

Rear surface passivation of ultra-thin CIGS solar cells using atomic layer deposited HfO_x

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Abstract. In this work, hafnium oxide layer is investigated as rear surface passivation layer for ultra-thin (550 nm) CIGS solar cells. Point contact openings in the passivation layer are realized by spin-coating potassium fluoride prior to absorber layer growth. Contacts are formed during absorber layer growth and visualized with scanning electron microscopy (SEM). To assess the passivating qualities, HfO_x was applied in a metal-insulator-semiconductor (MIS) structure, and it demonstrates a low interface trap density in combination with a negative density of charges. Since we used ultra-thin devices that are ideal to probe improvements at the rear, solar cell results indicated improvements in all cell parameters by the addition of 2 nm thick HfO_x passivation layer with contact openings.

Keywords: Solar cells / ultra-thin films / copper indium gallium selenide / surface passivation layer / hafnium oxide

1 Introduction

Today, CIGS based thin-film solar cells have achieved significant efficiency values, up to 23% [1]. With its tunable bandgap, being able to be transparent and flexible, it is widely preferred for thin-film applications. However, if the thickness of the absorber layer is chosen below 500 nm, that is, ultra-thin, the conversion efficiency will decrease. The reason for this lower efficiency can be explained by the detrimental impact of increased back surface recombination and insufficient absorption due to decreased absorber layer thickness. Different approaches are being investigated to overcome these problems. At the back contact the application of a passivation layer, with or without optical structures to increase reflection, has provided the most promising results [2–6]. In this study, the proposed method is to use a dielectric layer as a rear surface passivation layer with contact openings realized by spin-coated alkali solution prior to CIGS layer growth. This method has

been proven to make contact openings in AlO_x [4,5]. In this contribution we use hafnium oxide (HfO_x) as the dielectric layer, since it is proven to be a good passivation layer for c-Si and MOS structure by creating chemical and field-effect passivation, see [7–10]. HfO_x is also tested before for CIGS solar cells as front and rear surface passivation layer, see [11,12]. In [12], it is concluded that HfO_x has the potential to be an effective rear surface passivation layer with an appropriate contacting approach, like nano-patterning. In here we will apply a fast, cost-effective and simple approach, to create contact openings inside the hafnium oxide layer, and obtain an increase for all the solar cell parameters.

2 Experimental section

The proposed rear surface passivated solar cell structure is the following: SLG/Si(O,N)/Mo/ HfO_x /KF/CIGS/NaF/CdS/i-ZnO/ZnO:Al/Ni-Ag-Ni Grids, as shown in Figure 1a. Solar cells have 550 nm thick, single-stage CIGS absorber layers with an active area of 0.5 cm². 7nm NaF

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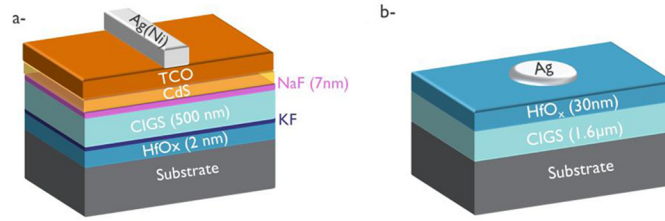


Fig. 1. Sample structure of (a) passivated solar cell and (b) MIS structure (*Substrate: SLG/Si(O,N)/Mo*).

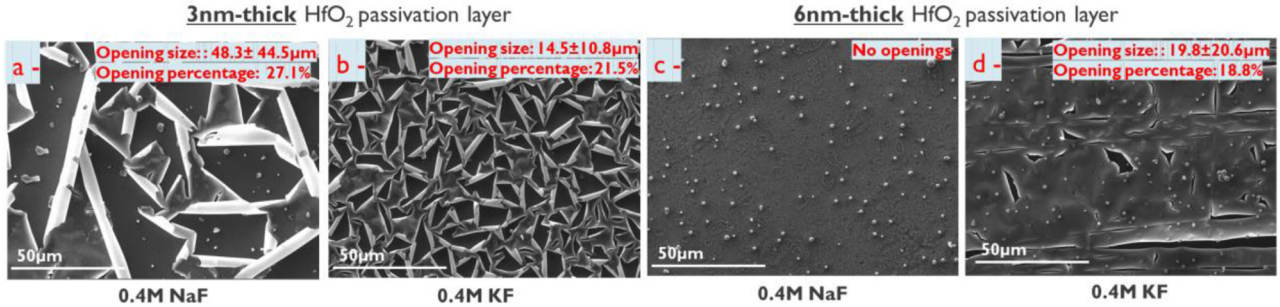


Fig. 2. SEM pictures of the test samples, (a) 3 nm thick HfO_x and (c) 6 nm thick HfO_x with 0.4M NaF, (b) 3 nm thick HfO_x and (d) 6 nm thick HfO_x with 0.4M KF solution. The opening sizes and areas were calculated via Gwyddion [9] (Magnification: 800 \times).

was added after absorber layer growth. No Ga-grading was used, and the $([\text{Cu}]/([\text{Ga}]+[\text{In}])),$ CGI ratio was approximately 85% and $([\text{Ga}]/([\text{Ga}]+[\text{In}])),$ GGI ratio was approximately 31%, determined with XRF measurement. 2 nm HfO_x was deposited via ALD at 250 $^\circ\text{C}$, and a growth rate of 0.14 nm/cycle with Tetrakis-EthylMethylAmino Hafnium (TEMAH) as the precursor and H_2O as the reactant. KF was spin-coated on the HfO_x layer. The reference sample has 0.4 M KF, but no passivation layer. The MIS, on the other hand, has the following structure: SLG/Mo (300 nm)/CIGS (1.6 μm) / HfO_x (30 nm)/Ag grids. Solar cells were characterized with current-voltage (J-V) and external quantum efficiency (EQE) measurements. From the dark J-V curves, the saturated current density (J_0) values were extracted. The MIS structure was characterized with capacitance-voltage (C-V) measurement. Contact openings were monitored via scanning electron microscopy (SEM).

3 Results

3.1 Creation of the openings

To study the creation of the openings inside the dielectric layer, we used a spin-coated alkali solution and then selenized the samples. The idea is to mimic the absorber layer deposition environment and to observe the effects of selenium environment on the combination of the di-electric and alkali solution. Since we know from our group's previous study, contact openings created spontaneously during the absorber layer deposition [4]. In line with our previous work on the AlO_x passivation layer [4], our first intention was using NaF salt as our contacting approach. However, as can be seen from Figure 2, we cannot obtain

good, that is, small and well-distributed openings in the 3 and 6 nm HfO_x . For KF however, smaller and well distributed opening were observed, for both 3 and 6 nm thick HfO_x layers. As a result, we decided to use the KF solution to create the contacts in the HfO_x layer when applied as back contact passivation layer in solar cells, Figure 1a.

3.2 Capacitance-Voltage (C-V) measurement

In order to analyze the passivating properties of the HfO_x dielectric layer, C-V measurement was done on the MIS structure, with the aim to extract the interface trap density (D_{it}) and density of charges (Q_{eff}). The sketch of the associated MIS structure is shared in Figure 1b.

Figure 3a shows the C-V curves at different frequencies. The Q_f value was estimated from the following equation [8]:

$$Q_f = \frac{c_{ox}(\varphi_{ms} - V_{fb})}{e}$$

where $\varphi_{ms} = 4.5$ eV, the estimated work function difference between silver (Ag) and CIGS, the oxide capacitance per unit area, $c_{ox} = 12$ nF, and e is the elementary charge in Coulombs. The flat band voltage, V_{fb} , is extracted as 0.5 V at 10 kHz, see Figure 3b. The Q_f is then calculated to be $Q_f = -8.6 \times 10^{12} \text{ cm}^{-2}$. This high concentration of negative Q_f values reduce the net concentration of minority carriers at CIGS rear surface [9]. In other words, due to the Coulomb repulsion that creates a built-in electric field shielded the minority carriers to recombine at the rear surface, the negative Q_f values indicate the field-effect passivation [10]. To assess the chemical passivation, D_{it} values were also determined [13]. The D_{it} value is

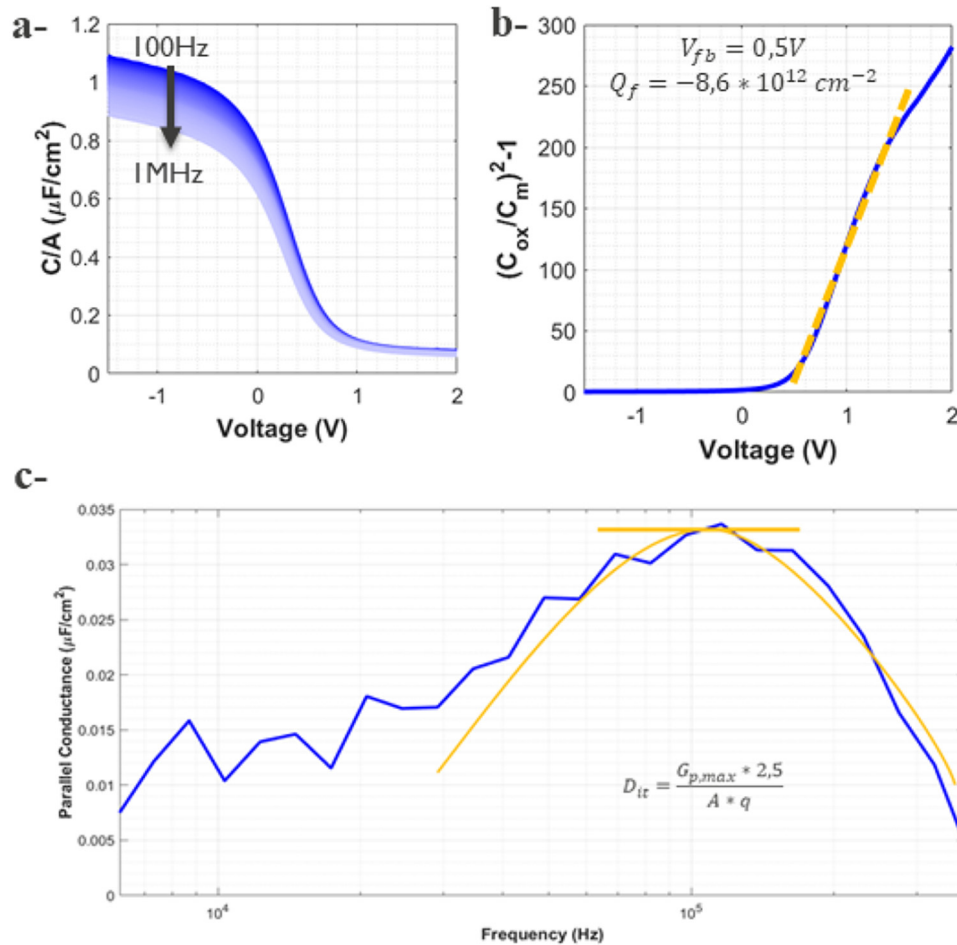


Fig. 3. (a) Capacitance-voltage (C-V) graph, (b) $(C_{ox}/C_m)^2 - 1$ as a function of voltage and (c) parallel conductance as a function of frequency.

respectively extracted with the Conductance method [14], and the High-Low Frequency Capacitance method [15], and it is estimated to be 6.1×10^{11} and 4.8×10^{11} , Figure 3c. These two values of D_{it} fall in the expected order of magnitude for passivation properties of HfO_x layers, and imply effective chemical passivation. According to the literature, annealed HfO_x layers result in better Q_f and D_{it} values [16,17]. The HfO_x passivation layer was annealed naturally during absorber layer deposition at $540^\circ C$, in this study. However, we could not perform C-V measurement at degrees higher than $300^\circ C$ for MIS structure due to experimental limitations. For $300^\circ C$, Q_f and D_{it} values and the polarity of the charges did not change.

3.3 Solar cell results

Solar cells were prepared with 2 nm HfO_x layer and various amount of KF solution were deposited, reference solar cell is also has KF prior to CIGS deposition. The electrical parameters of the devices were analyzed in this section. The arithmetic average of the six cells for each parameter, that is, J_{sc} , V_{oc} , FF, J_0 , and η , for each combination is shown in Figure 4.

In this study, we used single-stage, un-graded, and ultra-thin CIGS absorber. Hence, the cell parameters for the reference sample are not on the same level as the record efficiencies that are shared in the introduction section (Fig. 4). However, deploying a passivation layer at the rear surface resulting in increased V_{oc} values, which is the proof of the reduction in recombination. Decreased J_0 values, on the other hand, correlate with V_{oc} values and support this assumption.

The best V_{oc} , that is, 595 mV, was achieved with a 2 nm thick HfO_x layer in combination with 0.4 M KF (Fig. 4a). The associated J_0 value for this sample is the lowest value that we measured, which is $4 \times 10^{-9} A/cm^2$ (Fig. 4b). However, this sample does not have the lowest average J_0 values. The reason for that can be associated with the J-V curve of that sample (Fig. 4c). As can be seen from the J-V curve, there is a cross-over phenomenon that is mostly caused by high series resistance problems. For that sample, we believed that unoptimized contact openings lead to such high series resistance which ends up high J_0 and low FF when we compared it to the 0.6 M KF sample. One of the most significant improvements is observed in the FF of the solar cells, especially with a sample that has a 2 nm thick HfO_x layer with 0.6 M KF. The reason for this improve-

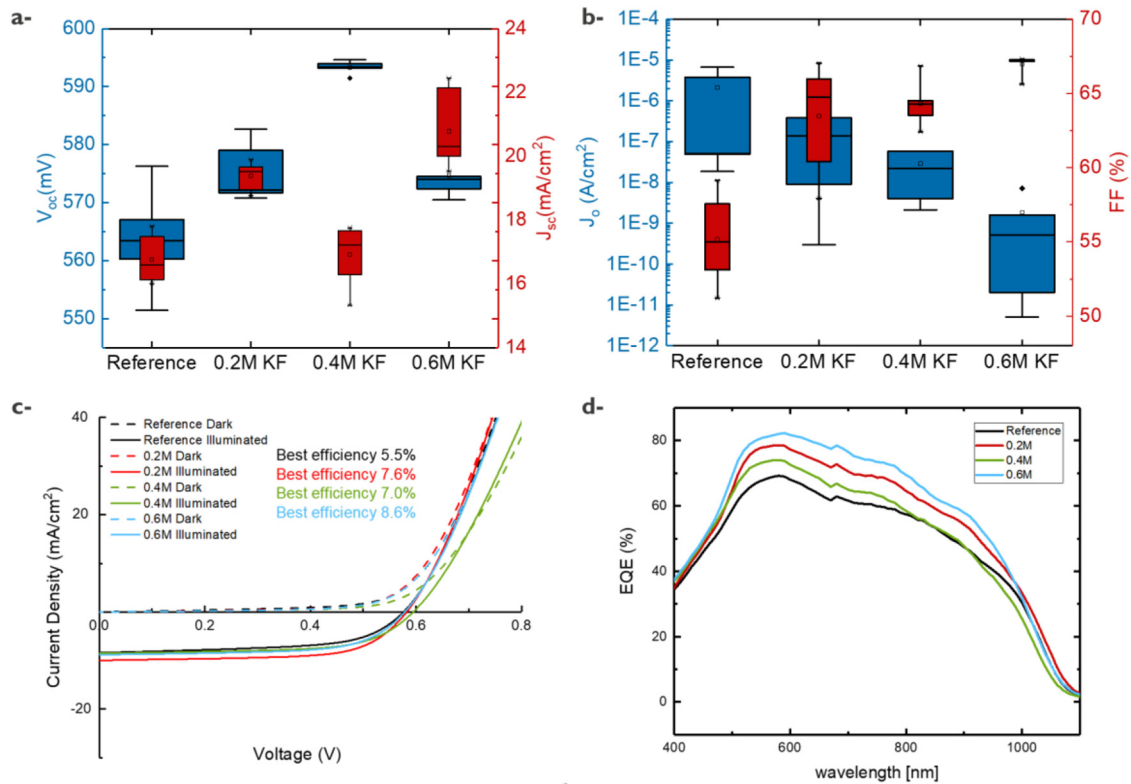


Fig. 4. J-V parameter comparison between reference (bare) and passivated ultrathin CIGS solar cells: (a) Voc (left axis) and Jsc (right axis), (b) J_0 (left axis) and FF (right axis), (c) J-V curves with best efficiency values and (d) EQE responses for different KF molarity with 2 nm thick HfO_x layer.

ment is due to the high shunt (R_{sh}) and the low series (R_s) resistance of this sample. Since the FF is inversely proportional to R_{sh} and proportional to R_s , $FF_{sh} = FF(1 - 1/R_{sh})$, and $FF_s = FF(1 - R_s)$, this can explain the noticeable increase in FF [18]. When we investigate the relation between FF and J_0 values, it can be seen that decreased J_0 values result in increased FF, as expected, see Figure 4b. The short circuit current density (J_{sc}) values are enhanced for all combinations (Fig. 4a). The increase in J_{sc} can be seen in the EQE responses of the samples. We observed better performances for all combinations in comparison to reference cell throughout most of the spectrum (Fig. 4d). As a result, increases in power conversion efficiencies were achieved for all combinations (Fig. 4c). For the solar cell with 2 nm HfO_x and 0.6 M KF, there was an absolute 3% increase of the efficiency.

4 Conclusion

We have shown that HfO_x has a potential to be used as a rear surface passivation layer for CIGS solar cells. With 2 nm thick HfO_x layer in combination with a spin coated KF solution, we managed to create contact openings inside the dielectric layer during selenization. We gained 3% absolute increase in power conversion efficiency for the passivated solar cell, attributed to an increase in all cell parameters. With a MIS structure the quality of the layer were determined. The increased Voc and decreased

J_0 values, in combination with the negative Q_f and low D_{it} values prove that a rear surface passivation effect is created with 2 nm thick HfO_x layer. As a result, we reached 595 mV of Voc for ultra-thin (550 nm), single-stage CIGS solar cells. Furthermore, we believed that this study will be shed a light on using HfO_x as the rear surface passivation layer for CIGS solar cells because it is still open for further optimizations. The contact openings and the thickness of the dielectric layer can be further optimized. Even, the tunneling effect should also be tested for layers thinner than 2 nm.

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Author contribution statement

All authors contributed equally to this work.

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