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Interdiffusion of Zinc-Stannate Buffer Layer and Cadmium Sulfide Heterojunction and Its Correlation with $CdCl_2$ Treatment

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Abstract:

In this paper, a highly transparent and conductive Zinc Stannate (Zn_2SnO_4) buffer layer is integrated between the transparent conductive oxide (TCO) layer and the Cadmium Sulfide (CdS) window layer to improve the optical properties of (TCO\Zn2SnO4\CdS\CdTe) heterojunctions in CdTe\CdS solar cells. This buffer layer is used to reduce the excess interdiffusion between the window and absorber layers when Ultra-thin CdS window layer, d < 100 nm, is employed, and post $CdCl_2$ treatment is applied at high temperature after deposition of CdTe layer. The fabricated Zinc Stannate (Zn_2SnO_4) buffer layer was found to have ideal transmission, reflectance and absorption properties which helped in introducing good optical properties in the short wavelengths. It has been found that using the Zn_2SnO_4 buffer layer enhanced the short circuit current *Jsc* and the open circuit voltage *Voc* of the solar cells that used Ultra-thin CdS thickness (80nm) by preventing TCO\CdTe direct contact, and led to improved solar cells' performance and reproducibility.

Keywords: Interdiffusion, Zinc Stannate, Buffer Layer, Ultra-Thin CdS, TCO.

Introduction:

In multilayer with heterojunction photovoltaic devices such as solar cells, it is well known that light interference occurs(Jordan 1993). Light absorption in the window layers and reflection at the interfaces reduces transmission and, eventually, the overall device performance(Ferekides, Balasubramanian et al. 2004). Thus, optical losses can be minimized by reducing the window-layer absorption which effectively enhances short circuit current (Jsc) and improve device performance(Ma, McCamy et al. 2013). This is, in CdS\CdTe solar cells, obtained by reducing the CdS window layer thickness to improve the blue spectral response. However, reducing the thickness of this layer too much, less than 100nm, can produce poor device performance due to many reasons (McCandless, Moulton et al. 1997). Firstly, ultra-thin CdS will impact the open circuit voltage (Voc). Also, ultra-thin CdS layer might be consumed totally due to the interduffusion occurs during heat treatment and post $CdCl_2$ treatment that is an important treatment for making high-efficiency CdTe solar cells by increasing grain size, grain-boundary passivation, CdS\CdTe interface alloying, and reducing lattice mismatch between the CdS and CdTe heterojunction(Wu, Asher et al. 2001). Thus, this will lead to produce localized TCO\CdTe junctions that results poor device parameters (Voc and fill factor), and also increase the pinhole formation probability(Bapanapalli 2005).

Therefore, inserting additional highly resistive transparent buffer layer between the TCO and the CdS layers has been introduced to produce high (Voc) by preventing TCO\CdTe junction formation, as well as produce high (Jsc) when CdS layer is thinned. Also, it could help reduce stresses between these different layers which improve adhesion during the CdCl2 post-treatment(Wu, Asher et al. 2001, Young, Moutinho et al. 2002).

Many different materials have been used as buffer layers in different solar cells types, such as ZnO and SnO_2 using different fabrication methods and conditions (Liang, Zhang et al. 2012, Shen, Wang et al. 2017, Wen, He et al. 2017). In this work, we are introducing a Zn_2SnO_4 buffer layer between a TCO\CdS device structures fabricated by PLD to address all the benefits mentioned above. The properties of Zn_2SnO_4 thin film layer were presented firstly. After that, three structures of solar cells were discussed. The first structure was TCO\CdS\CdTe As-deposited without buffer layer and any treatment. The second structure was TCO\CdS\CdTe with $CdCl_2$ post-treatment only. The third one was TCO\Zn_2SnO_4\CdS\CdTe that has buffer layer with $CdCl_2$ post-treatment to study the significance of using Zn_2SnO_4 buffer layer and its correlation with $CdCl_2$ post-treatment. Ultra-thin CdS layer of 80nm has been fabricated as a window layer to fabricate the device with 50nm thickness of Zn_2SnO_4 and 1.5µm CdTe absorber layer, and its results were compared with thicker CdS layer of 120nm. Considerable improvements of optical and electrical properties have been found by using Zn_2SnO_4 buffer layer with a noticeable linkage with $CdCl_2$ post-treatment even though Ultra-thin window was used, which will eliminate layer thickness limitations.

Experimental Work:-

Thin films of Zn_2SnO_4 buffer layer were prepared by Pulsed Laser Deposition (PLD) technology described in details in our pervious group publications (Li, Liu et al. 2012, Ding, Ming et al. 2013) directly on (TEC-7) glass substrate coated with TCO. This substrate has the lowest resistivity value in the NSG TEC™ range (7-8 ohm/sq) with 2.2mm typical thickness. The typical thickness (50nm) of the buffer layer which was modified and will be reported in our next paper was fabricated at $200C^0$. After that, (120nm - 80nm) thicknesses of CdS and 1.5µm of CdTe layers were manufactured by PLD to form the depletion region of the solar cells. Heat treatment was carried out at $450C^0$ and $CdCl_2$ treatment at $350C^0$ in (¼) O_2/Argon for 15min that were identified to be the ideal conditions in our previous investigations(Zeng, Harrison et al. 2016). The back contact (B.C.) mixture of graphite, cooper, and HgTe was used to form small cells with electrode (Silver) as a final step. Layers' thicknesses were obtained using a (KLA-Tencor P16) profiler.

Results and Discussion:-

The optical properties of Zn_2SnO_4 buffer layer were characterized by using a UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950) within 200–2000 nm spectral range. These properties which include optical transmittance, absorptance and reflectance are shown in Fig 1a, 1b and 1c respectively. It can be revealed that the fabricated Zn_2SnO_4 buffer layer thin film exhibits near-zero absorptance, quite small reflectance and high optical transmittance particularly in the visible range and higher. These results showed good match with other research groups(Bapanapalli 2005, Mereu, Le Donne et al. 2015). The bandgap calculation that was estimated by using the Tauc equation(Grahn 1999) shows that the Zn_2SnO_4 buffer layer has a wide and close to ideal optical bandgap of (~3.4 eV)(Bapanapalli 2005).

Atomic Force Microscopy (AFM) study was carried out by using a WiTec Alpha 300 confocal Microscopy system to investigate structural characteristics of the fabricated Zn_2SnO_4 buffer layer and obtain its surface roughness. Fig. 2 shows that the fabricated films have smooth surface and rounded small grain size that can be attributed to the relatively low fabrication temperature ($200C^0$) used to prepare the films. Films surfaces show good uniformity due to good distribution of the materials on the substrate during the fabrication process. This was found by measuring the thickness of the layer (50nm) from different directions and sides, which showed almost similar values of the thickness. An average surface roughness of ~18Å was found by this measurement which was close to the ideal film properties. These good structure characteristics of the fabricated Zn_2SnO_4 film have a good match with previous reported results (Mereu, Le Donne et al. 2015), and were ideal to be used as a buffer layer. Therefore, we have then fabricated solar cell layers to form a solar cell device in the forms shown in Fig. 3 (a) without buffer layer and (b) with buffer layer.

The performance of these solar cells was measured by using a CHI660D electrochemical work-station, a solar simulator at 1.5 AM to provide a solar spectrum, and a Newport 69911 spectrometer. The results are shown in Table 1 and represented in Fig. 4, in which it can be seen that the As-deposited device without a Zn_2SnO_4 buffer layer and $CdCl_2$ treatment show very poor parameters including open circuit voltage *Voc*, short circuit current density *Jsc*, Fill Factor *FF* and overall performance for both CdS thicknesses of 120nm and 80nm. This is well known to be attributed to the low temperature used to fabricate these layers at 200 C^0 that introduce poor structure properties and low CdTe layer doping as it has been already investigated previously(Kadhim, Harrison et al. 2016, Zeng, Harrison et al. 2016).

After exposing the device to the $CdCl_2$ treatment at $450C^0$ as described in the experimental part above, the solar cells that has 120nm CdS thickness show improved *Voc*, *Jsc*, *FF* and efficiency η (5.1%), (See Fig.4). These improvements applied to the huge $CdCl_2$ treatment effects that is well known to offer many substantial benefits including recrystallizations, increased grain growth, grain-boundary passivation, increased CdS\CdTe interface alloying, and reduced lattice mismatch between CdS\CdTe layers (Dharmadasa 2014, Spalatu, Hiie et al. 2015).

However, after reducing the CdS layer from 120nm to 80nm to improve the short wavelengths optical range, all solar cells parameters with overall performance were dropped down drastically. This is due to the excessive material interdiffusion between Ultra-thin CdS layer and CdTe layer which probably led to consume the whole CdS layer during the high applied temperature. Also, as the CdS thickness is thinned, the probability of pinhole formation is increased, causing localized TCO\CdTe junctions with inferior (Voc and fill factor) device parameters, and adversely impact device open circuit voltage (Voc). In contrast, the same cells with Ultra-thin CdS layer of (80nm) were significantly improved and able to maintain high and improved solar cells parameters after inserting a Zn_2SnO_4 buffer layer between TCO\CdS as shown in the last column of Table 1 as well as relations shown in Fig. 4.

These cell results have demonstrated that improved performance of TCO\CdS\CdTe devices can be obtained by integrating a Zn_2SnO_4 buffer layer into CdS\CdTe devices. They show that solar cells in (TEC 7glass\TCO\Zn_2SnO_4\CdS\CdTe) device structure with Ultra-thin CdS layer of (80nm) has been fabricated with improved *Jsc* of (20.4 mA/cm^2). Even though the CdS is very thin, the fabricated device retained a high *Voc* (701 mV) and *FF* (47.7%) due to the addition of a Zn_2SnO_4 buffer layer which results in higher conversion efficiency of (6.8%). The improved solar cells parameters are attributed to the Zn_2SnO_4 buffer layer that acting as a non-conductive stop-etch layer, that significantly reduces device shunting, and this has a quite similarity with results obtained previously(Matin, Amin et al. 2009).

We have further studied the adhesion behavior to investigate surfaces stress, and found that inserting a Zn_2SnO_4 buffer layer can improve the adhesion significantly after $CdCl_2$ treatment as it is shown in Table 2. This study carried out on a total of 68 devices that all exposed to 100% saturated $CdCl_2$ solution soak and following thermal anneal, then was investigated for adhesion. A total of (50) devices had the Zn_2SnO_4 buffer layer within their structure while the other (18) devices had not. It has been found that among the (18) solar cells devices that were without the buffer layer, only one of them had good adhesion. On the other hand, (46) devices with the buffer layer had good adhesion. This result shows that integrating a Zn_2SnO_4 buffer layer provides better adhesion and reduces the stress consequently. This was also supported by the results reported previously(Rojo, Korevaar et al. 2012). Therefore, much greater process scope can be addressed when optimizing the CdCl2 treatment step and this has effective manufacturing ramifications.

Figure 5 shows the standard J-V curve of our solar cells devices. Poor J-V properties were recorded for devices without buffer layer and $CdCl_2$ treatment. Appling $CdCl_2$ treatment introduced some improvements but not a lot (η = 2.2 %) due to using Ultra-thin CdS. On the other hand, considerable improvements in device performance (η = 6.8 %) even when thinner CdS window layer is applied by integrating a Zn_2SnO_4 buffer layer into a TCO-based CdS/CdTe cell. Our results showed good coincide partially with what have been already introduced in some results reported in the literature(Matin, Amin et al. 2009, Kephart, Geisthardt et al. 2013). Therefore, the performance of CdS/CdTe cells with the Zn_2SnO_4 buffer layer is far from optimized, and we expect that high level of understanding of the physics and chemistry of how Zn_2SnO_4 buffer layers affect CdS/CdTe devices will result to improved enhancements in device performance.

Conclusion:

In order to reduce the optical losses in solar cells, Ultra-thin CdS window layer (120nm - 80nm) has been used in fabricating CdS\CdTe based solar cells. Then, integrating a highly conductive and transparent Zn_2SnO_4 buffer layer between TCO and CdS was found to be very beneficial in producing high device performance. It is found to help minimizing the excessive material interdiffusion at the interfaces and preventing the formation of direct contact between TCO and CdTe layers when Ultra-thin CdS (80nm) is used and high $CdCl_2$ temperature treatment is applied.

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Also, using the buffer layer has enhanced the adhesion properties of the fabricated devices which would be very significant point in manufacturing fields. Moreover, improved solar cells parameters including *Jsc*, *Voc*, and *FF* were obtained, as well as high conversion efficiency of (6.8 %) was calculated from devices used only (80nm) CdS layer and a Zn_2SnO_4 buffer layer. More investigations on the correlation between the buffer layer thickness and window and absorbed layers from one side, and heat treatment conditions from another side would open the door for very interested improvements in solar cells production.

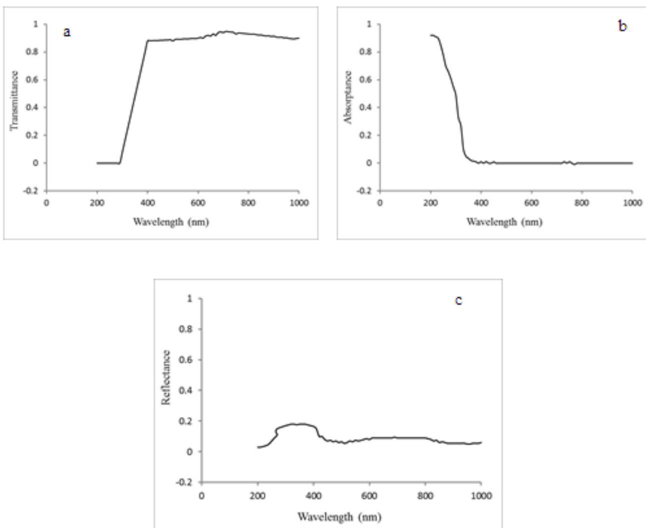

Figure 1: a) The transmittance, b) absorptance, and c) reflectance of a Zn_2SnO_4 thin film

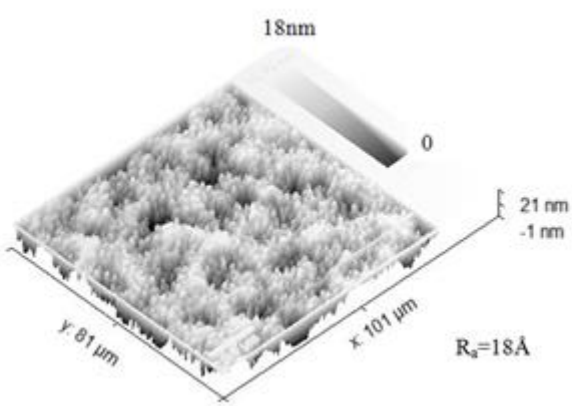

Figure 2: Atomic Force Microscopy (AFM) study of Zn_2SnO_4 thin film

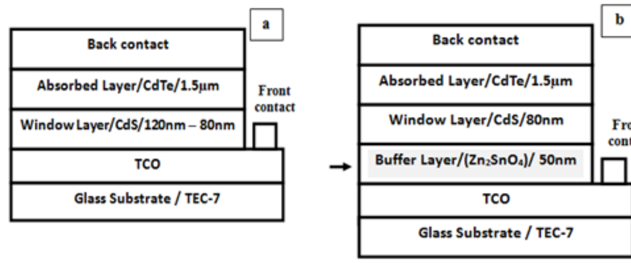

Figure 3: Structures of the solar cells: (a) Conventional baseline case structure and (b) Modified structure with a Zn_2SnO_4 buffer layer integrated between TCO\CdS for higher conversion efficiency

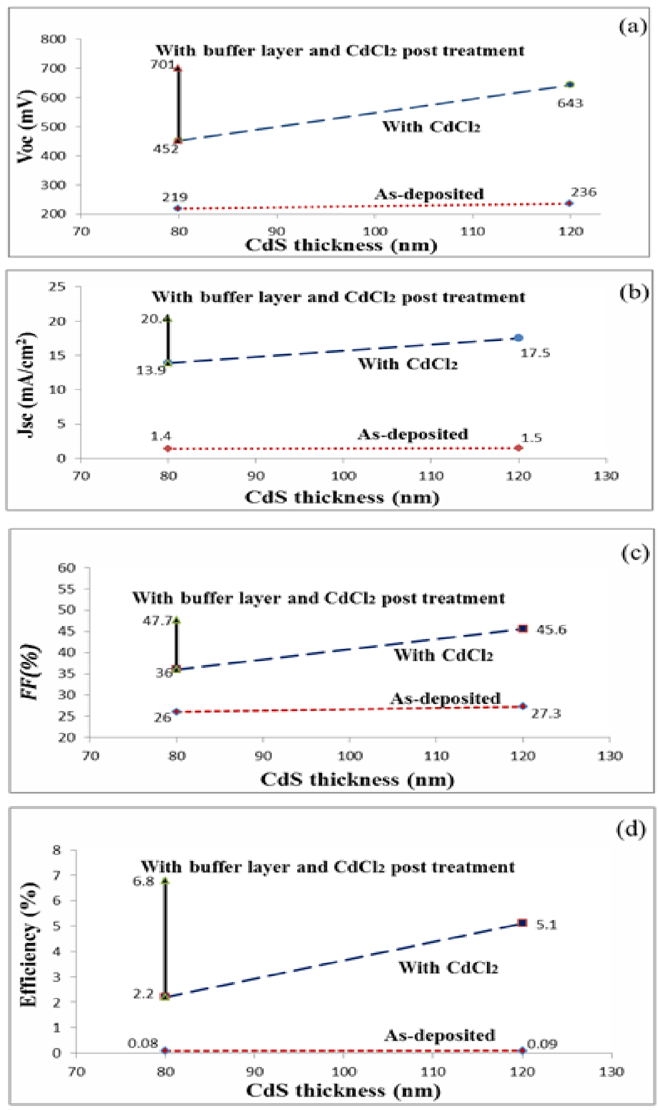

Figure 4: Effect of integrating Zn_2SnO_4 buffer layer, $CdCl_2$ treatment and CdS film thickness on cell output parameters

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Table 1: Show solar cell parameters in different conditions

Sample Condition	As-fabricated (No buffer layer and No $CdCl_2$ doping)		With $CdCl_2$ doping only		With (Zn_2SnO_4) buffer layer and $CdCl_2$ doping
CdS thickness (nm)	120	80	120	80	80
Voc (mV)	236	219	643	452	701
Jsc (mA/cm²)	1.5	1.4	17.5	13.9	20.4
FF (%)	27.3	26	45.6	36	47.7
η (%)	0.09	0.08	5.1	2.2	6.8

Table 2: Show solar cell adhesion properties with and without the Zn_2SnO_4 buffer layer

Solar Cells Devices	Solar Cells without (Zn_2SnO_4) buffer layer	Solar Cells with (Zn_2SnO_4) buffer layer
Total	18	50
Good adhesion	1	46
Edges Blister	11	3
Completely peeled off	6	1

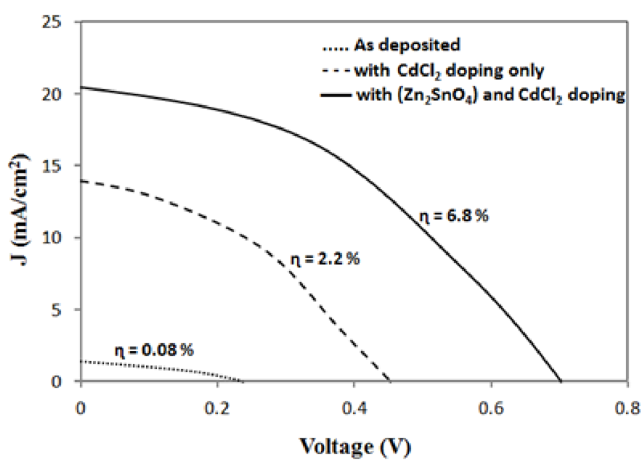

Figure 5: *J-V* Characteristics of solar cells devices that have Ultra-thin CdS (80nm), and fabricated with and without a Zn_2SnO_4 buffer layer and $CdCl_2$ treatment

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