Three-dimensional structures based on ZnO/CdS and ZnO/(Zn,Mg)O core-shell nanowires embedded in Cu(In,Ga)S₂ for solar cell applications

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Abstract. Thin film and core-shell nanowire heterostructures containing copper indium gallium sulfide Cu(In,Ga)S₂ (CIGS) as light absorber are fabricated by low cost, solution based processes. The unique structures consist of ZnO and CdS or (Zn,Mg)O core-shell nanowire arrays embedded inside CIGS thin films for solar cell applications. Nontoxic (Zn,Mg)O buffer layer deposited by atomic layer deposition is proven to be suitable for replacing solution grown CdS for fabricating CIGS nanowire solar cells. A systemic comparison of device performance is made between the CIGS nanowire solar cells and their thin film counterparts with different final treatment temperatures. Overall, the nanowire devices show higher efficiency than the corresponding planar structures fabricated under similar conditions. Effect of nanowire on the solar cell performance is further studied by using nanowires of various lengths, which reveals that the longer nanowire arrays resulted in a higher short circuit current. This study represents the first working CIGS nanowire solar cells reported so far and provides an opportunity for investigating the mechanism of nanowire solar cells using a well-defined material system.

Keywords: CIGS, ZnO, Core-shell nanowires, Photovoltaics.

Introduction

Solar energy conversion is a highly attractive process for clean and renewable power for the future. The layered structure of $\text{Cu(In,Ga)(Se,S)}_2/\text{CdS/ZnO}$ has proven itself to be a worthwhile photovoltaic combination achieving record efficiencies upwards of 20% [1]. These record efficiencies have been obtained through vacuum-based approaches. However, the high cost of vacuum-based fabrication processes become a barrier to affordable solar cells as an energy source. As a result, solution-based approaches have become the focus of many studies which have achieved record efficiencies of 15% for copper-indium-gallium-disulfide (CIGS) materials [2, 3]. These highly efficient devices have been fabricated on a 2-dimensional design, i.e. multilayers of thin film structures.

In the last few years, an emerging solar cell design is to transfer the typical planar structure into a 3-dimensional one by utilizing 1-dimensional nanostructures to build devices in an “up and out” fashion [5, 6, 7]. There are three main reasons that make the 3-dimensional design more favorable. First, by implanting nanostructures, the charge carriers do not need to travel for a long distance for being separated and collected. It facilitates the efficient collection of photogenerated carriers in materials, especially those with low minority-carrier diffusion lengths. Second, a high aspect ratio of the nanostructures increases the surface area on a similarly sized device, thus increasing the area of the pn-junction for improved charge separation. Third, the nanostructures lead to light scattering and trapping effect, which enhance light absorption and therefore help the energy conversion efficiency.

Although nanowire structures are promising design for solar cell applications, so far the device performance has not been as good as its planar counterpart. Some examples include but are not limited to the materials of CdS/CdTe [8], Si [9], TiO_2 [10], Dye-sensitized [11], and CIS

[12, 13]. Most photovoltaic devices based on nanostructures show significant lower efficiencies than the planar structures. Some issues related to the device fabrication, materials control, and surface properties need to be addressed prior to achieving high efficiency nanowire solar cells.

In this study, we take an initial step to fabricate CIGS nanowire solar cells by embedding the core-shell structure of ZnO nanowires and two different buffer layers of cadmium sulfide (CdS) and magnesium-doped zinc oxide ((Zn,Mg)O) inside the CIGS films. In order to achieve this nanowire solar cell, a superstrate configuration has to be used in our solution based processes instead of the standard procedures for CIGS solar cell preparation. In fact, non-solution based CIGS devices in a superstrate configuration have previously shown an efficiency of 10% [4]. But a solution-processed superstrate device has not been reported so far. A typical device structure is shown in Figure 1. The left panel shows a typical planar structure of CIGS solar cells. Each layer of the materials is deposited in the sequence as it appears from the bottom to the top in this standard CIGS solar cell structure. The right panel shows the structure of a nanowire solar cell and its sequence of material deposition from bottom to the top, which leaves the Mo contact as the last step for deposition. This latter procedure is just opposite to the standard the CIGS fabrication and referred to as superstrate process. This superstrate configuration is necessary for fabricating CIGS nanowire solar cells since ZnO nanowires need to be deposited before the deposition of CIGS films.

The photovoltaic effects of the nanowire structures are studied and compared with their corresponding planar configurations. An efficiency of 12.5% was achieved for a traditional planar structure of the solution processed CIGS. However, the superstrate structures shows only 3.1% efficiency with an optimized final treatment. In comparison, the CIGS nanowire solar cells achieve efficiencies of 3.5% and 5% respectively for using CdS and (Zn,Mg)O buffer layers.

Effects of nanowire length on the solar cell performance are also studied, which further confirms the positive impact of nanowires on the device performance in superstrate configuration.

Although the overall efficiency of the CIGS nanowire solar cells is still low, this study presents a first working CIGS nanowire device and opens up a new opportunity to fully investigate the nanowire solar cells for a well-developed and very promising photovoltaic material system.

Figure 1. Schematic of ZnO/(Zn,Mg)O/CIGS thin film and nanowire solar cell structures.

2. Experimental

ZnO nanowire structures were grown using a low temperature, solution based electrochemical approach on ITO thin films [14-17]. The method used was developed by Cui and Gibson in which a potential was applied to a conducting substrate for well controlled growth in a solution of zinc nitrate and hexamine [16]. By applying a potential during the growth, vertically aligned ZnO NWs were deposited onto conducting substrates without a seed layer. Zinc nitrate of 0.5000 g and hexamine of 0.2352 g are mixed in 200 mL of deionized water and heated to 92 °C. A potential of -2.6V is applied across a working electrode; in this case, the ITO coated glass. A gold wire is placed into the solution as the counter electrode. Different deposition times of 0, 5, 10, 15, 30, 45, and 60 min are used in order to achieve nanowires of

different densities and lengths. Deposition time of zero min means a layer ZnO thin film deposited without NWs as a control.

Buffer layer CdS is usually deposited using an ammonia-enhanced process for CIGS solar cell applications. However, an ammonia-free method was used in this study to avoid ZnO etching during CdS deposition [18]. In this approach, cadmium acetate ($(\text{CH}_3\text{CO}_2)_2$) was mixed with thioacetimide (CH_2CSNH_2) in de-ionized water. The solution was stirred by a magnetic bar and kept at 80 °C during deposition.

Alternative buffer layer (Zn,Mg)O is prepared by atomic layer deposition (ALD). The Zn precursor was diethylzinc (DEZ). The Mg doping was achieved by adding an Mg pulse step periodically in the thermal-ALD growth cycle involving the standard DEZ and H_2O sequence. All DEZ and H_2O pulses were 0.06 s, followed by 5 s purges in each case. A high purity of Ar was used as the process gas. A background pressure of 0.17 Torr and substrate temperature of 200 °C were used for optimal Mg incorporation. The doping concentration of Mg was controlled to range from 0% to 24.16%, which give a band gap change from 3.3eV to 3.7eV. The film thickness is 60-80 nm.

CIGS thin film was deposited by a solution process developed by researchers at IBM [2]. It involves using a hydrazine solution to dissolve the metals into precursor solutions. The precursor solutions are mixed into a final solution so that the appropriate composition is achieved in the CIGS films. The final solution is spin coated onto the desired substrate. An initial heat treatment is applied to dry the sample 290 °C by a hotplate in order to remove the hydrazine and leave behind a uniform thin film. The spin coating and drying are repeated to achieve the desired film thickness. Afterwards, the final treatment is performed by placing the films in a tube furnace in the presence of sulfur at different temperatures.

A typical sequence for fabricating traditional structure of CIGS solar cells involves sputtered Mo back contact, CIGS, CdS or (Zn,Mg)O buffer layer, i-ZnO, and AZO window. The (Zn,Mg)O, i-ZnO, and AZO were deposited by ALD. Superstrate device structures are fabricated by reversing the above process, starting with ITO glass as a window layer and finishing by depositing Mo contact. For NW solar cell fabrication, the ZnO NWs was deposited on ITO glass substrates, coated with the buffer layer, and then embedded inside CIGS layer. Before depositing Mo contact, the NW structures with CIGS were treated in a tube furnace at different temperatures.

Structural morphology is examined by scanning electron microscopy (SEM). The solar cell devices have sizes in a centimeter scale and were scribed into $3 \times 3 \text{ mm}^2$ small cells for testing. Dark and illuminated current-voltage (I-V) characterization of the solar cells were performed by a Keithley 2400 source meter under AM1.5 spectrum using a solar simulator.

3. Results and Discussion

3.1 Thin film solar cells of traditional structure

Investigation on replacing CdS by other materials including (Zn,Mg)O have been performed in vacuum deposited CIGS solar cells [19]. It has been shown that (Zn,Mg)O is a suitable replacement as a buffer layer for CdS. Use of (Zn,Mg)O is more favorable than CdS because it is much more environmentally friendly without toxic materials and its bandgap is tunable by changing amount of Mg in ZnO which may have a desired band alignment with CIGS [20, 21]. (Zn,Mg)O also has a higher optical transmission than that of CdS. By changing the amount of Mg doping in the (Zn,Mg)O buffer layer, the solar cell performance has been optimized. Under the optimum conditions, the photovoltaic devices based on both CdS and (Zn,Mg)O buffer layers

were found to have similar energy conversion efficiencies. The best devices with optimum (Zn,Mg)O buffer layer have a typical ratio among Zn, Mg, and O of 0.65:0.35:1. This level of Mg doping raises the band gap from 3.3 eV for undoped ZnO to 3.64 eV for $\text{Mg}_{0.35}\text{Zn}_{0.65}\text{O}$. Figure 2 shows SEM cross section images of typical solar cell device structures with both CdS and (Zn,Mg)O buffer layers. The images show distinguished layers of the materials. Due to the small thickness of CdS (MgZnO), i-ZnO, and AZO, it is hard to see their interfaces.

Significant efforts have been made to replace the CdS with (Zn,Mg)O due to its toxic nature. Improvement of band alignment at the interface between CIGS and (Zn, Mg)O is important to maintain or improve the solar cell device performance. It has been found that the conduction band offset can be improved by increasing the band gap of (Zn,Mg)O. There is a large conduction band discontinuity when CdS or ZnO buffer layer is used. The increase of the band gap of the buffer layer by doping Mg into ZnO helps improve the conduction band alignment, and therefore helps the charge transportation. It was reported that the larger band gap energy of (Zn,Mg)O is necessary to create suitable conduction band offset at the interface of CIGS and (Zn,Mg)O in order to obtain a robust heterojunction [20].

Figure 2. SEM images of traditional CIGS thin film devices with (a) CdS and (b) (Zn,Mg)O as buffer layers.

Figure 3 shows the performance of standard CIGS thin film solar cells respectively using (Zn,Mg)O and CdS buffer layers prepared otherwise under similar conditions. The final treatment temperature was 650 C. Both devices have similar short circuit current I_{sc} , open circuit voltage V_{oc} , and fill factor FF. They also show the same power conversion efficiency η of about 12.5%, in comparison to the record efficiency of 15% using solution processed CIGS. It is demonstrated that the ALD deposited (Zn,Mg)O can be used to replace CdS as buffer layer for solution deposited CIGS solar cells without a negative impact on their performance.

Figure 3. I-V of standard CIGS thin film solar cells with CdS and (Zn,Mg)O as buffer layers.

The device parameters are listed in the inset.

3.2 Thin film solar cells of superstrate structure

Thin film devices were also fabricated in a superstrate configuration by reversing the deposition procedures. After the solar cells are fabricated, final heat treatments were performed in the presence of sulfur at different temperatures. Figure 4 shows the I-V curves of these superstrate devices with CdS and (Zn,Mg)O buffer layers. Overall, their performance is much worse than the devices of traditional structure. This may be resulted from the final heat treatments which degrades the interface quality.

For the devices with CdS as buffer layers, the as-prepared solar cell shows no photovoltaic effect because the final treatment is necessary to have crystalline CIGS. After treated at 350 °C, a weak photovoltaic effect was observed. The device performance was continuously improved up to a temperature of 450 °C at which the short circuit current is 7.2 mA/cm². Above this temperature, the photovoltaic effect disappears and the I-V curves become straight lines. This

result indicates that the p-n junction was destroyed by the high temperature final treatment. Similar phenomenon was observed in the superstrate structures with (Zn,Mg)O as buffer layer. The device performance shows improvement as the final treatment temperature is raised up to 550 °C. However, this new buffer layer seems to be able to tolerate a higher treatment temperature. The optima power conversion efficiency for the solar cell with CdS buffer layer is 1.38% after final treatment at 450 °C and that with (Zn,Mg)O buffer layer is 3.1% after treatment at 550 °C. This observation suggests that the (Zn,Mg)O buffer layer and the corresponding p-n junction can survive at higher temperatures than that of CdS with CIGS. The higher final treatment temperature helps the crystallization of CIGS, which in turn enhances the device efficiency. Note that the superstrate structures reported here using solution processed CIGS show much lower efficiency than those fabricated in a vacuum process [4]. This may be because the solution processed CIGS needs final treatment for crystallization and the treatment also degrade the interface quality.

Figure 4. Current voltage curves of superstrate CIGS thin film devices with (a) CdS and (b) (Zn,Mg)O buffer layers after final treatments at different temperatures.

In addition, the composition of CIGS was precisely controlled in the starting materials and also measured by energy dispersive x-ray spectroscopy after each final treatment using reference samples. Table 1 lists the composition of CIGS treated at different temperatures. It was found that the composition of Cu, In, and Ga are relatively stable while the big change was found in that of Se and S. Se content quickly drops while the sulfur content increases at the same time after the samples were treated in presence of S at higher temperatures. Overall, the combination of S and Se remains about 51% in the samples.

Table 1. Composition of CIGS at different treatment temperatures.

Temperature (°C)	Cu	In	Ga	Se	S
290	24.21	20.17	4.67	50.36	0.59
350	24.8	18.87	4.76	5.65	45.92
400	23.76	18.06	5.75	5.63	46.8
450	24.08	18.31	4.32	2.69	50.6
500	25.31	18.36	5.13	2.05	49.15
550	24.4	18.34	5.31	0.61	51.34
650	24.55	17.12	6.41	0.32	51.6

The CIGS samples were also investigated by x-ray photoemission spectroscopy (XPS). In order to get a clean surface, the sample was Ar ion etched for 5 min at 1 kV. These measurements confirm that single phase CIGS materials were obtained and the material compositions are consistent with those obtained by EDX measurements. The detailed XPS peaks of Cu, In, Ga, and S are shown in Figure 5. All elements show single symmetric peaks, indicating they possess only one chemical state. The peak positions are also consistent with previous reports in the literature [22, 23]. Note that both $2p^{3/2}$ and $2p^{1/2}$ peaks are shown for sulfur while only one peak is shown for Cu ($2p^{3/2}$), In ($3d^{5/2}$), and Ga ($2p^{3/2}$).

Figure 5. XPS spectra of Cu (a), In (b), Ga (c), and S (d) taken from CIGS thin film after treated at 650 °C.

3.3 Nanowire solar cells

Nanowire devices were fabricated in a superstrate configuration by reversing the deposition procedures due to the fact that ZnO nanowires have to be deposited prior to the growth of CIGS layer. Figure 6(a) shows an SEM cross section image of typical ZnO nanowires vertically aligned on ITO glasses. The nanowires have an average length of 1 μm and diameter of about 100 nm, which are tunable by changing growth conditions and time.

The ZnO/CdS core-shell nanowires are fabricated by coating the ZnO nanowires with CdS by a solution process. Figure 6(b) shows an SEM cross section image of the core-shell nanowire arrays. The average diameter of the ZnO/CdS core-shell nanowires is significantly larger than the pure ZnO nanowires. The thickness of the CdS shell is about 30 nm, which can be controlled by tuning the deposition conditions. Because the CdS is deposited by a hydrothermal process in solution, CdS can be deposited in the deep gap between the nanowires. Therefore the ZnO nanowires can be completely covered by CdS layers. The surface of the core-shell nanowires becomes rough as compared to the bare ZnO nanowires because of the nanocrystalline structure of CdS layer.

Figure 6. SEM images of (a) ZnO nanowires and (b) CdS coated ZnO nanowires.

The core-shell structures of ZnO/(Zn,Mg)O are achieved by deposition of (Zn,Mg)O onto ZnO nanowires by an ALD process. Figure 7 shows the SEM images of the bare ZnO nanowires and ZnO/(Zn, Mg)O core-shell structures. The ALD is expected to have uniform and conformal coating for core-shell structure deposition. One can see from the SEM images that the diameter of the nanowires is increased and the surfaces become rough after coating (Zn,Mg)O layer onto ZnO.

Figure 7. SEM images of (a) ZnO nanowires and (b) (Zn,Mg)O/ZnO core-shell nanowires.

The light absorber of CIGS is deposited onto the core-shell nanowire structures by the solution process, which allows for CIGS to be deposited within the spaces between the nanowires. After CIGS deposition, the nanostructures underwent a final treatment at different temperatures similar to the superstrate thin film devices. Figure 8 displays SEM images of a thin CIGS coating on ZnO/CdS and ZnO/(Zn,Mg)O core-shell nanowire arrays. The thin CIGS coating is shown here to illustrate the capability of the solution process in depositing CIGS into the deep spaces between nanowires. One can see that the core-shell nanowires are completely coated with CIGS layer. Note that the actual devices may have thicker layer of CIGS coatings in order to effectively absorb light and achieve reasonable efficiency. A complete nanowire solar cell is achieved after Mo contact is deposited onto CIGS layer.

Figure 8. SEM images of core-shell nanowire arrays with thin CIGS coatings: (a) CIGS/CdS/ZnO structure and (b) CIGS/(Zn,Mg)O/ZnO structure.

The I-V curves taken from the nanowire solar cells with CdS and (Zn,Mg)O buffer layers are shown in Figure 9. Similar to the superstrate thin film devices, the performance of nanowire devices is significantly affected by the final treatment temperature. For ZnO/CdS core-shell structure, the device performance shows an improvement until 450 °C. At the treatment temperature of 500 °C, the device loses its photovoltaic effect. The optima efficiency achieved at 450 °C is 2.18%. This phenomenon is also observed in the superstrate thin film solar cells using CdS as buffer layer. The solar cell using ZnO/(Zn,Mg)O core-shell nanowires show an improvement in performance up to 550 °C. Above this treatment temperature, the device performance becomes much worse than those treated at 550 °C. The efficiency of the device treated at 550 °C is 4.1%. Again this observation is similar to the superstrate thin film devices using (Zn,Mg)O as buffer layer. It is believed that the degradation of the interface quality between buffer layer and CIGS at high temperatures causes the loss of photovoltaic effects. It

seems also to indicate that the thermal stability of the (Zn,Mg)O buffer layer is better than that of CdS.

Figure 9. The I-V curves of CIGS nanowire solar cells with (a) ZnO/CdS and (b) ZnO/(Zn,Mg)O core-shell structures achieved at different final treatment temperatures.

One can see from Fig. 9(b) that the significant change in the shape of I-V curve occurs in the temperature range from 350 to 500 °C. The observed changes in I-V curves are believed to be associated directly with the change of shunt and series resistance as a result of heat treatment. The increase of treatment temperature helps to increase the shunt resistance, which causes the I-V curve to become flat around short-circuit (zero voltage). Similarly, the treatment also causes the series resistance to decrease, which increases the slope of I-V curve around the open-circuit voltage (zero current). Therefore, the I-V curves show significantly difference in their shapes.

3.4 Effects of nanowires on solar cell performance

In order to see the impact of nanowire on the solar cell performance, a comparison between the superstrate thin film and nanowire devices is made. Figure 10 shows the I-V curves from

those thin film and nanowire devices prepared under similar conditions. One can see that, under each treatment temperature, the nanowire solar cells show an improvement in terms of short circuit current as compared to their thin film counterparts. For the devices with CdS buffer layer and treated at 450 °C, the superstrate thin film structure shows an efficiency of 1.38% while the superstrate nanowire device has an efficiency of 2.18%. For those devices with (Zn,Mg)O buffer layer and treated at 550 °C, the superstrate thin film structure has an efficiency of 3.1% while the superstrate nanowire solar cell shows an efficiency of 4.1%. These results suggest that the use of nanowire indeed helps improve the solar cell performance.

Figure 10. Comparison between superstrate thin film and nanowire solar cells after different final treatment temperatures. Two sets of buffer layers of CdS (a) and (Zn,Mg)O (b) are shown.

In order to confirm the impact of ZnO nanowires on CIGS solar cell performance, further studies are made by changing the length of ZnO nanowires. Change of deposition time leads to the control of ZnO nanowire length. Figure 11 shows the ZnO nanowire arrays grown for 5 and 60 min. One can see that the nanowire length increases with growth time while the density and diameter does not show significant increase. The diameter seems to increase at longer growth

time. Figure 12 shows the average length of ZnO nanowires as a function of growth time. At 5 min, the nanowires are short and their average length is about 1.4 μm . As the growth time is increased to 60 min, the average length of the nanowires increases to 2.1 μm . This control of nanowire length provides the possibility to investigate the influence of nanowire length on the solar cell performance.

Figure 11. SEM images of ZnO nanowires grown for (a) 5 min-top view, (b) 60 min-top view, (c) 5 min-cross-section view, and (d) 60 min-cross-section view.

Figure 12. Average length of ZnO nanowires as a function of growth time.

In this experiment, (Zn,Mg)O buffer layer is used as an example and the final treatment temperature is chosen at the optima value of 550 °C. Figure 13 shows the I-V curves taken from the solar cells using nanowires with different lengths. The device of zero min refers to a superstrate thin film device without growing ZnO nanowires. It is found that those devices using nanowires with large lengths have better performance. The short-circuit current increases significantly as the nanowire length is increased. The open circuit voltage is also improved. The nanowire length directly affects the surface area of the P-N Junction. The nanowires also aid in increasing the light absorption and charge collection. It is hard to distinguish which factors may affect the solar cell performance more. However, it is shown that the nanowire incorporation in CIGS solar cells indeed improves the device performance. In general, the embedded nanowire arrays bring several advantages for solar cell performance. First, the nanowire arrays form a special structure for light trapping, which enhances the light absorption by the CIGS layers due to the multiple scattering inside the absorption layer. Second, the large surface area of nanowires

causes the p-n junction formed between CIGS and the core-shell nanowires to have large area. This increased the p-n junction area helps the efficiency for charge separation occurred on the interface. Third, the protrusion of nanowires into CIGS films helps charge collection. In planar structure, the charge has to travel across the film to reach the collection electrode. However, the nanowire cores in this nanowire solar cells act as nanoelectrodes for charge collection. Therefore, the charge collection is enhanced due to the presence of nanowires. All of these effects help the efficiency of nanowire solar cells although side effect may also exist such as the increased recombination when p-n junction area is increased. The observed increase in efficiency in the CIGS nanowire solar cells is believed to be a combination of these effects.

The success fabrication of working CIGS/(Zn,Mg)O nanowire solar cells provide the opportunity to further investigate the impact of nanowires on solar cell performance and some underlying mechanisms. For example, the effects of interface on charge separation and recombination play a critical role in solar cell devices. However, the detailed science about the interface is complicated and not yet fully understood. The nanowire solar cells provide a huge room for tuning the interface area through the change in the size and density of nanowires. By careful design, the investigation of nanowire solar cells will help to answer some of questions related to interface.

Figure 13. The I-V curves of superstrate nanowire devices with ZnO/(Zn,Mg)O core-shell nanowires of different lengths.

Conclusions

The CIGS nanowire solar cells based on ZnO/CdS and ZnO/(Zn,Mg)O core-shell structures have been fabricated by using solution processes. (Zn,Mg)O buffer layer was found to be better suited for nanowire nanowire solar cell fabrications because of its better thermal stability than CdS during the CIGS final heat treatment. As compared to the thin film superstrate structures, the CIGS nanowire solar cells using both CdS and (Zn,Mg)O buffer layers show an improvement in efficiency. It was also shown that the length of core-shell nanowires affects the nanowire solar cell performance. Longer nanowires help increase the short circuit current which may be resulted from the improved charge separation and collection. This study present the first working CIGS nanowire solar cells, opening up the opportunity to further understand the mechanism underlying and make efficient CIGS nanowire solar cells for applications.

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