



Defect levels in CuGaSe₂ by modulated photocurrent spectroscopy

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ABSTRACT

Results of high frequency modulated photocurrent spectroscopy (HF MPC) performed on epitaxial and polycrystalline CuGaSe₂ thin films are presented. Frequency and temperature scans of MPC in the high frequency regime are compared, and the advantages of the second mode of measurement over the first one are demonstrated. Electronic parameters of defect levels in Cu-rich and Ga-rich stoichiometry are obtained and discussed in comparison to the literature data on defect levels derived from capacitance junction techniques. An attempt to correlate levels observed by MPC technique with material stoichiometry has been made.

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1. Introduction

Deep defect levels in chalcopyrites of Cu(In,Ga)(S,Se)₂ (CIGS) family which might have an impact on recombination properties of solar cells are a subject of continuing interest and investigation. Some work has been done by use of capacitance methods as admittance spectroscopy and DLTS [1–5], mostly on solar cells, but also on Schottky devices [6]. Despite this fact the picture of intrinsic defect levels is still far from being complete. In case of devices, interpretation of capacitance spectroscopy results is not straightforward because of the presence of interface and also because of distortions brought by electric field [7]. Metastabilities induced by voltage bias and illumination do not make the interpretation any easier.

Modulated photocurrent (MPC) is a technique developed for investigation of defect levels in thin films, originally proposed by Oheda [8]. It is based on the measurement of a phase shift between photoexcitation pulse and photocurrent response, brought by a presence of traps. The technique has been previously used for investigation of energetic distributions of defect levels in amorphous semiconductors [8–10] but it has also been once applied to CIGS [11]. In [11] the MPC spectra were explained by superposition of the Gaussian distribution of traps centered around 250 meV and exponential tail of levels with characteristic energy of 60 meV. Metastable behavior of the MPC spectra has been there reported.

In this work we apply MPC method to the epitaxial and polycrystalline thin films of CuGaSe₂ of various stoichiometries. The main goal is to identify deep levels typical for Cu-rich and Ga-rich compositions of CGS. This knowledge should be indispensable for

proper identification of levels in the absorbers of CIGS solar cells, and it should help also differentiate between interface and bulk levels in the CIGS devices.

2. Experiment

2.1. Samples

Samples were prepared at the Laboratory for Photovoltaics, University of Luxembourg. Epitaxial CuGaSe₂ samples were grown on semi-insulating GaAs by metal organic chemical vapor epitaxy (MOVPE). Details of the samples preparation and growth control process of epitaxial CGS with various stoichiometries are given in [12,13]. Basing on preceding work on CuGaSe₂ [12] low temperature (10 K) photoluminescence spectra have been employed to indicate the stoichiometry of the samples.

Polycrystalline CGS was grown on soda lime glass by physical vapor deposition (PVD). The stoichiometry of these samples was also estimated by comparing the low temperature PL spectra to the PL spectra of samples of known stoichiometry.

Gold electrical contacts in a co-planar geometry were evaporated on both types of the samples. The thickness of the samples is about 300 nm in the case of epitaxial layers and 2 μm for polycrystalline samples.

The list of samples investigated in this work together with their estimated stoichiometry is given in Table 1.

2.2. Method

In the MPC spectroscopy a sample in the co-planar geometry is illuminated by a beam with two components – constant Φ_{dc} and alternating Φ_{ac} . A modulus of the alternating component of the

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Table 1
Investigated samples, their stoichiometry estimated from low temperature photoluminescence spectra and energy levels derived from MPC.

Sample	Cu/Ga	Defects
epi-1	0.8	D1, D2, D3
epi-2	0.9	D1, D2
epi-3	1.1	D3
epi-4	1.2	D3
pc-1	<1	D2
pc-2	>1	D4
GaAs	Not applicable	S1

photocurrent (i_{ac}) and a phase shift between excitation light and the current response (ϕ) is measured. Brüggemann showed that frequency values corresponding to the maxima of the phase shift are directly related to emission rates of the defect level at a given temperature [14].

$$e_t = 2\pi f_{max} = \xi_0 T^2 \exp(-E_A / k_B T). \quad (1)$$

Later works show that this relation is true only if measurement conditions are such that the influence of recombination on defect occupation can be neglected (so called high frequency regime-HF MPC) [9]. Otherwise phase shift is distorted by correction function [10] and depends also on constant component of the excitation light. For sufficiently high dc light intensity defects fall into recombination regime and the phase shift approaches zero value – this mode of measurement is considered by low frequency MPC (LF MPC) [9].

The measurement setup was similar as one described in [11,15]. Measurements in the temperature range between 90 and 340 K were carried out using liquid nitrogen cryostat. As an excitation light source a 50 mW laser diode with a wavelength peak emission of 650 nm was used. Maximum available flux was $4 \times 10^{18} \text{ s}^{-1} \text{ cm}^{-2}$, attenuated if needed by neutral density filters in the range between 10^{-5} and 0.1 of Φ_{max} . Alternating illumination amplitude was kept at a level of 5% of constant illumination flux. Modulation frequencies from 1 Hz to 10 kHz were obtained using Hewlett-Packard 33120A function generator. Amplitude of the ac photocurrent and sample response phase shift were measured using SR 810 DSP Lock-in amplifier, in conjunction with Keithley 428 current amplifier.

Best resolution and signal to noise ratio is obtained in MPC measurements if the dc photocurrent is much higher than the dark current. In case of epitaxial samples the AC signal could be measured in the wide range of excitation light fluxes from $10^{-4} \Phi_{max}$ to Φ_{max} . Investigations on polycrystalline samples have been more difficult to conduct since resistivity of the samples is lower and satisfying signal to noise ratio is obtained only at excitation intensities higher than $\Phi_{max}/100$.

3. Experimental results and discussion

All data presented in the following paper were obtained for measurement conditions required by high frequency mode. In order to determine a transition frequency between the modes plot of the $\cos(\phi)/i_{ac}$ versus frequency was used. According to [9] in the range of frequencies corresponding to low frequency mode a plateau should be observed. In Fig. 1 the data for sample epi-4 as an example are shown. The transition frequencies between HF and LF modes are marked by the symbol “X”.

Phase shifts in the MPC method can be measured either at constant temperatures by using frequency scan mode or by using several constant frequencies while scanning temperature. In pure high frequency regime results provided by both methods should in principle be the same [16]. However, temperature scan provides results less dependent on phase shifts introduced by the setup – during frequency scan a setup correlated phase shifts which may well

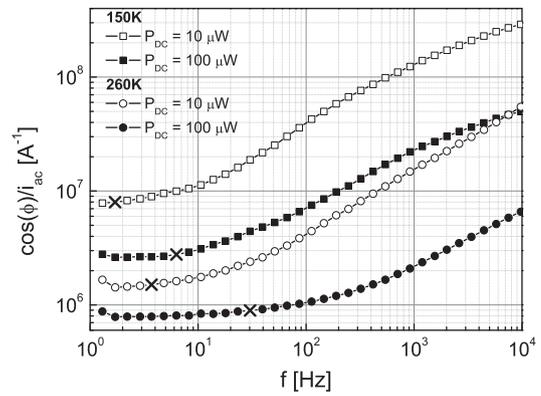


Fig. 1. Influence of the constant light bias power and temperature on the plot $\cos(\phi)/i_{ac}$ for the sample epi-4. By “X” symbols are marked transition frequencies from the low frequency to the high frequency mode.

depend also on frequency, can shift the maxima introducing additional errors into the results. We have also observed that peaks' position in $\phi(T)$ measurement are better resolved, with maxima position less sensitive to photon flux value, and disappear only when level evidently falls into recombination regime, while corresponding peaks in $\phi(f)$ scan shift with light intensity. This is illustrated in Fig. 2 where results belonging to a level D3 observed in sample epi-4 are shown. On $\phi(T)$ spectra at the excitation frequency of 66 Hz (top figure) two distinct peaks at temperatures 150 K and 260 K are clearly resolved (one of them disappears at high photon flux due to falling into recombination regime). The same maxima in the frequency scan mode (bottom figure) strongly depend on photon flux, thus providing less reliable results.

The example of the MPC temperature scans for the sample epi-2 featuring levels labeled D1 and D2 is shown in Fig. 3(a). Similar sets of data were obtained for all samples and various light intensities, and provided values of emission rates from deep levels as a function of temperature. Hence Arrhenius plots were created, activation energies and attempt-to-escape frequencies by using formula (1) were

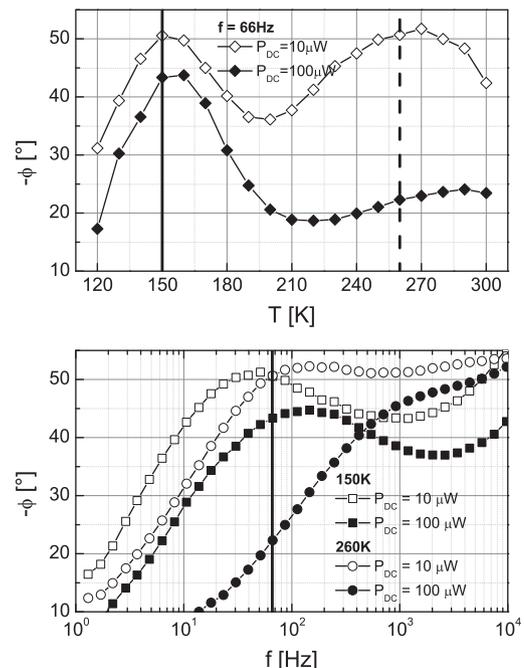


Fig. 2. MPC spectra measured in the sample epi-4 for two different constant excitation fluxes in the temperature scan (top) and frequency scan (bottom) mode.

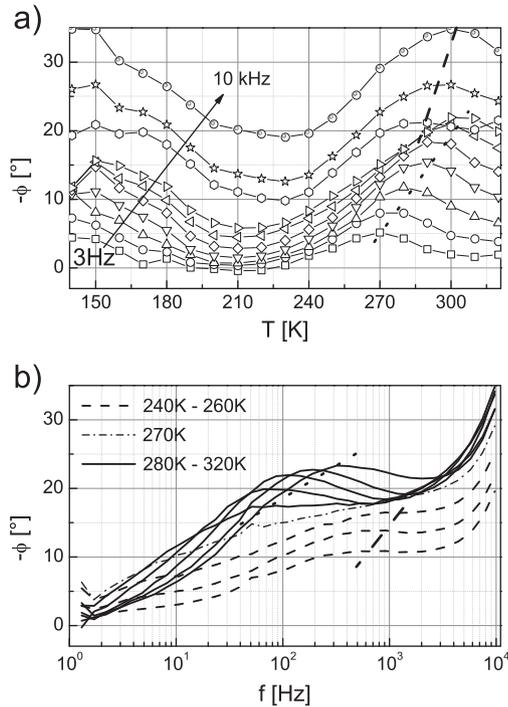


Fig. 3. Phase shift as a function of temperature (a) and frequency (b) for the sample epi-2. In both figures the maxima corresponding to states D1 and D2 are indicated by broken and dotted lines respectively. Note how a signal dominated by the D1 level at lower temperatures disappears and the level D2 becomes visible in frequency scan mode.

calculated. We will discuss here only those levels which have been found in at least two different samples. Arrhenius plots for these levels are presented in Fig. 4. Lines represent literature data obtained by use of PITS [15] in case of GaAs and admittance spectroscopy in case of CGS [1]. The activation energies and the values of preexponential factors are collected in Table 2. In Table 1 the levels observed in each of the investigated samples are listed.

Distinction between signals labeled D1 and D2 is not straightforward. Temperature range at which both signals occur overlap and slopes of their Arrhenius plots look very similar at a first glance (Fig. 5). But when we examine the MPC spectra in the frequency scan mode it is obvious that there is a contribution from two separate levels (Fig. 3(b)) and at higher temperature the signal from level D1 begins to takeover the D2. In the temperature scan both defects are well separated and occur as a two distinct peaks at different frequency ranges (Fig. 3(a)).

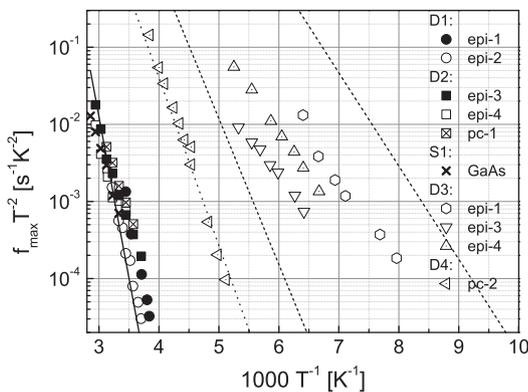


Fig. 4. Arrhenius plot of the emission rates derived from the positions of the phase shift maxima measured in the temperature scan mode. Lines show literature data: continuous line – GaAs (PITS data [14]), dashed lines – Cu-rich, dotted line – Ga-rich CGS (admittance spectroscopy of polycrystalline absorbers [1]).

Table 2

Electronic parameters of levels observed in the HF MPC. ξ_0 is the preexponential factor in Eq. (1), $\nu_0 = \xi_0 T^2$.

Defect	E_A [meV]	ξ_0 [$s^{-1} K^{-2}$]	$\nu_0(T=300 K)$ [s^{-1}]
D1	720 ± 70	10^{10}	10^{15}
D2	440 ± 40	5×10^4	4×10^{10}
D3	200 ± 30	4×10^4	4×10^9
D4	490 ± 10	5×10^8	5×10^{13}
S1	450 ± 30	7×10^4	6×10^9

Additional complication to proper interpretation of MPC data is brought by the fact that epitaxial samples with Cu-poor stoichiometry were highly compensated, so their conductivity was at least comparable with that of the substrate. Thus we can not exclude that levels belonging to GaAs contributed to the MPC response. This ambiguity has to be considered in case of the level labeled D1 which was observed only in the Cu-poor epitaxial samples. Its activation energy equal to 720 ± 70 meV – close to midgap together with high value of the preexponential factor (of order of $10^{15} s^{-1}$ at 300 K) are close to the parameters of deep level discovered in semi insulating undoped GaAs: according to [15] this deep state parameters are: $E_A = 830$ meV and $\nu_0(T=300 K) = 4 \times 10^{15} s^{-1}$. It has to be mentioned that it is difficult to observe this level by MPC because its position in the gap and the Fermi level position in the undoped GaAs are very close to each other, hence very small quasi Fermi level splitting (i.e. very small Φ_{DC}) is necessary. However 300 nm thick CuGaSe₂ constitutes as a neutral density filter and it is possible that proper measurement condition for observation of that level is thus attained.

In this section we will discuss the assignment of a level labeled D2 with activation energy equal to 440 meV. D2 level appeared in Cu-poor stoichiometry, in both epitaxial and polycrystalline samples. No levels exhibiting similar properties were observed in CuGaSe₂ Cu-rich samples. We have to mention though that the measurements carried out by us on GaAs substrate without coverage with CGS revealed a level (labeled S1) which occurs in very similar temperature and frequency range. Strong argument that level D2 belongs nevertheless to the chalcopyrite is provided by the fact that we have observed the level coinciding with S1 also in polycrystalline sample on glass substrate. Still, D2 state in Cu-poor CGS has to be confirmed by other techniques, e.g. capacitance spectroscopy.

State labeled D3 occurred in all investigated epitaxial samples, regardless of stoichiometry. Dispersion of activation energies obtained in various samples is minor, but preexponential factor differs from sample to sample, as shown in Fig. 4. In the sample epi-2 the level D3 gives contribution to the phase shift only in the frequency

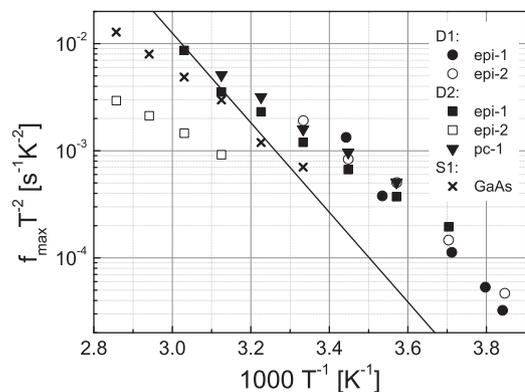


Fig. 5. Arrhenius plot of the emission rates corresponding to D1 and D2 levels. Presented is transition from state D1 (open circles) to state D2 (open squares) showed in Fig. 3(b).

scan, still even then the experimental points fall into similar range of temperatures/frequencies as in the other samples.

No levels with parameters similar to D3 have been observed in both polycrystalline samples. Although a defect level with activation energy near 200 meV has been observed in admittance spectroscopy and DLTS [1,5], it features three orders of magnitude higher value of preexponential factor thus it is unlikely it corresponds to D3.

Very good agreement between literature data derived from admittance spectroscopy performed on solar cells with Ga-rich CGSe [1] and defect labeled D4 found in pc-2 sample has been observed. Although nominally this sample should be Cu-rich, the low temperature PL spectra [unpublished data J. K. Larsen] indicate some signal contribution typical of Cu-poor phase.

4. Summary

We have reported the first systematic study on defect levels in CuGaSe₂ epitaxial and polycrystalline layers by modulated photocurrent spectroscopy. In all epitaxial samples a relatively shallow 200 meV level has been observed. Good agreement between admittance and MPC results has been found for the 490 meV level observed in one of the polycrystalline samples proving that this level indeed belongs to the CGS bulk. We discuss the interpretation difficulties with assignment of the levels found in Cu-poor layers caused by GaAs-related states with similar electronic parameters. To resolve the ambiguities, the capacitance techniques have to be applied to epitaxial CuGaSe₂ samples and investigation of the MPC spectra on thicker CGS epitaxial layers is

planned. Our work proves that MPC technique is a valuable tool which might help assign levels observed by use of various techniques to specific intrinsic defects.

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