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Admittance measurements on CIGS solar cells

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Thin film solar cells based on polycrystalline CIGS absorbers are one of the most promising candidates for the low-cost and efficient large-scale solar energy conversion devices. Electronic transport properties of ZnO/CdS/Cu(In,Ga)Se_2 solar cells were investigated by means of admittance measurements in a frequency range from 600 Hz to 1 MHz and a temperature range from 80 to 300 K. Dependent on the sample under investigation, one characteristic frequency (inflection point) corresponding to an activation energy between 80 and 160 meV or two points corresponding to an activation energy about 400 meV have been observed. Analysis of the measured frequencies and obtained activation energies provides information on the equilibrium Fermi level position at the CdS/CIGS interface.

Keywords: admittance, heterojunction, solar cells, ternary compounds.

1. Introduction

Thin film solar cells employing polycrystalline ternary semiconductor $CuInSe_2$ and Ga containing alloys as absorber (CIGS), provided with CdS buffer layer and ZnO window are one of the most promising candidates for the low-cost and efficient large scale solar energy conversion devices. Despite improvements in solar cells efficiency and significant progress in understanding of their electronic properties, electronic processes limiting device performance [1] as well as properties of polycrystalline bulk materials and their interfaces have not been explained satisfactorily yet. Admittance spectroscopy was proposed as a tool to identify the discrete traps many years ago [2]. This technique is being continuously developed [3] and with deep level transient spectroscopy (DLTS) allows to determine energy distribution of defects. In this work admittance spectroscopy yielded valuable information on the band diagram of the investigated devices.

2. Experimental

The investigated samples were standard ZnO/CdS/Cu(In,Ga)Se_2 thin film solar cells obtained by the coevaporation method on Mo-coated glass substrate. Two of them (S-509 and JW-5) were fabricated in Ångstrom Solar Center, Uppsala University [4] and one (MG-407) in IPE, Stuttgart University [5]. Their structure represents a n^+-n-p heterojunction well suited for admittance spectroscopy. Admittance measurements were performed using precision Hewlett-Packard HP 4204 LCR meter in the frequency range from 20 Hz to 1 MHz at zero bias. Measuring ac signal amplitude was 50 mV. The admittance data were evaluated assuming a parallel equivalent circuit. Samples were mounted on a sample stage cooled by liquid nitrogen inside vacuum chamber allowing to vary temperature between 80 and 300 K. The sample JW-5 was treated by "damp heat" process, 1000 hours in 85% relative humidity and temperature of about 85°C which caused decrease in its efficiency to about 9%, from initial value 14% [6]. Light induced metastabilities were investigated in the sample MG-407. The illumination was realised by 100 W halogen lamp.

3. Theory

The capacitance of CdS/CIGS junction consists of two independent elements: from free carriers and from defect states. Contribution from free carriers depends on the width of the space charge layer. This capacitance is determined by the response of the majority carriers limited by the dielectric relaxation time

$$\tau_{rel} = \frac{\varepsilon}{\sigma} \tag{1}$$

where σ denotes the conductivity and ε is the dielectric constant. For high frequencies exceeding τ_{rel}^{-1}, an absorber behaves as a pure dielectric and capacitance reduces only to the value determined by the sample geometry. Due to thermally activation of σ, the critical frequency will be thermally shifted. Charging and discharging of trapping levels give additional contribution to the junction capacitance. This additional capacitance can be observed only if the modulating ac field allows establishing equilibrium state between the occupation of the defect states and the

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free carriers. Capacitance corresponding to discrete defect states C_t depends on measuring frequency ω

$$C_t \propto \frac{\omega_0^2}{\omega_0^2 - \omega^2} \tag{2}$$

where ω_0 is the inflection point of the capacitance function (inflection of the characteristic step). The value of ω_0 depends on the effective density of the band, thermal velocity, capture cross-section for carriers and thermal activation energy from the defect states E_a. Temperature dependence of ω_0 can be written in the following form

$$w_0 \propto T^2 \exp\left(-\frac{E_a}{kT}\right) \tag{3}$$

Neglecting temperature dependence ~T^2 arising from temperature dependencies of thermal velocity and density of band, using Arrhenius plot of the maxima of dC/dω vs. lnω the activation energy from the family of temperature and frequency dependent admittance measurements can be obtained.

4. Results

Typical capacitance spectra of the ZnO/CdS/Cu(In,Ga)Se_2 solar cells for sample MG-407 are presented in Fig. 1. These results are typical for CIGS solar cells – only one capacitance step can be observed. In the temperature range between 80 and 160 K capacitance decreases from high to low frequency capacitance in one frequency decade. Similar results for the sample S-509 were obtained. Admittance spectra yield only one low temperature capacitance step that shifts to the higher frequencies after light soaking [7]. According to Refs. 1 and 8, the low temperature step can be produced by high density of donor-type interface states at the CdS/CIGS interface (activation energy 160 meV). The energy activation shift dependent on illumination intensity indicates a distribution of interface states on CdS/CIGS interface. Arrhenius plots for different measur-

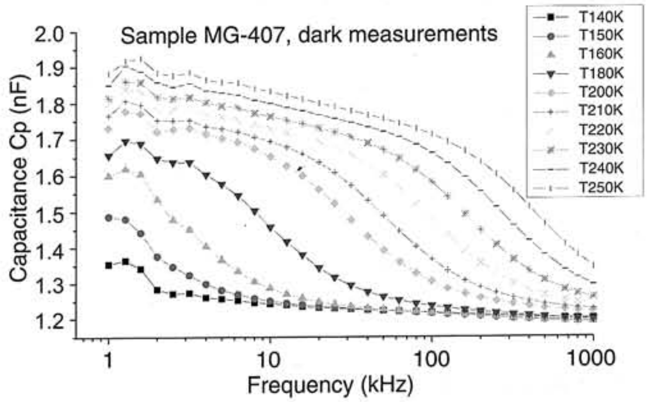

Fig. 1. Capacitance spectra of the ZnO/CdS/Cu(In,Ga)Se_2 solar cells, sample MG-407.

ing condition are presented in Fig. 2. As it can be seen in this figure, Arrhenius plots are not perfectly linear what makes their analysis not so clear. Some authors make attempt to interpret this nonlinearity as a result of thermally assisted tunneling [9].

There is no significant shift of activation energy when admittance measurements at reverse bias are made in comparison to zero bias conditions. It means that Fermi level is pinned at the interface by interface states. Capacitance spectra for sample JW-5 are presented in Fig. 3. In this sample, after „damp heat", the high-frequency capacitance decreases and the second capacitance step arises. There is no shift of this step after the light soaking. From the comparison of these spectra to the reported data [1] it can be concluded that high temperature step corresponds to the bulk defects (hole traps) in the absorber (activation energy 420 meV). These two effects can be explained assuming that "damp heat" treatment reduces significantly the grain boundaries passivation.

Activation energies for investigated samples, obtained using Arrhenius plot, are presented in Table 1.

The band diagram for ZnO/CdS/Cu(In,Ga)Se_2 solar cells and the interface states localisation are presented in Fig. 4. The activation energy E_a obtained from admittance

Table 1. Activation energies

Sample	Conditions	Activation energy (meV)	
		Low temperature step	High temperature step
S-509	Initial (dark)	150	
	1 hour light soaking before cooling	80	
JW-5	Initial (dark)	160	420
	1 hour light soaking before cooling	100	390
MG-407	Initial (dark)	200	
	1 hour light soaking before cooling	140	
	2 hours light soaking before and during cooling	80	
	Reverse bias	195	

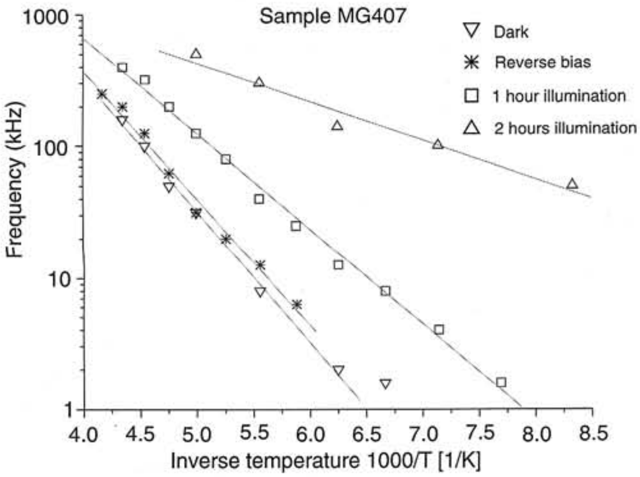

Fig. 2. Activation energy changes caused by different measurement conditions.

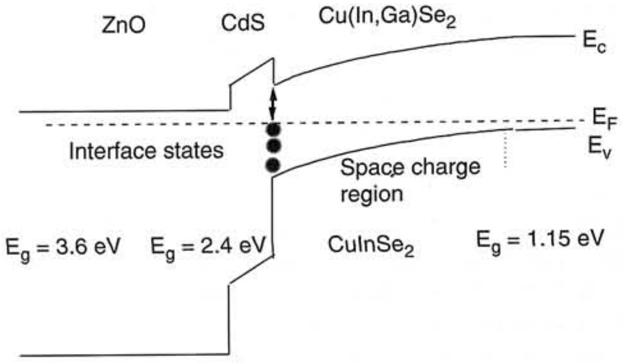

Fig. 4. Localisation of interface states – band diagram for $ZnO/CdS/CuInSe_2$ solar cell.

measurements using Eq. (3) corresponds to E_c–E_f at the interface. Obtained results are consistent with published in another papers [1,3].

5. Conclusions

Admittance measurements have shown that defect spectra of efficient photovoltaic devices obtained at Ångstrom Solar Center are similar to that fabricated at IPE, Stuttgart University and reported in the literature. Only one inflection point in C(ω) characteristic corresponding to interface levels is observed. Its activation energy indicates that Fermi level is pinned close to conduction band at the interface. Light soaking increases further the inversion at the interface, which is beneficial from the point of view of photovoltaic performance.

In the devices of lower efficiency which have been subjected to "damp heat" treatment, the signal which we have attributed to grain boundaries appeared.

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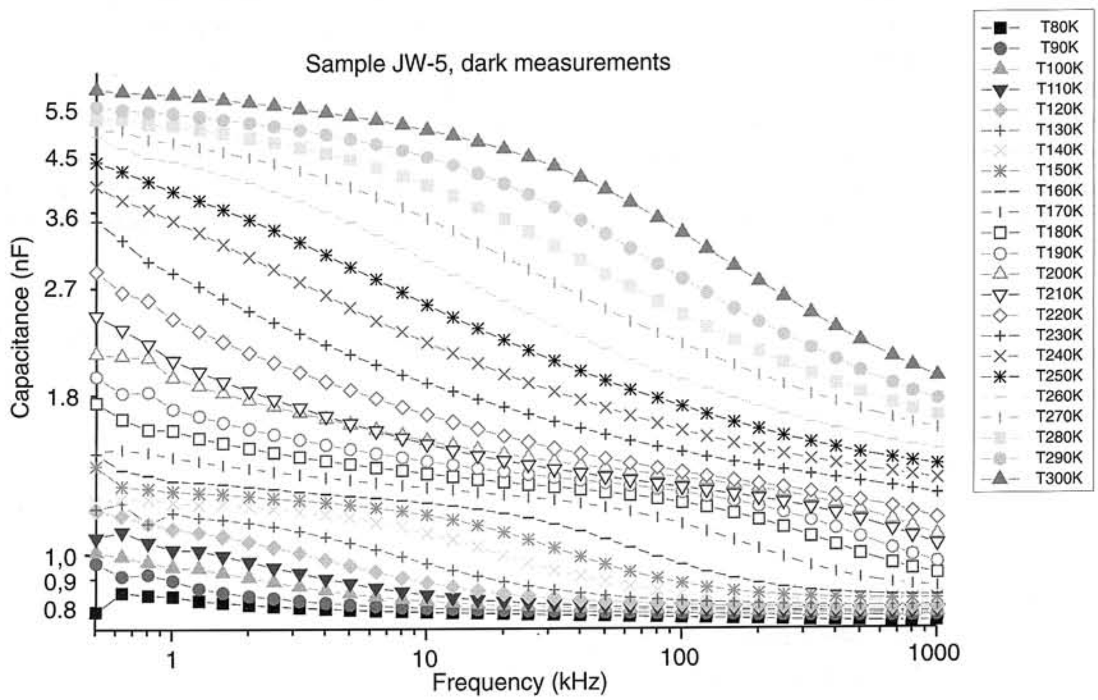

Fig. 3. Capacitance spectra of the $ZnO/CdS/Cu(In,Ga)Se_2$ solar cells, sample JW-5.

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