Structure optimization on the photoelectric and photocatalytic properties of Cu_2S and ZnO complex films

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Abstract: Cu_2S and ZnO complex films were deposited on glass substrates, by means of radio frequency (RF) magnetron sputtering device. The impact of the thickness of ZnO and Cu_2S on the whole transmittance, conductivity, and photocatalysis was investigated. The photoelectric and photocatalytic properties of the complex films were studied by optical spectrometry and four point probes measurements, respectively. To evaluate the Transparent Conductive Oxide (TCO) films and compare their photoelectric performance, the figure of merit (FOM) is introduced. The photocatalytic activities of the ZnO/Cu_2S/ZnO complex films were evaluated by comparing the degradation of methyl orange under UV irradiation. In order to guide the experiments in theory, numerical simulations of the optical properties of complex films were carried

out. In experiments, the thickness of the ZnO layers was varied between 0 and 60 nm and those of Cu_2S were between 0 and 120 nm. Low sheet resistance and high transmittance were obtained, and the optimal photocatalytic efficiency of ZnO(15 nm)/Cu_2S(60 nm)/ZnO(60 nm)/glass complex films can reach 72%.

Keywords: Multilayers, Thin Films, Sputtering, Optical Properties.

1 INTRODUCTION

ZnO has been a heated object in recent years, as a potential ultraviolet, blue and other visible optical device materials owing to its wide and direct band gap 3.1-3.3 eV.[1-4] Additionally, polycrystalline ZnO has been found for numerous interesting applications, such as piezoelectric transducers transparent conducting films.[5-9] But the wide band gap n-type ZnO is limited in its application because it is electrically too large in various environments.[10] New materials must be developed with optical properties superior to the present pure ZnO and with lower resistivities than pure ZnO. At present, the main research objective of developing new materials for transparent conductive oxides films is to achieve higher transmittance and lower resistivity in visible range. Recently, a combination of dielectric, semi-conductor and metal were used to produce highly transparent conducting oxides.[11-14] p-type semiconductors are important materials for developing optoelectronic devices such as large area flat-panel displays, solar cells and light-emitting diodes. As a kind of p-type semiconductor, Cu_xS attracts much attention of researchers because of electrical and optical properties. Cu_xS has five crystalline phases

such as Cu_2S, $Cu_{1.95}S$, $Cu_{1.8}S$, $Cu_{1.75}S$ and CuS. From this set of copper sulfides, Cu_2S is considered to be a promising material as absorber of visible light, due to its band gap energy 1.2-2.4 eV.[15-16] Besides, the combination of p-type and n-type materials leads to application of p-n junction devices in the future. Furthermore, ZnO and Cu_2S complex films have a good photocatalytic performance.[17] They can completely destruct the undesirable contaminants in both liquid and gaseous phase by using solar or artificial light illumination.[17-18] As we know, the efficiency of photocatalytic reaction is determined by the absorption ability of light and high separation rate of photo-induced electron-hole pair. There are many different Cu_2S fabrication methods, such as electrode position, sol-gel, hydrothermal, however the use of radio frequency (RF) magnetron sputtering is rare.[19] In this paper, ZnO/Cu_2S/ZnO complex films were fabricated by RF magnetron sputtering. Their transparent, conductive and photocatalytic properties were investigated. In order to get a better sandwich structure, numerical simulation and fabrication of ZnO/Cu_2S/ZnO multilayer were carried out for optimizing a multilayer system. The influence of the top ZnO layer thicknesses are the focus of the study and discussion.

2 EXPERIMENTAL

ZnO/Cu_2S/ZnO complex films were deposited on glass substrates using a Zn target (99.9% purity, 50 mm diameter) and a Cu_2S target (99.9% purity, 50 mm diameter) by RF magnetron sputtering. The glass substrates were

ultrasonically cleaned in acetone and alcohol, and rinsed in deionized water in sequence then dried in flowing nitrogen gas. The working chamber was pumped down to 5×10^{-4} Pa before deposition. The ZnO was deposited in O_2 and Ar mixed atmosphere with O_2/Ar pressure ratio 1:4, correspondent to a deposition pressure of 0.6 Pa. The Cu_2S film was deposited in a pure Ar atmosphere, with a deposition pressure of 0.6 Pa. For the ZnO/Cu_2S/ZnO combination, bottom ZnO thickness was fixed at 60 nm, and the Cu_2S layer thickness was fixed at 60 nm. The top ZnO was varied from 0 nm to 60 nm.

The photodegradation of methyl orange was chosen to evaluate the photocatalytic activity of our samples. The photocatalytic reaction was carried out in a beaker containing the prepared sample (2.5×2.5 $cm^{2)}$ and 30 ml of 10^{-4} M methyl orange aqueous solution. The solution was irradiated with a 175 W mercury lamp with central wavelength of 365 nm. The temperature of methyl orange aqueous solution was kept at 30 ℃ during experiment process. Each 10 minutes of radiation, the concentration of methyl orange was examined using the AvaSpec-2048 type dual-channel fiber optical spectrometer by collecting the absorbance of the methyl orange.

The thickness of the films were monitored using the quartz crystal oscillator film-thickness apparatus (FTM-V, Taiyao Vacuum Tech.). The UV-visible and near-infrared photometer was used to measure the transmittance in the visible and near-infrared regions with the automatic source selection mode. And the sheet resistance of films was measured using the four-point probe method

(RTS-8, Four Probes Tech).

3 RESULTS AND DISCUSSION

3.1. Simulation and experiments

Numerical simulation of the optical transmittance of the complex film has been carried out in order to guide the experimental work. The characteristic matrix M of the stratified medium given by Born[20] was used in this computer program. The characteristic matrix of the whole ZnO/Cu_2S/ZnO/glass complex films can be expressed as:

$$M = M_{ZnO}(n_1, k_1) M_{Cu_2S}(n_2, k_2) M_{ZnO}(n_3, k_3)$$

Where n_i and k_i are the refractive index and extinction coefficient, respectively, of corresponding medium layer. For each combination of Cu_2S and ZnO layer thicknesses in the ZnO/Cu_2S/ZnO/glass complex films, the values of the transmittance at normal incidence are calculated using the equation for T.[20] In the simulation, the optical constants n and k for the ZnO and Cu_2S are important. The constants n and k for the ZnO can be used from the AvaSoft software, but under present conditions, we don't have the comprehensive description of the optical constants of the Cu_2S. In this situation, we use the modified optical constants of the ZnS to replace the constants of the Cu_2S, and the modified constants are used for the numerical simulation of the optical properties of the ZnO/Cu_2S/ZnO multilayer films.

Dependence of the simulated maximum transmittance of the multilayers on the thickness of top ZnO layer in the condition of fixed middle Cu_2S and bottom

ZnO layer thicknesses for each curve is shown in Fig. 1. At the fixed Cu_2S thickness (60 nm), the seven curves represent seven different thicknesses of the bottom ZnO layers (40 to 100 nm, spacing for 10 nm) in this graph. It is observed that when the top ZnO thickness is or nearly equal to bottom ZnO thickness, the transmittance reaches a maximum value.

It is found that the variations in simulated optical transmittance are basically consistent with the experimental results. For example, Fig. 2 gives a good result about the comparison between simulation and experimental transmission spectrum of ZnO(30 nm)/Cu_2S(60 nm)/ZnO(60 nm) multilayer (a)and ZnO(60 nm)/Cu_2S(60 nm)/ZnO(60 nm) multilayer(b).

3.2. Properties influenced by top ZnO layer

A series of complex films with different top ZnO layer thicknesses were prepared at O_2/Ar ratio of 1:4. Fig. 3 presents the optical transmittance spectra of the ZnO/Cu_2S/ZnO complex films with different layer top ZnO thicknesses for fixed thickness of Cu_2S layer (60 nm) and bottom ZnO(60 nm) layer. It is seen that in the visible light region, when the top ZnO film gets thicker, the transmittance gets bigger. Additionally, for the five different thickness of the films, in the visible light region, the partial maximum value of each transmittance appears in a same location, near the wavelength of 600 nm.

In the research on resistance property, Fig. 4 indicates that the trend of the curve presents firstly increase and then decrease, and the maximum sheet resistance appears in 45 nm and a marked decline appears in 60 nm. Three

layers structures can realize the goal to limit resistance under threshold value. (for example 190 Ω/□).

To evaluate the Transparent Conductive Oxide (TCO) films and compare their photoelectric performance, the figure of merit (FOM) is introduced. FOM=T^{10}/Rs was defined by Haacke. T is the optical transmittance and Rs is the sheet resistance. The figure of merit of ZnO/Cu_2S/ZnO/glass complex films for different thickness is shown in Fig. 5. It is obvious that in the visible light and infrared regions, as the ZnO layer thickness increases, the film has much better FOM value.

The change of photocatalytic activity is exhibited in Fig. 6. The degradation rates were varied from 55% to 72%. When the thickness of top ZnO layer is 45 nm, the degradation rate is worst among the five samples. When the thickness of top ZnO layer is 15 nm, the best degradation rate is approximate to 72%.

4 CONCLUSION

ZnO/ Cu_2S /ZnO complex films as transparent conducting coatings have been deposited by simultaneous RF magnetron sputtering. Numerical simulation of the transmittance was carried out to guide the experiments. The changes in top ZnO layer thicknesses were found to affect the photoelectric and photocatalytic properties of the films. ZnO(60 nm)/Cu_2S(60 nm)/ZnO(60 nm)/glass complex film has higher transmittance and lower resistivity in visible light range. The photocatalytic performance of ZnO(15 nm)/Cu_2S(60 nm)/ZnO(60 nm)/glass film improve effectively. It was found that the complex

film can be optimized to have a low sheet resistance about 140 Ω/sq. The research proves that different complex film component ratio has obvious effects on the properties of film. While complex film component ratio is reasonable, the complex film excellent performance can be achieved better.

Acknowledgements

We acknowledge partial financial supports from Jointly Funded Project (No. 61179055) of Chinese Civil Aviation Authority, National Natural Science Foundation of China, Talent Grant (2013-ZQXY-05） of Educational Commission of Guangdong Province, China and Jilin University Science and Technology Innovation Fund (No. 450060487476 and No.450060497067).

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Figure captions page:

Fig. 1 The simulation maximum transmittance of the multilayers on the thickness of top ZnO layer (The thicknesses of middle Cu_2S is 60 nm and bottom ZnO layer thicknesses for each curve)

Fig. 2 Comparison between simulation and experimental transmission spectrum of ZnO(30 nm)/Cu_2S(60 nm)/ZnO(60 nm)/glass multilayer and ZnO(60 nm)/Cu_2S(60 nm)/ZnO (60 nm)/glass multilayer

Fig. 3 The transmittance diagram of ZnO/Cu_2S/ZnO/glass complex films

Fig. 4 The sheet resistance of ZnO/Cu_2S/ZnO/glass complex films

Fig. 5 The figure of merit of ZnO/Cu_2S/ZnO/glass complex films

Fig. 6 The photocatalytic activity of ZnO/Cu_2S/ZnO/glass complex films

Figures

Fig. 1

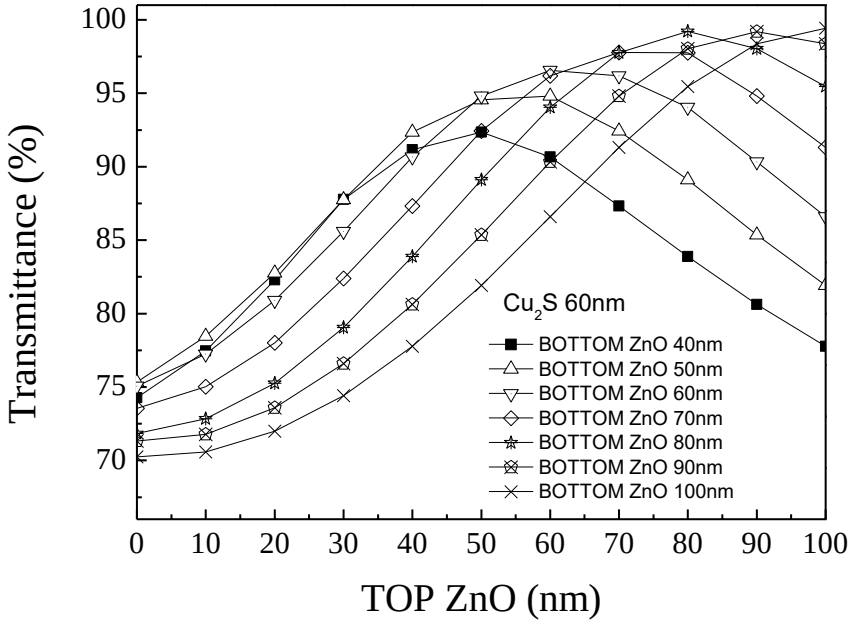


Fig. 2

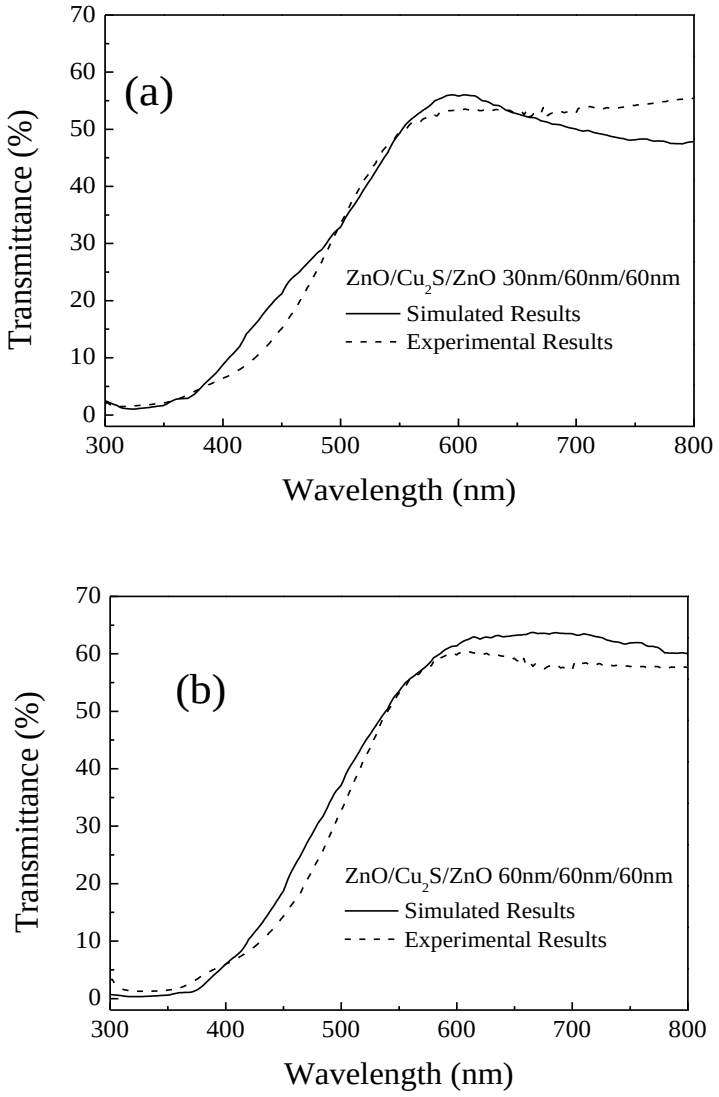

(a)
Transmittance (%)
Wavelength (nm)
ZnO/Cu2S/ZnO 30nm/60nm/60nm
Simulated Results
Experimental Results
(b)
Transmittance (%)
Wavelength (nm)
ZnO/Cu2S/ZnO 60nm/60nm/60nm
Simulated Results
Experimental Results

Fig. 3

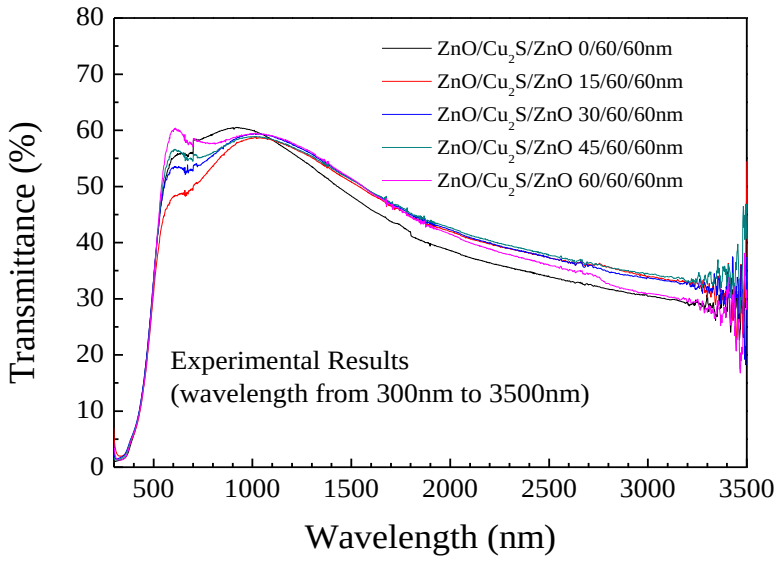

Transmittance (%)
Wavelength (nm)
ZnO/Cu2S/ZnO 0/60/60nm
ZnO/Cu2S/ZnO 15/60/60nm
ZnO/Cu2S/ZnO 30/60/60nm
ZnO/Cu2S/ZnO 45/60/60nm
ZnO/Cu2S/ZnO 60/60/60nm
Experimental Results
(wavelength from 300nm to 3500nm)
0
10
20
30
40
50
60
70
80
500
1000
1500
2000
2500
3000
3500

Fig. 4

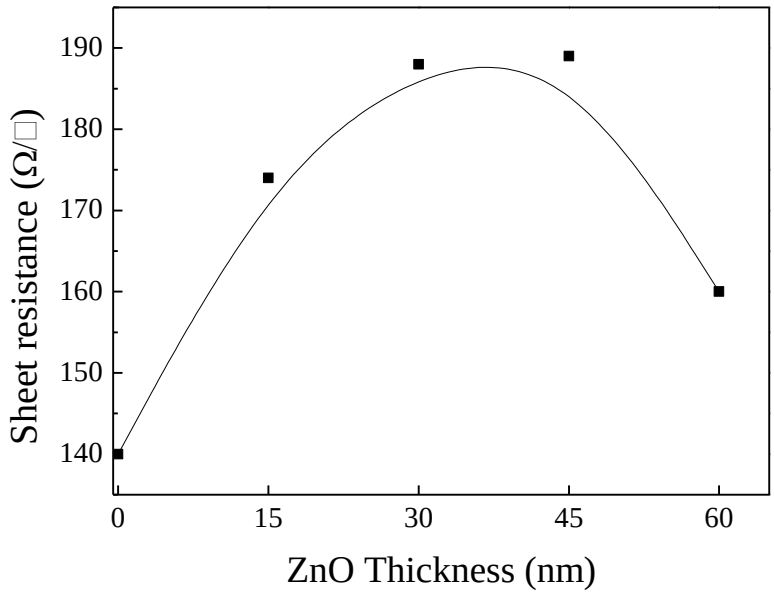

Sheet resistance (Ω/□)
190
180
170
160
150
140
0
15
30
45
60
ZnO Thickness (nm)

Fig. 5

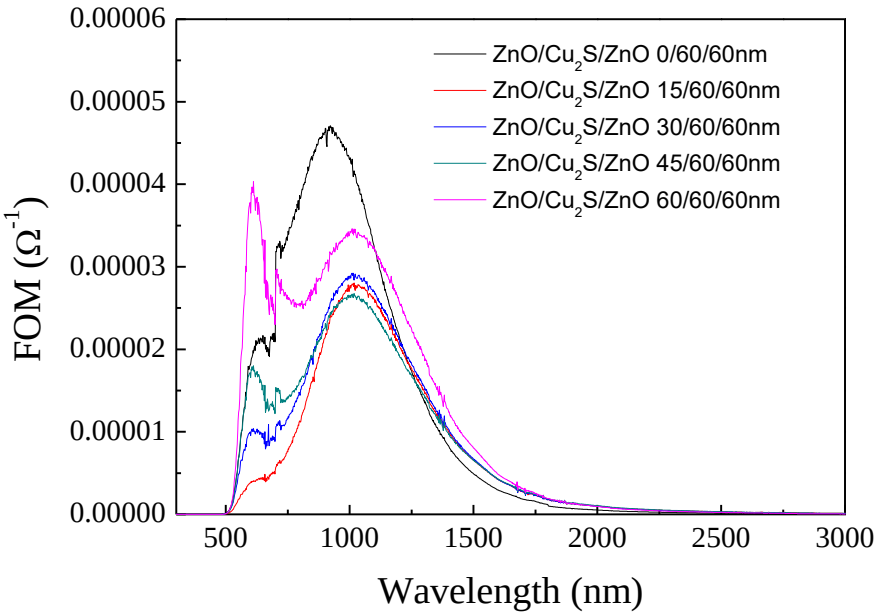
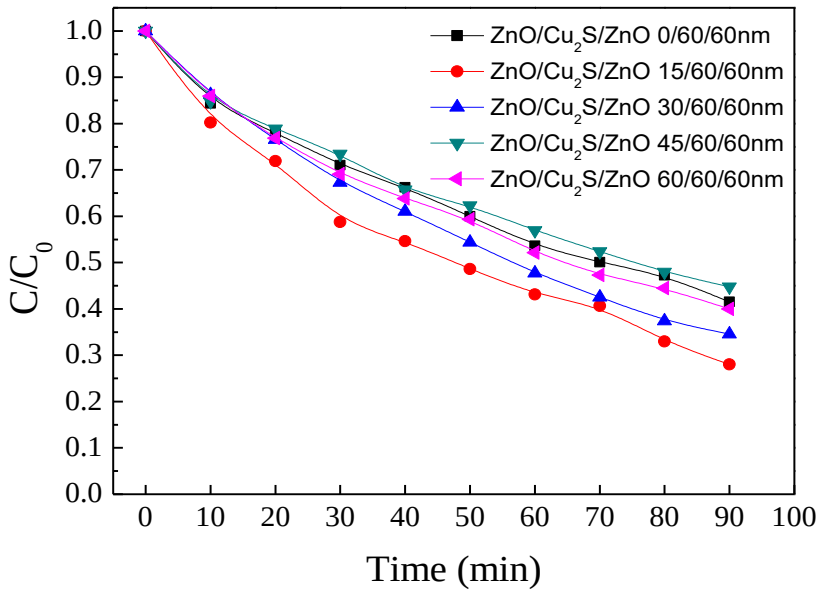

0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000
FOM (Ω-1)
500
1000
1500
2000
2500
3000
Wavelength (nm)
ZnO/Cu2S/ZnO 0/60/60nm
ZnO/Cu2S/ZnO 15/60/60nm
ZnO/Cu2S/ZnO 30/60/60nm
ZnO/Cu2S/ZnO 45/60/60nm
ZnO/Cu2S/ZnO 60/60/60nm

Fig. 6


ZnO/Cu2S/ZnO 0/60/60nm
ZnO/Cu2S/ZnO 15/60/60nm
ZnO/Cu2S/ZnO 30/60/60nm
ZnO/Cu2S/ZnO 45/60/60nm
ZnO/Cu2S/ZnO 60/60/60nm
C/C0
Time (min)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
10
20
30
40
50
60
70
80
90
100