Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2008) 5039–5043
applied surface science
www.elsevier.com/locate/apsusc

Physical properties of ZnS thin films prepared by chemical bath deposition

T. Ben Nasr [a,*], N. Kamoun [a], C. Guasch [b]

[a] *Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis (2092) El Manar, Tunisia*
[b] *Institut d'Electronique du Sud UMR 5214, Université de Montpellier II, Place Eugène Bataillon, CC082, 34095 Montpellier, France*

Received 10 August 2007; received in revised form 26 January 2008; accepted 31 January 2008
Available online 4 March 2008

Abstract

Zinc sulphide thin films are deposited on SnO_2/glass using the chemical bath deposition technique. X-ray diffraction and atomic force microscopy are used to characterize the structure of the films; the surface composition of the films is studied by Auger electrons spectroscopy, the work function and the photovoltage are investigated by the Kelvin method. Using these techniques, we specify the effect of pH solution and heat treatment in vacuum at 500 °C. The cubic structure corresponding to the (1 1 1) planes of β-ZnS is obtained for pH equal to 10. The work function ($\Phi_{material} - \Phi_{probe}$) for ZnS deposited at pH 10 is equal to −152 meV. Annealing at 500 °C increases Φ_m (by about 43 meV) and induces the formation of a negative surface barrier. In all cases, Auger spectra indicate that the surface composition of zinc sulphide thin films exhibits the presence of the constituent elements Zn and S as well as C and O as impurity elements.

Keywords: Zinc sulphide; Chemical bath deposition; Physical properties

1. Introduction

Zinc sulphide (ZnS) thin films with a wide direct band gap and n-type conductivity are promising for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells. In optoelectronics, it can be used as light emitting diode in blue to ultraviolet spectral region due to its wide band gap of 3.7 eV at room temperature [1]. Several techniques such as molecular beam epitaxy [2], H_2 plasma chemical sputtering [3], MOCVD [4], MOVPE [5], liquid phase techniques such as electrochemical deposition [6], and chemical bath deposition (CBD) [7–8] have been used to produce ZnS thin films. Among them, chemical bath deposition is the least costly, low temperature technique. The CBD process uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. In the most typical experimental approach, substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion, added base and a complexing agent. The latter is used to control the speciation of the metal ion. Ammonia and hydrazine are popular choices as the complexing agent in the CBD of ZnS thin films [9].

In the present paper, we report the preparation of ZnS thin films by chemical bath deposition and physical characterization of the thin layers. The effect of pH and heat treatment on structural, morphological, and electronical properties of these films is investigated with the aim of finding the best conditions for the deposition process.

2. Experiments

The chemical bath deposition of ZnS on tin oxide (SnO_2) coated glass substrates are carried out from a chemical bath technique. The deposition of zinc sulphide thin films by CBD technique in zinc chloride–ammonia–thiourea system consists of complexation of the zinc cations by the ammonia and the consecutive reaction with the sulphide ions provided by the hydrolysis of thiourea. The chemical bath solution was constituted of: 0.315 g of zinc chloride ($ZnCl_2$: 0.077 M), 0.162 g of thiourea ($CS(NH_2)_2$: 0.071 M), 5.44 ml of 28% ammonia solution (NH_4OH: 1.39 M), and 3.34 ml of hydrazine hydrate (N_2H_4: 2.29 M). The deposition is carried out in a 30 ml beaker at a temperature of 90 °C and for a deposition time of

* Corresponding author. Tel.: +216 98524797; fax: +216 71885073.
E-mail address: tarek.ben-nasr@laposte.net (T. Ben Nasr).

0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.01.173

3 h. After the deposition, the samples are taken out from the bath, washed in distilled water and dried at 80 °C for 15 min in a hot air oven. The film deposition is carried out with the same bath composition for different pH values, ranging from 10 to 11.5. A hydrochloride acid solution is added into the chemical bath to adjust the pH at the suitable value.

The X-ray diffraction (XRD) spectra are obtained by means of BRUKER AXS D8 ADVANCE using Cu K_α monochromatic radiations. The wavelength, accelerating voltage, and current are respectively 1.5418 Å, 40 kV, and 20 mA. AFM is carried out with a Veecoo Dimension 3100 atomic force microscopy, in the so-called "Tapping mode" of imaging. Auger measurements are carried out with a Riber system equipped with a cylindrical mirror analyser (CMA) and working on the first derivative mode. In order to get information on the work function Φ of the film, we used the Kelvin method which allows us to determine the contact potential difference $(\Phi - \Phi_m)/q$ between the surface of these samples and a stable metallic probe surface. The metallic probe (work function Φ_m) vibrates in front of the investigated surface (work function Φ). By means of a compensation voltage, E, we equalize the surface potentials of the probe and of the sample and cancel the electric field ε between them. Then $(\Phi - \Phi_m)/q = E$. As $\varepsilon = 0$, there is no modification of Φ by the measurement technique and, therefore, the compensation voltage yields the true value of $\Phi - \Phi_m$.

3. Results and discussion

3.1. Structural and morphological properties

The obtained ZnS films are homogeneous with a good adherence to the substrate. Generally, the ZnS material can form wurtzite type structure or cubic. The CBD-derived ZnS films are amorphous or consisted of ZnO or $Zn(OH)_2$ [10]. Changes of crystallinity for different pH values of the chemical bath are investigated by XRD measurement. Fig. 1 shows the diffraction patterns for the polycrystalline ZnS films before annealing and deposited at different pH ranging from 11.5 to 10. Annealing at high temperature in vacuum does not improve the films crystallinity. There is one main peak, observed at the diffraction angles of 28.8°, for the ZnS films prepared in this study. This peak is assigned to the cubic phase β-ZnS of the plane (1 1 1). A decreasing of the pH value from 11.5 to 10 is found to improve the crystallinity of the film. In fact, the (1 1 1) peak intensity increases with decreasing pH and at pH 10 the ZnS films indicate better crystallinity (Fig. 1d). For a comparison, see Dona and Vidal [10,11] who obtained amorphous or poorly crystalline ZnS thin films by CBD method. Also, we note the presence of the unwanted phase β-$Zn(OH)_2$ corresponding to the (2 2 0) plane. With decreasing pH to 10 the intensity of the undesirable phase decreases which reveals that our films deposited at pH 10 of the chemical bath are essentially formed by the β-ZnS phase. In our previous work [12], we show that an increase of the pH leads to more OH^- ions in the solution, which tend to combine readily with zinc without leaving enough zinc for ZnS growth on the substrate. In other words, slow growth rates keep enough Zn in the solution on the form of $Zn(OH)_2$. This result is also indicated by thickness measurements estimated by the double weight method using an ultraprecision balance, which show thinner layer at greater pH. To summarize, for the same deposition time, films grown at low growth rate (pH 11.5) are thinner and have lower absorption, whereas, films grown at higher growth rate (pH 10) are thicker and have higher absorption.

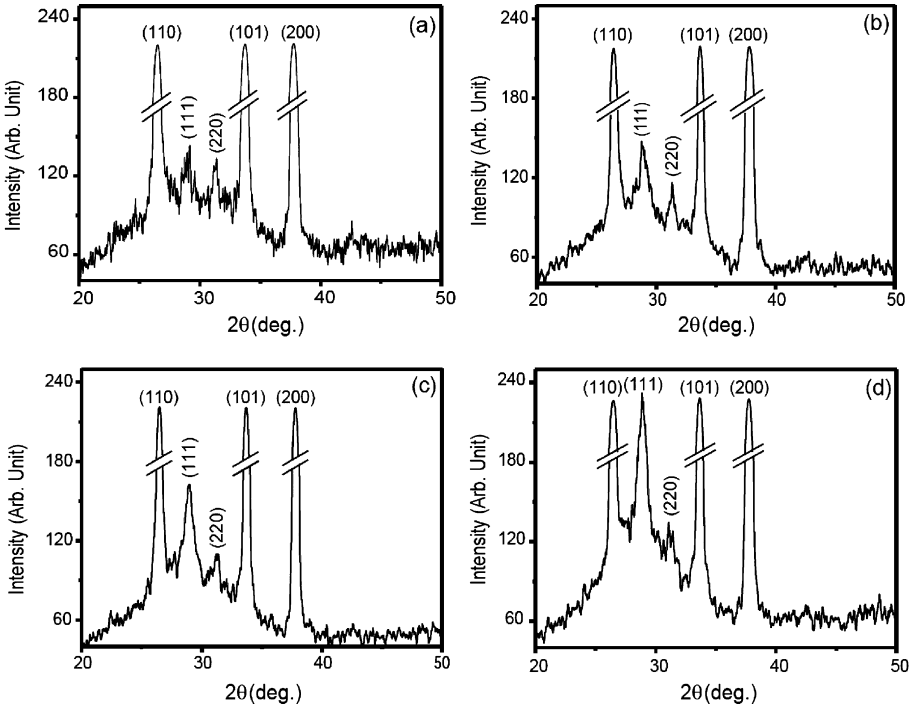

Fig. 1. X-ray diffraction patterns of ZnS thin films deposited on SnO_2/glass substrates at different pH solutions, (a) 11.5, (b) 10.99, (c) 10.48 and (d) 10; the line labelled (1 1 1) corresponds to β-ZnS; (2 2 0) to β-$Zn(OH)_2$; and (1 1 0), (1 0 1), (2 0 0) to SnO_2.