Applied Surface Science 258 (2011) 649–656

Contents lists available at ScienceDirect

Applied Surface Science

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

Fabrication and characterization of indium sulfide thin films deposited on SAMs modified substrates surfaces by chemical bath deposition

Xu Meng[a,b], Yongjuan Lu[a,c], Xiaoliang Zhang[a,c], Baoping Yang[b], Gewen Yi[a], Junhong Jia[a,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China
[b] College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou, 730050, China
[c] Graduate School of Chinese Academy of Sciences, Beijing, 10049, China

ARTICLE INFO

Article history:
Received 14 January 2011
Received in revised form 28 June 2011
Accepted 5 July 2011
Available online 3 August 2011

Keywords:
Indium sulfide
Thin films
Self-assembled monolayers
Photoelectrochemical property
Micropattern

ABSTRACT

In an effort to explore the optoelectronic properties of nanostructured indium sulfide (In_2S_3) thin films for a wide range of applications, the In_2S_3 thin films were successfully deposited on the APTS layers (–NH_2-terminated) modified ITO glass substrates using the chemical bath deposition technique. The surface morphology, structure and composition of the resultant In_2S_3 thin films were characterized by FESEM, XRD, and XPS, respectively. Also, the correlations between the optical properties, photocurrent response and the thickness of thin films were established. According to the different deposition mechanisms on the varying SAMs terminational groups, the positive and negative micropatterned In_2S_3 thin films were successfully fabricated on modified Si substrates surface combining with the ultraviolet lithography process. This offers an attractive opportunity to fabricate patterned In_2S_3 thin films for controlling the spatial positioning of functional materials in microsystems.

1. Introduction

In recent years, there has been increasing interest in III–VI semiconductor materials for their potential applications in optoelectronic, photovoltaic industries and photoelectrochemical solar cell devices [1]. One of the most promising alternative materials is In_2S_3 thin films, which is a chalcogenide n-type semiconductor with a wide energy band gap (2.0–2.8 eV) and is a non-toxic material. Owing to its stability [2–6], optical [7], optoelectronic [8], and electronic [9,10], it can be applied to many technologies, such as luminophors, solar cell devices, optoelectronic [8,9,11–13], and heterojunction for use in photovoltaic electric generators [13]. There are several reports about solar cells based on Cu(In, Ga)Se_2–In_2S_3 heterostructures that have achieved efficiencies as high as 15.7% [14–16]. Meanwhile, In_2S_3 can be a base material in the deposition of compound semiconductors such as $CuInS_2$ [17–22], $CuInSe_2$ [15,23], $AgInS_2$ [24], $CuAgInS_2$ [25].

As we know, the shape, phase, and size of inorganic nanocrystals and microcrystals are the determinant elements in varying their electrical, optical, and other properties [26]. Various techniques, such as chemical vapour deposition [27], physical vacuum deposition [28], atomic layer epitaxy [29], successive ionic layer adsorption and reaction (SILAR) [7], spray pyrolysis [30], and chemical bath deposition (CBD) [14,31,32] have been utilized to prepare In_2S_3 thin films. Among these methods, even through the uniform and high quality films are synthesized by physical techniques, they are correspondingly expensive and highly energy consuming. CBD is known to be a simple, no requirement for sophisticated instruments, low temperature, and convenient for large area deposition technique [33,34]. CBD is a slow process, which facilitates the better orientation of the crystallites with improved grain structure [35].

Patterning techniques are very important for fabricating thin film devices and patterned structures are eventually required in most of microsystems for controlling the spatial positioning of functional materials [36]. A self-assembled monolayer grown on the substrates provides a way to regulate surface properties and control crystal heterogeneous nucleation and growth for the preparation of various inorganic thin films [24,37–43]. Self-assembled monolayers (SAMs) with different terminated groups have been used as templates combining with ultraviolet lithography [44], scanning probe lithography [45], microcontact printing [42], and electron-beam patterning [46] to fabricate micro- and nanoscale patterned structures for applying in most of functional materials, such as microelectronic, sensors, electrical and optical devices, MEMS, and photonic systems.

In this work, we introduce a convenient, time-saving route for deposition of the transparent n-type conducting In_2S_3 thin films on the self-assembled monolayer (SAMs)-modified ITO glass and p-type Si(1 0 0) substrates with CBD method. In addition, the positive and negative micropatterned In_2S_3 thin films were successfully

* Corresponding author. Tel.: +86 931 4968611; fax: +86 931 8277088.
E-mail address: jhjia@licp.cas.cn (J. Jia).

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doi:10.1016/j.apsusc.2011.07.036

fabricated on Si substrates with $-NH_2/-CH_3$ and $-NH_2/-OH$ terminated silane SAMs with CBD method combining with the ultraviolet lithography process. The detailed time-dependent evolutions of surface morphology, crystal phase and composition of the resultant In_2S_3 thin films were characterized to understand the formation process and growth mechanism of In_2S_3 thin films. Also, the correlations between the optical properties, photocurrent response and the thickness of thin films were established to continue studying thin films with special using In_2S_3 materials. Extensively fabricating of patterned In_2S_3 thin films can provide an attractive procedure to control the spatial regulation In_2S_3 thin films for investigating the innovative photoelectrochemical properties of In_2S_3 thin films in the succeeding research.

2. Experimental

2.1. Materials and substrate surface modification

Analytical grade Indium sulfate ($In_2(SO_4)_3$), triethanolamine ($N(CH_2CH_2OH)_3$, TEA), thioacetamide (CH_3CSNH_2, TAA) with purities better than 98% were purchased commercially and used as received. 3-aminoproyl triethoxysilane (APTS, 99%) and octadecyltrichlorosilane (OTS, 95%) were purchased from Aldrich. All chemicals were used without further purification.

The substrates used for the present study were ITO-coated glass and p-type Si(1 0 0), cut into $1 \times 2\,cm^2$ and $1 \times 1\,cm^2$ pieces, respectively. Prior to SAMs assembling, the substrates were ultrasonically cleaned by subsequently soaking them in an ultrasonic bath in deionized water, acetone, and isopropyl alcohol for 10 min respectively, followed by thoroughly rinsing them with deionized water, and drying with a nitrogen gas flow. The Si(1 0 0) substrates were immersed in Piranha solution (H_2O_2: H_2SO_4 = 3:7) at the 90 °C for 1 h and then rinsed thoroughly with deionized water. The procedure for assemble APTS or OTS SAMs on the substrates has been described in details in our previous papers [36,47].

2.2. Deposition of indium sulfide thin films

For the deposition, aqueous solutions of 0.01 M Indium sulfate, 0.03 M thioacetamide (TAA) and 0.03 M triethanolamine (TEA, complexing agent) were mixed together in a 50 mL glass beaker and the pH value of the solution was controlled to 2.2 and 2.3 by adding 0.1 M H_2SO_4 into the reaction mixture. The substrates with APTS layers were placed vertically to the bottom of the beakers to avoid the effect of gravity, the temperature of the reaction mixture was maintained 80 °C, and deposition time was varied from 28 to 90 min. The deposited films were rinsed with deionized water to remove loosely adhered particles on the films and then dried with a nitrogen gas flow.

2.3. Fabrication of the patterned In_2S_3 microarrays

Positive patterns were produced by irradiating the OTS-SAM surface through a mask with 130 μm feature size under UV light (125 W UV mercury lamp, λ = 365 nm) for approximately 3 h in air. UV-irradiation causes the formation of silanol regions in exposed areas. Then, the patterned substrate was immersed in the hexane solution of APTS for 3 h to assemble APTS on the silanol regions. Finally, the substrate was removed from the solution and ultrasonically washed with hexane for 3 min and dried with a nitrogen gas flow, resulting in a patterned $-NH_2/-CH_3$-terminated SAMs surface. Similarly, only the procedure of exposing the APTS layers selectively to UV light was needed in the negative patterns fabrication, resulting in a patterned $-NH_2/-OH$-terminated SAMs surface. The patterned SAMs of the positive and negative were immersed in the previous aqueous solution for the deposition of the patterned In_2S_3 microarrays.

2.4. Characterization

The surface morphologies of In_2S_3 thin films were examined by a JSM-5600LV field-emission scanning electron microscope (FESEM, Japan). The structure and the phase composition were analyzed by X'pert PRO X-ray diffraction (XRD, Netherlands) with Cu Kα radiation (λ = 1.5406 Å) at a scanning speed of 1.2°/min. The chemical states of the elements on the films were determined using a PHI5702 multifunctional X-ray photoelectron spectroscope (XPS, USA). The XPS analysis was conducted at 400 W and pass energy of 29.35 eV, using Al Kα (1486.6 eV) radiation as the excitation source, and the binding energy of contaminated carbon (C1s = 284.6 eV) was used as reference. The optical absorption was measured by a UV–vis spectrophotometer (U-3010, Japan) within the wavelength range of 300–900 nm. The photocurrent response was measured by an electrochemical workstation (CHI660d, China) with a three-electrode system, in which In_2S_3 thin films, a platinum wire, and saturation calomel electrode were used as the working electrode, the counter electrode, and reference electrode, respectively. A 125 W UV mercury lamp (λ = 365 nm) was used as the light source. The electrolyte, aqueous $HClO_4$ (0.1 M) solution, was freshly prepared using double deionized water.

3. Results and discussion

3.1. Time-dependent evolutions of morphologies and film thickness

The In_2S_3 thin films were successfully deposited on the APTS layers ($-NH_2$-terminated) modified ITO glass substrates using chemical bath deposition technique. The deposition temperature and aqueous solution were kept constant to avoid the differences. In order to understand the formation process and growth mechanism of In_2S_3 thin films, detailed time-dependent evolutions of morphology were studied by the FESEM. As shown in Fig. 1, initially, the density of nucleation was so low that continuous thin films can be hardly observed at the first 28 min, but formed some active nucleation spots (Fig. 1a). However, some continuous spherical clusters were formed on the APTS layers surface with the deposition time was extended to 30 min (Fig. 1b), but there are still no obvious In_2S_3 nanorods formed. After 40 min, the quantity of spherical clusters soars expeditiously with the increasing number of the active nucleation spots (Fig. 1c). When the deposition time was prolonged to 50 min, the particle shape changed from spherical clusters to nanorods (Fig. 1d). By the reaction time of 60 min, In_2S_3 nanorods have assembled into compact thin films on $-NH_2$-terminated APTS layers and a uniform surface was obtained (Fig. 1e). When the deposition time was prolonged to 90 min, the thin films became more uniform and compact (Fig. 1f). From this, it can be seen that the In_2S_3 thin films are composed of nanorods with about 50 nm in diameter and at least about 150 nm in length have uniformity throughout the surface. This architecture would be more fascinating to form an organic–inorganic hybrid photovoltaic cell with a suitable p-type layer [48,49]. The variation of thin films thickness with different deposition times is shown in Fig. 2. There is a continuous increase of thin films thickness with the increase of deposition time, while the growth rate decreases gradually. The maximum thickness of 500 nm was attained after a deposition period of 90 min. After 90 min, the thickness was no longer to change obviously, which can be attributed to the equilibrium of two competing processes taking place in the deposition solution: one process includes the heterogeneous precipitation and