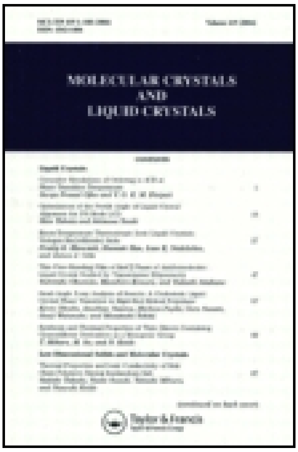

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P-type Copper Oxide Thin Films Deposited by Vacuum Thermal Evaporation

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Using vacuum thermal evaporation combined with post-deposition annealing, we obtained p-type copper oxide films with a hole concentration on the order of 10^{16} cm^{-3} *and Hall mobility of over 5* cm^2 V^{-1} s^{-1}*. These properties are in the range that can be used for an active layer of p-channel thin film transistors. We used air thermal annealing to convert n-type conduction of as-deposited films to p-type conduction, and determined that vacuum thermal annealing did not change the n-type conductivity of the as-deposited films.*

Keywords Annealing; copper oxide; evaporation; p-type

Introduction

Hydrogenated amorphous silicon (a-Si:H) and polycrystalline silicon (p-Si) technologies are currently the mainstream technologies used in large area flat panel electronics. a-Si:H and p-Si films are essential in producing flat panel displays (FPDs) such as thin film transistor liquid crystal displays (TFT-LCDs) and active matrix organic light-emitting diodes (AM-OLEDs). In addition to FPDs, thin film solar cells and flat panel sensors use silicon films. These silicon thin film technologies are reaching limits as the advent of new products requiring higher performance and lower cost thin film semiconductors such as AM-OLEDs and system-on-panel (SOP) FPDs. Silicon thin films cannot satisfy these demands due to the low performance of a-Si:H and the high production costs of poly-Si. Oxide semiconductor technologies are expected to be promising solutions to overcome the limits of silicon technologies. Carrier mobility and the production costs of oxide semiconductors are comparable to the carrier mobility of p-Si and the production costs of a-Si:H, respectively. Significant efforts have been made to develop commercial technologies for oxide semiconductors. The majority of these efforts focus on n-type oxide semiconductors [1–3] due to difficulties in obtaining p-type oxide semiconductors with appropriate properties for semiconductor devices such as thin film transistors.

The advantages of p-type semiconductors over n-type semiconductors are considerable. P-channel TFTs composed of p-type semiconductors are better at driving AM-OLEDs.

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Because TFTs are connected to the bottom anodes of OLEDs, if an n-channel TFT is used, the variation in voltage drop over the OLED affects the drain current of the TFT. However, the variation does not affect the drain current of a p-channel TFT in saturation mode. Complementary metal oxide semiconductor (CMOS) circuits composed of p- and n-channel TFTs are necessary for fabricating high performance periphery circuits on glass substrates such as gate drivers and data drivers. Studies have been performed on p-type oxide semiconductors of several material systems based on zinc oxide [4,5], tin oxide [6,7], and copper oxide [8,9]. Zinc oxide has intrinsic n-type conduction properties. Doping processes have been studied in order to obtain p-type conduction properties from zinc oxide films. However, the instability of the p-type conduction of zinc oxides has not been clearly solved until now. Tin monoxide (SnO) and cuprous oxide (Cu_2O) have p-type conduction properties in the crystalline phase. Researchers have described obtaining p-type semiconducting films using SnO [6,7] and Cu_2O [8,9] that have properties applicable to active layers of TFTs. Pulsed laser deposition (PLD) and sputtering methods have been mainly used in studies to obtain the p-type oxide semiconductor films on glass substrates for TFTs. PLD is not suitable to the process using large substrates. In addition, it is difficult to obtain stable p-type films using sputtering methods. Studies of p-type oxide semiconductors for TFTs on glass substrates are at an early stage; thus, further studies on materials and processes are needed to achieve a practical technology.

We examined the properties of copper oxide thin films deposited by vacuum thermal evaporation using Cu_2O powder as a source material. Post-deposition annealing conditions were evaluated to obtain proper characteristics that are adoptable as an active layer for TFTs. The vacuum thermal evaporation method can be used in depositing thin films on large area substrates. In addition, the costs for the equipment, operations, and materials used in this method are lower than those of other thin-film deposition methods such as PLD, plasma-enhanced chemical vapor deposition, and sputtering. Thus, the proposed materials and process can provide a practical way to obtain low-cost stable p-type oxide semiconductors.

Experiments

Vacuum thermal deposition of copper oxide films was carried out using a CETUS OL100 evaporation system (SELCOS, Korea) at a pressure of under 5×10^{-6} Torr. Resistance heating using tungsten boats was used to evaporate 99.99% Cu_2O power purchased from Sigma-Aldrich (USA). There was no substrate heating, and the surface temperature of the substrate was kept under 80°C. The deposition rate was 1 Å/s, and 0.5 mm-thick Eagle XG glass (Samsung Corning Precision Glass, Korea) substrates were used to fabricate the samples. The film thickness was fixed at 200 nm. After the evaporation process, the samples were thermally annealed. Thermal annealing in a vacuum was performed using a vacuum probe station (OmniProbe, Woosin CryoVac, Korea), and was performed in air in an electric box furnace (DongSeo Science, Korea). Carrier density and Hall mobility were obtained through Hall effect analysis using an HMS-3000 Hall effect measurement system (Ecopia, Korea) at room temperature. Samples were stored in a nitrogen environment between measurements and processes to avoid unintentional changes of the properties.

Results and Discussion

The carrier concentration and Hall mobility obtained from our Hall effect measurements versus the duration time of thermal annealing in air are shown in Figs 1(a) and (b),

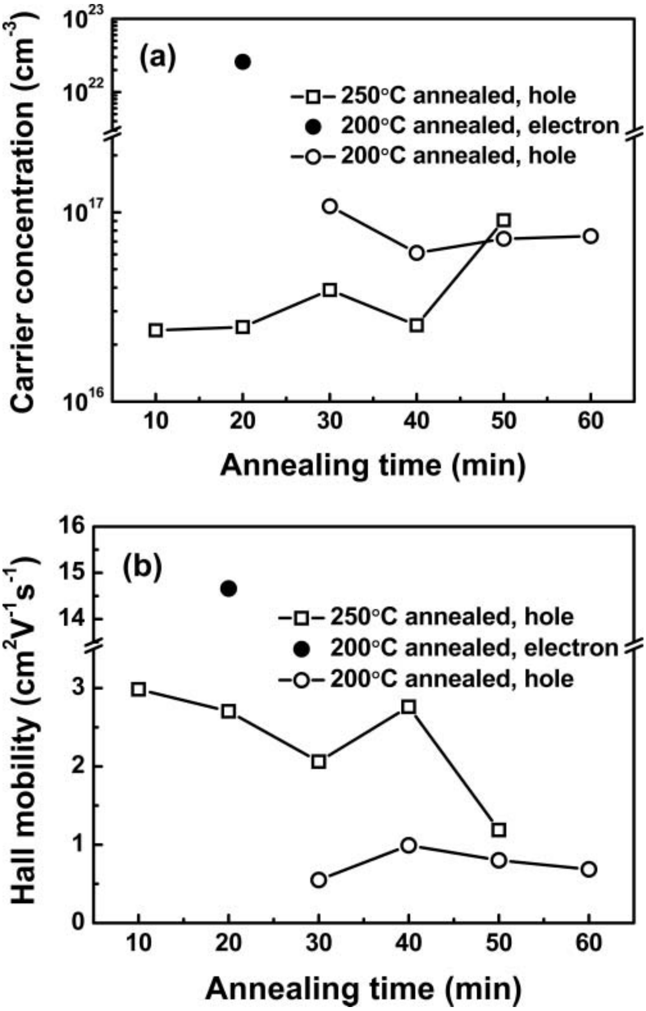

Figure 1. (a) Carrier concentration, and (b) Hall mobility obtained from Hall effect measurements according to the duration time of thermal annealing in air.

respectively. The as-deposited films had n-type conduction properties with an electron density of 2.4 × 10^{22} cm^{-3} and Hall mobility of 1.3 cm^2 V^{-1} s^{-1} (these are not shown on the graph). For the 200°C annealed samples, a brief (20 min) annealing gave a slightly higher electron density of 2.6 × 10^{22} cm^{-3} and a much higher Hall mobility of 14.6 cm^2 V^{-1} s^{-1} than the as-deposited samples. As the annealing time increased, copper oxide films showed p-type conduction properties with a hole concentration on the order of 10^{16} cm^{-3} and Hall mobility of under 1 cm^2 V^{-1} s^{-1}. For the 250°C annealed samples, p-type conduction was obtained even with a short annealing time of 10 min. The hole concentration was on the order of 10^{16} cm^{-3} and the Hall mobility was over 1 cm^2 V^{-1} s^{-1}. The carrier concentration and Hall mobility obtained from the Hall effect measurements versus the air thermal annealing temperature are shown in Figs 2(a) and (b), respectively. The annealing time was 2 h. The sample annealed at 50°C showed slightly higher electron density and lower Hall mobility than those of the as-deposited sample; the electron density

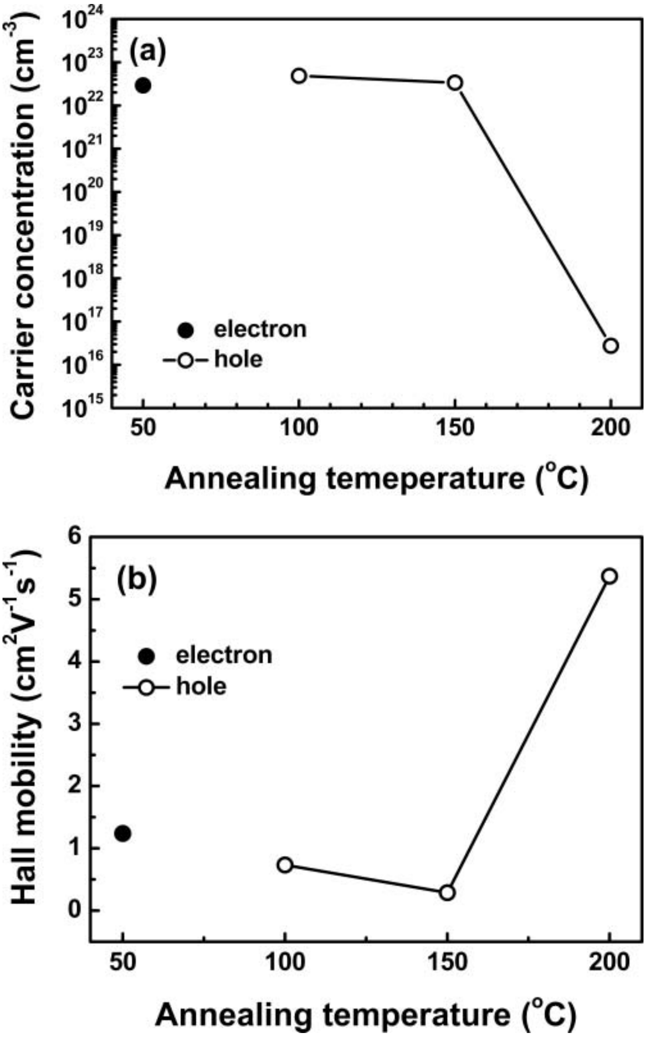

Figure 2. (a) Carrier concentration, and (b) Hall mobility obtained from Hall effect measurements according to the air thermal annealing temperature.

and Hall mobility were 2.9×10^{22} cm^{-3} and 1.24 cm^2 V^{-1} s^{-1}, respectively. Samples annealed at higher temperatures had p-type conduction properties. The hole density decreased from on the order of 10^{22} cm^{-3} to 10^{16} cm^{-3} as the annealing temperature increased from 100°C to 200°C. Hall mobility increased from under 1 cm^2 V^{-1} s^{-1} to over 5 cm^2 V^{-1} s^{-1} as the annealing temperature increased.

Copper vacancies in Cu_2O films acted as acceptors, causing p-type conduction [9]. As shown in Fig. 2(a), a higher annealing temperature caused a lower hole concentration; the higher temperature made more stable Cu_2O structures so that copper vacancies generating the holes could be reduced. As the annealing time increased, the conduction properties changed from n-type to p-type, as demonstrated by the results of the 200°C air thermal-annealed samples shown in Fig. 1. In the case of 250°C annealing, p-type conductivity was obtained from the 10 min annealed sample in contrast to the 200°C annealing case in which 30 min of annealing time was required to obtain p-type conductivity. Based on our results, both temperature and time seemed to be the factors promoting the oxidation process. As shown in Figs 1 and 2, higher mobility was obtained from samples with lower carrier concentration.

Carrier concentration and Hall mobility obtained from Hall effect measurements versus the vacuum thermal annealing temperature are shown in Figs 3(a) and (b), respectively. The annealing pressure was about 0.1 Torr and the annealing time was 1 h. All samples annealed in a vacuum had n-type conduction properties; the electron density was kept at the order of 10^{22} cm^{-3} and there were no noticeable changes in the electron density. Hall mobility increased from 1.4 cm^2 V^{-1} s^{-1} to 11.4 cm^2 V^{-1} s^{-1} as the annealing temperature increased.

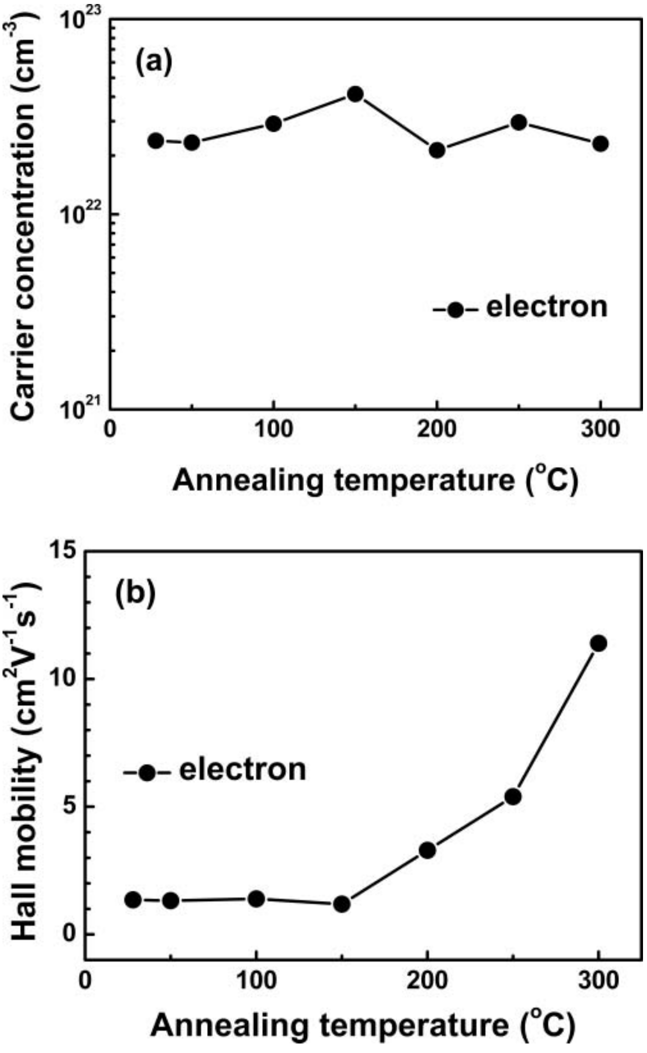

Figure 3. (a) Carrier concentration, and (b) Hall mobility obtained from Hall effect measurements according to the vacuum thermal annealing temperature.

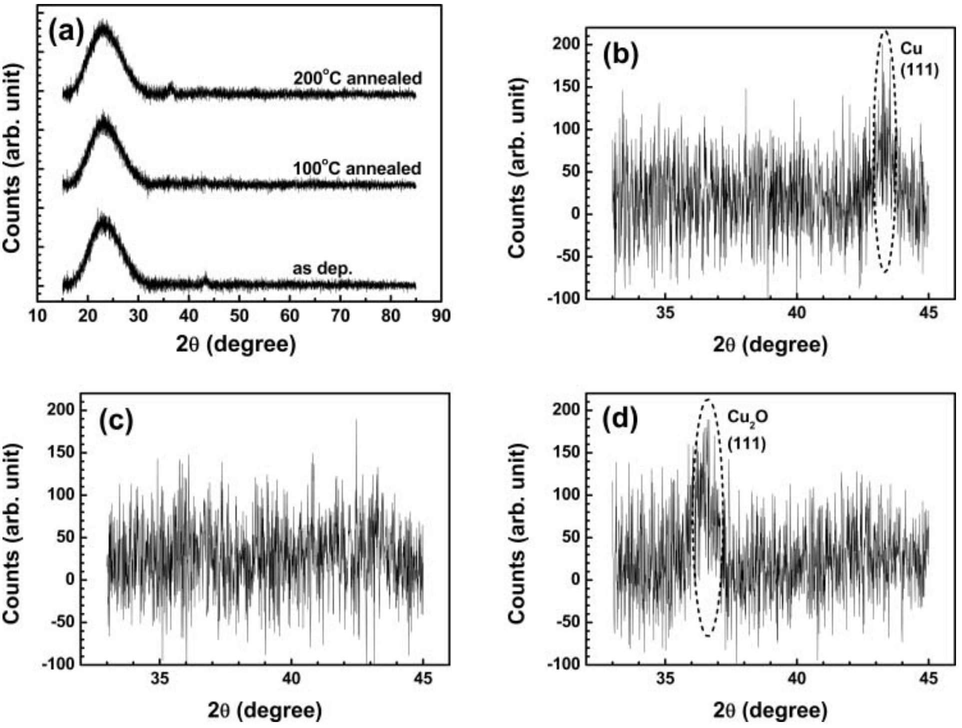

Figure 4. (a) XRD results from as-deposited, 100°C, and 200°C air thermal-annealed copper oxide films, (b) peak from as-deposited sample, (c) result from 100°C air thermal-annealed sample, and (d) peak from 200°C air thermal-annealed sample.

In contrast to air thermal annealing, vacuum thermal annealing did not change the conduction type: n-type conduction was retained, and the carrier concentration was nearly unchanged by vacuum thermal annealing. Hall mobility increased as the annealing temperature increased. The lack of oxygen inhibited the oxidation process causing the p-type Cu_2O phase. A higher annealing temperature could cause the crystallization of the as-deposited amorphous films; therefore, mobility could increase according to the increase in annealing temperature.

X-ray diffraction (XRD) results of the copper oxide films are shown in Fig. 4. XRD peaks from as-deposited, 100°C, and 200°C air thermal-annealed copper oxide films are shown in Fig. 4(a). The peak shapes appeared to be those of an amorphous phase; however, a few weak crystalline peaks could be found. Fig. 4(b) shows the results from an as-deposited sample. A peak at about 43.4° was identified as the peak from the Cu (111) plane [8]. As shown in Fig. 4(c), the 100°C air thermal-annealed sample had no peaks. As shown in Fig. 4(d), the 200°C air thermal-annealed sample had a peak at 36.6°□ that was identified as the peak from the Cu_2O (111) plane [8].

Optical transmittance data of as-deposited, 1 h, and 2 h annealed films are shown in Fig. 5(a). Thermal annealing was performed in air at 200°C. Longer annealing gave higher transmittance in the visible range, as shown in the figure. Derivatives of the optical transmittance shown in Fig. 5(a) are shown in Fig. 5(b). We obtained the approximate optical band gap from the maximum points of the derivatives [10]. The estimated optical band gap of air thermal-annealed films was about 2 eV.

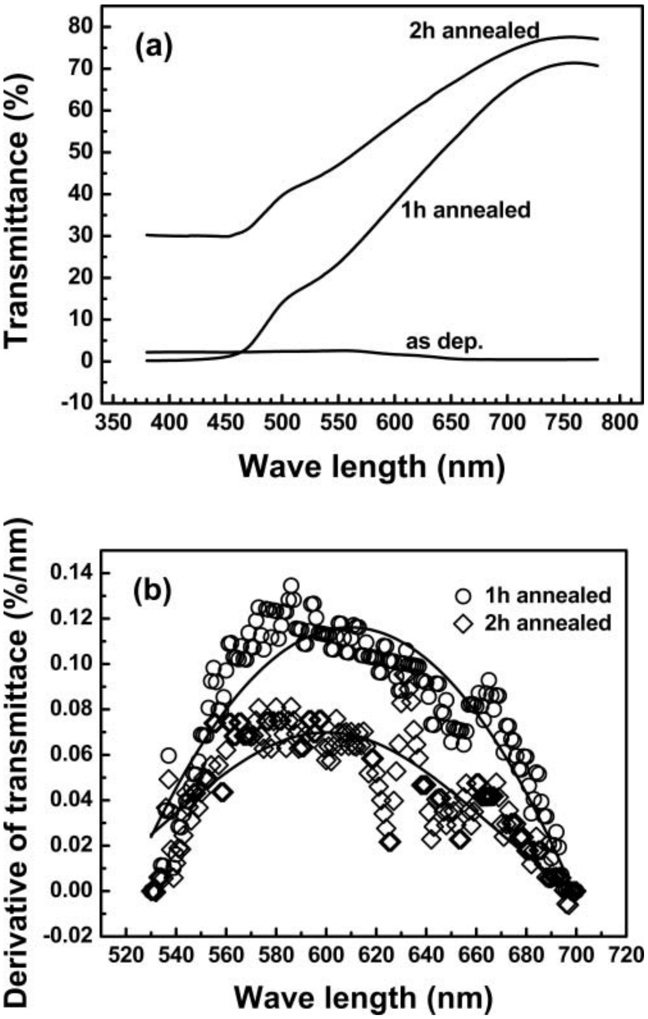

Figure 5. (a) Optical transmittance data from as-deposited, 1 h, and 2 h air thermal-annealed copper oxide films, and (b) derivatives of optical transmittance data of 1 h and 2 h air thermal-annealed copper oxide films. Solid lines represent Gaussian fitting.

Copper oxide films deposited by vacuum thermal evaporation using a Cu_2O source had a mixed phase composed of a main amorphous phase and a partial crystalline phase. As-deposited films had a copper phase; the Cu (111) peak from XRD data and the n-type conduction of as-deposited films support this observation. As the evaporation process was performed at a high vacuum (on the order of 10^{-6} Torr), the oxygen content in the deposited films seemed to decrease; therefore, the deposited films had a near-copper phase. Air thermal annealing converted n-type conductivity of as-deposited films to p-type conductivity; the oxygen supply from the air and the elevated annealing temperature prompted the oxidation process that converted the copper phase to a copper oxide phase. As the annealing temperature increased, oxidation was enhanced; the copper (111) XRD peak disappeared, and the Cu_2O (111) XRD peak appeared as the annealing temperature increased. The optical band gap of 2 eV obtained after the air thermal annealing was similar to the previous data from Cu_2O films[11,12]. Therefore, the optical property shown in Fig. 5 could be evidence of a Cu_2O phase after air thermal annealing.

Conclusions

We studied copper oxide films deposited by vacuum thermal evaporation using a Cu_2O powder source. As-deposited films showed n-type conductivity, and XRD peak analysis revealed that the films had a partial Cu (111) crystalline phase mixed with a major amorphous phase. P-type Cu_2O films were obtained using this process combined with thermal annealing after the deposition. Air thermal annealing converted the n-type conduction to p-type conduction, and a hole concentration on the order of 10^{16} cm^{-3} and a Hall mobility of over 5 cm^2 V^{-1} s^{-1} were obtained after the post-deposition air thermal annealing. A hole concentration of 10^{16} cm^{-3} was low enough for an active layer of TFT, and a Hall mobility of 5 cm^2 V^{-1} s^{-1} was adoptable as an active layer for the TFTs.

From this study, we obtained copper oxide films that could be used as an active layer for p-channel TFTs, and determined the post-deposition annealing conditions required to produce proper p-type copper oxide films. Our results with low cost and easy-to-process p-type copper oxide could be useful in developing commercial oxide-semiconductor technologies.

Acknowledgment

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