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Impact on Development of ZnS Nanoparticles Thin Film Deposited by Chemical Bath Deposition and Spin Coating

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Abstract*: Research comparing the advantages of spin coating and chemical bath deposition is going, and there are varied views on these methods. Here, we used spin coating and chemical bath deposition to prepare thin films of ZnS nanoparticles. The film was analysed by photoluminescence (PL) spectrophotometry, field emission scanning electron microscopy (FE-SEM), ultraviolet spectroscopy (UV-Vis), and energy-dispersive X-ray (EDX) spectroscopy. The UV-Vis spectra revealed that the wavelength of ZnS is between 220 nm - 320 nm while the PL spectra showed a peak centred in the blue region. Both spin coating and chemical bath deposition rendered spherical nanoparticles but of different sizes 17.9 nm and 21.2 -25.7 nm, respectively. It was concluded that each method has its potential. This work can help researchers choose a suitable method for fabricating thin films, depending on the aims and objectives of their work.

Keywords: nanoparticles thin film, chemical bath deposition, spin coating

I. INTRODUCTION

The deposition of thin films of nanoparticles on substrates using diverse methods is still a topic of interest among researchers. Typically, ZnS thin films are synthesized by methods such as thermal evaporation [1], spray pyrolysis [2, 3], sputtering [4, 5, 6], pulsed laser deposition [7, 8], chemical vapor deposition [9, 10], successive ionic layer adsorption and reaction (SILAR) [11], chemical bath deposition [12, 13, 14, 15, 16], chemical deposition [17], chemical precipitation [18, 19, 20], spin coating [21, 22, 23, 24, 25, 26], dip coating [22, 28, 29, 30], green synthesis [31, 32, 33, 34], electro-deposition [35], and thermolysis [36, 37, 38, 39, 40]. Each method has its advantages based on the aim of the study. Researchers widely favour the methods of spin coating and chemical bath deposition due to their simplicity as compared to other processes. Chemical bath deposition has a greater commercial value than either thermal evaporation or sputtering and has recently attracted the attention of researchers due to its simplicity, convenience, reproducibility, large-area scaling, and suitability for commercial-scale production [41]. Nabachandra et al. [42] mentioned that the chemical bath deposition method is employed because of its advantages like low cost, low deposition temperature, and easy coating of smooth and uniform layers on large surfaces. This method is also attractive for modelling studies. Kostoglou et al. [43] developed a model for the fabrication of CdS thin films using chemical bath deposition. They tried to develop and optimise model equations based on a population balance formulation. Notably, the chemical bath deposition method was first used in 1946 to prepare PbS films for infrared applications. It is currently used to obtain semiconductor films on a large-scale. Essentially, a thin film deposition process involves three steps: (i) creation of atomic/molecular/ionic species, (ii) transport of these species through a medium, and (iii) condensation of the species. The basic principle involved in the synthesis of thin films by the chemical bath deposition method is the controlled precipitation of the desired compound from a solution of its constituents [41]. Spin coating and its allied process dip coating are well-known methods that are less expensive and less complicated. Spin coating is a process in which a flat surface is coated by a thin film of a liquid aided by the fast rotation of the surface. A spin coater is essentially a turntable maintained under vacuum conditions or mechanical parts. A liquid is deposited at the centre of the substrate which is placed on the turntable. This is followed by a high-speed rotation (thousands of rotations per minute) of the turntable. The liquid spreads outwards to the edge of the substrate and forms a thin film of relatively uniform thickness. Some researchers have modified this technique by combining it with the self-assembly approach. Arif et al. [44] used metal tape as a barrier during the spinning process to prevent the solution from spreading outwards from the glass substrate. The thickness of the coating layer depends on the fluids viscosity, fluid density, angular velocity of the turntable, and the total time for which the sample is rotated [45]. Therefore, it is essential to understand the effects of various control variables on the thickness and uniformity of the thin film, since semiconductor devices require smooth and uniform photoresist films of predictable and reproducible thickness.

II. METHODOLOGY

In this study, a thin film of ZnS nanoparticles were prepared using the spin coating and chemical bath deposition methods. We aimed to analyse the characteristics of the films prepared by these two methods.

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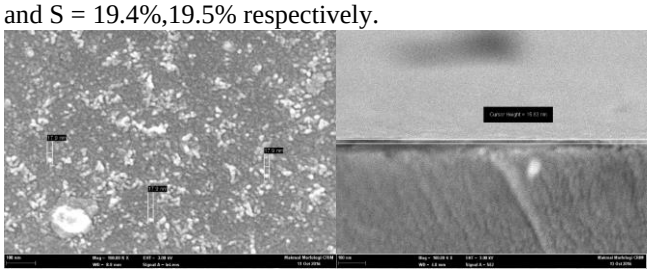
First, a ZnS solution was produced via the sol-gel technique. Sol-gel technique was chosen because of its many advantages such as ease in the control of the film composition, and cost-effective and easy fabrication of large-area films [41]. The clear solution was prepared using dehydrated zinc acetate (ZAD), thiourea, ethanol, ethylenediaminetetraacetic (EDTA) as a surfactant and distilled water. A clear solution was obtained after 48 h of stirring. For the spin coating method, the ZnS sol was deposited on a glass substrate using a spin coater. The sample was rotated with high efficiency at a speed of 2000 rpm for 20 s. For the chemical bath deposition process, the ZnS sol was deposited onto a glass slide and exposed to air for 15 mins. Both samples were annealed at 500˚C to reduce material defects. The thin films were then cooled to room temperature (23.7˚C -32.7˚C). The experiments were initially performed using chemicals that have been provided to produce ZnS nanoparticles thin film via two methods. Optical characterisation of the samples was carried out using UV-Visible spectroscopy (LAMBDA 950 Perkin Elmer), and photoluminescence spectrophotometry (FLSP920 Edinburgh Instruments). In contrast, the structural and compositional analysis of films was carried out via X-ray diffraction (D8 Advance Bruker), field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (Supra 55Vp).

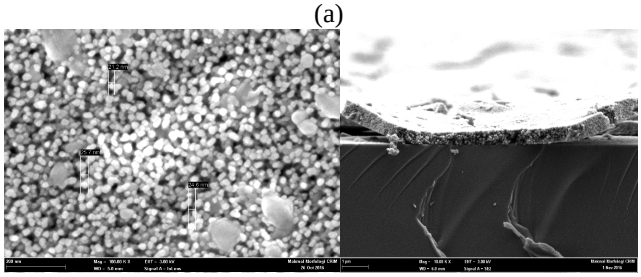
III. RESULTS AND DISCUSSION

A. Perspectives on FE-SEM images and EDX spectra

FE-SEM images were obtained for the ZnS thin films deposited on glass substrates in order to study the surface of the thin films, especially their size and pattern. FE-SEM images for both ZnS thin films show that the nanoparticles are approximately spherical with a slight difference in size. The spin coating method produced a smaller size of nanoparticles (17.9 nm) as compared to the chemical bath deposition method (21.2 nm – 25.7 nm). It is expected that the spin coating method will produce a smaller size because of the high speed (2000 rpm) and duration (20 s) of the spinning process. During this process, the particles get distributed rapidly and do not have much time to adhere to the glass substrate. The FE-SEM image for the thin film prepared with the chemical bath deposition method was clear due to the larger size of the nanoparticles as compared to the spin coating method. End side of a thin film for both methods proved the occurrence of nanoparticles on a glass substrate. A single thin layer can be seen clearly in Fig. 1(a) with a film thickness of 15.63 nm. The chemical bath deposition method rendered multiple layers of the film with a good arrangement of the nanoparticles; moreover, the film was devoid of the bulk component. This method helped to perfectly create a uniform layer which can be attributed to the duration of the deposition process. The film was deposited on to the glass slide within 15 min; previous studies mention that the duration of deposition can affect the outcome of the thin films. A slight increase in the grain size follows from the increase of the deposition time but does not impact the surface roughness [46]. EDX analysis for both methods confirmed the presence of zinc (Zn) and sulphur (S) in ZnS, the spectra of which are shown in Fig. 2. The proportion of constituent elements measured for the spin coating and chemical bath deposition processes was Zn = 80.6%, 80.5% and S = 19.4%,19.5% respectively.

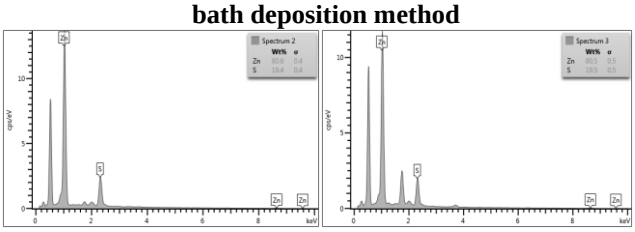


(a)



(b)

Fig. 1.Nanocrystalline thin film produced at the heating temperature 500 °C using (a) spin coating (b) chemical bath deposition method



(a) **(b)**

Fig. 2. EDX spectra (a) spin coating method (b) chemical bath deposition method

B. Perspectives on Photoluminescent (PL) spectra

Photoluminescent spectra for the Zn:S ratio of (1:1 and 1:3) with the concentration factor can be seen in Fig. 3. A comparison of the PL and UV spectra reveals that both spectra present the same results. All thin films were excited at 250 nm, but different factors led to the emission of wavelengths corresponding to different colours. The Zn:S ratio exhibited two emission peaks at 390 nm and 450 nm, while the concentration factor exhibited three emission peaks at 440 nm, 450 nm and 470 nm. The broad and robust peak observed at 390 nm is attributed to the near-band-edge emission of ZnS. The emission at 440 nm, 450 nm and 470 nm can be attributed to the recombination of electrons at the surface sulphur vacancy with the holes at the valance band [18, 21, 47]. The recombination process is evident from the electrons trapped in the energy gap of ZnS. The impact of spin coating and chemical bath deposition impact are seen to be focused on the Zn:S ratio. The sample prepared by the chemical bath deposition method exhibited a more substantial peak than that prepared by the spin coating method; this is evident from the spectra and correlates well with the results obtained from the FE-SEM images.

As seen in Fig. 1(b), the chemical bath deposition method rendered a larger size of ZnS nanoparticles. Hence, the nanoparticles could absorb more energy and exhibited more intensity of emission. In other words, the broadening of the emission peak can be attributed to the size distribution and increase in the surface states owing to the increase in the surface to volume ratio of the nanoparticles [48].

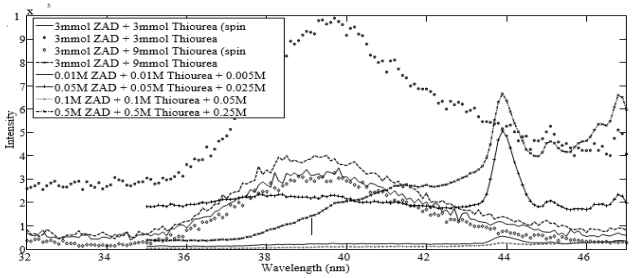


Fig. 3. Photoluminescence spectra of ZnS nanocrystals at different method, a ratio of Zn to S and concentration.

C. Perspectives on the Absorption spectrum

The optical properties of the ZnS nanoparticles can be interpreted from the absorption spectra shown in Fig. 4, wherein clear peaks can be seen within the range of 220 -320 nm. The six samples which were analysed showed different broadening wavelengths. The Zn:S ratios of 1:1 and 1:3 also had an impact on the absorption characteristics; the absorption was higher for a more excellent ratio. This phenomenon is similar to that observed for the concentration factor. Regarding Fig. 4, the concentration influenced the outcome of the absorption region, with a greater concentration rendering a broader absorption peak in a higher wavelength region. A shift in the optical absorption spectrum is known to take place due to the quantum confinement effect, which occurs in the case of nanoparticles when the particle size becomes comparable with or smaller than the Bohr radius of an exciton [18]. Generally, a higher concentration would produce a larger size of particles; the same goes for the ratio of Zn to S. However, the resulting spectrum shows a blue shift which is different from that observed for bulk ZnS [21].

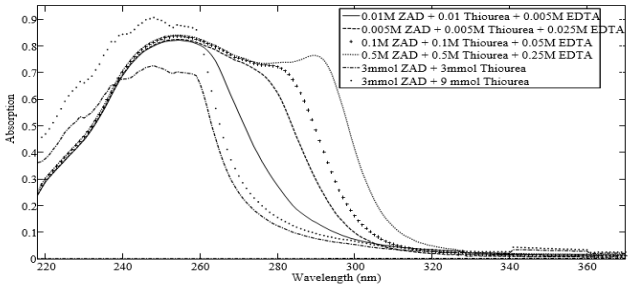


Fig. 4. UV-Visible absorption spectra of ZnS solutions

IV. CONCLUSION

In the present work, thin films of spherical ZnS nanoparticles were prepared via the conventional methods of spin coating and chemical bath deposition. The XRD patterns indicate the presence of thiourea, zinc sulphide and zinc oxide. The PL spectra exhibited a blue emission, while the absorption edge appears in the range of 220 nm -320 nm. The chemical bath deposition method rendered a larger size of nanoparticles, and the samples exhibited more excellent absorption and emission of energy than those prepared by the spin coating method. This conventional process is a simple, well-known, and beneficial method to synthesises thin films of semiconductor nanoparticles. This work can help researchers choose a suitable method to fabricate thin films in future based on structural mainly.

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