IOP Conf. Series: Materials Science and Engineering **211** (2017) 012025 doi:10.1088/1757-899X/211/1/012025

Influence of oxygen flow rate on structural, optical and electrical properties of copper oxide thin films prepared by reactive magnetron sputtering

Thitinai Gaewdang* and Ngamnit Wongcharoen

Physics Department, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

*Email: thitinai.ga@kmitl.ac.th

Abstract. In this research, copper oxide thin films were prepared by reactive dc magnetron sputtering method on glass substrates with oxygen flow rate in the range of 1-10 sccm. From XRD patterns, formation of Cu_2O cubic structure or CuO monoclinic structure was controlled by adjusting oxygen flow rate. Nanocrystallite size of the as-grown films was observed by AFM. From transmittance spectra, direct energy gap varied between 1.97 and 2.55 eV. Electrical conductivity and Hall effect measurements were performed on the films with van der Pauw configuration. The positive sign of the Hall coefficient confirmed the p-type conductivity in all studied films. Important electrical parameters of films as a function of oxygen flow rate were observed. With low resistivity and high mobility values, the films prepared at oxygen flow rate of 8 sccm are identified as suitable candidates for fabrication as absorber layer in solar cell devices.

1. Introduction

Oxides of copper are well-known to show p-type conductivity and have many advantages for catalysts, chemical sensors and solar energy conversion application. Non-toxic, economic, abundant availability and relatively simple formation of oxide make 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 [1]. Cu_2O and CuO belong to cubic and monoclinic structures with band gap of 2.1-2.6 eV and 1.9-2.1 eV, respectively [2]. It has been demonstrated by varying the deposition conditions, films phase such as Cu_2O, CuO and Cu_4O_3 can be obtained and this also leads to different stoichiometry for a given phase. The optical transmittance and electrical resistivity of the films are two critical parameters in evaluating the performance of photovoltaic cells and electrochromic devices. A variety of deposition techniques have been employed for the growth copper oxide films. Among these thin films deposition techniques, reactive magnetron sputtering is one of the industrially practiced techniques for preparing of uniform films on large area substrates with required chemical composition. In this paper, copper oxide thin films were obtained through reactive dc magnetron sputtering on glass substrates with different oxygen flow rates. 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.

2. Materials and methods

The copper oxide films were deposited by reactive dc magnetron sputtering from a high purity Cu target of 99.99% with diameter of 50 mm and thickness 3 mm. Oxygen and argon were used a reactive gas and working gas, respectively. In order to study the effect of oxygen flow rate and eliminate the action of sputtering pressure, the sputtering pressure was kept at 0.73 Pa, with a variation of oxygen flow rate in the range of 1-10 sccm and an argon flow rate in the range of 12-32 sccm. A diffusion pump was used to achieve a base pressure of 6.90×10^{-3} Pa. The substrate temperature during deposition was not intentional controlled. Target to substrate distance was kept constant at 100 mm. Sputtering time was 30 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 Park XE-100 AFM. The EDS spectra were recorded with a Zeiss EVO MA 10 Scanning Electron Microscopy. Optical transmission measurements were performed with UV-VIS double beam spectrophotometer in the wavelength range of 300-1,000 nm. FTIR spectra were performed by Thermo Scientific Nicollet 6700 in the range between 450 and 4000 cm^{-1}. Electrical properties of the films were evaluated by Hall effect and resistivity measurements in the van der Pauw configuration at room temperature.

3. Results and discussion

3.1 *Structural properties*

Figure 1 shows XRD patterns of Cu-O films grown on glass substrates as a function of oxygen flow rate $R(O_2)$. For $R(O_2)$ at 1 sccm, the as-grown films showed amorphous characteristics. In contrast, the XRD spectra of the films grown at 2 and 4 sccm showed the well-resolved two diffraction peaks. These peaks corresponded to the reflection of (111) and (200) planes of standard JCPDS data card of Cu_2O phase (JCPDS No. 74-1230). For $R(O_2)$ at 6 sccm, two diffraction peaks corresponded to the (-111) and (111) of CuO phase (JCPDS No. 80-76). When $R(O_2)$ increased to 8 sccm intensity of (-111) and (111) diffraction peaks decreased and then disappeared at $R(O_2)$ of 10 sccm attributed to amorphous phase. Inadequate or excessive oxygen atoms leads the films difficulty crystallise [3]. That is because oxygen atoms are reflected from the target and collided the substrate with appreciable energy, thereby causing nucleation. However, too much oxygen content will decrease the presence of Cu atoms in the vapor phase, thereby hindering nucleation. Simillar behavior was observed in TiO_2 films [3], that too much oxygen content also make the films become amorphous phase.

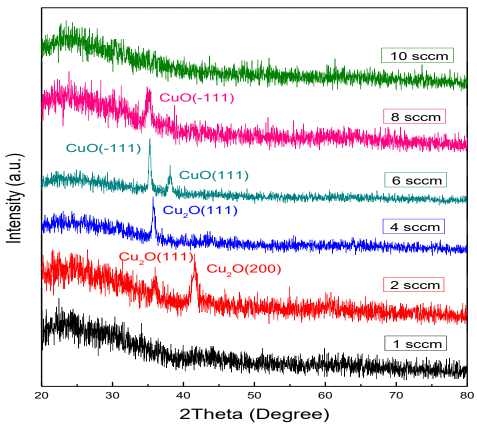

Figure 1. XRD patterns of Cu-O films as a function of $R(O_2)$.

AFM images of the films prepared as a function of $R(O_2)$ are shown in figure 2. The films formed at $R(O_2)$ of 1 sccm showed isolated particles with different sizes due to a low deposition rate and deficient O_2 content for reacting with Cu precusor atoms. At $R(O_2)$ of 2 sccm, AFM image showed that the films crystallised in pillar shape with average roughness and particle size of 3.82 and of 31.25 nm, respectively. With increasing the $R(O_2)$ from 4 to 6 sccm, the surface roughness of the films with pillar shape decreased from 2.84 to 2.29 nm but the particle size increased from 33.20 to 36.88 nm. However, the pyramidal shape of particles at film surface was noticed at $R(O_2)$ of 8 sccm with average roughness and particle size of to 1.75 and of 37.10 nm. At $R(O_2)$ of 10 sccm, flattened surface with different particle sizes in irregular shape was observed.

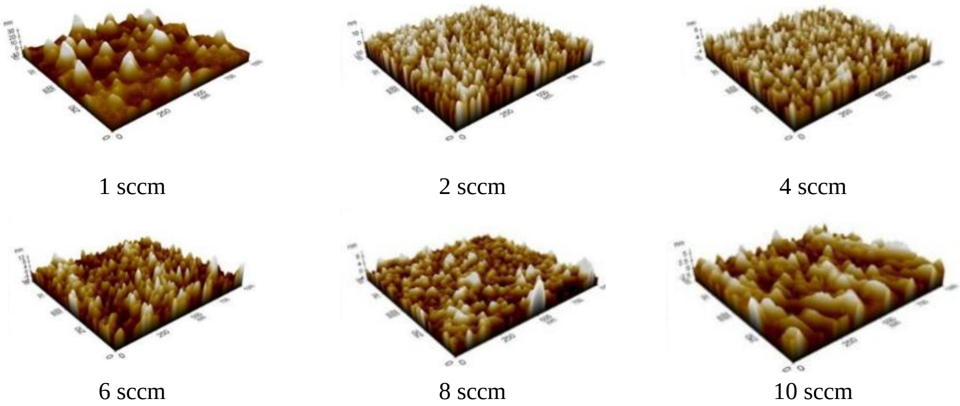

Figure 2. AFM images of Cu-O films as a function of $R(O_2)$.

3.2 Optical properties

Figure 3 shows transmittance spectra of Cu-O films obtained from various oxygen flow rates. From the transmittance spectra, the absorption coefficient (α) was calculated using relationship of Sunds $\alpha = (1/d)\ln(1/T)$ where T is transmittance and d is film thickness. The absorption coefficient (α) and the incident photon energy (hν) according to Tauc relationship $(\alpha h\nu)^2 = A(h\nu - E_g)$ where A and E_g are constant and energy gap values, respectively. The E_g can be determined by extrapolation of the linear portion of the curve to the photon energy axis. Figure 4 shows the curve of $(\alpha h\nu)^2$ vs. photon energy (hν) of the films obtained from various oxygen flow rates. The dependence of E_g on $R(O_2)$ of the films in the range of 1.97- 2.55 eV is shown in figure 5. Figure 6 shows the FTIR spectra of Cu-O films as a function of $R(O_2)$. The nature of peaks are presented in table 2. The peaks with wave numbers of ~630 and ~770 cm^{-1} are characteristics of the stretching vibration of Cu(I)-O and Cu(II)-O bonds, respectively [4,5].

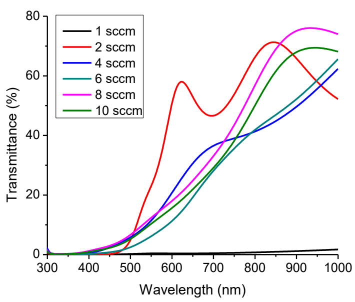

Figure 3. Transmittance of Cu-O films as a function of $R(O_2)$.

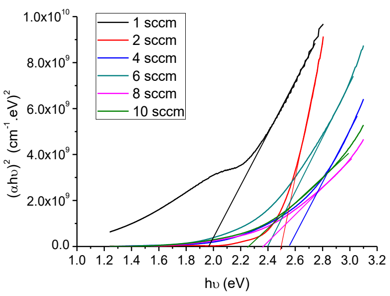

Figure 4. $(\alpha h\nu)^2$ vs. hν plot of Cu-O films as a function of $R(O_2)$.

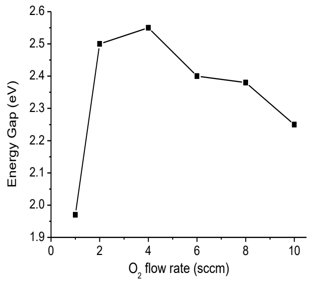

Figure 5. Variation of E_g of Cu-O films as a function of $R(O_2)$.

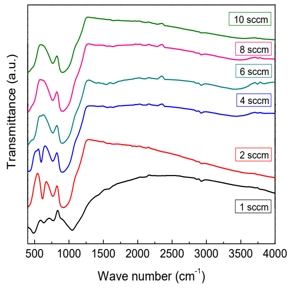

Figure 6. FTIR spectra of Cu-O films as a function of $R(O_2)$.

Table 1. FTIR spectra of Cu-O films as a function of $R(O_2)$.

$R(O_2)$ (sccm)	Peak of FTIR (cm^{-1})	Phase	Assignments Vibration Mode	[Ref.]
1	485 630 770 1046	CuO Cu_2O CuO Cu(OH)	Cu(II)-O Cu(I)-O Cu(II)-O Cu-OH	[5,6] [4,7,8] [5] [6]
2	615 765, 918	Cu_2O CuO	Cu(I)-O	[9,10]
4	610 764, 905 3438	Cu_2O CuO Hydroxyls of absorbed water	Cu(II)-O Stretching vibration of OH^-	[4,5]
6	764, 904 3407	CuO Hydroxyls of absorbed water	Cu(II)-O Stretching vibration of OH^-	
8	764, 907 1641 3495	CuO Surface absorbed water Hydroxyls of absorbed water	Bending vibration Stretching vibration of OH^-	[4,5]
10	764, 907 3400	CuO Hydroxyls of absorbed water	Cu(II)-O Stretching vibration of OH^-	

3.3 Electrical properties

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 exhibited p-type conductivity. Variations of the resistivity, carrier concentration and mobility against $R(O_2)$ are shown in figure 7. Carrier concentration (n) was 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) was determined using the relation $\mu=1/ne\rho$ where ρ is resistivity. Resistivity of the films increased from 2.01 attain maximum at 1.85×10^3 Ω.cm with $R(O_2)$ increased from 1 to 6 sccm and then decreased to 10.25 Ω.cm when $R(O_2)$ further increased to 10 sccm. The carrier concentration initially decreased with an increase $R(O_2)$ down to 6 sccm and then increased with an increase in $R(O_2)$. The variation of mobility value showed the similar behavior to resistivity. These results indicate that the resistivity, carrier concentration and mobility of the films are sensitive to $R(O_2)$. The films prepared at oxygen flow rate of 8 sccm revealed a low resistivity and high mobility values. So, they are identified as suitable candidates for fabrication as absorber layer in solar cell devices.

IOP Conf. Series: Materials Science and Engineering **211** (2017) 012025 doi:10.1088/1757-899X/211/1/012025

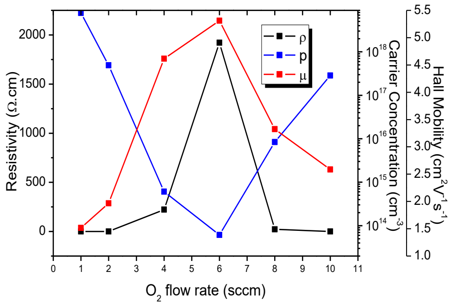

Figure 7. Variations of ρ, p and μ of Cu-O films as a function of $R(O_2)$.

4. Conclusion

The influence of oxygen flow rate $R(O_2)$ on the structural, optical and electrical properties of copper oxide thin films grown by reactive dc magnetron sputtering was investigated. The results revealed the structural properties of the obtained films strongly depended on $R(O_2)$. The nanocrystallite copper oxide thin films with cubic structure were formed at $R(O_2)$ values of 2 and 4 sccm. Then, transition to monoclinic structure at $R(O_2)$ values of 6 and 8 sccm was observed. Out of the above $R(O_2)$ ranges, amorphous phase was dominant. The average particle size of the films around 30 nm was observed by AFM. Influence of oxygen flow rate on optical and electrical properties of the as-grown films was also investigated. These results showed a better understanding of the growth behavior and other relevant properties of the deposited copper oxide thin films as a function of $R(O_2)$. The effect of other growth parameters such as deposition temperature, deposition time and thickness on the optoelectronic properties of the films will be planned to investigate in the near future.

References

[1] P K Ooi, S S Ng, M J Abdullah, H Abu Hassan and Z Hassan 2013 *Mater. Chem. Phys* **140** p 243
[2] S Cho 2013 *Met. Mater. Int* **191** p 327
[3] B X Zhao, J C Zhou and L Y Rong 2010 *Trans. Nonferrous Met. Soc. China* **20** p 1429
[4] D GuoD, L Wang, Y Du, Z M Ma and L Shen 2015 *Mater. Lett* **160** p 541
[5] J S K Arockiasamy and J Irudayaraj 2015 *Ceramic International* **42** p 6198
[6] M Fterich, F B Nasr, R Lefi, M Toumi and S Guermazi 2016 *Mater. Sci. Semicon. Processing* **43** p 114
[7] M A Bhosale and B M Bhanage 2016 *Adv. Powder Tech* **27** p 238
[8] K Kaviyarasan, S Anandan, R V Mangalaraja, T Sivasankar and M Ashokkumar 2016 *Ultrasonics Sonochemistry* **29** p 388
[9] A Chen, H Long, X Li, Y Li, G Yang and P Lu 2009 *Vacuum* **83** p 927
[10] K Kardarian, D Nunes, P M Sberna, A Ginsburg, D A Keller, J V Pinto, J Deuermeier, A Y Anderson, A Zaban, R Martins and E Fortunato 2016 *Sol. Energy & Sol. Cells* **147** p27

Acknowledgment

This work is supported by King Mongkut's Institute of Technology Ladkrabang under grant number A118-59-038.