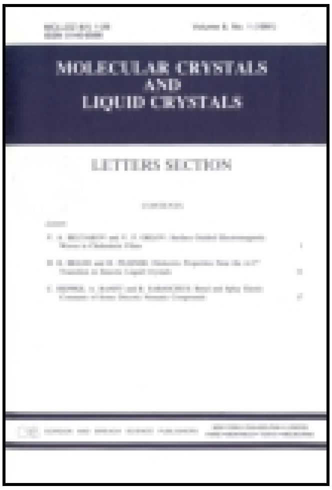

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Properties of Cu_2O Thin Films for All-Oxide Solar Cells

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Published online: 17 Nov 2014.

Mol. Cryst. Liq. Cryst., Vol. 598: pp. 62–68, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.933299

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Properties of Cu_2O Thin Films for All-Oxide Solar Cells

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In this work, p-type Cu_2O thin films deposited by RF magnetron sputtering for Cu_2O based all metal oxide solar cells were studied as a function of oxygen partial pressure ratio at room temperature. The Cu_2O (111) x-ray diffraction peaks were indicated as a function of oxygen partial pressure ratio. Optical band gap energies of as-deposited Cu_2O thin films ranged from 1.88 to 1.96 eV as a function of oxygen partial pressure ratio. The resistivity and mobility of the p-type Cu_2O thin film with an oxygen partial pressure ratio of 2.4% was 2×10^4 Ω·cm and 15.1 $cm^2/V{\cdot}s$, respectively.

Keywords Cu_2O; RF magnetron sputtering; oxygen partial pressure ratio

Introduction

Common forms of copper oxide are cuprous oxide (Cu_2O), cupric oxide (CuO), and paramelaconite (Cu_4O_3) [1–3]. The Cu_2O is a p-type metal oxide semiconductor with Cu vacancies [4,5]. The p-type Cu_2O has been studied for many applications such as the absorption layer of metal oxide solar cells, the channel layer of thin film transistors, and gas sensors. As the absorption layer of metal oxide solar cells, p-type Cu_2O has many advantages such as low cost, non-toxicity, high Hall mobility, 2.1 eV direct band gap, high minority carrier diffusion length, and high optical absorption coefficient ($>10^5$) in the visible region [6–8]. In addition, theoretical light conversion efficiency of Cu_2O-based metal oxide solar cells is about 20% [9–11]. The deposition of Cu_2O thin films have been investigated by thermal oxidation, electro deposition, thermal evaporation, sol-gel, spray pyrolysis, chemical vapor deposition, molecular beam epitaxy, plasma deposition, pulsed laser deposition, DC reactive sputtering, and RF magnetron sputtering [12–28]. Among them, RF magnetron sputtering has many advantages such as easily controlled material composition and film thickness uniformity. Despite these advantages, the Hall mobility of Cu_2O thin films showed low values below 10 $cm^2/V{\cdot}s$ [29]. In this study, we aim to fabricate an optimal and high mobility (above 10 $cm^2/V{\cdot}s$) p-type Cu_2O semiconductor structure using RF magnetron sputtering as a function of oxygen flow rate.

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Experimental Details

Deposition of Cu_2O Thin Film

The Cu_2O thin films were deposited on glass substrates by RF magnetron sputtering using a Cu_2O ceramic target (purity 99.9%, 2 inch, LTS Inc.). The vacuum chamber was initially evacuated to 2.6×10^{-4} Pa using a turbo molecular pump. The working pressure was maintained at 0.65 Pa (5 mTorr). The oxygen partial pressure ratio $[(O_2/(Ar + O_2))\times 100]$ was controlled by using mass flow controllers (MFC). The Ar gas flow was alternated between 8 and 10 sccm. The O_2 gas flow was alternated between 0.1 and 0.7 sccm. The ratio of oxygen flow, denoted as PO_2, was varied from 0% to 6.54%. The detailed sputtering parameters are shown below in Table 1.

Film Characterization

The thicknesses of the Cu_2O thin films were measured using a surface profilometer (KLA-Tencor, Alpha-step D-100). Crystallinity of Cu_2O thin films were examined by X-ray diffraction (XRD, D/MAX-2200, Rigaku) with a Cu Kα radiation ($\lambda = 1.5418$ Å) X-ray source at 40 kV and 20 mA over the scanning angle (2θ) from 20° to 80°. The surface resistivity was measured by using a four-point probe (AIT Co., Ltd., CMT-SR1000N). The optical properties were measured by UV/vis spectrometry (Hewlett-Packard HP8453). In addition, the electrical conductivity, carrier concentration, and mobility were measured by using a Hall effect measurement system (HMS-3000, Ecopia).

Results and Discussion

The thicknesses of the Cu_2O thin films were fixed at 1μm. Figure 1 shows XRD diffraction peaks of the Cu_2O thin films as a function of oxygen partial pressure ratio. Diffraction peaks of as-deposited Cu_2O thin films with oxygen partial pressure ratio from 1 to 2.4% indicated the Cu_2O (111) peak. Diffraction peaks of as-deposited Cu_2O thin films with oxygen partial pressure ratio after 3.2%, indicated the CuO (002) peak. The absence of this peak with oxygen partial pressure ratio of 0 may have been due to evacuation of ionized oxygen before it reached the substrate. In the work of Noda et. al., the XRD patterns of thin films deposited at oxygen partial pressure ratio from 2.5 to 4% did not include the Cu_4O_3 (202) peak in this paper [30]. Figure 2 shows the optical absorbance spectrum of Cu_2O thin films deposited at PO_2 of 1, 2.4, 3.2, 4.7, 5.6, and 6.5%. Absorbance of all the films was over 10% below 550 nm. Figure 3 shows the optical transmittance spectrum of Cu_2O thin films deposited at the same PO_2 values as in Fig. 3. Transmittance of all the as-deposited films was 0% from 300 to 700 nm, regardless of the oxygen partial pressure ratio. The

Table 1. Sputtering parameters

Target	Cu_2O (99.9%)
RF power	100 W
Substrate	Glass
Substrate temperature	Room Temperature
Oxygen partial pressure ratio $\frac{O_2}{Ar+O_2} \times 100$	$0 \sim 6.5\%$
Thickness	1 μm

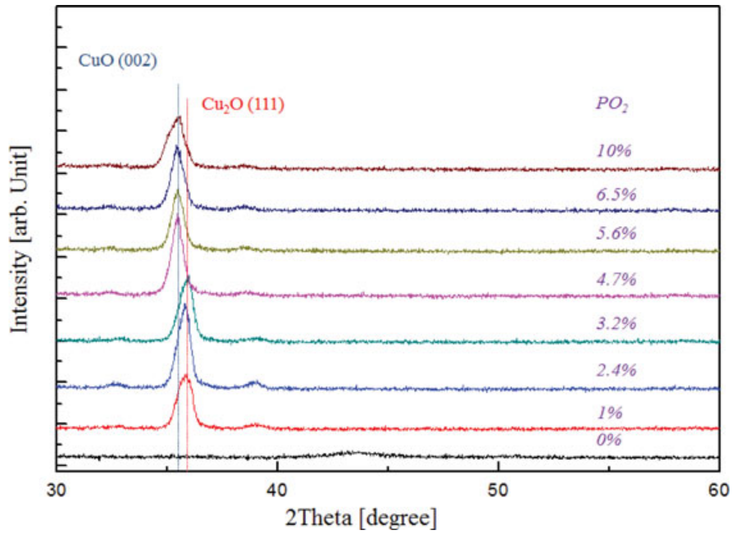

Figure 1. Variation in crystalline phase of sputter deposited films with changing PO_2 using Cu_2O target.

opacity of the thin films decreased with increasing PO_2. Figure 4 shows the optical band gaps of all the Cu_2O thin films. The relation between the absorption coefficient (α) and the photon energy ($h\nu$) can be determined by Equation below [31].

$$(\alpha h\nu) = A\sqrt{(h\upsilon - Eg)} \quad (1)$$

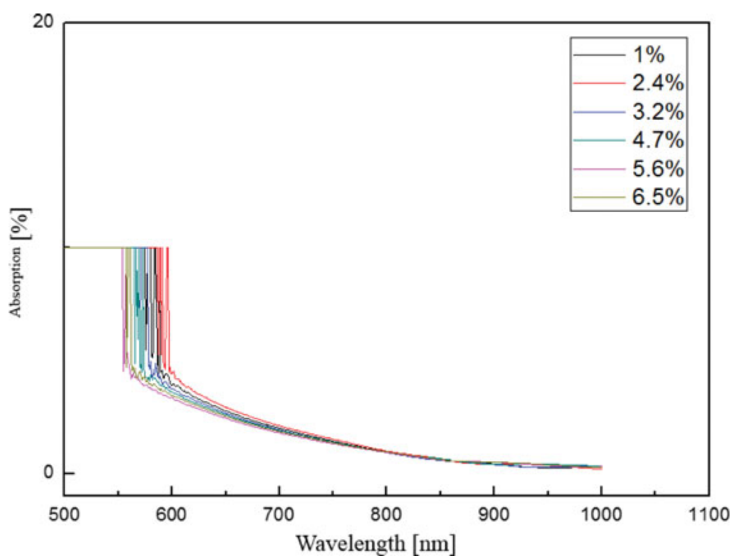

Figure 2. Variation in optical absorption spectra of sputter deposited films with changing PO_2 using Cu_2O target.

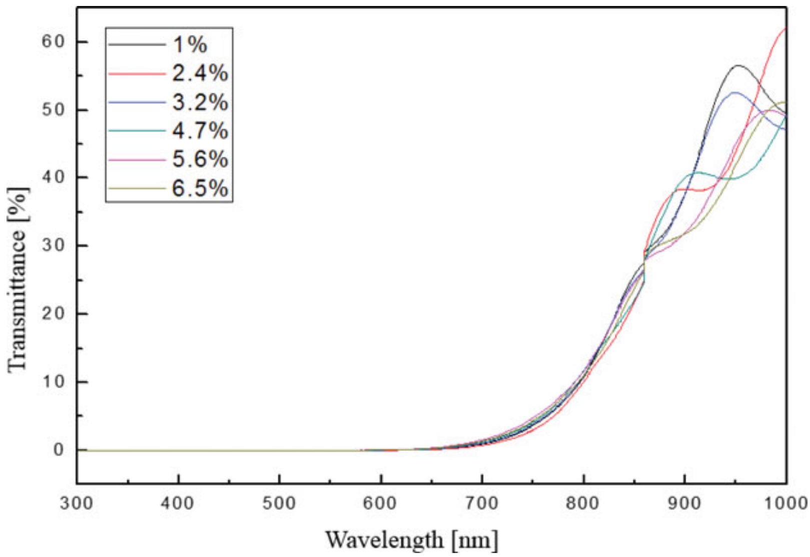

Figure 3. Variations in optical transmittance spectra of sputter deposited films with changing PO_2 using Cu_2O target.

Where A is a constant and Eg is the optical band gap of the material. The optical band gaps of Cu_2O thin films deposited at different PO_2 values from 1.0 to 3.2% were calculated as 2.02 to 2.06 eV, and 4.7∼6.5% were calculated as 1.92 to 1.96 eV. The optical band gap of theoretical Cu_2O material was reported to be 2.1 eV. However, the observed optical band gaps of Cu_2O thin films in this study were smaller than 2.1 eV. The results we obtained is similar to typical value that reported in previous researches. At the conditions of oxygen partial pressure ratios used, the Cu_2O thin films may have contained some amount of CuO

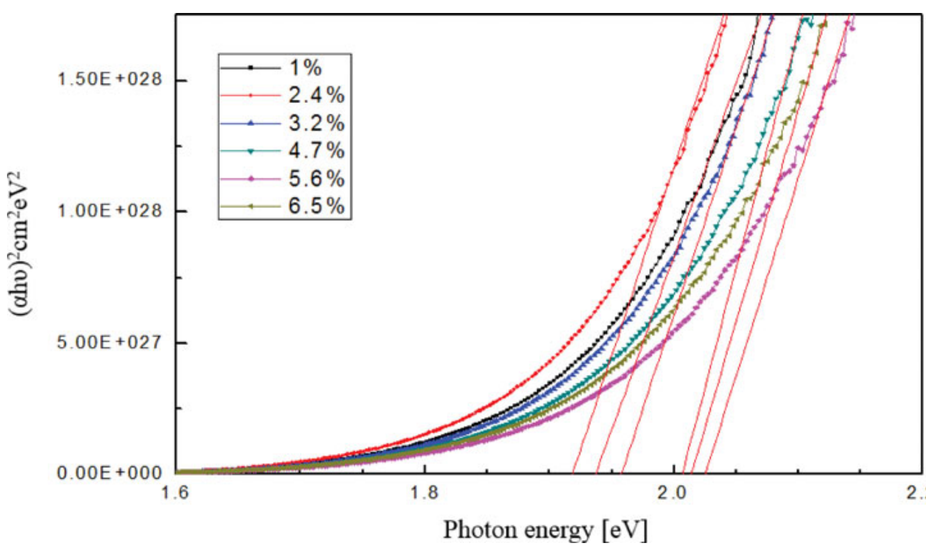

Figure 4. Tauc plot of absorption coefficient α of Cu_2O target-based films.

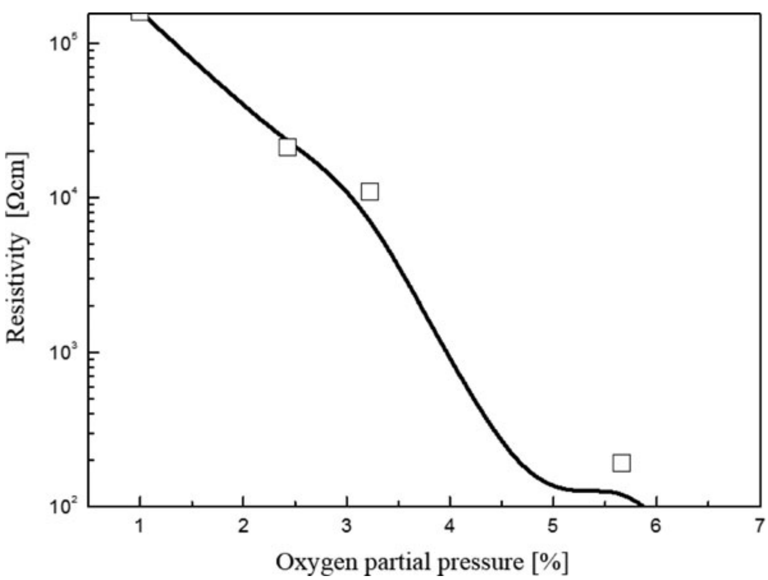

Figure 5. The electrical sheet resistance of Cu_2O thin films and CuO thin films.

in their crystal structure owing to the low density of oxygen. The band gap of CuO is approximately 1.3–2.0 eV [32,33], which could lower the bulk band gap of a film from the 2.1 eV theoretical band gap of Cu_2O. The Hall mobility depended on the oxygen flow rate. Figure 5 shows the electrical sheet resistance of Cu_2O thin films and CuO thin films. As the oxygen partial pressure ratio increased, the resistivity decreased. The suggested cause of the decrease in resistivity was an increase in Hall mobility. Figure 6 shows the Hall

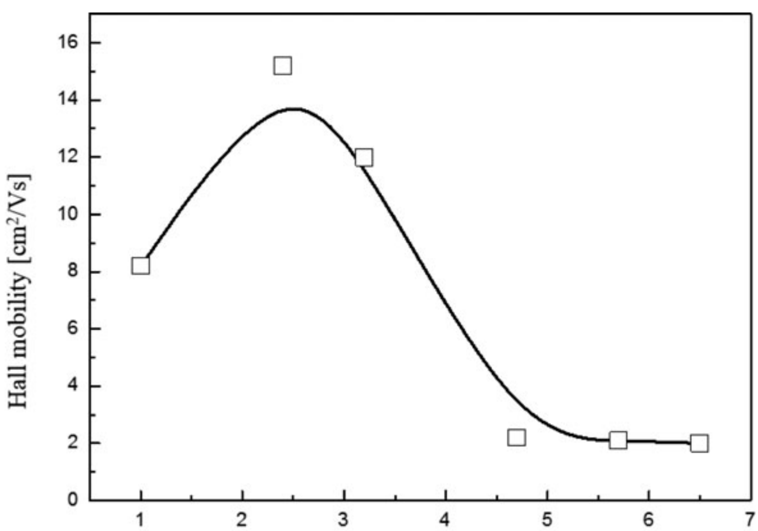

Figure 6. The mobility of Cu_2O thin films as a function of oxygen flow rates.

mobility of Cu_2O thin films and CuO thin films. At the small PO_2 region below 2.4%, the hall mobility of Cu_2O thin films were increased with increment of the oxygen partial pressure ratio. The crystalline domain size was calculated from the width of XRD peaks using Scherrer's equation [34].

$$D = K\lambda/\beta cos\theta \tag{2}$$

where D is the average crystalline domain size, β is the full width at half maximum (FWHM), $K = 0.94$, $\lambda = 1.540598$ Å, and θ is the diffraction angle. The Cu_2O thin films deposited at an oxygen partial pressure ratio of 1% were found to have the largest particle size.

Conclusions

The p-type Cu_2O thin films were deposited on glass substrates by RF magnetron sputtering with Cu_2O ceramic target as a function of oxygen partial pressure ratio. The $Cu_2O(111)$ diffraction peaks were strongly indicated with oxygen partial pressure ratio of 2.4%. The optical band gap energy of Cu_2O thin film with oxygen partial pressure ratio of 2.4% indicated 1.93 eV. The resistivity and mobility of p-type Cu_2O thin film indicated 2×10^4 $\Omega\cdot$cm and 15.1 $cm^2/V\cdot s$ with oxygen partial pressure ratio of 2.4%. In our results, as-deposited p-type Cu_2O thin films with oxygen partial pressure ratio of 2.4%. Achieved an optimal structure and higher mobility than other oxygen partial pressure ratio.

Acknowledgments

This work was supported by the Human Resource Development Program (NO. 20124030200010) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by Korea Government Ministry of Trade, Industry and Energy.

References

[1] Samarasekara, P., Kumara, N. T. R. N., & Yapa, N. U. S. (2006). *J. Phys. Condens. Mater.*, *18* 2417
[2] Pierson, J. F., Thobor-Keek, A., & Billard, A. (2003). *Appl. Surf. Sci.*, *210* 359
[3] Rai, B. P. (1988). *Solar Cells*, *25* 265
[4] Nolan, M. & Elliott, S. D. (2006). *Physical Chemistry Chemical Physics*, *8* 45
[5] Sieberer, M., Redinger, J., & Mohn, P. (2007). *Physical Review B*, *75* 3
[6] Akimoto, K., Ishizuka, S., Yanagita, M. *et al.* (2006). *Sol. Energy*, *80* 715
[7] Figueiredo, V., Elangovan, E., Goncalves, G., Barquinha, P., Pereira, L., Franco, N., Alves, E., Martins, R., & Fortunato, E. (2008). *Appl. Surf. Sci.*, *254* 3949
[8] Rafea, M. A. & Roushdy, N. (2009). *J. Phys. D: Appl. Phys.*, *42* 015413
[9] Olsen, L. C., Addis, F. W., & Miller, W. (1982). *Solar Cells*, *7* 3
[10] Rai, B. P. (1988). *Solar Cells*, *25* 3
[11] Berezin, A. A. & Weichman, F. L. (1981). *Solid State Communications*, *37* 2
[12] Figueiredo, V., Elangovan, E., Goncalves, G. *et al.* (2008). *Appl. Surf. Sci.*, *254* 3949
[13] Mahalingam, T., Chitra, J. S. P., Chu, J. P. *et al.* (2005). *Sol. Energy Mater. Sol. Cells*, *88* 209
[14] Al-Kuhaili, M. F. (2008). *Vacuum*, *82* 623
[15] Ray, S. C. (2001). *Sol. Energy Mater. Sol. Cells*, *68* 307
[16] Ottosson, M., & Carlson, J. O. (1996). *Surf. Coat. Technol.*, *78* 623
[17] Lee, H. H., Lee, C., Kuo, Y. L., & Yen, Y. W. (2006). *Thin Solid Films*, *498* 43
[18] Zhu, H., Zhang, J., Li, C. *et al.* (2008). *Thin Solid Films*, *517* 5700

[19] Han, S., Chan, H. Y., Kuo, L. T., & Tsai, C. H. (2008). *Thin Solid Films*, *517* 1195
[20] Chen, A., Long, H., Li, Y., , Yang, G., & Lu, P. (2009). *Vacuum*, *83* 927
[21] Sivasankar Reddy, A., Uthanna, S., & Sreedhara Reddy, P. (2007). *Appl. Surf. Sci.*, *253* 5287
[22] Perretta, A., Jayaaraj, M. K., Nocera, A. D. *et al.* (1996). *Phys. Status Solid (a)*, *155* 399
[23] Rastkar, A. R., Niknam, A. R., & Shokri, B. (2008). *Thin Solid Films*, *517* 5464
[24] Ghosh, S, Avasthi, D. K., Shah, P. *et al.* (2000). *Vacuum*, *57* 377
[25] Yang, W. Y., Kim, W. G., & Rhee, S. W. (2008). *Thin Solid Films*, *517* 967
[26] Pierson, J. F., Petitjean, C, & Horwat, D (2009). *Plasma Process and Polymers*, *6* 399
[27] Sivasankar Reddy, A., Sreedhara Reddy, P., Uthanna, S. *et al.* (2006). *Phys. Status Solid (a)*, *203* 844
[28] Sivasankar Reddy, A., Venkata Rao, G., Uthanna, S. *et al.* (2005). *Physica B*, *370* 29
[29] Li, B. S., Akimoto, K., & Shen, A. (2009). *J. Cryst. Growth*, *311* 1102
[30] Noda, S., Shima, H. & Kinaga, H. A. (2013). *Journal of Physics: Conference Series*, *433* 012027
[31] Tauc, J., Grigorovici, R., & Vancu, A. (1966). *Physica Status Solid*, *15* 627
[32] Ray, S. C. (2001). *Solar Energy Materials & Solar Cells*, *68* 3–4
[33] Balamurugan, B., &Mehta, B. R. (2001). *Thin Solid Films*, *396* 90–96
[34] Scherrer, P. (1918). *Göttinger Nachrichten Gesell*, *2*, 98