Anisotropic delafossite-type CuFeO₂ thin films deposited by electrospinning with rotating collector

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Delafossite CuFeO₂ anisotropic thin films were prepared by electrospinning method with rotating collector. The pure phase CuFeO₂ anisotropic thin films were prepared by heat treatment at 773 K in the air for 600 s and 1023 K under nitrogen for 600 s. Besides, an electrospinning process rotation speed influence on the CuFeO₂ film formation. The delafossite-type CuFeO₂ films were identified by X-ray diffraction and field emission scanning electronic microscopy. High-speed rotating collector were used to prepare the anisotropic thin film. Glass substrates were fixed on a rotating collector and rotated at speeds of 100–3000 rpm. The optical and electrical properties of the prepared CuFeO₂ thin film were measured by ultraviolet–visible spectrometry and two-point probe method, respectively. The electrical resistance of the macroscopically anisotropic CuFeO₂ thin films in the parallel and vertical directions showed a difference of 2–3 orders.

Key-words : Delafossite materials, CuFeO₂, Anisotropic thin film, Electrospinning, Optical properties, Electrical properties

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1. Introduction

Transparent conducting oxides (TCOs) are semiconductors combining visible light transparency and high electrical conductivity in a single material. Thin films of TCOs are utilized in a wide range of applications, such as flat panel displays, light emitting diodes, photovoltaic cells, energy-efficient windows, removal of metal ions, photocatalysts, gas sensors and biomedical products. The TCOs are currently used in n-type TCOs, in which F- doped SnO₂ (FTO) and Sn-doped In₂O₃ (ITO) are applied in the market for unipolar devices. In contrast, p-type TCOs are comparatively less improved and less widely utilized.

The delafossite structure obeys the general ternary oxide chemical composition of MₓM₃₋ₓO₂. It is divided into two groups: monovalent cations (M₁ = Ag⁺ and Cu⁺) and trivalent cations (M₃₋ₓ = Al³⁺, Fe³⁺ or Cr³⁺). Especially, copper delafossites [Cu(I)M(III)O₂] have attracted interest due to their wide ranges of electrical conductivity and optical transparency as compared to other ternary oxides. The delafossite properties of CuAlO₂ film were first reported by Kawazoe et al. in 1997 for a highly conductive p-type TCO. Since then, a series of the p-type TCOs based on Cu-incorporating oxides, such as CuInO₂, CuCrO₂, CuFeO₂, CuCrO₂, and SrCu₂O₂, has been found as a consequence of efforts in material investigation following the design methodology. Especially, CuFeO₂, a delafossite series of p-type semiconductors, has excellent conductivity and photocatalytic activity at room temperature due to its band gap of 1.3 eV. CuFeO₂ powder has a small grain size, high surface area, and good adsorption behavior. CuFeO₂ thin films can be prepared using techniques such as pulsed laser deposition, radio-frequency sputtering, electrochemical deposition, and chemical solution methods. M. Lalanne et al. reported the preparation of CuFe₁₋ₓCrₓO₂ solid solution by standard solid-state reaction, but the preparation of Cu-based delafossite nanomaterials and thin films is very difficult by solid state reaction.

Electrospinning is an effective method of processing viscous solutions into continuous fibers with diameters ranging from the micrometer to the nanometer range. This method is extensively used in many areas, such as optics, filtration, biological scaffolds, chemical sensors, and nanocable preparation. It is also used for the continuous preparation of one-dimensional materials, polymer com-
posites and ceramic film.\(^{24-26}\) Moreover, electrospinning is cost effective and can be performed at room temperature with optimized atmosphere conditions.\(^{27}\) Generally, an electrospinning system has three major parts: a spinneret, a high voltage power supply and a grounded collecting plate. Such an electrospinning system utilizes a high voltage to inject a charge of polarity into the prepared polymer solution, which is accelerated towards a collector of opposite polarity.\(^{28,29}\) In this preparation, a polymer solution is held by its surface tension at the end of a capillary needle, and the charge is induced on the solution surface by an external electric force. Mutual charge repulsion creates a force opposite to the surface tension of the polymer solution. When the applied electric field reaches a critical value, the repulsive electrical force overcomes the surface tension of the polymer solution. Finally, a charged jet of the precursor solution is ejected from the capillary tip and is whipped rapidly in the space between the capillary tip and rotating collector plate. This action leads to evaporation of the solvent behind a polymer film.\(^{14,30}\) This paper demonstrates a unique CuFeO\(_2\) anisotropic thin film with uniform diameter prepared by electrospinning process.

2. Experimental procedure

2.1 Preparation of precursor

Figures 1 and 2 shows the CuFeO\(_2\) fiber was prepared by the electrospinning method.\(^{30}\) First, cupric nitrate and ferric nitrate were mixed at the equal molar ratio and dissolved in dimethylformamide (DMF)/ethanol solution. This prepared solution was mixed at a volumetric ratio of 1:1, and added in different molar ratio of ethanol/DMF solvent to form 0.05, 0.1, 0.2 and 0.3 M of CuFeO\(_2\) solutions. After that, CuFeO\(_2\) solutions were mixed with 18.5 wt.% PVP gel solution at dissolved in DMF/ethanol solvent at a volumetric ratio of 0.8:1 to form the final precursor. In the electrospinning preparation, the metal precursor was placed in a glass syringe (5 ml) equipped with a stainless steel needle. The metal precursor loaded syringe was attached to a ring stand that was 15 cm above a grounded bowl-shape stainless steel rotator. A high-voltage power source was connected to the stainless steel needle at the syringe with the feeding rate was 0.2 ml/h and the applied voltage was 20 kV to form electrospinning jet. After the electrospinning process, CuFeO\(_2\) fibers were annealed in different temperature conditions of 773 and 1023 K.

The prepared CuFeO\(_2\) anisotropic thin films were characterized by physical and chemical characterization techniques. The crystal phase structure of the prepared thin films was identified by X-ray diffraction studies (XRD, Bruker D2 Phaser) with Cu K\(\alpha\) radiation (\(\lambda = 0.15418\) nm). The surface arrangement of the thin film was studied

![Fig. 1. Flowchart for electrospinning preparation of CuFeO\(_2\) thin film.](image1)

![Fig. 2. Schematic illustration of electrospinning preparation of CuFeO\(_2\) thin film.](image2)
by field emission scanning electronic microscopy (FESEM, Hitachi S-4700). The optical properties of the CuFeO$_2$ thin film were identified by using a ultraviolet-visible (UV–Vis) spectrometer (UV–Vis SHIMADZU 2600) at wavelengths of 220–1100 nm, and the electrical properties were measured by two-point probe method.

3. Results and discussion

3.1 XRD and SEM studies

The structure of the deposited CuFeO$_2$ thin film was identified from the XRD analysis, as shown in Fig. 3. The diffraction pattern of the CuFeO$_2$ thin film (JCPDS No. 75-2146) exhibited three well-defined main reflections of a typical delafossite structure. According to the XRD pattern, a pure phase of CuFeO$_2$ thin film was obtained after heat treatment at 773 K in air for 600 s and 1023 K under nitrogen for 600 s. This result is concordant with previously reported CuFeO$_2$ thin film.$^{31,32}$

Figures 4(a)–4(d) shows SEM images of the anisotropic CuFeO$_2$ thin films prepared by the electrospinning deposition on glass substrates fixed on rotating collector at different rotation speeds (100–3000 rpm). The SEM observation revealed that the CuFeO$_2$ thin film presented progressively more consistent orientation as the rotation speed was increased. When the jet velocity of spun fiber matched with the line speed of collector, the aligned fiber was obtained on the substrate which fixed on rotating collector. The line speed of collector was faster than the jet velocity of spun fiber, the fiber will break when they were deposited on the substrates. When the line speed of collector was slower than the jet velocity the fiber will randomly deposit on the substrate. These results exhibit that jet velocity could be estimated about fiber alignment form on the rotating drum. Therefore, when the rotation speed reached 3000 rpm, the film was broken slightly. Because, when rotation speed lower than 2000 rpm, jet velocity could follow the collector but faster than the 3000 rpm thin film could not follow and broken by strains.$^{33,34}$

Figures 5(a)–5(d) shows the average thicknesses of the CuFeO$_2$ thin films were 1490 nm (100 rpm), 700 nm (1000 rpm), 630 nm (2000 rpm), and 720 nm (3000 rpm), respectively.

![Fig. 3.](image1.png) The XRD pattern of CuFeO$_2$ thin film annealed at 773 K in air for 600 s and then at 1023 K in nitrogen for 600 s.

![Fig. 4.](image2.png) SEM morphology structure of CuFeO$_2$ thin films deposited on glass substrates by electrospinning at different rotation speeds: (a) 100 rpm, (b) 1000 rpm, (c) 2000 rpm, (d) 3000 rpm.
3.2 Optical properties

The optical transmission spectra of CuFeO$_2$ anisotropic thin films were identified within the wavelength range of 300–1400 nm. Figure 6 shows the optical transmittance spectra of CuFeO$_2$ thin films prepared at different rotation speeds and heat treated at 773 K in the air for 600 s and 1023 K under nitrogen for 600 s. The obtained transmittances in the visible region of the thin films prepared at different rotation speeds were 44% (100 rpm), 48.3% (1000 rpm), 52.9% (2000 rpm), and 57.09% (3000 rpm). The diffusion transmittances in the visible region of the films prepared at different rotation speeds were 12.37% (100 rpm), 14.2% (1000 rpm), 13.87% (2000 rpm), and 15.17% (3000 rpm), respectively (Fig. 7). After measuring the total transmittances and diffusion transmittances, we calculated the transmittance haze by the following formula (1):

$$\text{Transmittance haze} (\%) = \frac{\text{Diffuse transmittance}}{\text{Total transmittance}}$$

(1)

Table 1 lists the transmittance haze percentages of CuFeO$_2$ thin films prepared at different rotation speeds and heat

![Fig. 5. Cross-section SEM images of CuFeO$_2$ thin films deposited on glass substrates by electrospinning at different rotation speeds: (a) 100 rpm, (b) 1000 rpm, (c) 2000 rpm, (d) 3000 rpm.](image1)

![Fig. 6. UV–Visible transmittance spectra of CuFeO$_2$ thin films at different rotation speeds and heat treated at 773 K in air for 600 s and 1023 K under nitrogen for 600 s.](image2)

![Fig. 7. UV–Visible diffusion transmittance spectrum CuFeO$_2$ thin films at different rotation speeds and heat treated at 773 K in air for 600 s and 1023 K under nitrogen for 600 s.](image3)
treated at 773 K in air for 600 s and 1023 K under nitrogen for 600 s. The transmittance haze percentages were 28.2% (100 rpm), 29.4% (1000 rpm), 26.3% (2000 rpm), and 26.6% (3000 rpm), respectively. The corresponding absorption exhibited the electron excitation from the valence band to the conduction band, which can be used to determine the optical bandgap. Moreover, the simple parabolic bands \( N(E) \propto E^{1/2} \) and direct transitions expressed in Eq. (2).

\[
\alpha(v)n_{s}hv(hv - E_g)^{n}
\]  
(2)

where \( n = 1/2 \) for the direct bandgap and 3/2 for forbidden transitions in the quantum-mechanical sense; \( \alpha \) is the absorption coefficient; \( A \) is a constant; \( n_s \) is the refractive index, which is assumed to be a constant over energy variation; \( E_g \) is the optical bandgap; and \( h\nu \) is the photon energy of the material under investigation.\(^{35-37} \) As shown in Fig. 8, the band gaps of CuFeO\(_2\) thin films prepared at different rotation speeds and heat treated at 773 K in air for 600 s and 1023 K under nitrogen for 600 s were estimated at 2.05, 1.99, 2 and 2.1 eV, respectively. The band gap energy is dependent on the crystal structure, microstructure, and chemical compositions of materials. In addition, the band gap energy changes can be attributed to the increasing the grain size and improvement of the crystallinity of the thin film after the annealing process. Therefore, the structural changes and band gap energy of CuFeO\(_2\) thin film is attributed by different annealing process and rotation speed.\(^{38,39} \)

### Table 1. UV–Visible transmittance haze of CuFeO\(_2\) thin films prepared at different rotation speeds after annealing at 773 K in air for 600 s and then at 1023 K in nitrogen for 600 s

| Rotation speed | Haze  |
|---------------|-------|
| 100 rpm       | 28.2% |
| 1000 rpm      | 29.4% |
| 2000 rpm      | 26.3% |
| 3000 rpm      | 26.6% |

### Table 2. The values of resistance of different directions of CuFeO\(_2\) thin films with line speed of collector

| Rotation speed | Line speed of Collector | Resistance (Ω) | Resistance (Ω) |
|----------------|-------------------------|----------------|----------------|
| 100 rpm        | 0.78 m/s                | 1.2 × 10\(^6\) | 3.41 × 10\(^8\) |
| 1000 rpm       | 7.86 m/s                | 5.47 × 10\(^8\) | 5.188 × 10\(^9\) |
| 2000 rpm       | 15.70 m/s               | 2.297 × 10\(^9\) | 3.257 × 10\(^9\) |
| 3000 rpm       | 23.55 m/s               | 8.846 × 10\(^9\) | 1.015 × 10\(^10\) |

3.3 Electrical properties

Table 2 shows the line speed of collector and the resistance of CuFeO\(_2\) thin films prepared at different rotation speeds and heat treated at 773 K in air for 600 s and 1023 K under \( N_2 \) for 600 s. The line speed of collector is increased for increasing the rotation speeds such as 0.78 m/s (100 rpm), 7.86 m/s (1000 rpm), 15.70 m/s (2000 rpm) and 23.55 m/s (3000 rpm) respectively. Figure 9 shows a schematic diagram of the resistance measurement by the two-point probe method. The values of parallel resistance were 1.2 × 10\(^6\) Ω (100 rpm), 5.47 × 10\(^8\) Ω (1000 rpm), 2.297 × 10\(^9\) Ω (2000 rpm), and 8.846 × 10\(^9\) Ω (3000 rpm), respectively. The values of vertical resistance were 3.41 × 10\(^6\) Ω (100 rpm), 5.188 × 10\(^9\) Ω (1000 rpm), 3.257 × 10\(^9\) Ω (2000 rpm), and 1.015 × 10\(^10\) Ω (3000 rpm), respectively. The electrical resistance of macroscopically anisotropic CuFeO\(_2\) thin film confirmed, the line speed of collector of 15.70 m/s (2000 rpm) showed nearly a two-order difference between the parallel and vertical directions.

4. Conclusion

In summary, CuFeO\(_2\) anisotropic thin films were successfully fabricated on the glass substrate by the electrospinning method. The XRD diffraction patterns indicated that pure phase CuFeO\(_2\) thin film can be obtained by heat treatment at 773 K in air for 600 s and 1023 K under nitrogen for 600 s. The SEM morphologies of the thin film showed progressively more consistent orientation as the rotation speed increased from 100 to 3000 rpm. However, the CuFeO\(_2\) thin film was broken slightly when the rotation speed reached 3000 rpm. The transmittances in the visible region of thin films prepared at different rotation speeds were 44% (100 rpm), 48.3% (1000 rpm), 52.9% (2000 rpm), and 57% (3000 rpm), respectively. The haze percentages in the visible region were 28.2% (100 rpm), 29.4% (1000 rpm), 26.3% (2000 rpm) and 26.6% (3000 rpm). Notably, the electrical conductivity of the
anisotropic CuFeO₂ thin film prepared at the rotation speed of 2000 rpm (15.70 m/s) showed a difference of nearly two orders between the parallel and vertical directions.

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References
1) X. Zhu and Y. Sun, J. Mater. Chem. C, 5, 1885–1892 (2017).
2) T. Minami, Semicond. Sci. Tech., 20, S35–S44 (2005).
3) C. G. Granqvist, Sol. Energy Mater. Sol. Cells, 91, 1529–1589 (2007).
4) K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, and H. Hosono, Science, 300, 1269–1273 (2003).
5) Z. Wang, P. K. Nayak, J. A. C. Rescas and H. N. Alshareef, Adv. Mater., 28, 3831–3892 (2016).
6) J. Patzsch, I. Balog, P. Krau, C. W. Lehmann and J. J. Schneider, RSC Adv., 4, 15348–15355 (2014).
7) S. Kameoka, T. Tanabe and A. P. Tsai, Catal. Lett., 100, 1–2 (2005).
8) S. Kameoka, T. Tanabe and A. P. Tsai, Appl. Catal. A-Gen., 375, 163–171 (2010).
9) H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi and H. Hosono, Nature, 389, 939–942 (1997).
10) M. Shimode, M. Sasaki and K. Mukaida, J. Solid State Chem., 20, 16–20 (2000).
11) T. W. Chiu, Y. C. Yang, A. C. Yeh, Y. P. Wang and Y. W. Feng, Vacuum, 87, 174–177 (2013).
12) S. M. Thahab, A. H. Omran and I. Abdulah, Mat. Sci. Semicon. Proc., 41, 436–440 (2016).
13) T. W. Chiu and P. S. Huang, Ceram. Int., 39, S575–S578 (2013).
14) T. C. Chao, T. W. Chiu and Y. Fu, Ceram. Int., 44, S80–S83 (2018).
15) T. W. Chiu and Y. S. Lu, Ferroelectrics, 491, 149–154 (2016).
16) X. H. Pan, W. Guo, Z. Z. Ye, B. Liu, Y. Che, H. P. He and X. Q. Pan, J. Appl. Physiol., 105, 113516 (2009).
17) T. Joshi, T. R. Senty, R. Trappen, J. Zhou, S. Chen, P. Ferrari, P. Borisov, X. Song, M. B. Holcomb, A. D. Bristow, A. L. Cabrera and D. Lederman, J. Appl. Phys., 117, 013908 (2015).
18) S. Z. Li, J. Liu, X. Z. Wang, B. W. Yan, H. Li and J. M. Liu, Physica B, 407, 2412–2415 (2012).
19) A. Barnabe, E. Mugnier, L. Presmanes and P. Tailhades, Mater. Lett., 60, 3468–3470 (2006).
20) E. Mugnier, A. Barnabe, L. Presmanes and P. Tailhades, Thin Solid Films, 516, 1453–1456 (2008).
21) C. G. Read, Y. Park and K. Choi, J. Phys. Chem. Lett., 3, 1872–1876 (2012).
22) H. Chen and J. Wu, Appl. Surf. Sci., 258, 4844–4847 (2012).
23) H. Y. Chen and J. Wu, Thin Solid Films, 520, 5029–5035 (2012).
24) A. Leviet, M. V. Reddy, R. Jose, B. V. R. Chowdari and S. Ramakrishna, J. Phys. Chem., 114, 664–671 (2010).
25) J. H. Chai and S. S. Wu, Beilstein J. Nanotechnol., 4, 189–197 (2013).
26) Q. Ma, J. Wang, X. Dong, W. Yu, G. Liu and J. Xu, J. Mater. Chem., 22, 14438–14442 (2012).
27) N. Bhardwaj and S. C. Kundu, Biotechnol. Adv., 28, 325–347 (2010).
28) D. Liang, B. S. Hsiao and B. Chiu, Adv. Drug Deliv. Rev., 59, 1392–1412 (2007).
29) T. J. Sill and H. A. Vonrecum, Biomaterials, 29, 1989–2006 (2008).
30) E. Process, J. Doshi and D. H. Reneker, J. Electrostat., 35, 151–160 (1995).
31) E. K. Im, Z. J. Iang and N. O. Kwangsoo, Jpn. J. Appl. Phys., 39, 4820–4825 (2000).
32) A. Bera, K. Deb, K. K. Chattopadhyay, R. Thapa and B. Saha, Microelectron. Eng., 162, 23–26 (2016).
33) B. Ahmad, S. Stoyanov, E. Pelan, E. Stride and M. Edirisinghe, Food Res. Int., 54, 1761–1772 (2013).
34) Z. Sun, J. M. Deitzel, J. Knopf, X. Chen and J. W. Gillespie, Jr., J. Appl. Polym. Sci., 125, 2585–2594 (2012).
35) A. Bera, K. Deb, S. Sinthika, R. Thapa and B. Saha, Mater. Res. Express, 5, 015909 (2018).
36) T. W. Chiu, J. H. Shih and C. H. Chang, Thin Solid Films, 618, 151–158 (2016).
37) Y. H. Lin, T. W. Chiu and J. H. Park, Ceram. Int., 44, S22–S25 (2018).
38) R. S. Yu, Y. F. Lee and Y. S. Lai, ECS J. Solid State Sci. Technol., 5, 646–652 (2016).
39) A. H. O. Alkhayatt, S. M. Thahab and I. A. Zgair, Optik, 127, 3745–3749 (2016).