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Fabrication and properties of pure-phase Cu_2O co-doped with zinc and indium

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ABSTRACT

Cuprous oxide (Cu_2O) thin films co-doped with zinc (Zn) and indium (In) were fabricated with direct current (DC) magnetron sputtering. The sputtering voltage of the Cu target was fixed while that of the alloy target of Zn and In was varied. It is found that when the alloy target voltage is below 310 V, pure-phase Cu_2O can be obtained while a further increase in the alloy target voltage will result in the presence of metallic copper. The surface morphologies, the atomic ratios of the Zn and In, and the grain size do not have a linear dependence on the sputtering voltage of the alloy target. Higher concentration doping will decrease the lattice constant of Cu_2O. Pure-phase samples doped with Zn and In have relatively higher transmittance and larger optical band gaps. The n-type conduction of Cu_2O co-doped with Zn and In is realized when the sputtering voltage of the alloy target is 310 V. Zn and In atoms are found to exist as Zn^{2+} and In^{3+} in the films and they are possible donors for the n-type conduction.

1. Introduction

Cuprous oxide (Cu_2O) can be applied in photocatalysis and photovoltaics because it has many advantages including a direct band gap (the forbidden band gap width is 2.1 eV), the abundance of copper on the earth and no toxicity, etc. Theoretical works show that the conversion efficiency of solar cells based on the pn homojunction of Cu_2O can reach 20% [1–3]. In experiments, however, the highest conversion efficiency of solar cells based on the pn homojunction of Cu_2O is just 1.06% [4–8], far below the theoretical prediction and that of Cu_2O heterojunction solar cells (cf., 6.39% [9], 8.1% [10]). The reason for the difference between the theory and the experiments might be that the n-type layer used in these Cu_2O pn homojunctions which were fabricated with electrodeposition is not truly n-type [11,12]. As a matter of fact, Cu_2O is naturally a p-type semiconductor with copper vacancies as the acceptors. Theoretical works have shown that undoped Cu_2O is always of p-type conduction, while experiments have demonstrated that the n-type conduction of the undoped Cu_2O fabricated with electrodeposition is due to the surface accumulation of Cu^{2+} ions [11,12]. Therefore, doping Cu_2O to realize its n-type conduction is necessary and intriguing. In this regard, Cu_2O has been doped with many elements [13–17], such as group-IV elements [13], indium [14,15], and Zn [16,17]. To this end, Cu_2O co-doped with Zn and In has not been studied yet.

Here, we fabricate Cu_2O co-doped with Zn and In of different concentrations and study their structural, optical and electrical properties. It is found that Cu_2O co-doped with Zn and In can turn to n-type conduction with an increase in the sputtering voltage of the alloy target.

2. Experiments

All the samples were prepared with a multi-target direct current (DC) magnetron sputtering system (JGP 450, SKY Technology Development Corporation Limited, Chinese Academy of Sciences). The targets were a copper disk (with the purity of 99.999%) and an alloy disk of metallic zinc and indium (both have the purity of

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99.999% and the atomic ratio of zinc to indium is 1:1). K9 glass and Si (100) were used as the substrates. The films deposited on Si substrates were only used for scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements. The substrates were ultrasonically washed in acetone, ethanol and de-ionized water. The washing time was 15 min in each liquid. The base pressure of the sputtering chamber was 6.0×10^{-4} Pa. During sputtering, the flow rates of O_2 and Ar were 1.0 standard cubic centi-meter per minute (*sccm*) and 20.0 *sccm*, respectively, and the work pressure of the sputtering chamber was fixed at 2 Pa. The substrates rotated with the substrate holder at a speed of 0.46π (rad/s) and the substrate temperature was 673 K. The sputtering power (voltage × current) for the Cu target was always 350 V × 43 mA. The sputtering power for the alloy target was 260 V × 25 mA, 270 V × 30 mA, 280 V × 40 mA, 290 V × 55 mA, 310 V × 50 mA and 320 V × 55 mA, respectively. Before film deposition, the targets were sputtered for 5 min in order to clean the target surface. The sputtering for film deposition lasted for 1 h. After the film deposition, the target power, gas flow and substrate heater were all switched off. The chamber was pumped until the substrates cooled down to room temperature naturally.

The crystal structure, transmission and thickness of the samples were measured with X-ray diffraction (XRD, D/max 2500 PC, 18 kw, Cu Kα radiation), a UV/VIS spectrophotometer (Perkin-Elmer, Lambda 900) and a surface profiler (Veeco Dektak 3ST). Atomic force microscopy (AFM, Veeco, multimode V) was used to obtain the surface morphology of the samples through tapping mode. Energy dispersive X-ray spectroscopy (EDX, Oxford Link ISIS) was used to measure the content of the films. Hall effect measurements (Bio Rad, HL 5500PC) were conducted at room temperature to obtain the carrier concentration and conduction type, etc. The sample for Hall effect measurements has a square size of 10.0 mm × 10.0 mm and the four electrodes were at the corners of the square. X-ray photoelectron spectroscopy (XPS, Physical Electronics, PHI-5802 with a monochromatic Al Kα X-ray source of 1486.6 eV and the C 1s was calibrated to be 284.6 eV) was used to detect the chemical states of the elements in the samples.

3. Results and discussion

The thicknesses of the samples deposited with the alloy target voltages to be 260, 270, 280, 290, 310 and 320 V are 67, 83, 102, 121, 168 and 280 nm, respectively. The surface morphologies of all the samples were obtained with AFM measurements and the AFM images of all the samples are present in Fig. 1. From Fig. 1, it can be found that the surfaces of the samples deposited at 270 V, 280 V and 290 V (as shown in Fig. 1 (b), (c) and (d), respectively) are smoother than that deposited at 320 V. The grains of the samples are homogenously distributed, similar to that of the Cu_2O samples deposited with successive ions layer absorption and reaction techniques [18]. The compositions of the samples were measured with EDX and the atomic percentages of copper, zinc and indium of all the samples are shown in Fig. 2. The atomic percentages of the three metals change with an increase in the sputtering powers but the relation is not linear or monotonic. The total atomic percentage of Zn and In increases with an increase in the sputtering voltages of

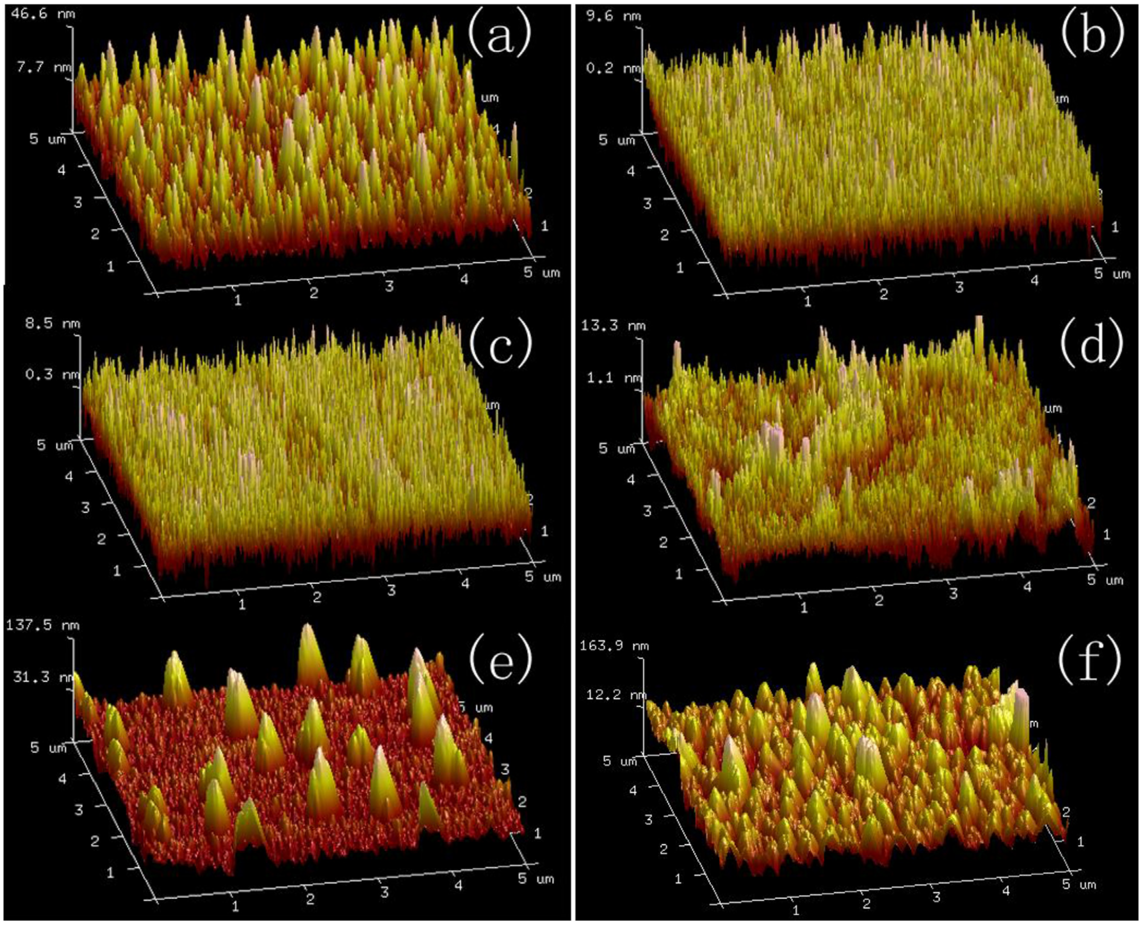

Fig. 1. The AFM images of doped Cu_2O thin films prepared at different sputtering voltages of the alloy target. (a) 260 V; (b) 270 V; (c) 280 V; (d) 290 V; (e) 310 V; (f) 320 V.