Defect levels in the epitaxial and polycrystalline CuGaSe$_2$ by photocurrent and capacitance methods

Adam Krysztopa,$^{1,8}$ Malgorzata Igalson,$^1$ Yasuhiro Aida,$^{2,3}$ Jes K. Larsen,$^2$ Levent Gütay,$^2$ and Susanne Siebentritt$^2$

$^1$Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warszawa, Poland
$^2$Laboratory for Photovoltaics, University of Luxembourg, 41, rue du Brill L-4422 Belvaux, Luxembourg
$^3$Device Development Center, TDK Corporation, Ichikawa, Chiba, 272-8558, Japan

(Received 25 June 2011; accepted 17 October 2011; published online 23 November 2011)

The defect levels in epitaxial and polycrystalline wide bandgap chalcopyrite CuGaSe$_2$ with various stoichiometry deviations were investigated using modulated photocurrent spectroscopy. The results were analyzed as a function of light intensity and Fermi-level position. Comparison of the results from epitaxial and polycrystalline material distinguished levels belonging to intrinsic defects and their correlation with the material stoichiometry. We also compared the fingerprints of defect levels by MPC to the results derived from capacitance spectroscopy performed on Schottky diodes fabricated on both epitaxial and polycrystalline layers. This allowed us to attribute unambiguously levels observed in the capacitance response to bulk point defects. In the final conclusions we provide information on the electronic parameters of nine defect levels observed in CuGaSe$_2$ and their correlation with the material stoichiometry. These results should help to identify intrinsic defects that are important for the photovoltaic performance of solar cells based on chalcopyrites.


I. INTRODUCTION

Ternary compound CuGaSe$_2$ (CGSe) belongs to the chalcopyrite family and is considered an interesting material for photovoltaic applications, due to its bandgap value of 1.68 eV in tandem solar cells.\cite{1} The first attempts to produce CGSe-based solar cells were made in 1977 (Romeo et al.$^2$) and led to the fabrication of a device with a conversion efficiency of 5%.$^3$ Despite many years of investigation no scientific group has yet been able to significantly improve the performance of these cells. The low efficiency stemming from the low open circuit voltage is still not fully explained. As well as explanations based on the large conduction band discontinuity at the CdS/CGSe heterointerface,$^4$ some experimental evidence indicates the influence of intrinsic defects on $V_{oc}$ limitation.$^5$ Theoretical studies dealing with this problem$^6,^7$ indicate that intrinsic defects such as V$_{Se}$ or Ga$_{Cu}$ might play an important role.

Despite the undoubtedly important role of intrinsic defects for the performance of CGSe solar cells, we do not have much information on their basic electronic properties. A few papers have described ab initio calculations of intrinsic defect formation in CuGaSe$_2.$ $^6,^8,^9$ Some other have examined defect levels using the Hall effect and photoluminescence measurements, reporting activation energies from shallow donor-like and acceptor-like defects.$^{10,11}$ A deeper acceptor state with an activation energy of 390 meV has also been reported.$^{11}$ In CGSe-based solar cells deep levels have been studied using junction capacitance spectroscopy.$^{12,13}$ Jasenek et al.$^{12}$ reported data on defect signatures including thermal activation energies and emission coefficients in absorbers with both Cu-rich and Cu-poor stoichiometry: A1 with an activation energy $E_A = 190-240$ meV and emission coefficient $\zeta_0 = (1-9) \times 10^3 \text{s}^{-1} \text{K}^{-2}$ and A2 with $E_A = 375-395$ meV and $\zeta_0 = 2 \times 10^8 - 2 \times 10^9 \text{s}^{-1} \text{K}^{-2}$, depending on the metastable state. Cu-poor-based solar cells exhibit two more acceptor states: A3 ($E_A$ around 130 meV, $\zeta_0$ in the order of $5 \times 10^7 \text{s}^{-1} \text{K}^{-2}$) and A4 ($E_A = 250 \text{ meV}, \zeta_0 = 2 \times 10^6 \text{s}^{-1} \text{K}^{-2}$). The cells also showed a strong dependence of recombination loss on the A4 concentration.

The inherent experimental problems associated with the interpretation of admittance spectroscopy applied to ZnO/buffer/CGSe heterojunction solar cells include the differentiation between interface and bulk defects.$^{14}$ The high electric field across the space charge region of the junction up to $10^6 \text{ Vm}^{-1}$ may also have a significant impact on the results obtained using capacitance junction techniques.$^{15}$ These difficulties and distortions do not play a role in modulated photocurrent (MPC) experiments. The method is based on measuring a phase shift between excitation and the photocurrent response introduced by capture and emission processes involving deep trap levels. Here thin films with ohmic contacts in a coplanar geometry are used and therefore only bulk defect level signatures are obtained. In addition, there is a much lower electric field in the sample. We should also add that the choice of samples suitable for MPC measurements is not limited by the ability of the material in given composition or doping level to form a good Schottky or heterojunction.

In this work we present the results of modulated photocurrent spectroscopy on epitaxial and polycrystalline CGSe with various stoichiometries. By using epitaxially grown CGSe it is possible to investigate defect levels in samples...
with a strictly defined composition and high homogeneity. Thus it should be possible to relate defect levels to material composition. Comparison of data on the epitaxial and polycrystalline samples should allow us to distinguish bulk defect level signatures in CGSe regardless of its morphology, the presence of grain boundaries, etc. Whenever possible, defect level spectra derived from MPC data are compared to the defect signatures obtained using capacitance spectroscopy methods, deep level transient spectroscopy (DLTS) and admittance spectroscopy (AS). Thus, we provide direct proof that peaks are better resolved in this mode. In Ref. 21 we have also shown the advantages of the temperature scan (T-Scan) over the frequency scan (f-Scan) mode in acquiring the MPC spectra – in the temperature scan phase shifts introduced by experimental set-up does not distort the positions of the maxima and that peaks are better resolved in this mode. In the T-Scan a phase shift is presented as a function of temperature for a set of frequencies, in analogy to the temperature scan of DLTS.

Herberholtz et al. derived an expression for the phase shift in the case of discrete level in the bandgap of semiconductor—situation typical in mono- and polycrystalline semiconductors. Analyzing the expression for the phase shift they showed that in the case of negligible retrapping typically assumed in the MPC calculations, the maximum of (negative) phase shift at a temperature \( T \), for a given frequency window \( f_m \), corresponds to the emission rate from the level:

\[
e_{T} = 2 \pi f_m = \xi_0 T^2 \exp \left( \frac{-E_A}{k_B T} \right).
\]

If the processes of recombination and recapture of emitted carriers are ignored and a temperature-independent capture cross section is assumed, the activation energy \( E_A \) corresponds to the deep level distance from the nearest band: \( E_c - E_i \) or \( E_v - E_x \) and pre-exponential factor \( \xi_0 T^2 \) is equal to \( \sigma N v_{th} \) where \( \sigma \) is the electron (hole) capture cross section, \( N \) is the effective density of states in the conduction (valence) band, \( v_{th} \) is the thermal velocity of the carrier, and \( \xi_0 \) is the emission parameter, which, for this simple case is temperature- and enthalpy-independent. Unfortunately, in photoelectrical methods such as MPC it is theoretically impossible to achieve measurement conditions in which interaction with only one band is present (no recombination), but we will show later that we can define optimum settings allowing us to minimize deviation from these conditions. Another disadvantage of MPC is its inability to straightforwardly determine whether observed energy level is an electron or a hole trap situated in the upper or lower half of the bandgap, especially if intrinsic material is investigated. If the Fermi level is situated near one of the bands the position of the level can be determined but carrier emission from the level is distorted by the capture of free electrons or holes. In the presence of free carriers the positions of the phase shift maxima are distorted by a factor proportional to the electron and hole densities and level parameters: \( \omega_0 = n c_n + p c_p \). The modified expression for \( \omega_m \) includes influence of capture processes on defect-related time constant:

\[
\omega_m' = \sqrt{\omega_n^2 + \omega_p^2}.
\]

where \( n \) and \( p \) are, respectively, the electron and hole concentration under illumination, \( c_n \) and \( c_p \) are the capture coefficients for electrons and holes.

II. PRINCIPLES OF MODULATED PHOTOCURRENT SPECTROSCOPY

Modulated photocurrent spectroscopy (MPC) is a photoelectrical technique originally introduced by Oheda and developed by Brüggemann et al. The method is based on illumination of a biased sample in a coplanar contact geometry by photons with energy higher than the semiconductor bandgap. Photon flux has two components: constant (\( F_{dc} \)) and sinusoidal alternating (\( F_{ac} \)). Photo-generated electrons and holes interact with deep levels in the bandgap and thus contribute to the splitting of various quasi-Fermi levels and a change in the interaction between charge carriers and defect levels. If capture and emission processes dominate (for sufficiently low DC light intensity), the released carriers make a significant contribution to the phase shift – this mode is known as the High Frequency mode of modulated photocurrent (HF-MPC). If recombination processes dominate (for high enough light intensity) the phase shift rapidly drops to zero – this is the case in the Low Frequency MPC mode (LF-MPC). The transition frequency between the LF and HF mode is determined experimentally according to a method detailed in Ref. 20. A description of this procedure applied to CGSe layers can be found elsewhere. In Ref. 21 we have also shown the advantages of the temperature scan (T-Scan) over the frequency scan (f-Scan) mode in acquiring the MPC spectra – in the temperature scan phase shifts introduced by experimental set-up does not distort the positions of the maxima and that peaks are better resolved in this mode. In the T-Scan a phase shift is presented as a function of temperature for a set of frequencies, in analogy to the temperature scan of DLTS.

Epitaxial and polycrystalline thin films of CuGaSe\(_2\) were grown in the Laboratory for Photovoltaics, University of Luxembourg. All investigated samples, which differed by geometry (coplanar and Schottky diodes), morphology (epitaxial and polycrystalline) and composition, are listed in Table I. Epitaxial layers in coplanar contact geometry (300-nm and 800-nm thick) were grown by Metal Organic Vapor Phase Epitaxy (MOVPE) on a semi-insulating undoped GaAs (SI GaAs) substrate. Layers used in the Schottky diodes were 1.4-\( \mu \)m thick and grown on Zn-doped (p-type) GaAs. Details of the growth process are presented elsewhere. Polycrystalline CGSe (3-\( \mu \)m thick) with various stoichiometries were grown using a three-stage Physical
TABLE I. CuGaSe₂ samples investigated in this work: the numbering used in the composition column indicates the increased deviation from stoichiometry: (1) to the highest deviation; (2) in the case of the Cu-poor samples and (2) in the case of the Cu-rich ones, as deduced from the analysis of PL spectra.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Sample</th>
<th>Composition</th>
<th>Thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Epitaxial samples</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>co-planar</td>
<td>eCuP1</td>
<td>Cu-poor (2)</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>eCuP2</td>
<td>Cu-poor (3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>eCuP3</td>
<td>Cu-poor (1)</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>eCuP4</td>
<td>Cu-poor (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>eCuP5</td>
<td>Cu-poor (3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>eCuR1</td>
<td>Cu-rich (1)</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>eCuR2</td>
<td>Cu-rich (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>eCuR3, eCuR4</td>
<td>Cu-rich (1)</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Schottky diodes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>eSchCuP</td>
<td>Cu-poor (3)</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>eSchCuR</td>
<td>Cu-rich (2)</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>Polycrystalline samples</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>co-planar</td>
<td>pcCuP1, pcCuP2</td>
<td>Cu-poor</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>pcCuR1, pcCuR2</td>
<td>Cu-rich</td>
<td>3</td>
</tr>
<tr>
<td><strong>Schottky diodes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pcSchCuP</td>
<td>Cu-poor</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>pcSchCuR1, pcSchCuR2</td>
<td>Cu-rich</td>
<td>3</td>
</tr>
</tbody>
</table>

Deep level transient spectroscopy and admittance measurements on Schottky diodes were carried out in an optical helium cryostat at temperatures ranging from 20 K to 340 K. For admittance spectroscopy a HP4284A RLC meter was used, with the AC voltage amplitude set to 50 mV, and the frequency from 100 Hz to 1 MHz. DLTS measurements were carried out using a Boonton 7200 capacitance bridge in conjunction with a high-resolution National Instrument PCI-6521M DAQ card. The capacitance transient was subsequently analyzed using lock-in type averaging with window rates between 5 and 2000 s⁻¹.

IV. EXPERIMENTAL RESULTS

A. Conductivity of thin film samples

The electrical properties of the epitaxial CGSe were strongly dependent on the sample composition. Cu-poor epitaxial samples exhibited low conductivity, of the order of 10⁻⁴ Sm⁻¹ at room temperature, with an activation energy for conductivity of approximately 700 meV (see Fig. 1). The only exception was the near stoichiometric Cu-poor sample eCuP3, which exhibited lower activation energy around 350 meV although its room temperature conductivity appeared to be within the same range. Epitaxial Cu-rich CGSe showed the opposite—conductivity was at least 3 orders of magnitude higher with much lower activation energies (below 150 meV) and varying from sample to sample. Values of conductivity of investigated epitaxial samples agree with the data reported previously. As mentioned already all epitaxial Cu-poor samples are almost semi-insulating with the Fermi level located near the middle of the bandgap. This makes them ideal candidates for MPC measurements. On the other hand, the photoconductivity of the substrate layer in such highly resistive samples complicates interpretation of the results, as will be shown in the next section. The situation is slightly worse in the case of Cu-rich samples, yet their very high photoconductivity compensates for their higher doping level, thus making them suitable for MPC investigations.

Polycrystalline samples did not show any correlation between conductivity and stoichiometry, and all showed
similar conductivity and temperature dependence with activation energies in the range of 100–170 meV. The most important feature for interpretation of the MPC results measured in polycrystalline Cu-poor samples was their much higher conductivity in comparison to the Cu-poor epitaxial samples which might be due to the absence of sodium in MOCVD process.

B. Modulated photocurrent

In a previous paper we demonstrated the usefulness of modulated photocurrent spectroscopy for investigating deep levels in the bandgap of CuGaSe₂. We observed four defect levels and estimated their electronic parameters, in particular their energy depths. We showed that measurement conditions such as the magnitude of the constant part of the excitation light, using the frequency scan or temperature scan to estimate the electronic parameters, and the conductivity of the samples related to the equilibrium Fermi-level position, etc., have an impact on the final results. In Ref. 21, we also showed that in the case of low-conductivity samples the impact of the substrate is not negligible and thus we can observe mixed MPC signals originating from both the CGS layer and GaAs substrate.

In the following sub-sections we will address in detail the above-mentioned problems. The conclusions include indications for optimal measurement conditions.

1. Influence of the measurement conditions

Varying the constant part of the photoexcitation intensity produces changes in the splitting of quasi Fermi levels. Depending on the parameters of the defect levels (i.e., energetic distance between a level and the band edge and capture cross sections) different defect states can be probed. Some of these levels are able to respond and contribute to the phase shift (emission-dominated mode), and some, for which recombination prevails over thermal emission fall into the recombination regime. In the transition region a decrease in the phase shift values is observed, which may be a source of distortion of the electronic parameters of trap levels derived from MPC. This should also be kept in mind when analyzing the data.

MPC experiments employing various light intensities allow us to probe different defect levels in the bandgap of the semiconductor. This makes the method very useful but one has to be careful when choosing measurement parameters in order to maintain the High Frequency regime in the probed states. Otherwise an increase in recombination probability may alter the estimated values of the emission rates and hence introduce large distortion of the values of trap parameters derived from the experiment. An example of the influence of light intensity is presented in Fig. 2 for sample eCuR3. These data belong to the levels labeled E3 and E4 in the further discussion. Two separate and well-defined peaks at high (E3) and low temperatures (E4) are evident for small light intensities (in this case $F_{dc} = 10^{15} \text{s}^{-1}\text{cm}^{-2}$ – Fig. 2(a)). With the increase in the constant part of the excitation light intensity, the high temperature E3 peak disappears as the defect level begins to fall into the recombination regime.

In some cases the structure of the spectra is quite complex, as two or more electron states are probed simultaneously. Figure 3 shows the MPC spectra in the temperature scan mode for the eCuP3 sample at two light intensities: (Fig. 3(a)) $F_{dc} = 10^{15} \text{s}^{-1}\text{cm}^{-2}$ and (Fig. 3(b)) $F_{dc} = 10^{17} \text{s}^{-1}\text{cm}^{-2}$. In this example the MPC signal belongs to the levels labeled E4, E6, and E7. Arrhenius plots derived from these data are shown in Fig. 4(a). At $10^{15} \text{s}^{-1}\text{cm}^{-2}$ the

![FIG. 2. The MPC spectra of the eCuR3 sample at two different DC light intensities: (a) $F_{dc} = 10^{15} \text{s}^{-1}\text{cm}^{-2}$; (b) $F_{dc} = 10^{17} \text{s}^{-1}\text{cm}^{-2}$. Transition from the emission to recombination mode for level E3 was observed at the higher light intensity.](image)

![FIG. 3. The low temperature part of the MPC spectra for the eCuP3 sample at different DC excitation intensities: (a) $2 \times 10^{15} \text{s}^{-1}\text{cm}^{-2}$; (b) $10^{17} \text{s}^{-1}\text{cm}^{-2}$. The broad peaks visible in the plot (a) correspond to E7 and E6. As DC light power increases, E6 falls into the recombination regime and exposes the response belonging to the E4 state.](image)
overlapping peaks contribute to a broad spectrum and separation of the peaks is impossible in many cases. With good accuracy only the maxima of highest amplitude, in this case corresponding to the E6 and E7 levels, can provide meaningful data. With higher light intensity some of these levels fall into the recombination regime, exposing the response from another defect level—E4 (indicated by an arrow in Fig. 4(a)).

The equilibrium carrier concentration under dark conditions may also have an impact on MPC spectra. The high concentration of majority carriers greatly enhances the recombination probability, in effect increasing the emission rates derived from the experiment. Figure 4(b) shows the emission rates versus reciprocal temperature for E4. With the increase in the sample conductivity (indicated by an arrow) the Arrhenius plots of the emission rates show changes in the activation energy and pre-exponential factor—both parameters decrease with increasing of holes concentration. According to Kounavis,24 the most reliable results should be obtained for samples with the lowest conductivity.

2. Influence of the substrate

As reported in Ref. 21 one of the major problems arising from the low-conductivity CGSe layers typical of Cu-poor composition is the influence of the GaAs substrate on the results. At high temperatures we observe a response belonging to the mixture of CGSe levels coexisting with those characteristic of GaAs. This effect is typical in 300-nm thick epitaxial Cu-poor layers. Various phenomena are observed depending on the light intensity: either a characteristic transition between two probed states (open squares in Fig. 5) at \( F_{dc} = 10^{16} \text{ s}^{-1} \text{cm}^{-2} \) or separate states at the lower photon flux of \( F_{dc} = 10^{11} \text{ s}^{-1} \text{cm}^{-2} \) (open triangles). For comparison the results obtained for the bare SI GaAs substrate are shown in Fig. 5 (asterisks), in which we note that the experimental points in the narrow temperature range around 300 K, interpreted as an originated from the D2 state in Ref. 21 in fact may be an artifact associated with the transition between the level belonging to CGSe and the S1 level observed in SI GaAs.

In order to unambiguously identify the levels belonging to CGSe we performed measurements on the 800-nm thick epitaxial sample. Here only a level labeled E1 was observed (Fig. 5). Thus, we conclude that some of the levels observed in the 300-nm sample in the high temperature range belong to the substrate instead. This conclusion is supported by the results of photocurrent transient spectroscopy (PITS) on GaAs reported in Ref. 28: the parameters of one level observed in the 300-nm samples were relatively consistent with those obtained by Longeaud et al. using PITS (\( E_a = 640 \text{ meV}, \zeta_0 \approx 5 \times 10^{10} \text{ s}^{-1} \text{K}^{-2} \)). Case of the E2 level is different: no such level has been observed in GaAs; therefore, we believe it belongs to chalcopyrite despite of fact that it has not been observed in 800 nm thick CGSe samples.

We stress though that after careful comparison of the MPC results from the CGSe epitaxial layers and semi-insulating GaAs (by both MPC and PITS) there was no other evidence suggesting the influence of the substrate. We conclude that all other defect levels observed in the CuGaSe_2 epitaxial layers belong to the chalcopyrite. The Arrhenius plots of these levels are displayed in Fig. 6.

3. Polycrystalline CGSe thin films

MPC measurements were also performed on polycrystalline CuGaSe_2 layers with both Cu-poor and Cu-rich composition. The main goal was to identify the differences and similarities between defect spectra in these two types of material. The polycrystalline layers differ from the epitaxial ones not only by their different morphology and the presence of grain boundaries, which affect photocurrent transport, but also by their conductivity—this is much higher in the case of Cu-poor samples (see Fig. 1). Polycrystalline Cu-poor CGSe also exhibits large non-exponential photoconductivity transients after a light impulse.29 They belong, as previously reported, to the relaxation related to configuration changes.
between acceptor and donor configuration of amphoteric defects, namely, $V_{Se}^{-}V_{Cu}^{+}$ divacancies.\textsuperscript{6} This feature makes the MPC measurements more difficult as it hinders and distorts thermally activated signals. Thus, a thermally activated process attributed to a deep level was detected only in one of the Cu-poor polycrystalline samples.

In the case of the Cu-rich composition the stretch-exponential photocurrent transients did not significantly disturb the MPC spectra, but peaks in $\frac{e\tau T^2}{C_0}$ were broader and smaller than for the epitaxially grown thin films. In addition, higher excitation light intensities had to be used in comparison to the epitaxial samples, otherwise photocurrent values were below detection limit. This may be attributed to e.g. different defect concentrations or Fermi level pinning on grain boundaries. An exception was the MPC response belonging to the level labeled PC1 in the pcCuR2 sample, which was observed over a wide range of light fluxes from $10^{15}$ $s^{-1}cm^{-2}$ to $10^{18}$ $s^{-1}cm^{-2}$. Most levels observed in the polycrystalline thin films, with the exception of the levels labeled PC1 and PC2, were consistent with those found in the epitaxial layers. Figure 7 shows all levels observed in the polycrystalline samples against a background of the corresponding levels in the epitaxial samples. This is evidence that they all belong to intrinsic bulk defects in CuGaSe\textsubscript{2}. Otherwise, if they originated from the GaAs, they would not be observed in polycrystalline thin films, or if they originated from interface states, they would not be observed in MPC.

C. Capacitance spectroscopy

In order to determine which of the defect levels detected by MPC also appear in the spectrum of levels observed by capacitance methods, we carried out investigations using DLTS and AS on Schottky diodes. These experiments were expected to help distinguish between majority and minority carrier traps and locate them in the appropriate part of the bandgap.

An example of the admittance spectrum measured in the epitaxial Schottky diode eSchCuR is shown in Fig. 8(a). The position of the step corresponding to the emission rate from the trap level is defined by almost the same formula as (1) (differing only by a factor of 2\textsuperscript{17}). The Arrhenius plot of these emission rates is shown in Fig. 6 and the correspondence between that level and the MPC level E4 can readily be observed. Apart from this level in the Cu-rich sample, only one other level labeled E5 was detected in the Cu-poor epitaxial Schottky diode.

Level E6 and E7, which were detected in the epitaxial samples by MPC, were also observed by admittance
spectroscopy but in the polycrystalline Schottky diodes. Level E7 is particularly interesting, because it seems to be responsible for doping in the very Cu-rich material. As shown in Fig. 8(b), the capacitance step due to this level that was observed in sample pcSchCuR2, which had the highest deviation from stoichiometry, was exceptionally large. The high frequency capacitance value indicated that depleted part of the device exceeded its total width. This means that this step corresponds to a carrier freeze out, and the Arrhenius plot of the emission rate in this case gives the depth of the shallow acceptor responsible for doping. This observation provides a plausible explanation for why we were not able to observe the E7 defect by MPC in the Cu-rich samples. It is not that the defect is not present in Cu-rich composition, but, on the contrary, that in this case it is the main acceptor responsible for the p-type doping. An acceptor level with an activation energy of 150 meV like E7 has been reported previously.30

All results obtained via capacitance spectroscopy are compared to the MPC data in Figs. 6 and 7 for epitaxial and polycrystalline samples, respectively. These show that the majority of levels were confirmed by both methods. Only the deepest levels E1, E2, E3, and PC2 were not detected in any of the Schottky diodes investigated in this study, which suggests that they are minority carrier traps.

V. DISCUSSION

Defect levels observed in both the epitaxial and polycrystalline CGSe are labeled E1 to E7, whereas those found only in the polycrystalline material are labeled PC1 and PC2. Figures 6 and 7 show the Arrhenius plots for the most representative sets of data for these levels. The defect level parameters such as activation energies and emission coefficients derived from these plots are presented in Table II. Information on specific defect properties and the composition of the samples in which they were observed is also included. We will now discuss the properties of the levels found in CGSe by MPC while taking into account the results of admittance and DLTS spectroscopy on both polycrystalline and epitaxially grown Schottky diodes. We will also attempt to describe their basic properties on the basis of their reaction to such parameters as light intensity, Fermi-level position, etc.

Level E1 was observed in all epitaxial Cu-poor samples. As discussed in the previous section we ruled out the possibility that it belongs to the GaAs substrate and determined the value of its activation energy $E_A = 600 \pm 50$ meV and the emission parameter $\zeta_0$ in order of $10^8$ s$^{-1}$K$^{-2}$. It is worth mentioning that the activation energies of conductivity measured in the epitaxial Cu-poor samples had similar values, and thus it is possible that the E1 state is responsible for the Fermi-level pinning in Cu-poor material. This hypothesis is supported by the observation that the MPC signal belonging to E1 was found for all light intensities used—a feature signifying that the concentration of these defect states is very high.

Level E2 was observed by MPC in only one Cu-poor sample at very low excitation light intensity. It is possible that the E2 state may easily fall into the recombination regime—an activation energy value of 800 meV places it almost in the middle of the CuGaSe$_2$ bandgap, and this makes it a good candidate for the recombination center.

A deep level labeled E3 was observed in the epitaxial samples in Cu-rich composition (eCuR3 and eCuR4). This was characterized by the same activation energy as E1, but a two-fold larger emission parameter $\zeta_0$. This signal was strongly dependent on light intensity. Well-defined peak was observed at low intensities, but as intensity increased, it was less and less distinct and thus determination of the defect parameters became difficult or impossible. These properties could be explained by the very low concentration of defects responsible for the E3 signature in Cu-rich samples; hence the quasi Fermi levels could be shifted easily beyond the defect, after which the level falls into the recombination regime. The sensitivity to light intensity is a characteristic difference between E1 and E3. Bearing in mind that they both feature the same activation energy we may speculate that in fact E1 and E3 comprise the same structural defect of the CuGaSe$_2$, present at much lower concentrations in the Cu-rich composition and therefore harder to detect. In addition, we should remember that the conductivity of the Cu-rich samples is much higher than that of the Cu-poor ones. As explained earlier this may have an impact on the emission parameters determined from the Arrhenius plot, and produces a difference between pre-exponential factors of the same level detected in material differing by many orders of magnitude in their doping concentrations.

<table>
<thead>
<tr>
<th>Defect level</th>
<th>$E_A$ [meV]</th>
<th>$\zeta_0$ [s$^{-1}$K$^{-2}$]</th>
<th>Occurrence</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>550 – 650</td>
<td>$10^2 - 7 \times 10^4$</td>
<td>epi CuP</td>
<td>Minority carrier trap</td>
</tr>
<tr>
<td>E2</td>
<td>800 ± 30</td>
<td>$=8 \times 10^3$</td>
<td>epi CuP (?)</td>
<td>Easily falls into recombination regime</td>
</tr>
<tr>
<td>E3</td>
<td>550 – 580</td>
<td>$2 \times 10^2 - 2 \times 10^4$</td>
<td>epi CuR</td>
<td>Minority carrier trap</td>
</tr>
<tr>
<td>E4</td>
<td>100 – 400</td>
<td>$100 - 10^{10}$</td>
<td>epi and poly, CuP and CuR</td>
<td>Capture-limitation?</td>
</tr>
<tr>
<td>E5</td>
<td>150 – 250</td>
<td>$10^3 - 4 \times 10^8$</td>
<td>epi, very CuP</td>
<td>Majority carrier trap</td>
</tr>
<tr>
<td>E6</td>
<td>90 – 130</td>
<td>$6 \times 10^4 - 4 \times 10^5$</td>
<td>epi CuP and poly CuR</td>
<td>Majority carrier trap</td>
</tr>
<tr>
<td>E7</td>
<td>150 ± 10</td>
<td>$4 \times 10^3 \pm 2 \times 10^5$</td>
<td>epi slightly CuP, poly very CuR</td>
<td>Main acceptor in the polycrystalline very Cu-rich</td>
</tr>
<tr>
<td>PC1</td>
<td>350 – 530</td>
<td>$4 \times 10^3 - 2 \times 10^{10}$</td>
<td>poly CuP and CuR</td>
<td>Majority carrier trap?</td>
</tr>
<tr>
<td>PC2</td>
<td>350</td>
<td>$10^3$</td>
<td>poly CuP and CuR</td>
<td>Minority carrier trap</td>
</tr>
</tbody>
</table>
A signal labeled E4 was observed in the modulated photocurrent in all epitaxial samples both in the Cu-poor and Cu-rich composition at temperatures ranging from 100 to 200 K. The same level was also observed in the epitaxial Cu-rich Schottky junction (see Fig. 6). E4 was also detected in polycrystalline thin films in Cu-rich composition but only at very low excitation intensities \( F_{dc} = 10^{15} \text{s}^{-1} \text{cm}^{-2} \). DLTS and RDLTS measurements performed on the pcSchCuR1 sample (see Fig. 7) also showed this signal, the parameters of which agreed not only with our MPC data, but also with those reported for Cu-rich CGSe-based solar cells (A2 state derived from the AS reported by Jasenek et al.\textsuperscript{[12]}). We found the properties of E4 to be quite unique. As mentioned earlier (see Sec. IV B 1) the parameters of level E4 depend very strongly on the sample properties—activation energy and emission parameters vary across a wide range: the activation energy varies between 100 meV and 400 meV and the emission coefficient by 8 orders of magnitude. The parameters for other levels do not vary as much. For one particular set of measurement conditions the parameters of E4 were consistent with the A4 level observed by Jasenek et al.\textsuperscript{[12]} in Cu-poor solar cells. The Arrhenius plots obtained for that level for various samples and measurement conditions indicate a common origin despite various activation energies, which was confirmed by the Meyer-Neldel plot of emission parameters versus activation energies shown in the insert of Fig. 9. All these extraordinary properties of E4 suggest a mechanism other than simple capture and emission from the defect level. This level is observed in the admittance spectrum of the Schottky diode with the Schottky barrier around 600 meV, so we conclude that it must be an acceptor. On the other hand it should be impossible to observe a capture–emission process from the acceptor type defect in the MPC experiment when the equilibrium Fermi level lies closer to the valence band than this level. The only reasonable explanation of this phenomenon is a capture-limited signal—strongly depending on the availability of holes. The DLTS and RDLTS experiments did not make the picture any clearer—a negative signal was observed in both experiments.

We should mention that for low-gallium baseline CIGS solar cells there is a continuing discussion about the interpretation of the so-called N1 signal, which has very similar properties.\textsuperscript{[14]} Further work, including MPC measurements on low-gallium layers, should shed more light on the origin of the E4 signal.

Within the same temperature range a state labeled E5 was observed in the epitaxial Cu-poor samples. This occurred much less frequently than E4, and only for excitation fluxes lower than \( 10^{15} \text{s}^{-1} \text{cm}^{-2} \). This level was also detected by admittance spectroscopy on the epitaxial CGSe Schottky diode in Cu-poor composition. Since we know that the Schottky barrier in this case, estimated from IVT measurements, was lower than 600 meV, we have to conclude that the E5 level was situated in the lower half of the bandgap.

Levels E6 and E7 were observed by MPC only in the Cu-poor 800 nm epi-samples. It has already been mentioned that the MPC signal from E6 strongly depends on the DC illumination level and that, with increasing \( F_{DC} \), it falls into the recombination regime. The E6 signature coincides with the border of the measurements range of our set-up and this may be the reason why it has been rarely observed. The properties of E7 differed, and in the eCuP3 sample, for example, it was observed in the wide range of excitation light flux. The signatures of both levels were confirmed by AS on Cu-rich polycrystalline Schottky diodes: pcSchCuR1 (E6) and pcSchCuR1 (E7) (see Fig. 7). These properties provide information about the energetic position of both states in the bandgap of CuGaSe\(_2\): they must be majority carrier traps situated near the valence band. On the basis of the AS results, we showed in the previous section that E7 is the level responsible for doping in the pcSchCuR2 sample with the highest deviation from stoichiometry. In photoluminescence experiments acceptors with similar activation energies were observed and E6 may correspond to A2 and E7 to A3 according to Ref. 31.

The PC1 level was observed in the polycrystalline samples of both Cu-poor (AS) and Cu-rich composition (AS, MPC). It was observed by MPC in a wide range of DC illumination fluxes \( (10^{15} \text{s}^{-1} \text{cm}^{-2}) \) to \( 10^{18} \text{s}^{-1} \text{cm}^{-2} \), which suggests a very high concentration. A level with a similar signature was also reported in solar cells with a baseline CIGS absorber of Cu-poor composition.\textsuperscript{[12]} The same question as in the case of the E4 response arises here: why is a deep electroni-
cally active defects in the chalcopyrite family CuGaSe\(_2\)

VI. SUMMARY

We have presented a systematic study of the electronically active defects in the chalcopyrite family CuGaSe\(_2\)
using modulated photocurrent. The utility of the MPC method as a tool for the investigation of defect levels in chalcopyrites has been proven and its experimental limitations as a defect level spectroscopy technique have been discussed. A good level of agreement between the signatures of defect levels obtained by MPC and by capacitance spectroscopy has been demonstrated.

By correlation of the results derived from MPC, capacitance junction spectroscopy, and the temperature dependence of the dark conductivity, we can reach some conclusions about the nature of some of the defect levels. The levels labeled E5, E6, E7 (and probably PC1) belong to acceptor-like defects. Judging from the values of the activation energies found for E3 and PC2 compared to the Fermi level position in the epitaxial Cu-rich, polycrystalline Cu-poor and Cu-rich samples, which were not far from the valence band edge, we place them in the upper half of the bandgap. This conclusion is supported by the fact that none of these levels was observed by the capacitance junction techniques, sensitive only to majority carrier traps. As a result of the Fermi level position in the middle of the bandgap in the Cu-poor epitaxial samples we were not able to observe the levels E1 and E2 levels by capacitance spectroscopy and we cannot reach unambiguous conclusions about their electrical activity. We can only say that E2 seems to be an efficient recombination center in the middle of the bandgap.

Interesting features exhibited by the E4 process were detected by both photoelectric and capacitance methods in poly and epitaxial samples. The nature of this level remains unclear but our MPC investigations showed that its specific properties resemble those of the N1 level in CIGS solar cells.

Summing up, by using MPC spectroscopy we distinguished seven defect levels appearing in both polycrystalline and epitaxial samples and two only in polycrystalline layers. Some of these were assigned to rather Cu-poor or Cu-rich composition. In future investigations we intend to include CuInSe2 material in the hope that obtaining defect level signatures in this compound will bring us closer to establishing a comprehensive picture of the defect levels in the chalcopyrite solid solutions Cu(In, Ga)Se2 employed as absorbers in solar cells.

ACKNOWLEDGMENTS

This work was supported by the Polish NCBiR and Luxembourgish FNR under the ERA-NET MATERA program.

A. Krysztopa is also grateful for the support of the European Union in the framework of the European Social Fund through the Warsaw University of Technology Development Programme.