Effect of deposition atmosphere on the structure and properties of Mg doped	Ảnh hưởng của môi trường lắng đọng đến cấu trúc và tính chất của các

CuCrO2 thin films prepared by direct current magnetron sputtering

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CuCr0.97Mg0.03O2 thin films were prepared by direct current magnetron sputtering under various percentage of oxygen flow rate (Pq) followed by post-annealed in N2 atmosphere. The microstructures, optical and electrical properties of the films were investigated. The film deposited in pure Ar atmosphere showed pure CuCrO2 phase, while the films deposited in O2 and Ar mixture atmosphere showed CuO and CuCr2O4 mixture phase. After post-annealed at 800 °C, the films deposited in O2 and Ar mixture atmosphere turned into c-axis oriented single-phase CuCrO2 which showed much better transparency and electrical conductivity than the film deposited in pure Ar. The film deposited in Pq = 40% with thickness of 350 nm showed the lowest resistivity of0.4 O cm and transmittance over 60% in visible light region.

1. Introduction

Delafossite oxides CuMO2 (M = Al, Cr, Ga, Fe, etc.) have been widely studied as p-type transparent conductive oxides (TCO) since Kawazoe et al. first reported the p-TCO film of CuAlO2 [1]. As the key component materials for active all-oxide transparent devices, the p-TCOs have potential applications in the emerging field of so-called "invisible cir-cuits" based on fully transparent p-n

màng mỏng CuCrO2 pha tạp Mg được chế tạo bằng phương pháp phún xạ magnetron dòng một chiều

TÓM TẮT

Chúng tôi chế tạo các màng mỏng CuCr0.97Mg0.03O2 bằng phương pháp phún xạ magnetron dòng một chiều với tỷ lệ lưu lượng oxy khác nhau (P0), sau đó ủ trong môi trường N2. Sau đó khảo sát vi cấu trúc, tính chất quang và điện của màng. Màng lắng đọng trong môi trường Ar tinh khiết cho cấu trúc đơn pha Cu CrO2, trong khi đó màng lắng đọc trong môi trường hỗn hợp O2 và Ar cho cấu trúc pha hỗn hợp CuO và CuCr2O4. Sau khi ủ nhiệt ở 8000C, các màng lắng đọng trong môi trường hỗn hợp khí O2 và Ar chuyển thành CuCrO2 đơn pha định hướng theo trục c có độ truyền qua và độ dẫn điện tốt hơn so với các màng lắng đọng trong Ar tinh khiết. Màng lắng đọng trong P0=40% có bề dày 350 nm cho điện trở suất thấp nhất là 0.4 Ω cm và độ truyền qua 60% trong vùng ánh sáng khả kiến.

[redacted]

junction, transistor and other rel-evant semiconductor devices [2]. However, the conductivities of these p-TCOs are much lower than those of n-TCOs, such as tin-doped indium oxide, ZnO [3,4], which severely restricts their applications. With the aim to enhance p-type conductivities, acceptor-doping on M-site or O-site as well as nonstoichiometric (excess oxygen and/or insufficient metal cations) in these delafossite oxides have been extensively studied [5-7].

The delafossite structure of $CuMO_2$ can be described as alternating close-packed Cu^{1+} layers (ab plane) and edge-shared MO_6 octahedra stacked along the c axis, and the rhombohedral 3R (R3m) or hexagonal 2H (P63/mmc) structures can be formed depending on the stacking of the layers [8]. Among Cu-based delafossites, $CuCrO_2$ is the most promising candidate of high-performance p-TCOs with the reported largest p-type conductivity at room temperature when Cr^{3+} sites was partly substituted by Mg^{2+} ions [9]. Moreover, $CuCrO_2$ has also been widely studied as photocatalyst [10], ozone sensor [11], thermoelectric [12] and multiferroic materials [13].

$CuCrO_2$ thin films have been prepared by pulsed laser deposition [14], sputtering [9,15], chemical vapor deposition [16], molecular beam

epitaxy [17], sol-gel methods [18] and chemical spray pyrolysis techniques [19]. Magnetron sputtering technique has the advantages of high deposition rate, good adhesion and large film dimension, which are cost-effective for the industrial producing [20]. The properties of the sputtered films mainly depend on the deposition parameters, such as target type, substrate temperature, substrate-target distance, sputtering power and atmosphere. There are a few studies about properties of magnetron sputtering fabricated $CuCrO_2$ thin films. Singlephase $CuCrO_2$ films were prepared by reactive magnetron sputtering using copper-chromium alloy target and the influence of postannealing temperature on the structure and optoelectronic properties of the films was studied. The lowest resistivity of 4.31 O cm with light transmittance of 62% at 600 nm was achieved [15]. N-doped $CuCrO_2$ thin films were prepared by radio frequency (RF) magnetron sputtering using a mixture of N_2O and Ar sputtering gas and the influence of N_2O vol.% (ranging 0-30%) on the properties of $CuCrO_2$ films was investigated. The lowest resistivity of 0.06 O cm with light transmittance of 50% at 600 nm was achieved [21]. The effect of Mg-doping on the properties of $CuCrO_2$ films was studied by RF sputtering. 5% Mg-doped films showed the lowest resistivity of 0.0045 O cm, but the transparency was only 30% in the visible range. Post-annealing at 900 °C

could improve the trans-parency to 40% but also lead to the increase of resistivity to about 1 ft cm [9]. However, there are few reports on the influence of sputtering oxygen flow rate percentage (PO) on the properties of CuCrO2 films since there is a popular belief that holes cannot be introduced by oxygen intercalation in CuCrO2 and some attempts to do this simply resulted in the secondary spinel phase formation of CuCr2O4 [9,22].
In this work, Mg doped CuCrO2 thin films were prepared by direct current (DC) magnetron sputtering followed by post-annealing at 800 °C in flowing N2 atmosphere. The influence of PO on the structural, optical and electrical properties of the films was studied. To avoid the am-biguous problems resulting from solid solubility limit, a moderate dopant concentration, 3 at.% Mg was selected.

2. Experimental details

Polycrystalline CuCr0 97Mg0 03O2 (CCMO) target for DC magnetron sputtering was prepared by conventional solid state reaction. Stoichio-metric Cu2O (99%), Cr2O3 (99%) and MgO (99%) were well mixed by ball-milling and then uniaxially pressed into pellet. The pellet was then sintered at 1100 °C in air for 20 h.

CCMO thin films were deposited on (00l) sapphire substrates by DC magnetron sputtering with a substrate

temperature of 400 °C, substrate-target distance of ~ 5 cm and sputtering power of 100 W. The base pressure of the sputtering chamber was 5 x 10-4 Pa. Varied PO = O2/(Ar + O2) of 0,25%, 40% and 50% was used while the total pressure was controlled constant at 0.5 Pa. In order to eliminate the incorporation of foreign molecules adsorbed on the surface of the target, a presputtering procedure was carried out for 10 min before allowing the sputtered species to reach the substrate. The as-deposited films were post-annealed in a tube furnace at 800 °C for 1 h in flowing N2 atmosphere to obtain the final resulted films.

The crystalline phases were investigated using X-ray diffractometer (XRD, Philips SmartLab™) operated at40 kV and 200 mA using Cu-Ka1 source (\ = 1.54059 A). Diffraction patterns were taken from 10 to 80° with a scanning speed of 2 °/min. Field emission scanning electronic microscope (FE-SEM; FEl-designed Sirion 200) was used to characterize the micromorphology of the thin films. The thicknesses of the films were measured by a stylus profilometer (Ambios Technology XP-2). Optical transmittance spectra were recorded using a UV-VIS-NIR spectrophotometer (CARY-5E) at a fixed incidence angle perpendicular to the film surface. Electrical properties were measured by the standard four-probe d.c. method using a source meter (Keithley 2400) with thermal evaporated Au electrodes as ohmic

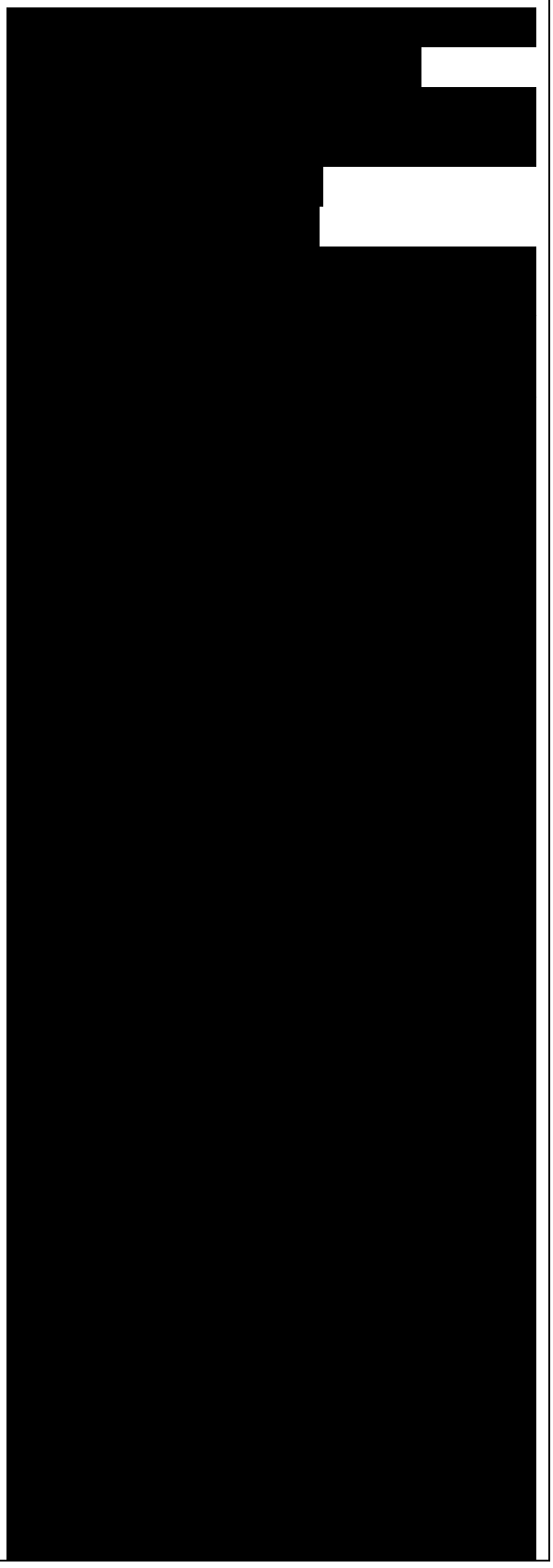
contacts.

Fig. 1. XRD pattern of the CCMO target for DC magnetron sputtering.

Fig. 2. XRD patterns of the as-sputtered CCMO films deposited at 400 °C and under various PO.

3.Results and discussion

Fig. 1 shows the XRD pattern of the CCMO target for sputtering pre-pared by conventional solid state reaction. All the diffraction peaks are identified as the rhombohedral 3R (R3m) delafossite structure (PDF #74-0983). Fig. 2 shows the XRD patterns of the as-sputtered CCMO films. Only the film deposited in pure Ar atmosphere was crystallized in the delafossite phase. lntroducing 25% O2 reactive gas during deposition resulted in a favored growth of CuCr2O4 and CuO phases over CuCrO2. This result is in good accordance with the report of Ref. [22] that CuCr2O4 is more stable in high O2 pressure and low temperature. For the films deposited in Po = 40% and 50%, except for diffraction peaks from the substrate, only two peaks located at 37.08°, 37.34° and 79.17", 79.50", respectively. Since CuO, Cu2O and CuCr2O4 all have strong diffraction peaks located at 36.5 -38 , CuO, CuCr2O4, Cr2O3 and CuCrO2 have diffraction peaks located at 79 -80 , it's likely to make a wrong decision to determine the crystalline phases solely from the XRD patterns. XPS was conducted to clarify the chemical state of Cu cations in the films. As shown in Fig. 3, the main Cu-2p components of the film deposited in Po = 50% are



located at 932.5 eV and 952.5 eV, which demonstrates that Cu cations are in the form of Cu2+. Additionally, intense satellite peaks between the 2p3/2 and 2p1/2 peaks are observed. These “shake-up” satellites result from metal-ligand charge transfer during the photo emission process, characteristic of copper oxides having a d9 configuration in the ground state. The whole Cu-2p spectra of films deposited in Po = 25% and 50% are similar to Refs. [23-25] which indicate CuO and/or CuCr2O4 are present in the film.

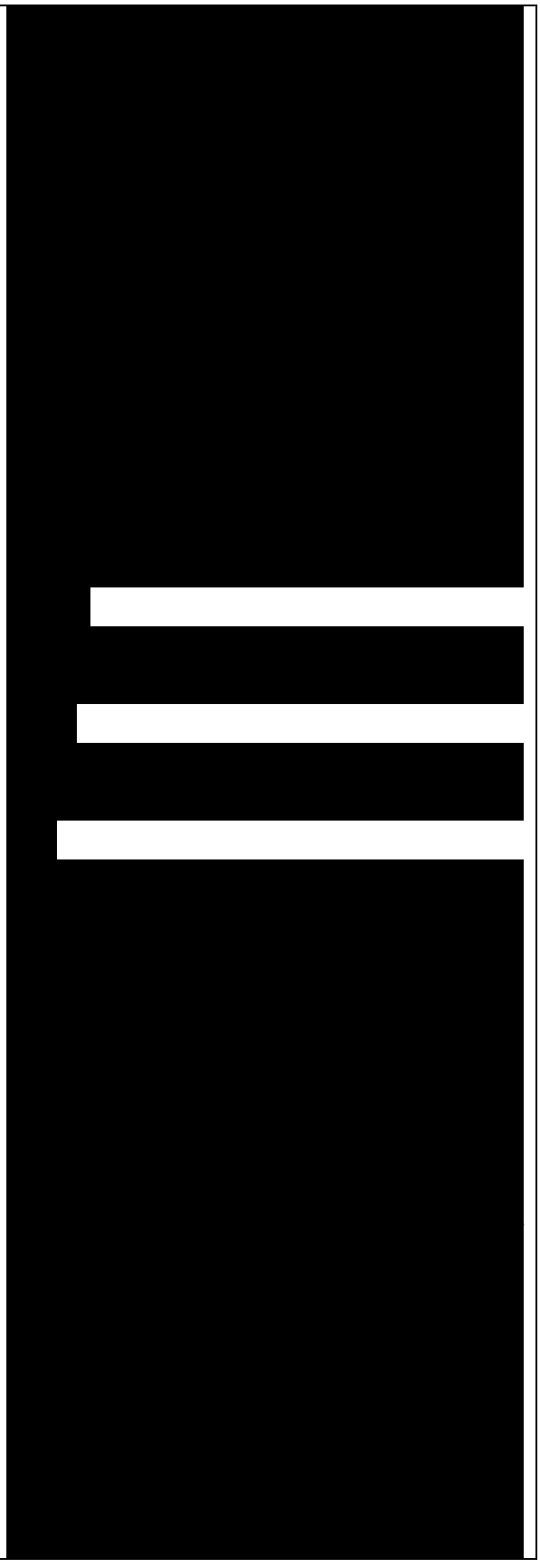


Fig. 3. Cu-2p spectra of the as-sputtered film deposited in PO = 25% and PO = 50%.

Fig. 4. XRD patterns of the CCMO films post-annealed at 800 °C in N2 atmosphere.

After post-annealed at 800 °C in N2 atmosphere, all the films are crystallized to pure delafossite CuCrO2 phase, as shown in Fig. 4. For the film deposited in pure Ar, no significant change in XRD pattern after annealing and the strongest diffraction peak is (012). For the films deposited in O2 and Ar mixture atmosphere, CuCr2O4 becomes instable at high temperature and decomposes into CuCrO2. The films tend to grow in c-axis orientation with the increase of PO. The diffraction intensity ratio of peaks (006) and (012) is 0.045 for PO = 0% and 14.4 for PO = 25%, while for the films deposited in PO = 40% and 50%, the diffraction peak (012) disappears and only

diffraction peaks of (00l) could be observed. This implies that oxygen content in the pristine films is essential for the c-axis oriented growth of $CuCrO_2$.

The surface morphologies of the post-annealed CCMO films are pre-sented in Fig. 5. All the films present densely arranged granular surface. The grain shapes of film deposited in PO = 0% are quite different from the others, which may be due to the non c-axis orientation growth. For the film deposited in PO = 25%, some grains are unusually large which make a rougher surface. For the films deposited in O_2 and Ar mixture atmosphere, with increase of PO, the grain boundaries become more and more apparent and the grain sizes become more and more evenly distributed. The average grain sizes also increase with increasing PO. For the film deposited in PO = 50%, granular and irregular spots appear on the surface of the grains, which may be due to incomplete annealing/decomposition process. The tiny secondary phase may be undetectable by XRD because the detection limit of XRD is above 5%.

Fig. 6(a) shows the optical transmittance of the post-annealed CCMO films in the range of 350-800 nm. The optical transmittance increases with the increase of the PO. Generally, the optical transmittance is influenced by the point defects, grain sizes, void defects, surface conditions and

thickness of the films [15]. In this study, the films thickness measured by stylus profilometer is 350 ± 40 nm. So, the film thickness may not be the main reason for this monotonic increase of transmittance with increasing PO. The point defects and grain sizes which are closely related to PO may contribute to the discrepancy of the transmittance. Point defects and grain boundaries acting as photon scattering centers could remarkably deteriorate the optical transmittance. The films deposited in pure Ar atmosphere may have many oxygen vacancy defects. These defects act as light scattering centers and decrease the optical transmittance. With increase of PO, the defects decrease and the average grain sizes increase, so the light scattered by grain boundaries decreases which results in increase of optical transmittance. The optical transmittance at wavelengths greater than 600 nm increases from 30% to 70% when the PO increases from 0% to 50%. Optical interference patterns are observed in Fig. 6(a). Considering that these films have almost the same thickness, the diversity of the interference patterns can be attributed to the changes of surface morphology which is closely related to PO. The direct optical band gap, Eg, was deduced by Tauc's relation (ahv)2 = A(hv — Eg) as shown in Fig. 5(b), where a denoted the absorption coefficient obtained by the relation, a = — ln (T)/d. As depicted in the inset of Fig. 6(b), the values of Eg for the

annealed films sputtered in PO = 0% — 50% were estimated to be 3.15-3.17 eV. These values are closely matched with the other reported values for Mg doped CuCrO2 films [26]. The film deposited in PO = 50% shows a blue-shifted band gap energy, which may be related to the improved crystalline quality.

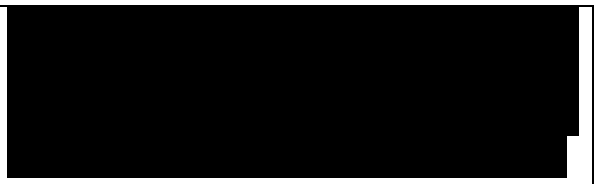
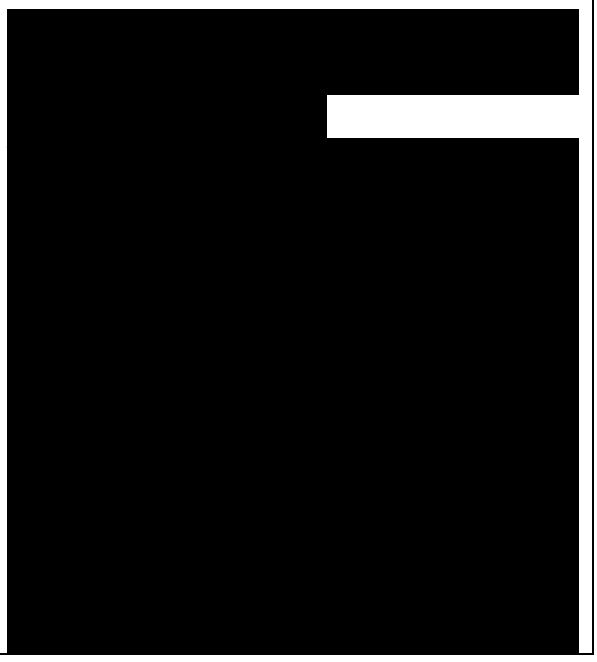


Fig. 6. (a) Optical transmittance spectra and (b) Tauc plots of the post-annealed CCMO films. Inset of Fig. 5(b) is plot of optical band gap.

Fig. 7 shows the changes of room temperature resistivity of the post-annealed CCMO films versus PO. The resistivity first decreases and then increases with increasing PO. The lowest resistivity 0.4 ft cm was obtained with PO = 40%, while the highest resistivity 3.5 ft cm was obtained with PO = 0%. The delafossite structure is anisotropic between in- and

Fig. 7. Variation of room temperature resistivity with PQ for the post-annealed CCMO films.



out-of-plane directions and the main conduction path is considered to be the closed-packed Cu1+ layers [27]. It was reported that in CuCrO2 single-crystal, electrical conductivity along the ab plane was 35 times higher than that along the c axis due to the structural anisotropy [28]. As observed in Fig. 4, the films show improved c-axis orientation with increasing PO. This may be the main reason for the decrease of resistivity with increasing

PO when PO < 40%. As seen in the SEM images, the grains become loosely stacked and distinct grain boundaries increase with an increase of PO. Besides, minor secondary phase appears for the films deposited in PO = 50%. These all may hinder carrier transport and aggravate the carrier scattering in the films, which result in the increase of resistivity for the film sputtered in PO = 50%.

4. Conclusions

$CuCr_{0.97}Mg_{0.03}O_2$ thin films were prepared by DC magnetron sputtering with post-annealing at 800 °C in N_2 atmosphere. The influence of PO on the microstructure, optical and electrical properties of the obtained films was studied. The film surface morphologies, such as grain size and preferred orientation, were found to be sensitive to PO. The films deposited in O_2 and Ar mixture atmosphere were c-axis ori-ented single-phase $CuCrO_2$ which showed much better transparency and electrical conductivity than the film deposited in pure Ar. The film deposited in PO = 40% with thickness of 350 nm showed the lowest resistivity of 0.4 ft cm and transmittance over 60% in visual light region. The results elucidated that, though excess oxygen could not introduce holes into $CuCrO_2$ films, but moderate oxygen could improve the c-axis orientation and crystalline quality of $CuCrO_2$ and thus improve the optical transmittancy and resistivity.
