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Review

Annealing and light effect on structural, optical and electrical properties of CuS, CuZnS and ZnS thin films grown by the SILAR method

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ABSTRACT

CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films were grown by successive ionic layer adsorption and reaction (SILAR) method on glass substrates at room temperature. The annealing temperature effect on the crystal structure, optical band gap and the light effect on the electrical properties of these films have been investigated. Scanning electron microscope (SEM) and X-ray diffraction (XRD) techniques were used for the investigation of structural properties of films. The SEM and XRD studies showed that the films are covered well with glass substrates and exhibit polycrystalline characterization. Using the absorption measurements, the band gap energies for CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films were found as 2.03, 2.14 and 3.92 eV at room temperature, respectively. The two-point-probe method was used for the investigation of electrical properties of films and it was found that the current increase with increasing light intensity and increasing rate in illuminated 500 W cm^{-2} films was greater than in others. There is an important increasing in the current values of the CuS and $Cu_{0.6}Zn_{0.4}S$ films which have annealed at 400 °C. But the annealed ZnS thin film has less current values than the as-grown film. This is the first study which led to deposition of the CuZnS thin films by using the SILAR method.

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Contents

1. Introduction

There has been increasing interest during the past few decades in semiconducting chalcogenide thin films, because of their wide

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application in various fields of science and technology, leading to a drastic cut in the cost of production of semiconductor devices. Metal chalcogenide films have been extensively studied, because of their potential application in electronic, optical and superconductor devices. These films have been prepared by the successive ionic layer adsorption and reaction (SILAR) and solution growth techniques (SGTs) are simple, cheap and convenient for large area deposition and have easy controllable parameter [1,2]. Also, solution growth technique is convenient technology for synthesizing nanostructure materials [3–6]. The SILAR method is an aqueous solution method based on sequential reactions at the substrate–solution interface for the deposition of thin films. In the SILAR method, concentration, pH and temperature of precursor solutions and the time duration for adsorption, reaction and rinsing are very important parameters. The SILAR apparatus used for the thin film deposition has been presented earlier [2].

As an important semiconductor with unique electronic, optical and chemical properties, CuS is a promising material with potential applications in many fields [7–9]. The CuS thin films have recently received considerable attention, due to numerous technological applications in achievement of solar cells [10,11] in photo thermal conversion of solar energy [12], as selective radiation filters on architectural windows [13]. The structural and optical studies showed a direct band gap of 2.36 eV [14], 2.2 eV and hexagonal crystal structure [15] for CuS thin films. The electrical resistances of CuS films in the dark and under illumination with tungsten lamp of 100 Wm^{-2} were also investigated and resistance values decreased with illumination [15]. The XRD study showed that the as-grown CuS film reveals amorphous nature of the material. This film was annealed at 250 °C in Ar ambient for 2 h and characteristic peaks of CuS film begin to increase with annealing temperature. After annealing of this film indicates polycrystalline nature [16]. The CuO has been extensively studied because of its applications in the field of lithium-ion batteries, catalysis and superconductors. Porous and hollow CuO doughnut-shaped architecture is prepared by thermal oxidation of CuS and Cu_2S in air under atmospheric pressure [17]. Due to the unique optical property of hollow CuS structures, these structures are envisaged to be used in novel building blocks for the advanced materials, solar cell devices and drug delivery system [18].

ZnS is an important semiconductor materials with an energy band gap $E_g = 3.65$ eV (bulk), which is the largest value of all II–VI compound semiconductors. ZnS is an n-type semiconductor with a wide direct band gap. Thus, it could be used for the fabrication of optoelectronics devices, such as blue light-emitting diodes, Mn-doped electroluminescent devices, electro-optic modulator and n-window layers of solar cells [19]. ZnS thin films have been grown on various substrates like silicon, glass, ITO and GaAs vs. [20–22]. The annealing temperature effect on optical band gap and the light effect on the electrical properties of ZnS thin films were investigated and it was found that optical band gap decrease with increasing annealing temperature and the annealed films have more resistance than the as-grown films [2]. Hollow structures show a lower density, higher surface area and distinct optical property. Hollow ZnS architecture is fabricated by employing $Zn_5(CO_3)_2(OH)_6$ microspheres as the sacrificial template [23]. ZnSe nanobelt arrays have been achieved via the thermal treatment of belt-like precursor and strong emission (578 nm) from the unique well-aligned ZnSe nanostructures reveals their potential as building blocks for optoelectronics devices [24].

$Cu_xZn_{1-x}S$ ternary alloy compounds are promising materials for a variety of optical device applications, such as electroluminescent and photoconductor devices and photovoltaic cells. Using the $Cu_xZn_{1-x}S$ ternary compound is the possibility of tailoring its semiconductor properties between values corresponding to the pure binaries. This fact allows adapting the material properties the device requirements.

In this study, CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films were grown by the SILAR method. The light and annealing temperatures effect on the structural, optical and electrical properties of these films have been investigated. Characterizations of the films were done by using XRD, SEM optical absorption measurements and two-point-probe method.

2. Experimental procedure

In this study, CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films were grown on glass substrates by the SILAR method at room temperature. This is one of the first studies which led to deposition of the $Cu_{0.6}Zn_{0.4}S$ thin films by using the SILAR method. The adsorption, reaction and rinsing times were chosen experimentally, so that deposition occurred layer wise and resulted in homogeneous thin film structure. For deposition of CuS thin films, 0.1 M $CuCl_2$ solution (pH~3) is used as cationic precursor and 0.05 M Na_2S solution (pH~12) is used as anionic precursor. The adsorption and reaction times of CuS were 30 s and rinsing time was 50 s. For deposition of ZnS thin films, 0.1 M $ZnCl_2$ solution (pH~5) is used as cationic precursor and 0.05 M Na_2S solution (pH~12) is used as anionic precursor. The adsorption and reaction times of ZnS were 20 s and rinsing time was 100 s. For deposition of $Cu_{0.6}Zn_{0.4}S$ thin films, the concentrations of copper chloride and zinc chloride were optimized to deposit good quality and stoichiometric $Cu_{0.6}Zn_{0.4}S$ composite thin films. Thus, (0.1 M $CuCl_2$+0.1 M $ZnCl_2$) solution is used as cationic precursor and 0.05 M Na_2S solution (pH~12) as anionic precursor. The adsorption and reaction times of $Cu_{0.6}Zn_{0.4}S$ were 30 s and rinsing time was 50 s. For rinsing purpose, sample quantity of purified water was used. We obtained CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films of 150, 125 and 110 nm thicknesses by repeating such SILAR cycles 40 times. Optimized preparative parameters for CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films are summarized in Table 1. The other $Cu_{1-x}Zn_xS$ structures are growth but we do not get high-quality films. So we decided to evaluate the $Cu_{0.6}Zn_{0.4}S$ samples. In the SILAR method concentration, pH and temperature of precursor solutions and the time durations for adsorption, reaction and rinsing are important. By making several experimental trials, CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films deposition conditions were optimized. These optimized values can be seen in Table 1.

The glass substrates were cleaned ultrasonically for 10 min first in acetone and then in an ethanole: water 1:1 solution. The substrates were dried and stored in desiccators.

The samples were annealed at 200, 300 and 400 °C for 3 min under nitrogen atmosphere for investigating the annealing effects on crystal structures, optical and electrical properties of thin films. For investigating the light effect on films, in dark and under 150,

Table 1
Optimized preparative parameters for CuS, $Cu_{0.6}Zn_{0.4}S$ and ZnS thin films.

Parameters	Precursors solutions					
	CuS		$Cu_{0.6}Zn_{0.4}S$		ZnS	
	$CuCl_2$	Na_2S	$CuCl_2$+$ZnCl_2$	Na_2S	$ZnCl_2$	Na_2S
Concentration (M)	0.1	0.05	0.1	0.05	0.1	0.05
Immersion time (s)	30	30	30	30	20	20
Recycle SILAR	40	40	40	40	40	40
pH	~3	~12	~4	~12	~5	~12

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