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Thickness-dependent optoelectronic properties of $CuCr_{0.93}Mg_{0.07}O_2$ thin films deposited by reactive magnetron sputtering

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ABSTRACT

$CuCr_{0.93}Mg_{0.07}O_2$ thin films were successfully deposited by DC reactive magnetron sputtering at 1123 K from metallic targets. The influence of film thickness on the structural and optoelectronic properties of the films was investigated. X-ray diffraction (XRD) results revealed that all the films had a delafossite structure with no other phases. The optical and electrical properties were investigated by UV–VIS spectrophotometer and Hall measurement, respectively. It was found that the optoelectronic properties exhibited a thickness-dependent behavior. The optical band gap and the average transmittance of the films showed a monotonous decrease with respect to the increase in thickness. The average transmittance in the visible region decreased from 67% to 47% as the thickness increased from ~70 nm to ~280 nm. Simultaneously, the conductivity of the films fell from 1.40 $S{\cdot}cm^{-1}$ to 0.27 $S{\cdot}cm^{-1}$. According to Haacke's figure of merit (FOM), a film with a maximum FOM value of about $1.72\times10^{-7}\ \Omega^{-1}$ can be achieved when the thickness is about 70 nm ($\sigma\approx$ 1.40 $S{\cdot}cm^{-1}$ and $T_{av.}\approx$67%).

1. Introduction

Transparent conductive oxides (TCOs) are materials that possess relatively high electrical conductivity and high optical transmittance in the visible light region. They are widely used in photovoltaic devices, flat panel displays, and light emitting diodes in the microelectronics industry [1–4]. In the last few decades, attention has been focused on n-type TCOs such as In_2O_3:Sn (ITO), ZnO:Al (AZO), and ZnO:Ga (GZO), some of which exhibit both transmittance of over 90% in the visible spectrum and high conductivity of about 10^4 $S{\cdot}cm^{-1}$ [5–8]. However, the performance of p-type TCOs is relatively poor; in particular, their conductivity is about 3–4 orders of magnitude lower than that of n-type TCOs [9–11]. In this case, the development of transparent p-n junctions is restricted by the slow progress of p-type TCOs. To date, almost no practical applications based on transparent p-n junctions have been developed. In 2000, H. Kawazoe et al. indicated that copper-based oxides with a delafossite structure had great potential as p-type TCOs [12]. In this type of oxide, because the energy level of the Cu*3d* orbital is comparable to that of the O*2p* orbital, the hybridization of these two orbitals can reduce the strong localization of hole carriers in the valence band and facilitate their migration [12]. These results are encouraging, since they confirm that it is possible to obtain p-type TCOs with high conductivity. $CuCrO_2$-based thin films with a wide band gap of 3.10 ~ 3.25 eV are considered to be particularly good candidates [13–15]. Many efforts have focused on them in the last decade [16–18].

Depending on the requirements of the applications, the thickness of TCO thin films varies from a few tens of nanometers to several micrometers. The films' thickness has a significant effect on their optoelectronic properties. This effect differs for various materials and even for the same material synthesized by different processes [19].

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Singh et al. reported the thickness-dependent optoelectronic properties of ZnO thin films in 2014 [20]. They found that, due to the quantum confinement effects in thinner films and the relaxation of the compressive stress effect in thicker films, the band gap of the films decreases as the thickness increases. Dong et al. investigated the influence of the thickness of $CuAlO_2$ thin films on their electrical properties and found that both carrier concentration and carrier mobility were enhanced with increases their thickness [21]. Pardo et al. studied the thickness-dependent transport properties of $Sr_4Fe_6O_{13}$ thin films and found that the conductivity of thicker films was degraded relative to that of thinner films [22]. The same result was also reported by Rabeh et al. for $CuInS_2$ thin films [23]. However, the mechanism remains unclear.

To the best of our knowledge, the influence of film thickness on the optoelectronic properties of $CuCrO_2$-based thin films remains uninvestigated. It may be important to understand how the thickness affects the performance of $CuCrO_2$-based films. In this work, $CuCr_{0.93}Mg_{0.07}O_2$ thin films with a delafossite structure were deposited by DC reactive magnetron sputtering. The evolution of the structural and optoelectronic properties with variations in film thickness are discussed.

2. Experimental details

2.1. Sputtering deposition

$CuCr_{0.93}Mg_{0.07}O_2$ thin films were deposited on fused quartz, silicon, and alumina substrates by DC reactive magnetron sputtering. An argon-oxygen mixture was used as the reactive gas. The working pressure was maintained at about 0.95 Pa. Pure copper, chromium, and magnesium targets (purity 99.99%, 50 mm in diameter and 3 mm thick) were mounted on balanced magnetrons and powered by pulsed DC supplies (Advanced Energy Pinnacle$^+$). A description of the reactor can be found elsewhere [24]. In our experiments, the films were first deposited at 1023–1123 K in order to verify the crystallization temperature of the $CuCrO_2$ delafossite structure. Then films with various theoretical thicknesses of 70–280 nm were deposited at 1123 K. The thickness was controlled by varying the deposition time from 10 min to 40 min. Other sputtering parameters are listed in Table 1.

2.2. Characterisation

The chemical compositions of the films were measured by energy dispersive spectroscopy (EDS). The structures were characterized by X-ray diffraction (XRD) using a BRUKER D8 focus diffractometer ($Co_{K\alpha1+\alpha2}$ radiations) in the Bragg-Brentano configuration. The thickness and morphological properties of the films were obtained with a JEOL JSM-7800F field emission scanning electron microscope (FE-SEM). The microstructures were observed from cross-sections of the films by JEOL JEM-2100 high resolution transmission electron microscopy (HR-TEM). The specimens were prepared by focused ion beam (FIB) milling before HR-TEM observation. Hall effect analysis was employed to characterize the electrical properties of the films. The optical properties were measured with a Shimadzu UV-3600 UV–VIS spectrophotometer using a sampling interval of 1.0 nm. The average transmittance in the visible region was obtained with the following equation:

$$T_{average} = \frac{\int_{\lambda_1}^{\lambda_n} T(\lambda)\,d\lambda}{\lambda_n - \lambda_1} \approx \frac{1}{m}\sum_{\lambda=\lambda_1}^{m} T(\lambda) \quad (m = \lambda_1, \lambda_2, \lambda_3 \ldots \lambda_n) \tag{1}$$

where $\lambda_1 = 400$ nm and $\lambda_n = 800$ nm.

Table 1
Sputtering parameters maintained during deposition of $CuCr_{0.93}Mg_{0.07}O_2$ thin films.

Target (metallic)	Cu	Cr	Mg
Discharge current (A)	0.16	0.73	0.15
Pulsed frequency (kHz)	50	50	50
Time off (μs)	5	5	5
Argon flow rate (sccm)	100	Draw distance (mm)	60
Oxygen flow rate (sccm)	10	Run duration (min)	10 → 40
Total pressure (Pa)	~ 0.95	Substrate temperature (K)	~1123

3. Results and discussion

3.1. Towards the delafossite structure

Before the deposition of the films of various thicknesses, the composition was confirmed by EDS measurement. According to the results reported by other authors [15,25–27], the optimal doping amount of magnesium in the films is lower than 10 at%. If too much magnesium is introduced into the films, $MgCr_2O_4$ impurity phase may form and the optoelectronic performance thus degraded [28,29]. In our previous work, we confirmed that $CuCr_{0.93}Mg_{0.07}O_2$ film crystallized *ex-situ* by post annealing with stoichiometric composition (ABO_2) possesses the optimal performance, with no other phases being detected [30]. Therefore, we fixed the film composition in the current work and first investigated the influence of the deposition temperature on the structural properties of the films. The films were deposited on hot substrates at 1023–1123 K for 30 min. Their structural properties as a function of the deposition temperature are shown in Fig. 1. In the film deposited at 1023 K, spinel structure $CuCr_2O_4$ (JCPDS: 00–026–0509) formed first. $CuCrO_2$ (JCPDS: 01–089–0539) phase with a delafossite structure crystallized when the deposition temperature was 1073 K. When the substrate temperature was further increased to 1123 K, the delafossite $CuCrO_2$ crystallization prevailed over the spinel $CuCr_2O_4$ structure.

Then delafossite $CuCrO_2$ films of various thicknesses were deposited at a fixed temperature of 1123 K. The thickness was controlled by adjusting the deposition time, which varied from 10 min to 40 min, corresponding to theoretical thicknesses of 70–280 nm, respectively. EDS analysis showed that the chemical content of the $CuCr_{0.93}Mg_{0.07}O_2$ films remained almost unchanged (Fig. 2).

3.2. Structural properties of $CuCr_{0.93}Mg_{0.07}O_2$ thin films

Fig. 3 shows the XRD patterns of the $CuCr_{0.93}Mg_{0.07}O_2$ films of various thicknesses. The delafossite structure was observed, and no additional phases were found. The peaks at about 41.13°, 42.54°, and 73.98° corresponded well to the diffraction lines of the (101), (012) and (110) planes of the $CuCrO_2$ phase. As the deposition time was increased, the $CuCrO_2$ peaks became more intense and sharper, which is associated with a larger mean grain size. The grain size, estimated with the Scherrer equation [31], progressively increased from 18 (± 0.4) nm to

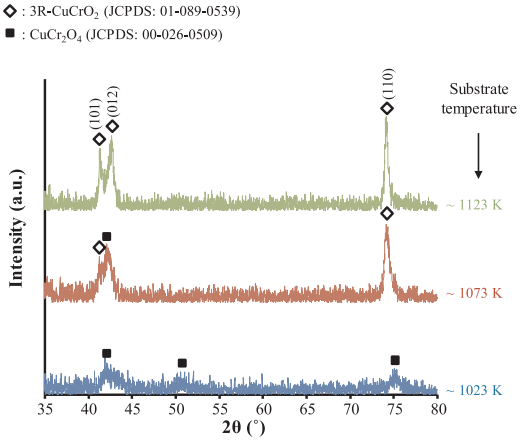

Fig. 1. X-ray diffractograms of the films deposited at different temperatures on fused quartz substrates for 30 min.