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Directly hydrothermal growth of $CdIn_2S_4$ nanosheet films on FTO substrates for photoelectric application

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ABSTRACT

In this paper, $CdIn_2S_4$ films composed of nanosheets have been directly deposited on fluorine-doped tin oxide (FTO) substrates using a simple hydrothermal method. The crystal structure, morphology, composition, and optical properties of the $CdIn_2S_4$ films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analyzer (EDX), X-ray photoelectron spectrum (XPS), and UV–vis spectra. In addition, the reaction conditions influencing the formation of $CdIn_2S_4$ films, such as reaction time and the sulfur source, were investigated. The L-cysteine acting as sulfur source was found to play an important role in the formation of the final films. A possible growth mechanism for the formation $CdIn_2S_4$ films on FTO substrates has been proposed. And the photoelectrochemical properties were also investigated.

1. Introduction

Cadmium indium sulfide ($CdIn_2S_4$) is a ternary chalcogenide which belongs to the family of ternary compound AB_2C_4 (A = Cu, Ag, Zn, Cd, etc.; B = Al, Ga, In; C = S, Se, Te). The band gap of $CdIn_2S_4$ reported in the literature is in the range of 2.1–2.7 eV, which matches the solar spectrum for energy conversion reasonably well [1,2]. It has recently been reported that the $CdIn_2S_4$ is a prospective material for photoelectrochemical solar cells [3–5]. In addition, it is also a material for application in photoconductors, photocatalysis, and light-emitting diodes [6–11].

It is well known that the physical and chemical properties of materials have a strong correlation with their shapes, size, and structures [12,13]. Thus, many efforts have been focused on the preparation of the $CdIn_2S_4$ material with various morphologies. For example, Jin-Ook Baeg et al. [1] have synthesized $CdIn_2S_4$ nanotubes and "marigold-like" nanostructures. Fan et al. [14] have fabricated $CdIn_2S_4$ hollow spheres, and Apte et al. [15] have synthesized hierarchical $CdIn_2S_4$ nanostructures via microwave-hydrothermal process. However, it is still a challenge to fabricate nanostructured $CdIn_2S_4$ material with structurally well-defined morphology onto a conductive substrate. This disadvantage imposes barriers in the construction of device because stronger binding of electrode films onto conductive substrate is a necessary prerequisite for the fabrication of devices, especially for solar cells [16]. On the other hand, attempts have been made to synthesize $CdIn_2S_4$ thin films by spray pyrolysis, vacuum evaporation, and hot wall epitaxy methods [17–19]. However, all these techniques require high temperature or a sintering step to obtain highly crystalline films. Compared with the above mentioned method, hydrothermal synthesis method is attractive because of its operational simplicity, good coating efficiency, and capability for large-scale production. Although hydrothermal synthesis has been widely used to prepare a variety of chalcogenide nanoparticles [20–22], studies on the hydrothermal preparation of chalcogenide thin films are very limited [23].

Herein, we report on a facile one-pot hydrothermal process to fabricate $CdIn_2S_4$ thin films with perpendicular nanosheets structure on FTO substrate. The formation of the $CdIn_2S_4$ microstructure was investigated. In addition, the optical and photoelectrochemical properties of the films were also studied.

2. Experiments

2.1. Preparation of $CdIn_2S_4$ films

All reagents were analytical grade and were used without further purification. Before deposition of $CdIn_2S_4$, FTO conductive glass (NSG GPOUP, TCO-17, 16 Ω sq^{-1}, 4 cm × 1.5 cm, with a thickness of 2.2 mm) was washed sequentially with acetone, ethanol, and distilled water in an ultrasonic cleaner. In a typical synthesis procedure, stoichiometric amounts of $CdCl_2{\cdot}2.5H_2O$·(0.068 g), $InCl_3{\cdot}4H_2O$ (0.176 g), and a double excess of L-cysteine (0.290 g) were dissolved in 30 ml distilled water and placed in a Teflon-lined stainless autoclave of 50 ml capacity. Then, the pretreated FTO was placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The autoclave was sealed, maintained at 160 °C for 3, 6, 12, 18 h, and cooled to room temperature naturally. Finally, the obtained homogeneous films deposited on the FTO substrate were washed repeatedly with distilled water and dried in air at room temperature.

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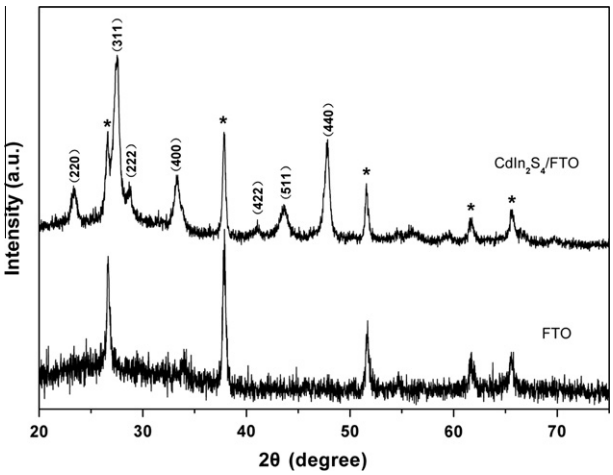

Fig. 1. XRD patterns of $CdIn_2S_4$ thin film on FTO substrate obtained at 160 °C for 12 h and FTO substrate.

2.2. Characterization

The phase analysis of the films was performed on a Bruker D8 X-ray diffractometer (40 kV, 40 mA) with Cu Kα radiation (λ = 1.5418 Å). The morphologies were characterized by field-emission scanning electron microscopy (FESEM, JEOL JEM-6700F Microscope). Compositional analysis of the films was carried out by energy dispersive X-ray spectrometer (EDX) attached with the SEM. The surface bonding states was studied using X-ray photoelectron spectroscopy (XPS) with a monochromated Alα ($h\upsilon$ = 1486.7 eV) source. Optical characterization of the films was performed on a UV-3150 spectrophotometer.

2.3. Photoelectrochemical measurements

The photoelectrochemical properties were investigated using a conventional three-electrode system. Films before and after heat treatment at 400 °C for 1 h in an Ar atmosphere were used as the working electrode, a platinum mesh as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was a 0.5 M Na_2SO_4 aqueous solution. The light source was a 500 W xenon lamp (spectra physics), and the light intensity was calibrated for AM 1.5 light at 100 mW cm^{-2} with a laser power meter (BG26M92C, Midwest Group). The current density–time and current density–voltage (J–V) response of the device was recorded using an electrochemical workstation (CH Instruments, Model CHI601C).

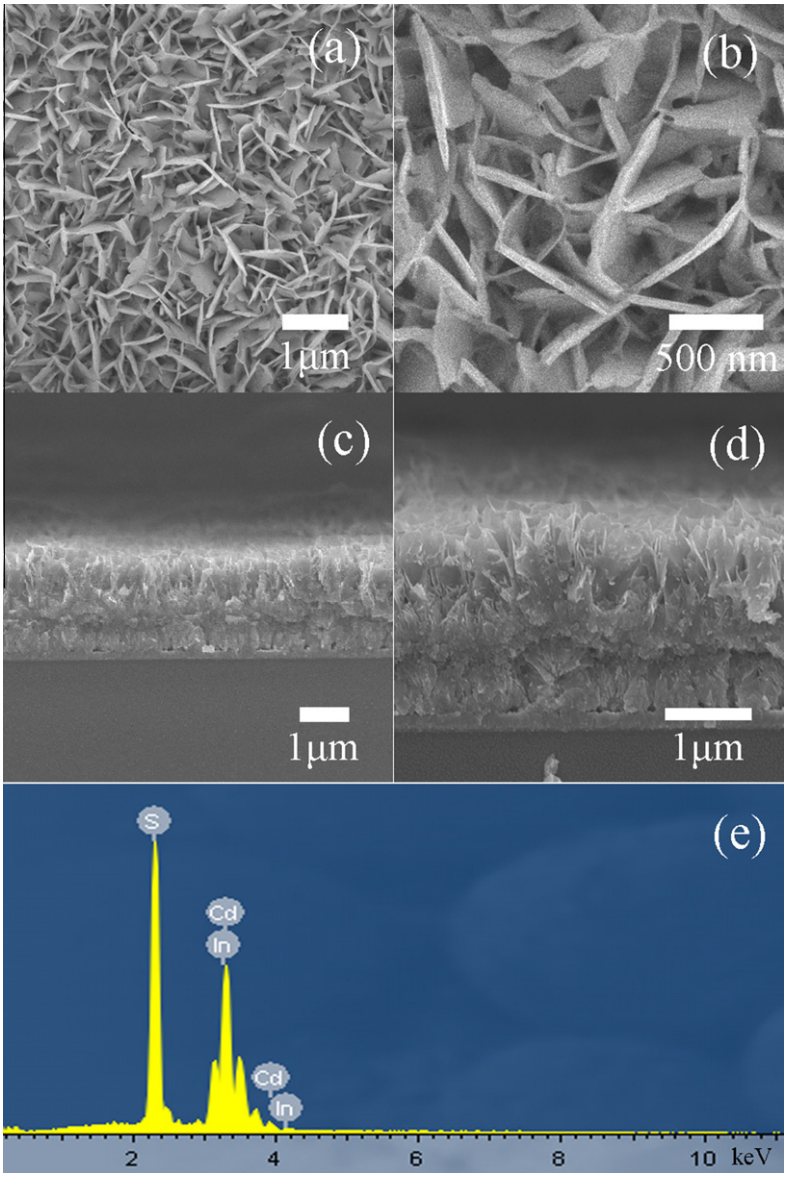

Fig. 2. (a and b) Top- and (c and d) cross-sectional SEM images of $CdIn_2S_4$ film obtained at 160 °C for 12 h. (e) EDX pattern of the $CdIn_2S_4$ film.