the recombination losses remains still to be confirmed.

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