Original Article

Influence of chemical composition on phase transformation and optoelectronic properties of Cu–Cr–O thin films by reactive magnetron sputtering

Du-Cheng Tsai\textsuperscript{a}, Zue-Chin Chang\textsuperscript{b}, Bing-Hau Kuo\textsuperscript{a}, Chung-Ming Chen\textsuperscript{a}, Erh-Chiang Chen\textsuperscript{b}, Fuh-Sheng Shieu\textsuperscript{a,*}

\textsuperscript{a} Department of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan, ROC
\textsuperscript{b} Department of Mechanical Engineering, National Chin-Yi University of Technology, Taichung 41170, Taiwan, ROC

\textbf{Article history:\textsuperscript{1}}
Received 13 November 2017
Accepted 21 May 2018
Available online 6 July 2018

Keywords:
Sputtering
Ceramic coating
Phase change
Coating process

\textbf{Abstract}

Cu–Cr–O films were co-sputtered from Cu and Cr targets on fused silica substrates. Then, these films were annealed at 700 °C for 2 h under controlled Ar atmosphere. \([\text{Cu}] / [\text{Cr}]\) ratio was increased from 0.59 to 2.02 by increasing the Cu-target power from 10 W to 52 W. When the film was prepared at Cu-target power of 10 W, a pure spinel CuCr\textsubscript{2}O\textsubscript{4} phase was formed in the film. As the Cu-target power increased to 22 W, the phase transformed gradually from spinel CuCr\textsubscript{2}O\textsubscript{4} to delafossite CuCrO\textsubscript{2}. Further increase of Cu-target power resulted in the appearance of an additional monoclinic CuO phase. The \([\text{Cu}] / [\text{Cr}]\) ratio was approximately 1 at Cu-target power of 22 W, which caused the film to exhibit pure delafossite CuCrO\textsubscript{2} phase and high crystallinity. Accordingly, optimum electrical conductivity and visible transparency were achieved for the pure CuCrO\textsubscript{2} film prepared at Cu-target power of 22 W with a figure of merit of \(1.51 \times 10^{-4} \Omega^{-1}\). The formation of the CuO and CuCr\textsubscript{2}O\textsubscript{4} phase was confirmed to deteriorated optoelectronic properties of films.

\(\copyright\) 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Transparent conducting oxide films with n-type conductivity, such as Sn-doped In\textsubscript{2}O\textsubscript{3} [1], Al-doped ZnO [2], and Sb-doped SnO\textsubscript{2} [3], are commonly used as transparent electrodes in touch panels, flat-panel displays, and solar cells. The development of p-type transparent conducting oxide films potentially led to the fabrication of transparent p–n junctions devices.

A series of p-type TCOs with delafossite structures such as CuAl\textsubscript{2}O\textsubscript{4} [4], CuCrO\textsubscript{2} [5], CuInO\textsubscript{2} [6], CuFeO\textsubscript{2} [7], and SrCu\textsubscript{2}O\textsubscript{2} [8] has been reported to exhibit good p-type conductivity. Among the Cu-based delafossites, CuCrO\textsubscript{2} has the highest p-type electrical conductivity. In addition, a transparent pn-junction has been demonstrated using p-type CuCrO\textsubscript{2} film and n-type ZnO film prepared by magnetron sputtering deposition [9].

Basing on the successful preparation of p-type CuAl\textsubscript{2}O\textsubscript{4} films [4], researchers have developed different thin-film deposition techniques for depositing delafossite materials. Preparation and characterization of CuCrO\textsubscript{2} thin films by pulsed laser
deposition [10], chemical vapor deposition [11], sol–gel [12], hydrothermal synthesis [13], and sputtering [14–16] have been reported. In processes involving electronic devices, sputtering deposition is one of the most widely used film deposition techniques for large-area substrates. In the sputtering deposition techniques for compound material films, a sintered polycrystalline source is often used as the target material. Barnabé et al. synthesized delafossite Mg-doped CuCrO₂ films by radio frequency (RF) magnetron sputtering technique using the CuCr₃₋₉ₓMgₓO₃₋₂O₂ target fabricated by sintering Cu₂O, Cr₂O₃, and MgO powders [15]. The film possesses a maximum Haak’s figure of merit (FOM) value of about 1.5 × 10⁻⁷ Ω⁻¹ after annealing under vacuum at about 600 °C for 4 h; its light transmittance can reach 63% in the wavelength between 400 and 800 nm, while the film’s electrical resistivity is about 0.71 Ω cm. However, sintering the polycrystalline CuCrO₂ source from commercial binary oxide sources is difficult using a solid-state reaction at temperatures higher than about 1000 °C for more than 1 day. Another effective way to prepare CuCrO₂ thin film is to deposit directly from Cu and Cr metal targets through reactive DC sputtering in an oxygen atmosphere in the dual-target sputtering system. This method not only eliminates the intermediate procedure of CuCrO₂ powder preparation, but also because of the higher conductivity of metal powders compared with CuCrO₂ powder, DC sputtering technique can more adequately be applied. Moreover, the chemical composition of films can affect phase transformation and modify opto-electronic properties themselves. ([Cu]/[Cr]) ratio in the films can be controlled by changing the individual target power in the dual-target sputtering system. The research and exploration of Cu–Cr–O with various [Cu]/[Cr] ratios is a worthwhile endeavor. Sun et al. have reported the preparation of Mg-doped CuCrO₂ films from metallic Cr, Cu, and Mg targets through DC reactive magnetron sputtering in a mixed Ar + O₂ atmosphere [16]. The best FOM value of about 2.17 × 10⁻⁸ Ω⁻¹ can be obtained when the film is annealed at 750 °C for 2 h under vacuum treatment. It shows an electrical resistivity of 3.70 Ω cm and a light transmittance of 54.23% in the wavelength between 380 and 780 nm.

In this study, we propose the synthesis of Cu–Cr–O thin films by DC reactive magnetron sputtering using Cu and Cr metallic targets. This method allows the perfect control of the [Cu]/[Cr] ratio during delafossite coating and possesses a higher deposition rate compared with RF sputtering. Phase and optoelectronic properties of the various Cu–Cr–O oxide films are significant for the fundamental understanding of their optoelectronic performance. This work aims to study the effects of film [Cu]/[Cr] ratio on the properties of the material, as well as analyze and explore its phase transformation, structure, and optical and electrical properties.

2. Experimental

Cu–Cr–O films were formed in a high-vacuum dual-target sputter deposition system by DC magnetron sputtering onto a fused silica substrate using Cu and Cr targets with diameters of 4 in. During dual-target sputter deposition, the distance between the target and the substrate was 50 mm and the deposition angle was 60° relative to the substrate. The sputtering system comprised a stainless steel vacuum chamber and a turbo molecular pump with a rotary pump, which provided an ultimate vacuum of 6.0 × 10⁻⁶ Torr before the gases were introduced to the system. The Cr-target power was fixed at 150 W, and the Cu-target power was set within the range of 10–52 W to obtain films with various compositions, phases, and optoelectronic properties. Prior to thin-film deposition, the target surface was cleaned by bombarding with Ar⁺ ions for 10 min. During the film sputtering deposition, Ar and O₂ gases were purged into the chamber at an O₂/(O₂ + Ar) gas mass flow ratio of 75%. The Ar flow rates and O₂ flow rates were set to be 12.5 and 37.5 sccm, respectively. The chamber pressure for film deposition was 3.0 × 10⁻⁵ Torr, and the film was deposited on fused silica substrate at room temperature. To increase the homogeneity of the film, the rotation speed of the specimen holder was set to 15 rpm. The films were deposited onto fused silica substrates at room temperature for 40 min. In our previous study, a post-deposition annealing at 700 °C in an inert atmosphere was necessary to form the delafossite structure, and a maximum FOM was observed [14]. This temperature was considered as the optimal temperature for the study. Thus, the specimens were then annealed under Ar (99.999% pure) atmosphere in the tube furnace under controlled partial oxygen pressure of 7.0 × 10⁻⁵ atm. The annealing temperature was kept constant at 700 ± 5 °C with a heating rate of 5 °C/min for 2 h. The specimens were cooled to room temperature at the same rate of 5 °C/min.

The chemical compositions of the coatings were determined by electron spectroscopy for chemical analysis (ESCA, PHI 500 VersaProbe) with monochromatic Al Kα radiation. X-ray diffraction (XRD, MAC SCIENCE MPXIII, BRUKER) measurements were carried out with a normalized grazing angle of incidence θ = 1°. The system was operated at 40 kV and 30 mA with Cu Kα radiation. The scanning speed was 0.25°/min with ±2θ angles ranging from 20° to 80°. The rotation speed of sample was 21,600/min. XRD analysis was performed on all deposited films to investigate the effects of post-annealing on the structures. Field emission scanning electron microscope (FESEM, JEOL JSM-6700F) was used to analyze the film morphology. An ultraviolet/visible spectrophotometer (UV–vis, HITACHI U3010) was used to measure light transmittance. The electrical properties of the film were determined using Hall-effect measurements (ECOPIA HMS-2000).

3. Results and discussion

Fig. 1 presents the elemental composition of the Cu–Cr–O coatings prepared at various Cu-target powers. As the Cu-target power increased, the Cu levels in the coatings linearly increased and caused a corresponding decrease in Cr content. As the Cu-target power increased from 10 W to 52 W, the Cu content increased from 14.6 at.% to 31.5 at.%, whereas, the Cr content decreased from 24.6 at.% to 15.6 at.%. The Cu/Cr ratio of the coatings prepared at Cu-target powers of 10, 14, 18, 22, 32, and 52 W was 0.59, 0.79, 0.86, 1.02, 1.29, 1.62, and 2.02, respectively. Moreover, it is observed that low Cu-target power resulted in high O₂ content, which may be attributed to the low deposition rates [17].
During the sputtering process, Cu and Cr reacted with O and were deposited onto the substrate. Given the low-temperature process and the size difference between varying constituent atoms, the as-deposited films assumed an amorphous structure regardless of the Cu-target power (not shown). The crystal structure of Cu–Cr–O films annealed at 700 °C with different Cu-target powers examined by XRD is shown in Fig. 2. A change in crystal phase was observed when the Cu-target power was increased. The results indicate that the film with Cu-target power of 10 W exhibited a single-spinel CuCrO$_3$ phase. By increasing the Cu-target power to 14 W, the delafossite CuCrO$_2$ phase started to appear with the decrease of CuCr$_2$O$_4$ phase. Scherrer’s formula [18] suggests that the grain size of the CuCrO$_2$ phase increases as the grain size of the CuCr$_2$O$_4$ phase decreases. The film displayed a single CuCrO$_2$ phase up to 22 W with the complete disappearance of the CuCr$_2$O$_4$ phase. At the time, the grain size of the CuCrO$_2$ phase had increased to ~22 nm. When the Cr power exceeded 32 W, an additional monoclinic CuO phase appeared and grew. The phase transformation and grain size of the Cu–Cr–O films annealed at 700 °C and prepared at various Cu-target powers are listed in Table 1. Based on the aforementioned results, the phase formation can be represented by the following generic equation.

During the sputtering process, the Cu and Cr reacted with O to form an amorphous Cu–Cr–O film [14].

\[
\mathrm{Cu-O}_\mathrm{ss} + \mathrm{Cr-O}_\mathrm{ss} \rightarrow \text{amorphous Cu-Cr-O}_\mathrm{ss} \quad (1)
\]

Then, the Cu–Cr–O films were annealed at 700 °C under Ar atmosphere and consequently formed crystalline phases. When the Cu-target power was too low, the available Cu for the formation of CuCrO$_2$ film was insufficient. Thus, the CuCr$_2$O$_4$ was formed [19]:

\[
\mathrm{CuO}_\mathrm{ss} + \mathrm{Cr}_2\mathrm{O}_3\mathrm{s} \rightarrow \mathrm{CuCr}_2\mathrm{O}_4\mathrm{s} \quad (2)
\]

When sufficient Cu (Cu/Cr ratio ~ 1.0) was present in the film prepared at a moderate Cu-target power, the reaction continued with CuO supplementing CuCr$_2$O$_4$ to form proper CuCrO$_2$ [19].

\[
\mathrm{CuCr}_2\mathrm{O}_4\mathrm{s} + \mathrm{CuO}_\mathrm{ss} \rightarrow 2\mathrm{CuCrO}_2\mathrm{ss} + \frac{1}{2}\mathrm{O}_2\mathrm{ss} \quad (3)
\]

Further increasing Cu-target power to above 32 W caused the excess CuO supplements to form monoclinic CuO phase [20].

\[
\text{Amorphous Cu-O}_\mathrm{ss} \rightarrow \text{Monoclinic CuO}_\mathrm{ss} \quad (4)
\]

Fig. 3 shows the SEM images of the Cu–Cr–O films annealed at 700 °C with different Cu-target power. Based on SEM observations, the film thickness increased to 122, 133, 164, 167, 171, 212, and 315 nm as the Cu-target power increased from 10, 14, 18, 22, 32, and 52 W, respectively, as shown in Table 2. The deposition rate likewise increased. This is because the higher Cu-target power provided more Cu atom on growing films and thus increased the film thickness [21]. The films prepared at Cu-target power of 10 W displayed a polygon-like surface appearance with void boundaries. The polygon-like surface was attribute to the formation of crystalline-like phase [22]. The void growth may be ascribed to the volumetric change, which was associated with grain growth and phase transformations. As the Cu-target power increased to 22 W, the film exhibited a significant grain growth and void size as a result of pure CuCrO$_2$ phase growth. When the Cu-target power was increased to 42 W, the polygon-like clusters became smaller, which may be associated with the coexistence of CuCrO$_2$ and CuO phases. However, further increasing the Cu-target power to 52 W resulted in larger polygon-like clusters, which may be attributed to the growth of the CuO phase.

ESCA is an important technique for analyzing the chemical states of films. Fig. 4a shows the Cu-2p of Cu–Cr–O films annealed at 700 °C with Cu-target power of 10 and 22 W with single spinel CuCrO$_2$ and delafossite CuCrO$_2$ phase, respectively, as confirmed by XRD analysis. For the films prepared with Cu-target power of 10 W, Cu-2p showed three intense peaks at 2p$_{3/2}$, 2p$_{1/2}$, and satellites. The Cu-2p$_{3/2}$ peak can be deconvoluted into two peaks, with a main peak at 932.0 eV representing Cu$^+$ cations and a minor peak at 934.4 eV representing Cu$^{2+}$ cations [23]. The satellites resulted from the metal-ligand charge transfer during the photoemission pro-
Table 1 – Phase structure, grain size, and volume fraction of the phases of the 700 °C-annealed Cu–Cr–O thin films as a function of Cu-target power.

<table>
<thead>
<tr>
<th>Cu-target power (W)</th>
<th>Phases observed</th>
<th>Average grain size (nm)</th>
<th>Volume fraction of the observed phases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CuCrO4</td>
<td>CuCr2O4</td>
</tr>
<tr>
<td>10</td>
<td>CuCr2O4</td>
<td>12.12</td>
<td>–</td>
</tr>
<tr>
<td>14</td>
<td>CuCr2O4 + CuCrO2</td>
<td>9.64</td>
<td>12.31</td>
</tr>
<tr>
<td>18</td>
<td>CuCr2O4 + CuCrO2</td>
<td>7.92</td>
<td>18.55</td>
</tr>
<tr>
<td>22</td>
<td>CuCrO2</td>
<td>–</td>
<td>22.68</td>
</tr>
<tr>
<td>32</td>
<td>CuO + CuCrO2</td>
<td>–</td>
<td>22.30</td>
</tr>
<tr>
<td>42</td>
<td>CuO + CuCrO2</td>
<td>–</td>
<td>22.17</td>
</tr>
<tr>
<td>52</td>
<td>CuO + CuCrO2</td>
<td>–</td>
<td>20.45</td>
</tr>
</tbody>
</table>

The grain size calculation based on Scherrer’s formula.
The volume fraction calculation based on the peak area ratio.

Fig. 3 – SEM micrographs of the Cu–Cr–O coatings prepared at various Cu-target powers: (a) 10 W, (b) 14 W, (c) 18 W, (d) 22 W, (e) 32 W, (f) 42 W, and (g) 52 W.

Table 2 – Summary of Hall effect measurement results, average visible transmittance, and thickness for the 700 °C-annealed Cu–Cr–O films prepared at various Cu-target powers. The μ is Hall mobility, N is the carrier density (hole), ρ is the electrical resistivity, and Φ is the FOM.

<table>
<thead>
<tr>
<th>Cu-target power (W)</th>
<th>Average visible transmittance (380–780 nm) (%)</th>
<th>μ (cm²/(V s))</th>
<th>N (×10¹⁸ cm⁻³)</th>
<th>ρ (Ω cm)</th>
<th>Φ (Ω⁻¹)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>48.97</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>122.8</td>
</tr>
<tr>
<td>14</td>
<td>42.92</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>133.1</td>
</tr>
<tr>
<td>18</td>
<td>46.65</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>164.1</td>
</tr>
<tr>
<td>22</td>
<td>58.31</td>
<td>0.303</td>
<td>4.016</td>
<td>5.13</td>
<td>1.51 × 10⁻⁸</td>
<td>166.9</td>
</tr>
<tr>
<td>32</td>
<td>51.28</td>
<td>0.292</td>
<td>3.789</td>
<td>5.65</td>
<td>3.80 × 10⁻⁹</td>
<td>170.6</td>
</tr>
<tr>
<td>42</td>
<td>37.17</td>
<td>0.176</td>
<td>3.391</td>
<td>10.53</td>
<td>1.02 × 10⁻¹⁰</td>
<td>212.8</td>
</tr>
<tr>
<td>52</td>
<td>17.74</td>
<td>0.086</td>
<td>2.632</td>
<td>27.78</td>
<td>3.52 × 10⁻¹⁴</td>
<td>315.0</td>
</tr>
</tbody>
</table>
cess [23]. This aspect indicates that Cu was present in the +2 valence state because other valence states of copper do not exhibit satellite features. The above results indicate that Cu+ and Cu2+ cations coexisted in the film, and the Cu2+ oxidation state could have originated from the CuCrO4 phase. The Cu+ oxidation state may be attributed to the CuCrO2 phase, which is an amorphous structure as observed by XRD analysis. For the film prepared at Cu-target power of 22 W, the observed satellites in the spectrum vanished. The binding energies of Cu-2p3/2 = 932.3 and Cu-2p1/2 = 952.0 eV were identified with a spin-orbit splitting energy of approximately 19.7 eV. This result confirms that the Cu+ oxidation state provided by the CuCrO2 phase existed in this film. Fig. 4b shows the Cr-2p and of Cu–Cr–O films annealed at 700 °C with Cu-target power of 10 and 22 W. Two intense Cr-2p peaks at Cr-2p3/2 = 576.0 eV and Cr-2p1/2 = 586.0 eV were observed in both films, and the spin-orbit splitting energy between the Cr-2p3/2 and the Cr-2p1/2 peaks was approximately 10.0 eV. This observation is in good agreement with the Cr3+ oxidation state in the films, which was derived from CuCr2O4 and CuCrO2 phases [23,24].

Fig. 5 shows the light transmittance and reflectance of the Cu–Cr–O films annealed at 700 °C with different Cu-target powers. The analysis results led to several findings. (1) The transition between absorption and transmission is very sharp for the film prepared at the Cu-target power of 22 W. When the Cu-target power was far from 22 W, the transition became more gradual. The transition region is called the “absorption edge.” Generally, the impurity phase or defects cause a gradual absorption edge. In other words, the very sharp absorption edge can be attributed to pure CuCrO2 phase with high crystallinity and large grain size. (2) CuCr2O4 has a strong response to the p-type semiconductor visible light photocatalyst band gap of about 1.4 eV [25]. However, the film with a single CuCr2O4 phase still exhibited a transmittance above the wavelength of 4.0 eV in this study. Based on the gradual feature of the film’s absorption edge and ESCA observation, the amorphous CuCrO2 may exist in the film. The CuCrO2 has a large band gap of about 3.1 eV, and its amorphous structure resulted in a band gap expansion compared with bulk crystalline, leading to transmittance in short wavelength [26]. (3) Among these films, the film prepared at Cu-target power of 22 W exhibited the highest visible transmittance of 58.31% (wavelength range of 380–780 nm) because the CuO and CuCr2O4 are p-type semiconductors with a narrow band gap of 1.2 and 1.4 eV [25,27], respectively. This finding presented lower visible light transmittance compared with the delafossite CuCrO2 with a wide band gap of 3.1 eV. Moreover, the relatively high crystallinity reduced light scattering and absorption, which contributed to high light transmittance. As the Cu-target power increased to 52 W, the visible transmittance decreased to 17.74%, which

![Fig. 4](image4.png)  
Fig. 4 – (a) Cu-2p and (b) Cr-2p spectrum of the Cu–Cr–O coatings prepared at Cu-target powers of 10 W and 22 W.

![Fig. 5](image5.png)  
Fig. 5 – (a) The light transmittance and (b) reflectance of the Cu–Cr–O coatings prepared at various Cu-target powers.
was ascribed to the incorporation of monoclinic CuO phase. (4) As the Cu-target power increased, the absorption edge revealed a significant red shift. In the Cu-target power range of 10–22 W, the phase transformed gradually from CuCr2O4 to CuCrO2. This result indicated that the blue shift of the absorption edge should occur as CuCr2O4 has a strong response to the p-type semiconductor visible light photocatalyst band gap of about 1.4 eV [25]. However, the films in this study exhibited a red-shift of the absorption edge, which may have resulted from the reduced amount of amorphous CuCr2O4 phase. In the Cu-target power range of 20–52 W, the amount of monoclinic CuO phase increased gradually, and the absorption edge red-shifted. (5) Plotting the Tauc’s relation of (\(\alpha\))2 versus \(h\nu\) can reveal the optical direct band gap of the thin films [28]. However, given the structurally disordered and/or multi-phase film, a direct energy gap was not present. The gradual absorption edge caused a large error in the measurement of a band gap. In this study, the direct band gap of CuCr2O4 film prepared by a Cu-target power range of 22 W was measured as 3.18 eV using Tauc’s method. The obtained optical band gap values were consistent with those in the literature [14,29]. (6) The increased film thickness at higher Cu-target power provided more absorption and resulted in lower transmittance especially of shorted wavelengths [30].

Table 2 shows the Hall effect measurement results of the Cu–Cr–O films annealed at 700 °C with different Cu-target power. When the Cu-target power was below 18 W, no electrical conductivity was detected by the Hall-effect measurements because films served as insulators. The CuO, CuCr2O4, and CuCrO2 are all p-type semiconductor materials, and their electrical resistivities vary according to reports by various authors. This finding may be due to the differences in composition and microstructure of the film investigated, the electrical behavior of which were not explained in full. In general, the reported electrical resistivity of CuCr2O4 is considerably higher than that of CuCrO2 [31–34]. Associated with the smaller grain size, the incorporation of CuCr2O4 phase in the film is believed to result in immeasurable conductivity. As the Cu-target power increased to above 22 W, the film’s conductivity became measurable in the Hall effect measurement. The electrical resistivity of the films increased from 5.13 Ω cm to 27.78 Ω cm, the corresponding carrier concentration decreased from 4.016 × 1018 cm−3 to 2.632 × 1018 cm−3, and the corresponding hole mobility decreased from 0.303 cm2/V s to 0.086 cm2/V s. Two factors that enhanced the electrical performance of the films when the Cu-target power was 22 W were identified, namely, (1) pure CuCr2O4 phase and (2) large grain size. Increasing the Cu-target power increased the amount of CuO phase present and decreased the amount of CuCrO2 phase with larger grain size, which was detrimental to electrical performance. To select a suitable film with optimal photoelectric performance, FOM was employed for the criterion of the films [35]. Here, FOM is defined as \(FOM = \frac{T}{\alpha} \frac{1}{R_{sh}}\), where \(T\) is the average transmittance and \(R_{sh}\) is the sheet resistance. As shown in Table 2, the highest FOM value of 1.51 × 10−8 Ω−1 was obtained when the film was prepared at a Cu-target power of 22 W. Compared to Mg-doped CuCr2O4 reported by Barnabé and Sun et al. [15,16], the present undoped CuCr2O4 film displays relatively smaller FOM value, which are attributable to lower hole concentration. To improve electrical performance, further research and development in the divalent cation-doped or nitrogen-doped CuCrO2 materials would still be required.

4. Conclusions

As-deposited films were prepared by magnetron co-sputtering using Cu and Cr targets under an O2 and Ar atmosphere and annealed at 700 °C in an Ar atmosphere. The [Cu]/[Cr] ratio in the films was controlled from 0.59 to 2.02 by changing the Cu-target power from 10 W to 52 W. The effects of these changes on the structure and optoelectronic properties of the films were investigated. At a low Cu-target power of 10 W, the pure spinel CuCr2O4 phase was found and no measurable conductivity was detected within the measurement limit of the Hall effect instrument. Further increasing the Cu-target power caused the CuO and CuCr2O4 to react with each other to form delafossite CuCrO2 phase. When the Cu-target power reached 22 W and the [Cu]/[Cr] ratio in the film was close to 1, a single delafossite CuCrO2 film was obtained and the grain size was increased. The film with pure CuCrO2 phase achieved a high visible transmittance of 58.31%, low electrical resistivity of 5.13 Ω cm, and the highest FOM of 1.51 × 10−8 Ω−1. By increasing the Cu-target power to 52 W, an additional monoclinic CuO phase was developed, which significantly deteriorated the optoelectronic properties. This study is significant for the fundamental understanding of optoelectronic performance. These results show the changes in the Cu content of the films that resulted in the formation of various oxide phase with various optoelectronic properties.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The authors gratefully acknowledge the financial support for this research by the Ministry of Science and Technology of Taiwan under Grant No. NSC 106-2221-E-005-026-MY3. The present work was also supported in part by the Center for Micro/Nano Science and Technology of the National Cheng Kung University and Innovation and Development Center of Sustainable Agriculture (IDCSA).

References


