A study to improve light confinement and rear-surface passivation in a thin-Cu(In, Ga)Se2 solar cell

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Abstract: Reducing the absorber layer thickness below 1 µm for a regular copper indium gallium di-selenide (CIGS) solar cell lowers the minimum quality requirements for the absorber layer due to shorter electron diffusion length. Additionally, it reduces material costs and production time. Yet, having such a thin absorber, reduces the cell efficiency significantly, due to incomplete light absorption and high Molybdenum/CIGS rear-surface recombination [1]. The aim of this research is to implement some innovative rear surface modifications on a 430 nm thick CIGS absorber layer to reduce both these affects: an aluminium oxide passivation layer to reduce the back-surface recombination and point contact openings using nano-particles for electrical contact. The impact of the implementation of all these rear-surface modifications on the opto-electrical properties of the CIGS solar cell will be discussed and analyzed in this paper.

Cover Letter

Submission letter for the contribution to E-MRS 2018, Symposium A Chalcogenide PV.

The present paper with the title A Study to improve light confinement and rear-surface passivation in a thin-CIGS solar cell is the contribution to Symposium A, Chalcogenide PV in E-MRS 2018 held in Strasbourg, France. The list of the authors is:

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***Reply to Editor and Referees**

I would like to thank you all for the constructive comments I have received from both editors and reviewers. I feel like they have helped me to improve the overall presentation and quality of the article. I hope that everyone will be satisfied with the way I have tried to adapt to their comments, while adjusting to the limitations imposed on me. All changes in the text are highlighted in yellow. That way you should be able to see them with ease.

Reviewer1:

1) Introduction:

First sentence needs a reference:

Thank you for pointing it out to me. I have added a reference in the corrected manuscript.

What is a standard absorber?

A standard absorber here means an absorber with a thickness of about 2-3 µm. The term "standard" was used to give comparison to a thinner (< 1 µm) absorber layer. But, to make is clearer, I have reframed the sentence.

It now reads "When compared to CIGS absorbers with a standard thickness of 2-3 µm, sub-micron absorbers (<1 µm)...."

Silver is not an alternative to ga but rather a complement:

Thank you for pointing it out to me. It escaped my attentiveness. The error has been corrected. It now reads " has gained greater interest;...."

2) Experimental:

First paragraph should be in introduction as it explains the motivation for the features dimensions.

You are absolutely right. I have made changes to the text to incorporate these changes. I think that it is now clearer and improves the structure of the manuscript.

How many cells are there for sample and why were the cells randomly selected? why not removing shunted ones and keep all the remaining ones?

There are a total of 32 cells in each sample (5cm by 5cm), out of which about 28 cells were characterized randomly as it expected that the composition (for instance the CGI and GGI ration) etc. are constant throughout. Thus, to improve the statistical data and make inferences about the obtained results, about 90% of the cells were measured. You are correct, shunted cells were not included in the average, hence out of 28, 3-4 cells (on average) were not considered and the average of remaining cells (nearly 25 cells) were presented. To make it clearer, the word "randomly" has been removed in the manuscript as most of the cells were measured.

3) Results:

How a value of 5% of contacting area was reached?

A particle rich CdS solution was created using a cadmium ammonium solution (cadmium precursor and ammonia as the complexing agent) and thiourea solution (sulphur precursor) at 64°C. The substrate was immersed into the chemical bath deposition (CBD) solution after X minutes of reaction time i.e. the time taken for the formation of CdS nano-particles. It was then allowed to remain in the CBD solution for Y minutes during which a CdS rich film was grown on the substrate surface. Initial experiments involved the optimization of the deposition parameters X and Y to obtain an optimal 5 % coverage. Post optimization, X and Y were experimentally found to be 4 and 5 minutes respectively for a surface coverage of about 5 % and the point opening diameter being 300±20 nm. Given the space constraints, I skipped explaining this part. I hope this clarifies the doubt.

Rs and Rp values should be shown as the J-V curves are very similar:

Thank you for pointing this out to me. I have added the information in the JV curves. The shunt resistance is lower for the reference, which is also seen in the shape of the JV curve.

Is silver really a low diffusion element in CIGS? please provide references:
Yes, to answer the question. I added the requested information with a small justification: the diffusion coefficient of Ag is less than that of copper. This could lead to silver segregation; high-temperature annealing could improve the diffusion coefficient of Ag.
This was however not done in the present work due to time and equipment constraints. I have also changed the sentence in the main manuscript to make it clearer. References for the same:
1) Xianfeng, Z., Kobayashi, T., Kurokawa, Y., & Yamada, A. (2012). Growth of Ag (In, Ga) Se2 films by modified three-stage method and influence of annealing on performance of solar cells. Japanese Journal of Applied Physics, 51(10S), 10NC05.
2) Zhang, X.F. and Kobayashi, M., 2017. Study on growth process of Ag (In Ga) Se_2 films by a three-stage co-evaporation method using molecular beam epitaxy apparatus. IEEE Photonics J, 9, p.8400109.
3) Dyson, B. F., Anthony, T., & Turnbull, D. (1966). Interstitial diffusion of copper and silver in lead. Journal of Applied Physics, 37(6), 2370-2374.

4) Language:
"efficiencies" is a colloquial term for "values of efficiency" and other terms like this one "bandgap" instead of "band gap" xxx % and not xxx%
Thank you for pointing it out to me. It has been corrected in the text to the best of my capability.

A good language review needs to be performed for instance beginning of section 3.2: "as explained in the previously, for ..." - there are several of this kind of mistakes, a paragraph cannot start with "from the table" - what table? with regards to what? paragraphs should not be linked to previous paragraphs, that is why they are paragraphs.
Thank you very much for pointing it out to me. I added some changes/ corrections in the sentences and paragraphs as per your feedback. This will make it less long and, hopefully, easier and clearer to read/understand paragraphs.

5) Other comments:
References have some mistakes and need corrections pex subscripts:
Thank you very much for pointing it out to me It has been corrected in the text to the best of my knowledge.

__**Reviewer 2:**__

1) General remarks:
The "light confinement" announced in the title is not highlighted in the entire article. All the results refer to rear passivation. Apart from that, this article give interesting results for ultrathin CIGS solar cell improvement. The point contact passivation seems to be a simple option to improve performances even if more investigations are needed particularly for the use of silver nanoparticles.
You are probably right, however, at the time of writing the abstract for the conference, the idea of Ag nano-particles was to serve 2 purposes 1) diffuse into the absorber (absorber improvements) and or 2) remain as nano-particles, which would then make them interesting for light confinement or both. Hence, the title was chosen to include this aspect of the work performed. However, as seen from the results, there were no significant improvements in the light confinement. Accordingly, the conclusions state that more work towards the same is needed as it is just a preliminary work.

2) Missing references:
In the first line of introduction "high efficiencies of about 22.9%" the authors should give the reference of this record efficiency.
Thank you for pointing it out to me. I have added a reference in the corrected manuscript.
In the seventh line of introduction part, "(the electron-hole pair is generated in the vicinity of the back contact)" The authors should give the references for this assertion.
Thank you for pointing it out to me. I have added a reference in the corrected manuscript.

In the fourth and fifth line "thin film solar cells like CIGS have very short minority carrier diffusion length thereby lifetime." The authors should give the references for this assertion.
Thank you for pointing it out to me. I have added a reference in the corrected manuscript.

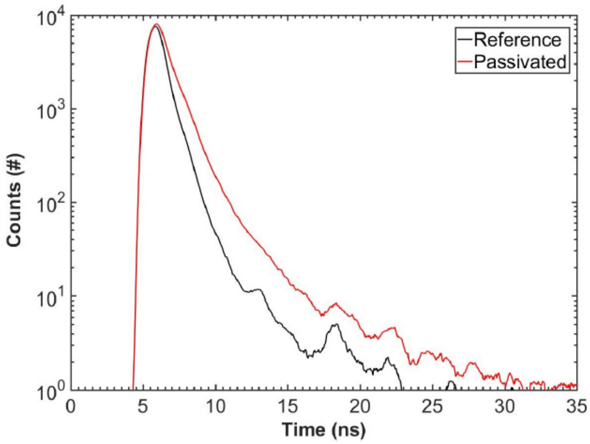
3) Experimental details:
The table 1 is unclear, add some columns.
Thank you for this suggestion. I have added 3 columns and modified the table. Indeed, I was finding it difficult to explain all the different steps for the 3-fabricated device in one table. Thank you. Hope this change makes the process steps much clearer.
4) Passivated thin-CIGS solar cell:
In the eighteenth line of the "Passivated thin-CIGS solar cell" paragraph, The sentence "(calculated using one-diode model developed by Hegedus et al. [11])" could be illustrated with a dark IV graph superposed with fit done with this model. A comparison between the three samples (reference, passivated and Ag passivated could be more explicit with the dark IV graph corresponding to these samples). Moreover, Table 2 and three can be completed with the results of fit model. This can add to the discussion comparison between series resistance, shunt resistance and saturation current, which should be changed because of passivation.
Thank you for mentioning this. I have added some of the values calculated using the Hegedus model in the results section as to give a better comparison. I have also added the series and shunt resistances in the JV curve. However, I have not added the series and shunt resistance values in the table as the other values like current /voltage are the average values, however, the ones presented in the figure are for one of the best performing devices. All the values given and explained in the results section use the values from the model for comparison.

In the thirty-fifth line of this paragraph, "This is possible as part of the light in the near infra-red region is reflected at the Al_2O_3/Mo interface into the CIGS absorber by light interference fringes.". I'm not agree with that because the thickness of the Al2O3 is too thin to induce optical modification. Moreover, the EQE spectra show an improvement in the 550-100 nm spectral range without any changes in the form of the EQE (no new resonance or shift), this is typically the effect of better carrier collection due to passivation and no effect of optical light trapping. However, in the case of Ag nanoparticles, a change in the form of EQE spectra (shift of resonances) can be attributed to back scattering of the light.
I would agree with you on the first part. For the passivated solar cell, a part of the light in the near infra-red region is reflected at the Al_2O_3/Mo interface into the CIGS absorber by light interference fringes. This leads to an improved current generation which is seen in the JV measurements. Also, the reflection is stronger for thicker Al_2O_3 layers, thus, only a marginal improvement in the J_{SC} was obtained in the present research (6 ±1 nm layer used). This would suggest that the enhanced J_{SC} is not only due to optical improvements but also due the electronic effects of the passivation layer. Therefore, explanations for the improved J_{SC} could be: 1) reduced rear interface trap density leading to a lower surface recombination velocity 2) higher minority charge carrier diffusion length due to an induced electric field caused by the Al_2O_3 layer and 3) improved reflection of light into absorber. This error escaped my vigilance and has been corrected in the manuscript.
It now reads : "Therefore, explanations for the improved J_{SC} could be: 1) reduced rear interface trap density leading to a lower surface recombination velocity [10] 2) higher minority charge carrier diffusion length due to an induced electric field caused by the Al2O3 layer [15] and 3) improved reflection of light into absorber [14]."

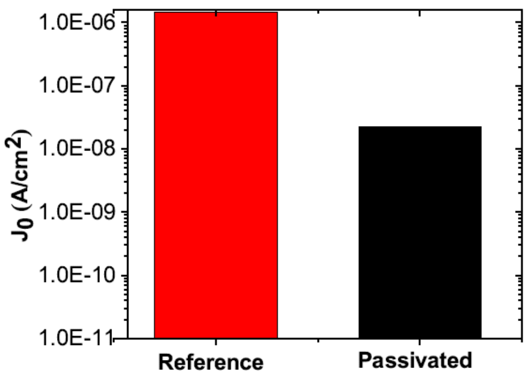
However, for the effects of silver nano-particles, I would be difficult to conclusively come to that conclusion as the effect of the selenization process on the nano-particles is still unclear. For instance, it is possible that the Ag-nano-particles partly improved the reflectance in the longer wavelength ranges, however the improvements in the absorber region still need further studies.

In the forty-eighth line of this paragraph," A higher charge carrier life time is also observed for the passivated device,". The authors should explain how they obtain this carrier lifetime (photoluminescence?):

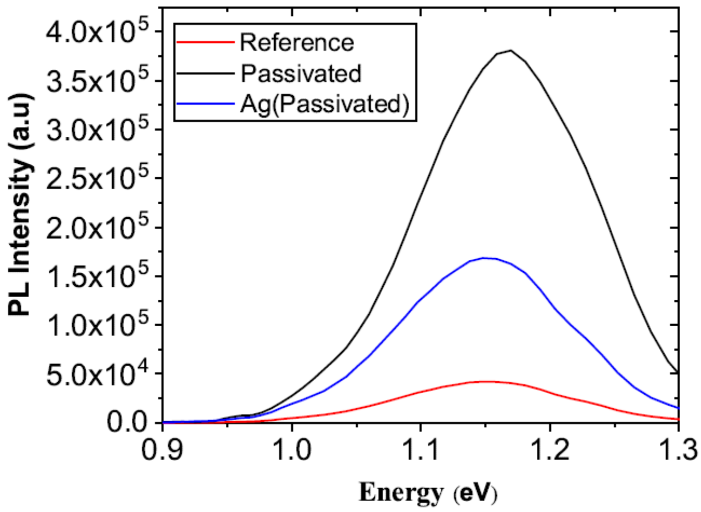
You are absolutely right. TRPL measurements and PL measurements were performed. The TRPL measurements (not in the) shows a slight improvement in the lifetime of the charge carriers for the passivated device. The intensity of the PL peak (not shown in the manuscript) is nearly 8 times higher for the passivated device when compared to the reference device. An amplified PL spectrum would suggest that non-radiative recombination is significantly reduced, and that the fermi-level spitting is more enhanced. he improvement in the PL spectrum is too large to be related to only the optical effects of the passivation layer, thus the Al_2O_3 improves the opto-electrical characteristics of the cell (improved interface quality). This can be explained as follows; the fermi-level splitting depends on the product of both the majority and minority charge carrier concentrations. Since the majority carrier concentration is identical in both the devices, this means that the minority carrier collection probability improved. This could be due to 1) increase in the diffusion length of the minority carrier due to added drift-field (electrons generated beyond the space charge region will drift towards the it and 2) reduced minority charge carrier recombination at the rear interface (lower surface recombination velocity). Thus, from the PL analysis, it is concluded that the nano-patterned Al_2O_3 layer decreases the number of active non-radiative defects in the CIGS device and thus reduces the rear interface recombination. Shown below are the figures for the same.



(a) Time resolved photoluminescence

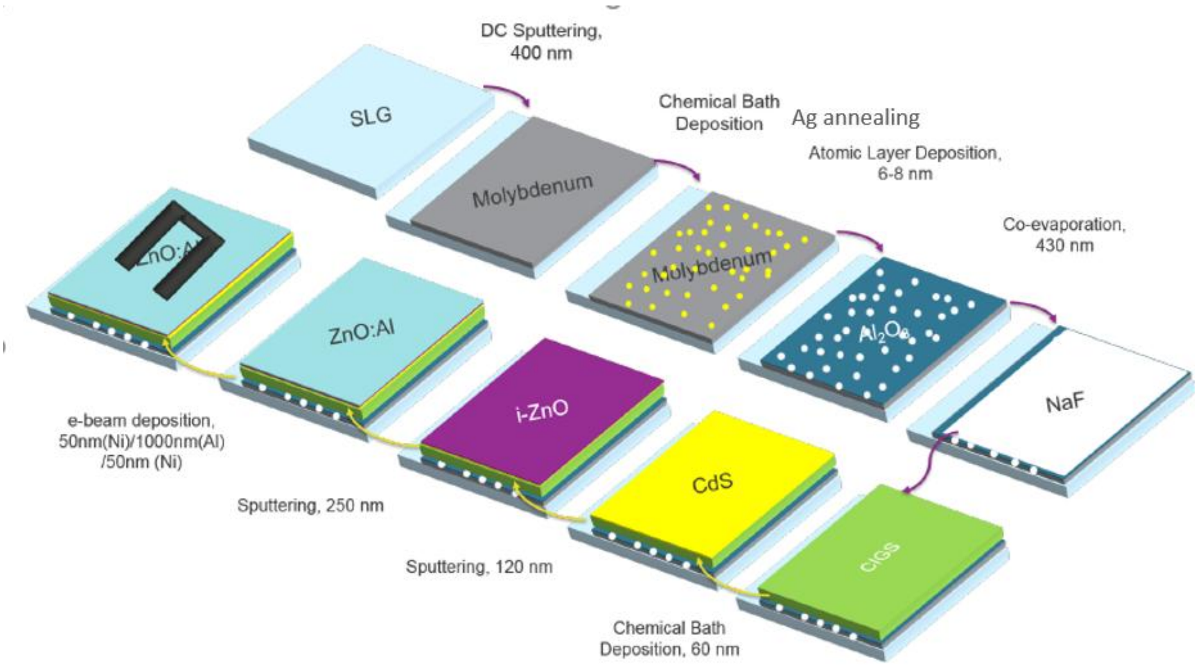


(b) Dark saturation current density



(c) PL measurements.

5) Passivated Ag-CIGS solar cells:
In the twenty-fifth line of the paragraph "Passivated Ag-CIGS solar cells", "to use of CdS nano-particles to create the contacts as explained in Table 1.". The method of fabrication is not clear. Maybe the author should include a schematic of the fabrication or detailed it in the text. We don't know if th Ag stay under Al2O3, if the CdS particle are removed by HCl or ultrasonic agitation?
Thank you for pointing it out to me. I have added a figure describing the process steps. However, given the space constraints, I don't think it will be feasible to add the picture in the main article.



This was make is easier and quick to understand the process steps as you have suggested.
Yes, the CdS particles are removed by ultrasonic agitation/HCl dipping. Yes, the Ag particles remain on the surface post Al_2O_3 deposition. However, some of the particles are lost 1) during the CdS removal step and 2) during the co-evaporation step. This requires more research, which is currently being carried out.

Figure 1:
The term "Microscopic Image" in the legend is not clear. It could be an atomic force microscope, a scanning electron microscope or an optical microscope, which could take this image. Please precise it.
Thank you for pointing it out to me. I have change it to "optical microscope" to be more precise.

*Highlights (for review)

- Rear surface passivation improves the open circuit voltage significantly.
- Well defined nano-point contacts lead to high fill factors.
- Unoptimized silver in the absorber affects cell performance.

A study to improve light confinement and rear-surface passivation in a thin-Cu(In, Ga)Se_2 solar cell.

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Abstract:

Reducing the absorber layer thickness below 1 μm for a regular copper indium gallium di-selenide (CIGS) solar cell lowers the minimum quality requirements for the absorber layer due to shorter electron diffusion length. Additionally, it reduces material costs and production time. Yet, having such a thin absorber reduces the cell efficiency significantly. This is due to incomplete light absorption and high Molybdenum/CIGS rear-surface recombination [1]. The aim of this research is to implement some innovative rear surface modifications on a 430 nm thick CIGS absorber layer to reduce both these affects: an aluminium oxide passivation layer to reduce the back-surface recombination and point contact openings using nano-particles for electrical contact. The impact of the implementation of all these rear-surface modifications on the opto-electrical properties of the CIGS solar cell will be discussed and analyzed in this paper.

1. Introduction:

Recently, power conversion efficiencies of about 22.9 % were obtained for small-area copper indium gallium di-selenide (CIGS) solar cells, however they were achieved with absorbers thicker than 1 μm [2]. When compared to CIGS absorbers with a standard thickness of 2-3 μm, sub-micron absorbers limit usage of critical feed-stock (reduced manufacturing costs), reduce the bulk defects (due to reduced bulk volume) and increase the potential for higher manufacturing throughput (reduced deposition times). Yet, for sub-micrometer CIGS solar cells, issues surrounding a highly recombinative rear interface (the electron-hole pair is generated in the vicinity of the back contact) and incomplete absorption of incident solar spectrum (partly due to low reflection at the Molybdenum (Mo) /CIGS interface) limit its usage. The combined effects of the same lead to a reduced open-circuit voltage (V_{OC}) and short circuit current (J_{SC}). One approach to reduce the rear interface recombination for instance would be to use a passivation layer; the passivation layer reduces the interface recombination by field effect and chemical passivation [3]. For a thin-CIGS solar cell, an ultra-thin film of aluminium oxide (Al_2O_3) can be used to passivate the rear interface. The use of an Al_2O_3 layer is justified as 1) first principle calculations by Hsu et al. [4] estimate a 35 % reduction in the interface trap density (Mo/CIGS) 2) a built-in field is created due to a high density of fixed negative charge which shields the minority charge carriers from getting recombined in the rear. Thus, by implementing an Al_2O_3 layer, the surface recombination velocity can be brought down to 100 cm/s (estimated from Solar Cell Capacitance Simulator [5]), leading to an enhanced V_{OC} [5].

As the Al_2O_3 layer is of non-conducting type, point contacts are necessary for electrical connection in the passivated cell. The size and distance between the point contacts (pitch) is determined by, among other parameters, the minority carrier diffusion length. When compared to c-Si solar cells (several hundred micrometers), thin film solar cells like CIGS have very short minority carrier diffusion length, thereby lifetime [6]. Thus, if a diffusion length of 0.5-1.25 µm is feasible, nano-sized openings (a few hundred nanometers in diameter) for a pitch varying from 1.25 to 2.5 µm (scaled from the Si-passivated emitter and rear cell design) is necessary for efficient carrier collection with the contacting area varying between 4-5 % (to minimize contact area between CIGS and Mo) [6].

The final bandgap of the material depends on the Ga content in the cell [7]. But, if the [Ga]/[Ga]+[In] (GGI) ratio is greater than 0.3, the performance of the device degrades, limiting the maximum achievable V_{OC} for the device [8]. Recently, the addition of silver (Ag) in a CIGS solar cell has gained greater interest; it reduces the defect density, lowers the structural disorder and increases the open circuit voltage for higher bandgap absorber layers [9]. Thus, in this research, an attempt was made to 1) implement a rear interface passivation layer and 2) introduce silver into the absorber of a passivated cell. The results of passivated device and the silver incorporated passivated device are discussed and compared to a reference solar cell.

2. Experimental Details:

A substrate configuration was used for cell fabrication (Figure 1). The Al_2O_3 layer was grown (using atomic layer deposition (ALD)) on a particle rich-cadmium sulfide (CdS) layer and subsequently, the particles were removed from the surface to create the point openings. The reason for choosing CdS nano-particles (NPs) is twofold 1) CdS is used as the buffer layer in the cell, hence the same chemical bath deposition solution can be used (cost saving) 2) the particle size varies from 200 nm to 500 nm, more or less the optimal size required in this case. Post ALD, particle removal was done in many ways such as i) dil. HCl immersion and ii) ultrasonic agitation (Figure 2). For ALD deposited Al_2O_3 layers thicker than 8 nm, particle removal was unsatisfactory. The highly conformal and self-limiting nature of ALD reactions means that the CdS particles embedded in very thick Al_2O_3 layers are irremovable. Thus, an ultra-thin 6±1 nm layer of Al_2O_3 was deposited to tackle two issues 1) blistering [10] and 2) unsatisfactory particle removal.

For the silver passivated CIGS devices, an ultra-thin layer (~15 nm) of silver was evaporated on to the Mo/CIGS interface and then annealed at 375°C in a nitrogen environment for roughly 30 minutes. Silver nano-particles are created as a result, with the average particle size being 550±20 nm. The idea to use silver NPs comes from Yin et al. [11] who reported that silver NPs at the rear surface of the cell (at the Mo/CIGS interface) tend to diffuse into the CIGS absorber during the high temperature deposition process. The steps involved in the fabrication of the passivated device is given in Table 1.

3. Results and Discussion:

3.1 Passivated thin-CIGS solar cell

To study the effects of the suggested rear surface modifications (passivation layer and Ag) on device performance, a plain reference, passivated cell and a passivated cell with Ag NPs (Ag passivated) at the rear surface were all fabricated in a single run; the molybdenum, absorber, buffer layer and front contacts are all deposited in the same run. Soda lime glass substrates used in this research had an alkali barrier layer. Hence, to counter this and avoid the so called 'roll over' effect [12], an ultra-thin sodium fluoride ((NaF), (3-4 nm)) layer is deposited pre-CIGS deposition (note, this is done for all the devices). In all cases, a 430 nm CIGS absorber was used with the GGI ratio being 0.29±0.1.

In every device, about 28 cells (32 cells per device, each 0.5 cm^2) were electrically characterized. The statistical results for V_{OC}, fill factor (FF) and efficiency (η) are summarized in Table 2 (shunted cell results were discarded). The above table shows that there is an improvement in the electrical performance of the passivated device when compared to the reference. For the reference device, the average value of efficiency was 7.2 % whereas, for the passivated device it was 8.5 %, an improvement of 1.3 % abs. On average, a 65 mV improvement in the open-circuit voltage was recorded for the passivated device, with the highest recorded V_{OC} value being 604.4 mV. Using conductance-voltage measurements, the doping concentration was calculated and found to be similar for both the devices; 1.9×10^{16} cm^{-3} for the reference device and 1.1×10^{16} cm^{-3} for the passivated device. Thus, the rational reason for an improved V_{OC} would be improved rear-surface passivation and reduced surface recombination velocity due to the Al_2O_3 layer. Remarkably, the fill factors for the passivated are acceptable and in fact, higher when compared to the reference cells; 62.1 % for the passivated device when compared to 59.4 % for the reference. Good fill factors indicate a well-defined and nearly optimized contact area in contrast to low FF values, which together with a high series resistance, is indicative of non-optimized electrical contacts. A relatively low average series resistance of 1.3 Ωcm^{-2} (calculated using one-diode model developed by Hegedus et al. [13]) and high FF for the passivated device suggests that random-nano patterned Al_2O_3 layer in terms of spacing and density, creates a proper and well-defined contacting area. The low series resistance also means that the carrier collection is not deeply affected by the large lateral distance needed by the charge carrier to reach the point contacts [14]. Furthermore, for an increased open-circuit voltage, the FF is expected to improve [14].

Both the devices have good-diode like behavior (from the dark JV curve not shown here) however, the reference device appeared to be slightly shunted (from the illuminated JV curve, Figure 3). The dark JV curve of the reference cell does not show any sign of shunting; the reference cells are affected by voltage-dependent current collection [14]. For thin-film solar cells with shorter diffusion lengths and higher absorption coefficients like CIGS, the current generation has a greater reliance on the electric field assisted drift [14]. Thus, the photo-current decreases with decreasing field or increasing forward bias. Lower diffusion lengths can be attributed to either higher bulk and/or rear interface recombination [10]. The same is not observed for the passivated device, hinting a reduced interface recombination (bulk remains the same in both the cases). Higher charge carrier life time is also observed for the passivated device (from TR-PL measurements, not shown here), and in the present case, the bulk remains unchanged. Hence it is attributed to passivating qualities of the Al_2O_3 layer.

Sufficiently good V_{OC} (>530 mV) and decent FF (>59 %) were obtained, however the efficiency was limited by the low J_{SC} values (< 24 $mAcm^{-2}$) in both the devices. Yet, when compared to the reference device, a slight improvement in the average J_{SC} was observed (+0.2 $mAcm^{-2}$). For the passivated solar cell, a part of the light in the near infra-red region is reflected at the Al_2O_3/Mo interface into the CIGS absorber by light interference fringes. However, the reflection is stronger for thicker Al_2O_3 layers, thus, only a marginal improvement in the J_{SC} (Figure 4) was obtained in the present research. This would suggest that the enhanced J_{SC} is not only due to optical improvements but also due the electronic effects of the passivation layer. Therefore, explanations for the improved J_{SC} could be: 1) reduced rear interface trap density leading to a lower surface recombination velocity [10] 2) higher minority charge carrier diffusion length due to an induced electric field caused by the Al_2O_3 layer [15] and 3) improved reflection of light into absorber [14].

3.2 Passivated Ag-CIGS solar cells:

For an Al_2O_3 passivated (rear) CIGS device, contacts are needed for efficient carrier collection. In the previous case, the CdS NPs used to create the contacts were removed from the surface. In this case however, it is necessary that the Ag particles remain on the surface. Thus, initially, the ALD deposition parameters were varied drastically to try and obtain non-conformal ALD growth. In doing so, it is possible that some regions of the cell or regions around complex 3-D structures (like the nano-particles) not be uniformly coated. The idea for non-conformal ALD growth can be explained as follows; in an idealized temperature window for ALD depositions, the growth per cycle (GPC) is weakly dependent on the temperature. However, outside that temperature window, the idealized ALD behavior can be lost due to the following reasons i) condensation: precursor gases can condense on the substrate surface which could prevent efficient purging [16] ii) lower temperature: limits completion of precursor reactions due to lack of sufficient reactivity and iii) desorption: the deposited film or the precursor gases may desorb from the surface, effecting the GPC [17]. Thus, an initial trial was made with an extremely thin non-conformal (non-conformal parameters like low temperature (from 150°C to 100°C), reducing pulse time for the TMA precursor (from 0.016 to 0.006 seconds) etc.) Al_2O_3 layer (5 nm) grown on the silver NPs. With these parameters, a thin-CIGS device was fabricated. By analyzing the results, it was absorbed that extremely low short circuit current (11 mA/cm^2), high series resistances and extremely low shunt resistances were obtained (about 9 Ωcm^2 and 33 Ωcm^2 respectively). The high series resistance and poor carrier collection suggests that the contacts were not well defined or created properly. Also, it is difficult to conclude if the contacts were a result of the non-conformal ALD or the pre-deposited NaF layer (currently under research). Thus, non-conformal ALD cannot be used as a controllable and repeatable method to create contacts. A different approach was tested to create contacts and keep the Ag NPs on the surface; to use of CdS NPs to create the contacts as explained in Table 1. The results of same are summarized in Table 2.

From Table 2, it is possible to see that there is an improvement in the open-circuit voltage (+28 mV when compared to the reference), yet the increase is not as high as in the case of a plain passivated device. The reduced open-circuit voltage can partially be explained by the lower doping concentration in the Ag-CIGS device (in the range of 10^{15} cm^{-3}), even lower than what was obtained for the plain passivated device. The FF was also reduced when compared to the plain passivated device; an average of 60.1% was obtained. This could be due to the CdS removal step; during the CdS nano-particle removal, even silver nano-particles could have partially been removed from the surface. Thus, the electrical contact area is increased and/or not optimized, which effects the fill factor.

An important trend observed in the present case is the slight improvement in the short circuit current (+0.6 mA/cm^2). The improvement in the short circuit current can also be seen in the external quantum efficiency (EQE) curves (Figure 4), where there is an improvement in the entire solar spectrum. Therefore, explanations for the improved J_{SC} could be due the combined effects of the passivation layer, the reduced disorder/defects in the CIGS structure due partial silver addition (hence an improved EQE spectra in the visible light region) and light scattering of the Ag NPs. However, further studies are needed to confirm the same. This is because silver has a low diffusion coefficient, hence higher temperatures are required to promote silver diffusion in the absorber [18, 19]. Since, in the present case, the CIGS deposition conditions were not varied significantly (for example the deposition temperature remained unchanged), it is more likely that the silver did not or partially diffused into the absorber (due to reduced CIGS absorber thickness). This possibly explains the reasonable shunt resistances obtained from the device. Moreover, for obtaining high quality Ag-CIGS devices, the uniformity of Ag in the absorber is essential, which in this case couldn't have been achieved. Consequently, moderate efficiencies were obtained (on average 7.8%) owing to the marginal improvements in the FF, J_{SC} and V_{OC}. The PL spectrum of the Ag-CIGS device was amplified when compared to the reference, however, it is more likely that it is a result of the passivation layer and not the Ag. Besides, there is no significant increase in the bandgap of the Ag-CIGS device (observed from both the photoluminescence spectra (not shown here) and the EQE) further proof of the lack of silver in the absorber. However, it must be noted that this was an initial trial made on such devices more and optimization studies are being researched actively.

4. Conclusions

In summary, an advanced architecture to integrate a rear surface passivation scheme in a thin-CIGS solar device was demonstrated. The modified rear surface consisted of an ultra-thin passivation layer with nano-sized point openings on its surface. A simple and technologically feasible method was demonstrated to generate nano-sized point openings without effecting the fill factor severely. Implementing Al_2O_3 passivation schemes impacts the cell performance positively; i) it reduces the rear interface defects ii) it lowers the rear interface recombination and iii) it improves the minority carrier diffusion lengths. Higher efficiencies were obtained owing to higher fill factors and open-circuit voltages, bringing down the efficiency losses when compared to a standard thin-CIGS device. Furthermore, an attempt was made to introduce silver into the absorber, however, more research and studies are needed in that aspect of the cell.

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Tables (if any)

Table 1: Overview of all the steps required for the fabrication of the different CIGS devices used. Note that V stands for the process being carried out and X meaning the process not being carried out.

Sr.	Process Description	Reference	Passivated	Ag (Passivated)
1	Mo/Soda lime glass (with alkali barrier) cleaning	V	V	V
2	Ultra-thin Ag layer; thermal evaporation	X	X	V
3	Ag nano-particles, annealing at 375°C	X	X	V
4	Particle rich CdS deposition, CBD	X	V	V
5	Al_2O_3 deposition; ALD (~7 nm)	X	V	V
6	CdS particle removal, point openings	X	V	V
7	NaF layer deposition (3-4nm)	V	V	V
8	CIGS, 1-stage co-evaporation (no Ga grading) (430nm)	V	V	V
9	Buffer layer (CdS), CBD (50 nm)	V	V	V
10	Window layer, RF sputtering	V	V	V
11	Ni/Al/Ni front contact, evaporation	V	V	V

Table 2: Statistical results for 25 randomly characterized solar cells under AM 1.5 spectrum, with each cell being 0.5 cm^2 in area. Both the reference and the passivated devices were deposited in the same run, have a thickness of about 430 nm with a constant GGI ratio of 0.29±0.1.

Device	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)	Saturation Current Density (Acm^{-2})
Reference	532±05	22.7±0.4	59.4±0.5	7.2±0.1	2.2×10^{-6}
Passivated	597±07	22.9±0.3	62.1±2	8.5±0.6	1.4×10^{-8}
Ag (Passivated)	560±07	23.3±0.3	60.1±2	7.8±0.6	6.4×10^{-7}

Figures (if any)
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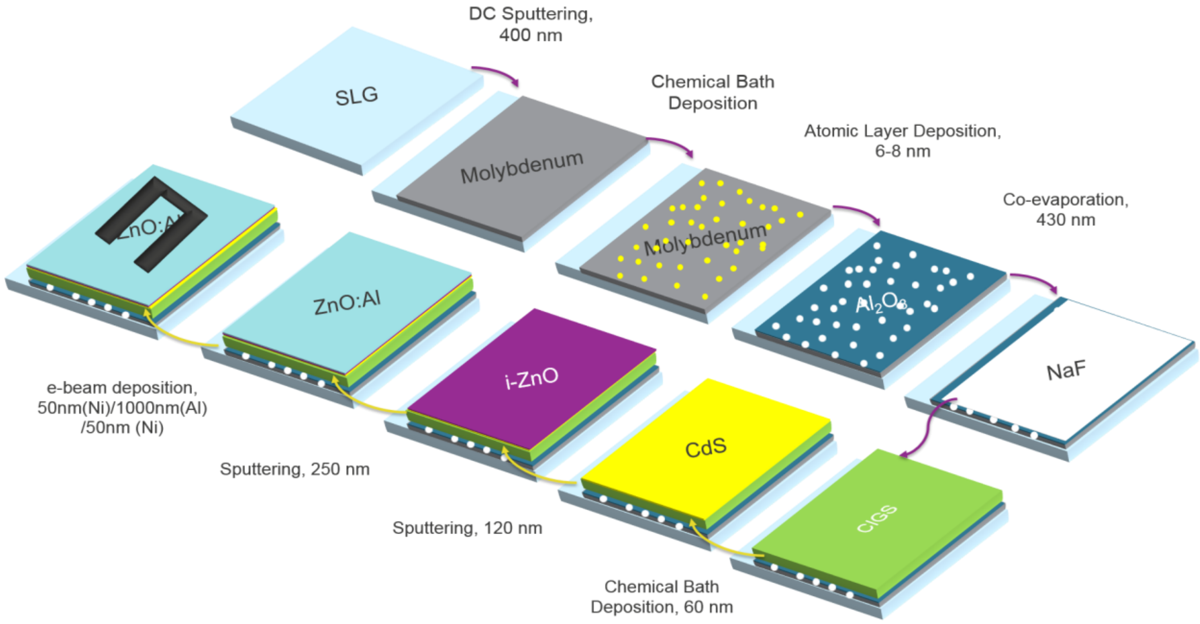

Figure 1: The various steps involved in the fabrication of a passivated CIGS device. A 1-stage co-evaporation process is used for the absorber deposition.

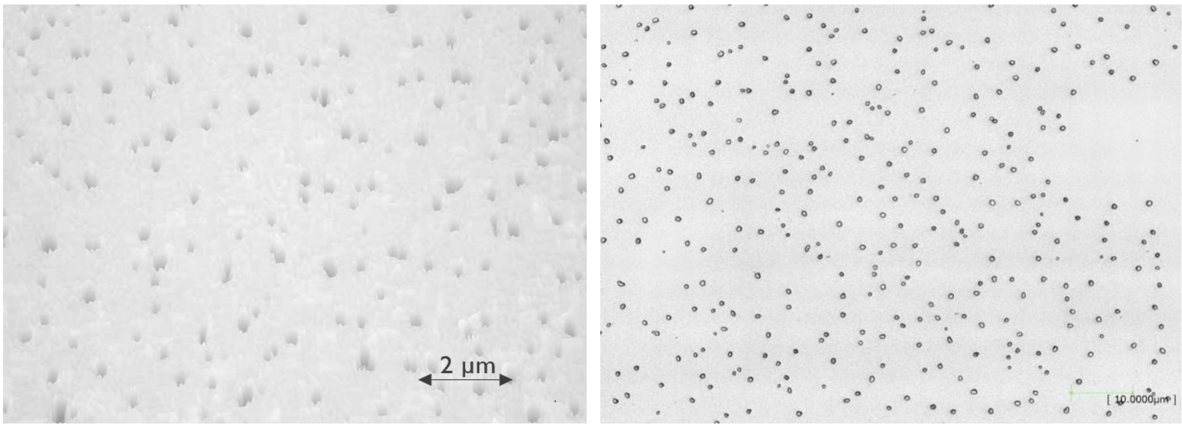

Figure 2: Optical Microscopy images of 1) point contacts post CdS removal and 2) Ag NP post annealing.

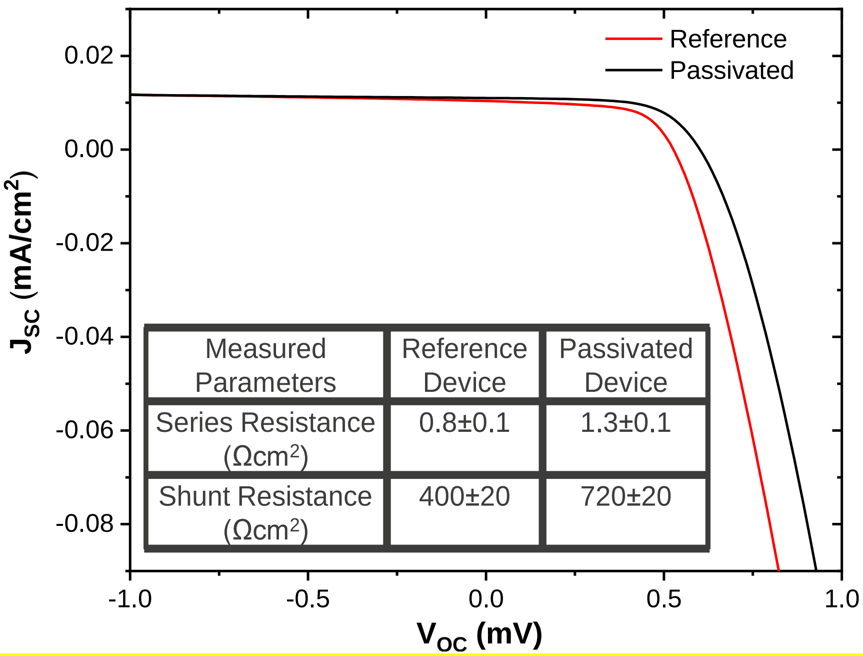

Figure 3: Representative illuminated JV curves for the reference and passivated devices. From the illustration, it is noted that 1) for the passivated device the open circuit voltage is increased 2) the reference device is shunted, effecting its fill factor.

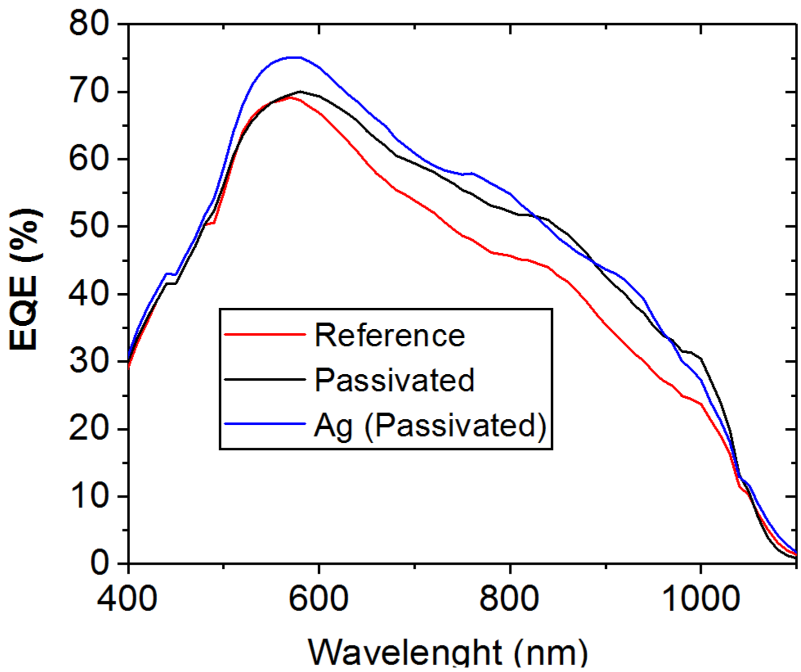

Figure 4: Representative EQE spectra for the best efficiency cell of the respective devices.