



An Energy Efficient Way to Produce Zinc-Based Semiconductor Thin Films via Chemical Bath Deposition Technique

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ABSTRACT

In this study, zinc oxide, zinc sulfide and zinc selenide semiconductor thin films were produced by Chemical Bath Deposition technique with and without annealing. The structural, surface and optical properties of the obtained thin films were determined to specify effect of annealing on thin film properties. Characterization results indicated that, the produced zinc-based thin films have polycrystalline nature. Both zinc sulfide and zinc selenide thin films have cubic and zinc oxide thin films have hexagonal structure. The surface morphologies of all thin films are homogeneous and compact. The optical band gap values of the obtained thin films are close to the band gap of zinc-based semiconductors. The annealing processes neither improved the crystal structures nor altered the band gap values of zinc-based thin films. Agreeable to characterization results, production of zinc-based thin films via chemical bath deposition technique without annealing is facile, economic and energy efficient so can be used for many thin film applications.

KEYWORDS

Solar cells, Thin films, Chemical bath deposition, Semiconductors.

INTRODUCTION

Energy demand which is constantly increasing due to technological development is currently supplied by traditional fossil fuels such as coal, natural gas, petroleum products, etc. [1]. Fossil fuels have some disadvantages: they are thermally inefficient when converted to final product (a); it causes environmental and health problems (b) and the most important point is the fossil fuel reserves in the world is limited (c). Vagueness of the fossil fuel prices in the future is also another important drawback about use of fossil fuels [2]. Evaluation of renewable energy sources is the key parameter to overcome energy crisis [3]. Renewable and clean energy resources can be classified as wind, biomass, hydro and solar energy.

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In semiconductor materials, zinc-based (zinc oxide, zinc sulphide and zinc selenide) which consist of II and VI group elements of the periodic table are significant elements to use in optical device technology [4]. Interest in II-VI materials stems from their wide band gap [5]. These materials are commonly used in applications of optoelectronic devices such as solar cells [6]. The advantages of zinc-based materials in comparison to other II-VI elements are that it is non-toxic, readily available and eco-friendly [7]. They can be obtained with high purity from cheap raw materials. Having wide band gap, high electron mobility and strong room-temperature luminescence are unique properties of Zinc oxide (ZnO) [8]. Because of these superior properties, ZnO is frequently used in the application of solar cells [9]. ZnO is also a promotive material for electronic, optoelectronic, information technology device and gas sensor applications due to its good electrical and optical properties [10]. Zinc sulphide (ZnS) is a wide band gap and direct transition semiconductor [11]. Because of its wide bandgap, ZnS has significant importance in light emitting diodes, cathode-ray tubes, thin film electroluminescence and window layers in photovoltaic cells application [12]. Zinc selenide (ZnSe) is another important II-VI group semiconductor material having a wide direct band gap [13]. It has an extensive application area in thin film devices, such as photoluminescent and electroluminescent devices and as an n-type window layer for thin film heterojunction solar cells [14].

Zinc-based thin films can be produced as a polycrystalline layer by conventional methods like as electron beam evaporation, Radio Frequency (RF) sputtering, pulsed laser deposition, ultrasonic spray pyrolysis, sol-gel method and chemical bath deposition technique [15]. These conventional techniques require high temperature annealing process to obtain high crystallinity. High temperature annealing process causes high energy consumption. In the method used in this work, there is no need to anneal as in other thin film deposition techniques. This provides energy savings.

In this work, zinc-based thin films have been synthesized on glass substrates, by Chemical Bath Deposition (CBD) technique and the structural, morphological and optical properties of the films have been investigated.

MATERIALS AND METHOD

Deposition technique and deposition process were given below in this section.

Chemical Bath Deposition technique

CBD is an easy method for production of thin films. This method is performed in a batch reactor, needs only a substrate to be immersed in a solution of aqueous precursors such as metal salts, complexing agents, and pH buffers. Highlights of CBD include cost-efficient, operation at atmospheric pressure, and scalability to large surface substrates [16]. In Figure 1, the schematic presentation of chemical bath deposition technique is shown.

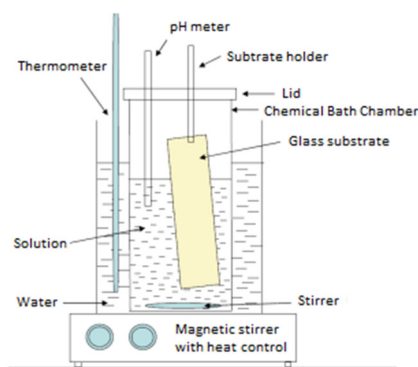


Figure 1. The schematic presentation of CBD technique

Cleaning process of substrates

In this study, glass slides were used as substrate to deposit semiconductor thin films. Glass substrates were immersed in acetone and methanol for 5 minutes in ultrasonic bath respectively, then cleaned with distilled water and dried at 25 °C.

Preparation of zinc oxide thin films

0.1M Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Sigma Aldrich) solution was prepared in distilled water of 100 ml. The solution was stirred with a magnetic stirrer for 15 minutes. Then, pH of the solution was arranged to 10 by dropping ammonia solution (28% v/v) (Merck). After the bath was prepared, substrates were immersed in the solution. The solution with immersed substrate was mixed with temperature-controlled magnetic stirrer for 30 min at 85 °C. Prepared thin films were cleaned with distilled water and dried at 25 °C.

Preparation of zinc sulfide thin films

Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], Tri-sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) and Thiourea (N_2SCH_4) from Sigma Aldrich were used synthesized ZnS films by CBD technique. 0.15M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.5M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 1M N_2SCH_4 solutions were prepared and then blended. pH value of the final solution was fixed at 10, by dropping 28% aqueous ammonia solution. The two glass substrates were submerged in the prepared bath. The bath temperature was set at 80 °C for 90 minutes. Prepared films were cleaned with distilled water and dried at 25 °C.

Preparation of zinc selenide thin films

Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and Selenourea [$\text{SeC}(\text{NH}_2)_2$] from Sigma Aldrich were used to synthesize ZnSe thin films by CBD method, as well as Hydrazine hydrate ($\text{N}_2\text{H}_5\text{OH}$) from Merck as a stabilizer. Firstly, 0.5M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.4M $\text{SeC}(\text{NH}_2)_2$ and 0.5M $\text{N}_2\text{H}_5\text{OH}$ solutions were prepared in equal volumes. 28% aqueous ammonia solution was used to fix the pH of final solution to 10. Glass substrates were submerged in the bath. The bath temperature was set at 80 °C for 90 minutes. Prepared films were cleaned with distilled water and dried at 25 °C.

The structural, surface and optical properties of the obtained thin films characterized by applying X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Ultra-Violet Visible (UV-Vis). Spectroscopy measurements, respectively.

RESULTS AND DISCUSSION

The crystal structure of the semiconductor thin films was investigated by XRD measurements which were performed by Panalytical Empyrean X-ray diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation in the 2θ range 20° - 80° with a scanning speed of $2^\circ/\text{min}$. The diffractometer reflection of the films was taken at the room temperature. An X-ray tube operated at 45 kV and 40 mA. According to XRD results, all produced zinc-based thin films have polycrystalline nature. The XRD diffraction pattern of the ZnO has matched completely with that of the hexagonal structured ZnO (ICDD: 98-003-1052), ZnS has matched with that of the cubic structured ZnS (ICDD: 98-004-2798) and ZnSe has matched with that of the cubic structured ZnSe (ICDD: 98-004-1983). In Figure 2, XRD spectra of zinc-based semiconductor thin films have been given comparatively.

As seen from the XRD results, the peak intensities of non-annealed zinc-based thin films are greater than the peak intensities of thin films annealed at 400 °C. For both non-annealed and annealed thin films' Full Width at Half Maximum (FWHM) values and the grain size values calculated with Scherer's formula are approximately the same.

The calculated average grain size value for both films is about 30 nm for ZnO, 23 nm for ZnS and 28 nm for ZnSe. According to these results, it seems that the annealing process does not have a healing effect on crystal structures of zinc-based thin films.

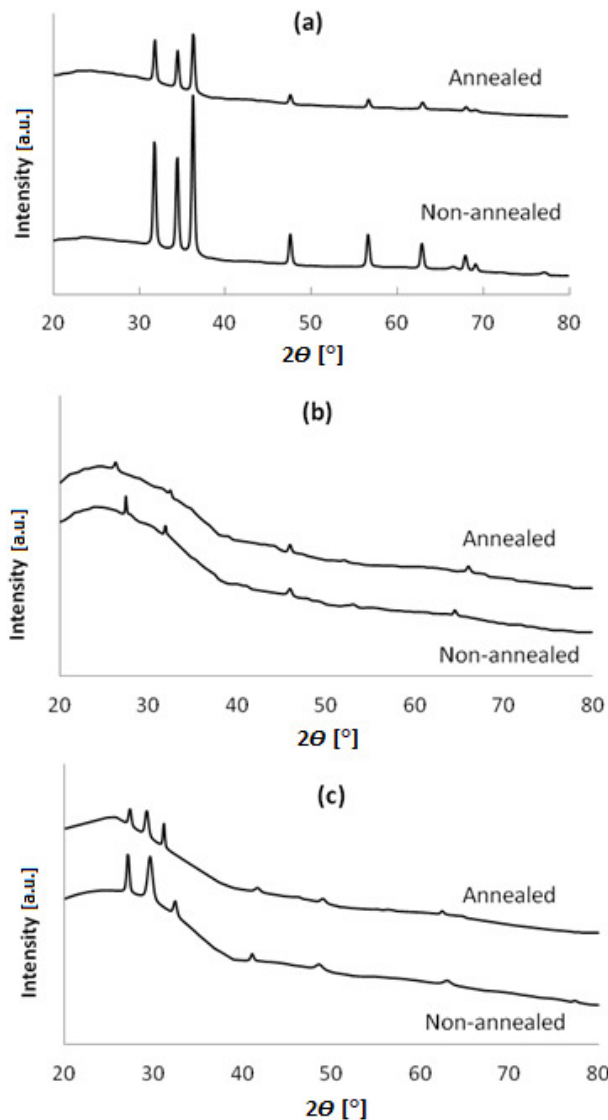


Figure 2. XRD spectra of: ZnO (a); ZnS (b) and ZnSe (c) thin films

Morphological properties of the films were determined by FESEM (Zeiss Supra 40VP). In Figure 3, FESEM pictures of zinc-based thin films are presented. When the images of ZnO (Figure 3a and Figure 3b) thin films are investigated, it is seen that the morphological structure is formed consistently and detached from each other by nanorods. It is also examined that the nanorods integrate to form a flower-like structure. In the ZnS (Figure 3c and Figure 3d) pictures, it is seen that the film surface is constituted by almost homogeneously distributed nanostructured particles. It is also shown that there are no aggregations and there are no vacancies on the surface, so that the nano-particles are kept together better. In the ZnSe (Figure 3e and Figure 3f) images, it is demonstrated that the surface of the film is occurred from small accumulations and nano-particles in alignment. The images of zinc-based thin films which are non-annealed and annealed at 400 °C are very similar to each other. According to these results, it is concluded that the annealing process does not have a healing effect on the morphological properties of zinc-based thin films. FESEM images of ZnO thin films [17], ZnS thin films [16] and ZnSe [18] thin films are consistent with the images in the literature.

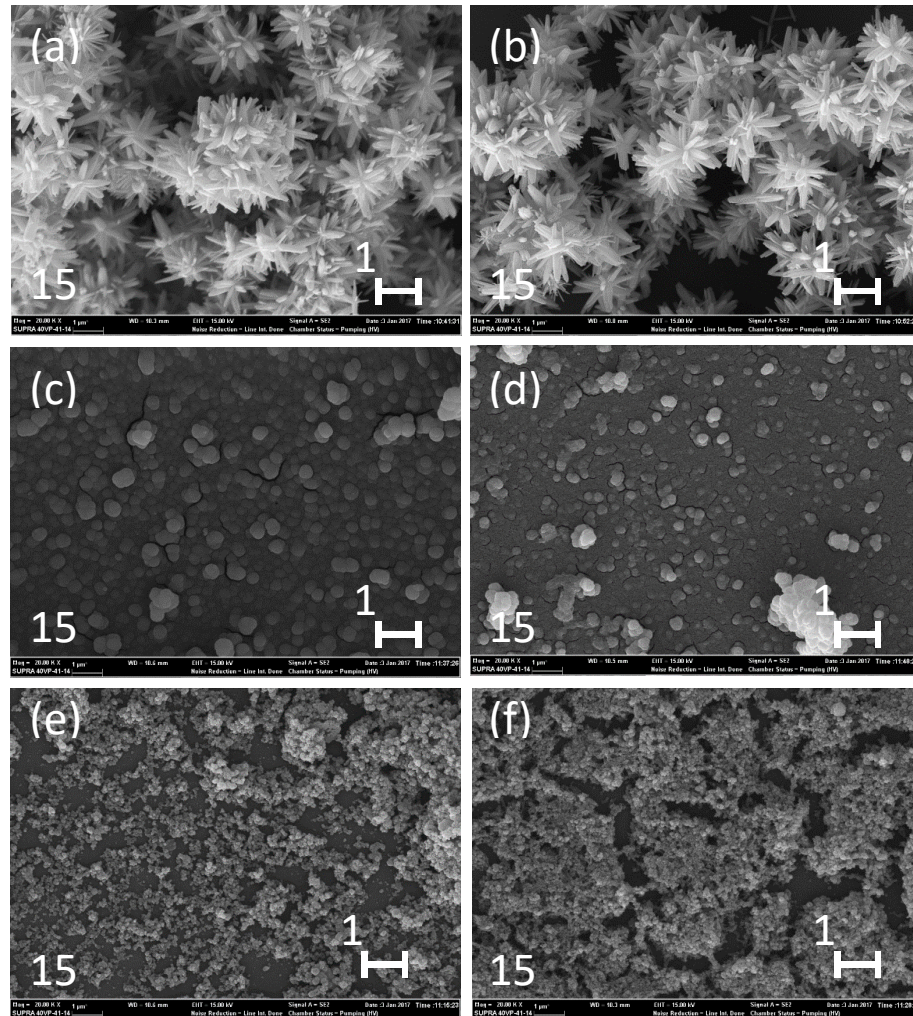


Figure 3. FESEM images of: non-annealed ZnO (a); annealed ZnO (b); non-annealed ZnS (c); annealed ZnS (d); non-annealed ZnSe (e) and annealed ZnSe (f) thin films

Perkin Elmer Lambda 25 UV-Vis Spectrometer between 300-1,100 nm wavelengths were used to carry out absorption studies to calculate the band gap of the semiconductor thin films. The band gap values of the produced semi-conductor thin films were calculated according to the Tauc Method [19]. $(\alpha h\nu)^2$ vs. $h\nu$ plots are given in Figure 4. The band gap values of the zinc-based thin films were determined from the point at which the linear part of the graph cuts the $h\nu$ axis. Table 1 showed that the band gap values of the zinc-based thin films.

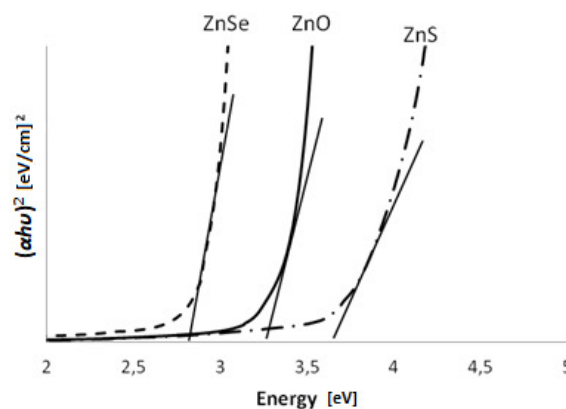


Figure 4. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of zinc-based thin films

Table 1. The band gap values of the zinc-based thin films

	Band gap value [eV]
ZnO	3.27
ZnS	3.61
ZnSe	2.82

The calculated band gap values of the obtained thin films are close to the band gap of zinc-based semiconductors which are stated in the literature [20-22]. It has also been observed that the annealing process does not cause a change in the band gap values of zinc-based thin films.

CONCLUSION

The zinc-based semiconductor thin films have been deposited on glass substrates by CBD technique and annealed at 400 °C in air. The structural, morphological and optical properties of the obtained films have been specified. It has been seen that zinc-based thin films have polycrystalline nature and consist of nanoparticles. The band gap values of the produced thin films are close to the band gap of zinc-based semiconductors. It has also been observed that the annealing process does not cause any change in the structural, morphological and optical properties of zinc-based thin films. According to these results, zinc-based semiconductor thin films can be produced by CBD technique, which is a simple and economical technique. The most important point is that in this technique there is no need to anneal as in other thin film deposition techniques. This also provides energy savings.

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NOMENCLATURE

Abbreviations

CBD	Chemical Bath Deposition
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
ICDD	The International Centre for Diffraction Data
RF	Radio Frequency
XRD	X-Ray Diffraction
UV-Vis	Ultra Violet Visible

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