Journal of Alloys and Compounds 614 (2014) 221–225

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Structural, electrical, optical and magnetic properties of p-type $Cu(Cr_{1-x}Mn_x)O_2$ thin films prepared by pulsed laser deposition

Xiaoshan Zhou, Fangting Lin *, Wangzhou Shi, Aiyun Liu

Key Laboratory of Optoelectronic Material and Device, Department of Physics, Shanghai Normal University, Shanghai 200234, PR China

ARTICLE INFO

Article history:
Received 29 March 2014
Received in revised form 4 June 2014
Accepted 18 June 2014
Available online 27 June 2014

Keywords:
Semiconductors
Magnetic films and multilayers
Microstructure
Electrical transport
Optical properties
Magnetization

ABSTRACT

$Cu(Cr_{1-x}Mn_x)O_2$ delafossite thin films ($0 \leqslant x \leqslant 15$ at.%), with a *c*-axis quasi-epitaxial orientation, were prepared by pulsed laser deposition. The effects of Mn content on microstructure and physical properties were investigated. Both the variation of lattice constant *c* and X-ray photoelectron spectroscopy reveal that the Mn ions substitute for Cr^{3+} as Mn^{3+} and Mn^{4+}. The proportion of Mn^{4+} is gradually increased with the Mn doping, leading to the changes of hole density and mobility. As a result, the p-type conductivity is decreased at first and then increased. The conduction mechanism is thermal activation between 130 and 300 K. It is indicated that the PLD method and the Mn^{3+}–O–Mn^{4+} and Mn^{3+}–O–Cr^{3+} double-exchange interactions are favorable to the high hole density and mobility, respectively. Meanwhile, the double-exchange interactions produce the near-room-temperature ferromagnetism. The saturation magnetization and Curie temperature are gradually increased with the Mn content. For optical properties, all thin films have a comparatively high transmittance for visible light, with the highest value 70% for $x = 15$ at.% at the wavelength of 750 nm. As increasing the Mn content, the transparency and direct optical bandgap exhibit the similar trend as the hole density. With the relatively balanced electrical, magnetic and optical properties, these pulsed-laser-deposition-grown $Cu(Cr_{1-x}Mn_x)O_2$ thin films are expected to become a promising p-type transparent diluted magnetic semiconductor material.

1. Introduction

In the semiconductor industry there is an uninterrupted evolution towards higher and higher integration which results in capability increase of devices and dimension reduction of elements. Hence numerous researches on multifunctional materials, e.g. diluted magnetic semiconductors (DMSs), ferroelectric semiconductors, ferroelectric photovoltaic materials and multiferroic materials, have been motivated in both technological and scientific fields. Oxide-based DMSs exhibit unique magnetic, magneto-electrical and magneto-optical effects as well as high transparency in the visible region. They can be used in spintronic devices and transparent optoelectronic devices, such as spin-valve transistors, spin light-emitting diodes, nonvolatile logic devices, transparent electrodes in flat panel displays, and window layers in solar cells.

Especially, p-type oxide-based DMSs have substantially aroused the researchers' enthusiasm, because theoretical predictions [1–3] pointed out that ferromagnetic coupling between magnetic ions could be formed more easily in p-type semiconductors due to hole carriers serving as a medium. In such a way, some key issues existing in the present DMSs are expected to be alleviated, e.g. small magnetization and low Curie temperature (T_C).

As one typical p-type transparent conducting oxide (TCO), $CuCrO_2$ delafossite with the ABO_2 structure is considered as an excellent candidate for the matrix semiconductor. Its conductivity ($\sigma = 220$ S cm^{-1}) is the highest one among all p-type TCOs [4], which is beneficial to the magnetic exchange mechanism [1–3]. Low-temperature ferromagnetism has been successively achieved in $Cu(Cr_{1-x}M_x)O_2$ (M = Mn [5], Ni [6,7], Al [8], Rh [9], Co [10]) ceramics. In 2011, Wang et al. [11] synthesized $Cu(Cr_{1-x}Mn_x)O_2$ thin films by chemical solution deposition and obtained room-temperature ferromagnetism which was ascribed to the double-exchange (DE) interaction between Mn^{3+} and Cr^{3+}. However, the highest transmittance in the visible range, about 65%, was not satisfactory, and the resistivity (ρ) increased rapidly with the Mn content. The lowest ρ value from un-doped $CuCrO_2$ film was 74 Ω cm, whereas those of Mn-doped ones were even about four orders of magnitude higher.

In our work, a physical method, pulsed laser deposition (PLD), was adopted to prepare *c*-oriented Mn-doped $CuCrO_2$ thin films. The near-room-temperature ferromagnetism is achieved, and the highest transmittance for visible light is improved by 5% compared with Ref. [11]. More important, the p-type conductivity is

* Corresponding author. Tel.: +86 21 64322726; fax: +86 21 64328894.
E-mail address: nounou7@163.com (F. Lin).

http://dx.doi.org/10.1016/j.jallcom.2014.06.127
0925-8388/

remarkably enhanced. In comparison with the similar compositions in Ref. [11], the σ values of our un-doped and Mn-doped $CuCrO_2$ films are respectively about two and three orders of magnitude higher. Our thin films possess relatively balanced electrical, optical and magnetic properties, showing promise for applications in multifunctional devices.

2. Experimental

$Cu(Cr_{1-x}Mn_x)O_2$ thin films (x = 0, 5, 10 and 15 at.%) were grown on $Al_2O_3(001)$ substrates by PLD (KrF excimer laser, λ = 248 nm). The targets were prepared by the solid-state reaction technique. High-purity (99.99%) CuO, Cr_2O_3 and MnO_2 powders based on the stoichiometric compositions were mixed, ground and calcined at 1050 °C for 24 h. Subsequently, the powders were pressed and sintered at 1200 °C for 48 h. The substrates with a size of 1.5 × 1.5 cm^2 were cleaned with ethanol and acetone in an ultrasonic cleanser and rinsed with deionized water. The substrate was set parallel to the target at a distance of 6 cm. In order to obtain uniform thin films, both the target and substrate were rotated at a speed of 6 rpm during the deposition. Thin films were deposited at 750 °C for 15 min in oxygen atmosphere with a pressure of 5 Pa. The base pressure was lower than 1×10^{-4} Pa. The pulse energy and repetition rate were fixed at 200 mJ and 8 Hz, respectively.

Crystal structure was analyzed by X-ray diffraction (XRD) on a Bruker D8 Focus diffractometer with Cu Kα radiation. The thickness of thin films was determined by a Bruker DektakXT Stylus Profiler. Valence states of ions were verified by X-ray photoelectron spectroscopy (XPS) using a Perkin–Elmer PHI 5000C ESCA system with Al Kα radiation. The DC resistivity was measured with a four-point probe configuration. The carrier type, density and mobility were determined at room temperature by a Lake Shore 7600 hall measurement system (HMS). The optical transmission spectra were recorded using an Aquila NKD-8000 spectrophotometer. The magnetization vs. magnetic field (M–H) curves and the magnetization vs. temperature (M–T) curves were measured on a Quantum Design PPMS-9T (EC-II) physical property measurement system (PPMS), with an applied magnetic field parallel to the film plane.

3. Results and analysis

3.1. Structural properties

3.1.1. XRD characterization

Fig. 1 gives the XRD patterns for $Cu(Cr_{1-x}Mn_x)O_2$ thin films. There is no structural difference among four samples. All films are crystallized in a single 3R-$CuCrO_2$ delafossite structure (JCPDF No. 89-0539). No evidence for impurity formation (e.g. manganese oxides) or phase separation is found. Therefore the Mn ions seem to have been incorporated into the host lattice, substituting for Cr^{3+}. Moreover, only (003), (006), (009) and (0012) diffraction peaks from $CuCrO_2$ delafossite are observed. It means that these films have a quasi-epitaxial growth orientation along the c axis. The Full-Width at Half-Maximum (FWHM) of (006) peaks ranges between 0.32° and 0.43°.

The calculated lattice constant c is plotted in the inset of Fig. 1, in accordance with 3R-$CuCrO_2$ (JCPDS No. 89-0539). With the Mn addition, the c value is increased at first; and then its increase slows down obviously; finally, it is remarkably decreased instead. According to Ref. [12], the ionic radii in Coordination (VI) are 0.615, 0.830, 0.645 and 0.530 Å, respectively, for Cr^{3+}, Mn^{2+}, Mn^{3+} and Mn^{4+}. Firstly, the existence of Mn^{2+} can be excluded. If the Mn valence were 2+, the increase of c would be much greater owing to the much larger size of Mn^{2+} than that of Cr^{3+}. Moreover, our ceramic targets were prepared using MnO_2 as raw material and sintered in air for a long time and the corresponding thin films were grown in oxygen atmosphere. During such a preparation process, Mn^{2+} is very unlikely to form, but Mn^{4+} is likely to exist. Combined with the variation in lattice constant, the Mn ions are deduced to replace Cr^{3+} in the mixed valence state: Mn^{3+} and Mn^{4+}. At x = 5 at.%, the Mn^{3+} ions are dominant over Mn^{4+}, leading to a 0.31% increase in c because the ionic radius of Mn^{3+} is larger than that of Cr^{3+}. As x is raised to 10 at.%, the proportion of Mn^{4+} ions is enhanced, and therefore c is increased by only 0.04% due to the smaller size of Mn^{4+} compared with Cr^{3+}. When x reaches 15 at.%, the proportion of Mn^{4+} is further enhanced. As a result, the c value no longer increases but decreases instead, even 0.30% lower than that of un-doped $CuCrO_2$.

3.1.2. XPS characterization

The XPS measurements were carried out to determine the valence states of ions. All thin films show similar results and the x = 15 at.% one is taken for example here as presented in Fig. 2. The typical Cu 2P XPS spectrum is observed in Fig. 2(a). Its line shape with no clear satellite is quite similar to that of Cu_2O (Cu^+). Hence the Cu ions are concluded to be in the monovalent state [5,13]. From Fig. 2(b), it can be seen that the Cr $2p_{3/2}$ peak is located at 576.1 eV and the energy difference between the Cr

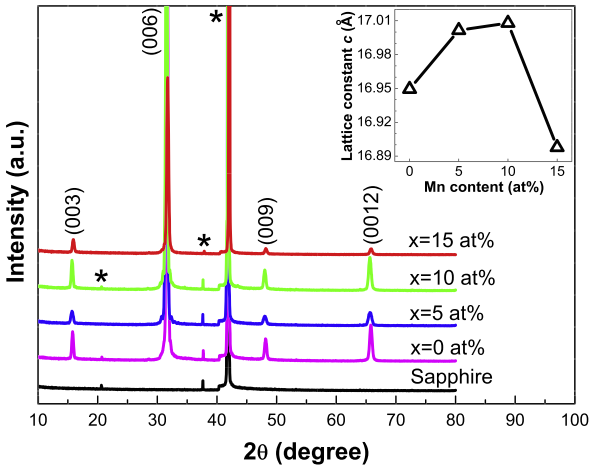

Fig. 1. XRD patterns of $Cu(Cr_{1-x}Mn_x)O_2$ thin films on sapphire substrates. The peaks marked by an asterisk (*) correspond to the substrate. The inset shows the composition dependence of lattice constant c.

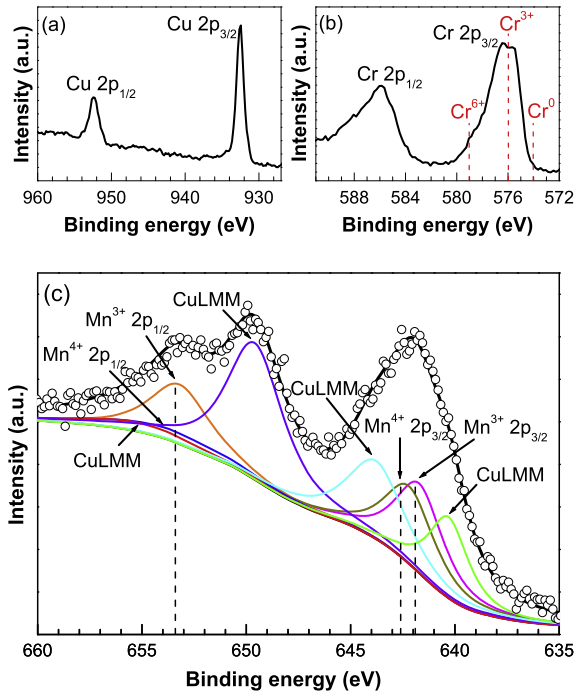

Fig. 2. XPS spectra of $Cu(Cr_{0.85}Mn_{0.15})O_2$ thin film: (a) Cu 2p XPS spectrum, (b) Cr 2p XPS spectrum, and (c) Mn 2p XPS spectrum where points and solid lines represent the experimental and fitting data, respectively.