Preparation of CuCrO_2 anisotropic delafossite-type thin film by electrospinning on glass substrates

Chia-Hsuan Weng

National Taipei University of Technology

Rong-JUN Huang

National Taipei University of Technology

Subramanian Sakthinathan

National Taipei University of Technology

Te-Wei Chiu (✉ tewei@ntut.edu.tw)

National Taipei University of Technology <https://orcid.org/0000-0002-2625-2906>

Chaofang Dong (✉ cfdong@ustb.edu.cn)

University of science and technology, Beijing

Research Article

Keywords: CuCrO_2 , Thin film, Anisotropic, Electrospinning, Electrical conductivity, Optical properties

Posted Date: February 17th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-203712/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Anisotropic CuCrO_2 thin films were successfully prepared on glass substrate by the electrospinning method followed by annealing at 600°C . The directionality of the nanowires increased with increases in rotation speed. In addition, the structural formation and optoelectronic behavior of the CuCrO_2 thin films have been studied by X-ray powder diffraction studies, transmission electron microscopy, field emission scanning electron microscopy, Hall effect measurement and UV-vis spectroscopy. The X-ray diffraction studies revealed a delafossite properties of the CuCrO_2 . The electrical conductivity in the parallel and vertical directions of the films produced at 2000–3000 rpm differed by two to three orders of magnitude. The optical transmittance properties of the CuCrO_2 thin films was improved by increasing the rotation speed.

1. Introduction

Transparent conducting oxides (TCO) are special semiconductors combining electrical conductivity and visible-range transparency in a single material [1]. They are used in a wide range of optoelectronic applications, such as photovoltaic cells, solar cells, flat panel displays, and gas sensors, and light emitting diodes [2–5]. The popular TCOs currently used are n-type, of which In-doped SnO_2 and F-doped SnO_2 dominate the market for unique properties [6]. However, improvements to modern optoelectronic devices are based on p–n junctions, so the development of p-type materials is important. At present, p-type TCOs are generally less evolved and less used than n-type TCOs. The CuAlO_2 was first described in 1997 for a highly conductive p-type TCO material [7]. A series of p-type TCOs based on Cu-incorporating oxides, such as CuCrO_2 [8], CuFeO_2 [9], CuInO_2 [10], and SrCu_2O_2 [11], have been established as a result of material discovery efforts following the principle. Hence, the improvement of p-type TCO materials is a worthy endeavor.

The CuCrO_2 is p-type TCO, it can be prepared by different techniques, such as chemical vapor deposition (CVD) [12], pulsed laser deposition [13–16], sol-gel techniques [17,18], hydrothermal synthesis [19], electron beam evaporation [20], sputtering [21–23] and so on. However, electrospinning is more interesting because it is conducted at room temperature [24]. It is also a simple technique for nanowire preparation [25]. There are three key components of an electrospinning system: a high voltage power unit, a spinneret, and a collecting plate. A voltage is applied to the metal source to inject a charge of a certain polarity into a loaded polymer solution, which is then expelled into an opposite polarity collector [26,27]. A polymer gel solution retained by its surface tension at the end of a tube is subjected to an electric field in the electrospinning. A charge is caused by the applied electric field on the liquid top surface. Repulsion of reciprocal charge produces a force that is directly opposite to the surface tension of the polymer. The repulsive electrical force surpasses the surface tension force when the applied electric field exceeds a critical value [28]. Eventually, from the tip of the tube, the charged polymer solution is expelled, forming a Taylor cone and becoming unstable. As a result, the jet is easily whipped between the capillary tip and the collector, resulting in solvent evaporation [29, 30]. In this article, we describe the preparation of CuCrO_2

films by a simple electrospinning method and investigations of the prepared CuCrO_2 films to determine their morphological structures, electrical and optical properties. The results indicated that the rotation speed and temperature influence the morphological structure of CuCrO_2 nanowires.

2. Experimental

2.1 Materials and approaches

Copper nitrate ($\text{Cu}(\text{NO}_3)_2$) and chromium (II) acetate were purchased from Aldrich and AVATOR. Ethanol and polyvinyl pyrrolidone (PVP) were purchased from Echo Chemical Co., Ltd. A study of field emission scanning electron microscopy (FE-SEM) was performed with a Hitachi S-470000. The material structure was identified with a JEOL 2100F transmission electron microscope (TEM). The elemental analysis (EDX) was performed with a HORIBA EMAX-ACT (model 51-ADD0009). The crystal structures were characterized with a GA-XRD PANalytical X'pert X-ray diffractometer (XRD). The optical transmission spectra were measured with a Shimadzu UV-2600 model spectrometer at a range of 200–1100 nm. The electrical conductance of the nanowires was measured with KEITHLEY 2634B two-point probe method at room temperature. The current voltage response of the sample was investigated by Hall measurement (Ecopia HMS-3000). To measure the electrical conductance, Al-doped ZnO (AZO) thin films were deposited by RF magnetron sputtering via scotch tape mask to form the electrode, as shown in Fig. 6.

2.2 CuCrO_2 thin film Preparation

The CuCrO_2 nanowire was prepared by a simple electrospinning method. The sol-gel method with CuCrO_2 precursor used for the film preparation is illustrated in Fig. 1. Chromium acetate and cupric nitrate were combined with molar ratio of 3:1, and the prepared composition was dissolved in $\text{CH}_3\text{CH}_2\text{OH}$ solution to obtain 0.2 M of the metal source solution. At the time, polyvinyl pyrrolidone (PVP) (1.5 g) of and ethanol (8.5 ml) were applied to the metal source solution (10 ml) to form the main precursor. After effective stirring at 80°C for 12 h, a sticky gel-like solution of CuCrO_2 /PVP precursor was achieved. The reaction precursor was put in a 5 ml syringe for the electrospinning process. The syringe was then clamped to a ring stand 5 cm above a stainless steel mesh that was grounded, bowl-shaped. A high-voltage power was attached to the precursor syringe's metal needle, which was linked to the syringe pump. The applied voltage was 16 kV, and the electrospinning precursor feeding rate was 0.12 ml/h. Anisotropic films were prepared using the high-speed spinning collector and the glass substrate was anchored on the roller. The CuCrO_2 nanowires were electrospun onto the glass substrate for 2.5 hours. Every sample was dried in an oven for 12 h at 80°C after electrospinning. The dried CuCrO_2 thin films were then vacuum-coated for 10 minutes at 600°C prior to characterization.

3. Results And Discussion

3.1. XRD analysis of CuCrO_2 thin films

The X-ray diffraction analysis (XRD) used to identify the crystal structure of the CuCrO_2 thin films, as shown in Fig. 2. The XRD pattern exhibited three main peaks, corresponding to the (006), (012) and (110) planes, which coincided with the typical delafossite structure of CuCrO_2 (JCPDF Card No. 39–0247). Moreover, based on the XRD pattern study, it was determined that the pure phase of CuCrO_2 was obtained by annealing at 600°C for 10 min.

3.2. Electron microscope studies of prepared CuCrO_2 thin films

Figure 3 presents the optical microscope analysis of CuCrO_2 thin films deposited on glass substrate at different rotation speeds (100–3000 rpm). As shown in Fig. 3 (A), slow spinning produced disordered nanowires. At a rotation speed of 1000 rpm, as shown in (Fig. 3 (B) and (C)), the nanowires were still somewhat disordered. At 2000 rpm and above, the nanowire alignment had a more homogeneous direction, as shown in Fig. 3 (D) and (E).

Figure 4 shows FE-SEM analysis of the CuCrO_2 thin films annealed at 600°C for 10 min in vacuum. The FE-SEM images verified that increasing the rotation speed resulted in better alignment of the nanowires in the depositing direction. The diameters of the nanowires were 112 to 375 nm. Figure 5 presents a cross-sectional FE-SEM image of the CuCrO_2 nanowires. The average thicknesses of the CuCrO_2 nanowires produced at the different rotation speeds were as follows: (A) 352 nm (100 rpm), (B) 340 nm (500 rpm), (C) 396 nm (1000 rpm), (D) 252 nm (2000 rpm), and (E) 240 nm (3000 rpm).

The CuCrO_2 structure on glass substrate was identified by TEM. The TEM samples were processed with a focused ion beam (FIB) with a Pt protective coating. The samples were then cut in the directions vertical and parallel to the spinning direction, as shown in Fig. 6. Figure 7A and Fig. 8A present TEM images of the CuCrO_2 thin films cut in the two directions. The parallel-direction TEM image clearly shows that the films were well attached to the AZO, and the vertical-direction TEM image exhibits that the films were deposited in layers on the AZO. The EDX analysis in Figs. 7 and 8 presents the mapping regions corresponding to (D) Cu, (E) Cr, (F) Al and (G) Zn elements. All results confirmed that the anisotropic CuCrO_2 thin films were successfully prepared on the AZO by electrospinning.

4. Optoelectrical Properties Of Delafossite-type CuCrO_2 Thin Films

4.1 Optical properties

The CuCrO_2 thin film optical transmission spectrum was examined at wavelengths of 220–1100 nm. Figure 9 displays the optical transmittance spectrum of thin CuCrO_2 films in vacuum condition at 600°C for 10 minutes. The transmittances of the samples were 55.8% (100 rpm), 69.6% (500 rpm), 75.2% (1000 rpm), 82.1% (2000 rpm), and 81.0% (3000 rpm) in the visible region. The diffusion transmittances of the films were 9.34% (100 rpm), 10.47% (500 rpm), 9.33% (1000 rpm), 8.13% (2000 rpm), and 4.15% (3000 rpm).

rpm) in the visible region, respectively (Fig. 10). We calculate the transmittance haze with Eq. 1 after calculating the diffusion transmittances and total transmittances.

$$\text{Transmittance Haze} = \frac{\text{Diffuse transmittance}}{\text{Total transmittance}} \quad (1)$$

Table 1 mentioned the transmittance haze results of the CuCrO₂ thin films annealed in vacuum at 600°C for 10 min. The results were 16.7% (100 rpm), 15.0% (500 rpm), 12.4% (1000 rpm), 9.9% (2000 rpm), and 5.1% (3000 rpm), respectively. Figure 11 presents the diffusion reflection spectra of the CuCrO₂ thin films annealed in vacuum at 600°C for 10 min in different rotating directions. The diffusion reflections were 18.5% (100 rpm), 11.2% (500 rpm), 14.2% (1000 rpm), 11.2% (2000 rpm), and 11.7% (3000 rpm) in the visible region, respectively. We determined the absorption with Eq. 2 from the transmittance, diffusion transmittances, and diffusion reflections.

$$T_{\text{total}} = T_0 + \text{Abs.} + R \% + D \% \quad (2)$$

The absorbance values were 16.36% (100 rpm), 8.73% (500 rpm), 2.27% (1000 rpm), 1.68% (2000 rpm), and 3.15% (3000 rpm). Table 2 lists all the values of total transmittance.

To evaluate the optical bandgap and absorption, which corresponds to the electron excitation from the valence band to the conduction band was used. For simple parabolic bands and direct transitions mentioned in Eq. 3

$$\alpha(\nu) n_o h\nu \approx (h\nu - E_g)^n \quad (3)$$

In the quantum-mechanical sense, where n is a constant of 1/2 for permitted transitions and 3/2 for prohibited transitions; n_o is the refractive index, $h\nu$ is the photon energy; and E_g is the bandgap energy of the material under investigation [22]. As shown in Fig. 12, the band gaps of CuCrO₂ thin films were estimated at 2.74, 2.69, 2.54, 2.81, and 2.69 eV, respectively [31–33].

4.2 3.6 Electrical properties

Figure 13 indicates the resistivity measured by the system of the two-point probe. The resistivity of CuCrO₂ thin films produced at different speeds of rotation and vacuum-recovered at 600°C for 10 minutes is shown in Table 3. The values of parallel resistivity were 6.79×10^7 (100 rpm), 2.12×10^7 (500 rpm), 1.68×10^6 (1000 rpm), 4.21×10^6 (2000 rpm), and 1.88×10^5 (3000 rpm), respectively. Those of vertical resistivity were 4.88×10^7 (100 rpm), 1.05×10^6 (500 rpm), 7.73×10^6 (1000 rpm), 2.67×10^9 (2000 rpm), and 6.03×10^7 (3000 rpm), respectively. The anisotropic CuCrO₂ thin films conductivities in the parallel and vertical directions differed by nearly two to three orders of magnitude. The differences for the rotation speeds of 2000 and 3000 rpm were especially obvious.

5. Conclusions

In this study, anisotropic CuCrO₂ thin films were successfully fabricated by electrospinning on glass substrate. The XRD patterns suggested that the pure phase of the CuCrO₂ thin film was achieved by annealing in vacuum at 600°C for 10 min. SEM revealed that higher rotation speeds resulted in better alignment of the nanowires, leading to better morphology of the CuCrO₂ thin films. Moreover, higher rotation speeds also produced films with higher transmittance values. The transmittances for the different rotation speeds were 55.8% (100 rpm), 69.6% (500 rpm), 75.2% (1000 rpm), 82.1% (2000 rpm), and 81.0% (3000 rpm) in the visible region, respectively. The haze results were 16.7% (100 rpm), 15.0% (500 rpm), 12.4% (1000 rpm), 9.9% (2000 rpm), and 5.1% (3000 rpm) in the visible region, respectively. The parallel and vertical electrical conductivities of the anisotropic CuCrO₂ thin films generated at 2000 rpm and 3000 rpm had differences of nearly two to three magnitude orders. In addition, higher rotation speeds yielded CuCrO₂ thin films with higher optical transmittance.

Declarations

Authorship contribution

Chia-Hsuan Weng: Conceptualization, Methodology, Software, Data curation, Writing-original draft. **Subramanian Sakthinathan:** Visualization, Investigation, Software, Writing, Validation. **Rong-Jun Huang:** Software, Validation. **Te-Wei Chiu:** Supervision, Methodology, Investigation, Supervision, Writing & editing. **Chaofang Dong:** Supervision.

Acknowledgement

This work was sponsored by the National Taipei University of Technology (NTUT-USTB-105-7). The author thanks to the Precision Research and Analysis Center, National Taipei University of Technology's (NTUT) for providing the measurement facilities.

Conflict of interest

There are no conflicts of interest to declare

References

1. R. Wei, X. Tang, L. Hu, J. Yang, X. Zhu, W. Song, J. Dai, X. Zhu, Y. Sun, J. Mater. Chem. C. **5**, 1885 (2017)
2. T. Minami, Semicond. Sci. Technol. **20**, S35 (2005)
3. J.F. Wager, Transparent electronics, Science. **300**, 1245 (2003)
4. C.G. Granqvist, Sol. Energy Mater. Sol. Cells. **91** 1529 (2007)
5. K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, H. Hosono, **300**, 1269 (2003)

6. Z. Wang, P.K. Nayak, J.A. Caraveo-Frescas, H.N. Alshareef, *Adv. Mater.* **28**, 3831 (2016)
7. H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, **389**, 939 (1997)
8. S. Wu, Z. Deng, W. Dong, J. Shao, X. Fang, *Thin Solid Films.* **595**, 124 (2015)
9. S.M. Thahab, A.H.O. Alkhayatt, I.A. Zgair, *Mater. Sci. Semicond. Process.* **41**, 436 (2016)
10. M. Shimode, M. Sasaki, K. Mukaida, *J. Solid State Chem.* **151**, 16 (2000)
11. O.T. Tambunan, H. Tukiman, K.J. Parwanta, D.W. Jeong, C.U. Jung, S.J. Rhee, C. Liu, *Superlattices Microstruct.* **52**, 774 (2012)
12. S.Y. Kim, J.H. Lee, J.J. Kim, Y.W. Heo, *Curr. Appl. Phys.* **12**, 123 (2012)
13. S. Mahapatra, S.A. Shivashankar, *Chem. Vap. Depos.* **9**, 238 (2003)
14. T.W. Chiu, K. Tonooka, N. Kikuchi, *Thin Solid Films.* **518**, 7441 (2010)
15. T.W. Chiu, K. Tonooka, N. Kikuchi, *Vacuum.* **83**, 614 (2008)
16. T.W. Chiu, K. Tonooka, N. Kikuchi, *Thin Solid Films.* **516**, 5941 (2008)
17. H.Y. Chen, C.C. Yang, *Surf. Coatings Technol.* **231**, 277 (2013)
18. T.W. Chiu, Y.A. Chen, H.C. Lee, S.Z. Hong, *Ceram. Int.* **41**, S213 (2015)
19. S. Zhou, X. Fang, Z. Deng, D. Li, W. Dong, R. Tao, G. Meng, T. Wang, X. Zhu, *J. Cryst. Growth.* **310**, 5375 (2008)
20. D.S. Kim, S.J. Park, E.K. Jeong, H.K. Lee, S.Y. Choi, *Thin Solid Films.* **515**, 5103 (2007)
21. N. Tsuboi, T. Moriya, S. Kobayashi, H. Shimizu, K. Kato, F. Kaneko, *Jpn. J. Appl. Phys.* **47**, 592 (2008)
22. T.W. Chiu, Y.C. Yang, A.C. Yeh, Y.P. Wang, Y.W. Feng, *Vacuum.* **87**, 174 (2013)
23. T.C.K. Yang, Y.L. Yang, R.C. Juang, T.W. Chiu, C.C. Chen, *Vacuum.* **121**, 310 (2015)
24. N. Bhardwaj, S.C. Kundu, *Biotechnol. Adv.* **28**, 325 (2010)
25. T.W. Chiu, Y.T. Chen, *Ceram. Int.* **41**, S407 (2015)
26. D. Liang, B.S. Hsiao, B. Chu, *Adv. Drug Deliv. Rev.* **59**, 1392 (2007)
27. T.J. Sill, H.A. von Recum, *Biomaterials.* **29**, 1989 (2008)

28. J. Doshi, D.H. Reneker, Electrospinning process and applications of electrospun fibers, J Electrostat, **35** 151 (1995)

29. A.L. Yarin, S. Koombhongse, D.H. Reneker, J. Appl. Phys. **89**, 3018 (2001)

30. E. Adomaviciute, R. Milasius, Fibres Text. East. Eur. **5**, 69 (2007)

31. E. Kim, Z.T. Jiang, K. No, Japanese J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap. **39**, 4820 (2000)

32. F. Lin, C. Gao, X. Zhou, W. Shi, A. Liu, J. Alloys Compd. **581**, 502 (2013)

33. T.W. Chiu, J.H. Shih, C.H. Chang, Thin Solid Films. **618**, 151 (2016)

Tables

Table 1. UV-Visible transmittance haze of CuCrO₂ thin films annealed in vacuum at 600 °C for 10 min in different directions.

Rotation speed	Haze (%)
100 rpm	16.7%
500 rpm	15%
1000 rpm	12.4%
2000 rpm	9.9%
3000 rpm	5.1%

Table 2. The detailed values (transmittance, diffusion, reflection and absorbance) of CuCrO₂ thin films.

T total (%)	100 rpm	500 rpm	1000 rpm	2000 rpm	3000 rpm
Transmittance	55.8 %	69.6 %	75.2 %	82.1 %	81.0 %
Diffusion	9.34 %	10.47 %	8.33 %	5.02 %	4.15 %
Reflection	18,5 %	11.2 %	14.2 %	11.2 %	11.7 %
Absorb	16.36%	8.73 %	2.27 %	1.68 %	3.15 %

Table 3. The detail values of different direction electrical resistance.

Rotation speed	Resistivity($\Omega\cdot m$) Parallel	Electrical resistivity($\Omega\cdot cm$) Parallel	Resistivity ($\Omega\cdot m$) Vertical	Electrical resistivity ($\Omega\cdot cm$) Vertical
100 rpm	6.79×10^7	2.78×10^3	4.88×10^7	2.00×10^3
500 rpm	2.12×10^7	8.40×10^2	1.05×10^6	4.16×10^1
1000 rpm	1.68×10^6	7.75×10^1	7.73×10^6	3.57×10^2
2000 rpm	4.21×10^6	1.24×10^2	2.67×10^9	7.83×10^4
3000 rpm	1.88×10^5	5.25×10^2	6.03×10^7	1.68×10^3

Figures

Figure 1

Schematic image of electrospinning experimental setup.

Figure 2

XRD pattern of CuCrO₂ nanowire deposited on glass substrate after annealing at 600 °C.

Figure 3

Morphology of as-spun precursor nanowires of CuCrO_2 thin films deposited on glass substrates. Speed of rotation: (A) 100 rpm, (B) 500 rpm, (C) 1000 rpm, (D) 2000 rpm, (E) 3000 rpm.

Figure 4

Morphology of CuCrO₂ thin films deposited on glass substrates and annealed at 600 °C. Speed of rotation: (A) 100 rpm, (B) 500 rpm, (C) 1000 rpm, (D) 2000 rpm, (E) 3000 rpm.

Figure 5

The cross-section SEM of CuCrO₂ thin films deposited on glass substrates and annealed at 600 °C for 10 min. Speed of rotation: (A) 100 rpm, (B) 500 rpm, (C) 1000 rpm, (D) 2000 rpm, (E) 3000 rpm.

Figure 6

Schematic diagram of the resistivity's in the vertical and parallel directions measured by FIB

Figure 7

(A) TEM, (B) STEM, (C) Mix and EDX-mapping of the parallel direction of the CuCrO_2 thin film (D) Cu, (E) Cr, (F) Al, (G) Zn.

Figure 8

(A) TEM, (B) STEM, (C) Mix and EDX-mapping of the vertical direction of the CuCrO₂ thin film (D) Cu, (E) Cr, (F) Al, (G) Zn.

Figure 9

UV-Visible transmittance spectra in different directions of CuCrO₂ thin films annealed at 600 °C.

Figure 10

UV-Visible diffusion transmittance spectra in different directions of CuCrO₂ thin films annealed at 600 °C.

Figure 11

UV-Visible diffusion reflection spectra in different directions of CuCrO₂ thin films annealed at 600°C.

Figure 12

Absorption edges and estimated energy gaps of CuCrO₂ thin films annealed at 600°C.

Figure 13

Schematic diagram of the measured resistivity.