Predictive TCAD of Cu_2ZnSnS_4 (CZTS) Solar Cells

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***Abstract*- We demonstrate the application of a calibrated simulation deck for Cu_2ZnSnS_4 (CZTS) solar cells developed by us for predictive device modeling. Specifically, we study the effect of non-idealities – series resistance (R_S), carrier lifetime (τ), surface recombination velocity (SRV) – as well as that of novel transparent conductor materials.**

***Keywords*- CZTS Solar cells, Surface Recombination, Series resistance, Carrier lifetime, Graphene, rGO.**

I. INTRODUCTION

CZTS is a promising absorber material for low-cost, high-efficiency solar photovoltaics because of its earth abundant and non-toxic constituents, high optical absorption coefficient ($\alpha \sim 10^4$ cm^{-1}) and optimal band gap (1.4-1.6 eV) [1,2]. CZTS solar cell efficiency, as reported in the experimental literature, has evolved to a maximum of 8.4% thus far [3]. The other measured cell parameters for the best (highest-efficiency) cell [3] from IBM Research are: 19.5 mA/cm^2 short circuit current density (J_{SC}), 661 mV open circuit voltage (V_{OC}) and 66% fill factor (FF). Technology computer-aided-design (TCAD) of CZTS cells has, however, lagged behind in reaching the point where models are calibrated to experimental data, and thereby provide confidence for predictive simulations. This is possibly because of the complex dependence of cell performance metrics on various material and device parameters. In prior work, we have presented a simulation deck for CZTS cells that is rigorously calibrated to the experimental data from the best device [4]. We point out that our work goes beyond prior CZTS solar cell modeling/simulation approaches [5-7] in the following ways: (a) matching to experimental EQE and J-V data, (b) realistic wavelength-dependent optical constants, and, (c) the use of measured electrical parameters e.g. carrier lifetime, doping and series resistance. Here, we demonstrate its application to modeling the impact of key technology parameters, namely effect series resistance, carrier lifetime, surface recombination velocity and transparent conductor material. This is expected to be of use to the device engineer designing a CZTS cell.

II. SIMULATION METHODOLOGY

Our deck calibration and predictive simulations are performed on a standard TCAD platform (Sentaurus device from Synopsys) for coupled optical and electrical simulations. The optical calculation is based on the transfer matrix method (TMM); its output is fed into the electrical simulation, viz. a semiconductor drift-diffusion, continuity and electrostatics solver. We have described the methodology in detail and provided the full, calibrated parameter set earlier [4].

III. PREDICTIVE SIMULATIONS

Here we have applied that calibrated simulation deck to study the sensitivity of the cell performance parameters to a couple of technologically relevant device parameters – the carrier lifetime and the series resistance, as well as the effect of replacing Al:ZnO as the top transparent conductor with monolayer graphene (MLG) and reduced graphene oxide (rGO).

A. Effect of Series Resistance

The series resistance (R_S) is one of major non-idealities in a solar cell. It arises from the resistance of the semiconductor regions, the contact metals, and their junctions. Its primary effect tends to be a reduction of the fill factor and thereby the efficiency; large R_S could also reduce the J_{SC}. We find in this case that as the series resistance increases from its ideal value of zero to 18 Ω-cm^2, the effect on the EQE, J_{SC}, V_{OC}, is nearly negligible but the fill factor (FF) is degraded severely (about 50%), with a consequent and proportionate decrease in the cell efficiency (η). This is shown Fig. 1. The slopes of the curves therein are indicative of significant benefit (penalty) from reduced (enhanced) series resistance in the CZTS cell. Specifically, we see that the FF and efficiency degrade at the rate of 1.94/ Ω-cm^2 and 0.25/ Ω-cm^2 respectively with respect to R_S.

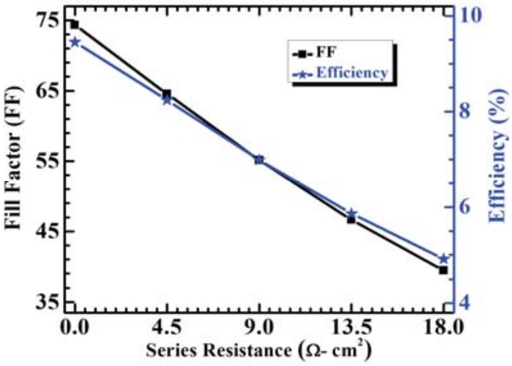

Fig.1. Effect of R_S on FF and η of the cell: these are degraded substantially as R_S increases from 0 (ideal) to18 Ω-cm^2.

B. Effect of Carrier Lifetime (τ)

Next we studied the effect of minority carrier lifetime (τ) on the cell performance, which parameterizes the average recombination time of the optically-excited excess charge carriers. We varied the lifetime from its experimentally measured value of 7.8ns in this case to 78ps – the effect on cell performance parameters are shown in Table I. While these are all dependent upon τ in principle, the cell parameters are not limited by it in the range of operation considered here. Thus, down to 0.78ns the lifetime is seen to have negligible effect on the cell performance. This indicates that the CZTS cell is fairly robust to smaller lifetimes that may result from sub-optimal processing. Only when going down to 78ps, the J_{SC} and efficiency η are found to reduce by 9% and 17% respectively.

TABLE I. CELL PARAMETERS WITH VARIATION OF LIFETIME (τ)

Carrier lifetime (τ ns)	**J_{SC} (mA/cm^2)**	**V_{OC} (mV)**	**FF**	**η (%)**
7.8	19.40	0.658	0.65	8.24
0.78	19.14	0.658	0.64	8.04
0.078	17.75	0.651	0.61	7.07

C. Effect of Surface Recombination at CdS/CZTS vs. CZTS/Mn interface

A fixed SRV ~10^8 cm/s (interface state density) has been used earlier for matching the simulated and experimental EQE. Here we model the effect of SRV on EQE, JV, Voc, Jsc and η by varying it from 10^5 cm/s to 10^8 cm/s. We find that the cell parameters are strongly affected by SRV, as shown in Fig.2. Then, in order to resolve the sensitivity of the cell parameters to the two interfaces in the device – CdS/CZTS (top surface) or CZTS/Mn (back contact) – we varied the SRV from 10^5 cm/s to 10^8 cm/s on both of them separately. We found that surface recombination at the top CdS/CZTS interface dominates over that at the back contact interface. High SRV here is seen to severely degrade short-circuit current and open circuit voltage, since the top surface region corresponds to the highest carrier generation rates for the CZTS cell. Clearly, a high-quality CdS/CZTS interface is essential to push this device to its performance limits.

D. Replacement of AZO with Graphene

Lastly, we use the calibrated simulation platform to assess the impact of a technology modification, namely inserting graphene in lieu of the transparent conducting oxide (TCO) material Al:ZnO (AZO). The latter has lower transmittance at short and near-infrared wavelengths [8], leading to lesser coupling of light to the absorber layer, and thereby to lower cell efficiency. Graphene, with a transmittance greater than 90% in the 350nm – 2200nm region [9], is therefore a promising replacement, which has already been tested in CdTe [10] and Cu(In,Ga)Se_2 (CIGS) [11] solar cells. Here, we have considered two cases: substituting AZO with mono-layer graphene (MLG) and reduced graphene oxide (rGO). This entails replacing the optical and electrical parameters of AZO with those of MLG and rGO [11, 12] in our simulation flow. Thence we arrived at the EQE (Fig. 3) and cell performance parameters (TABLE II). We observe that MLG enhances the transmittance at smaller wavelengths (300-450nm) compared to the reference (AZO) shown in Fig. 4, leading to an efficiency improvement of about 5%. On the contrary, rGO is seen to reduce the transmittance and thence lead to an efficiency reduction of 3%.

TABLE II. CELL PARAMETERS WITH AZO, MLG and rGO

Device Model	**J_{SC} (mA/cm^2)**	**V_{OC} (mV)**	**FF**	**η (%)**
AZO	17.05	0.658	0.65	7.32
MLG	17.92	0.658	0.65	7.66
rGO	16.44	0.651	0.66	7.07

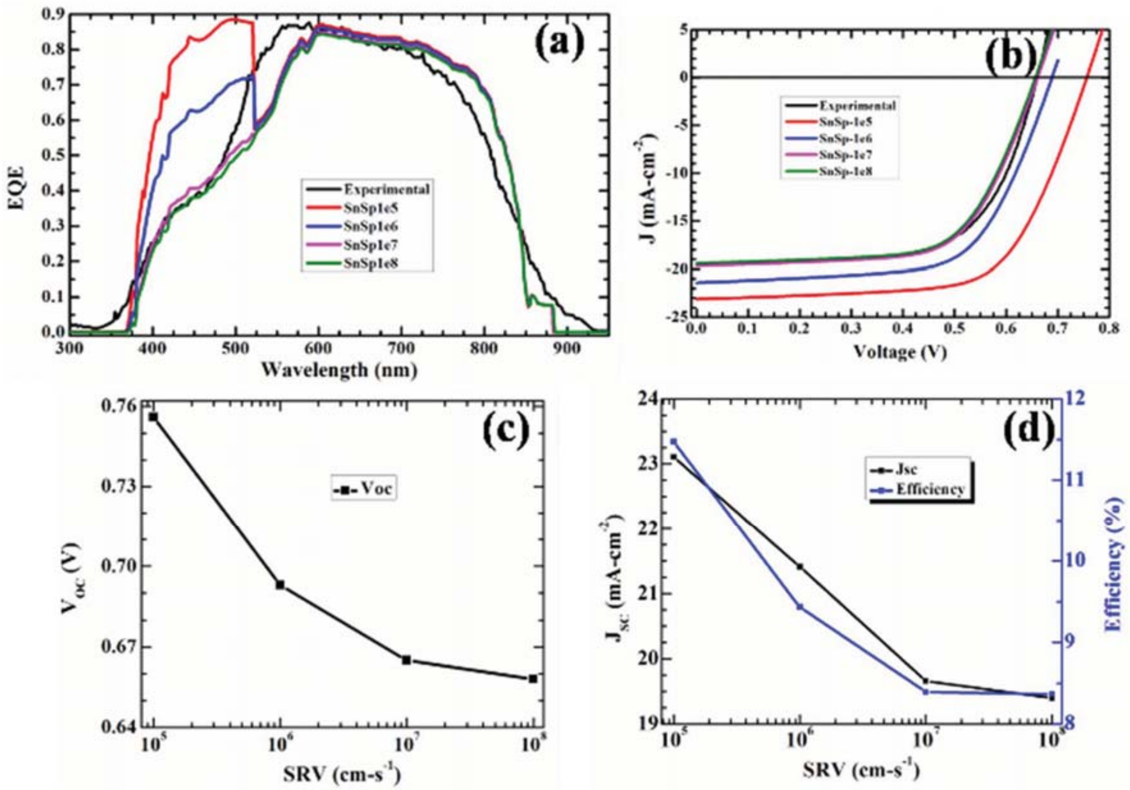

Fig. 2. Effect of Surface Recombination Velocity (SRV) on (a) EQE, (b) J–V characteristics, (c) V_{OC}, and, (d) J_{SC} and Efficiency.

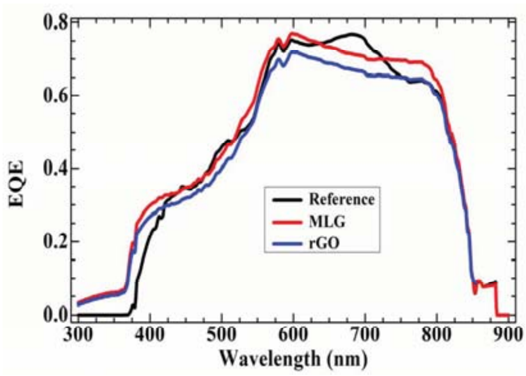

Fig. 3. EQE for MLG, rGO in comparison to reference AZO (without ARC). The higher EQE at lower wavelengths for MLG and rGO results in larger coupling of incident light to the absorber layer shown in Fig.4.

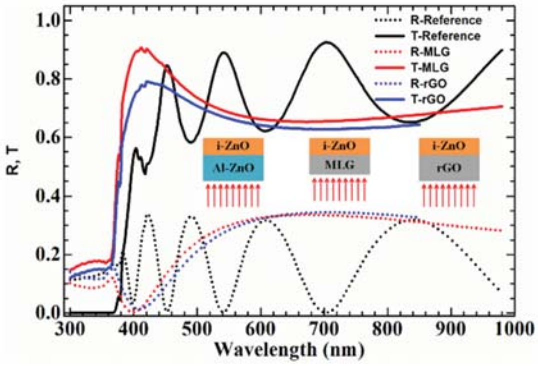

Fig.4. Reflectance (R – dotted line), Transmittance (T – solid line) for reference model (with AZO), with MLG and rGo (schematic diagrams are shown in inset). It is clearly scene in lower wavelength region enhanced transmittance with MLG, rGO as lower wavelengths will be absorbed by AZO.

IV. SUMMARY

In conclusion, we have used our calibrated deck of optical and electrical parameters to show its efficacy in enabling CZTS solar cell design, especially in analyzing the impact of key device parameter variation and novel technology options. We note that as more experimental data becomes available on CZTS cells the parameter values presented here may see some revision before settling down to established numbers.

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