Measuring Complex for Analysis of Recombination Deep Traps in Semiconductor Solar Cells

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Abstract — **Measuring complex for analysis of recombination deep traps in semiconductor solar cells based on the I-DLTS is described. Measuring complex can be used in the industry of semiconductor solar cells where is necessary to control deep traps concentration and required level of conversion efficiency and quality of solar cells.**

Keywords — *DLTS; I-DLTS; deep level; trap; semiconductor; solar cell*

I. INTRODUCTION

In the production of solar cells (SCs) the problem of improving the quality characteristics is solved continuously [1]. The main important characteristic of solar cells is the conversion efficiency of solar energy into electricity [2, 3]. Conversion efficiency is affected by different factors. One of the main is the presence of different types of processing induced or intrinsic structural defects [4]. Semiconductor materials and barrier structures (p-n, p-i-n, Schottky diodes) are used for solar cells manufacture inevitably have defects or deep traps. Defects form so-called deep energy levels (DLs) in the band gap of the semiconductor material. DLs are involved in the generation-recombination processes described by the Shockley-Read-Hall statistics [5] and form the recombination component of direct current through the rectifying junction [6].

In semiconductor diode based on materials with a small band gap and a large value of intrinsic concentration n_i (e.g. Ge) at room temperature the diffusion component dominates in the saturation current. For Si-based p-n junction generational component of current dominates and it is proportional to the n_i [6]. At forward bias on p-n junction in the generation-recombination processes in the depletion layer are determined by the processes of charge carriers' (CCs) capture also. The recombination current is added to the diffusion current through the junction [6]. In real SCs defects that create generation-recombination energy levels or DLs in the band gap present always. Therefore the direct current is also determined by the recombination of CCs in the depletion region of a diode. The conversion efficiency of solar energy in the real SC will decrease compared to the SC based on non defect ideal diode because open circuit voltage V_{XX}, the value of the direct current in the load I_L and the area of the rectangle of maximum power

on the current-voltage characteristic of the lightened SC decrease [4].

In Si-based SCs recombination current can lead to reduction conversion efficiency to 25% [7]. In the [8] the adverse influence of DLs on the performance of Si-based SCs was studied. Simple equation that explains the relationship of conversion efficiency η of solar energy into electricity is written as follow [6]:

$$\eta = \frac{FF \cdot I_L \cdot V_{XX}}{P_{in}}, \qquad (1)$$

where FF is the fill factor, P_{in} is the power of the SC radiation. The load current in the case p^+-n-junction consists of diffusion and recombination component [6]:

$$I_L = q\sqrt{\frac{D_p}{\tau_p}} \frac{n_i^2 S}{N_D} \exp\left(\frac{qV}{kT}\right) + \frac{q n_i N_t \sigma \langle \upsilon_T \rangle WS}{2} \exp\left(\frac{qV}{2kT}\right), \qquad (2)$$

where q is elementary charge, D_p is the hole diffusivity, τ_p is the hole lifetime, S is the area of the p^+-n-junction, N_D is the shallow donor impurity concentration in the n-type base, V is the voltage bias on SC, k is the Boltzmann constant, T is absolute temperature, N_t is DLs concentration, σ is the capture cross section of CCs, $\langle \upsilon_T \rangle$ is the average thermal velocity of CC, W is the width of the depletion region. The (1) and (2) show the conversion efficiency of solar energy depend on the presence of DLs complicatedly.

Another promising development of solar energy is associated with the manufacture of solar cells based on non-crystalline semiconductors, in particular based on a-Si:H (see e.g. time line of solar cell energy conversion efficiencies since 1976 reported by National Renewable Energy Laboratory (NREL) in the internet). In non-crystalline semiconductors charge carriers have less CCs mobility by several orders of magnitude than crystalline semiconductors. Electrical conductivity is determined significantly by hopping mechanism involving localized states [6]. Localized states are formed from structure defects (dangling bonds) in the material and act as recombination centers that reduce the lifetime of the CCs. The distribution of the density of localized states and their concentration in varying degrees affects on the concentration of

free CCs. In this regard the direct current in diode structures based on non-crystalline semiconductors is determined by process of drift and generation-recombination processes involving deep localized states.

Thus in the industry of SCs is necessary to control DLs in the depletion region because the increasing of the DLs concentration reduce the efficiency and quality of SCs.

II. SUBSTANTIATION OF MEASURING COMPLEX

Methods of investigation of electrical and optical active defects that create DLs in the band gap (mobility gap) in semiconductor diode structure based on the analysis of the frequency, electric field and temperature dependence of conductivity or admittance are well known. One of the most sensitive methods by the concentration of DLs up to 10^{-7} part of the free CCs concentration or $|N_D - N_A|$ is a deep level transient spectroscopy (DLTS) [9]. Relaxation spectroscopy as a method for the investigation of defects with DLs in semiconductor Schottky barrier structures, p-n-junctions, MIS structures was proposed by Lang in 1974 [9].

SCs are characterized by a rather large area of the junction which imposes certain requirements for the methods of SC's electrical parameters diagnostics. Large area of junction interface is larger than commonly studied with conventional diagnostic methods C-V, DLTS and admittance spectroscopy. In such diode-like structures electrical barrier capacitance and leakage current increase.

DLTS-spectrometers in many laboratories are often realized on the base of digital capacitance meter Boonton 7200. Maximum sensitivity to relative change in the measured capacitance of the sample is reached usually at the lower limit of measurement in the range 0-2 pF. On the other hand the dynamic range of the barrier capacitance may be one – two orders of magnitude. It is necessary to make a choice either to set a larger capacitance measuring limit or to measure capacitance transition towards the end of the transient. All of this leads to reduction of the method sensitivity at the minimum of the measured concentration N_t.

Due to the limitations of the conventional capacitance DLTS-method associated with increased requirements to the parameters of the test sample, the aim of this work is to develop a measuring complex based on the current version of DLTS-method (I-DLTS). In this paper the measurement complex including methods C-V, I-V, I-DLTS with electrical leakage current compensation for the study of electrical properties of test SC structures with electrical capacitance up to 10 nF is considered. This limit of capacitance and leakage current is increased due to the fact that the SCs and developed test elements in the test cell have the large geometric area.

In accordance these requirements a block diagram of the measuring complex of the I-DLTS, C-V and I-V characteristics shown in Fig. 1. C-V and I-V measurements are carried out before I-DLTS study. In the complex an electric method of creating of a nonequilibrium states of the test sample is provided. Thus the sample is placed in the measuring cell of the cryostat and periodically varying the bias voltage impulses from the pulse generator is supplied. Moreover the amplitudes

of the filling U_1 and emptying U_2 pulse voltages corresponding to time slots "pause" $(0 - t_p)$ and "impulse" $(t_p - t_1)$ are set independently of each other within ± 10 V using a voltage regulator in the generator (Fig. 2). The range of measured relaxation currents lies within $10^{-10}–10^{-5}$ A. The minimum of the current is provided by using the input stage current-voltage converter of the low noise operational amplifier LTC6244HV having unity gain frequency of 50 MHz and the input bias current less than 1 pA at RT. The maximum of the input current is determined by estimation of the maximum level of the leakage current of the test sample and the initial value of the current relaxation. Time duration of voltage impulses t_p and t_R are also adjusted in the range of $10^{-6} – 10$ s independently to each other. The signal from the output of the measuring cell in the helium closed type cryostat Janis CCS-400/204N is supplied to the current - voltage (I-V) converter. The conversion coefficient is adjusted in the range $10^3 – 10^9$ Ohm. The signal from the I-V converter goes to 16-bit analog-to-digital converter data acquisition board PCIe-6361 (manufactured by National Instruments) with a sampling frequency up to 2 MHz. Handling and storage of received data, control the temperature change of the sample is carried out in the programming environment LabView.

In the measuring complex a change of the studied relaxation time constant of electrical current transient is implemented by changing the temperature of the sample. Temperature control unit LakeShore335 allows to change the temperature in the measuring cell in the cryostat linearly within a temperature range of $7 – 500$ K. The linear temperature change is regulated within $0.1 – 3$ K/min. Temperature measurement is performed with a NIST calibrated sensor based on a silicon diode.

The current amplifier has sufficiently low input impedance (less than 1 kOhm) so the transition process due to recharge of barrier capacity of the sample ends about 10 μs for barrier capacity of the sample 10 nF. Current relaxation is described by the expression [10]:

$$i(t) = \frac{qSN_tW}{2\tau} \exp\left(-\frac{t}{\tau}\right), \qquad (3)$$

where t is the time, τ is the relaxation time determined by DL parameters [9]:

$$\tau = \left(\sigma\langle\upsilon_T\rangle N_C\right)^{-1} \exp\left(\frac{\Delta E_t}{kT}\right), \qquad (4)$$

where N_C is the effective density of states in the conduction band (for the n-type base), ΔE_t is the activation energy of the DL. The study of the temperature dependence of the current transient allows determining the temperature dependence of the relaxation time. The DL's activation energy and the capture cross section is estimated from the $\tau(T)$ by (3) and (4). According to these parameters the nature of the DLs identification may be carried out. The DL's concentration N_t is estimated by the amplitude of the I-DLTS-peak and evaluation of SC's conversion efficiency η may be carried out. DL's parameters are stored in the database of measuring complex and it allows to conclusion the suitability of technological

operations for the manufacture of SCs with the predicted or desired characteristics.

For p-i-n barrier structures based on non-crystalline semiconductors the energy spectrum of localized states is continuous. In the generation-recombination processes electrically active localized states with the density of states function $D(E)$ located in the depletion region near the quasi-Fermi level crossing all the i-region in a wide range of energies. Therefore, the signal of current relaxation is more complex.

The concentration of free electrons n in non-crystalline semiconductor can be determined from the ratio that takes into account the $D(E)$ [11]. The general form of the $D(E)$ function is not known, however, in practice, it is difficult to calculate the n. The free electrons concentration can be estimated from electrical conductivity measurements. The conductivity of a-Si:H is caused mainly by electrons because the holes mobility is approximately two orders of magnitude less than electron one. Thus, $n = \gamma/(q\mu_n)$ where γ is the conductivity, μ_n is the electron mobility, $\mu_n = 1 \div 10$ cm^{2}V^{-1}s^{-1} [11].

The conductivity in non-crystalline semiconductors is determined by the relation:

$$\gamma = \gamma_0 \exp\left(-\frac{E_C - E_F + W}{kT}\right),$$

where W is the activation energy of hopping conductivity in the case of localized states, E_C is the conduction band edge, E_F is the Fermi energy level, γ_0 is the conductivity at infinitely large temperature, $W = 0$ if the conductivity is related to the extended states [11]. The latter case usually observed at room temperature and higher.

The kinetics of DLs recharge is described using the Schokley-Read-Hall model. From the solution of appropriate kinetic equation the relaxation time of the electron emission process from DL is obtained [9]. For the non-crystalline semiconductor the relaxation time is proportional to the concentration of free electrons, which can be found from the electrical conductivity measurement.

As a result, we obtain the following simple equation for the relaxation time in the case of non-crystalline semiconductors:

$$\tau \propto n^{-1} \cdot \exp\left(\frac{\Delta E_t}{kT}\right) \propto \frac{\mu_n}{\gamma} \cdot \exp\left(\frac{\Delta E_t + W}{kT}\right).$$

Set of τ values at the different temperatures allows to determine the activation energy ΔE_t. Assuming that the pre-exponential factor is much less dependent on temperature than the exponential multiplier. The $\Delta E_t + W$ is determined from the Arrhenius plot in coordinates $\ln(\tau)$ versus T^{-1}. Energy W can be found by measuring the temperature dependence of the material conductivity.

Relaxation current signal from the I-V converter output is processed by the signal selection device according to the relaxation time (SD) that can select a signal with a certain relaxation time constant [9]. The presence of the SD gives to I-DLTS method its spectroscopic character. SD characterized by its transfer or correlation function which defines the extremum time constant corresponding to the maximum of output signal of the SD and I-DLTS spectrometer.

In the SD the signal relaxation is multiplied by the correlation function $w(t)$ (Fig. 2). The complex has several correlation functions as "double box-car", "lock-in", "Hi-Res-3", "GS-4" [12]. Rectangular correlation function or "lock-in" has a few significant advantages over other types of functions. First of all almost the influence of the leakage current structure is decreased. The reduction of constant component in the input signal by the multiplier is not less than 40 dB which is important for samples with a large area of the rectifying junction. Since the leakage current does not change with time, it is a constant component of the total current. By multiplying the signal on the "lock-in" function the sign of constant component at time t_3 is changed (Fig. 2). Since the time intervals $t_2 - t_3$ and $t_3 - t_4$ are equal each other (Fig. 2), then multiplying the integration signal will eliminate the constant component. Also interferences caused by charge capacitance of the structure under study are eliminated since the function $w(t)$ is produced with a certain time delay. The disadvantages of the multiplication on a "lock-in" correlation function should include smaller the signal – noise ratio compared to the exponential function. Moreover "lock-in" function does not proved a high resolution for the separation of transients with close in value relaxation times. In this case high resolution on relaxation time "Hires-3" or "GS-4" function is preferable to use which however does not allow compensating the constant component. We have developed additional algorithm of the leakage current component compensation in the current transient not less than 40 dB [13].
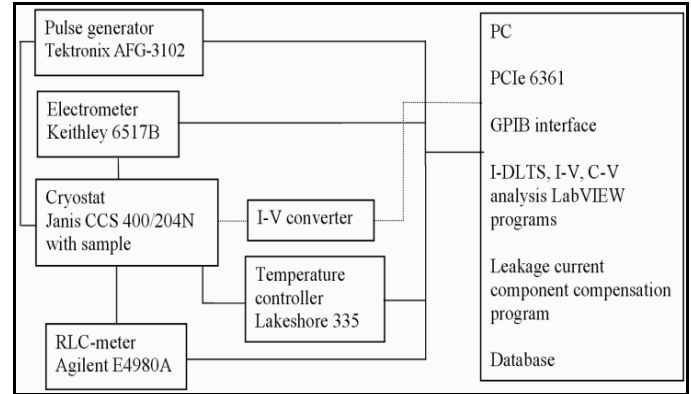

Fig. 1. Block diagram of measuring complex with I-DLTS, C-V and I-V diagnostic methods

To avoid the temperature deviations of DLTS peaks from the true position due to the lag filter operation the heating rate of the sample is not exceed 3 K/min. The filling of DLs by CCs is provided during the filling impulse voltage (Fig. 2). During the filling voltage impulse on the sample (time interval $0 - t_p$ in Fig. 2) there is the CC's capture on DLs. And during the reverse or emptying voltage impulse on the sample (time

interval $t_p - t_1$ in Fig. 2) there is a relaxation process of CC's emission from DLs that detected by the spectrometer.

Thus by changing the temperature of the investigated sample using a temperature controller and consequently changing time constant of DL or relaxation time constant τ when τ equals to the time constant of the SD τ_d in the output of the spectrometer at the temperature T_{max} a I-DLTS peak appears in the I-DLTS-spectrum. Repeating the same operation in different τ_d a set of temperatures T_{max} I-DLTS peaks and corresponding τ are obtained and the DL's activation energy is estimated from Arrhenius plot.
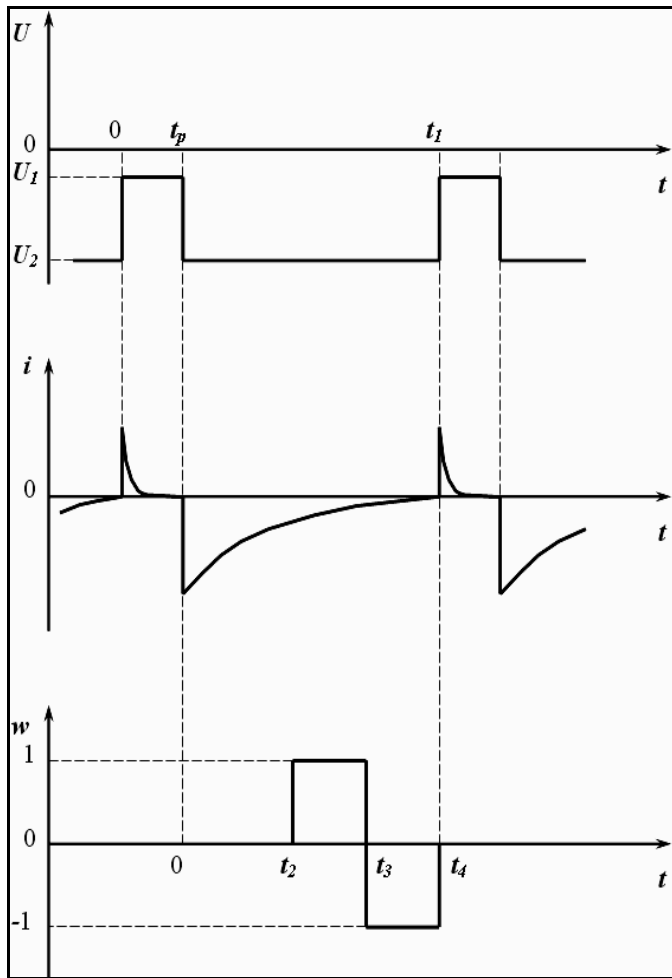

Fig. 2. Pulse sequences of impulse voltage on the sample $U(t)$, current transients $i(t)$ and correlation "lock-in" function $w(t)$

CONCLUSION

Thus in the paper features of construction and operation of the measuring complex for studying and control of recombination centers in solar cells based on crystalline or non-crystalline semiconductor materials are presented. A feature of the complex is the account of the specificity of the test objects semiconductor barrier structures with a larger area of the rectifying junction and increased leakage current and universality on the type of the test sample. The complex allows doing measurements in the temperature range $7 - 500$ K, in the range of relaxation times of $10^{-5} - 1$ s, in the sample with the maximum barrier capacity up to 10 nF, the current amplitude of relaxation in the range of $10^{-10} - 10^{-5}$ A. Received information about the recombination traps is stored in the special database and could be used to identify the nature of DLs that allows estimating the impact of DLs on the conversion efficiency of solar cells and making recommendations for optimization of solar cells construction design and manufacturing processes.

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