Room temperature deposition of amorphous p-type CuFeO_2 and fabrication of $\text{CuFeO}_2/\text{n-Si}$ heterojunction by RF sputtering method

TAO ZHU^{1,2,3}, ZANHONG DENG^{1,2}, XIAODONG FANG^{1,2,3,*}, WEIWEI DONG^{1,2},
JINGZHEN SHAO^{1,2}, RUHUA TAO^{1,2} and SHIMAO WANG^{1,2}

¹Anhui Provincial Key Lab of Photonics Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China

²Key Lab of Novel Thin Film Solar Cells, Chinese Academy of Sciences, Hefei 230031, China

³University of Science and Technology of China, Hefei 230026, China

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Abstract. Transparent conducting amorphous p-type CuFeO_2 (CFO) thin film was prepared by radio-frequency (RF) magnetron sputtering method at room temperature using polycrystalline CuFeO_2 target. Amorphous structure of as-deposited film was confirmed by XRD. XPS analysis convinced that the chemical state of Cu^+ and Fe^{3+} in the film, and the chemical composition of the thin films is close to the stoichiometry of CuFeO_2 . Surface morphology of the film was analysed by SEM studies. p-type nature and concentration of carriers was investigated by Hall effect measurement. The p–n heterojunction in the structure of $\text{Al/n-Si/p-CuFeO}_2/\text{Al}$ showed good rectifying behaviour with a forward and reverse currents ratio of 555 at 2 V. The turn-on voltage and reverse leakage current values were found to be 0.9 V and 4 μA at -2 V. Further, the conduction mechanism of forward bias voltage was controlled by thermionic emission (TE) and trap-space charge limited current (TCLC) mechanisms.

Keywords. RF sputtering; amorphous; CuFeO_2 ; p–n heterojunction.

1. Introduction

Amorphous transparent conducting oxides (a-TCOs) are highly favourable for optoelectronic applications in numerous devices such as photovoltaics and flat-panel displays because they have inherent advantages, such as low-temperature deposition of thin films on large and cheap substrates, and are expected to have robust properties with regard to lattice mismatch in p–n heterojunctions [1]. However, TCOs such as ZnO_{1-x} , $\text{ZnO} : \text{In/Al/F/B/Ga}$, $\text{In}_{1-x}\text{Sn}_x\text{O}_3$ and $\text{SnO}_2 : \text{F}$, Cd_2SnO_4 are all n-type materials, there are only a few reports on p-type TCOs, such as delafossite oxides CuMO_2 , SrCu_2O_2 , $\text{Ca}_3\text{Co}_4\text{O}_9$ and the newly reported $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ [2–5].

Delafossite oxides CuMO_2 (M is trivalent cation, such as Al, Cr, Fe, ...) have been studied intensively since Kawazoe *et al* [2] first reported p-type transparent conducting thin films of CuAlO_2 in 1997. The delafossite structure of CuFeO_2 (CFO) can be described as sheets of edge-shared FeO_6 octahedra alternatively stacked with close-packed Cu-ion layers, and the rhombohedral $3R$ ($R\bar{3}m$) or hexagonal $2H$ ($P6_3/\text{mmc}$) structures can be formed depending on the stacking of the layers [6]. CFO is a well-known p-type semiconductor with the largest conductivity at room temperature ($\sigma_{\text{RT}} = 1.53 \Omega^{-1}\text{cm}^{-1}$) among the delafossites, when an off-stoichiometric $\text{CuFeO}_{2+\delta}$ phase is formed [7].

Polycrystalline CFO thin films have been prepared by pulsed laser deposition, electrodeposition radio-frequency sputtering and sol–gel method with conductivity varied from insulation to $1.7 \Omega^{-1}\text{cm}^{-1}$ [8–14]. In our previous studies, the effects of oxygen partial pressure on the structural, optical and electrical properties of CFO thin films deposited on Al_2O_3 (001) substrate by RF sputtering were studied [15]. In this study, the optical and electrical properties of a-CFO film on quartz glass deposited by RF sputtering at room temperature was studied and p–n heterojunction in the structure of Al/n-Si/p-CFO/Al has been fabricated.

2. Experimental

Polycrystalline CFO target for RF sputtering was prepared by conventional solid-state reaction. Stoichiometric Cu_2O (99%) and Fe_2O_3 (99%) were well mixed by ball-milling and then calcinated at 900°C in flowing N_2 atmosphere for 10 h. The obtained powders were pelleted and finally sintered at 1000°C in flowing N_2 atmosphere for 4 h. CFO thin film was deposited on quartz glass substrate at room temperature under a deposition oxygen pressure $\text{O}_2/(\text{O}_2 + \text{Ar})$ of 1% with total gas pressure of 3 Pa. The substrate–target distance is 6 cm and sputtering power is 4 W cm^{-2} .

A Philips SmartLabTM 9 kW X-ray diffractometer (XRD) with $\text{CuK}\alpha$ source was used to identify the crystalline phases. Diffraction patterns were taken from 10 to 80° with a scanning speed of 4° min^{-1} . ESCALAB250 X-ray photoelectron

* Author for correspondence (xdfang@aiofm.ac.cn)

spectrometer was used to determine the chemical states of the thin films. The spectra were acquired after sputter cleaning with an Ar ion gun at 2 keV for 20 s and calibrated with respect to the C-1s peak at 284.8 eV. A Σ IGMA HD/VP (Carl Zeiss, Germany) field-emission scanning electron microscope (FE-SEM) was used to check the crystallization and microstructures. The film thickness was obtained by a profilometer (XP-2, AMBIOS Technology Inc., USA). Optical transmittance was recorded using a UV-vis-NIR spectrophotometer (CARY-5E) at a fixed incidence angle perpendicular to the film surface and within the range of 200–2500 nm. The d.c. resistivity of the film was observed with a four point probe configuration. The van-der-Pauw method was applied to measure carrier mobility and carrier density by Hall measurement system (HMS). The current–voltage characteristics of the diode in the dark was performed using a Keithley model 2400 digital sourcemeter.

3. Results and discussion

Figure 1 shows the XRD patterns of the CFO target and film. As shown in figure 1a, all the diffraction peaks of the target are identified as the rhombohedral 3R ($R\bar{3}m$) delafossite structure (PDF 75-2146). As for the film, except for diffraction peak from the substrate, there is a wide and low bump located at $35\text{--}40^\circ$ which is stemmed from the film. Such result suggests that the thin film was composed of amorphous phase, presumably due to room temperature deposition in which the crystallization was discouraged. Since the strongest peaks of CuO , Cu_2O , CuFe_2O_4 and Fe_3O_4 are located in this range, it is hard to examine the chemical state of the ions solely from the XRD pattern.

To analyse the chemical state of the thin film, XPS was carried out. The core-level spectra of Cu-2p, Fe-2p and O-1s of the film are shown in figure 2. The Cu-2p spectra of the film have two distinct and intense peaks with the binding energies (BE) of the $\text{Cu-2p}_{3/2} = 932.9$ eV and $\text{Cu-2p}_{1/2} = 952.7$ eV. The binding energy is in good agreement with the

literature reports for Cu^+ in CFO [12,14,16]. There are also broad and weak satellite peaks located at 940.8, 943.7 and 947.2 eV, indicating the presence of small amounts of Cu^{2+} state [17,18]. The $\text{Cu}^{2+}/\text{Cu}^+$ ratio is calculated to be 8.8%. This may be due to the formation of $\text{Cu}^+/\text{Cu}^{2+}$ by intercalation of excess oxygen into the CFO lattice. According to the close-packing principle, the structure of the space group $R\bar{3}m$ is in the form of closest packing, of which the packing index is usually 74.05%, while the actual packing index for delafossite CFO is about 53.50%. So in CuFeO_2 , it is possible to introduce excess oxygen without changing the structural symmetry [19]. Two strong peaks in the Fe-2p spectra with the binding energies of $\text{Fe-2p}_{3/2} = 711.2$ eV and $\text{Fe-2p}_{1/2} = 724.3$ eV were observed, indicating that the Fe^{3+} oxidation state is in good accordance with the reports of CFO [12,14,16]. Additionally, the O-1s spectra exhibit a single peak at 530.7 eV. The above results indicate that the thin

Figure 1. (a) XRD patterns of the CFO target and (b) a-CFO thin film on quartz substrate.

Figure 2. X-ray photoelectron spectra for (a) Cu-2p, (b) Fe-2p and (c) O-1s of the a-CFO thin film.

film is composed of amorphous CuFeO_2 phase. The atomic concentration of Cu, Fe and O were calculated from the integrated area of each spectrum. The calculated atomic concentration is Cu 24.5%, Fe 24.8% and O 50.7%, which is close to the stoichiometry of CFO.

SEM was used to investigate the surface morphology of the film. As shown in figure 3, the film exhibits a compact and uniform state. The thickness of the as-deposited film is around 130 nm with roughness of 4–5 nm. Figure 4a shows the optical transmission spectrum in the range of 200–2500 nm of the substrate and film. There is only one absorption edge observed in the film. The optical bandgap, E_{OPT} is deduced by Tauc's relation

$$(\alpha h\nu)^n = A(h\nu - E_{\text{OPT}}), \quad (1)$$

where α denotes the absorption coefficient obtained by the relation: $\alpha = -\ln(T)/d$. The nature of the bandgap is identified by the exponent n and an intercept of the plot $(\alpha h\nu)^n$ with photon energy, $h\nu$ yields the optical bandgap energy. The optical bandgap of the thin film was obtained using the $(\alpha h\nu)^n$ vs. $h\nu$ plot as seen in figure 4b, with $n = 2$ for direct bandgap transition. By extrapolating the straight portion of the curve, the direct bandgap of the thin film was estimated to be around 3.25 eV, which is in good agreement with the previous reports of CFO [12,20].

p-type nature and concentration of carriers were investigated by Hall effect measurement. The film shows positive Hall coefficient. The carrier mobility and carrier density were $1.89 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.80 \times 10^{17} \text{ cm}^{-3}$, respectively, making the resistivity $11.76 \Omega \text{ cm}$.

Heterojunction was fabricated in the structure of Al/n-Si/p-CFO/Al. The resistivity and carrier concentration of n-Si are $1\text{--}10 \Omega \text{ cm}$ and $1 \times 10^{15} \text{ cm}^{-3}$, respectively. The area of the junction was 0.19 cm^2 . The I – V characteristic between Al contacts on a-CFO is linear in the positive voltage region and approximate linear in negative voltage region (inset of figure 5). The dark I – V characteristic

Figure 3. SEM image of the a-CFO thin film.

Figure 4. (a) Optical transmittance spectra and (b) $(\alpha h\nu)^2$ vs. $h\nu$ plots of the a-CFO thin film.

Figure 5. I – V characteristics of $\text{CuFeO}_2/\text{n-Si}$ heterojunction diode at room temperature and the inset shows the I – V curve of Al contacts on CFO film.

Figure 6. Equilibrium energy band diagram of the heterojunction.

of the heterojunction exhibits a good rectifying behaviour with a $I_F/I_R = 555$ at 2 V indicating the formation of a diode as seen in figure 5 (I_F and I_R stand for the forward and reverse currents, respectively). The turn-on voltage and reverse leakage current values are found to be 0.9 V and 4 μ A at -2 V.

Figure 6 shows the energy band diagram of the junction. The electron affinity and bandgap values for CFO and n-Si are $\chi_{\text{CFO}} = 4.21$ eV [21], $E_{g \text{ CFO}} = 3.25$ eV and $\chi_{\text{Si}} = 4.05$ eV, $E_{g \text{ Si}} = 1.12$ eV [22], respectively. The model shows a small conduction band offset (0.16 eV) and a large valence band offset (2.29 eV). It is seen from figure 6 that the barrier to electrons is much higher than that of holes ($qV_D - \Delta E_c > qV_D - \Delta E_v$), so hole current will be predominant and electron current is negligible. Further, the valence-band edge in Si is lower than its peak in CFO, so thermionic emission theory (TE) can be used to analyse the charge transport mechanism. Because the saturation current in TE theory is independent of voltage, it exactly explains that the variation of $\ln I$ with V is near a straight line at small voltages ($0.025 \leq V \leq 0.425$) as seen in figure 7. The diode equation of the dark according to the TE theory is given as:

$$I = I_0(\exp(qV/nkT) - 1), \quad (2)$$

where I_0 is the saturation current, q the electronic charge, V the applied voltage, k the Boltzmann constant, T the temperature and n the ideality factor [23]. The saturation current based on TE mechanism can be given as:

$$I_0 = AA^*T^2 \exp(q\phi_b/kT), \quad (3)$$

where A is the diode contact area, A^* the effective Richardson constant ($A^* = 112 \text{ A cm}^{-2}, \text{ K}^2$ for n-Si) [24,25]. ϕ_b the effective barrier height at zero bias. The value of ϕ_b is calculated through the other form of equation (3) as:

$$\phi_b = kT/q \ln(AA^*T^2/I_0). \quad (4)$$

Figure 7. Variation of $\ln I$ vs. V for CuFeO₂/n-Si heterojunction diode at voltage range ($0.025 \leq V \leq 0.425$).

Figure 8. The forward I – V characteristics of the CuFeO₂/n-Si heterojunction diode in double logarithmic scale at room temperature.

Here, the value of I_0 was determined from the intercept of the best fit straight line as seen in figure 7. The calculated values of I_0 and ϕ_b were found to be 8.42×10^{-8} A and 0.79 eV, respectively. The value of the ideality factor n was obtained from the slope of the best fit straight line and the value was found to be 6.03. However, for ideal diodes, n varies between 1 and 2. The high value of ideality factor was attributed to poor interface and defects at the interface. According to Wang *et al* [2], the heterojunction diode can be modelled in different bias ranges by a series of diodes and resistances [26]. The ideality factor of the device is the sum of ideality factors of the individual junctions and may lead the ideality factor to much greater than 2 [27].

At higher voltages ($0.425 \leq V \leq 2$), the forward I – V characteristics of the diode was plotted in double logarithmic scale as shown in figure 8. The $\log I$ – $\log V$ curve is characterized by two different linear regions. If there are deep traps at the interface, the charge transport profile will be modified

and these modifications will affect the slopes of the $I-V$ characteristics, by applying the law of the current density changes in the form of $I \propto V^m$. The m values were obtained from the slopes of the two regions, by using a linear fit, and they were found to be 6.01 and 3.27, respectively. These values indicate that the conduction mechanism of two regions are controlled by trap-charge limited current (TCLC), where the exponent ($m \geq 2$) is dependent on the energy distribution of trap levels within the forbidden band [28].

4. Conclusions

Amorphous CuFeO₂ thin films were prepared by RF sputtering on quartz substrate at room temperature and the structural and optoelectronic properties of the film were studied. The optical transmission spectrum of the a-CFO thin film shows only one gradual absorption edge in the range of 200–2500 nm with a bandgap around 3.25 eV. The p–n heterojunction in the structure of Al/n-Si/p-CuFeO₂/Al was fabricated at room temperature. The heterojunction showed good rectifying behaviour with a forward and reverse currents ratio of 555 at 2 V. The turn-on voltage and reverse leakage current values were found to be 0.9 V and 4 μ A at –2 V. Analysis of the energy band diagram and log I –log V curve suggest that the conduction mechanism of the junction was controlled by TE and TCLC mechanisms.

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