Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 154 (2016) 171–176

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Structural, morphological and optical properties of ZnSe quantum dot thin films

I.T. Zedan [a,*], A.A. Azab [b], E.M. El-Menyawy [b]

[a] *Basic Science Department, High Institute of Engineering and Technology, El-Arish, North Sinai, Egypt*
[b] *Solid State Electronics Laboratory, Solid State Physics Department, Physical Research Division, National Research Centre, 33 El-Bohouth St., Dokki, Giza 12622, Egypt*

A R T I C L E I N F O

Article history:
Received 3 June 2015
Received in revised form 22 July 2015
Accepted 22 October 2015
Available online 24 October 2015

Keywords:
ZnSe
Quantum dots
Thin films
Photoluminescence
Optical constants

A B S T R A C T

ZnSe powder was prepared via hydrothermal technique using zinc acetate and sodium selenite as source materials. The prepared ZnSe powder was used for preparing film with different thickness values (95, 135 and 230 nm) via thermal evaporation technique. X-ray diffraction showed that the prepared powder has cubic zinc-blende structure with a space group, $F43m$. The high resolution transmittance electron microscope results show that the films are composed of spherical-shaped nanoparticles with a diameter in the range of 2–8 nm. The optical properties of ZnSe films with differing thicknesses are investigated by means of spectrophotometric measurements of the photoluminescence, transmittance and reflectance. The absorption coefficient of the films is calculated and the optical band gap is estimated. The refractive index of the films is determined and its normal dispersion behavior is analyzed on the basis of a single oscillator model, in which oscillator energy, dispersion energy and dielectric constant at high frequency are evaluated. Drude model is also applied to determine the lattice dielectric constant and the ratio of the carriers' concentration to their effective mass.

1. Introduction

There has been a great interest to control the shape and size of inorganic semiconductor nanoparticles. Many research works are contributing to understand their novel properties together with the structure relationship. Among inorganic semiconductor materials, II–VI semiconductor systems have many electronic and optoelectronic applications. ZnSe is an important member of the II–VI semiconducting materials having a wide direct band gap of 2.7 eV [1] at ambient conditions, small exciton Bohr diameter of 7.8 nm [2] and large exciton binding energy (22 meV) [3]. Due to such properties as well as their fantastic optical and electrical properties, ZnSe films have been extensively studied and introduced in advanced applications.

A special attention has been directed to synthesis and characterization of inorganic semiconducting nanocrystals and quantum dots (QDs). In comparison with traditional emissive material such as organic dyes and inorganic phosphor powders, QDs possess several advantages such as narrow and symmetric emission with tunable colors, broad absorption, zero scattering and reasonable stability behavior [4]. Studies on ZnSe nanoparticles with quantum size are interesting due to splendid characteristics, such as tunable blue-ultraviolet luminescence with high luminescent efficiency, wide band gap, low absorption coefficient and excellent transparency to infrared [5–7], which recommended it as an extremely important component in several electronic and optoelectronic applications including laser diodes, light emitting diodes, photodetectors [8–11], optical limiters for eye protection and optically controlled switching owing to nonlinear optical properties [12].

Inorganic nanoparticles have been prepared by various methods such as molecular beam epitaxy [13,14], chemical vapor deposition [15], reduction by ionizing radiation [16], thermal decomposition in organic solvents [17], chemical reduction or photoreduction in reverse micelles [18] and chemical reduction with or without stabilizing polymers [19,20]. It is realized from the literature, that the morphology of the nanoparticles is sensitive to the method of preparation [21]. In addition, most of these methods require the use of expensive materials and sophisticated equipment.

In this work, ZnSe is chemically prepared by simple and inexpensive hydrothermal method and the corresponding thin films are prepared via conventional thermal evaporation technique, in which their tunable structural, morphological and optical properties are investigated.

2. Experimental

All the chemical reagents were of analytical grade and used without further purification. ZnSe powder was prepared by a simple hydrothermal method using polyethylene glycol (PEG), sodium hydroxide (NaOH), sodium selenite ($NaSeO_3$), zinc acetate dihydrate ($ZnAc.2H_2O$), and hydrazine hydrate (HH). The PEG is used as a surfactant, whereas the HH is used as a complex reagent. NaOH is used for adjusting the pH of the solution to 14. In typical synthesis, 0.1 g of PEG and 4.8 g of NaOH were added to 100 ml of de-ionized water. After a few minutes

* Corresponding author.
E-mail addresses: islamzedan@hotmail.com, islamtaha@hotmail.co.uk (I.T. Zedan).

http://dx.doi.org/10.1016/j.saa.2015.10.016
1386-1425/

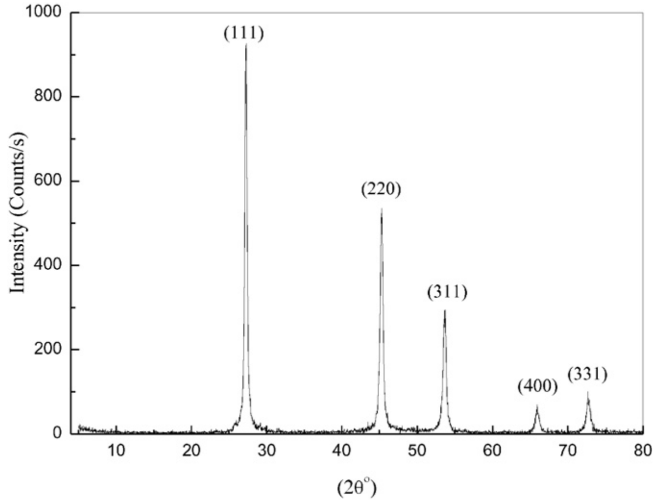

Fig. 1. X-ray diffraction pattern of ZnSe powder prepared by hydrothermal method.

of stirring, 2 mmol of $NaSeO_3$ and 2 mmol of $ZnAc.2H_2O$ were added to the solution and stirred until the reactants were dissolved completely. Then, 20 ml of hydrazine hydrate was added to the solution and transferred into a Teflon-lined stainless steel autoclave. The sealed vessel was kept in a furnace at a temperature of 150 °C for 10 h and then was left to cool down to room temperature. The precipitated ZnSe was washed several times with distilled water and dried at 80 °C for 30 min. The yield of ZnSe powder was calculated as 77%.

ZnSe films were prepared by conventional thermal evaporation by using coating unit (model E306 A, Edwards Co., England) under a base pressure of 3×10^{-6} Torr. The films were deposited onto glass and optical flat quartz substrates. Glass and quartz substrates were for X-ray diffraction and optical measurements, respectively. The film thickness was determined by using multiple beam interference technique. The crystal structure of the ZnSe in powder and thin film forms was investigated by using Expert PM-8203 diffractometer. A JEOL-2100 high resolution transmission electron microscope (HRTEM) is used to detect the particle shape and electron diffraction patterns of the films.

The photoluminescence (PL) emission spectra of the films were recorded at room temperature with a Shimadzu RF-1501 spectrophotometer. The measurements were achieved at excitation wavelength of 354 nm. The transmittance, T_m, and reflectance, R_m, were recorded at normal incidence in the wavelength range of 200–2500 nm using a double beam spectrophotometer (JASCO model V-570 UV–vis–NIR). The absolute values of the measured transmittance, T_m, and reflectance, R_m, are calculated, respectively, by the expressions given by [22]:

$$T = T_m(1-R_q) \quad (1)$$

$$R = R_m R_{Al}\left[(1-R_q)^2 + 1\right] - T^2 R_q \quad (2)$$

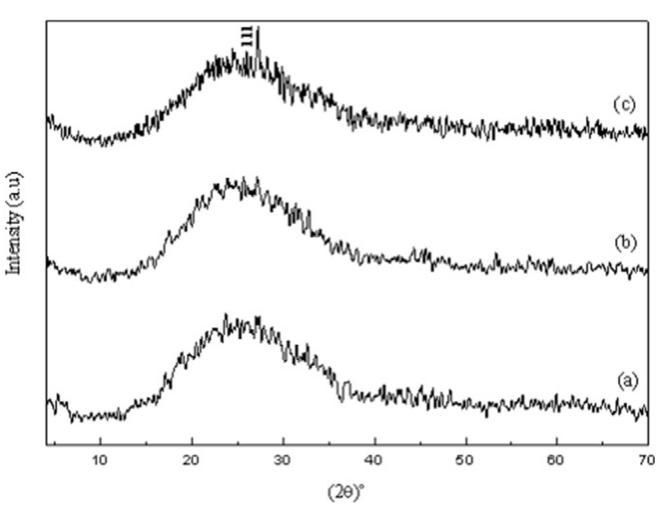

Fig. 2. X-ray diffraction patterns of as-deposited ZnSe films with different thicknesses: (a) 95 nm, (b) 135 nm and (c) 230 nm.

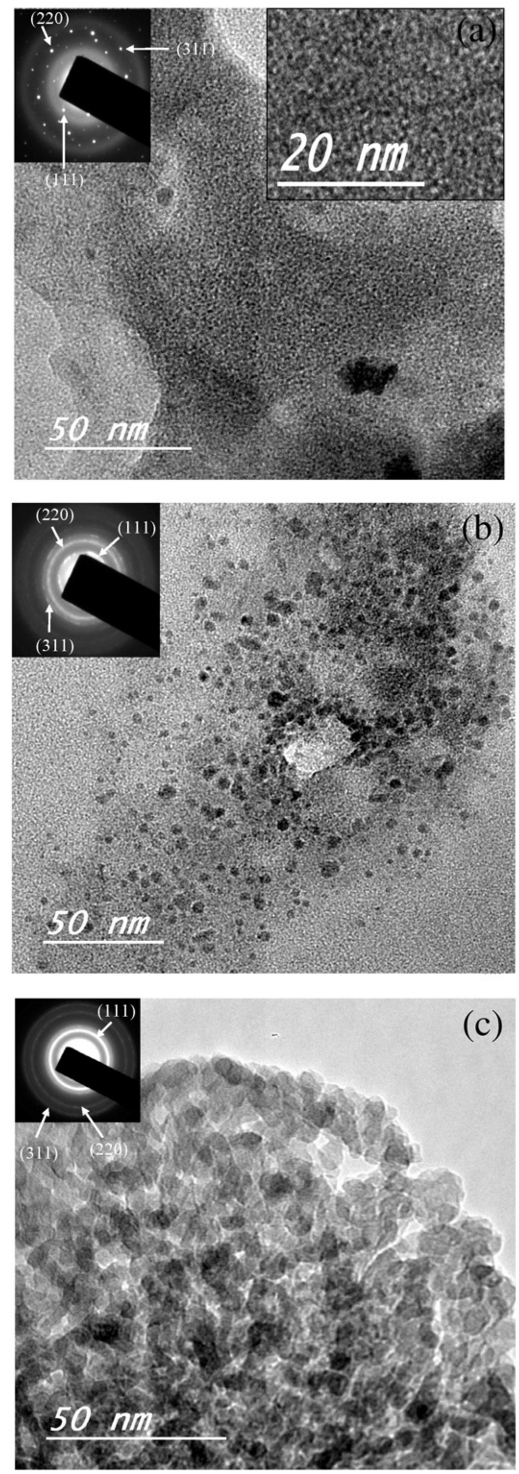

Fig. 3. HRTEM images of ZnSe QD films with different thicknesses: (a) 95 nm (b) 135 nm and (c) 230 nm.