Defects in the photovoltaic structures based on CuInSe$_2^+$

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This paper is dedicated to intrinsic defects in the absorber layer of thin film solar cells ZnO/CdS/CuInSe$_2$. A nature of shallow levels controlling the electrical properties of CuInSe$_2$ is briefly discussed. Most attention is given to the recent progress on experimental observations of deep levels. The examples of results obtained by junction techniques, DLTS, and admittance spectroscopy, are presented together with the short description of the employed methods. The data indicating which features of the spectra are due to bulk defect levels and to interface states are discussed.

1. Introduction

Chalcopyrite compound CuInSe$_2$ and related materials Cu(In,Ga)Se$_2$ and CuIn(S,Se)$_2$ are employed as absorbers in high efficiency thin film solar cells [1]. The electrical and photovoltaic properties of CuInSe$_2$ are controlled by intrinsic defects. Their concentration in a ternary semiconductor as CuInSe$_2$ is expected to be very high, so on that background the significance of extrinsic states is generally considered as negligible.

In general, intrinsic defects can introduce shallow levels in the energy gap controlling transport properties of the material and deep states acting as traps or recombination centers. The latter are particularly important for the performance of the photovoltaic devices. Within last few years the investigations based on junction capacitance techniques, deep level transient spectroscopy (DLTS), and admittance spectroscopy have brought some new information on the bulk and interface states in solar cells based on ternary chalcopyrites.

In this work after a brief description of the problems associated with intrinsic shallow defects in Cu-InSe$_2$, the review of the results on deep states provided by both junction techniques will be presented. Most of these data have been obtained for the standard thin film photovoltaic devices ZnO/CdS/CuInSe$_2$ fabricated in the Institute of Physical Electronics of Stuttgart University [2]. Some results for structures based on single crystal CuInSe$_2$ will be also shown in order to document which features of defect level spectrum are typical for the bulk material as well as for thin films.

2. Shallow states

It has long been known, that a conductivity type of CuInSe$_2$ depends on the predominant intrinsic defects which act as shallow donors or acceptors [3, 4]. For example, annealing in selenium vapour changes the material from n- to p-type conductive and that can be reverted by annealing in vacuum. The excess of indium or copper regarding to the stoichiometry also influences the conductivity type. In Table 1 the formation energies of various point defects in CuInSe$_2$ and their electrical activities predicted by a covalent model have been collected [4]. On the basis of the theoretical expectations and experimental data coming from investigation of electrical transport and photoluminescence one might try to assign observed in the experiment shallow donor and acceptor states to specific point defects. Since CuInSe$_2$ is usually strongly compensated material, it is generally believed that, depending on the stoichiometry, specific pairs of compensating defects dominate. In p-CuInSe$_2$ with excess of indium, which is employed as an absorber in the solar cells, the dominating pair of shallow defects is vacancy V$_{Cu}$

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(acceptor) and antisite In_{Cu} (compensating donor). Other point defects, giving shallow levels are probably V_{In}, V_{Se}, Cu_{In}, Cu_i. Still there are no theoretical or experimental evidences, which would univocally imply, that any defect listed in Table 1 acts as a deep trap or recombination center.

Table. 1. Creation energies and electrical activities of intrinsic defects according to covalent model of CuInSe2 [4].

Defect	Formation energy (eV)	Electrical activity
In_{Cu}	1.4	D
Cu_{In}	1.5	A
V_{Se}	2.4	A
V_{Cu}	2.6	A
V_{In}	2.8	A
Cu_i	4.4	D
In_{Se}	5.0	D
Se_{In}	5.5	A
Cu_{Se}	7.5	A
Se_{Cu}	7.5	D
In_i	9.1	D
Se_i	22.4	A

3. DLTS spectroscopy

3.1. Experimental method

Space charge junction methods are based on a fact that a capacitance of the junction depends on a total charge in the depleted region [5]. Limiting the discussion to the case of n⁺–p junction (Fig. 1.), which is a simplified model of CdS/CuInSe2 heterojunction, one can divide this charge to a fraction belonging to shallow acceptors of concentration N_a and to deeper acceptor-type states N_T. The capacitance of the junction depends on the sum of concentrations of empty shallow and deep states in the depletion layer and on the total voltage drop across the junction:

$$C = \sqrt{\frac{\varepsilon\varepsilon_o e(N_a + N_T)}{2(V_R + V_b)}}$$

The amount of charge accumulated in the deep states can be changed, e.g. by decreasing for an instant the reverse bias applied to the junction. The majority carrier traps, which will momentarily rise above the hole quasi-Fermi level E_{fh}, are then filled by holes.
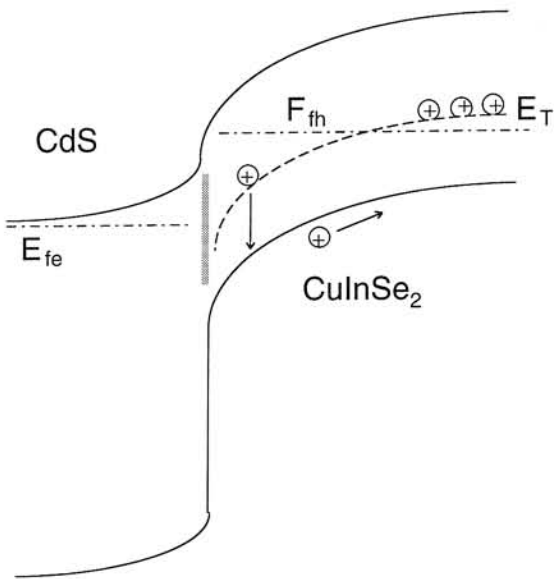

Fig. 1. Band diagram of CdS/CuInSe2 heterojunction under reverse bias. Hole and electron quasi-Fermi levels and a trap level E_T are indicated.

After the quiescent bias is returned, the capacitance of the structure is lower due to decrease of total negative charge in the depletion region. If $N_T \ll N_a$, the magnitude of the capacitance change is proportional to the concentration of filled traps. As the trapped holes are thermally emitted to the valence band, a capacitance transient is observed:

$$\Delta C(t) \sim n_T(t) = N_T \exp(-e_T t)$$

Thermal emission rate e_T depends on the electronic parameters of defect level: σ_h – capture cross section for holes, and E_T -trap level depth with respect to the valence band:

$$e_T = \sigma_h v_{th} N_v \exp(-E_T / kT)$$

Here v_{th} is a thermal velocity of holes, and N_v – density of states in the valence band. If emission rate e_T has been determined from the capacitance transients at several temperatures, one can obtain σ_h and E_T by constructing an Arrhenius plot. Additionally, from the total capacitance change after filling all traps, the concentration of traps can be calculated.

Very often it is difficult to obtain e_T by analyzing the capacitance transients, particularly when the concentration of traps is low. In that case the DLTS method is very convenient. It is based on the periodic filling of traps while temperature is scanned. By means of an electronic filter, the capacitance transient is compared after each pulse to the prefixed "emission rate window". When the thermal emission rate fits into the

"rate window" the maximum of DLTS signal is observed. After performing the temperature scans for several emission rate windows and determining the positions of DLTS peaks in the temperature scale, one can easily obtain the dependence of e_T on temperature.

3.2. Spectra of majority carrier traps

Typical DLTS spectrum of hole traps in single crystal p-CuInSe$_2$ measured for Schottky junction prepared on Bridgman-grown stoichiometric material is shown in Fig. 2. [6]. Arrhenius plot obtained from that data (Fig. 3.) gives the trap depth 0.26-0.28 eV above the valence band and cross section for holes of order of 10^{-14} cm^2. The DLTS peak due to that trap is much broader than expected for a discrete level and is accompanied by a tail of emission rates towards higher temperatures. That feature is also characteristic for DLTS hole trap spectrum of thin film photovoltaic structures (Fig. 4.) [7]. The defect state or rather distribution of states centered around 0.26 eV has been also observed in thin films by ac photoconductivity [8] and admittance spectroscopy [9] (see section 4). All these methods also show that with the states around 0.26 eV metastable phenomena are associated. An increase of DLTS and admittance signal, decrease of ac photoconductivity is observed after illumination or electron injection and persists at low temperatures. For explanation of these metastabilities a model of a defect strongly coupled to the lattice, which relaxes after a change of the charge state, has been proposed [7, 10].

An experimental observation, that the 0.26 eV hole traps do not usually appear in the efficient struc-
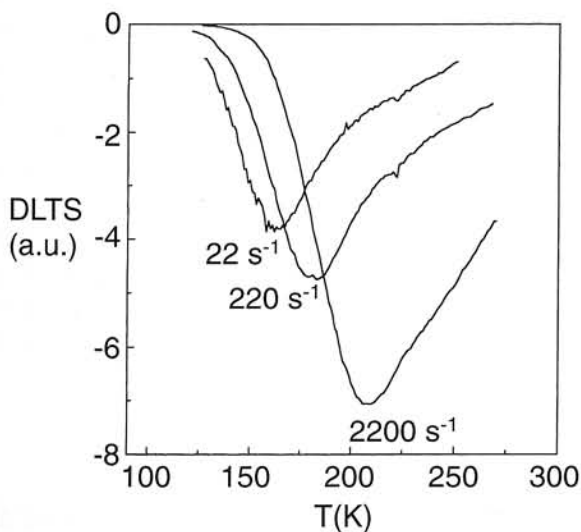

Fig. 3. Arrhenius plots for bulk trap hole traps ($\triangle$, $\square$) and electron trap (o) observed by DLTS. Open symbols are results for single crystal material, full symbols – for absorber layers in photovoltaic structures.

tures in which some indium has been replaced by gallium, but can again be observed in the structures based on CuGaSe$_2$ is also intriguing [11].

3.3. Spectra of minority carrier traps

Deep levels situated in the upper half of the band gap are of special interest from the point of view of establishing factors limiting device efficiency, since they can play a role of recombination centers for photoexcited carriers. They can be studied when

Fig. 2. DLTS spectra of hole traps obtained in single crystal Schottky junction In/CuInSe$_2$ for various emission rate windows [6].

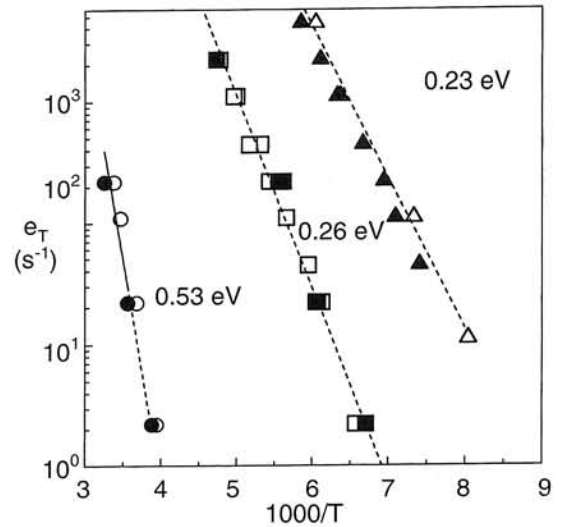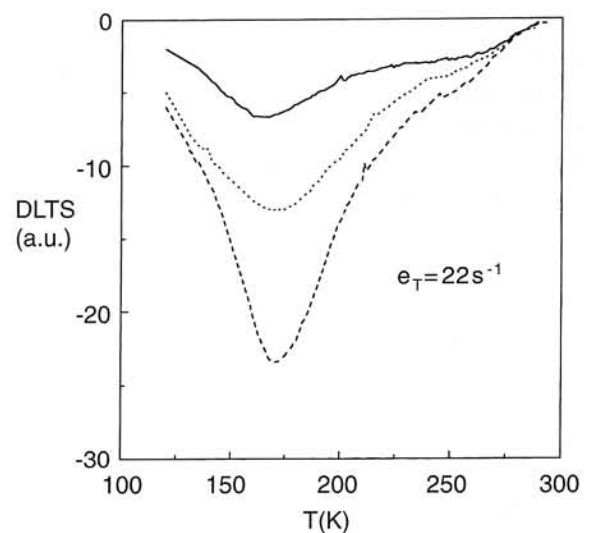Fig. 4. DLTS hole trap spectra in ZnO/CdS/CuInSe$_2$ solar cell. The metastable increase of the signal magnitude after illumination (dotted line) and electron injection (dashed line) is shown [7].
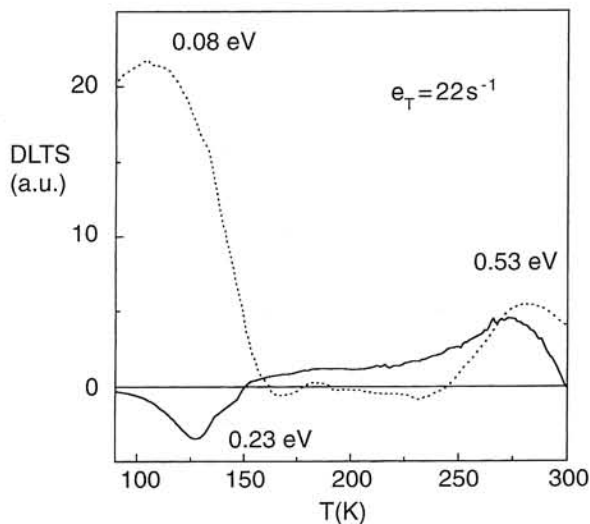
Fig. 5. Electron trap spectra obtained for CdS/CuInSe₂ devices by use of injection pulses: continuous line – single crystal CdS/CuInSe₂ heterojunction (a hole trap of energy 0.23 eV is also present); dashed line – thin film solar cell ZnO/CdS/CuInSe₂
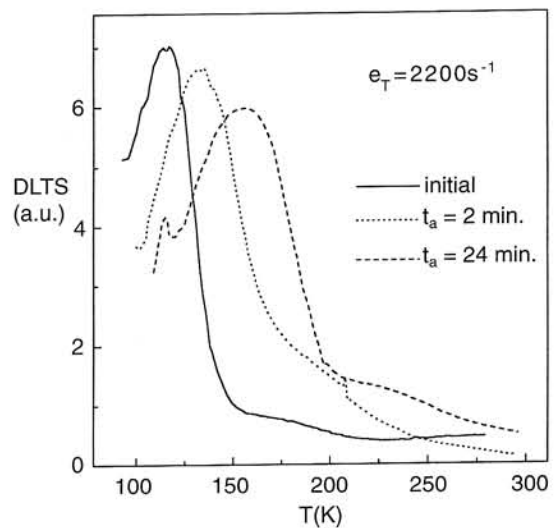

Fig. 6. Spectra of interface electron traps measured by optically induced DLTS in ZnO/CdS/CuInSe₂ device showing the influence of annealing in air at 200°C [13].

minority carriers are introduced into the depletion layer by band-gap light or injection pulses. A DLTS signal coming from the traps emitting minority carriers is positive, so it can be easily distinguished from the one due to the hole traps. However, since injection and illumination produces carriers of both signs within the depletion region, very effective recombination centers, which do not store charge, may be difficult to fill and hence can not be observed by DLTS.

In the spectrum of electron traps investigated by use of electron injection a deep level has been observed (E_T = 0.53 eV) [6, 8], which has been earlier found by studying of kinetics of dc photoconductivity [12]. That electron trap is observed also in both poly- and monocrystalline material (see Fig. 3 and 5.).

In the efficient photovoltaic devices a big maximum due to electron emission at low temperatures, characterized by an activation energy around 0.1 eV, is usually detected (Fig. 5). The measurements carried out by DLTS and admittance spectroscopy (see next Section) revealed, that this feature is related to electron traps at interface [13]. A presence of DLTS response due to interface states means, that a standard CuInSe₂-based solar cell is a MIS-type structure with depleted CdS layer, since only then a voltage pulse changes the occupation of interface levels.

As it has been mentioned, electron traps can also be investigated using pulsed light of energy higher than E_g. The example of that type of measurements is illustrated in Fig. 6, in which the DLTS spectra due to emission from electron interface traps obtained by optically induced DLTS are depicted. The effect of annealing in air at 200°C on the value of the emission energy (the longer the annealing the deeper an apparent energy level) is shown here [13].

Electron interface states can also be investigated by use of a modification of standard DLTS technique – reverse-bias DLTS (RDLTS) [14]. It has been found that RDLTS is much more convenient method for studying these levels than the conventional minority carrier DLTS employing light or injection pulses [15].
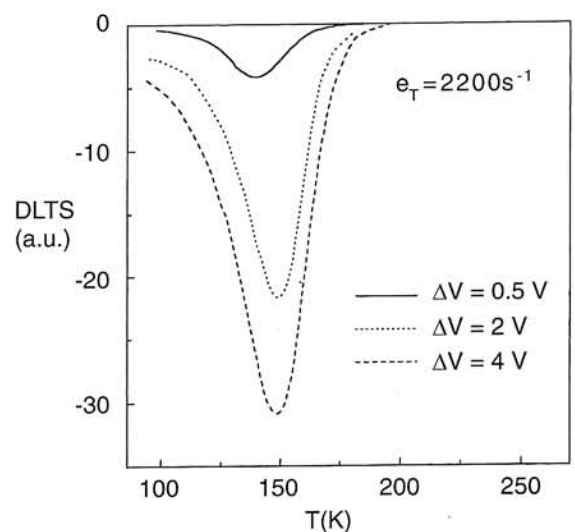

Fig. 7. RDLTS spectra due to interface traps obtained for ZnO/CdS/Cu(In,Ga)Se₂ device for various pulse heights |V| applied in the reverse direction to the zero-biased junction [15].

The spectrum of electron interface traps by RDLTS is not distorted by the metastable effects due to the electron injection and also by the majority carrier emission. In this method a voltage pulse in the reverse direction is applied to the junction. During the pulse the quasi-Fermi level for electrons at interface decreases with respect to the conduction band and interface states emit electrons. When the quiescent voltage is returned, electrons are captured back by these states and to the capture-related capacitance transient the DLTS processing is applied. The signal in that case has an opposite sign to the one due to emission, but the temperature dependence of the time constant remains the same. That is due to the fact, that the highest contribution to the capacitance transients comes from the states, for which the probability of capture is equal to that of emission. In Fig. 7. the RDLTS spectra for the photovoltaic device based on Cu(In,Ga)Se$_2$ are shown. One can observe that there is practically no change of RDLTS spectrum with the pulse height, which means that either the process due to discrete level is observed or the Fermi-level is very strongly pinned at interface.

4. Admittance spectroscopy

4.1. Method

In the DLTS measurements it is assumed, that the angular frequency ω of an ac signal employed by a capacitance bridge for measuring the junction capacitance is much higher, than the capture and emission rates characterizing deep levels under investigation. Thus the only states which are fast enough to follow the ac voltage are shallow acceptors (donors). But if that frequency is comparable to the emission rates from deeper traps, they also contribute to the capacitance [16]. Hence an increase of the capacitance is observed, when during the measurement at constant temperature the measurement frequency ω is gradually reduced. The same effect is observed, if measurement is made at constant ω while temperature increases. The capacitance change from the value to which only shallow states contribute to the value in which also deeper traps take part can be expressed by relation

$$C_{lf} - C_{hf} \propto \frac{e_T^2}{e_T^2 + \omega^2}$$

By analyzing of the derivative of $C(\omega)$ measured at various temperatures one can determine the dependence of emission rates on T, and, using Arrhenius plot, the electronic parameters of the traps.

4.2 Admittance spectra

The measurements of deep level spectra by the admittance spectroscopy confirmed, that in CuInSe$_2$ and CuGaSe$_2$-based devices there is a quasi-continuous broad distribution of energy levels around 0.25-0.30 eV with a tail towards midgap [9]. Therefore the density of states rather, than single level positions have been calculated from admittance data (Fig. 8).

In most photovoltaic structures there is also a high concentration of shallow states, which by comparing with DLTS data have been identified as electron traps. The influence of annealing in air at 200°C has been investigated and it has been found, that an apparent thermal activation energy from these traps increases from 0.12 eV to about 0.24 eV with the annealing time (Fig. 9.) [13]. These results, together with the dependence of the magnitude of the response due to that traps on the width of CdS layer, have been concluded in [13], that we observe here the response due to continuous distribution of donor-type states at CdS/CuInSe$_2$ interface. Thus an activation energy obtained in the experiment corresponds here to the electron Fermi-level position at interface.

By use of admittance spectroscopy the influence of incorporation of sodium and sulfur on the level spectra and efficiency of the devices has been studied [17]. It has been found that the best photovoltaic parameters and at the same time the lowest concentration of deep states are observed, if both elements simultaneously are incorporated in the absorber.
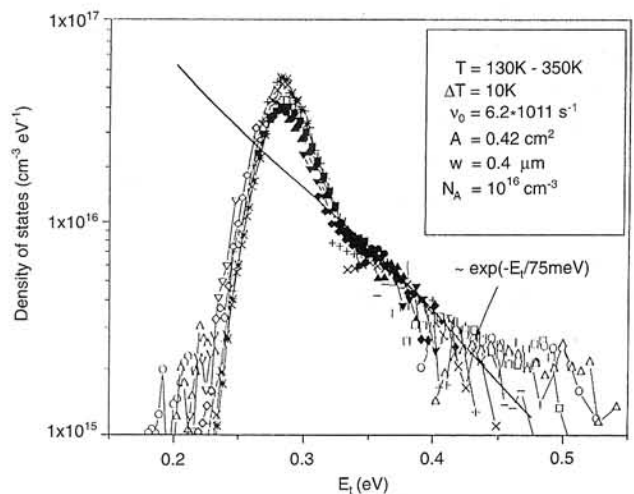

Fig. 8. The density of states in ZnO/CdS/CuInSe$_2$ device obtained by admittance spectroscopy [9]. The wide distribution of states around 0.28 eV is shown.
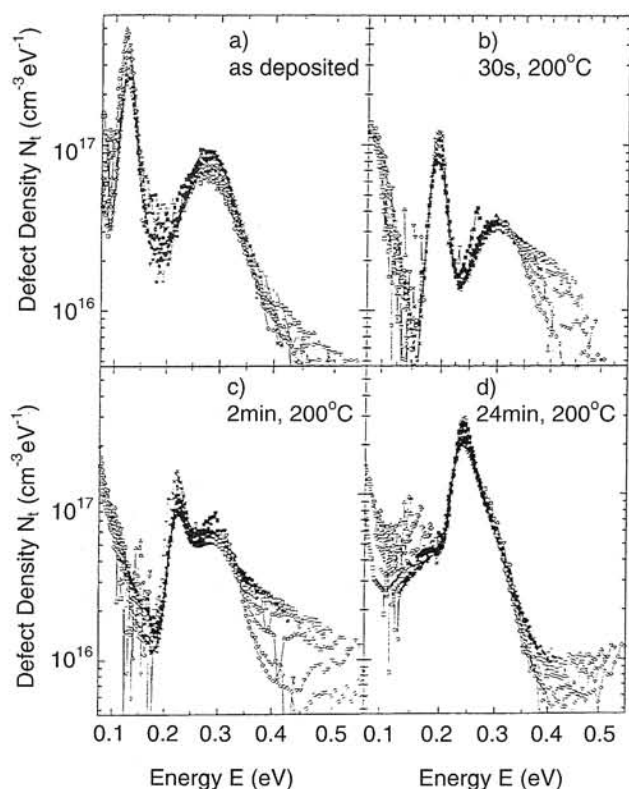
Fig. 9. The influence of annealing in air at 200°C on the density of states in ZnO/CdS/CuInSe$_2$ device obtained by admittance spectroscopy [13]. The position of shallower level due to electron interface trap changes with annealing time, while the 0.28 eV trap remains unchanged.

5. Discussion

In the discussion we will focus on the problem of the role of defect states detected by junction techniques and their influence on the photovoltaic parameters of solar cells. The data presented in Section 3 (see the Arrhenius plot in Fig. 3.) prove, that two hole traps – 0.23 eV and 0.26 eV and one electron trap 0.53 eV, which have been observed in both thin films and single crystals are related to the intrinsic bulk defects. The hole traps around 0.26 eV exhibit some features, which interpretation is still a subject of discussion. In the model proposed for explanation of metastable effects the apparent continuous distribution of levels is due to a defect relaxation and their presence or absence in the sample is a consequence of their relation to a defect, with three charge states of various thermal ionization energies and type of electrical activity [7, 10]. That defect, when neutral, should play a role of a weak recombination center. Since the metastabilities seem to be closely related to the well known effect of increase of efficiency of CuInSe$_2$-based solar cells resulting

from light-soaking [18], a full explanation of the nature of that phenomenon is crucial for understanding important factors influencing the performance of these devices.

The deep electron state 0.53 eV seems to be a typical trap - the investigation of dc photoconductivity indicates, that recombination is possible only after thermal activation of trapped electrons [12]. Within a model of the relaxing center, strongly coupled to the lattice, it might be also one of the three levels associated to the defect responsible for the metastable behavior.

The relation between the presence and density of the interface states in the structure and the efficiency of the device is not straightforward. The results of RDLTS and admittance spectroscopy prove, that Fermi-level is pinned very strongly at the interface and that is why the DLTS or admittance spectra give the impression, that they originate from a discrete level. The density of these states is very large, exceeding 10^{13} cm^{-2}eV^{-1}, even in the best cells. A fact, that they apparently do not restrain the performance of the devices may be attributed to the presence of n-type defected layer CuIn$_3$Se$_5$ adjacent to the interface [19]. That phase seems to separate the electrical junction from the metallurgical one and limits the interface recombination since holes are then minority carriers at CdS/CuInSe$_2$ interface.

6. Summary

The experimental results obtained by junction techniques prove, that these methods provide valuable data on bulk and interface levels in the photovoltaic structures based on CuInSe$_2$. The advantages of DLTS are, that it can easily distinguish between hole and electron trap levels by a sign of a signal and makes possible the determination of spatial distribution of levels. Admittance spectroscopy allows for investigation of defect-related processes in the conditions closer to thermodynamic equilibrium and exhibits higher sensitivity to the interface states. Presently we have introduced also a new technique, Laplace-DLTS [20], which is based on the numerical analysis of the capacitance transients by use of reverse Laplace transform [21]. That method displays much higher spectral resolution so the investigation of subtle details of the defect level spectra is possible.

Summing up, we have to say, that many issues concerning the electronic properties of defect centers and their role in the solar cells based on CuInSe$_2$ remain open and still are a subject of investigation and

discussion. We believe that a continuation of fundamental research, possibly closely linked to technology, is necessary for attaining further progress in the performance of photovoltaic devices based on the ternary compounds.

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