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Abstract

Cu_2O\ZnO nanowires (NWs) heterojunctions were successfully prepared by combining Atomic layer Deposition (ALD) and Electrochemical Deposition (ECD) processes. The crystallinity, morphology and photoconductivity properties of the Cu_2O\ZnO nanostructures have been investigated. The properties of the Cu_2O absorber layer and the nanostructured heterojunction were studied in order to understand the mechanisms lying behind the low photoconductivity measured. It has been found that the interface state defects and the high resistivity of Cu_2O film were limiting the photovoltaic properties of the prepared devices. The understanding presented in this work is expected to enable the optimization of solar cell devices based on Cu_2O\ZnO nanomaterials and improve their overall performance.

Keywords: Cu_2O\ZnO nanowires heterojunction, Electrochemical Deposition, Atomic Layer Deposition, photovoltaic solar cells.

1. Introduction

In the coming years, solar photovoltaic (PV) technologies are expected to grow further and become a major component of the worldwide electricity generation. Nowadays, PV cells are mainly based on silicon, as this leading technology is mature and presents high energy conversion efficiency [1, 2]. Other promising technologies are used and further explored for the development of solar cells, such as Cadmium Telluride (CdTe), Copper Indium Selenide (CIS) and organic materials [3, 4, 5]. Among them, the Cu_2O/ZnO heterostructure represents a promising candidate, as these oxide materials combination form a low-cost and environment-friendly photovoltaic device. On one hand, Cu_2O can be used as an absorber material, as it is a semiconductor presenting a band gap of 2 eV and a p-type conduction attributed to Cu vacancies [6]. Besides, Cu_2O presents a high optical absorption coefficient in the range of 2.10^5- $3.7.10^6$ cm^{-1} [7]. On the other hand, ZnO is a n type semiconductor characterized by a wide band gap of 3.3 eV, a large exciton binding energy (60 meV) and a high electron mobility (120 cm^2 V^{-1} S^{-1}) [8]. This n-type semiconductor is able to ensure the efficient charges separation and collection. Several groups have focused their attention on Cu_2O\ZnO based solar cells, [9, 10, 11, 12, 13, 14] and the highest efficiency measured was 1.52% [15]. Therefore, novel manufacturing processes and better understanding of the devices are required to get closer to the theoretical maximum efficiencies.

Cu_2O\ZnO heterojunction solar cells has been manufactured using different routes, such as the chemical synthesis of a ZnO film on thermally oxidized copper sheets [16], the photochemical deposition of Cu_2O on a chemically deposited ZnO layer [17] or the sputtering of Al-doped ZnO layer onto electrodeposited Cu_2O films [9]. Among these methods, electrodeposition is an attractive route, as it is a cost-effective process and as it may offer excellent contact to the absorber film (through a complete filling of physical voids).

The Cu_2O absorber layer thickness and the geometry of ZnO NWs have an important role on the photovoltaic performances of nanostructured Cu_2O\ZnO devices. Indeed, the Cu_2O absorber thickness should be chosen in order to obtain the highest light absorption and photocarrier collection, but a suitable depletion layer should be obtained [18] as the carrier diffusion length in Cu_2O is typically lower than 1 µm [19, 20]. This diffusion length considerably limits the efficiency of solar cells fabricated with planar films. Therefore, nanostructured cells using ZnO NWs as carrier collectors enable to tackle this issue and to reach considerably higher photocurrents [14].

The formation of a continuous Cu_2O\ZnO NWs heterojunction is the key to obtain the highest PV performance. Thus, the geometry of the ZnO NWs should be tuned to allow a total coating by the Cu_2O absorber [9, 13]. Crystalline ZnO NWs can be grown perpendicularly on ZnO seed layers using electrochemical deposition (ECD) processes. This ZnO seed layers is required for the growth of high quality nanowires array, and prevents any contact between the Cu_2O film and the Indium Tin Oxide (ITO) substrate.

Atomic Layer Deposition (ALD) is a very appropriate technology for the deposition of this ZnO film, as this vapor phase deposition technique allows for the preparation of conformal films with sub-nanometer thickness control [21].

In this work, we report for the first time the combination of scalable ALD and ECD for the preparation of Cu_2O/ZnO NWs solar cells. ALD has been used to prepare ZnO seed

layers on ITO substrate, and ZnO NWs were grown using a cost-effective electrochemical deposition (ECD) process. Another ECD process was then used to deposit the Cu_2O absorber within the NWs in order to form the heterojunction. The crystallinity, morphology and photoconductivity properties of the Cu_2O\ZnO nanostructures are investigated, and the photocurrent response is discussed.

2. Materials and Methods

Lactic acid ($C_3H_6O_3$, 85%), Copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$, 85%), sodium hydroxide (NaOH) , Zinc chloride ($ZnCl_2$), potassium chloride (KCl) and diethyl zinc (DEZ) ($Zn(CH_2CH_3)_2$, 95%) were purchased from Sigma Aldrich and used as received. The ITO coated glass substrates were purchased from KINTEC Company, Hong Kong. The initial substrates on which the Cu_2O\ZnO NWs cells were prepared cells consisted of a ~120 nm thick ITO layer (resistivity 10 Ω.m) on glass.

Before the Cu_2O\ZnO NWs heterojunction deposition, the ITO substrates were cleaned using successively acetone and isopropanol in an ultrasonic bath (15 minutes each) and then rinsed with water.

2.1. Atomic Layer Deposition of ZnO

The ALD process was performed in order to prepare the ZnO seed layers on ITO glass substrates. ALD of ZnO was carried out in a home-built reactor using sequential exposures of DEZ and H_2O separated by Argon purge at a substrate temperature of 60°C (at flow rates of 100 sccm). Briefly, the process consisted of 0.2 s pulses and 40 s exposure of DEZ, 60 s of Argon purge followed by 2 s pulse and 40 s exposure of H_2O, and a final 60 s Argon purge was used to complete the ALD cycle [22, 23]. Using 100, 200 and 300 ALD cycles, we prepared ZnO films of 20, 40 and 60 nm thicknesses, respectively [23, 24, 25].

2.2 Electrochemical deposition of ZnO NWs and Cu_2O

The electrodeposition process was performed in a classical three-electrodes electrochemical cell. First, the ZnO NWs were prepared on the substrates (ZnO ALD films) immersed in an aqueous solution containing 5.10^{-4} M and $1.0.10^{-1}$ M $ZnCl_2$ and KCl, respectively (under continuous bubbling of oxygen) [26, 38, 39, 40]. The electrodeposition was carried out at the fixed potential of -1.0V versus Ag/AgCl using an Autolab PGSTAT30 potentiostat. The deposition time was 150 minutes and the reaction temperature was kept at 80°C [26]. Then, the as-prepared ZnO NWs were annealed for 30 minutes at 400 °C and used as the working electrode.

Next, Cu_2O has been deposited. The electrochemically synthesis was aimed to fill the gaps between the NWs and to get the absorber layer. The electrodeposition process was carried out for 60 minutes at the constant current of -1.0 $mA.cm^{-2}$ in 100 ml of aqueous solution containing 0.2 M $CuSO_4$ and 3 M lactic acid. The electrolyte temperature was kept at 40°C and the pH value of the solution was adjusted to approximately 12.5 by addition of NaOH. Three Cu_2O\ZnO NWs samples were prepared using the different ZnO seed layers (presenting thicknesses of 20, 40 and 60 nm). Please note that the basic deposition solution at pH 12.5 did not etch the ZnO NWs [14, 19].

Finally, a 200 nm thick gold layer was deposited on the Cu_2O layer through a shadow mask by direct current sputtering (at a power of 28 W), and the connection was made through an Indium contact deposited on the ITO. The effective area of the heterojunction is 0.5 cm^2. The schematic representation of the heterojunction cell is given in Figure 1.

2.3. Characterization

Morphological properties were investigated by Scanning electron microscopy (SEM) using a HITACHI-S4800. The crystallinity studies have been carried out using X-ray diffraction (XRD) and powder XRD with a PANalytical Xpert-PRO diffractometer (Cu Kα radiation). The absorption measurements were performed using a UV/Vis/NIR spectrophotometer (Jasco V-570). I-V curves were measured in order to get a glance on the photovoltaic properties of the Cu_2O\ZnO heterojunctions. The photovoltaic parameters were evaluated under 1 Sun (AM 1.5 G, 100 mW/cm^2 at 25°C) with a solar simulator (LS0106) connected to a Keithley 2400 Source Meter.

3. Results and discussion

3.1. Morphology and microstructure

Figure 2 shows SEM images of ZnO NWs and Cu_2O\ZnO NWs structures with ZnO seed layers presenting different thicknesses, namely 20, 40 and 60 nm. First, as observed on the cross-section views (Figure 2(a), (b) and (c)), the ZnO nanowires presenting diameters of around 60 nm are uniformly and vertically aligned to the substrate. The increase in the NWs average length from L1=580 nm, to L2=650 nm and L3=740 nm is related to the thickness of the seed layer of 20, 40 and 60 nm respectively. The NWs diameter increase with thicker ZnO seed layer was expected, as this observation has been made previously in the literature [41]. However, according to the SEM images (Figure 3S in Supporting Information), we cannot confirm a significant change of the NWs diameter as a function of the seed layer thickness. The absence of a strong dependence of the ZnO NWs diameter and the ZnO seed layer thickness may be due to the small differences between the thicknesses of ZnO seed layer used in this study. The increase in the NWs average length as a function of the seed layer thickness can be explained by the fact that thicker ZnO seed layers enhance the crystal sizes [27] and

decrease the competition of the growth between neighboring NWs. As a result, the vertical alignment was improved and the NWs length increases.

The electrodeposition of Cu_2O on the ZnO NWs sees to enable the preparation of a continuous film on the top of the NWs as depicted in the top view images (figure 2 (d, e, f)). Besides, no defects such as pinholes or pores could be observed on the top of Cu_2O surface that would prevent the direct contact between Au and ZnO and reduce the leakage current through the heterojunction. Figure 2(g) and Figure 1S (supporting information) enable the comparison of the cross section SEM images of all samples. From Figure 2(g), one can note that the Cu_2O films present approximately the same thickness of 2.4 μm for the three samples. In addition, Cu_2O seem to coat the ZnO NWs conformally and thus to fill the gaps between the nanowires.

Next, XRD measurements were performed to study the crystallinity of the synthesized Cu_2O\ZnO NWs heterostructures. As observed in Figure 3, the diffraction peak at $2\theta = 34.46°$ corresponds to the (002) crystal plan according to hexagonal ZnO NWs crystalline phase in the three samples. This peak indicates a clear c-axis orientation of the nanowires during ECD process, and it is consistent with JCPDS card (01-080-0074). The intensity of this peak increases gradually when the thickness of ZnO seed layer increases, which may be due to the increase of ZnO NWs length.

In addition to the presence of the ZnO NWs, diffraction peaks at (111), (200) and (220) can be seen. These crystal planes correspond to the cubic phase of Cu_2O (JCPDS: 01-078-2076). The strong intensity of the (111) peak compared to the others peaks indicates a preferential growth of the Cu_2O film through the (111) direction, which can be controlled by varying the pH of the electrochemical solution [9, 28]. The growth of Cu_2O with this preferential orientation on the top of ZnO NWs with the c-axis orientation leads indeed to a good crystallographic

matching [15]. Finally, the characteristic peaks of Cu and CuO are not observed suggesting that no metallic oxide phase was formed during the electrodeposition process of Cu_2O.

The average grain size dimensions of Cu_2O films along (111) planes were calculated using the Debye–Scherrer relation. The calculated values were found to be 74.2 nm, 69.3 nm and 43.4 nm for ZnO seed layers of 20, 40 and 60 nm, respectively. The decrease of the grain size is likely to be related to the microstrain developed in the Cu_2O film during the electrodeposition process. The microstrain (ε) was calculated using the formula below [42]

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad (1)$$

It has been found that the calculated values of the microstrain increase for thicker ZnO seed layers (1.65×10^{-3}, 1.94×10^{-3} and 3.13×10^{-3} for 20, 40 and 60 nm, respectively).

This increase of the ε confirms the presence of a significant contraction on the Cu_2O film electrodeposited on the top of the most vertical aligned NWs. Thus, the grain size decreases when the ZnO NWs length increases.

3.2. Optical analysis

To evaluate the band edge of Cu_2O\ZnO NWs, optical absorption measurements were performed and compared to the absorption spectra of a Cu_2O film prepared by ECD process on ITO substrate (Figure 4). All Cu_2O\ZnO NWs samples are characterized by a similar strong absorption, which reaches a maximum value at 74% of the incident light, and by an absorption edge detected at 600 nm. Similar features are observed for the Cu_2O film that correspond to the exitonic band gap of Cu_2O, suggesting that no trace amount of Cu^{2+} impurities was incorporated in the Cu_2O film during the ECD process [29]. One can note the absence of the absorption edge of the excitonic band gap of ZnO NWs, which might be due to the strong absorption of the Cu_2O layer.

The fluctuations in the absorbance, detected at wavelengths lower than the absorption edge, suggest interferences oscillations that may be linked to the formation of a continuous Cu_2O thin film with a smooth surface. To calculate the Cu_2O film band gaps, we used the Tauc formula [30]:

$$(\alpha E)^2 = (E - Eg) \qquad (E = h\upsilon) \qquad (2)$$

Where α is the absorption coefficient. The results of $(\alpha h\upsilon)^2$ versus $h\upsilon$ are given in the supporting information (Figure S2).

The values of the band gap energies of Cu_2O for the different samples measured are estimated at 2eV (close to the theoretical 2.05 eV) [11, 12, 31]. We can assume that Cu_2O in all the samples have the same band gap energy value of 2 eV, since the electrodeposition time of Cu_2O film was kept constant for all samples, resulting in similar thicknesses and strain.

3.3. I-V analysis

Figure 5(A) shows the dark current-voltage (I-V) curve of the Cu_2O\ZnO NWs structure with various thicknesses of the ZnO seed layer. We observe a current rectification behavior confirming that a p–n heterojunction (core–shell) nanostructure is formed. Besides, high leakage-current at voltages less than 0 V appears.

The rectification behavior of Cu_2O\ZnO NWs heterojunction was estimated by applying a bias ranging from -0.5 V to +0.5 V to the samples. It was found a rectification ratio of 2.9, 2.0 and 1.8 for Cu_2O\ ZnO NWs\ $ZnO_{ALD\ 20\ nm}$, Cu_2O\ ZnO NWs\ $ZnO_{ALD\ 40\ nm}$ and Cu_2O\ ZnO NWs\ $ZnO_{ALD\ 60\ nm}$, respectively. Figure 5(B) depicts the I–V characteristics under illumination of the different samples and their photovoltaic parameters are listed in Table 1. The open circuit voltage (Voc), the short circuit current density (Jsc) and the fill factor exhibit low values, whereas, the series resistances (Rs), which mainly depend on the resistivity of Cu_2O film remain extremely high. The high Rs of these structures was probably due to the

small Cu_2O grain sizes (from 43 to 74 nm) that may introduce grain boundaries on the film and increase the possible recombination rate of the photogenerated carriers. We suggest that ECD of Cu_2O resulted in the formation of a resistive film. In addition, the extremely low Jsc and low F.F values may confirm the high resistivity of Cu_2O film.

The Voc is reported to be highly dependent on the Cu_2O film thickness, due to improved light absorption and presumably due to a change in the crystal defect concentration with increasing thicknesses. The Voc is highly dependent on the interface state densities [18] but it is not affected by the NWs length [19].

Influence of the thickness of Cu_2O film on photovoltaic parameters

The absorber layer is a key factor to obtain the desired good photovoltaic parameters. We believe the electrodeposition of an appropriate thickness of Cu_2O film may lead to the proper light absorption and to high values of Voc and Icc.

When Cu_2O\ZnO NWs heterojunction is formed, a wide depletion zone is created due to the low doping level in Cu_2O. If the Cu_2O thickness is insufficient, the Voc value is considerably hindered. Musselman *et al.* calculated the thickness of Cu_2O film necessary to reach a suitable value of Voc (in the range of 0.4 to 0.7 V) by resolving Poisson's equation at the heterointerface. It was found that a tap thickness between 2.3 and 3 µm was necessary [19]. Thus, it was expected that for a 2.4 µm Cu_2O thickness used in our samples, a reasonable Voc would be obtained. In our case, low Voc (approx. 0.06V) were obtained, despite the Cu_2O layer of 2.4 µm thickness. Consequently, other mechanisms taking place in the nanomaterials are linked to these low values, such as traps and recombination centers in the Cu_2O material.

Influence of Interface state on photovoltaic parameters

To improve the photovoltaic parameters, the architecture of Cu_2O\ZnO NWs must present good crystallographic qualities with a minimum of local shuntings and grain boundaries to reduce recombination at the interfaces. SEM images indicate that the electrodeposition of Cu_2O film fills the spaces between nanowires with a good conformality and achieves good crystallographic qualities of the Cu_2O\ZnO NWs heterojunction.

However, it is not easy to achieve a good heterojunction because ZnO and Cu_2O crystal faces contain different atomic arrangements. These differences introduce a significant number of defects at the interface states. Interface states can influence the built-in potential of the heterojunction and hence its photovoltaic properties [32, 33, 34].

To confirm the presence of interface states, we calculated the lattice mismatch given by the relation:

$\Delta a\backslash a = 2(a_2-a_1)\backslash a_2+a_1$ [33].

Where a_1, a_2 are the lattice constant of ZnO and Cu_2O respectively (a_1= 3.25 Å, a_2= 4.25 Å).

The lattice mismatch between Cu_2O (111) and ZnO (002) was 27.1%. This large value therefore induces a significant number of defects at the interface. Most of Vbi can have been formed in Cu_2O due to the low doping level obtained in the electrodeposition process. The doping values are 10^{12} -10^{14} cm^{-3}[8, 35, 36], significantly lower than the ZnO carrier concentration (10^{18} cm^{-3})[11, 37].

The defects existing in the interface states reduce the value of Vbi, and a drastic reduction of Voc value is therefore expected as well. Thus, holes can easily cross the barrier to recombine with a trapped electron at an interface state, resulting in charge carrier collection decrease and a significant decrease of the photovoltaic parameters.

The lattice mismatch and our PV parameters measurements suggest the presence of a large number of defects at interface states. In fact, dark J–V curves for the three samples presented higher reverse-bias leakage currents which resulted in current flow across the

Cu_2O\ZnO heterojunctions. We believe that a high resistivity of Cu_2O film and the interface recombinations are responsible for the low photovoltaic parameters measured. It was expected that the large amount of light absorbed through the NW heterojunction would induce a much larger amount of charge carrier generation.

Indeed, better photon absorption phenomenon did not translate into a good collection of charge because of the unbalance between the optimum thickness for a good optical absorption of light in the collection region (lower than 1µm) and the optimum Cu_2O film thickness necessary to achieve a fully developed depletion zone (space charge region, generally above 2 µm). Therefore, more investigations must be carried out in order to find the appropriate balance between these two phenomena. In addition, other factors not studied here, such as electrolyte composition and deposition time should be taken into consideration in the future to better understand their effects. We believe these research efforts will help to minimize the interface states and enhance the electrical properties of the Cu_2O oxide layer.

Conclusion

This study brought insights on the synthesis and characterization of Cu_2O\ZnO NWs heterojunctions prepared using Atomic layer Deposition (ALD) and Electrochemical Deposition (ECD) processes. ALD has been used to deposit ZnO seed layers on ITO substrates, whereas ZnO NWs have been grown using a cost-effective ECD process. Another ECD process was then used to deposit the Cu_2O absorber within the NWs in order to form the heterojunction. The crystallinity, morphology and photoconductivity properties of the Cu_2O\ZnO nanostructures were investigated, and the measurements carried out confirmed the good crystallography properties of the oxide layers. A large light absorption in the Cu_2O material has been confirmed, and the bandgap of the Cu_2O absorber has been estimated at 2 eV. The photovoltaic behavior of such heterojunctions was also examined under AM 1.5 G and

under dark using I-V curves. A current rectification behavior has been observed, but the photovoltaic parameters, such as the Voc, Jsc and FF exhibited low values. We believe that the high density of interface states and the high resistivity of Cu_2O film were the main reason of the limitation of these parameters. Although further research efforts are necessary in order to decrease interfacial recombinations and to improve the electrical properties of the Cu_2O films, the understanding presented in this work is expected to enable the optimization of solar cell devices based on Cu_2O\ZnO nanomaterials.

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