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Advance in Cu_2O-ZnO Solar Cells and Investigation of Cu_2O-ZnO Heterojunction Fabricated by Magnetron Sputtering

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Abstract: Cu_2O-ZnO heterojunction has shown great potential for photovoltaic application due to the low-cost, non-toxicity, abundance and variety of preparation methods. However, the resistivity of the Cu_2O film in present ZnO-Cu_2O heterojunction solar cell is relatively high, which seems to be the major problem for the low photoelectric conversion efficiency. Cu_2O films were prepared using reactive direct current magnetron sputtering. The microstructures and properties were characterized using X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and Hall-effect measurements. The influences of $q_V(\mathrm{Ar}):q_V(\mathrm{O_2})$ on the structures and properties of deposited films were investigated. Single-phase Cu_2O film with a resistivity of 88.5 Ω · cm, a Hall mobility of 16.9 $cm^2 \cdot V^{-1} \cdot s^{-1}$ and a carrier concentration of 4.19×10^{15} cm^{-3} were obtained at $q_V(\mathrm{Ar}):q_V(\mathrm{O_2}) = 90:0.3$. The as-deposited Cu_2O films have a great improvement in electrical performance and have more advantage in photovoltaic application compared with that prepared by electrochemical deposition or thermal oxidation. On that basis, the Cu_2O-ZnO heterojunctions were fabricated in reversed growth sequence and the band alignments of the heterojunctions were given to investigate their potential application in solar cells. Possible areas for future work in this field were outlined and some suggestions were made based on our investigation of the Cu_2O-ZnO heterojunctions fabricated by magnetron sputtering.

Key words: compound semiconductor; Cu_2O-ZnO heterojunction; solar cell; resistivity; band alignment
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Cu_2O-ZnO 太阳能电池的研究进展及磁控溅射法制备 Cu_2O-ZnO 异质结的研究

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摘要：Cu_2O-ZnO 异质结具有成本低廉、环境友好及制备方法多样等优点，在太阳能电池领域有很好的应用前景。Cu_2O 薄膜的高电阻率和低载流子浓度是制约其效率提高的主要原因。本文采用磁控溅射法，在 $q_V(\mathrm{Ar}):q_V(\mathrm{O_2}) = 90:0.3$ 时得到单相 p 型 Cu_2O 薄膜，电阻率为 88.5 Ω · cm，霍尔迁移率为 16.9 $cm^2 \cdot V^{-1} \cdot s^{-1}$，载

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流子浓度为4.19 × 10^{15} cm^{-3}。并结合 Cu_2O-ZnO 异质结能带结构的研究,对 Cu_2O-ZnO 异质结太阳能电池今后的研究提出了一些建议。

关 键 词: 化合物半导体; Cu_2O-ZnO 异质结; 太阳能电池; 电阻率; 能带结构

1 Introduction

The ideal material for future photovoltaic applications should be a compromise between cost, efficiency, toxicity, relative abundance and environmental friendliness. Recently, there is renewed interest on Cu_2O with respect to solar-cell applications. Cuprous oxide(Cu_2O) is a natural p-type direct band semiconductor with a gap of 2.17 eV, good mobility and high minority carrier diffusion length. According to the Shockley-Queisser limit(SQL)[1], it was predicted a maximum efficiency of about 20% for single junction Cu_2O solar cells, but current experimental data are only about 4%[2]. Although there have been a few reports on Cu_2O homojunction solar cells[3], reproducibility is not so good due to the unclear formation mechanism of n-type Cu_2O. Zinc oxide (ZnO) is an intrinsic n-type semiconductor with a direct band gap of 3.37 eV and high electron mobility. Cu_2O-ZnO heterojunction is considered promising material for photovoltaic application. In this context, we summarized the main achievements of heterojunction solar cells based on Cu_2O-ZnO during the past ten years. The high resistivity of the Cu_2O film in present ZnO-Cu_2O heterojunction solar cells seems to be the major problem for the low efficiency. In this work, we prepared Cu_2O films by magnetron sputtering in expect to improve the electrical performance, and measured the band alignments of the Cu_2O-ZnO heterojunctions in order to investigate their potential application in solar cells.

2 Fabrication Methods and Performance of Present Cu_2O-ZnO Heterojunction Solar Cells

Thus far, the Cu_2O-ZnO heterojunction has been fabricated by several methods.

2.1 Electrochemical Deposition

Electrochemical-deposition is easily scaled, inexpensive and can produce uniform films on various substrates. It is usually performed using a three-electrode cell in aqueous electrolytes of precursors. High density of interface states resulting from the aqueous synthesis and poor minority carrier transport were identified as the factors limiting the performance of as-deposited solar cells. The electrodeposited Cu_2O-ZnO solar cells with the highest efficiency of 1.28% was fabricated by Izaki *et al.*[4], where the polarization of the substrate seems to be very important. Electrodeposition can also be used to synthesize hexagonal Cu_2O nanotube arrays[5], which could be interesting in fabrication of nanostructured Cu_2O-ZnO solar cells.

2.2 Thermal Oxidation/Sputtering or Plused Laser Depositon (PLD)

Cu_2O-ZnO solar cells with good performance[6-9] are fabricated by depositing ZnO on Cu_2O sheet prepared by oxidizing Cu sheets. The typical oxidation procedure includes annealing of the Cu sheets, oxidation in air and annealing of the Cu_2O film. The purity of Cu sheets has a significant impact on the quality of the Cu_2O. A number of pre-and post-oxidation treatments involving cleaning, etching, polishing, annealing *etc.* have been suggested in the literature. ZnO films can be deposited by various methods, *e. g.*, plused laser deposition (PLD), vacuum arc plasma evaporation (VAPE), ion beam sputtering, metal-organic chemical vapor deposition (MOCVD).

2.3 Sputtering and Other Methods

Magnetron sputtering is commonly used in the preparation of thin films. However, no report on the cells fabricated from sputtered Cu_2O and ZnO can be found in the literature, which is probably attributed to the poor crystal quality of the deposited thin films. Previously, Hsueh *et al.*[9] reported the fabrication of magnetron sputtered p-Cu_2O onto vertical n-ZnO nanowires prepared by a self-catalyzed vapor-liquid-solid (VLS) method and obtained a conversion effciency of 0.1%.

A light-assisted electrodeposition of the ZnO continuous layer on the Cu_2O layer has been revealed by Fariza *et al.*[10]. Rectification feature was observed in the constructed ZnO/Cu_2O diode, but no solar cell efficiency was reported. In some nanostructure Cu_2O-ZnO heterojunction solar cells, a novel wet chemistry route[11] was used to synthesize Cu_2O nanoparticles and a self-catalyzed vapor-liquid-solid (VLS) method or hydrothermal method was used to prepare ZnO nanowires.

2.4 Performance

The exploratory studies on the Cu_2O-ZnO heterojunction solar cells in the past ten years are summarized in Table 1. There are mainly three deposition techniques: electrochemical deposition, thermal oxidation and sputtering/PLD/VAPE/MOCVD. The cell structures were bilayer thin films, Cu_2O thin film on ZnO nanowires or Cu_2O nanoparticles drop-cast into ZnO nanowires, in some cases with an inserted thin buffer layer. The ZnO was either undoped or highly doped with elements Mg, Al or Ga. The efficiencies range between 0.1% and 4.08%.

Table 1 Solar-cell performances of various Cu_2O-ZnO heterojunctions

Structure	Preparation methods	Solar cell performance				Author
		$I_{sc}/(mA\cdot cm^{-2})$	V_{oc}/V	FF	$\eta/\%$	
Cu_2O thin film/ZnO nanowires	Sputtering/(VLS) method	2.35	0.13	0.29	0.1	Hsueh[9]
Cu_2O/ZnO bilayer	Electrochemical deposition	1.98	0.34	0.32	0.24	Hussain[12]
Cu_2O thin film/ZnO nanowires	Electrochemical deposition	4.4	0.28	0.39	0.47	Musselman[13]
Cu_2O/ZnO: Mg bilayer	Electrochemical deposition/MOCVD	3	0.57	0.42	0.71	Duan[14]
Cu_2O/ZnO bilayer	Electrochemical deposition	3.8	0.59	0.58	1.28	Izaki[4]
ZnO/Cu_2O bilayer	VAPE/Oxidizing Cu sheet	6.94	0.41	0.53	1.52	Minami[6]
ZnO/Cu_2O bilayer	Ion beam sputtering/Oxidizing Cu sheet	6.78	0.59	0.5	2.01	Mittiga[7]
ZnO/Cu_2O bilayer	PLD/Oxidizing Cu sheet	10.1	0.69	0.55	3.83	Minami[8]
ZnO/Cu_2O bilayer	PLD/Oxidizing Cu sheet	10	0.72	0.59	4.08	Nishi[2]

3 Our Work on Cu_2O-ZnO Heterojunction Fabricated by Magnetron Sputtering

As shown in Table 1, the electrochemical-deposited Cu_2O-ZnO solar cells exhibited the highest efficiency of 1.28%, while most of the Cu_2O/ZnO solar cells with efficiency larger than 1.5% were fabricated on Cu_2O sheet prepared by thermal oxidation method. High concentration of interface states at the heterointerface introduced by etching during device fabrication will lead to poor carrier collection in electrochemical-deposited solar cells. Other limitations in the performance include crystal orientation, grain sizes, and the minority carrier transport length. However, the resistivity of the electrodeposited Cu_2O films was reported to be $10^4 \sim 10^6\ \Omega\cdot cm$[15], while the resistivity of oxidized Cu_2O substrate was on the order of $10^3\ \Omega\cdot cm$, which seems to be the major problem for the low efficiency. So far, there is no report on the cells fabricated from sputtered Cu_2O in the literature, although the magnetron sputtered Cu_2O film is expected to reach a resistivity lower than $10^3\ \Omega\cdot cm$. In our work, the Cu_2O films were prepared by magnetron sputtering. The electrical properties of Cu_2O films and band alignments of the Cu_2O-ZnO heterojunctions were measured to investigate their potential application in solar cells.

3.1 Experiments

Cu_2O and ZnO films were prepared in a magnetron sputtering system with a base pressure of 10^{-3} Pa. Before deposition, the glass substrates were ultrasonically cleaned in acetone, ethanol and deionized water each for 10 min, and subsequently dried with flowing nitrogen gas. The Cu_2O films were deposited by reactive direct current (DC) magnetron sputtering using a metallic copper target (99.99%) at the substrate temperature of 400 ℃ in an argon-oxygen (Ar-O_2) ambience. To obtain a single phase of Cu_2O, the O_2 flow rate was kept at 0.3 cm^3/min, and the Ar flow rate was varied from 60 to 90 cm^3/min with the total pressure maintained at 0.5 Pa. The ZnO films were deposited by radio frequency (RF) magnetron sputtering using a sintered ZnO target (99.99%) in pure Ar ambience. The band alignments at the interfaces of the Cu_2O/ZnO and ZnO/Cu_2O heterojunctions were investigated. Crystal structures were characterized by X-ray diffraction (XRD) using a XPERT-PRO system with a source of Cu Kα ($\lambda = 0.154\,06$ nm). Electrical properties were measured by Hall measurements in Vander Pauw configuration (BIO-RAD HL5500PC) at room temperature (RT). The core-levels and valence-band (VB) spectra were measured by X-ray photoelectron spectrometer (XPS, AXIS ULTRADLD with a 1 486.6 eV Al Kα monochromatic X-ray radiation source).

3.2 Result and Discussion

Fig. 1. shows the XRD patterns for the films obtained at various $q_V(Ar):q_V(O_2)$ with a sputtering pressure of 0.5 Pa. At a lower $q_V(Ar):q_V(O_2)$ of 60:0.3, the films are characterized to be mixed phase of Cu_2O and CuO. Single phase of Cu_2O films are obtained when $q_V(Ar):q_V(O_2)$ is larger than 80:0.3. As shown in Fig. 1, diffraction peaks at 36.5°, 42.4°, 61.5° and 73.7° are corresponding to the (111), (200), (220) and (311) crystal planes of cubic-structured Cu_2O (JCPD card No. 65-3288). We also verified the purity of the Cu_2O film which we obtained by XPS, as shown in Fig. 2. The $Cu2p_{3/2}$ peak is fit into a single peak at a binding energy of 932.47 eV with good symmetry. No sub-peak attributed to the Cu (Ⅱ) in CuO is observed, the shake-up satellite structures located at 940 ~ 945 eV that is usually appear in CuO are not seen either.

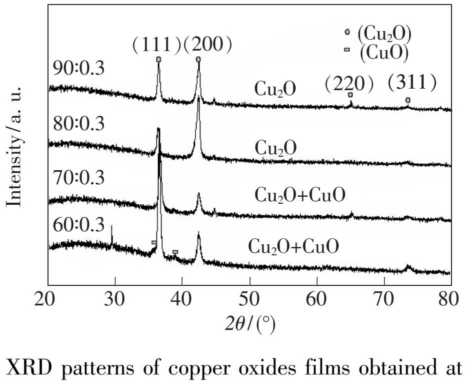


Fig. 1 XRD patterns of copper oxides films obtained at various $q_V(Ar):q_V(O_2)$ ratios with the sputtering pressure of 0.5 Pa

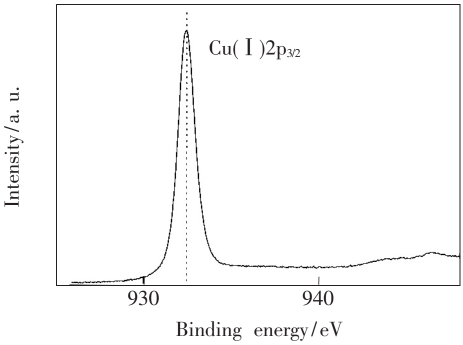


Fig. 2 The $Cu2p_{3/2}$ XPS spectrum from a single-phase Cu_2O film

The electrical properties of all copper oxides films are shown in Fig. 3. Hall measurements at RT show that all the copper oxide films are p-type with resistivities lower than 600 Ω · cm. The single-phase Cu_2O films deposited at $q_V(Ar):q_V(O_2) = 90:0.3$ exhibit a resistivity of 88.5 Ω · cm, a Hall mobility of 16.9 $cm^2 \cdot V^{-1} \cdot s^{-1}$ and a carrier concentration of 4.19×10^{15} cm^{-3}. The copper oxides films mixed with CuO deposited at $q_V(Ar):q_V(O_2) = 60:0.3$ and $q_V(Ar):q_V(O_2) = 70:0.3$ exhibit higher resistivity due to the decrease of carrier concentration and Hall mobility.

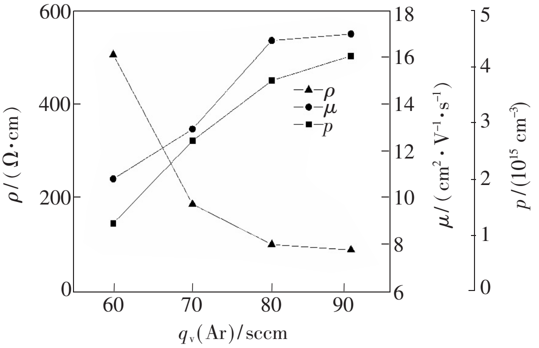
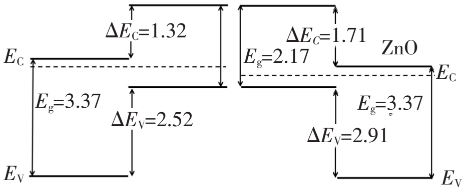


Fig. 3 Resistivity, Hall mobility and carrier concentration measured by Hall effect measurements for Cu_2O thin films deposited at various $q_V(Ar):q_V(O_2)$.

The actual band offsets between ZnO and Cu_2O

films prepared by magnetron sputtering have been investigated. Using X-ray photo-electron spectroscopy (XPS), the valence band offset (VBO) of the Cu_2O/ZnO heterojunction (where Cu_2O was deposited on ZnO) were measured to be 2.91 eV, while for ZnO/Cu_2O (where ZnO was deposited on Cu_2O), the CBO were determined to be 2.52 eV. The schematic diagrams of the band alignments of the two kinds of heterojunctions are drawn as Fig. 4. Assuming that the Fermi level in n-ZnO is close to conduction band minimum in ZnO, and Fermi level in p-Cu_2O is close to valence band maximum in Cu_2O, the upper limit of thermodynamic open circuit voltage (V_{oc}) is estimated to be 0.46 eV for Cu_2O/ZnO and 0.85 eV for ZnO/Cu_2O, respectively. In addition, the recombination of majority carriers increases with the increase of CBO. Therefore, considering the band alignments, the ZnO/Cu_2O structure is expected to harvest higher photovoltaic power conversion efficiency than the Cu_2O/ZnO.



ZnO on Cu_2O Cu_2O on ZnO

Fig. 4 Schematic diagrams of ZnO/Cu_2O and Cu_2O/ZnO heterojunctions

4 Conclusion

In summary, we prepared Cu_2O films using direct current reactive magnetron sputtering. The $q_v(Ar):q_v(O_2)$ ratio is a crucial parameter in achieving pure phase of Cu_2O. The phase purity of the Cu_2O was observed from XRD, and confirmed by XPS. It shows that the obtained Cu_2O films have a resistivity lower than 100 Ω · cm, which indicates a great improvement in electrical performance than electrochemical-deposited or thermal-oxidized Cu_2O films. Future work should be planned to lower the resistivity of the Cu_2O films by doping (N or Si) or other treatment. In addition, the measured VBO of ZnO/Cu_2O heterojunction is smaller than that of Cu_2O/ZnO heterojunction. Based on the band alignments consideration, the ZnO/Cu_2O structure is expected to have more advantage in photovoltaic application than Cu_2O/ZnO structure.

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