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GREEN SYNTHESIS OF ZnS THIN FILMS BY CHEMICAL BATH DEPOSITION

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Semiconducting zinc sulphide (ZnS) has been demonstrated that is an excellent candidate for substituting the possible toxic materials as CdS as n-type material on optoelectronic devices, and photocatalytic materials. The Chemical Bath Deposition technique (CBD) is very simple: it requires temperatures below 100°C, a reactor that can be a beaker and the reaction can be carried out at atmospheric pressure. This study report a simple and green route for coating ZnS thin films onto glass-slide substrates by the CBD method, without the use of any complexing agents. Effects of vacuum annealing at various temperatures on the optical, structural and photocatalytic properties of nanocrystalline ZnS thin films were investigated. The ZnS thin films were prepared by a simple, economical and green synthesis, avoiding the use of any high-toxicity complexing agents. The chemical-bath-prepared ZnS thin films were obtained at 65°C on glass substrates. The band gap of the films varied in the range 3.28 to 3.64 eV. The photocatalytic activity of the ZnS thin films was evaluated by employing the degradation of aqueous methylene blue solution at a concentration of 2×10^{-5} mol L^{-1}. The ZnS thin-film sample annealed in a vacuum atmosphere at 200°C exhibited the highest photocatalytic activity.

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Keywords: ZnS, CBD, Thin film, Optical properties, Photocatalytic properties

1. Introduction

ZnS is one of the most promising chalcogenide semiconductors due to its great variety of applications. It is the principal semiconductor in thin films that can be substituted with effectively no toxic elements in a buffer layer in solar cells such as CdTe and copper indium gallium selenide, nanosized sensors, photodetectors, photodiodes, flat-panel displays, spectrally selective filters, electroluminescent devices and photocatalysts [1-10]. ZnS is an important II–VI compound semiconductor, crystallising in two phases, cubic-type zinc blende and hexagonal-type wurtzite, with band gaps of 3.66 and 3.74 eV respectively [11]. Two important optical properties, high transmission and high refractive index over a wide wavelength range, make it a very useful material with a great variety of applications. TiO_2 and ZnO are recognised as good photocatalyst materials, and much research has been done with the aim of improving the properties, particularly the photocatalytic properties, of these two materials; however, their production is still expensive and the process slow. An alternative material for use in photocatalytic processes is ZnS, grown by an economical and simple route such as the chemical bath deposition (CBD) technique. The CBD technique is very simple: it requires temperatures below 100°C, a reactor that can be a beaker and the reaction can be carried out at atmospheric pressure. In many previous studies [1-10],

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researchers have varied the complexing agent in order to improve the characteristics such as crystalliſnity, thicknesses, morphology and higher Zn atomic ratio, the most used complexing agents being ammonia, triethanolamine, tartaric acid, hydrazine hydrate, ammonium chloride, trisodium citrate, ethylenediaminetetraacetic acid disodium and mixtures of one, two or three of these components [12-25].

In this study, we report a simple and green route for coating ZnS thin films onto glass-slide substrates by the CBD method, without any complexing agents. We also investigated the effects of thermal annealing in a vacuum atmosphere on the optical, morphological and photocatalytic properties.

2. Experimental method

2.1 Reagents

Zinc acetate ($Zn(OOCCH_3)_2$, J.T. Baker, 99%) and thioacetamide (CH_3CSNH_2, J.T. Baker, >99%) were used to prepare deposition solutions. Highly pure water (≈18 MΩ) was used in the preparation of all solutions.

2.2 Procedure

In a similar manner as described before [35-36], the ZnS thin films were grown on Corning glass slides by the CBD technique at a temperature of 65 ± 2°C and with a deposition time of 120 min. The samples were prepared by immersing the substrates vertically in aqueous solution. The reagents used for the preparation were zinc acetate (0.07 M) and thioacetamide (0.35 M), being sources of Zn and S, respectively. The temperature was kept at 65 ± 2°C with a hot plate equipped with a magnetic stirrer. After growth, the thin films were rinsed in highly pure water with ultrasonic cleaning for 10 min. The average thickness of the films was 102 up to 235 ± 5 nm. The photocatalytic activity test was performed with 3.5 mL of an aqueous solution of methylene blue (MB) at a concentration of 2×10^{-5} mol L^{-1}. The thin films were placed in a quartz cell with dimensions of 1 cm × 1 cm × 4 cm and were irradiated with a commercial germicidal lamp (λ = 252 nm, 11 W). A rectangular sample with an area of 2 cm^2 was inserted into the interior of the quartz cell. The reaction vessel was fixed at 4.5 cm from the irradiation lamp. The irradiation times were 1 to 5 hours in steps of 1 hour. The residual concentration was quantified by UV–visible absorption spectroscopy at 663 nm, calibrated previously with external calibration standards (2, 1.5, 1.0, 0.5 and 0.25×10^{-5} mol L^{-1}). The ultraviolet-visible (UV-Vis) spectra of the films were measured on a Genesys 10S spectrophotometer with an uncoated glass substrate placed in the reference beam. The atomic concentrations of the various elements composing the films were measured by electron dispersion spectroscopy (EDS) using a Philips XL30-ESEM. XRD measurements were performed with a RIGAKU Ultima IV using Cu-Kα radiation (λ = 1.54 Å). Film thickness was measured on a Sloan Dektak IIA.

3. Results and discussion

The ZnS overall reaction could be expressed in agreement with the reaction proposed for the thioacetamide by Sugimoto et al [37] on the formation of CdS (eq 1) and the following reactions (eq 2 and 3) in aqueous media.

$$CH_3CSNH_2 \rightarrow CH_3CN + 2H^+ + S^{2-} \quad (1)$$

$$Zn(OOCCH_3)_2 \rightarrow 2(OOCCH_3)^- + Zn^{2+} \quad (2)$$

$$Zn^{2+} + S^{2-} \rightarrow ZnS \quad (3)$$

Figure 1*a–d* shows the surface morphologies of ZnS thin films after annealing at different temperatures in a vacuum atmosphere. The annealing temperatures were 150 to 300°C with steps of 50°C. The thicknesses of the obtained films are 235, 209, 179, 108 and 102 nm obtained at 27 (as prepared), 150, 200, 250 and 300ºC respectively. All the figures show an aggregate on the surface of 100 to 300 nm and the thin films have an aggregate in the bulk of approximately 20 to 50 nm; the samples are free of pinholes and cracks. The size of the aggregates increases as a function of the annealing temperature. Independently of the annealing temperature in a vacuum atmosphere, the samples display a nanocrystalline nature.

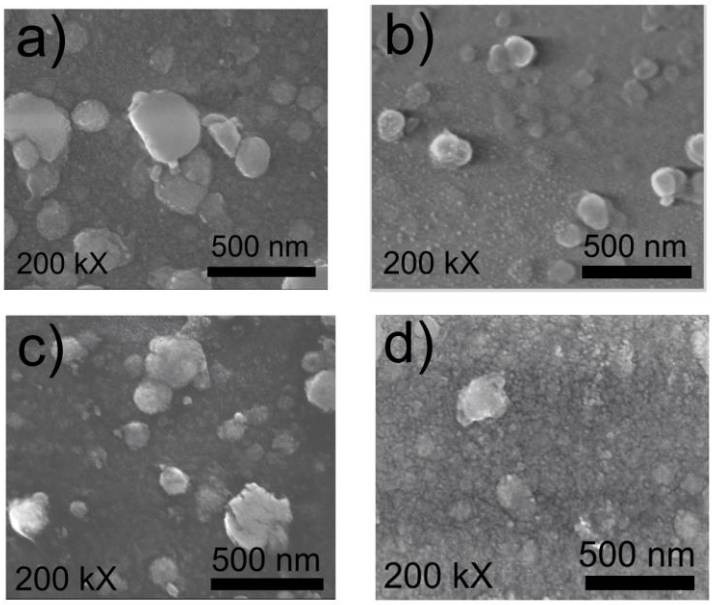

Fig. 1 SEM images of the ZnS thin films, annealed in vacuum atmosphere at a) 150°C, b) 200°C, c) 250°C and d) 300°C

Figure 2 shows the variation of the concentration of zinc and sulphur in the ZnS thin films as a function of the annealing temperature in a vacuum atmosphere. The atomic percentage of sulphur decreases as the temperature increases, and the atomic percentage of zinc increases as the temperature increases. The sulphur concentration decreases from 41.8 to 36.33 at.-% as an effect of the annealing temperature due to physical properties, such as the sulphur has a low melting point (112.8°C), a boiling point of 444.67°C and an ionisation energy of 10.36 eV.

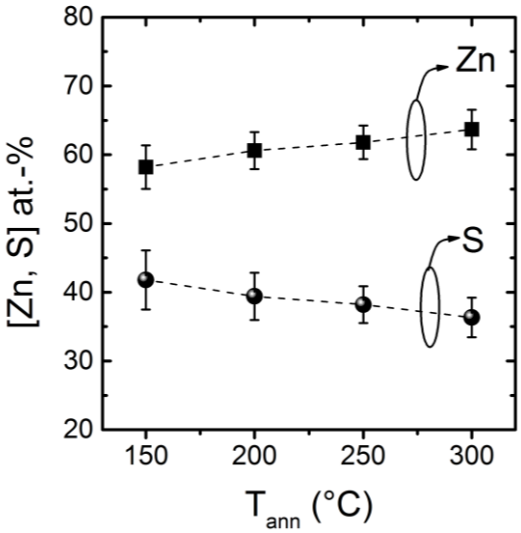

Fig. 2. Variation of the atomic percentage of Zn and S in ZnS thin films as a function of the annealing temperature in a vacuum atmosphere.

X-ray diffraction patterns are displayed in Fig. 3 with peaks of low intensity at 2θ values of 28.76°, 40.58°, 57.31°, 66.70° and 78.11°, corresponding to planes (111), (220), (311), (400) and (331), which can be identified as sphalerite ZnS with a cubic structure (PDF#05-0566). The peaks apparently are lost for annealing in a vacuum atmosphere at 100–200°C; for the annealing temperature of 250°C the peaks are more visible. These results are consistent with the SEM images.

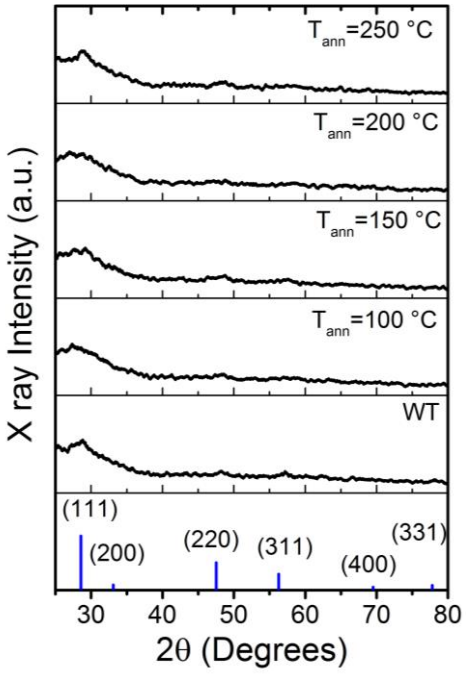

Fig. .3 X-ray diffraction patterns of ZnS films as a function of the vacuum annealing temperature (100–250°C). WT: without annealing

Thermogravimetric analysis (TGA) of ZnS without any annealing process is presented in Fig. 4. The temperature ranges and percentages of mass losses during the decomposition are presented as weight percentage and the first derivate of weight over time. The thermogram indicated four stages of mass loss at 82.04, 205.49, 311.88 and 376.85 ºC respectively, in the first

stage (80–210ºC) could be associated with loss of water adsorbed on the surface and the removal of acetonitrile. In the second stage (210-380ºC) could be attributed to the elimination of groups that containing oxygen. The weight of the sample remains almost unchanged from 475 to 800ºC. The total mass lost in all the thermogram was 5.47 %.

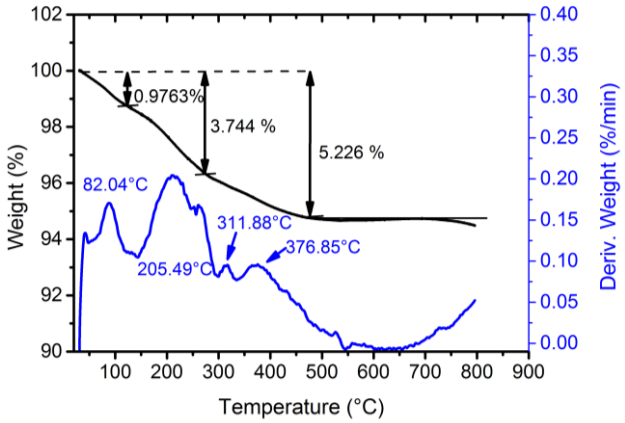

Fig. 4 Thermogravimetric analysis of ZnS as a function of temperature.

Figure 5 shows the UV–visible transmittance spectra in the wavelength range 300 to 1100 nm for ZnS thin films after annealing at 100–300°C in a vacuum atmosphere. The average transmittance (T) values of the samples are approximately in the range of 77 to 85% and increase with the annealing temperature. The absorption edge shift to greater wavelengths is indicative of the fact that the band gap decreases. These transmittance results are consistent with reports in the literature [26-28].

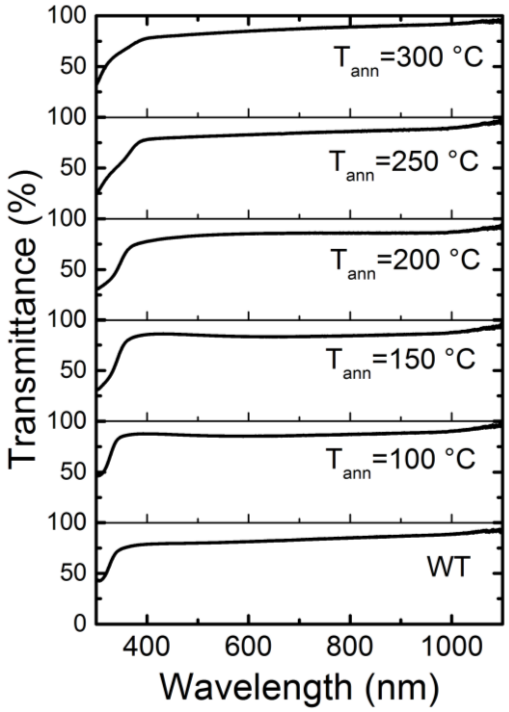

Fig. 5 UV–visible transmittance spectra of ZnS thin films annealed in a vacuum atmosphere. WT: without annealing

The optical band gap (E_g) was estimated with the Tauc theory and a plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient and $h\nu$ is the photon energy. E_g values varied in the range 3.28–3.64 eV as can be observed in Fig. 6. The highest E_g value corresponds to the as grown ZnS thin film without any annealing treatment. Figure 6*a* shows the band gap calculations by an extrapolation of the linear portion for direct band gaps and Fig. 6*b* displays the variation of E_g with annealing temperature in a vacuum atmosphere. The shifting of E_g to lower values as the annealing temperature increases can be attributed to defects generated due to the loss of sulphur in the films caused by the increase in heat treatment temperature, which is consistent with the EDS results (Fig. *2*) and quantum confinement effect due to the size of the aggregates.

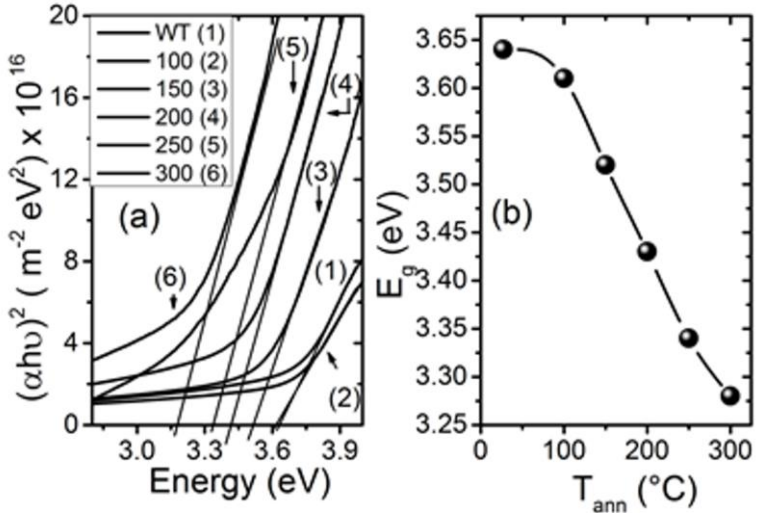

Fig. 6 Variation of the band gap of ZnS thin films annealed in a) vacuum atmosphere: a computation of the band gap; b) band gap versus annealing temperature

The results of Table 1 were obtained for ZnS thin films of good quality reported in the literature [26-34], but very toxic chemicals were used as complexing agents and pH controlling agents, such as hydrazine and ammonium compounds. The properties that were determined in the studies cited in Table 1 are very similar to those of our study, but, in the present work, the films were developed without the use of any toxic materials as complexing agents and pH controllers. This research work demonstrates that it is possible to obtain ZnS thin films with good properties by a very simple and a real green route.

Table 1. Reagents, complexing agents and pH controllers used in the development of ZnS thin films and some important properties

Reagents, complexing agents and pH controllers	**Temperature of bath/°C**	**Deposition time/min**	E_g**/eV**	T**/%**	**Ref.**
$Zn(OOCCH_3)_2/SC(NH_2)_2/NH_3/Na_3$-citrate	80	240	3.80–3.73	70–85	[26]
$ZnSO_4/CH_3CSNH_2/NH_3$	60	120	3.95–3.85	70–90	[27]
$ZnSO_4/SC(NH_2)_2/Na_3C_3H_5O_7/NH_4OH$	70–85	80	3.98–3.88	70–88	[28]
$ZnSO_4/SC(NH_2)_2/(NH_4)_2SO_4/N_2H_4/NH_3$	80–82	120–240	3.74–3.65	80–90	[29]
$ZnSO_4/SC(NH_2)_2/C_6H_5O_7Na_3/N_2H_4/NH_3$	70	120	3.88–3.72	75	[30]
$ZnCl_2/SC(NH_2)_2/NH_4NO_3/KOH$	50–90	60–140	4.11–3.53	–	[31]
$ZnSO_4/SC(NH_2)_2/N_2H_4/NH_4OH$	80	60	4.0–4.2	70–80	[32]
$ZnSO_4/SC(NH_2)_2/N_2H_4/NH_3$	70	120	3.87–3.83	70–80	[33]
$ZnNO_3/SC(NH_2)_2/N_2H_4/NH_4OH/NH_3$	RT	480–1200	3.83–3.66	15–40	[34]
$Zn(OOCCH_3)_2 \bullet 2H_2O/CH_3CSNH_2$	**65**	**120**	**3.64–3.28**	**75–85**	**This work**

In order to investigate their prospective application as photocatalytic material, the ZnS thin films, without annealing and with thermal annealing in a vacuum atmosphere at temperatures of 100–300°C in steps of 50°C, were used as catalysts in the degradation of methylene blue (MB) under germicidal light (λ = 252 nm) at room temperature. Figure 7*a* exhibits the photobleaching in terms of the change in the concentration of MB for ZnS thin films annealed at different temperatures in a vacuum atmosphere. The thin films annealed in a vacuum atmosphere at 150 and 200°C show the best results for the photodegradation of MB in aqueous solution, the ZnS thin film annealed at 200°C being the better sample, as shown by its effect on the MB degradation. Additionally, it is important to comment that the ZnS thin film that was obtained directly from the chemical bath reactor (without annealing) exhibited the worst performance in the degradation of MB. There is a thermal effect on the ZnS thin films, and the annealing in a vacuum atmosphere is beneficial for their structural and optical properties as good catalytic materials. Figure 7*b* displays the absorption spectra of an aqueous solution of MB at time intervals of 1, 2, 3, 4 and 5 hours in the presence of the ZnS sample annealed in a vacuum atmosphere at 200°C.

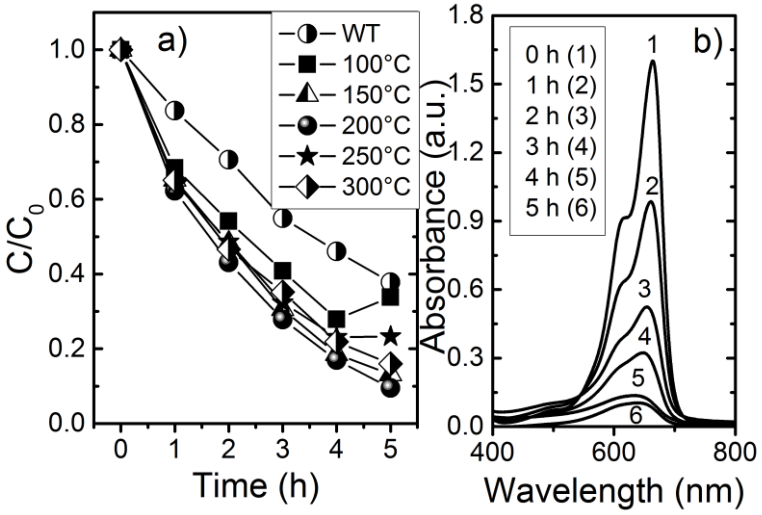

Figure 7 a) Change in the concentration of MB in the presence of ZnS thin films annealed at different temperatures. b) The time-dependent absorption spectra of MB in the presence of the ZnS thin film vacuum annealed at 200°C

4. Conclusions

A simple, green and economical synthesis of nanocrystalline ZnS thin films was carried out. Morphological, compositional, structural, optical and photocatalytic properties are dependent on the temperature of the annealing in a vacuum atmosphere. The transmittance was above 75% for all samples and the band gap varied from 3.28 to 3.63 eV, these values being dependent on the vacuum annealing temperature. The best photodegradation of MB was observed for a ZnS sample vacuum annealed at 200°C, showing 92% degradation, similar to values when using TiO_2. In this synthesis are not necessary a regulator of pH or complexing agent in order to obtain ZnS thin films of good quality. In other words, a heat treatment in an inert atmosphere (vacuum) is only necessary to improve the properties of ZnS obtained by chemical bath deposition technique.

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