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Influence of pH on properties of ZnS thin films deposited on SiO_2 substrate by chemical bath deposition

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ABSTRACT

This work focuses on the study of zinc sulfide (ZnS) thin films prepared by chemical bath deposition. The effect of the pH ranging from 10.0 to 10.75 on quality of ZnS thin films on SiO_2 substrate is investigated. The effect of pH on the surface showed that the variation of pH has a significant effect on the morphology of the ZnS thin films. The sample with pH value of 10.50 was uniform, free of agglomerates with band gap energy about 3.67 eV. The resistivity of ZnS thin films on SiO_2 substrate with different pH value were about 10^7 Ω cm.

1. Introduction

Zinc sulfide (ZnS) thin films is an important semiconductor material with large band gap (3.7 eV) [1], high transmittance in the visible range [2] and with a range of potential applications in optoelectronic devices [3]. Various techniques have been used to prepare ZnS thin films, such as chemical vapor deposition (CVD) [4], molecular beam epitaxy (MBE) [5], pulsed laser deposition (PLD) [6] and chemical bath deposition (CBD) [7,8]. The CBD method is the most convenient, is simple and inexpensive method. Studies on the deposited of ZnS thin films have been discussed on different parameters; substrates [9,10], zinc sources [11], deposition time [12], influence of pH on ZnS films over glass [13], growth rate [14]. Nevertheless, to the best of our knowledge reports of the effect of pH on ZnS thin films on SiO_2 substrate by chemical bath deposition have not been described. In the current work, the effect of the pH value in the aqueous solution, ranging from 10.0 to 10.75, on structural, morphological, optical properties and electrical resistivity of the ZnS thin films on SiO_2 substrates is reported.

2. Experimental

The ZnS thin films were deposited by immersion of the SiO_2 ($2 \times 2\ cm^2$) substrates in a CBD solution prepared from 2.5 ml of 0.15 M zinc acetate, 0.8 ml of 0.5 M tri-sodium citrate and 2.5 ml of 1 M thiourea. The temperature of the solution was kept at 80 °C ± 1 °C for 90 min. The pH was adjusted from 10.0 to 10.75 by adding ammonium hydroxide/ammonium chloride solution. Four set of samples were prepared of 10.0, 10.25, 10.50 and 10.75 values of pH. After deposition, the ZnS films were cleaned in an ultrasonic bath with methanol followed by distilled water rinse and dried with N_2. The ZnS films were characterized using different techniques. The morphology was analyzed in a Zeiss SUPRA 40 SEM with an operating voltage of 15 kV. The crystalline structure was analyzed in a Rigaku Ultima III X-ray diffractometer with CuKα (λ)=1.54 Å, operated at 40 kV and 44 mA. The optical properties were studied using a Cary 100 UV–vis spectrophotometer. The electrical characteristics were determined using current–voltage (*I–V*) measurements in a 4200 Keithley Semiconductor characterization system.

3. Results and discussion

Fig. 1 shows SEM images obtained for ZnS thin films deposited at different pH value in order to study the surface morphology. In this work, the surface shows that a small variation of pH has a significant effect on the morphology of the ZnS film. Fig. 1(a) shows that ZnS thin films deposited on SiO_2 substrate are not homogenous and the formation of a small amount of ZnS agglomerates. Fig. 1(b), corresponding to samples prepared to a pH value of 10.25, have poor uniformity and irregular grains are uniformly distributed on the

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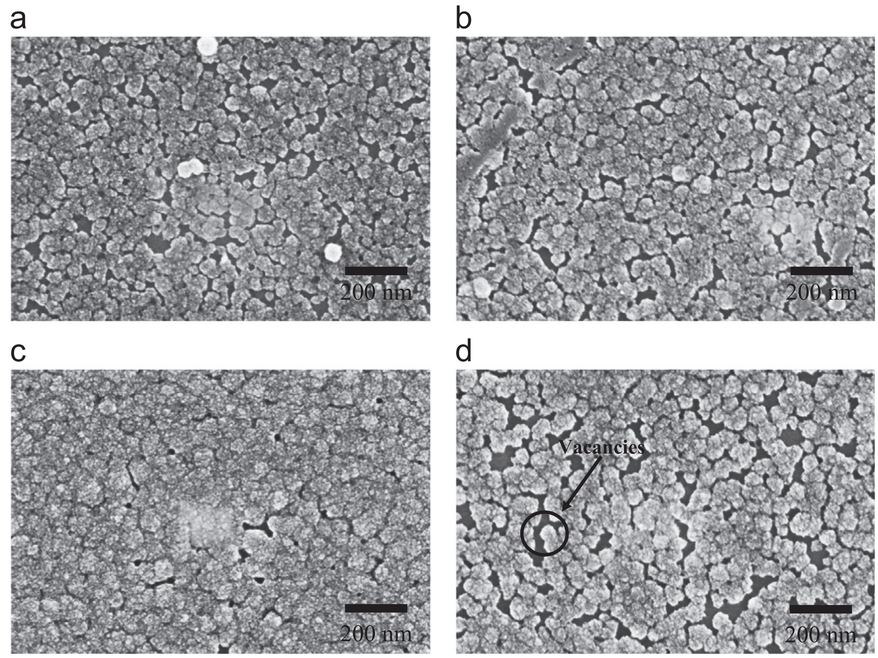

Fig. 1. Surface morphology of ZnS films grown on SiO_2 with different pH: (a) 10, (b) 10.25, (c) 10.50, and (d) 10.75.

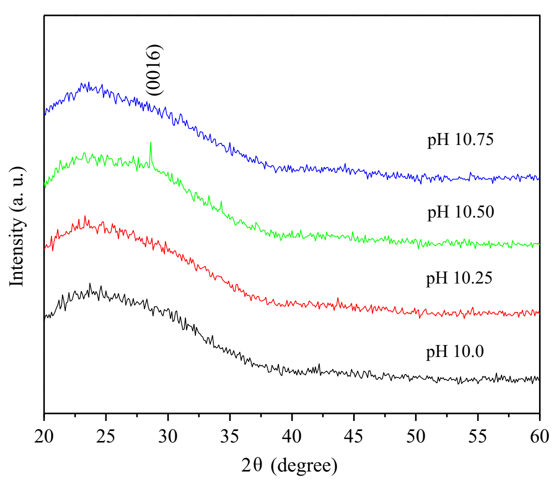

Fig. 2. X-ray diffraction pattern of ZnS film grown on SiO_2.

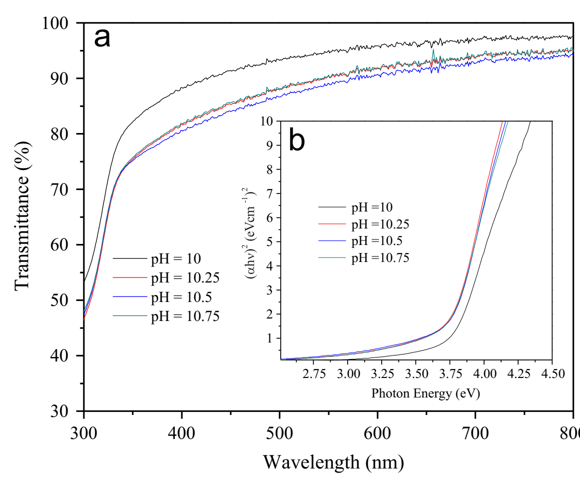

Fig. 3. Optical transmittance spectra (a) and (b) curves of *hv-ahv*^{2} for ZnS thin films.

surface. The same morphology is showed for the samples prepared to a pH = 10.75 (Fig. 1(d)). On the other hand, films with the pH value of 10.50, exhibit more homogeneity, free of agglomerates, as shown in Fig. 1(c). However, it is possible to observe that still some vacancies were present in the surface of these samples. The adhesion of the films to the substrate was through cluster-cluster growth mechanism, where high concentrations of Zn^{2+} ions are present, allowing large grains and the presence of pinhole on the surface of the films [15]. The resulting thicknesses were about of 50–55 nm for ZnS films deposited with different pH value. Fig. 2 shows the XRD patterns of the ZnS films deposited with different pH value grown on SiO_2. The results show that no peaks corresponding to cubic or hexagonal ZnS planes were observed for the thin films deposited with pH: 10.0, 10.25 and 10.75. However, XRD patterns of the ZnS thin films deposited with pH = 10.50 showed a peak at 28.55° corresponding to the (0016) [JCPDS No. 89 2433 (ZnS/Hex)] plane [16]. No characteristic peaks of phase ZnO impurity were observed. Fig. 3(a) shows the optical transmittance at different pH: (a) 10.0, (b) 10.5 and (c) 10.75. The ZnS thin films indicates a good transmission for an average transmittance of 75–90%. It can be observed that the transmittance of the films decreases rapidly with the increase the pH, which is mainly caused by reducing pinholes. The values of the energy band gap, E_g, were calculated by plotting $(\alpha h\upsilon)^2$ vs. $h\upsilon$ on the *x*-axis, where α, h, and υ are absorption coefficient, Planck constant, and frequency, respectively [17]. The Fig. 3(b) shows the variation of the optical bang gap is a function of pH value; it varies from 3.68 to 3.73 eV, these values are close to those reported by the literature for chemical bath deposited ZnS thin films [18]. Electrical properties were characterized by current–voltage (*I–V*) measurments. The Au/Cr/ZnS/SiO_2 structure was using gold (Au) metal contacts with 100 nm, Cr (10 nm), ZnS ($\approx$ 50 nm) and SiO_2 (100 nm). The resistivity was calculated with Ohm's law [19]. The electrical resistivity of ZnS thin films on SiO_2 substrate with different pH value were about 10^7 Ω cm, as shown in Fig. 4. These values are of the same magnitude than those reported [20], these resistivity values may be due to the presence of some fractures in the surface of the film.

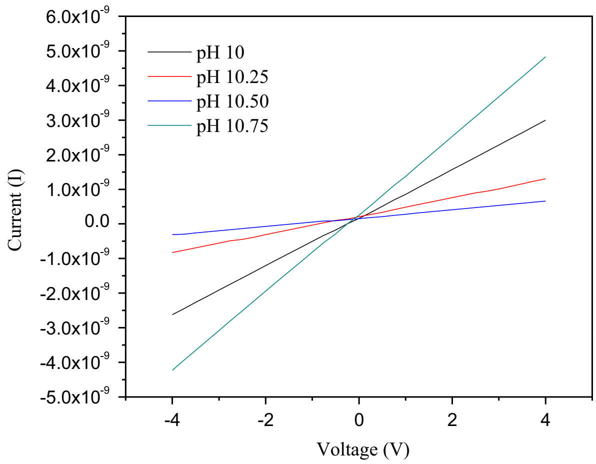

Fig. 4. Resistance of ZnS Thin Films.

4. Conclusions

This work presents the successful preparation of ZnS thin films deposited on SiO_2 substrate by a chemical bath deposition at 80 °C using different pH values, and using the non-toxic complexing agent Na_3-citrate. The morphology, optical properties depend strongly of the pH value. The ZnS thin films at pH = 10.50 showed a compact and smooth surface, and excellent transmission in visible high range. The band gaps E_g are found to decrease from 3.73 eV to 3.68 eV when the pH value increases. The properties obtained for these thin films have potential applications in optoelectronic devices.

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