

Modifications of structural and optical properties of copper oxide thin films by thermal annealing

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The structural modification of copper oxide thin films was investigated by controlling the thermal annealing atmosphere and temperature, which in turn affected their optical and electrical properties. Copper oxide thin films were deposited by spray pyrolysis deposition at 300 °C to give a uniform surface consisting of submicron-size grains with cubic Cu₂O crystalline structure. As the Cu₂O thin films were thermally annealed at less than 700 °C, they were transformed into the CuO phase. However, a mixed phase of CuO and Cu₂O was observed at temperatures above 800 °C. As the thermal annealing temperature was increased from 400 to 700 °C, the optical bandgap energy of the copper oxide thin films was decreased from 2.54 to 1.91 eV and the electrical charge carrier concentration was decreased gradually due to the improved crystalline quality. In this way, the crystalline structure of the copper oxide and its corresponding optical and electrical properties could be controlled by thermal annealing.

Key words: CuO, Cu₂O, Spray pyrolysis deposition, Thermal annealing.

Introduction

Copper oxide semiconductors have received strong attention for application to optical, electrical, and chemical devices such as solar cells, light-emitting diodes, transparent heaters, thin film transistors, and photocatalysts [1-7]. Copper oxide forms two stable crystalline phases: CuO and Cu₂O [5-7]. Cu₂O has a direct energy bandgap between 2.1 and 2.6 eV [8-10]. The many advantages offered by Cu₂O thin films include a long minority carrier diffusion length, a high hole concentration of 10¹⁶-10¹⁹ cm⁻³, and a high hole mobility of 50-100 cm²/V·sec at room temperature [8-10]. Therefore, they have been applied to the light absorbing layer or hole transport layer of solar cells and of photoelectrochemical cells for water decomposition [8-10]. The other crystalline phase, CuO, exhibits *n*-type semiconductor properties with a bandgap energy of 1.3-2.1 eV and offers chemical stability, non-toxicity, and low cost processing [11-14]. These characteristics make these oxides a promising material system for optoelectronic applications.

Recent research on the fabrication of copper oxide thin films has included hydrothermal processing, electro-deposition, sputtering deposition, atomic layer deposition, and ultrasonic-assisted spray pyrolysis deposition (SPD) [8-13]. SPD has received strong attention because it provides comparatively low cost processing and offers a larger area for mass production compared to other

vacuum technologies [12, 13]. In principle, SPD is a hybrid method of a wet process and chemical vapor deposition. Metal compounds dissolved in a source solution are transferred in the form of a spray and are thermally decomposed on the substrate surface to nucleate and grow the thin film [12, 13]. The structural and optical properties of the copper oxide thin films in the SPD system are influenced by the source flow rate, growth atmosphere, and substrate temperature [12]. For copper oxide, the formation of Cu₂O with a cubic structure and CuO with a monoclinic structure is sensitive to the deposition temperature and atmosphere, which makes it difficult to control these two crystalline phases [12]. In addition, the effect of post thermal annealing on the structural, electrical, and optical properties of the copper oxide thin films has not been fully elucidated. In this paper, we investigated the effect of thermal annealing atmosphere and temperature on the structural properties of the copper oxide thin films deposited by SPD and their corresponding effects on the films' optical and electrical properties.

Experimental Procedure

Fabrication

Copper oxide thin films were deposited on glass substrates using ultrasonic-assisted SPD. The glass substrates were cleaned in acetone, methanol, and deionized (DI) water for 5 min to remove organic pollutants and then loaded into a commercial SPD system (Nano SPD-TV500, Ceon, Korea). The source solution was prepared by dissolving 2 mM of copper

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acetylacetonate ($\text{Cu}(\text{acac})_2$, Sigma Aldrich), used as a chelating agent to improve the $\text{Cu}(\text{acac})_2$ solubility, and 4 mM of ethylenediamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$, Sigma Aldrich) in methanol. The solution was stirred at room temperature for 4 hrs and finally changed to a clear and homogeneous solution. The copper oxide thin films were deposited at 300 °C using an N_2 carrier gas for 60, 120, and 180 min. The N_2 flow rate was maintained constant at 15 L/min. To investigate the effect of thermal annealing on the optical and electrical properties of the copper oxide thin films, rapid thermal annealing (RTA, ECOPIA RTP-1300) was performed at temperatures between 400 and 800 °C in the N_2 and O_2 atmosphere. The thermal annealing time was fixed at 5 min with a ramping rate of 25 °C/min. The flow rate of the atmosphere gas was 10 L/min.

Characterization

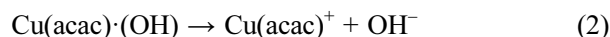
The morphologies of the copper oxide thin films were observed by scanning electron microscopy (SEM, Hitachi S-4800). The crystalline structure of the copper oxide thin films was measured by X-ray diffraction (XRD, PANalytical Empyrean). The electrical properties of the copper oxide thin films were characterized using Hall effect measurement (HMS-3500, ECOPIA). The transmittance and UV-visible absorption spectra of the copper oxide thin films were measured by using a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent).

Results and Discussion

The copper oxide thin films were deposited at 300 °C to fabricate the Cu_2O crystalline structure. Previous results reported for the SPD-growth of copper oxide thin films showed that the divalent Cu_2O was preferentially deposited rather than the CuO phase at temperatures lower than 400 °C [12]. To investigate the structural evolution during the deposition, the deposition time was varied from 60 to 180 min. Figure 1 shows the surface and cross-sectional SEM images of the copper oxide thin films deposited on the glass substrate with variation of the deposition time. As shown in Fig. 1(a), surface of the copper oxide thin films showed a uniform morphology consisting of nano-crystalline grain. Because

the growth temperature was lower than 400 °C, the atomic mobility on the substrate surface can be very low. This results in the formation of nano-crystalline grains. As the growth time was increased from 60 to 120 and to 180 min, larger grain size consisting of nano-crystalline particulates were observed. The limited surface atomic diffusion enabled the small grain size to be maintained even as the deposition time was increased, as shown in Figs. 1(b) and (c).

To investigate the crystalline structure of the copper oxide thin films, XRD was measured for the samples with different deposition times. As shown in Fig. 2, the XRD results for the samples mainly showed two peaks at 36.44° and 42.32°, which correspond to the (111) and (200) planes of the cubic Cu_2O (space group: $Pn-3m$; $a = 0.428 \text{ nm}$, JCPDS 78-2076) crystal, respectively. Because the thin films comprised small domains of Cu_2O sized less than 20 nm, the diffraction peaks were broad, which can be expected from the Scherrer equation relating the XRD peak broadness and the domain size. The absence of any additional peaks in the diffraction results indicates that no unintentional chemical species, such as CuO or Cu metallic compounds, were formed even with increasing deposition time. The overall reactions for the formation of the nanostructures can be summarized by the following reactions. The copper acetylacetonate [$\text{Cu}(\text{acac})_2$; $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$] used as the copper source is dissolved in the aqueous solution via the following reactions [12, 15]:



The chelating agent, ethylenediamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$), increases the solubility of the copper acetylacetonate by chelating the Cu cations by two amine-based ligands. The agent also promotes the uniform deposition of Cu_2O thin films on the substrate by preventing the random reaction between Cu cations and OH^- anions even at low temperature around 300 °C [16].

To investigate the effect of thermal annealing on the

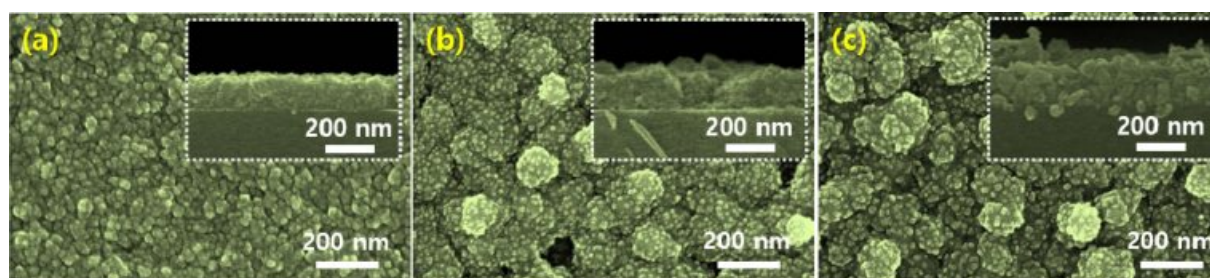


Fig. 1. Plane-view and cross-sectional-view SEM images of the copper oxide thin films with different deposition times: (a) 60 min, (b) 120 min, and (c) 180 min.

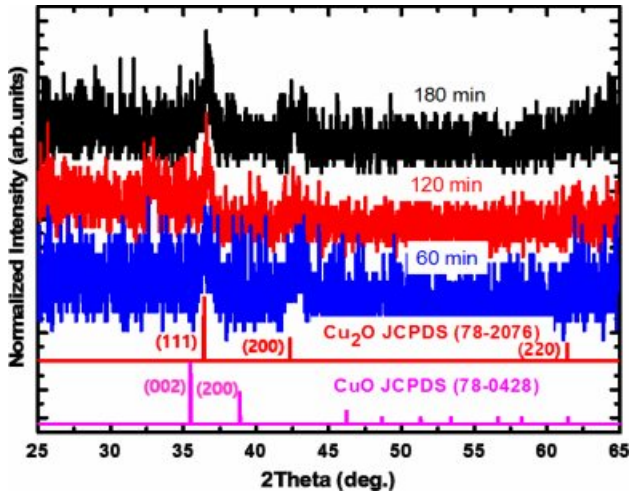


Fig. 2. Normalized θ - 2θ XRD patterns of the copper oxide thin films with different deposition times.

structural and optical properties of the Cu_2O thin films, the deposited thin films were annealed in the RTA system. Figure 3 shows the optical transmittance results of the Cu_2O thin films for the as-deposited film and for that thermally annealed at 600 °C in N_2 and O_2 gas atmosphere. The as-deposited Cu_2O thin film showed a transmittance over 80% at the wavelength around 600 nm. After the Cu_2O thin film was thermally annealed at 600 °C in N_2 and O_2 gas atmosphere, the transmittance decreased drastically in the visible spectral range and was maintained in the infrared spectral range. In general, the increase of the light absorption in the oxide thin film is originated from the phase transformation or increased defect formation. In this case, the increase of absorption would be attributed to the increased point defect during the annealing process. The optical transmittance decreased further when the annealing atmosphere was in the N_2 gas, which was attributed to the increased generation of oxygen vacancy-related point defects in the N_2 atmosphere because of high vapor pressure of oxygen atoms. The oxygen vacancy-related point defects produce free charge carriers to increase the absorption of light [17]. This result indicates that thermal annealing in O_2 atmosphere is better for avoiding the generation of oxygen vacancy-related point defects.

To investigate the dependence of the optical and structural properties on the thermal annealing temperature, the Cu_2O thin films were thermally annealed between 400 and 800 °C in O_2 atmosphere. Figure 4 shows the temperature-dependent structural evolution of the Cu_2O thin films. At an annealing temperature of 400 °C, the peaks corresponding to Cu_2O phase disappear. As the temperature is increased from 500 to 700 °C, new peaks appear at 35.5° and 38.9°, which correspond to the (002) and (111) planes of the monoclinic CuO phase (space group: $C2/c$; $a = 0.32501 \text{ nm}$, $b = 0.343 \text{ nm}$, c

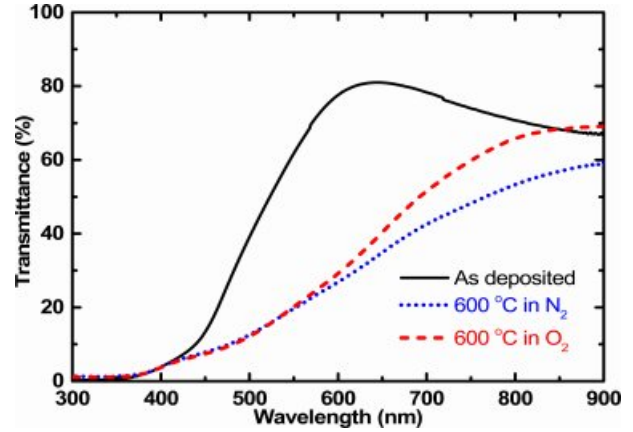


Fig. 3. Transmittance spectra of the copper oxide thin films that were thermally annealed at 600 °C in N_2 and O_2 atmosphere.

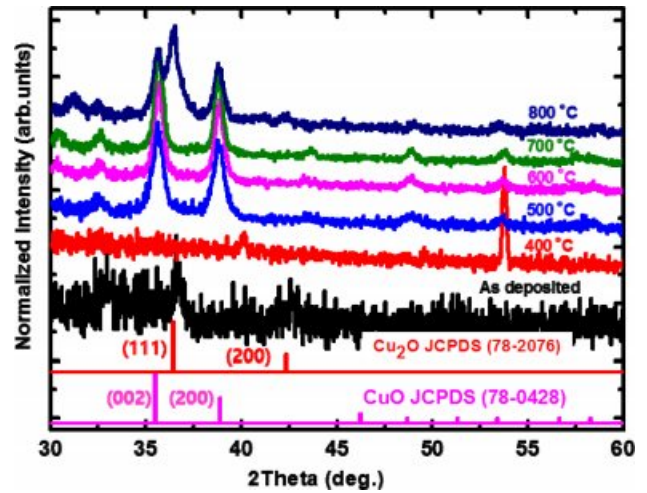


Fig. 4. Normalized θ - 2θ XRD patterns of the copper oxide thin films according to the thermal annealing temperature in O_2 atmosphere.

$= 0.5131 \text{ nm}$, $\beta = 99.549^\circ$, JCPDS 78-0428) [18]. This was attributed to the ionization of the Cu element into the Cu^+ ion to form a Cu_2O phase at temperatures lower than 400 °C, but into the divalent Cu^{2+} ions to form a CuO phase at temperatures higher than 500 °C. The full-width at half maximum of the peak became narrower as the temperature was increased to 700 °C, which indicates the improved crystalline quality of the copper oxide thin films. At temperatures higher than 800 °C, another peak corresponding to the (111) plane of the Cu_2O phase starts to appear, which leads to the formation of a mixed phase of CuO and Cu_2O . As the temperature is increased further, the CuO phase becomes unstable and is transformed into the Cu_2O phase by evaporation of the oxygen atoms.

Figure 5 shows the dependence of the optical properties of copper oxide thin films on temperature. As shown in the inset of Fig. 5(a), the as-deposited Cu_2O thin film shows a brown surface because the energy bandgap of Cu_2O is 2.1-2.6 eV. As the annealing temperature is

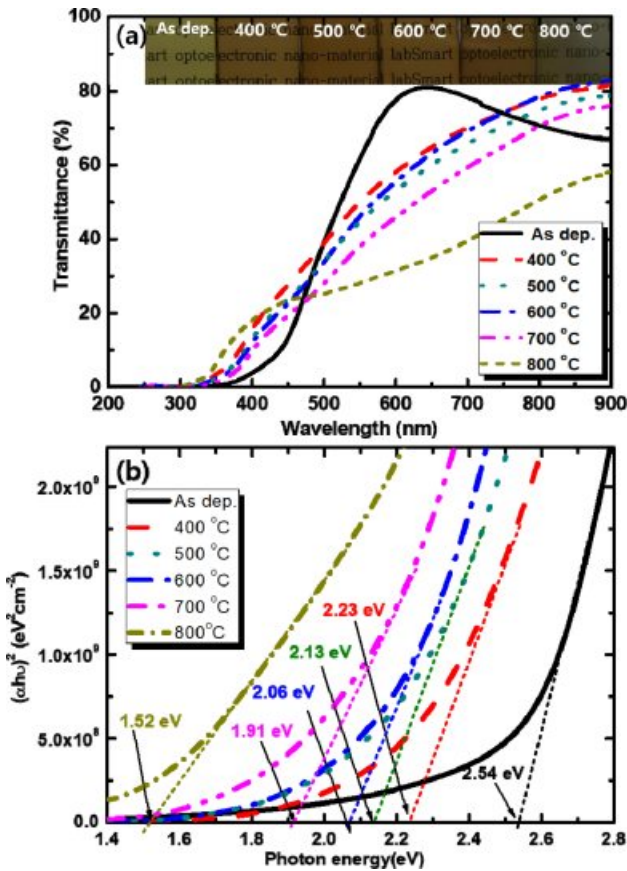


Fig. 5. (a) UV-vis optical absorption spectra of the copper oxide thin films according to the thermal annealing temperature in O_2 atmosphere. The inset shows the sample images observed by the naked eyes. (b) Specific absorption band edges calculated from Tauc-plot studies. Variation of $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) to obtain the direct band gap of the copper oxide thin films.

further increased up to 700 °C, the sample becomes reddish. The transmittance decreases gradually as the annealing temperature is increased from 400 to 700 °C. The bandgap energy of the samples was estimated by plotting the photon absorption coefficient (α) versus the photon energy ($h\nu$), as shown in Fig. 5(b). The optical bandgap energy was estimated by the Tauc and Davis-Mott expression [19]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (5)$$

In the equation, A and E_g are the proportional constant and the bandgap energy, respectively, and n is a characteristic constant that determines whether the electronic transition is direct ($n=0.5$) or indirect ($n=2$) [19]. The plots were well fitted for $n=0.5$, indicating that the copper oxide was a direct bandgap material. The bandgap energy of the as-deposited Cu_2O thin film was determined to be 2.54 eV, which is similar to the reported bandgap energy of the bulk Cu_2O [7-10]. As the annealing temperature is increased from 400 to 800 °C, the estimated optical bandgap energy decreases

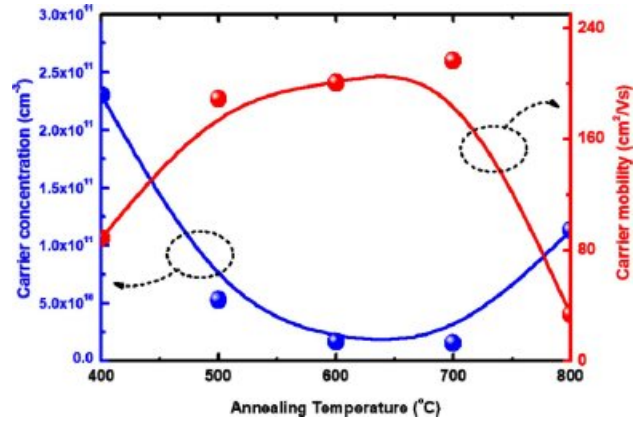


Fig. 6 Charge carrier concentration and carrier mobility of the copper oxide thin films according to the thermal annealing temperature.

from 2.23 to 1.52 eV. The bandgap energy of the CuO is 1.3~2.1 eV [10-12]. Therefore, these results indicate that the as-deposited Cu_2O phase changes to CuO phase as the annealing temperature is increased. This result is consistent with the XRD structural investigations.

To investigate the effect of thermal annealing on the electrical properties of Cu_2O thin films, Hall effect measurement was performed at room temperature. The copper oxide thin films showed highly resistive n -type characteristics with only a small amount of charge carrier concentration in the order of 10^{11} cm^{-3} . As shown in Fig. 6, the charge carrier concentration decreases while the carrier mobility increases, as the annealing temperature is increased up to 700 °C. This was attributed to the improved crystalline quality of the CuO as the annealing temperature was increased. Because the copper oxide thin films were annealed in an oxygen atmosphere, their crystalline quality was improved without evaporation of oxygen from the thin film, as shown in the XRD results. As the thermal annealing temperature is increased further up to 800 °C, the charge carrier concentration increases but the mobility decreases, because the decomposition of the CuO crystalline phase above this temperature leads to the formation of various point defects. Therefore, the copper oxide phase can be modified by thermal annealing, which enables their optical and electrical properties to be controlled. These findings will support the development of improved copper oxide-based optoelectronic devices.

Conclusions

In conclusion, we investigated the structural evolution of copper oxide thin films by controlling the thermal annealing, which in turn affected their optical and electrical properties. The XRD and SEM results showed that the as-deposited copper oxide thin films were composed of small grains with Cu_2O phase. As these Cu_2O thin films were thermally annealed between 500

and 700 °C, they were transformed into the CuO phase. Thermal annealing at 800 °C resulted in the formation of a mixed phase of CuO and Cu₂O. As the thermal annealing temperature was increased from 400 to 800 °C, the optical bandgap energy of the copper oxide thin films decreased from 2.54 to 1.52 eV. The electrical charge carrier concentration of the copper oxide thin films was decreased gradually as the thermal annealing temperature was increased from 400 to 700 °C due to the improved crystalline quality. Therefore, the crystalline structure of the copper oxide thin films could be modified by thermal annealing, which enabled their optical and electrical properties to be controlled. Considering the optical and electrical properties of copper oxide thin films, the temperature between 500 and 700 °C in the O₂ gas atmosphere can provide the optimal thermal annealing condition.

Acknowledgements

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References

1. R. N. Briskman, *Sol. Energy Mater. Sol. Cells* 27 (1992) 361-368.
2. B. P. Rai, *Sol. Cells* 25 (1988) 265-272.
3. X. Deng, Q. Zhang, E. Zhou, C. Ji, J. Huang, M. Shao, M. Ding, and X. Xu, *J. All. Comp.* 649 (2015) 1124-1129.
4. R. Laskowski, P. Blaha, and K. Schwarz, *Phys. Rev. B* 67 (2003) 075102-075110.
5. J. T. Zhang, J. F. Liu, Q. Peng, X. Wang, and Y. D. Li, *Chem. Mater.* 18 (2006) 867-871.
6. H. Zhu, J. Wang, and G. Xu, *Cryst. Growth Des.* 9 (2009) 633-638.
7. A. S. Zoolfakar, R. A. Rani, A. J. Morfa, A. P. O'Mullane, and K. Kalantar-zadeh, *J. Mater. Chem. C* 2 (2014) 5247-5270.
8. R. Wick and S. D. Tilley, *J. Phys. Chem. C* 119 (2015) 26243-26257.
9. J. Luo, L. Steier, M.-K. Son, M. Schreier, M. T. Mayer, and M. Grätzel, *Nano Lett.* 16 (2016) 1848-1857.
10. Y. Yang, D. Xu, Q. Wu, and P. Diao, *Sci. Rep.* 6 (2016) 35158.
11. Md. A. Hossain, R. Al-Gaashani, H. Hamoudi, M. J. A. Marri, I. A. Hussein, A. Belaidi, B. A. Merzougui, F. H. Alharbi, and N. Tabet, *Mat. Sci. Semicon. Proc.* 63 (2017) 203-211.
12. I. S. Han and I. K. Park, *Kor. J. Mater. Res.* 28 (2018) 516-521.
13. C. Y. Kim, S. G. Cho, S. Park, and D. K. Choi, *J. Ceram. Process. Res.* 10 (2009) 851-854.
14. M. Y. Lee, S. H. Kim, and I. K. Park, *Physica B* 500 (2016) 4-8.
15. Y. C. Zhang, J. Y. Tang, G. L. Wang, M. Zhang, and X. Y. Hu, *J. Crystal Growth* 294 (2006) 278-282.
16. K. Chen, C. J. Chiang, and D. Ray, *Mater. Lett.* 95 (2013) 172-174.
17. L. Wang, Y. Yang, and T. J. Marks, *Appl. Phys. Lett.* 87 (2005) 161107.
18. I. Kaya, C. Cetin, H. Aydin, Z. Katircioğlu, B. Z. Büyükbekar, M. S. Yavuz, M. Uyaner, V. Kalem, and H. Akyildiz, *J. Ceram. Process. Res.* 16 (2015) 648-655.
19. J. Tauc, *Opt. Acta Int. J. Opt.* 17 (1974) 952-952.