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Insulator materials for interface passivation of $Cu(In,Ga)Se_2$ thin films

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***Abstract*— In this work, Metal-Insulator-Semiconductor (MIS) structures were fabricated in order to study different types of insulators, namely, aluminum oxide (Al_2O_3), silicon nitride (Si_3N_x) and silicon oxide (SiO_x) to be used as passivation layers in $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells. The investigated stacks consisted of SLG/Mo/CIGS/insulator/Al. Raman scattering and Photoluminescence measurements were done to verify the insulator deposition influence on the CIGS surface. In order to study the electrical properties of the CIGS-insulator interface, capacitance vs. conductance and voltage (C-G-V) measurements were done to estimate the number and polarity of fixed insulator charges (Q_f). The density of interface defects (D_{it}) was estimated from capacitance vs. conductance and frequency (C-G-f) measurements. This study evidences that the deposition of the insulators at high temperatures (300 ºC) and the use of sputtering technique cause surface modification on the CIGS surface. We found that, by varying the SiO_x deposition parameters, it is possible to have opposite charges inside the insulator, which would allow its use in different device architectures. The material with lower D_{it} values was Al_2O_3 when deposited by sputtering.**

***Index Terms*— chemical passivation, $Cu(In,Ga)Se_2$ (CIGS), field-effect passivation, interface, passivation, solar cells, thin films**

I. INTRODUCTION

CURRENTLY, thin film solar cells based on $Cu(In,Ga)Se_2$ achieve an impressive world record of power conversion efficiency of 22.8 % [1]. With material quality being the improvement of choice in the last decade for CIGS technology, in recent years a bigger focus improving the interface quality has been made. At the front interface, a post deposition treatment (PDT) that is constituted by the incorporation of alkali elements reduces the front interface recombination significantly [2]–[6]. While the exact mechanisms of the PDT process that lead to an increase in the electrical performance of the solar cells and its full effects are still being discussed, a study has shown that there is a formation of a nano-patterned layer [7]. At the rear interface, the introduction of a nano-patterned insulator layer that passivates the interface led to improvements in the power conversion efficiency of ultrathin CIGS solar cells of up to 2 % [8]–[14]. In those cases the point contacts assure electrical contact while the passivation is made by an insulator made of Al_2O_3. The insulator materials have the potential to passivate the CIGS interface by lowering the number of interface defects, called chemical passivation, and by creating a built-in electrical field that repels carriers, called field-effect passivation [15], [16]. For the first studies, Al_2O_3 was the material of first choice as it is one of the best passivating materials in Si technology. For CIGS, an investigation of other oxide materials was performed as buffer layers in different solar cells configurations [17], [18] and as passivation layer [19] with different insulators than those studied in this work.

We report the study of several insulator materials, namely Al_2O_3, SiO_x and Si_3N_x, to be used as passivation materials in CIGS solar cells. For this purpose, we use an inverted metal-insulator-semiconductor (MIS) structure: SLG/Mo/CIGS/insulator/Al with the rear contact made of Mo. This architecture has the advantage that the CIGS growth is done in a similar way as for regular solar cells and the disadvantage that it does not allow for annealing of the insulator layers as it might cause CIGS surface modification which can lead to interpretation problems. The annealing can change the insulator properties, namely the polarity of the fixed insulator charges Q_f, and reduce de number of interface defects D_{it} [20]. Hence, our study is relevant for cases where no annealing of the insulators is made, which is the case of alternative CIGS architectures, such as superstrate [21] or novel ones. Besides applying MIS measurements for the determination of interface traps density and fixed insulator charges concentration and electrical polarity, we also focus our attention in understanding

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how the deposition conditions influence or cause CIGS surface modification.

II. Experimental

The main focus of this work is the study of the effects of several insulators, namely Al_2O_3, Si_3N_x and SiO_x on the CIGS interface properties. The samples started as soda-lime glass substrate, Mo rear contact (thickness of 350 nm), $Cu(In_{1-x},Ga_x)Se_2$ as absorber layer (thickness of 2 µm) and CdS (thickness of 70 nm). The CdS was deposited on top of CIGS to prevent air exposure of the CIGS during handling [22], [23]. The deposition of these layers were according to the Ångström solar cell baseline [24]. The samples names used henceforward are presented in TABLE I.

TABLE I
SAMPLE NAMING. LF MEANS LOW-FREQUENCY DEPOSITION AND HF, HIGH-FREQUENCY DEPOSITION.

Sample Name	*Sample Description*	*Structure*
Ref	CIGS reference sample	SLG/Mo/CIGS/CdS
Al_2O_3 – S	Al_2O_3 deposited by sputtering	SLG/Mo/CIGS/Al_2O_3
Si_3N_x	Si_3N_x deposited by PECVD at 150 ºC, HF	SLG/Mo/CIGS/Si_3N_x
Al_2O_3 – ALD	Al_2O_3 deposited by ALD	SLG/Mo/CIGS/Al_2O_3
SiO_x – 300 ºC	SiO_x deposited by PECVD at 300 ºC, HF	SLG/Mo/CIGS/SiO_x
SiO_x – 150 ºC, HF	SiO_x deposited by PECVD at 150 ºC, HF	SLG/Mo/CIGS/SiO_x
SiO_x – 150 ºC, LF	SiO_x deposited by PECVD at 150 ºC, LF	SLG/Mo/CIGS/SiO_x

Before the insulator deposition, a 10 % (w/w) HCl etch was done during 2 min to remove the CdS layer and to leave the CIGS surface pristine [25]. Subsequently, the samples were taken to the deposition tools in a matter of seconds to avoid CIGS air exposure.

The insulators were deposited with 50 nm and using different techniques: i) Al_2O_3 by RF sputtering at 1500 W, Ar injection with a flow of 200 sccm and deposition pressure of $5x10^{-3}$ mbar; ii) Si_3N_x by Plasma Enhanced Chemical Vapor Deposition (PECVD) at 150 ºC, High Frequency (HF) of 13.56MHz, plasma power of 30 W and as precursor gases NH_3, $SiH_{4\text{-}5}$ and N_2; iii) SiO_x by PECVD at three different deposition conditions: a) 300 ºC, HF, plasma power of 30 W and as precursor gases N_2O, $SiH_{4\text{-}5}$ and N_2; b) 150 ºC, HF, plasma power of 30 W and as precursor gases N_2O, $SiH_{4\text{-}5}$ and N_2; c) 150 ºC, Low Frequency (LF) of 380kHz, plasma power of 60 W and as precursor gases N_2O, $SiH_{4\text{-}5}$ and N_2; iv) Al_2O_3 by atomic layer deposition (ALD) at 200 ºC, using as precursor gases Trimethyl aluminum (TMA) as aluminum source and H_2O as oxygen source.

To create the MIS structure, metal aluminum layer contacts were deposited by thermal evaporation, with a thickness of 400 nm. The final scheme of one MIS structure and a representative SEM cross-section are depicted in Fig. 1. Each sample had 10 circular contacts with diameters of 1 mm, 5 contacts with diameters of 2 mm and 6 contacts with diameters of 3 mm.

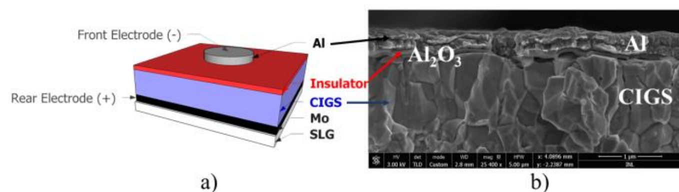

Fig. 1. a) Scheme of MIS structure: SLG/Mo/CIGS/insulator/Al. The molybdenum thickness is 350 nm, the CIGS is 2 µm, the insulator 50 nm and the aluminum layer 400 nm (bilayer of 200 nm each). The image is not at scale. b) SEM cross-section of sputtered Al_2O_3.

Raman spectroscopy was performed, using a Confocal Raman Microscope 300 R (WiTec) with green laser (excitation wavelength of 532 nm), 1 mW of power and a Zeiss objective of 100x in the backscattering configuration. Photoluminescence (PL) was performed with a YAG, class 3B laser with a 15 kHz repetition rate and 1 ns pulse length with a beam spot of 3 mm and excitation wavelength of 532 nm. An average illumination intensity of 1 mW was used. Scanning electron microscopy (SEM) cross-section was carried out, using a NovaNanoSEM 650 tool with an acceleration voltage of 3 kV.

C-G-f measurements were done using an Agilent E4890 A with 30 mV (V_{RMS}), 0 V_{bias} from 20 Hz to 1 MHz in frequency. C-G-V measurements were done in the same tool with 30 mV (V_{RMS}) and a frequency of 10 kHz. The ac electrical behavior of the MIS structures for the referred frequency range, was modeled using ZSimpWin 3.50 software [26], where different equivalent circuits were tested. The software fits impedance data by varying resistance and capacitance values of a user defined model circuit.

III. Results and Discussion

A. CIGS surface modifications

One of the objectives of this study was to understand if the deposition of the insulators caused any surface modifications to the CIGS. In order to study surface morphological changes, Raman spectroscopy was performed and representative curves are shown in Fig. 2.

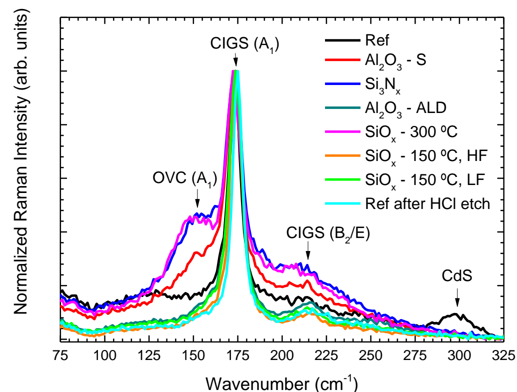

Fig. 2. Representative Raman spectra of all samples.

All the samples reveal the CIGS A_1 mode peak located at 172 cm^{-1} [27]. However, some of the samples, but not the reference one, show a shoulder in the low energy side of the referred CIGS peak. The shoulder, accordingly to the literature, is directly related with an order vacancy compound (OVC) [27], [28]. Al_2O_3 – S, Si_3N_x and SiO_x – 300 ºC samples show the

OVC layer hinting to the fact that there was some surface modification during the insulator deposition whereas Al_2O_3 – ALD and both SiO_x deposited at 150 ºC do not seem to cause modification to the CIGS surface, within the precision and accuracy limits of this equipment.

A probable reason for the OVC layer appearance is a CIGS surface modification [27] which could possibly be related to: i) the high energy sputtering method; ii) the high temperatures involved in the insulator deposition (300 ºC); or iii) the HCl etch.

It is known that sputtering causes CIGS surface modification [29], [30] while the HCl etch should not cause any surface change [25]. To understand if the HCl etch caused CIGS surface modification, a Raman measurement was conducted before and after the HCl etching. The spectra of the reference sample and the etched sample show the same peaks, thus, it is safe to conclude that the HCl etch is not affecting the CIGS surface.

PL was used to qualitatively study the CIGS opto-electronic properties, as shown in Fig. 3. In general, more recombination channels result in a wider emission and in an increase in the number of emission peaks, which ultimately lead to a worse solar cell electrical performance [31]–[33]. Both SiO_x samples deposited at 150 ºC and the Al_2O_3 sample deposited by ALD have only one narrow emission peak. The samples Al_2O_3 – S, Si_3N_x and SiO_x – 300 ºC show broad emissions. Consequently, a higher number of recombination channels should be present in the latter samples compared with the former ones. Besides having a narrow emission, both 150 ºC, SiO_x samples have a blue shift in energy of its peak position as compared with the emission from the reference sample. Such blue shift can either represent a higher bandgap value (unlikely due to the same CIGS processing in these samples) or passivation of shallow defects [34], [35]. The Al_2O_3 – S, Si_3N_x and SiO_x – 300 ºC samples have an emission which is characterized by two peaks. One of the peaks is located at the same energy as the one found in the reference sample and a second peak located at higher energetic positions. It is clear that the samples with the SiO_x deposited at 150 ºC and the Al_2O_3 deposited by ALD have a lower number of recombination channels affecting their electronic structure, a behavior similar to the reference sample but with different values of full width at half maximum (FWHM). To summarize the PL data, the samples that show several peaks, are likely to have several recombination channels, whereas the ones with the emission similar to the reference sample, kept the same recombination mechanism.

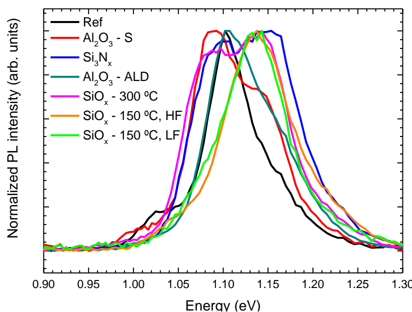

Fig. 3. Photoluminescence spectra of all samples.

A clear relation between Raman and PL measurements is observable: for Al_2O_3 – S, Si_3N_x and SiO_x – 300 ºC samples, CIGS-surface modifications are likely present. These samples involve deposition methods that are energetic and high temperature processing, hence, there is enough energy to induce surface modifications. The other samples, presenting similar PL and Raman results with the reference sample, indicate no CIGS surface modification.

B. Interface electrical measurements

To study the insulators passivation effect, two parameters were estimated: fixed insulator charges, Q_f, and interface defects density, D_{it}, in the CIGS-insulator interface.

The fixed insulator charges, Q_f, is estimated using the following equation [36]:

$$Q_f = \frac{C_{in}(\phi_{MS} - V_{fb})}{A \times q} \quad (1)$$

where A is the front metal contact area, q is the elementary charge, C_{in} is the insulator capacitance, V_{fb} is the flat-band voltage. Φ_{MS} is the work function difference between metal and semiconductor and can be determined by [19], [36]:

$$\phi_{MS} = \phi_M - \left(\chi + \frac{E_g}{2} + \frac{kT}{q} ln \frac{N_a}{n_i}\right) \quad (2)$$

$$n_i = \sqrt{N_C N_V e^{\frac{-E_g}{kT}}} \quad (3)$$

where Φ_M is the aluminum work function, (4.26 eV [37]), χ is the CIGS electron affinity (4.25 eV [38]), E_g is the CIGS bandgap (1.15 eV [24]), k is the Boltzmann constant, T is the temperature, N_a is the acceptor concentration (5×10^{15} cm^{-3} [19], [20]), n_i is the intrinsic carrier concentration, being calculated using equation (3) [19], N_c is the conduction-band density of states (7×10^{17} cm^{-3}) and N_v is the valence-band density of states (1.5×10^{19} cm^{-3}) [19], [39]. We note that when possible these values were experimentally calculated with CIGS fabricated in the same conditions as of this study and in these conditions, Φ_{MS} reaches a value of -0.97 V. However, it is expected some variability in the Al work function, as well as, in the CIGS affinity values due to Ga content profile. We tested this hypothesis by changing Φ_M from 4.06 eV to 4.26 eV and χ from 4.25 eV to 4.5 eV and only minor changes to Φ_{MS} were observed. Despite this evidence, as Φ_{MS} is used to calculated Q_f its absolute values should be seen with care, instead a comparison can be performed, as the CIGS and the aluminum is the same in all samples. In order to use equation (1), it is assumed that other insulator charges have a reduced effect on the Q_f measurements and that the interface traps plays a negligible role [36], a common assumption in the literature but that has yet to be fully proved [40]–[42].

C-V-f measurements were done to determine the C_{in} and V_{fb} parameters necessary to the calculation of Q_f. C_{in} is the insulator capacitance value extracted from the strong accumulation regime in the C-V curve. Taking into account the CIGS p-type conductivity, the accumulation regime is found at negative bias. To get the values of flat-band voltage (V_{fb}), the graphical method [43] is used and the following equation is considered:

$$\left(\frac{C_{in}}{C_m}\right)^2 - 1 = 0 \qquad (4)$$

where C_{in} is the insulator capacitance value, extracted in the C-V strong accumulation regime, and C_m is the measured capacitance.

A representative graph of the C_{in} and flat-band voltage (V_{fb}) extraction is shown in Fig. 4.

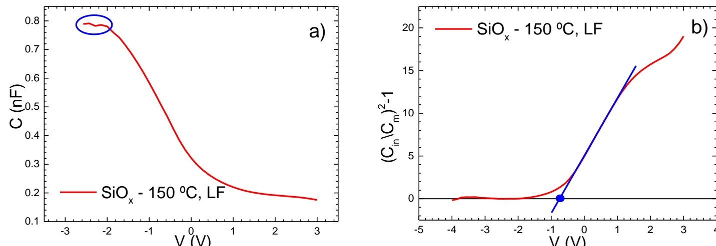

Fig. 4. Sample SiO_x – 150 ºC, LF. MIS with front contact of 1 mm: a) Representative C-V curve. The blue circle corresponds to the region where the C_{in} value is extracted; b) Representative V_{fb} extraction through the graphical method. The intercept of the fitted slope corresponds to –0.66 V.

Averages and standard deviation for the Q_f values of the MIS structure with front contact diameter of 1 mm are found in TABLE II. The large area MIS were not measured for reasons explained further in the text.

TABLE II: Q_f VALUES TAKING INTO ACCOUNT THE AVERAGE C_{in} AND V_{fb}. MIS WITH FRONT CONTACT DIAMETER OF 1 mm.

	$Q_f \times 10^{11}$ (cm^{-2})
Al_2O_3 – S	+3.6
Si_3N_x	+3.2
Al_2O_3 – ALD	+4.1
SiO_x – 300 °C	+4.0
SiO_x – 150 °C, HF	+2.8
SiO_x – 150 °C, LF	-0.6

It is necessary to understand that the Reference sample does not form a MIS structure, hence, it was not possible to calculate the electrical parameters such as the Q_f and the D_{it}. Considering TABLE II, it was expected that the same material had the same polarity of the fixed charges, as it is shown for the Al_2O_3 samples. However, an interesting observation is that for SiO_x – 150 ºC by changing frequency, in the deposition, it is possible to invert the polarity of the fixed insulator charges. Moreover, the insulator with positive charges (SiO_x – 150 ºC, HF) can be used in solar cells architectures that prefer field-effect passivation for holes, while the insulator with negative charges are more appropriate for rear passivation of current CIGS solar cells architectures as their field-effect passivation should repeal electrons.

This preliminary analysis shows that the interface Q_f values are not intrinsic to each insulator and that its concentration can be modified with growth properties.

The studied MIS structures had diameters of 1, 2 and 3 mm. However, during some of the C-V measurements, untypical behaviors appeared for the 2 and 3 mm MIS devices. Untypical behaviors of the large contact area devices observed were caused by a resistive behavior instead of a single capacitive one. An ideal MIS structure can be characterized by the equivalent circuit represented in Fig. 5 a). In this circuit, C_p and G_p correspond to the frequency-dependent capacitance and the frequency-dependent conductance, respectively, associated to the interface-traps whereas C_{in} is the capacitance created by the insulator [36], [44], [45]. In such ideal equivalent circuit, shunt conduction in the insulator is neglected which can be a problem for leaking current in the capacitor. In that case, a more realistic equivalent circuit would be the one represented by Fig. 5 b), where a G_s is now present. However, for the case of Fig. 5 b), there are still no established models for parameters extraction with these circuit conditions. To identify if our devices were being heavily affected by insulator shunts, measured the frequency dependent impedance behavior. Afterwards, this data was fitted to the equivalent circuit of Fig. 5 b), and values of G_s were extracted using the software ZSimpWin, which provide us with values of each electric component present in the circuit. Such procedure is needed as the measurement device considers the equivalent circuit shown in Fig. 5 c) and the measured values are C_m and G_m.

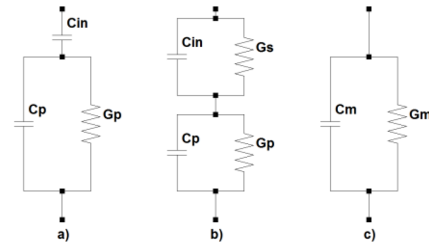

Fig. 5. Equivalent MIS circuits for conductance measurements: a) including interface-trap effect [45]; b) Same circuit of a), considering a possible series conductance; c) device's measured circuit.

The extracted values for series conductance, G_s, are shown in TABLE III. As hinted from the C-V measurements, the series conductance values increase with increasing contact diameter. These results indicate that while for small font contact diameters the electrical measurements are consistent with the circuit represented in Fig. 5 a), this is not the case for the other diameters. The results for 3 mm of the Al_2O_3 – ALD sample are not represented since the error values were too high, showing the need for even more complex equivalent circuits. Henceforth, only results for 1 mm MIS structures will be shown.

TABLE III: AVERAGE AND STANDARD DEVIATION OF SERIES CONDUCTANCE FOR DIFFERENT TOP CONTACT DIAMETERS.

G_s (nS)	*1 mm*	*2 mm*	*3 mm*
Si_3N_x	20.9 ± 6.70	92.9 ± 26.2	(1.34 ± 0.28) x10^5
Al_2O_3 - ALD	2.77 ± 1.25	14.7 ± 12.6	-
SiO_x - 300 °C	11.3 ± 1.70	38.0 ± 5.00	146 ± 49.0
SiO_x - 150 °C, HF	25.4 ± 17.1	302 ± 201	1.00 x10^3
SiO_x - 150 °C, LF	17.2 ± 6.70	103 ± 11.0	302 ± 54.0

Another important parameter for interface passivation is the density of interface defects (D_{it}). For a comparison between the D_{it} values of each sample, the conductance method, introduced by Nicollian and Brews [44] was used. This method does not

assume the leakage current through the insulator, thus, *Gs* does not appear in equation (5). The value G_p for the ideal MIS structure represented on Fig. 5 a), is given by [44], [45]:

$$\left(\frac{G_p}{\omega}\right) = \frac{\omega G_m C_{in}^2}{G_m^2 + \omega^2 (C_{in} - C_m)^2} \tag{5}$$

where ω is the angular frequency, G_m and C_m are the measured conductance and capacitance, respectively, and C_{in} is the capacitance of a C-V curve measured in the strong accumulation regime [36], [44], [45]. Plotting (Gp/ω) against frequency, *f,* will yield a maximum in the energy loss mechanism [20], [45] as shown in a representative plot in Fig. 6. The relation is given by [20], [36]:

$$D_{it} = \left(\frac{2.5}{A \times q}\right)\left(\frac{G_p}{\omega}\right)_{max} \tag{6}$$

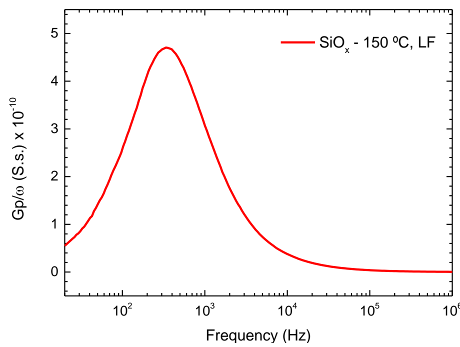

Fig. 6. Representative (G_p/ω) against f curve of sample SiO_x – 150 ºC, LF. MIS with 1 mm.

The extracted D_{it} values are summarized in TABLE IV. Surprisingly most of the samples show D_{it} values within the same order of magnitude, being the notable exception the sputtered Al_2O_3 sample. This is a remarkable result as the sputtering of Al_2O_3 was shown previously to cause some surface modifications and one would expect a higher number of electrical traps compared with samples with reduced surface modifications. While we cannot discard modifications to the composition of the Al_2O_3 layer itself in the sputtering deposition, the biggest difference compared with the ALD sample is the presence of an OVC layer. In the literature there are several hypothesis that the OVC layer improves the interface, like for instance due to a similar crystal structure and better band alignment [46]–[49]. Such improvement might be an explanation for the superior results achieved with the sputtered Al_2O_3 sample in comparison with the ALD Al_2O_3.

There are models to represent the (Gp/ω) data, namely the single level defects and continuous distributions of defects [36]. Fittings were done to our data, and the most suitable model in our case is the single level defect. Moreover, it was possible to extract D_{it} values through the fittings, and the values were found to be lower than the ones calculated using equation (6), however they followed exactly the same trend of the calculated values in the present paper. Such fact is a good indication that comparisons of the D_{it} values between samples are possible to be made. However, the presented values should not be considered absolute values as a more detailed analysis has to be performed in the future to understand what is the most accurate D_{it} extraction technique.

TABLE IV: D_{it} AVERAGE AND STANDARD DEVIATION VALUES OF MIS WITH DIAMETER OF 1 mm FOR EACH SAMPLE.

	D_{it} ×10^{12} ($eV^{-1}cm^{-2}$)
Al_2O_3 – S	0.8 ± 0.03
Si_3N_x	1.6 ± 1.0
Al_2O_3 – ALD	3.8 ± 1.4
SiO_x – 300 °C	3.1 ± 1.9
SiO_x – 150 °C, HF	5.7 ± 3.2
SiO_x – 150 °C, LF	0.9 ± 0.09

IV. CONCLUSIONS

In this work we studied the influence of depositing several insulator materials on CIGS with the objective of being used as interface passivation layers. We focused our attention in two different types of effects: i) identification of CIGS surface modifications during the deposition of the insulator; and ii) comparison of the electrical effect on the interface between CIGS and passivation layer. For surface modification we identified two trends: a) the appearance of an OVC layer; and b) unchanged samples. It was shown that the deposition of the insulator with either sputtering or high temperatures (300 ºC) causes the appearance of an OVC layer at the CIGS surface. Such fact was probed by Raman, and also seen in PL measurements by increased number of recombination channels.

With regard to the electrical measurements of the MIS structures, we determined that large areas lead to increased shunting between the Al contact and the Mo, which had to be dealt with by using sufficiently small values of front contact area.

For the fixed insulator charges, the values were found to be similar between each other with the same positive electrical polarity, however for the SiO_x deposited by LF, the values were found to be negative. The opposite polarity of the fixed charges mean that the same insulator can be used for different passivation roles. On the subject of density of interface defects, the insulator with lower D_{it} values compared with the others insulators, was Al_2O_3 deposited by sputtering. We note that a complete study of these effects has to be a continuous effort and more information, like defect energy and defect cross section, is needed in order to fully understand the effects of interface defects on the CIGS performance.

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