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Structure and electrical properties of $CdIn_2O_4$ thin films prepared by DC reactive magnetron sputtering

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ABSTRACT

$CdIn_2O_4$ thin films were prepared by direct-current (DC) reactive magnetron sputtering. The structure, surface morphology and the chemical composition of the thin films were analyzed by X-ray diffraction (XRD), atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. The electrical properties of the films prepared in different oxygen concentration and annealing treatment were determined, and the effects of the preparing conditions on the structure and electrical properties were also explored. It indicates that the $CdIn_2O_4$ thin films with uniform and dense surface morphology contain mainly $CdIn_2O_4$, In_2O_3 phases, and CdO phase is also observed. The XPS analysis confirms the films are in oxygen-deficient state. The electrical properties of these films significantly depend on the preparing conditions, the resistivity of the films with the oxygen concentration of 4.29% is $2.95 \times 10^{-4}\ \Omega$ cm and the Hall mobility is as high as 60.32 cm^2/V s. Annealing treatment can improve the electrical performance of the films.

1. Introduction

Transparent conducting oxides (TCOs) have attracted considerable attention for wide application in optoelectronic devices such as flat-panel displays, photovoltaics, invisible security circuits and heat reflectors [1,2]. Usually high conductivity of many TCOs such as Sn-doped In_2O_3 (ITO), Sb-doped SnO_2 and Al-doped ZnO is achieved by doping which can increase the carrier density. However, the increase of carrier density deteriorates optical transparency [3,4]. Ternary oxides thin films such as $CdIn_2O_4$ and Cd_2SnO_4 can be n-type materials without any doping. Wu et al. [5] have produced pure phase spinel $CdIn_2O_4$ films with the conductivity of 4300 S/cm and mobility of 44 cm^2/V s. They have drawn attention as a potential alternative to ITO.

$CdIn_2O_4$ thin films have been prepared by various physical and chemical deposition techniques, for instance, radio-frequency (RF) reactive sputtering [6], DC reactive sputtering [7], RF reactive magnetron sputtering [5], chemical vapor deposition [8] and co-precipitation [9]. The electrical and optical properties of the $CdIn_2O_4$ thin films prepared by these methods have been reported [5–7], but the structure and electrical properties of that prepared by DC reactive magnetron sputtering are less known [10]. Since DC reactive magnetron sputtering is a widely applied commercial method, it is necessary to obtain the properties of $CdIn_2O_4$ thin films prepared by this method. In this paper, $CdIn_2O_4$ thin films with low resistivity and high mobility prepared by DC reactive magnetron sputtering were reported, and the structure and electrical properties of the thin films prepared in different conditions were studied.

2. Experimental details

In the Ar + O_2 atmosphere, $CdIn_2O_4$ thin films were prepared by DC reactive magnetron sputtering with the power of 50 W. A

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60 mm diameter Cd–In alloy was used as the target, Cd and In (purity of 99.99%) atom ratio was 1:2. Transparent glass (30 mm × 25 mm × 1 mm) was used as the substrate. Prior to deposition, the substrates were degreased and cleaned ultrasonically in acetone, ethyl alcohol and distilled water. The distance between the target and substrate was 75 mm. In order to avoid contamination of the films, the chamber was evacuated to a base pressure of 6.0×10^{-4} Pa by a turbo molecular pump backed with a rotary pump, and the target surface was treated with presputtering for 5 min. Oxygen and argon gases were introduced into the chamber independently through two mass flow controllers. The mass flow of argon gas was fixed at 29.0 sccm, and the mass flow of oxygen was controlled to change the ratio of between Ar and O_2. The total pressure of the Ar + O_2 mixture was ~3.1 Pa. The substrate temperature was measured by a platinum–rhodium thermal couple. The preparing time was 45 min for all the samples. Furthermore, some thin films were annealed in stable N_2 flow at 400 °C for 60 min.

The structure of the films was determined by X-ray diffraction (XRD) with a D/Max-RB diffractometer, which used the Cu K_α line (λ = 1.504056 Å). The power was 1200 W and the scan speed was 8.0000°/min. The surface morphology of the films was investigated with a SPI3800N atomic force microscope (AFM); the scan area was 500 nm × 500 nm. The chemical compositions were analyzed by a PHI-5400 type X-ray photoelectron spectroscopy (XPS) with monochromatic Mg K_α (1254 eV) radiation source. In order to obtain actual information, Ar^+ etching was employed to eliminate the contamination such as C and O on the surface of the films for 15 min before scanning the films, the XPS analysis chamber was about 5.0×10^{-8} Torr, and the X-ray energy was 12 kV × 20 mA. Binding energies were referenced to the C1s peak at 284.8 eV. The electrical properties were measured by Hall effect measurements (HL5500PC) using a Van der Pauw configuration.

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows XRD patterns of the as-deposited and annealed $CdIn_2O_4$ thin films. It reveals that the films deposited at substrate temperature of 250 °C are mostly polycrystalline, containing mainly $CdIn_2O_4$ and In_2O_3 phases. CdO phase is also observed in the present work, which has been predicted to exist by Budzynska et al. [7] and found in the films prepared by RF reactive sputtering [6,11]. However, CdO phase is not observed in the as-deposited and annealed films deposited at substrate temperature of 16 °C. In addition, it can be seen from Fig. 1(b) that only (2 2 2) diffraction peak for In_2O_3 phase and no $CdIn_2O_4$ phase are observed in the as-deposited thin films. It can be concluded that higher substrate temperature is very necessary to improve the crystallization of $CdIn_2O_4$ thin films, so we investigated mainly on the $CdIn_2O_4$ thin films deposited at higher substrate temperature in the following work. Furthermore, the diffraction peaks of the annealed films deposited at substrate temperature of 250 °C and 16 °C strengthen and full width at half maximum (FWHM) β becomes smaller, therefore, the average crystallite size becomes bigger according to Scherrer's formula [12]. On the other hand, there are some new diffraction peaks appearing in the annealed thin films deposited at the substrate temperature of 16 °C. These results demonstrate that annealing treatment is advantageous to the crystallization of $CdIn_2O_4$ thin films.

$CdIn_2O_4$, In_2O_3 and CdO are cubic structure; the standard lattice parameters for $CdIn_2O_4$, In_2O_3 and CdO are 9.115 Å, 10.12 Å and 4.725 Å [powder diffraction files (PDF) card no. 740841, no. 760152 and no. 780653 from Joint Committee of Powder Diffraction Standard (JCPDS)], respectively. The lattice parameters for $CdIn_2O_4$,

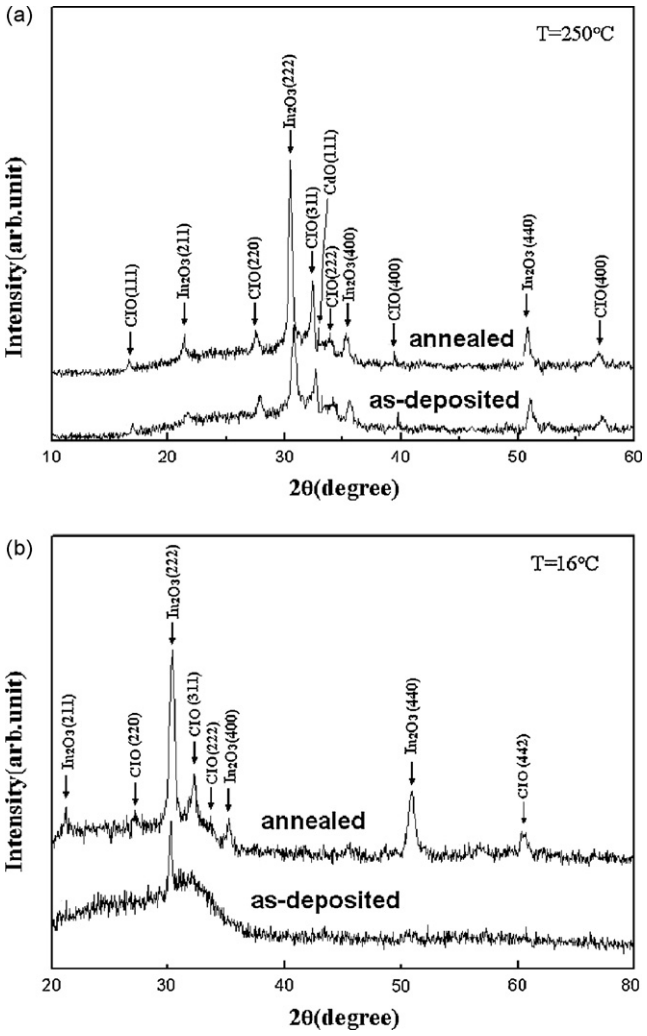

Fig. 1. XRD patterns of the as-deposited and annealed $CdIn_2O_4$ thin films. (a) The substrate temperature of 250 °C, (b) the substrate temperature of 16 °C (CIO denotes $CdIn_2O_4$ in the patterns).

In_2O_3 and CdO derived from the XRD spectra of the annealed films deposited at the substrate temperature of 250 °C are 9.1516 Å, 10.1626 Å and 4.7185 Å, respectively. The lattice parameters of the films deposited at the substrate temperature of 16 °C for $CdIn_2O_4$ and In_2O_3 are 9.2108 Å and 10.2117 Å, respectively. The lattice parameters for $CdIn_2O_4$, In_2O_3 in the two kinds of the films are both bigger than the corresponding standard values, but that for CdO is slightly smaller than the standard one. Because of the small percent of CdO, the whole effect of $CdIn_2O_4$, In_2O_3 and CdO will result in the expansion behavior in both kinds of the above thin films, which is due to the presence of point defects such as oxygen vacancies or the interchange between Cd^{2+} and In^{3+} [11].

3.2. Surface morphology

The surface morphology of the $CdIn_2O_4$ thin films was investigated by AFM. The typical two and three-dimensional surface morphology of thin films prepared in different oxygen concentrations are shown in Figs. 2 and 3, respectively. Fig. 2 demonstrates that the films are dense, uniform and composed of spherical grains. There is a congregative trend for the grains in the annealed films deposited at oxygen concentration of 4.29% and substrate temperature of 250 °C. Fig. 3 shows that all samples exhibit columnar structure features, which are desirable for good

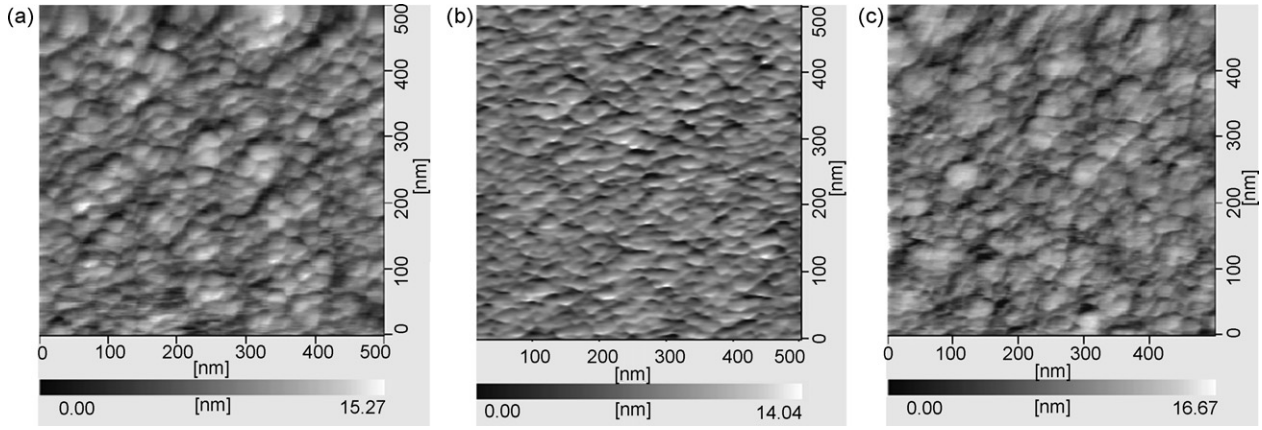

Fig. 2. Two-dimensional AFM surface morphology of the $CdIn_2O_4$ thin films prepared in different oxygen concentrations (a) 4.29%, (b) 9.38%, and (c) 4.29% after annealing treatment.

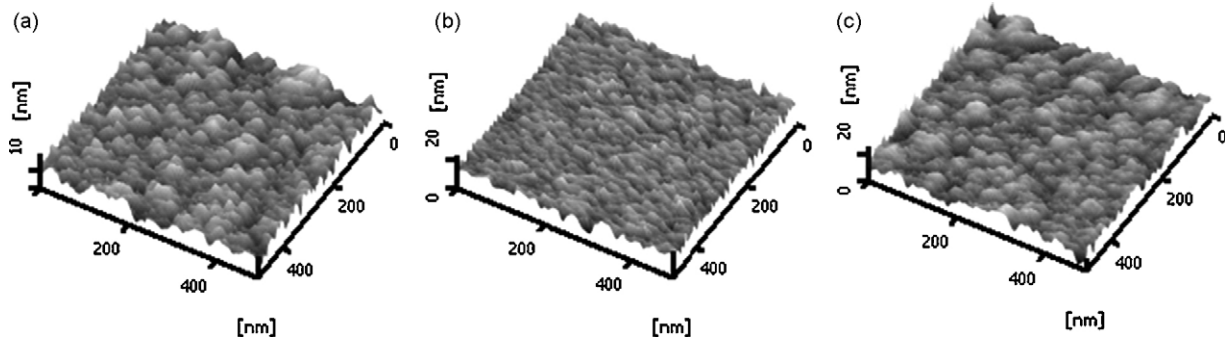

Fig. 3. Three-dimensional AFM surface morphology of the $CdIn_2O_4$ thin films prepared in different oxygen concentrations (a) 4.29%, (b) 9.38%, and (c) 4.29% after annealing treatment.

Table 1
The relationship between preparing conditions and surface roughness, average crystalline size

Sample	Preparing conditions		Surface roughness (nm)		Average crystalline size (nm)
	Oxygen concentration (%)	Treatment	R_{rms}	R_a	
1	4.29	As-deposited	2.4	1.92	35
2	4.29	Annealed	2.6	2.00	36
3	9.38	As-deposited	2.1	1.60	20

electrical properties since the films with columnar grains will have fewer grain boundaries.

In order to study the morphology of the films more clearly, the surface roughness and average crystalline size were calculated and shown in Table 1. The average crystalline size with oxygen concentration of 4.29% determined from AFM surface morphology is larger than that with oxygen concentration of 9.38%. Due to the annealing treatment supplies energy to the grains for congregating, the crystalline size increases slightly after annealing treatment, but these grains have not congregated completely, and the behavior is in great agreement with the results of XRD. Both the R_a (average roughness) and R_{rms} (root mean square roughness) calculated from AFM surface morphology decrease with increasing oxygen concentration, but increase after annealing treatment. However, the roughness of all the films is still low to satisfy the application in optoelectronic devices.

3.3. Chemical compositions

Fig. 4 shows XPS survey scan spectra of the as-deposited and annealed $CdIn_2O_4$ thin films deposited at oxygen concentration of

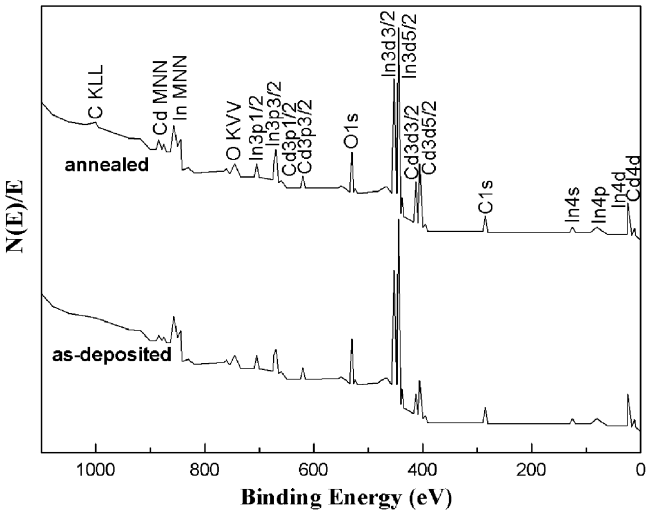

Fig. 4. XPS survey scan spectra of the as-deposited and annealed $CdIn_2O_4$ thin films deposited at oxygen concentration of 4.29% and substrate temperature of 250 °C.

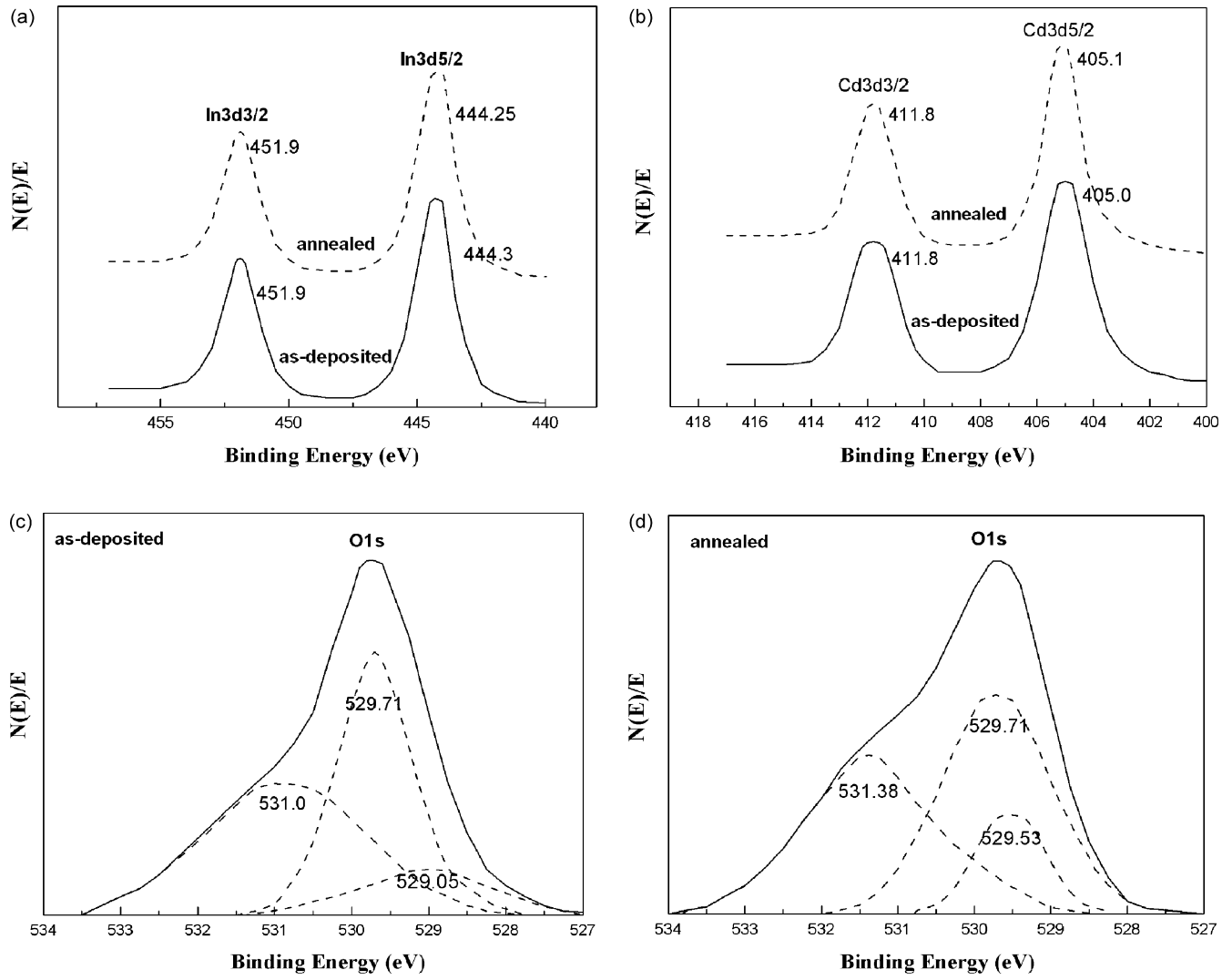

Fig. 5. Narrow scan XPS spectra of the as-deposited and annealed $CdIn_2O_4$ thin films (a) In3d, (b) Cd3d, (c) O1s before annealing treatment, and (d) O1s after annealing treatment.

4.29% and substrate temperature of 250 °C. The films contain Cd, In, O and C elements. Auger peaks of Cd MNN, In MNN, O KVV and C KLL are also observed. The atomic ratios of In3d:Cd3d:O1s are 3.68:1:4.02 and 2.88:1:2.77 for the as-deposited and annealed samples, respectively. The results indicate the films are off-stoichiometry, and the oxygen percent in the as-deposited sample is larger than that in the annealed one, thus it can be concluded that there are higher oxygen vacancies concentration in the annealed sample.

Narrow scan XPS spectra of In3d and Cd3d for the as-deposited and annealed $CdIn_2O_4$ thin films are shown in Fig. 5(a) and (b), respectively. The binding energies of In3d3/2 and In3d5/2 are found to be 451.9 eV, 444.3 eV and 451.9 eV, 444.25 eV for the as-deposited and annealed samples, respectively, these data are similar to each other. The binding energy of In3d5/2 can be attributed to the In^{3+} bonding state [13]. The binding energies of Cd3d3/2 and Cd3d5/2 for the as-deposited sample are 411.8 eV and 405.0 eV, respectively, which are very close to that for the annealed one. The binding energy of Cd3d5/2 can be attributed to the Cd^{2+} bonding state, which is in agreement with the previous report [14].

Narrow scan XPS spectra of O1s for the as-deposited and annealed $CdIn_2O_4$ thin films are shown in Fig. 5 (c) and (d), respectively. The O1s peaks have double peaks called main peak and shoulder peak, such phenomenon is common for oxides containing cation in multiple valence states [15]. An attempt is made for Gaussian curve fitting, and the results show the films consist of three components. The binding energies of O1s are 531.0 eV, 529.71 eV, 529.05 eV and 531.38 eV, 529.71 eV, 529.53 eV for the as-deposited and annealed thin films, respectively. The peaks at 529.05 eV and 529.53 eV correspond to the binding energy O^{2-}1s from CdO, while the peaks at 529.71 eV correspond to the binding energy O^{2-}1s from In_2O_3 [14]. According to the previous report [16], the O1s spectra contain two states called oxygen-deficient and oxygen-sufficient states. The two peaks with the binding energy O^{2-}1s from CdO and In_2O_3 correspond to oxygen-sufficient state, in which Cd ions and In ions are full complement with their neighboring O^{2-} ions, while the peaks at 531.0 eV and 531.38 eV correspond to the oxygen-deficient state. Owing to an electron charge density in the region of an oxygen vacancy reduces the screening of the O^{2-}1s electrons from their nucleus at the nearest-neighbor O^{2-} ions, the binding energy in oxygen-deficient state is higher than that in oxygen-sufficient state. Since annealing treatment can cause more oxygen vacancies, the binding energy of O1s in the annealed films is larger than that in the as-deposited ones; this phenomenon is very similar to that of increasing oxygen concentration [17]. The

Table 2
The XPS results of the O1s spectra

Preparing conditions	Binding energy (eV)	FWHM (eV)	Area percent (%)
As-deposited	531.00	2.40	40.88
	529.71	1.30	46.45
	529.05	3.12	12.68
Annealed	531.38	2.21	41.41
	529.71	1.73	45.22
	529.53	1.10	13.36

magnitude of the shift to higher binding energies depends on the oxygen deficiency concentration.

The XPS results of the O1s spectra are shown in Table 2, the ratios of oxygen-deficient area to oxygen-sufficient area for the as-deposited and annealed films are 0.69 and 0.71, respectively. It can be inferred that there are more vacancies for the annealed thin films. Each oxygen vacancy offers two electrons; the annealed sample must have larger numbers of electrons. Since $CdIn_2O_4$ is an n-type material, the electrical properties of these films strongly depend on the electron concentration; the increase of the ratio indicates the annealed films will improve the electrical performance [18]. This is confirmed by the following investigation on the electrical properties.

3.4. Electrical properties

Fig. 6 shows the resistivity of the as-deposited and annealed $CdIn_2O_4$ thin films deposited at substrate temperature of 250 °C in different oxygen concentration. It can be found that the resistivity increases with increasing oxygen concentration. According to the report [19], the main reason of $CdIn_2O_4$ thin films conducting electricity is intrinsic point defects; the prevailing native point defect mechanism in the films is the formation of oxygen vacancies which become donors. In order to maintain the local charge neutrality, two quasi-free-electrons are bounded around donors. The equation is written in standard Kröger–Vink notation as follows:

$$\begin{aligned} &O_O^x \Leftrightarrow V_O^{\bullet\bullet} + \frac{1}{2}O_2 + 2e \\ &n = 2[V_O^{\bullet\bullet}] \end{aligned} \quad (1)$$

As a reactive gas, oxygen plays an important role to determine the structure, composition and electrical performance of the $CdIn_2O_4$ thin films. If the oxygen concentration is high enough, it tends to obtain the stoichiometric films with fine grains and fewer point defects, and the surface roughness of the films is smaller than that of the oxygen deficiency. However, the films with larger resistivity are disadvantage for applications. Therefore, lower oxygen concentration is recommended to prepare $CdIn_2O_4$ thin films with excellent electrical performance. It is necessary to point out that the oxygen concentration should not be too low, otherwise the obtained thin films have poor transparency. In our experiments, we found the best oxygen concentration is 4.29%, the resistivity of the films is $2.95 \times 10^{-4}\ \Omega$ cm, the carrier concentration is $3.508 \times 10^{20}\ cm^{-3}$ and Hall mobility is as high as 60.32 cm^2/V s. The resistivity of the films prepared by DC reactive magnetron sputtering is lower than that prepared by RF reactive sputtering [6], but slightly higher than that prepared by RF reactive magnetron sputtering and DC reactive sputtering [5,7], while the Hall mobility of the films prepared by DC reactive magnetron sputtering is higher than that prepared by other techniques [5–7]. As the demand for thinner and higher performance devices increases, future TCOs are demanded to have not only lower resistivity but also higher optical transparency [4]. The resistivity is inversely proportional to the carrier concentration and mobility; nevertheless, higher carrier concentration will decrease optical transparency. Therefore, the best way to satisfy the demand for the future TCOs is to improve the Hall mobility. Although the resistivity of $CdIn_2O_4$ thin films is slightly higher than the commercial ITO ($\sim 1.79 \times 10^{-4}\ \Omega$ cm), the mobility of the $CdIn_2O_4$ thin films is much higher than ITO ($\sim$28.3 cm^2/V s) [3]. $CdIn_2O_4$ thin films with excellent performance may be a potential alternative to ITO.

In addition, annealing treatment is effective to improve the electrical properties of the films. Fig. 6 also shows that the resistivities of all samples decrease after annealing treatment; the resistivity for the films with the oxygen of 4.29% is as low as $2.00 \times 10^{-4}\ \Omega$ cm. The result confirms the inference from the XPS analysis. This result can be explained as follows: firstly, annealing treatment can give off the dissolved surplus oxygen which can capture free electrons in the surface of the films; secondly, it can also separate out the oxygen atom which stayed between crystals. Meanwhile, the higher the oxygen concentration is, the more sharply the resistivity decreases. This behavior is due to the films with higher oxygen concentration have larger numbers of dissolved surplus oxygen atoms, annealing treatment can give off much more numbers of oxygen atoms from the films.

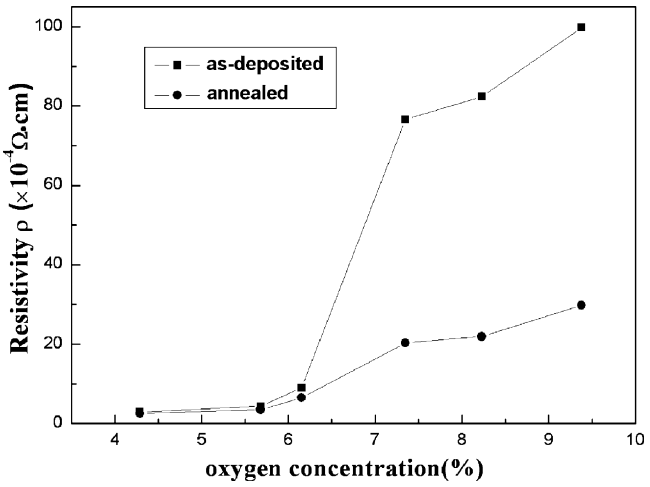

Fig. 6. The resistivity of the as-deposited and annealed $CdIn_2O_4$ thin films deposited at the substrate temperature of 250 °C in different oxygen concentration.

4. Conclusions

$CdIn_2O_4$ thin films with excellent performance were prepared by DC reactive magnetron sputtering, and the structure and electrical properties of the thin films were analyzed. It is found that higher substrate temperature and annealing treatment are advantageous to improve the crystallization of $CdIn_2O_4$ thin films; lower oxygen concentration is a benefit to obtain thin films with larger crystalline grains but a slightly rougher surface. The XPS analysis indicates that the $CdIn_2O_4$ films are in oxygen-deficient state; the oxygen vacancies are responsible for the electrical properties. The resistivity of the films prepared at the oxygen concentration of 4.29% is $2.95 \times 10^{-4}\ \Omega$ cm, the carriers concentration and Hall mobility are $3.508 \times 10^{20}\ cm^{-3}$ and as high as 60.32 cm^2/V s, respectively. The resistivity decreases to $2.00 \times 10^{-4}\ \Omega$ cm after annealing treatment. Lower oxygen concentration, higher substrate temperature and annealing treatment are favorable to prepare $CdIn_2O_4$ thin films with excellent electrical performance.

Acknowledgments

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