

Synthesis and Room Temperature Ferromagnetism in Fe-Doped CuAlO₂ Semiconductor

CHEN Chen¹, DONG Chengjun^{1,2}, WANG Biao³, HUANG Jiangqiang¹, WANG Yiding^{1*}

(1. State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China; 2. Department of Materials Science, Jilin University, Changchun 130012, China; 3. Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China)

Abstract: The synthesis and characterization of Fe-doped CuAlO₂ semiconductor were reported. The samples were synthesized by a simple and cost effective spin-on technique from solid state reaction of Cu₂O and Al₂O₃ on sapphire (001) substrate. Appropriate ethyl-cellulose (EC) and terpineol are useful for the formation of Fe-doped CuAlO₂ films. X-ray diffraction (XRD) revealed the growth of pure delafossite CuAlO₂ phase ruled out elemental metallic Fe clusters in all the Fe incorporated CuAlO₂ films. The existence of ferromagnetism at room temperature is evidenced by well-defined hysteresis loops. Specially, the saturation magnetization (M_s) values at room temperature have been monotonously enhanced with the increase of Fe composition from 1% to 5%.

Key words: Fe-Doped CuAlO₂; delafossite structure; ferromagnetism

1 Introduction

Exploring of ferromagnetic semiconductors with Curie temperature (T_c) at or above room temperature (RT) has received huge research interest due to their potential applications in designing the materials for spintronics devices by manipulating both charge and spin simultaneously^[1]. Following the theoretical prediction by Dietl *et al* of room temperature ferromagnetism in Mn doped ZnO and GaN^[2], a variety of transition metal (TM) doped oxides, such as ZnO^[3,4], In₂O₃^[5,6], TiO₂^[7,8], and SnO₂^[9,10] were investigated extensively. However, most of the experimental and theoretical efforts have so far mainly focused on n-type oxide semiconductors, somehow ignoring the existence of pristine p-type oxide-based diluted magnetic semiconductors (DMSs). A recent discovered transparent p-type oxide semiconductor, CuAlO₂ with wide band gap energy of about 3.5 eV (direct) and 1.8

eV (indirect)^[11] could open an avenue to a series of novel applications. Then, the theoretical calculation based on CuAlO₂ using first-principles showed that the ferromagnetic states of (Cu, Fe) AlO₂ are one of highly stabilized, which can be candidates of the ferromagnetic DMSs^[12]. The magnetic properties of Mn-doped transparent CuAlO₂ semiconductor have been reported by Zhang *et al*^[13]. Meanwhile, the improvement in thermoelectric properties of CuAlO₂ by adding Fe₂O₃ has been published^[14]. However, the experimental evidence in room temperature ferromagnetism in Fe-Doped CuAlO₂ is still highly expected. Roundly understanding the magnetic behavior in Fe-doped CuAlO₂ semiconductor will facilitate its potential applications in spintronic devices.

In this work, Fe-doped CuAlO₂ has been successfully synthesized by solid state reaction from Cu₂O and Al₂O₃ by adding Fe₂O₃. Firstly, the reagents were milled and mixed with appropriate ethyl-cellulose (EC) and terpineol. Precursor films have been prepared by spin-coated technique with sapphire (001) serving as the substrate. Thereafter, the CuAlO₂ films were obtained from the coated films by annealing at the temperature of 1 150 °C in air. Moreover, we systematically investigate the influence of Fe on the magnetic properties of CuAl_{1-x}Fe_xO₂ with $x=0.00-0.05$ prepared under the same synthesis conditions.

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CHEN Chen(陈晨): Ph D; E-mail: cchen19831102@gmail.com

*Corresponding author: WANG Yiding(王一丁): Prof.; Ph D; E-mail: wangyiding48@yahoo.com.cn

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2 Experimental

All samples of $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ film with $x=0.00-0.05$ were synthesized by solid state reaction on the sapphire (001) substrate. Stoichiometric mixture of the powders of Cu_2O , Al_2O_3 , and Fe_2O_3 with purity of 99.99% was milled for 10 h, and then was mixed with proper amount of ethyl-cellulose (EC) and terpeneol. The films were spin-coated onto sapphire (001) substrates at a speed of 8 000 rpm for 30 s. After that, the samples were dried at 60 °C for 10 min, and then preheated at 350 °C for 3 h to evaporate the solvent and remove organic residues in air. Finally, all deposited films were annealed at 1 150 °C for 3 h in a corundum tube furnace and a natural cooling was maintained after finishing the annealing. Before deposition, sapphire substrates were subjected to clean sequentially with acetone, ethanol, and deionized water in an ultrasonic cleaner. Because of the low Fe content, weighing error can be lessened by increasing the molar fraction of reagents. Furthermore, a physical balance with a precision of three decimal figures was used for weighing.

The obtained samples were structurally characterized using X-ray diffraction (XRD, BRUKER, D8 ADVANCE) with an incident X-ray wavelength of 1.540 Å. To investigate the surface and cross-section morphology of films, field emission scanning electron microscopy (FE-SEM) images were carried out on a JEOL JEM-6700F microscope. The surface chemical composition and bonding states were further studied by X-ray photoelectron spectroscopy (XPS) using monochromated Al α ($h\nu=1\,486.7$ eV) source in ESCALAB 250Xi XPS system. All the XPS spectra were accurately calibrated by the C 1s peak (284.6 eV). Finally, a vibrating sample magnetometer (Lake Shore7410) was used for the room temperature magnetic measurements.

3 Results and discussion

The top view FE-SEM micrograph of pure CuAlO_2 film grown on sapphire (001) substrate has been shown in Fig.1. It is obviously seen that the grain size is of asymmetry without porosity in order of micron. Significantly, none of obvious difference is observed in terms of CuAlO_2 doped with Fe (not shown here).

The phase purity and crystal structure of the $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ ($x=0.00-0.05$) films prepared have

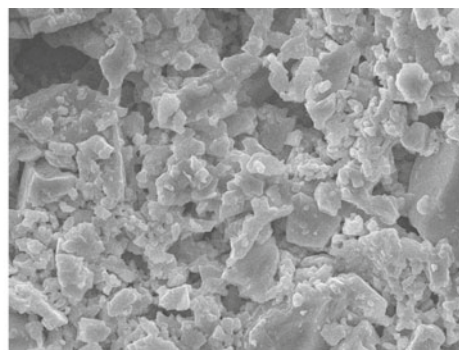


Fig.1. FE-SEM surface image of pure CuAlO_2 film

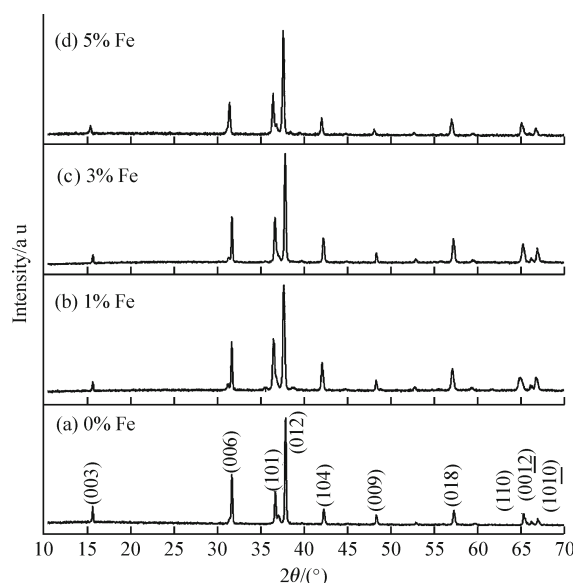


Fig.2 X-ray diffraction spectrum of $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ films with $x=0.00-0.05$

been analyzed by X-ray diffraction (XRD). The XRD patterns, as shown in Fig.2, of pure CuAlO_2 and Fe-doped CuAlO_2 films matched well with that of the standard delafossite CuAlO_2 (JCPDS card 77-2493, space group: $R\bar{3}m$)^[16]. For the Fe-added $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$, no diffraction peak corresponding to any other secondary phase such as Fe clusters, CuO , Fe_2O_3 and CuFeO_2 phases were observed, which is in good agreement with other Fe doped CuAlO_2 publication^[14]. This means that the Fe has been doped into the CuAlO_2 crystal structure to form a solid solution. Both the lattice parameters a and c were found to slightly increase from 2.85 to 2.87 Å and 16.86 to 16.99 Å, respectively, as the concentration of Fe is increased from 0 to 5%. Since the ion radii of Fe (valence of +2 (0.92 Å) or +3 (0.65 Å)) is always smaller than Cu^{1+} (0.95 Å) but larger than Al^{3+} (0.55 Å)^[14], as such, the decrease of c lattice constant could be detected if Fe ions are doped at the Cu-sites. The lattice parameters of a and c show the tendency of subtly increase with respect to Fe content increasing for our samples. Thus,

it is reasonable concluded that Fe ions substitute for the Al-site but not the Cu-site, which is following the other results of Fe doped CuAlO_2 ^[14]. Particularly, all films with a strongly oriented (012) have been confirmed by XRD measurements as well which will facilitate the development of the p-type oxide-based DMSs materials.

X-ray photoelectron spectroscopy (XPS) was carried out to determine the existence and valence of Fe element. A typical XPS spectra of $\text{CuAl}_{0.95}\text{Fe}_{0.05}\text{O}_2$ sample showed the indexed peaks corresponding to Cu, Al, Fe, and O, calibrated by C 1s (284.6 eV) as shown in Fig.3. The Cu $2p_{3/2}$ component in Fig.4(a) is centered at 933.27 eV binding energy with a full width at half maximum (FWHM) of around 1.7 eV. The Cu $2p$ spectra are dominated by a simple spin-orbit split doublet of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ distanced away from 19.85 eV each other. This reflects a Cu $3d^{10}$ configuration in the final state deriving from Cu^{1+} , which is well consistent with other results^[17]. The Al $2p$ peak is found at 74.32 eV and O 1s peak of being at 531.23 eV, which are identified as the valence of oxygen to be the chemical state -2 and aluminum to be +3, respectively.

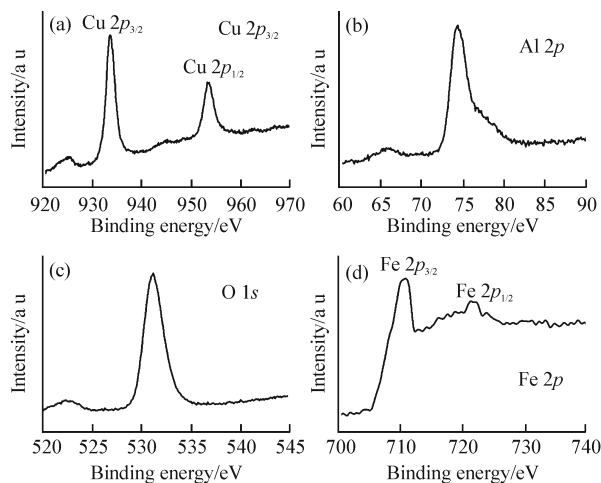


Fig.3 A typical XPS pattern of the Cu $2p$, Al $2p$, O $1s$, and Fe $2p$ spectral regions for $\text{CuAl}_{0.95}\text{Fe}_{0.05}\text{O}_2$

As shown in Fig.3(d), the peak of Fe $2p_{3/2}$ located at 709.9 eV and the peak of Fe $2p_{1/2}$ positioned at 721.6 eV, respectively. Moreover, we also check that the peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ for metal Fe are located at 706.75 eV and 719.95 eV from XPS handbook. This excludes the formation of iron metal clusters in our samples. So, both the peak position and the energy difference between Fe $2p_{3/2}$ and Fe $2p_{1/2}$ indicate that Fe element exists in the ion form, with the valence of +2 and/or +3, which is referenced to other observation^[18].

Considering XRD and magnetic measurements together, we believe that Fe element incorporates into the lattice frame of CuAlO_2 by substituting the position of Al atoms. Subsequently, those samples were used for magnetic measurements.

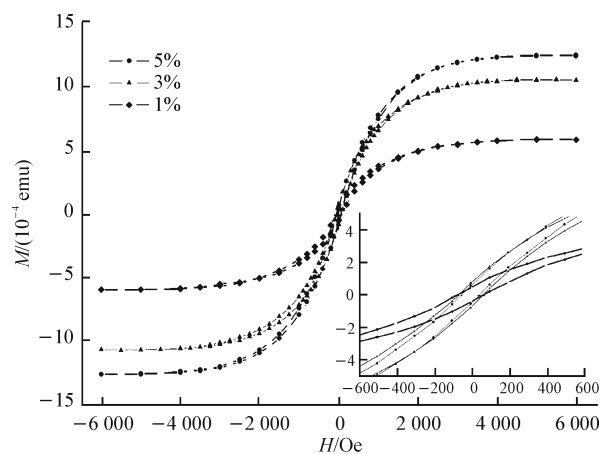


Fig.4 Magnetization (M) versus magnetic field (H) of $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ films with $x=0.01-0.05$ measured at room temperature, and enlargement of the low-field region (inset)

The magnetic properties of $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ were determined by vibrating sample magnetometer (VSM) at room temperature. Fig.4 showed the magnetic loops of samples $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ films with $x=0.01-0.05$, which is convincingly evidence of room temperature ferromagnetic behavior according to well-defined hysteresis loops. Apparently, the coercivity (H_c) values are 67.28, 73.13, and 43.88 Oe for Fe composition of 1%, 3%, and 5%, respectively (Fig.4, inset). However, the saturation magnetization (M_s) values at room temperature have been monotonously increased from 5.98×10^{-5} emu to 1.26×10^{-4} emu with the increase of Fe content from 1% to 5%. The room temperature ferromagnetism, in our case, is not supposed to arise from the metallic Fe cluster, nor from any secondary iron oxide phases according to the XRD and XPS analysis. Furthermore, the diamagnetism of pure CuAlO_2 sample has been identified in our recent investigations^[15]. Thus, the observed ferromagnetism is essentially intrinsic in origin to some extent. Up to now, the origin of ferromagnetism in DMSs is not very clear, even if various models have been put forward^[8, 19]. It is believed that the double exchange interaction is the dominant exchange mechanism in term of $(\text{Cu,Fe})\text{AlO}_2$ upon calculated density of states (DOS)^[12]. It is recently found that the weak magnetism of the material may derive from the polarised unpaired electrons nearby defects^[20]. Obviously, much more effort is involved to explore the magnetic properties of CuAlO_2 -based

DMSs into a practical state.

4 Conclusions

CuAl_{1-x}Fe_xO₂ films with $x=0.00-0.05$ were successfully synthesized on sapphire substrate using spin-on technique assisted by proper ethyl-cellulose (EC) and terpeneol. Considering the structure and magnetic properties together, we believe that Fe element incorporates into the lattice frame of CuAlO₂ by substituting the position of aluminium atoms and results an intrinsic ferromagnetism at room temperature. The synthesized Fe-doped CuAlO₂ may open up significant potential for theoretical research and application of CuAlO₂-based DMSs spintronic device.

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