ภาคผนวก

ตารางไฟล์มาตรฐาน JCPDS ของสารประกอบ CdS

Pattern : 75-1546 **Radiation =** 1.540600 **Quality :** Calculated

Cd S

Cadmium Sulfide

Lattice : Face-centered cubic **Mol. weight =** 144.47

S.G. : F-43m (216) **Volume [CD] =** 197.14

a = 5.82000 **Dx =** 4.868

Z = 4 **I/Icor =** 14.05

ICSD COLLECTION CODE : 031075
TEST FROM ICSD : No R value given.
TEST FROM ICSD : At least one TF missing.

*Calculated from ICSD using POWD-12++, (1997) primary reference :

*Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., volume 62, page 260, (1925) :
Ulrich, F., Zachariasen, W.

Radiation : CuKa1 **Filter :** Not specified

Lambda : 1.54060 **d-sp :** Calculated spacings

2th	I	h	k	l
26.505	100	1	1	1
30.699	22	2	0	0
43.969	47	2	2	0
52.076	33	3	1	1
54.579	5	2	2	2
63.932	6	4	0	0
70.468	11	3	3	1
72.585	5	4	2	0
80.842	10	4	2	2
86.902	7	5	1	1

ตารางไฟล์มาตรฐาน JCPDS ของสารประกอบ CuO

Pattern : 80-1268 **Radiation =** 1.540600 **Quality :** Calculated

Cu O

Copper Oxide

Lattice : Monoclinic
S.G. : C2/c (15)

a = 4.68330
b = 3.42080
c = 5.12940
a/b = 1.36907
c/b = 1.49947

Beta = 99.57
Z = 4

Mol. weight = 79.55
Volume [CD] = 81.03
Dx = 6.520
I/Icor = 4.00

ICSD COLLECTION CODE : 069094
TEMPERATURE FACTOR : ATF
REMARKS FROM ICSD : REM TEM 11.
REMARKS FROM ICSD : REM RVP.

*Calculated from ICSD using POWD-12++, (1997) primary reference :

*J. Solid State Chem., volume 89, page 184, (1990) :
Brese, N.E., O'Keeffe, M., Ramakrishna, B.L., von Dreele, R.B.

Radiation : CuKa1
Lambda : 1.54060

Filter : Not specified
d-sp : Calculated spacings

2th	I	h	k	l
32.548	7	1	1	0
35.466	37	0	0	2
35.566	92	-1	1	1
38.769	100	1	1	1
38.974	29	2	0	0
46.277	2	-1	1	2
48.743	28	-2	0	2
51.419	1	1	1	2
53.534	10	0	2	0
56.773	1	0	2	1
58.376	14	2	0	2
61.567	19	-1	1	3
65.870	14	0	2	2
66.292	14	-3	1	1
67.987	9	1	1	3
68.175	16	2	2	0
68.951	<1	-2	2	1
71.725	<1	-3	1	2
72.498	6	3	1	1
73.045	<1	2	2	1
75.059	5	0	0	4
75.298	8	-2	2	2
79.812	<1	0	2	3
80.191	2	-2	0	4
82.397	4	-3	1	3
83.184	4	2	2	2
83.701	4	3	1	2
*83.701	4	4	0	0
86.602	1	-4	0	2
86.811	1	-2	2	3
88.096	<1	1	1	4
89.877	5	-1	3	1

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Effect of Oxidation Temperature on the Properties of CuO Thin Films Prepared by Thermal Oxidation of Sputtered Cu Thin Films

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Keywords: CuO thin films, XRD, SEM, Persistent photoconductivity

Abstract. CuO thin films were obtained through thermal oxidation of dc magnetron sputtered metallic Cu films on glass substrates. Thermal oxidation process was performed in air at temperature ranging 300-500 °C. From XRD patterns, CuO single phase of monoclinic structure was formed at oxidation temperature beyond 450 °C whereas amorphous phase with very small grains was obtained at oxidation temperature below 450 °C. The positive sign of the Hall coefficient confirmed the p-type conductivity in all studied films. From transmission spectra, direct band gap value is varied between 2.17 and 2.83eV. From the transient photoconductivity measurements, persistent photoconductivity (PPC) behavior was observed. The decay current data were better fitted with the multiple exponential functions resulting into five slow decay times. Density of trap states corresponding to its decay time was also evaluated from the decay current data.

Introduction

Oxides of copper are well-known to show p-type conductivity and have many advantages for catalysts and solar energy conversion application. Non-toxic, economic, abundant availability and relatively simple formation of oxide makes copper oxide as an interesting material [1]. Two common forms of copper oxide are cuprous oxide (Cu_2O) and cupric oxide (CuO). A meta-stable copper oxide, Cu_4O_3, which is an intermediate compound between the previous two, has also reported [2]. Cu_2O and CuO belong to cubic and monoclinic structures with band gap of 2.1-2.6 eV and1.9-2.1eV, respectively. The growth of high quality p-type CuO thin films is essential for fabricating p-n junction-based oxide devices, such as solar cells, light emitting diodes and transistors. The optical transmittance and electrical resistivity of the films are two critical parameters in evaluating the performance of photovoltaic cells and electrochromic devices. In this paper, CuO thin films were obtained through thermal oxidation of dc magnetron sputtered metallic Cu films on glass substrates. The physical properties of the films were studied in order to find the possibility to use them in p-n junction low cost thin film solar cells.

Experimental

Copper thin films were grown on glass substrates by using dc magnetron sputtering from a home-made circular planar magnetron sputtering system. A circular planar magnetron of 60 mm diameter was used as the magnetron cathode. The magnetron target assembly was mounted on the top plate of the sputter chamber such that the sputtering could be done by sputtering down configuration. A continuously variable dc power supply of 630 V and 2.6 A was used a power source for sputtering. A 60 mm diameter and 3 mm thick pure copper (99.99%) used as sputter target. Pure argon was used as sputter gas. The flow rate of argon was controlled by AALBORG mass flow controller. Before deposition of each batch, the target was sputtered in pure argon atmosphere for 5 min to remove oxide layer if any on the surface of target. The sputtering conditions maintained during the growth copper films are given in Table 1. The as-deposited copper thin films were oxidized in tubular furnace at temperature ranging from 300-500 °C in air for 60 min. The crystal structure of these films was checked by X-ray diffraction technique with a Brucker

D 8 diffractometer using CuK_α radiation. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope. Optical transmission measurements were performed with UV-VIS double beam spectrophotometer in the wavelength range of 220-1,000 nm. The band gap (E_g) of the transparent films was determined by using the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ where α is the absorption coefficient, A is a constant and $h\nu$ is the photon energy. Electrical properties of the films were evaluated by Hall effect and resistivity measurements in the van der Pauw configuration at room temperature.

Table 1 List of some conditions for preparing CuO thin films

Conditions	Parameters	Values
Sputtering	Target	Cu
	Argon flow rate (sccm)	15
	Target to substrate distance (cm)	10
	Bias voltage (V)	370
	Current (mA)	80
	Substrate temperature (°C)	25
	Working pressure (torr)	$3.6x10^{-3}$
	Sputtering time (min)	6
Oxidized in air	Temperature (°C)	300-500
	Time (min)	60

Results and Discussion

Fig. 1 shows XRD patterns of CuO films as a function of oxidation temperature. XRD patterns of the films oxidized at temperature below 450 °C show amorphous characteristics. In contrast, the XRD spectrum of the films oxidized at 500 °C shows the well-resolved two diffraction peaks. These peaks correspond to the reflection of (-111) and (111) planes of standard JCPDS data card of CuO (JCPDS No. 80-1268). The crystallite size was calculated using Scherrer's formula, neglecting peak broadening due to residual stresses in the films, $L = 0.9\lambda/(\beta\cos\theta)$ where β is the broadening of diffraction line measured at half its maximum intensity in radian and λ is the wavelength of X-rays (0.1540 nm). The calculated value of L is about 15 nm. SEM images of CuO films obtained from oxidation temperature during 300-500 °C were shown in Fig. 2. When the films were oxidized below 350°C, the morphology does not change much and shows better uniformity in free surface. However, oxidation temperatures higher than 350 °C, small pores over the films were observed.

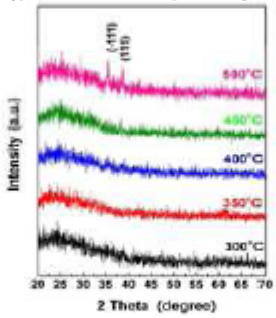

Fig. 1 XRD patterns of CuO films as a function of oxidation temperature.

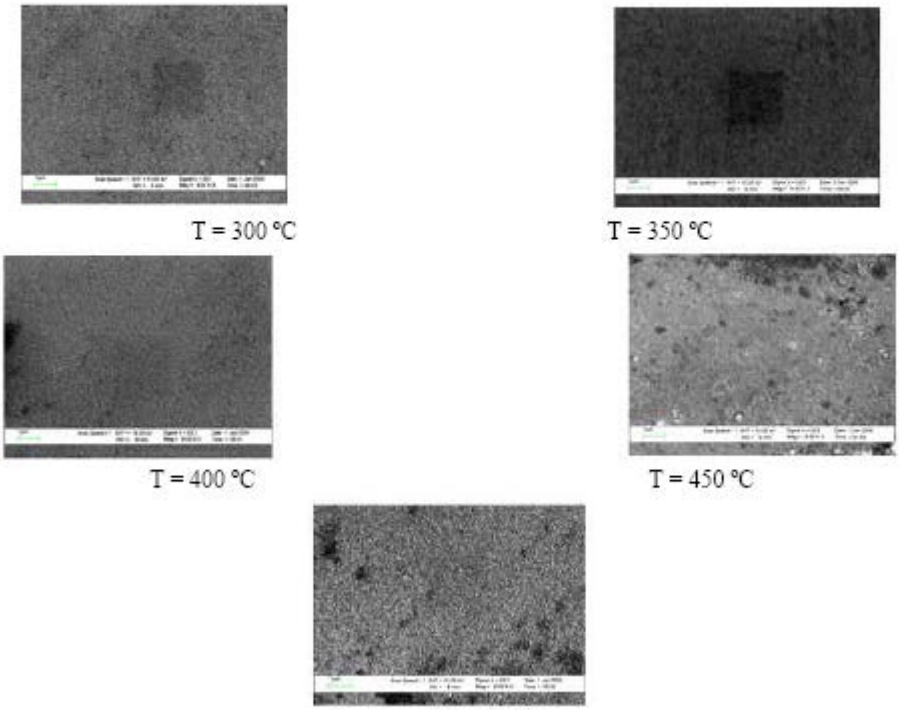

Fig. 2 SEM images of CuO films obtained from oxidation temperature between 300-500 °C.

Fig. 3 shows transmittance spectra of CuO films obtained from oxidation temperature during 300-500 °C. From the transmittance spectra we have also calculated band gap of films with different oxidation temperatures. The absorption coefficient (α) is calculated using the equation $\alpha = (1/d)\ln(1/T)$ where T is transmittance and d is film thickness. The absorption coefficient (α) and the incident photon energy (hν) related by $(\alpha h\nu)^2 = A(h\nu - E_g)$ where A and E_g are constant and band gap values, respectively. The E_g can be determined by extrapolation of the linear portion of the curve to the photon energy axis. Fig. 4 shows the curve of $(\alpha h\nu)^2$ vs. photon energy (hν) of the films obtained from oxidation temperature at 500 °C. Two allowed direct transition band gap were obviously observed. The smaller band gap value (E_{g1}) should correspond to the major CuO phase. The bigger band gap (E_{g2}) is possibly attributed to the parasitic phase of Cu_2O which cannot be observed by XRD due to too small amount of Cu_2O content in the bulk of films. The variation of E_{g1} and E_{g2} was shown in Fig. 5. The E_{g1} decreases from 2.41 to 2.17 eV with oxidation temperature increases from 300 to 400 °C and then increases to 2.19 eV when oxidation temperature further increases to 500 °C. The similar behavior is also observed in E_{g2}. These results indicate that E_{g1} and E_{g2} are sensitive to the oxidation temperature.

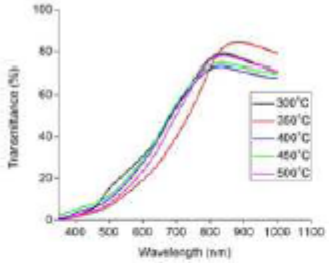

Fig. 3 Transmittance of CuO films obtained from oxidation temperature between 300-500 °C.

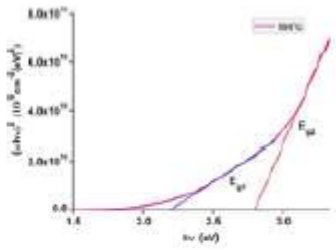

Fig. 4 $(\alpha h\nu)^2$ vs. hν plot of CuO films obtained from oxidation temperature at 500 °C.

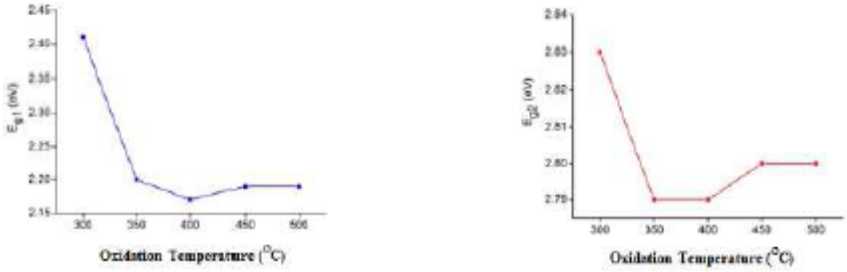

Fig. 5 Variation of band gap of CuO films as a function of oxidation temperature.

Electrical properties of the films were evaluated by Hall effect and resistivity measurements in the van der Pauw configuration. We found that all studied films are exhibited p-type conductivity. Variations of the resistivity, carrier concentration and mobility against oxidizing temperature are shown in Fig. 6. Carrier concentration (n) is derived from the relation $n=1/eR_H$ where R_H is the Hall coefficient and e is the absolute value of the electron charge. The carrier mobility (μ) is determined using the relation $1/ne\rho$ where ρ is resistivity. Resistivity of the films increases from 5.01×10^2 to attain maximum at $7.50\times10^3\Omega$.cm with oxidation temperature increasing from 300 to 400 °C, and decreases to 1.88×10^3 Ω.cm when the oxidation temperature further increase to 500°C. The mobility initially decreases with an increase in oxidation temperature up to 400 °C and then increases with an increase in oxidation temperature. The variation of carrier concentration shows the similar behavior to mobility. These results indicate that the resistivity, carrier concentration and mobility of the films are sensitive to the oxidation temperature.

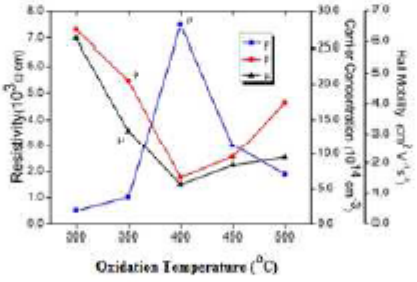

Fig. 6 Variations of the resistivity, carrier concentration and mobility against oxidation temperature.

The photocurrent response of the films oxidized at 500 °C was measured by two probe method using halogen lamp as a light source. Two silver electrodes with area 0.05 cm^2 was made on the

sample surface. The photocurrent response of the films oxidized at 500 °C was shown in Fig. 7. The sample was connected to the experimental setup and maintained in darkness under a constant applied bias of 6 V to stabilize the current. After the stabilization period, the current was recorded in the following sequences: 30 s in darkness, 400 s under illumination and, finally, 400 s in the darkness. Under illumination, the current increases immediately because a lot of carriers were exited by light illumination. After the illumination period, the persistent photoconductivity (PPC) effect of the films oxidized at 500 °C occurred in darkness. The decay of PPC in Fig. 7 can be described by multiple exponential functions [3,4] as

$$I = I_{dark} + (I_0 - I_{dark}) \sum_i \exp(-\frac{t}{\tau_i})$$

where I_{dark} is the current measured in darkness, I_0 is the PPC buildup level near the moment of light excitation being removed, τ is the PPC decay time constant. The normalized decay current in darkness as shown in Fig. 8, which follows the illumination period, indicates the persistent of charge carrier traps in the films [5]. In Fig. 8 the dash line is the measured data and the solid line is the least squares fit data by the multiple exponential functions as described above. According to the function of fitting curve in Fig. 8 we calculated that the five τ values are 120.77, 208.33, 414.94, 884.96 and 1504.95 s. Method for calculating the trap densities corresponding to the PPC decay constant was reported in the literatures [6-8]. The corresponding trap densities are $1.38x10^{11}$, $1.03x10^{11}$, $7.90x10^{10}$, $6.70x10^{10}$ and $5.89x10^{10}$ cm^{-2}.

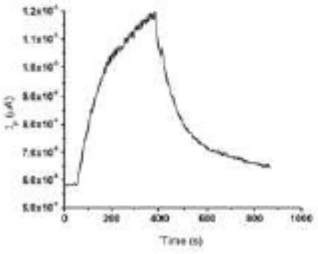

Fig. 7 Photocurrent response of CuO films obtained from oxidation temperature at 500 °C.

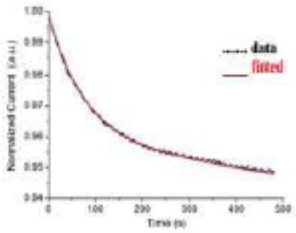

Fig. 8 Normalized decay time of CuO films obtained from oxidation temperature at 500 °C.

Summary

CuO thin films were obtained through oxidation of metallic Cu films deposited on glass substrates by dc magnetron sputtering method. It is shown that the CuO single phase of monoclinic structure was formed at oxidation temperature beyond 450 °C where amorphous phase with very small grains, confirmed by SEM images, was obtained at oxidation temperature below 450 °C. All studied films are p-type semiconductors with band gap of 2.17-2.83 eV. The photocurrent response of films oxidized at 500 °C was measured by two probe using halogen lamp as a light source. The decay current data were better fitted with the multiple exponential functions. Five slow decay times and five trap densities values are 120.77, 208.33, 414.94, 884.96, 1504.95 s and$1.38x10^{11}$, $1.03x10^{11}$, $7.90x10^{10}$, $6.70x10^{10}$, $5.89x10^{10}$ cm^{-2}, respectively.

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