Effect of annealing treatment on the structural, optical and magnetic properties of ZnSe thin films grown by spray pyrolysis

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Abstract

Many investigations and reviews show that II-VI compound semiconductor 1-D nanostructures have a great potential for the future electronic and optoelectronic applications. As an important II-VI semiconductor, ZnSe is one of the most significant materials with prominent applications in this issue. In the present work, we firstly provide a comprehensive investigation of the magnetic properties like magnetization and magnetic susceptibility of ZnSe nanostructures as a 1-D quantum many body. The magnetic study of this metal reveals a ferromagnetic-antiferromagnetic transition upon annealing. Magnetization shows a step-like behavior with pronounced plateaus in a specific magnetic field interval at low temperature. This subject has not been investigated in the previous works. In the experimental part, by the spray pyrolysis technique, thin films of ZnSe are deposited on glass substrates (at two different substrate temperature), then annealed in vacuum at 400°C for 1 hour. Hereby, we investigate the morphology, structural and optical properties of ZnSe thin films using field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and UV-vis spectrophotometer measurements. XRD analysis reveal that annealed films grown
on glass substrate at 400°C are polycrystalline in nature with cubic zincblende structure. By annealing, the grains size, the diameter and density of the particles increase. The UV-vis measurements display a red-shift of the absorption edge from the as-deposited to annealed ZnSe thin films as compared to its value for the ZnSe thin films. The band-gaps of the annealed samples are estimated about 2.71 eV, which are in consistence with the band gap of ZnSe thin films. The average transmittance of the annealed samples are over 80% close to the infrared wavelength range. Finally, a good comparison is carried out between obtained results from magnetic measurements and experimental analysis of the structural and optical properties of the material under consideration.

**Keywords:** ZnSe thin films, Optical properties, Magnetic susceptibility, Magnetization

**2010 MSC:** 00-01, 99-00

1. Introduction

In the current decade, great interests on Zinc selenide (ZnSe) nanostructures have been stimulated due to their worthful potentials for both fundamental physical researches and applications in constructing nanoscale electric and optoelectronic devices [1, 2, 3]. ZnSe is an II-VI semiconductor material that has unique physical properties, such as a fairly wide and direct band gap (2.7 eV at room temperature), low optical absorption and high optical transparency (∼90%) in the visible and infrared spectral regions [4]. ZnSe films, therefore, have several potential applications such as electro optics devices [5, 6], optical coatings, thin film transistors and heterojunction solar cells [7, 8], etc.

Current CdS is widely utilized as buffer layer material for solar cells. Due to the noxious nature of CdS layers, much consideration has been intensive on developing Cd-free buffer layers. One of the most ideal substitutions of CdS is ZnSe. ZnSe is not only environment responsive but also has higher band gap than CdS (∼2.4 eV), subsequently ZnSe buffer layer may conduct even higher energy photons to the absorber layer of the solar cell. There are some previous
reports revealing that it is possible to construct ZnSe based solar cells with efficiency > 11% [8, 9]. Moreover, it has possible applications in red, blue and green light emitting diodes, photovoltaic, laser screens, thin-film transistors, and photoelectrochemical cells [3].

Magnetic properties of metals have attracted intense interest from researchers due to their potential implementations at low temperature as well as higher temperature in condensed matter physics [10, 11, 12, 13, 14, 15, 16]. There are a few studies on the magnetic properties of material a:ZnSe (a denotes a specific metal) in the literature. For instance, magnetic properties of Mn:ZnSe have been experimentally investigated by S. Acharya et al [17]. Also, magnetic properties of granular MTJ systems, formed by an ensemble of Fe nanoparticles embedded in a ZnSe epilayer have been investigated by A. R. de Moraes et. al. [18]. Magneto-optical studies conducted with annealed CdZnSe/ZnSe quantum dots, also the effect of an externally applied magnetic field on the electronic structure of thermally annealed CdZnSe/ZnSe have been reported so far [19]. Subsequently, we will discuss the magnetic properties of ZnSe thin films theoretically, as well as the optical and electrical properties of such a material experimentally.

Various methods have been used to synthesize high quality thin films such as spray pyrolysis (SP) [20], thermal evaporation [21], metal-organic chemical vapor deposition (MOCVD) [22], electro-deposition [23], pulsed laser deposition [24], atomic layer deposition [25], sputtering [20, 27] and chemical bath deposition (CBD) [3]. Among these various techniques, spray pyrolysis (SP) technique has some advantages [28, 29]. For instance, it is easy, inexpensive and flexible to do, on top of that it is an applicable way to synthesize materials in the form of powders and films. It is also well known that the structural and optical properties of a thin films depend extremely on the conditions in which the deposition has been carried out and also performing of annealing treatment. For annealing treatment, various annealing parameters such as temperature, time, atmosphere and pressure could be mixed.

Formerly, the influence of annealing parameters on the properties of ZnSe
thin film have been studied in solid state physics and condensed matter. As prominent examples: Bacaksiz et al. [30] showed that annealing temperature of 200°C-400°C does not distort the major (111) crystallographic quality but affects the degree of preferred orientation of ZnSe thin film deposited at substrate temperature of −73°C and 275°C. Besides, there was no significant change in optical band gap with annealing temperature. The annealing process reduced the electrical resistivity of the film deposited at −73°C, but contrary trend was observed for the film deposited at 275°C. Kale and Lokhande [31] reported that the thermal annealing transmuted metastable cubic phase into stable polycrystalline hexagonal phase, slightly reduced the optical band gap and electrical resistivity of the ZnSe thin films prepared by chemical bath deposition method. C. B. Oh et al. [32] prepared low resistivity p-type ZnSe epilayer by annealing the ZnSe film in \(N_2\) environment. In this work, ZnSe thin films were deposited on the glass substrates by spray pyrolysis technique and annealed at 400°C in vacuum for 1 h. The effects of annealing treatment on the structural and optical properties of the films have been investigated and discussed.

The paper is organized as follows. In Sec. 2, ZnSe thin films have been considered as a 1-D spin lattice, then we theoretically investigate the magnetic properties of such a material using computational ALPS package. In Sec. 3, we give a short description of the experimental methods utilized, while the results and their analysis are presented in Sec. 4 for the structural and optical properties of the ZnSe thin films. The conclusions are drawn in Sec. 5.

2. Magnetic properties: Theoretical background

ZnSe has two commonly available allotropes: hexagonal wurtzite (W) and cubic zinc-blende (ZB) spin configurations. To numerate and simulate the thermodynamic parameters like magnetization and magnetic susceptibility we consider zinc-blende (ZB) spin structure as shown in Fig. 1.

To demonstrate magnetic properties of the semiconductor 1-D nanostructure ZnSe, we calculated magnetization and magnetic susceptibility using a QMC
method with the stochastic series expansion implementation from Algorithms and Libraries for Physics Simulations (ALPS) \cite{33,34} of a giant ZnSe with a \( N = 80 \) spin ground state. Figure 2 shows the magnetization curve with respect to the magnetic field at both low and high temperatures. The periodic boundary condition has been considered. At low temperature and weak magnetic fields, we do not observe magnetization plateau until magnetic field gets further than \( gH/|J| = 25 \). Here, there is a steep increasing of the magnetization curve upon increasing the magnetic field. First magnetization plateau \( M/\beta gN = \frac{1}{2} \) appears in the field interval \( 25 \leq gH/|J| \leq 100 \). According to the notation in this section, we are labeling applied characters as: \( g \) is Landé g-factor, \( \beta \) is Bohr magneton, \( k \) is Boltzmann constant, \( J \) indicates the coupling constant between Zn and Se particles, and \( N \) denotes the number of particles. With further increase of the magnetic field, one can see that there are several interesting short plateaus in the interval \( 100 \leq gH/|J| \leq 400 \). For \( gH/|J| > 400 \) magnetization of the spin model reaches its saturation value.

In order to get further information about the magnetic properties of this applicable material in the real world, we have performed magnetic susceptibility measurements vs temperature at fixed external magnetic field. We first consider zero-field magnetic susceptibility \( g^2\beta^2N/|J|\chi \) of the ZnSe system, the results of which are shown in Fig. 3(a). The inset shows the temperature dependence of
Figure 2: The magnetization of a giant ZnSe with a $N = 80$ spin ground state as a function of magnetic field $B$ at low temperature $kT/|J| = 4$. The coupling constant between adjacent atoms has been obtained as $J = 209 \text{ cm}^{-1}$ in Ref. [35, 36]. The inset shows magnetization curve against magnetic field at high temperature $kT/|J| = 300$. 

\[ M = \frac{1}{\beta N} M \]
Figure 3: (a) Temperature dependence of zero-field magnetic susceptibility $\frac{g^2 \beta^2 N}{|J|} \chi$ vs. $T$. (b) Temperature dependence of $\frac{g^2 \beta^2 N}{|J|} \chi$ at fixed value $H = 0.5 \frac{|J|}{g}$. The inset shows the corresponding temperature dependencies of $\frac{g^2 \beta^2 N}{|J|} \chi T$. The total number of particles has been taken as $N = 80$. 
the product of magnetic susceptibility times the temperature \( \frac{g^2 \beta^2 N}{|J|} \chi T \), where \( T \) is the temperature. The temperature dependence of both functions at weak magnetic field is presented in Fig. 3(b). We see that the behavior of magnetic susceptibility is not so different from zero-field case. Generally, \( \chi T \) obeys a Curie law over, nearly, the full temperature range with \( C \approx 0.3 \frac{g^2 \beta^2 N}{|J|} \). As can be seen from the insets in Fig. 3, the value of \( \frac{g^2 \beta^2 N}{|J|} \chi T \) in the vicinity of weak magnetic fields does approach the free-ion value at high temperatures. The decrease in \( \frac{g^2 \beta^2 N}{|J|} \chi T \) between \( T = 300 \frac{|J|}{k} \) and \( T = 2 \frac{|J|}{k} \) is due to an antiferromagnetic coupling.

In Fig. 4 we display \( \frac{g^2 \beta^2 N}{|J|} \chi T \) and \( \frac{g^2 \beta^2 N}{|J|} \chi \) as functions of the temperature in the presence of various external magnetic fields \( H = 100 \frac{|J|}{g} \) (Fig. 4(a)), and \( H = 300 \frac{|J|}{g} \) (Fig. 4(b)).

The ferromagnetic exchange interaction predicts a \( N = 80 \) spin ground state with \( \chi T_{max} \approx 9 \frac{|J|}{g^2 \beta^2 N} \) at temperature \( T \approx 80 \frac{|J|}{k} \) and fixed magnetic field \( H = 100 \frac{|J|}{g} \), as shown in the Fig. 4(a). When the system is putted in the presence of a strong magnetic field (\( H = 300 \frac{|J|}{g} \)), the product \( \frac{g^2 \beta^2 N}{|J|} \chi T \) has a stimulating double peak between \( T = 300 \frac{|J|}{k} \) and \( T = 2 \frac{|J|}{k} \), which denotes a phase variation of the system. As it can be seen in the insets, upon cooling, \( \frac{g^2 \beta^2 N}{|J|} \chi \) remains relatively constant until \( kT/|J| = 20 \) and then increases abruptly. This rapid rise of \( \frac{g^2 \beta^2 N}{|J|} \chi \) suggests that predominantly ferromagnetic interactions are presented in this condition.

3. Experimental details

The glass substrates were ultrasonically cleaned sequentially in acetone, alcohol, and deionized (DI) water for 15 min, and were finally dried in air before deposition of thin films. ZnSe thin films were deposited on highly clean glass substrates at different temperatures of 380°C and 400°C using spray pyrolysis
Figure 4: Temperature dependence of the product $\frac{g^2\beta^2N}{|J|}\chi T$ versus $T$ at fixed value (a) $H = 100\frac{|J|}{g}$, and (b) $H = 300\frac{|J|}{g}$. The inset shows the corresponding temperature dependencies of $\frac{g^2\beta^2N}{|J|}\chi$. 
technique. In order to prepare spray solution, an aqueous solution containing 0.05 moles/lit ZnCl$_2$ and 0.05 moles/lit SeO$_2$ with the same ration of Zn:Se=1:1 were made. 100 mlit spraying solution was used for sample deposition. The spray flow rate was adjusted to about 4 mlit per minute and the solution was sprayed through a nozzle onto glass substrates using air as carrier gas with a pressure of 1.5 bars. The distance between the nozzle and the substrate was kept at 35 cm in all cases. During the spraying process the substrates were heated by an electrical heater. All samples were annealed in vacuum (about $1 \times 10^{-4}$ mbar) at 400°C for 1 h. ZnSe thin films prepared at different substrate temperature of 380°C and 400°C before and after annealing, named A1, A2, B1 and B2, respectively. Surface morphology of the sample was studied using field emission scanning electron microscope (FE-SEM Model: Hitachi s.4160). The XRD patterns of the sample were recorded by a D8-Advance Bruke diffractometer in the scanning range of 10° – 70°, using Cu K$_\alpha$ radiation having a wavelength of 1.5406Å. UV-visible spectra of the samples were measured in the spectral range between 300 and 1100 nm using Shimadzu UV-vis 1800 spectrophotometer. The thickness of the thin films estimated by PUMA software were between 210 nm and 230 nm.

4. Results and discussion

4.1. Structural properties and Surface morphology

XRD patterns of as-deposited (A1, A2) and annealed (B1, B2) samples have been shown in Figs. 5(a) and 5(b). Figure 5(a) shows as-deposited thin films are almost amorphous with ZnO impurity phase. The XRD patterns of the annealed films indicated that B1 is also amorphous but B2 is polycrystalline which has a cubic zinc blende structure with preferred (111) orientation. The XRD patterns contain a small amount of zinc oxide (ZnO) impurity. Our result on B2 sample is in good agreement with the previous studies [17, 37], grown by thermal evaporation and annealed in vacuum. However, hexagonal wurtzite structure and cubic zincblende structure, or sometimes a combination of both
phases have been observed for the ZnSe films deposited by another technique\cite{37,38}.

The structure of the ZnSe films generally depends on the deposition technique. This formation of the ZnSe phases were attributed to the enhancement of clusters, rearrangement of atoms and removal of residual stresses/defects during the film annealing. The crystallinity of B2 sample that deposited at substrate temperature of 400°C, was improved by formation of (111) and (200) diffraction peaks after annealing. This confirms upon annealing, the crystallinity of the film increases due to recrystallization of the as-deposited thin film\cite{39}. According to the Debye-Scherer equation, the crystallite size of B1 sample can be estimated by:

\[ D = \frac{K\lambda}{\beta'\cos(\theta)} \]

where \( K \) is the shape factor that was taken equal to 0.9, \( \lambda \) is the wavelength of X-ray source, \( \beta' \) is the full width at half maximum (FWHM) of diffraction peak and \( \theta \) is the Bragg diffraction angle in degrees.

The lattice spacing, \( d \), is calculated from the Bragg’s formula:

\[ d = \frac{\lambda}{2\sin(\theta)} \]

The lattice parameter, \( a \), for cubic ZnSe film can be determined using the relation

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \]  \hspace{1cm} (1)

Where \( h, k \) and \( l \) represent the Miller indices of the crystal planes. The dislocation density is given by the relation \( \delta = \frac{1}{D^2} \) \cite{40}, and the strain values \( \varepsilon \) have been evaluated by equation \( \varepsilon = \frac{\beta'\cos(\theta)}{4} \) \cite{37}.

Structural parameters of B2 sample obtained by characteristic of the (111) peak are summarized in Table II. The result shows that lattice constant of B2 deviates from the bulk, revealing that the film grains are strained, and that may be for the sake of the variation of nature and concentration of the native defects.

Figure 6 shows FE-SEM images of the samples. As can be seen Figs. 6(a) and 6(b) for sample A1 and A2 which were deposited at different substrate temperatures of 380°C and 400°C, the plan and surface structure of both samples are relatively the same, and increase of the substrate temperature has not sig-
Figure 5: (a) XRD patterns of the ZnSe thin films deposited at 380°C (A1) and 400°C (A2), and (b) after annealing B1 and B2, respectively.
Table 1: Structural parameter of B2 sample.

| Sample | (hkl) | 2θ(°) | d (Å) | a (Å) | ε    | δ × 10^{-3} nm² | D (nm) |
|--------|-------|-------|-------|-------|------|-----------------|--------|
| B2     | (111) | 26    | 3.37  | 5.83  | 0.0009 | 6.7             | 38.4   |

Figure 6: (a) and (b) FESEM images of the ZnSe thin films deposited at 380° C and 400° C (A1 and A2, respectively), (c) and (d) after annealing at 400° C (B1 and B2, respectively).

Significant impact on the morphology of the film. On the other hand, Figs. 6(a) and 6(b) exhibit that after annealing surface morphology for samples B1 and B2 have changed. Through the annealing the grain size of both B1 and B2 samples have been enhanced. As it is evidence for the film which is prepared on substrate temperature of 400°C (B2), the diameter and density of ZnSe particles increased. The average diameter of the grains in B2 sample is about 50 nm, however this element is likely dependent on the annealing temperature.
4.2. Optical properties

The optical properties of the ZnSe thin films were studied using the UV-visible spectrophotometer. Fig. 7 shows the optical transmission spectra of ZnSe thin films in the wavelength range of 300-1100 nm before and after annealing. The transmittance of as-deposited ZnSe samples (A1, A2) is over than 77% in the visible wavelength range. The transmittance spectrum after annealing (B1, B2 samples) depicts a high transmission of 80% in the visible and near infrared region. Similar results have been reported by Mangalaraj et al. [40] for ZnSe thin films prepared at different thicknesses using a vacuum evaporation technique on the glass substrates. As an important result, by inspecting Figs. 2 and 1 it can be estimated that in the range of annealing temperature where the material ZnSe has the maximum transmittance, magnetization $M/\beta g N$ changes smoothly upon increasing magnetic field, namely, all plateaus disappear in this condition. Furthermore, during annealing when the temperature increases, function $g^2 \beta^2 N/|J| - \chi T$ displays a double peak (in the presence of externally strong magnetic field).

From the transmission spectra, near the fundamental absorption edge, the values of the absorption coefficient, $\alpha$, can be calculated using the formula: $\alpha = 1/d \ln(1/T)$, where $d$ is thickness, and $T$ is transmittance of the ZnSe thin films. Figure 8 shows absorption coefficient of the films as a function of wavelength. The variation in absorption edge after annealing is most probably due to the enhancement in structural order and removal of residual stresses [42, 43]. The average thicknesses of the ZnSe thin films which were estimated by Puma software [44], have been listed in Table 2. The fundamental absorption which corresponds to the transition from the valence band to the conduction band, can be used to estimate the band gap of the semiconductor materials. The relation between absorption coefficient, $\alpha$, and the incident photon energy, $h\nu$, can be written as follows

$$(\alpha h\nu)^m = A(h\nu - E_g), \quad (2)$$

where $\alpha$, $h\nu$, $E_g$ and $A$ are, respectively, absorption coefficient, photon energy,
Figure 7: Transmittance spectra of the ZnSe thin films deposited at 380°C and 400°C (A1 and A2, respectively), after annealing at 400°C (B1 and B2, respectively).

band gap. \( m \) is a constant equal to \( 1/2 \) or \( 2 \) for direct or indirect band gap semiconductor. Via this equation, we can find out the optical band gap \( (E_g) \) by extrapolating linear part of the curve \((\alpha h \nu)^2\) versus \((h \nu)\) as shown in Fig. 9. The corresponding optical band gap values to the samples are listed in Table 2. Results prove that the optical band-gap values related to the ZnSe thin films after annealing are less than those before annealing. It is well known that the absorption edge is dramatically associated to the size of nanoparticles. As the SEM analysis manifested, the grain size of ZnSe thin films after annealing are larger than before annealing, therefore this difference in band gap may be attributed to quantum-confinement effects [45]. The calculated values of the band gaps after annealing are in a well accordance with band gaps of the films deposited by spray pyrolysis (2.64-2.70 eV [46]) and thermal evaporation (2.76 eV [4]) methods. By inspecting XRD pattern, the higher band gaps of the as-deposited samples (A1, A2) may be due to the presence of the ZnO impurity which remarkably influences on the ZnSe band gap.
Figure 8: absorption coefficient of the ZnSe thin films deposited at 380° C and 400° C (A1 and A2, respectively), after annealing at 400° C (B1 and B2, respectively).

Figure 9: $\alpha h\nu$ versus $h\nu$ plots of the ZnSe thin films deposited at 380° C and 400° C (A1 and A2, respectively), after annealing at 400° C (B1 and B2, respectively).
Table 2: Energy gaps and thicknesses of the ZnSe thin films for investigated samples.

| Sample | Band gap (eV) | Thickness (nm) |
|--------|---------------|----------------|
| A1     | 3.98          | 230            |
| A2     | 3.87          | 220            |
| B1     | 2.76          | 215            |
| B2     | 2.71          | 210            |

5. Conclusions

To summarize, we have theoretically investigated the magnetic properties of the ZnSe thin films that is one of the most common species of II-VI compound semiconductor 1-D nanostructures by simulating the magnetization and magnetic susceptibility for a giant ZnSe spin system with a $N = 80$ spin-$1/2$ ground state. To do so, we have implemented QMC method characterized by ALPS package. Consequently, we observed magnetization plateau $M/\beta g N = \frac{1}{2}$ in the field interval $25 \leq gH/|J| \leq 100$. With further increase of the magnetic field several fractional plateaus appear, actually the magnetization behaves as a step function of the magnetic field at low temperature. We found that such a material reaches its saturation in the presence of a strong magnetic field, and when the temperature increases the magnetization curve becomes smooth.

Furthermore, we have investigated the magnetic susceptibility and also the product of magnetic susceptibility times the temperature for the ZnSe spin system. The bulk magnetic susceptibility data in ZnSe are indicative of a ferromagnetic interaction between Zn and Se at low temperature. On the other hand, the magnetization data in ZnSe demonstrate that the spin ground state has a phase variation ferromagnetic-antiferromagnetic upon increasing the magnetic field. When a strong magnetic field is applied, on cooling, the $\frac{g^2 \beta^2 N}{|J|} \chi T$ product for the ZnSe gradually increases with decreasing temperature to reach its maximum, then sharply decreases, reaching a specific value that varies upon changing the magnetic field strength. Interestingly, for the magnetic field in-
terval $100 \leq gH/|J| \leq 400$ at which the magnetization curve is a step-like function of the magnetic field, the product of magnetic susceptibility times the temperature has double peak at lower temperatures. These theoretical results of magnetic properties may prove useful in experimental studies of semiconductor 1-D nanostructures.

In the experimental part, ZnSe thin films have been deposited onto glass substrates at two different substrate temperatures of $380^\circ$C and $400^\circ$C using the spray pyrolysis technique, then annealed in vacuum at $400^\circ$C for 1 h. We have investigated the annealing effects on the morphology, structural and optical properties of samples under testing. The obtained outcomes proved that the optimal conditions for formation of crystalline ZnSe thin films are substrate temperature of $400^\circ$C and then anneal at $400^\circ$C in vacuum for 1 h. The XRD results indicated the crystal structure of the ZnSe thin film grown on glass substrate at $400^\circ$C and annealed in vacuum at $400^\circ$C for 1 h has the zinc-blende structure, with preferential orientation along (111), and the grain size of about 38.4 nm. The average transmittance of all ZnSe thin films were over 77% in the near infrared wavelength range. Band-gaps of the annealed samples were observed about 2.71 eV, which are in consistence with the band gap of ZnSe thin films. The band-gap of as grown samples were about 3.98 eV which near to the band gap of ZnO.

we ultimately concluded that in the range of annealing temperature where the crystal structure of the ZnSe thin film grows on the glass substrate and has a maximum transmittance, the magnetization $M/\beta g N$ behaves as a smooth function with respect to the magnetic field without plateau. It can be interpreted that during annealing process function $\frac{g^2\beta^2 N}{|J|} \chi T$ shows a double peak upon increasing the temperature in the presence of externally strong magnetic field.

Acknowledgments

H. Arian Zad acknowledges the receipt of the grant from the ICTP Affiliated Center Program AF-04.
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