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Admittance spectroscopy of Cu2ZnSnS4 based thin film solar cells

P. A. Fernandes,1,2,a) A. F. Sartori,1 P. M. P. Salomé,1  J. Malaquias,1 A. F. da Cunha,1
M. P. F. Graça,1 and J. C. González3
1I3N and Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago,
3810-193 Aveiro, Portugal
2Departamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto,
Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal
3Departamento de Física, Universidade Federal de Minas Gerais, 30123-970 Belo Horizonte,
Minas Gerais, Brazil

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In this report, we propose an AC response equivalent circuit model to describe the admittance measurements of Cu2ZnSnS4 thin film solar cell grown by sulphurization of stacked metallic precursors. This circuit describes the contact resistances, the back contact, and the heterojunction with two trap levels. The study of the back contact resistance allowed the estimation of an back contact barrier of 246 meV. The analysis of the trap series with varying temperature revealed defect activation energies of 45 meV and 113 meV. The solar cell’s electrical parameters were obtained from the J-V curve: conversion efficiency, 1.21%; fill factor, 50%; open circuit voltage, 360 mV; and short circuit current density, 6.8 mA/cm2. © 2012 American Institute of Physics.

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a device characterized by a series resistance, $R_s$, and a parallel capacitance and resistance, $C_j$ and $R_j$, respectively. The first element models all the contact and material resistances, such as Mo contact, ZnO:Al front window and Ni:Al contact grid and the loop describes the CZTS/CdS heterojunction AC response. An extra loop is added for the circuit M2, formed by $R_b$ and $C_b$ which models the behaviour of a non-ohmic Mo-MoS$_2$/CZTS electrical back contact. In the last model, M3, two capacitor-resistor ($C_1 - R_1$, $C_2 - R_2$) pairs have been added to the CZTS/CdS network to account for recombination centers in the CZTS layer. Additional C-R pairs in the CdS/CZTS heterojunction section did not show visible improvements in the fittings results.

Fig. 2(b) shows the measured admittance for a temperature of 293 K and the fitting results for the three models. The fitting deviations for the admittance module, $|Y|$, versus frequency are shown in Fig. 2(c). These results show that model M3 is the most suited one. For a low frequency regime, $f < 500$ Hz, all models present satisfactory fitting results with deviations smaller than 5%. In this regime, the AC response of the device is dominated by the capacitance of the junction, $C_j$. To improve the fittings for a higher frequency regime, the back contact loop must be added, as shown in model M2 and M3. Note that the maximum fitting deviation decreases from $\sim 25\%$ (M1) to $\sim 8\%$ (M2). In this regime, the capacitance behavior of the solar cell is given by the relation $C \sim (1/C_j + 1/C_b)^{-1}$. The inclusion of the trap states reduces the error to below 2% (M3). Similar results were obtained for the other temperatures.

The extracted resistances values, $R_b$, $R_j$, $R_1$, and $R_2$, are presented in Fig. 3(a). All these parameters show an exponential increase with decreasing temperature, as shown in the logarithmic plot in Fig. 3(a). $R_j$ seems to be well fitted using the relation $1/R_j = G_j = G_0 \times \exp(T/T_0)$, where $G_j$ is the junction conductance, $G_0$ and $T_0$ are constants. This behavior is known as temperature assisted tunneling and is
common on low mobility semiconductors. In fact, this feature was confirmed by Hall measurements in samples grown by a similar process. The temperature variation of the capacitance $C_j$, $C_1$, and $C_2$ is presented in Fig. 3(b). These variables show a decrease with decreasing temperature. The heterojunction capacitance, $C_j$, is characterized by a step decrease at $\approx 280 \text{K}$, a plateau at $6.5 \pm 0.2 \text{nF cm}^{-2}$ and another step decrease at $\approx 140 \text{K}$. The low temperature step may be explained by carrier freezing out and $C_j$ should tend to the heterojunction geometrical capacitance, which should be close to 0.5 nF cm$^{-2}$. The other variables do not seem to have any distinguishable temperature dependence within the experimental apparatus resolution or it could be hidden below the measurements errors, $R_i = 1.2 \pm 0.5 \text{Ω cm}^2$ and $C_j = 98 \pm 25 \text{nF cm}^{-2}$. According to Gunawan et al., the presence of a potential barrier can be defined by $R_b = \frac{k_b T}{e A^*} \exp \left(\frac{\phi_b}{k_b T}\right)$, where $A^*$ is the effective Richardson constant and $\phi_b$ is the barrier height at the interface. Fig. 3(c) presents the curve $\ln (R_b T)$ vs. $1/T$, from which high temperature $\phi_{b1}$ was extracted with a value of 246.4±13.0 meV. It is interesting to note that for a lower temperature the same curve also allow the estimation of a barrier with a different height, $\phi_{b2}$, of 70.0±10.0 meV. The nature of this result is unclear but it could be related to the fact that the back contact device is formed by two interfaces, Mo/MoS$_2$/CZTS and Mo/MoS$_2$. Attempts to model separately these two interfaces were not successful. Fig. 3(d) shows an Arrhenius plot of the characteristic frequency, $\omega_0$, defined as $\omega_0 = \frac{1}{R_b T}$, where $i = 2$, for each trap level. The thermal emission depth of the defect, $E_A$, can be extracted following the expression $\omega_0 = \frac{\zeta_i T^2}{\exp \left(\frac{E_A}{k_b T}\right)}$, where $\zeta_i$ is the thermal emission prefactor. The defect activation energies obtained were (44.7±0.7) meV and (112.7±3.5) meV. The shallower defect, $E_{A1}$, has a transition energy higher than the one obtained by Chen et al. of $\approx 20 \text{meV}$ for the $V_{Cu}$ defect.

Photoluminescence studies of samples grown by a similar process pointed to defect activation energies values close to the ones of $E_{A1}$. On other hand, the deeper defect, $E_{A2}$, seems to be close to the Cu$_{2x}$ defect activation energy of 120 meV.

In summary, we propose an AC response equivalent circuit that consists of a series connection of three sections. The first loop comprises all series resistances of the device. The second describes the back contact behavior in the AC regime. The temperature study of the back contact shunt resistance shows a near room temperature barrier height of 246 meV. The third section describes the behavior of CZTS/CdS heterojunction containing two trap levels. The analysis of the latter allowed the determination of a defect’s activation energy of 45 meV and 113 meV.

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