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Intensity modulated short circuit current spectroscopy for solar cells

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ABSTRACT

Understanding charge separation and transport is momentously important for the rectification of solar cell performance. To probe photo-generated carrier dynamics, we implemented intensity modulated short circuit current spectroscopy (IMSCCS) on porous Si and $Cu(In_x,Ga_{1-x})Se_2$ solar cells. In this experiment, the solar cells were lightened with sinusoidally modulated monochromatic light. The photocurrent response of the solar cell as a function of modulation frequency is measured as the optoelectronic transfer function of the system. The optoelectronic transfer function introduces the connection between the modulated light intensity and measured AC current of the solar cell. In this study, interaction of free carriers with the density of states of the porous Si and $Cu(In_x, Ga_{1-x})Se_2$ solar cells was studied on the basis of charge transport time by IMSCCS data.

1. Introduction

$Cu(In_x,Ga_{1-x})Se_2$ (CIGS) and porous Si solar cells prompt considerable interest due to their adjustable band gap for optimum sunlight absorption, high optical absorption coefficient, and high conversion efficiency. These properties enable their use in many engaging applications in space power systems.

The performance of a solar cell relies acutely on the electronic transport properties. Characterization of carrier transport, trapping, and recombination are the major problems in solar cells studies. In this study, the photo-generated charge transports in porous Si and $Cu(In_x,Ga_{1-x})Se_2$ solar cells were investigated by optoelectronic admittance spectroscopy, otherwise called intensity modulated short circuit current spectroscopy.

IMSCCS measurement provides information on the dynamics of charge transport. IMSCCS measures the periodic photocurrent response to light intensity that includes small amplitude sinusoidal modulation on a large steady state background level and allows the effects of trapping to be taken into account explicitly. The frequency resolved response shows a phase lag with respect to the excitation signal because of the internal electron transport of the carriers [1].

Steady state solutions of generation/collection for the mobile excess electrons density is given by [2]

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2}-\frac{n-n_0}{\tau_n}+\alpha\Phi\exp(-\alpha x) \quad (1)$$

where D is the diffusion coefficient of the electrons, n the electron density under illumination, n_0 the equilibrium electron density in dark condition, τ_n the electron lifetime (referred to recombination), α the absorption coefficient, and Φ the incident photon flux. τ_n and D vary with light intensity observed experimentally and hence Eq. (1) is non-linear [3,4]. Eq. (1) can be solved under limiting conditions, such as small amplitude perturbation of incident light intensity of the form

$$\Phi=\Phi_0[1+\delta\exp(i\omega t)] \quad (2)$$

where ω is the modulation frequency and $\delta \ll 1$ in order to allow linearization of the system response. Φ_0 and $\delta\Phi_0$ are the DC and AC components of the incident photon flux, respectively.

The frequency dependent modulation of carrier density is depicted by a semicircle in the fourth quadrant of the complex plane with a minimum at $\tau_n=(\omega_{min})^{-1}=(2\pi f_{min})^{-1}$ for the trap free case. If one wants to take a more careful approach, trapping and detrapping must be considered. The IMSCCS response stems fundamentally from the delay time related with electron transport from the injection site to the other contact. For the electron traps located at a given energy within the band gap, the solution of the continuity equation includes the effects of trapping and detrapping of carriers. In this case, the terms effective diffusion length (D_{eff}) and average transport time (τ_d) are introduced.

Superimposed light intensity in the IMSCCS experiment is given by $\Phi=\Phi_m\exp(i\omega t)$. The photocurrent response in the external circuit also fluctuates periodically $i=i_m\exp[i(\omega t-\varphi)]$ and is characterized by frequency dependent amplitude i_m and phase angle φ. Trapping, detrapping, and recombination of the photo-generated carriers during transport determine the phase angle. The optoelectronic admittance

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or optoelectronic transfer function is defined as $T = \frac{i}{e\Phi} = \left(\frac{i_m}{e\Phi_m}\right)\exp(-i\varphi)$. T can be thought of as the AC equivalent of quantum efficiency, considering the interaction of free carriers with density of states in the gap [5]. IMSCCS provides a study of electronic transport under steady state conditions for the photocurrent flow and occupation of electronic states when the trapping charge carriers play an important role in the electronic properties of the device. The characteristic time of the optoelectronic transfer function gives the average transit time of the electrons through the system if the lifetime of the electrons for recombination is considerably longer than transit time. The study, presented here, focuses mainly on the fundamental aspects of transport characteristics and not on the mapping of band gap states.

2. Experimental

Porous Si and $Cu(In_x,Ga_{1-x})Se_2$ solar cells studied in this work were prepared by the Institute of Fundamental Problems for HighTechnology, Ukrainian Academy of Sciences, and Institut für Physikalische Elektronik, Stuttgart University, Germany, respectively. Detailed information about preparation of these solar cells can be obtained from Refs. [6,7].

Fig. 1 shows a schematic overview of the IMSCCS measurement set-up, consisting of a HP4192A impedance analyzer, a homemade LED driver, LED groups, a TDS 220 digital oscilloscope, an *I–V* converter preamplifier, an IBM compatible PC, and a reference photodiode. The preamplifier available for use in our system was a current-to-voltage converter amplifier, incorporating a Burr-Brown OPA637 operational amplifier. The high gain-bandwidth product and slow rate of the voltage amplifier were particularly beneficial at short times (10 ns–1 μs), while the current amplifier had a far superior signal-to-noise performance and adequate bandwidth for use at longer times (greater than 1 μs).

The light source used in our experiments was the LED (Hamamatsu) group. The LED group (λ=660 nm) provided both DC and AC components of illumination. About 1% of the LED group light intensity was modulated, thus creating a modulated photon flux $e\Phi$. The monochromatic light beam was broadened using a beam expander (from Roithner Lasertechnik). The light spot provided was about as large as the contact area (7.5 mm^2) using a LED group equipped with a

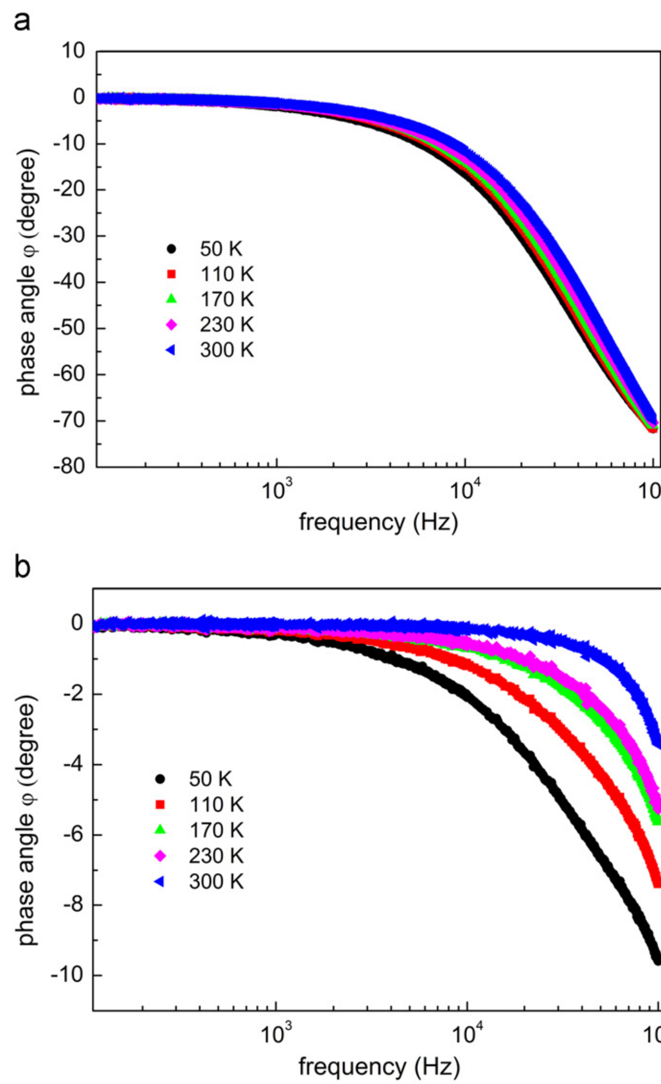
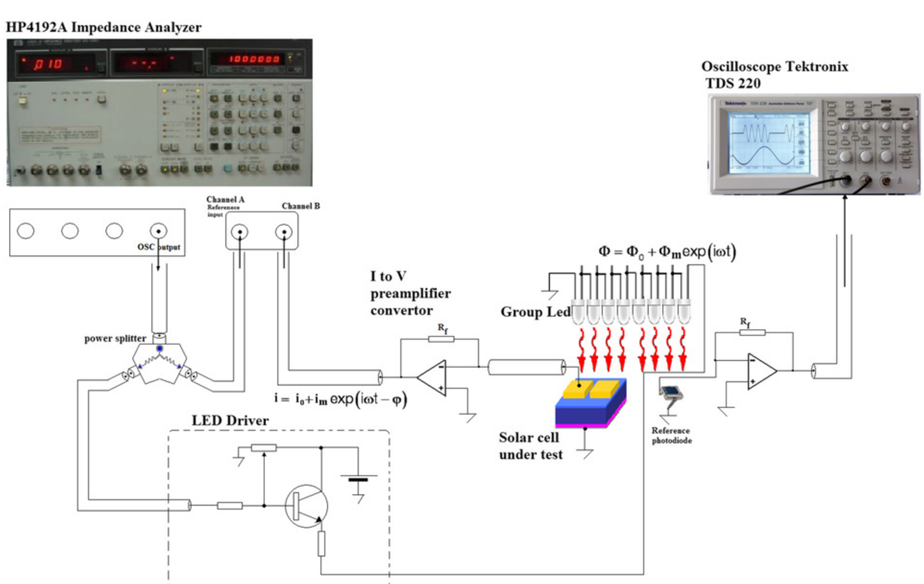


Fig. 2. Phase angle as a function of frequency of (a) porous Si and (b) Cu $(In_x,Ga_{1-x})Se_2$.



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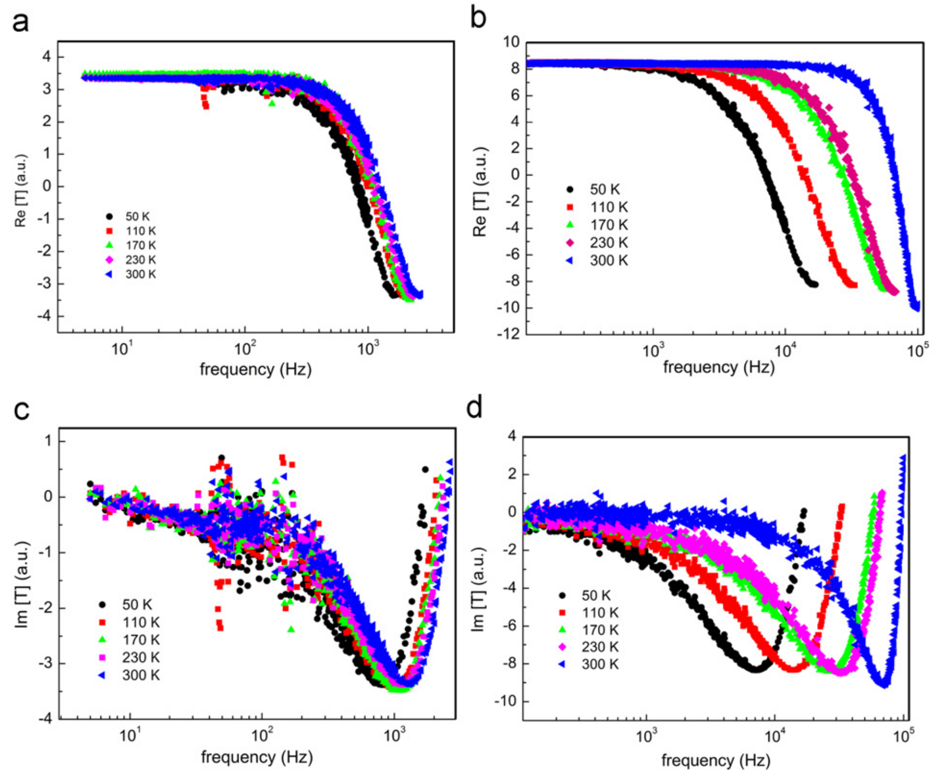

Fig. 3. Real and imaginary parts of optoelectronic admittance of porous Si (a, c) and Cu(In_x, Ga_{1-x})Se_2 (b, d) as a function of modulation frequency and temperature.

special diaphragm. In this way, it was ensured that the spot was homogeneous within an error of 7% over the entire sample. Illumination homogeneity at the place of the sample was measured using a XY positioner equipped with a small area photodiode, through which uniformity values of illumination could be measured with an accuracy of 5%. The whole response of the experimental set-up was measured using a reference photodiode for every temperature and subtracted from the measured experimental data to assure accurate measurement result.

Light intensity was measured using a calibrated photodiode (Siemens BPW-34; rise time less than 50 ns). Sinusoidal excitation was provided by a red LED driven via a homemade LED driver and by an oscillator output of HP4192A. The magnitude of modulated light intensity was tracked by a short circuit current of the reference photodiode. The short circuit current of the reference photodiode was amplified by the current-to-voltage converter (preamplifier) and the amplified signal was fed to a scope for assured absolute light intensity at the place of the sample. The amplitude of the modulated short circuit current and its phase shift with respect to the excitation were detected by a HP4192A impedance analyzer in conjunction with a homemade current (*I*–*V* converter; OPA637) preamplifier. The measurement was performed inside evacuated close-cycle OXFORD He cryostats with an ITC 502 intelligent temperature controller. A delay of a few seconds between subsequent measuring steps was built into the program to assure steady-state conditions for the measurement of temperature. The ITC 502 temperature controller had an auto-PID mode with an RS-232 computer interface. Therefore, cooling and heating rates as well as other parameters are systematically controlled by a PC.

3. Results and discussion

Transport and bulk recombination in inorganic materials are usually too quick to be analyzed by the IMSCCS technique [8]. Carrier transport is slower in organic semiconductors such as dye sensitized solar cells than in inorganic semiconductors and can be easily studied by IMSCCS [9,10].

In inorganic semiconductors, charge transfer to/from surface states and surface recombination processes can be studied by IMSCCS. Using the IMSCCS technique, steady state conditions are disturbed by small amplitude sinusoidal intensity light, thereby systematically varying the number of injected carriers. The photocurrent, which is the external electrical response at the short circuit, is monitored as the modulation frequency increases. The predicted IMSCCS response appears in the lower complex plane. The rate limiting dynamics for charge transports inducing the electrical response begins to lag behind the optical perturbation. Diffusion, trapping, and detrapping of photo-injected carriers from any point to substrate contact introduce a time delay between carrier injection and collection. This delay appears as a phase lag in the photocurrent response to intensity modulated light.

Fig. 2a and b shows that light excitation frequency is dependent on phase angle characteristics of porous Si and Cu(In_x,Ga_{1-x})Se_2 in the temperature range of 50–300 K. Temperature did not affect the phase angle frequency characteristics of porous Si. On the other hand, Cu(In_x,Ga_{1-x})Se_2 characteristics were strongly affected by temperature. In addition, the phase angle magnitude, in other words the photocurrent response lag with respect to excitation signal, decreased with increase in temperature. This may stem from temperature passivated trap centers in the Cu(In_x,Ga_{1-x})Se_2 solar cell. Especially around room temperature, phase angle had low values, which is a strong evidence that Cu(In_x,Ga_{1-x})Se_2 is a faster device than porous Si.

Diffusion, trapping, emission, and recombination of the photogenerated carriers during transport determine the phase angle. The trapping rate is directly proportional to thermal velocity of electrons in the conduction band, density of vacant traps, and their capture cross section. The thermal detrapping rate depends on

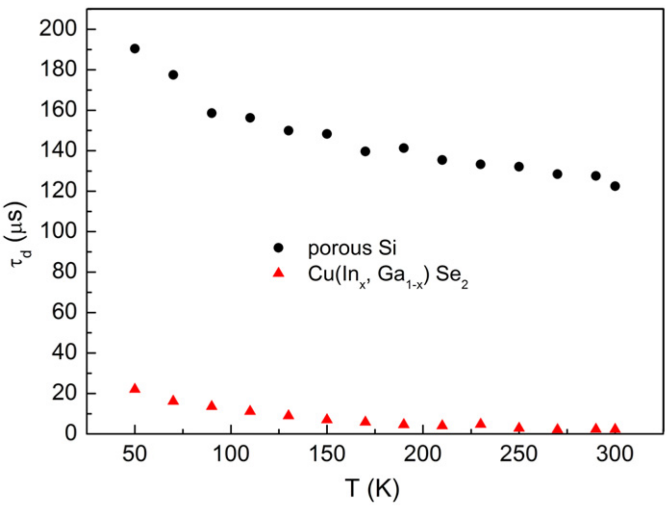

Fig. 4. Transport time as a function of temperature for porous Si ($\tau_d = 1.22 \times 10^{-4} + 1.25 \times 10^{-4}\exp(-(T/93.28))$) and $Cu(In_x,Ga_{1-x})Se_2$ ($\tau_d = 1.4 \times 10^{-6} + 3.78 \times 10^{-5}\exp(-(T/78.91))$).

temperature and trap depth. If there is a distribution of traps, the trapping rate depends on trap density at the quasi-Fermi level and the detrapping rate is related to the position of the quasi-Fermi level relative to the conduction band [2,4]. Therefore, temperature dependent frequency–phase angle characteristics give us information on thermal velocity of electrons in the conduction band, vacant trap density, capture cross section, trap depth, trap density at the quasi-Fermi level, and the position of the quasi-Fermi level.

Fig. 3a–d displays the real and imaginary parts of the optoelectronic admittance of porous Si (a, c) and $Cu(In_x, Ga_{1-x})Se_2$ (b, d) as a function of modulation frequency ($f = \omega/2\pi$) and temperature. Real and imaginary values of optoelectronic admittance are given in arbitrary units. Using these data, the frequency dependent cell response can be interpreted at different temperatures. In this respect, the measuring frequencies that result in the lowest imaginary component in the IMSCCS plot are of special interest. The average transport time (τ_d) may be estimated from the graphical minimum of the imaginary part as $\tau_d = (\omega_{min})^{-1} = (2\pi f_{min})^{-1}$. Considering a certain penetration depth of light, τ_d gives an estimation of only the average time that photo-injected electrons need to reach the back contact.

The calculated transport times are given in Fig. 4. As seen in the figure, transport times of the cells are sensitive to temperature. Transport times of $Cu(In_x,Ga_{1-x})Se_2$ are shorter than those of porous Si by a factor varying between 10 and 100 at any temperature. Fig. 4 also displays that as temperature increases transport times of the two cells decrease exponentially. The calculated small transport time values of the $Cu(In_x,Ga_{1-x})Se_2$ cell are attributed to decrease in trap density at the quasi-Fermi level as temperature increases and shortened trapping and detrapping times with increase in temperature [11]. The long transient time values of the porous Si solar cell with respect to the $Cu(In_x,Ga_{1-x})Se_2$ solar cell may stem from localized states in the porous Si band gap. It is well known that these localized states are induced by the amorphous matrix in porous Si [12].

4. Conclusion

In this study, an IMSCCS measurement set-up was constructed and optoelectronic admittances of inorganic solar cells were measured. Excitation frequency dependent phase angle characteristics and average charge transport times of the porous Si and $Cu(In_x,Ga_{1-x})$ Se_2 solar cells were obtained in the temperature range 50–300 K. It was shown that temperature was a striking parameter for phase angle and charge transport time. The IMSCCS results indicate that $Cu(In_x,Ga_{1-x})Se_2$ is a faster device than porous Si.

References

[1] J. Halme, Performance limiting factors in flexible dye solar cells, Doctoral Dissertation, Helsinki University of Technology, Faculty of Information and Natural Sciences, Department of Applied Physics, 2009, pp. 9–67.

[2] A.C. Fisher, L.M. Peter, E.A. Ponomarev, A.B. Walker, K.G.U. Wijayantha, Intensity dependence of the back reaction and transport of electrons in dye-sensitized nanocrystalline TiO_2 solar cells, J. Phys. Chem. B 104 (2000) 949–958.

[3] F. Cao, G Oskam, G.J. Meyer, P.C. Searson, Electron transport in porous nanocrystalline TiO_2 photoelectrochemical cells, J. Phys. Chem. 100 (1996) 17021–17027.

[4] L. Dloczik, O. Ileperuma, I. Lauermann, L.M. Peter, E.A. Ponomarev, G.J. Redmond, Dynamic response of dye-sensitized nanocrystalline solar cells: characterization by intensity-modulated photocurrent spectroscopy, Phys. Chem. B 101 (1997) 10281–10289.

[5] D. Vanmaekelbergh, J. van de Lagemaat, R.E.I. Schropp, Observation and explanation of quantum efficiencies exceeding unity in amorphous silicon solar cells, Sol. Energy Mater. Sol. Cells 41–42 (1996) 537–542.

[6] Ö. Tüzün, Ş. Altındal, Ş. Oktik, Frequency and voltage dependent surface states and series resistance of novel Si solar cells, Mater. Sci. Eng. B 134 (2–3) (2006) 291–295.

[7] L. Stolt, K. Granath, E. Niemi, M. Bodegaerd, J. Hedström, S. Bocking, M. Carter, M. Burgelman, B. Dimmler, R. Menner, M. Powalla, in: Proceedings of the 13th European Photovoltaic Solar Energy Conference, Nice, France, 1995, pp. 1451–1455.

[8] P.M. DiCarmine, O.A. Semenikhin, Intensity modulated photocurrent spectroscopy (IMPS) of solid-state polybithiophene-based solar cells, Electrochim. Acta 53 (11) (2008) 3744–3754.

[9] C. Grasso, M. Nanu, A. Goossens, M. Burgelman, Electron transport in $CuInS_2$-based nanostructured solar cells, Thin Solid Films 480–481 (2005) 87–91.

[10] G. Franco, L.M. Peter, E.A. Ponomarev, Detection of inhomogeneous dye distribution in dye sensitised nanocrystalline solar cells by intensity modulated photocurrent spectroscopy (IMPS), Electrochem. Commun. 1 (2) (1999) 61–64.

[11] U. Rau, H.W. Schock, Electronic properties of $Cu(In,Ga)Se_2$ heterojunction solar cells—recent achievements, current understanding, and future challenges, Appl. Phys. A 69 (1999) 131–147.

[12] O. Bisi, S. Ossicini, L. Pavesi, Porous silicon: a quantum sponge structure for silicon based optoelectronics, Surf. Sci. Rep. 38 (2000) 1–126.