Materials Science in Semiconductor Processing 75 (2018) 269–275

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Annealing atmosphere effects on the surface properties of Cd_2SnO_4 thin films obtained by RF sputtering

Shengqiang Ren[1], Tianyu Tang[1], Yuan Liu, Chuang Li, Lili Wu, Wei Li, Jingquan Zhang*, Wenwu Wang, Lianghuan Feng

Institute of Solar Energy Materials and Devices, College of Materials Science and Engineering, Sichuan University, No. 24 South Section 1, Yihuan Road, Chengdu 610065, China

ARTICLE INFO

Keywords:
Cd_2SnO_4 thin film
Annealing
Surface properties
Work function
Fermi level

ABSTRACT

Cd_2SnO_4 (CTO) thin films were prepared by RF sputtering technique from a CTO target and then annealed under Ar or Ar/CdS atmosphere. The detailed characterizations on the surface properties of as-deposited, Ar-annealed, and Ar/CdS-annealed CTO thin films were carried out by AFM, XPS, UPS, etc. The surface properties of the films are greatly dependent on the annealing atmosphere. Ar/CdS atmosphere promotes the grains to grow but slightly increases the surface roughness. Cadmium atoms sublimated off the CTO thin films during the annealing process and this sublimation can be suppressed under Ar/CdS atmosphere, which causes the surface of CTO thin films not homogeneous as inside. The fundamental band gap is determined to be 2.83 eV. The Fermi level position is 1.7 eV above the valence band maximum for the as-deposited films, while it shifts to 2.98 eV and 3.21 eV for the films annealed in Ar and Ar/CdS atmospheres, respectively. Work function for the Ar/CdS-annealed films is about 0.16 eV higher than the Ar-annealed ones. These results could be used to design high efficiency thin film solar cells and water photolysis devices, in which the efficiency is sensitive to the surface properties of TCO thin films.

1. Introduction

Transparent conducting oxides (TCOs) thin films have been widely used in microelectronics, optoelectronics and other fields [1,2]. Although the TCOs thin films of binary compounds, such as In_2O_3: Sn, SnO_2: F, ZnO: Al, etc., have been used in the devices of OLED, and solar cells. But the study for the TCOs thin films of ternary compounds, such $Cd_{2-x}Sn_xO_4$, $Zn_{1-x}Mg_xO$ etc., are paid extensive attention because their energy band structure including electron affinity or band gap can be modulated by changing the composition [3–5]. These can bring a more elastic space for the design and preparation of the device and be especially important for the heterojunction optoelectronic devices, such as solar cells of CdTe and $CuInSe_2$.

Cd_2SnO_4 (CTO) thin films have low resistivity, low surface roughness, high mobility and high transparency [6–8] and have been used in the preparation of CdTe solar cells [9,10] and perovskite solar cells [11]. CTO thin films can be prepared by sputtering [6,12], chemical bath [13] and spray pyrolysis [14], etc. Amongst the above techniques, the RF sputtering method achieves the lowest resistance of CTO thin films with good optical transmission [12].

The as-deposited CTO thin films are often annealed to improve the electrical and optical properties and the cadmium-containing atmosphere was generally necessary to get the lower resistivity and the higher mobility in this annealing process [6,15]. The theory calculation results show that the Sn_{Cd} antisite defect is the most probable donor under Cd-rich conditions [16]. However, the study of CTO annealing in cadmium-containing atmosphere has mainly focused on the specific process, such as the dependence of CTO thin film bulk properties on the annealing configuration in the CdS atmosphere [17]. The annealing effects on the surface composition, work function, and the mechanism for improving of the electric ability of CTO thin films in the cadmium-containing atmosphere are rarely reported. Anyway, the studies of surface characteristics are very important for interfacial matching of heterojunction devices.

In this paper, the surface morphology, composition, Fermi level position and work function of CTO thin films were studied in detail based on the measurements of AFM, XPS, UPS, PL, etc.

* Corresponding author.
E-mail address: zh_jq2000@263.net (J. Zhang).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.mssp.2017.11.017
Received 1 July 2017; Received in revised form 29 September 2017; Accepted 12 November 2017

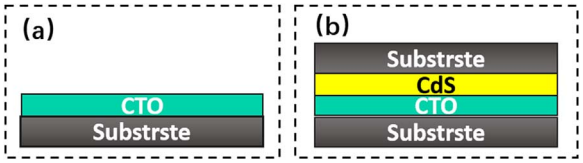

Fig. 1. Schematic diagram of the CTO thin films annealed in different atmospheres (a) Ar, (b) Ar/CdS.

2. Experimental techniques

2.1. Preparation

The CTO thin film was deposited on a borosilicate glass substrates (Corning Eagle XG) having a thickness of 1 mm from a Cd_2SnO_4 compound target (99.999% purity, Leshan Kaivada Photoelectric Technology Co, Ltd, China) at room temperature by radio-frequency magnetron sputtering. The chamber was initially evacuated to a pressure of 3.0–3.8 × 10^{-6} Torr and a mixture of 99.999% pure argon and 99.99% pure oxygen was then introduced using two mass flow meters of flow rate 47.5 and 2.5 sccm respectively to maintain the chamber pressure at 11.25 mTorr. The 100 W power was applied by a 13.56 MHz radio-frequency source with an auto-match network controller (R1001 RF power supply, AEREN Co, US). After sputtering, some samples were annealed at 680 °C for 40 min in Ar or Ar/CdS atmosphere, respectively. As shown in Fig. 1, CdS atmosphere was created by contact of 100 nm CdS thin film prepared by chemical bath deposition technique on the same substrates [18,19].

2.2. Characterization

The film thickness was measured with a step profiler (XP-2, Ambios Technology Inc. USA). The structure was characterized by X-ray diffraction (XRD, Dandong Fangyuan Instrument Co. Ltd., China). The surface morphology and surface roughness were studied by field emission scanning electron microscope (SEM, Hitachi S-4800) and atomic force microscope (AFM,Bruker Nano Inc. DI Multimode 8), respectively. The film composition was analyzed by energy dispersive X-ray spectroscopy (EDS, INCA, Inca Oxford) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo-Fisher Scientific). Smallest detectable element concentration was about 100 ppm for EDS and 1000 ppm for XPS. XPS was performed using the Ar+ ions (500 eV) to clean the thin film layers (sample current 2 μA) for 60 s and the Ar+ ions (2 kV) to etch the thin film layers. Monochromatic Al Kα radiation ($h\nu$ =1486.6 eV) was employed as excitation. The binding energy of the peaks was adjusted by fixing the C1s peak at 284.8 eV and the core level peaks were analyzed using a nonlinear Shirley-type background.

The electrical properties versus temperature measurements were measured using van der Pauw method through a Hall effect system, which consists of a Keithley 7065 Hall effect card, 6485 picoammeter, 2182 A nanovoltmeter, and 6220 constant current source, and then the resistivity, Hall mobility and carrier concentration were obtained. The samples were placed in a cryostat cooled by liquid nitrogen (Janis VPF-100S), and the temperature was controlled by the Lake Shore 335 temperature controller at 80–400 K. The samples size is of the order of 10 × 10 mm^2. The contacts were made by soldering with high purity indium on the four corner of samples. The optical transmission spectra were measured in the wavelength range of 300–1000 nm (in 1 nm intervals) with a UV–Vis–NIR grating spectrophotometer (Perkin-Elmer Lambda 950) equipped with an integrating sphere of 150 mm diameter. The band-to-band emission peak was determined by photoluminescence (PL) measurement using a FLS980 fluorescence spectrometer (Edinburgh Instruments). A Xe lamp was used as excitation source and the excitation wavelength was 390 nm.

The work function was measured by ultraviolet photoelectron spectroscopy (UPS, ESCALAB 250Xi, Thermo-Fisher Scientific). All samples were cleaned with deionized water in an ultrasonic bath and then dried with nitrogen before being measured. UPS was performed using a Helium (He–I) gas discharge lamp with an excitation energy of 21.22 eV and an energy resolution better than 200 meV. The Fermi energy level was calibrated using pure Au metal. The temperature and the pressure in the chamber were maintained at 20 °C and 2.3–3.8 × 10^{-8} Torr during the measurement.

3. Results and discussion

3.1. Morphology, structure, and chemical composition

Fig. 2 shows the surface morphology of the CTO thin films. In Fig. 2a, uniform and nearly spherical nano-grains are distributed on the surface of as-deposited CTO thin films with average roughness (R_a) of about 1.3 nm (Fig. 2d), and their grain sizes are estimated about

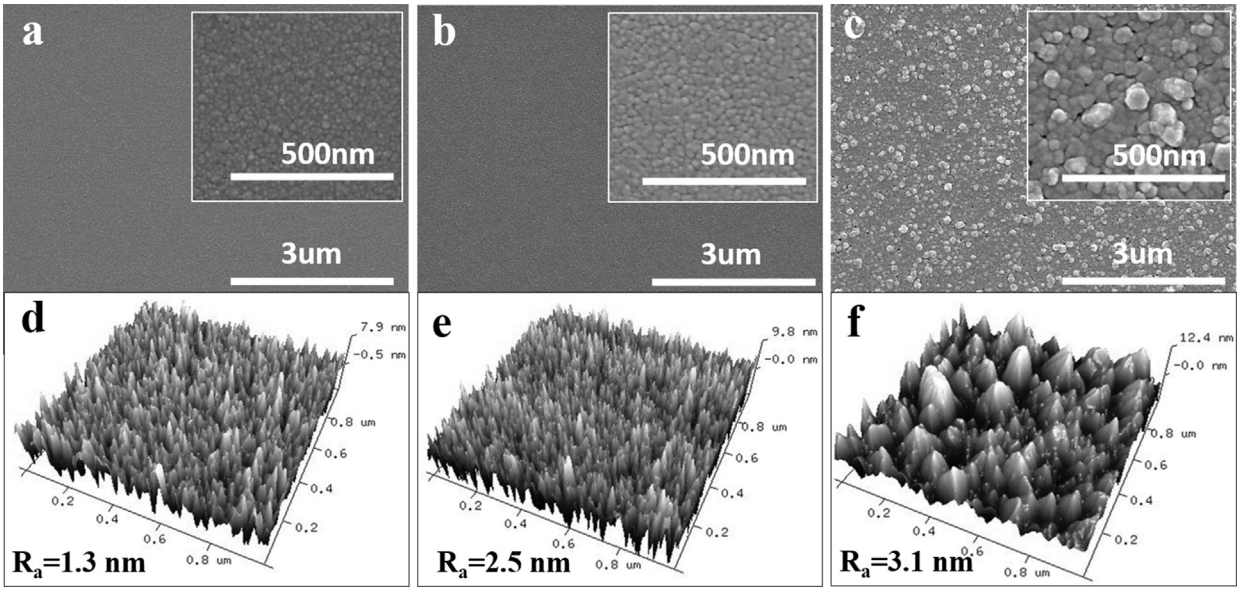

Fig. 2. SEM (a-c) and corresponding AFM (d-f) images of as-deposited (a, d), Ar-annealed (b, e) and Ar/CdS-annealed (c, f) CTO thin films. Insert images in (a-c) show the magnified details of sample surface obtained with SEM.