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Annealing temperature effect on the structural, optical and electrical properties of ZnS thin films

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ABSTRACT

Zinc sulfide thin films were prepared on glass substrates at room temperature using a chemical bath deposition method. The obtained films were annealed at temperatures ranging from 100 to 500 °C in steps of 100 °C for 1 h. The films were characterized by X-ray diffraction (XRD), Raman spectroscopy, energy dispersive X-ray analysis (EDX), optical absorption spectra, and electrical measurements. X-ray diffraction analysis indicates that the deposited films have an amorphous structure, but after being annealed at 500 °C, they change to slightly polycrystalline. The optical constants such as the refractive index (n_r), the extinction coefficient (k), and the real (ε_1) and imaginary (ε_2) parts of the dielectric constant are calculated depending on the annealing temperature. Aside from the ohmic characteristics of the I–V curve, a nonlinear I–V curve owing to the Schottky contact is also found, and the barrier heights (ϕ_{bn}) for Au/n-ZnS and In/n-ZnS heterojunctions are calculated. The conductivity type was identified by the hot-probe technique.

1. Introduction

Zinc sulfide (ZnS) is found in nature as zinc-blende (also called sphalerite or β-ZnS and with a cubic structure) and wurtzite (α-ZnS, which is a hexagonal structure). The names of these minerals are used to designate the corresponding crystal structures. Large, high-quality β-ZnS crystals are found in nature and can also be grown in the laboratory at relatively low temperatures [1], whereas the hexagonal structure corresponds to a high temperature phase [2]. ZnS has a wide band gap (~3.6 eV). It is a II–VI compound semiconductor material and is commercially used in solar cells [3], infrared windows [4], and phosphor materials by doping with transition or rare-earth metals [5,6]. There has been growing interest in developing techniques to prepare semiconductor ZnS thin films.

ZnS thin films are produced using various techniques, including radio frequency (RF) magnetron sputtering [7], chemical vapor deposition (CVD) [8], and solvothermal [9] and chemical bath deposition [10]. Among these, chemical bath deposition (CBD) is the least costly low-temperature technique to deposit large-area thin films of semiconductors [11]. CBD is a technique in which thin films are deposited on substrates immersed in dilute solutions containing metal and chalcogenide ion sources. A chelating agent is used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. The technique under these conditions relies on the slow release of chalcogen ions into a solution in which the free metal ion is buffered at a low concentration. Film formation on the substrate takes place when the ionic product (IP) exceeds the solubility product (SP). However, generally, the films obtained by the CBD method are either amorphous or poorly crystallized. Therefore, annealing at high temperature is needed to improve the crystallinity of the films [12].

In this work, we report on the deposition of ZnS thin films at room temperature using a chemical bath deposition technique. The influence of the annealing temperature on the structural, optical, and electrical properties of the films has been studied. The obtained film shows slight crystallization after annealing at 500 °C. Raman features of the annealed (500 °C) film were investigated in order to obtain information about the phonon-dispersion relation because there have been very few reports on the first-order, second-order, and third-order Raman spectra of ZnS films. The Raman spectra of annealed ZnS films (500 °C) were obtained at room temperature and showed linewidths characteristic of first-order TO_l and LA, second-order TO_Γ and LO, and third-order LO Raman phonons. Moreover, it should be noted that the electrical characteristics of as-deposited and annealed (400 °C) In/n-ZnS and Au/n-ZnS Schottky contacts, which were formed at room temperature, were investigated using current–voltage (I–V) measurements. According to a review of the literature, ideality factors and barrier heights of ZnS films using current–voltage characteristics have not been previously examined. The performance and stability of metal

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semiconductor (MS) structures are of vital importance to all electronic and optoelectronic devices [13]. However, the fundamental physical mechanisms that determine Schottky barrier diode parameters such as the ideality factor n and barrier height ϕ_{bn} are still not fully understood. The popularity of such studies, which is rooted in their importance to the semiconductor industry, has not assured uniformity of the results or of their interpretation. Schottky barrier diodes are among the simplest MS contact devices.

2. Experimental details

A ZnS thin film was prepared by first mixing 1.25 ml of 1 M $ZnSO_4.7H_2O$, 1.5 ml of 3.75 M triethanolamine [$(HOCH_2CH_2)_3N$], 1 ml of ammonia/ammonium chloride (NH_3/NH_4Cl, pH=10.55) buffer solution, 0.05 ml of 0.66 M tri-sodium citrate ($C_6H_5Na_3O_7$), 0.5 ml of 1 M thioacetamide (CH_3CSNH_2), and enough deionized water to make total solution volume of 25.05 ml. The solution was stirred for a few seconds with a magnetic stirrer, and then, a clean glass substrate was introduced into the solution vertically. The deposition was made at room temperature. ZnS films were nucleated onto the submerged surfaces including the beaker walls over about 24 h for a single deposition run. For two deposition runs, the thin film obtained from the first run was submerged into freshly prepared solution for 24 more hours. The same bath was repeated up to four times. At the end of the deposition run, the layer was rinsed in deionized water. The color of the film was light green. The film was heated at 100, 200, 300, 400, and 500 °C for 1 h in an air oven to study how this would affect the structural, optical, and electrical properties.

The X-ray diffraction (XRD) spectra for the samples prepared by multiple depositions were measured using an X-ray diffractometer (Rigaku Rint 2000) with Cu-Kα_1 monochromatic radiation at 40 kV and 30 mA. Compositional analysis of the films was performed by energy dispersive X-ray (EDX) measurements in an SEM (Zeiss SUPRA 50 VP). The Raman spectroscopy was performed at room temperature using a Raman spectrometer (Bruker Senterra) with a 532 nm (20 mW) Ne laser line as an excitation source. Optical transmission data were obtained by a UV–vis spectrophotometer (Shimadzu UV-2101PC). The current–voltage (I–V) measurements were performed using an HP4140B pA meter/DC voltage source and an HP34401 Model Digital multimeter. Metal contacts were obtained by a vacuum evaporation method (Leybold Heraus 300 Univex).

3. Results and discussion

3.1. Structural characterization

The X-ray diffraction patterns for as-deposited and annealed (500 °C) ZnS films are shown in Fig. 1. The diffractogram (Fig. 1a) does not show any diffraction lines except for a broad diffraction pattern for 2θ angles in the range 20–40°, which indicates that the film phase is amorphous when it is deposited. However, Fig. 1b indicates that the deposited film has become slightly polycrystalline after being annealed at 500 °C. The annealed film showed a diffraction peak at a 2θ value of ~29.38°. The peak was identified as originating from the (0 0 8) plane of the hexagonal phase of ZnS based on our previous report [14] (compare with PDF card no: 39-1363). It can be concluded that post-deposition annealing slightly improves the crystallinity but does not transform the type of ZnS crystal structure in the film as in Refs. [15,16] in which as-deposited ZnS and ZnS:Cu,Ga films were completely transformed to ZnO and ZnO:Cu,Ga films after annealing in air.

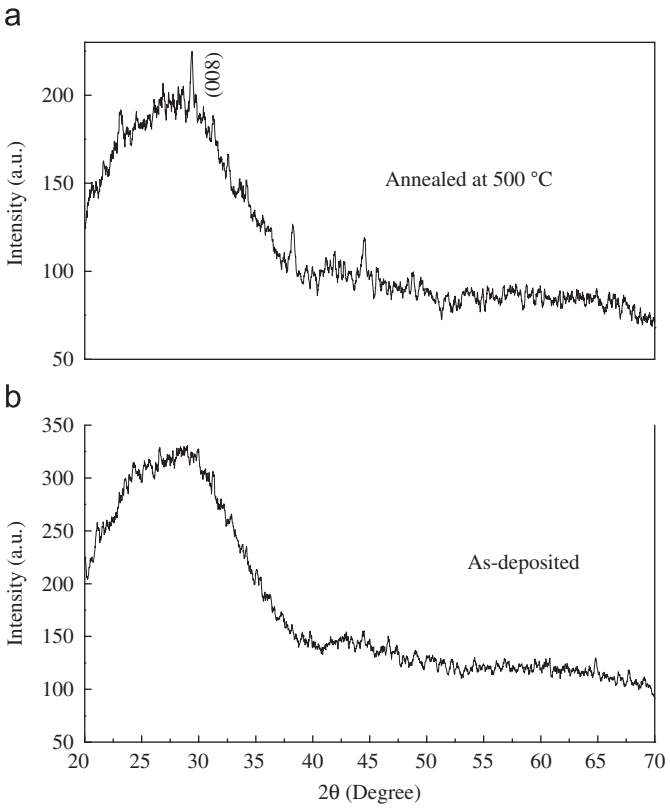

Fig. 1. XRD patterns of the ZnS films that were (a) as-deposited at room temperature and (b) annealed at 500 °C.

Raman spectroscopy is used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light that is usually sourced from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, which results in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. In addition, Raman spectroscopy can be used to observe other low-frequency excitations of the solid such as plasmons, magnons, and superconducting gap excitations. The spontaneous Raman signal gives information on the population of a given phonon mode by the ratio between the Stokes (down-shifted) intensity and the anti-Stokes (up-shifted) intensity. Finally, infrared and Raman spectra for the lowest energy structures can be obtained for possible detection and identification of these small clusters in experiments. The Raman spectra of annealed ZnS films are shown in Fig. 2 and the first-, second-, and third-order Raman phonons and their compositions are also given in Table 1. The first-order Raman phonon observed at ~478 cm^{-1} corresponds to $[TO_l+LA]_\Sigma$. The second-order Raman phonons observed at ~546 cm^{-1} and ~778 cm^{-1} might originate from $2TO_\Gamma$ and $2LO$, respectively. The Raman phonon modes $[TO_l+LA]_\Sigma$ and $2TO_\Gamma$ reported by Raman spectra were in good agreement when compared with Ref. [17]. The third-order Raman phonons observed at ~1082 cm^{-1} can be assigned as $3LO$ (see Table 1). The second- [$2LO$] and third [$3LO$]-order Raman phonons are also consistent with the literature [18]. The energy difference between the vibrational ground and excited states for each of the four vibrational modes in the Raman spectrum was calculated in the range 0.0593–0.1342 eV and listed in Table 1 using the following equation:

$$\Delta E = h\nu = h\omega c \quad (1)$$