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Effect of Laser Fluence on Structural Transformations and Photoluminescence Quenching of Zinc Selenide Nanoparticles Thin Films

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Abstract

We reported in this work the growth of ZnSe nanoparticles thin films deposited on glass substrates were synthesized by a pulsed laser deposition (PLD) method. The as obtained films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV-VIS Spectrophotometer, and Photoluminescence (PL) spectra. X-ray diffraction study confirmed the transformation the cubic phase of ZnSe nanoparticles into hexagonal phase by increase the laser fluence from (4.77-5.97) J/cm^2. The particle size variations were achieved by varying the laser fluence of prepared films. XRD studies and TEM images confirmed the nanometer size was found to lie in the range of 12-80 nm. A UV-VIS study was carried out to measure the band gap of the ZnSe nanoparicles thin films and it showed a blue shift with respect to the bulk value. The PL spectra at room temperature (300K) of the films showed the decrease of maximum values at at 522 nm(2.379), 521 nm (2.3838) and 520 nm (2.3882 eV) for the laser fluences (4.77, 5.57 and 5.97 J/cm2), respectively. We assigned the variation due a larger number of non-radiative recombination centers appears in the films.

Keywords: Zinc selenide, Photoluminescence, Thin films, Nanoparticles, PLD method.

Introduction

Semiconductor nanoparticles have been extensively studied from experimental and theoretical viewpoints, owing to their potential applications, consequent to their size dependent optical properties. Among all semiconductor nanoparticles, zinc selenide (ZnSe) is an interesting material with many applications in various fields such as optoelectronics, photocatalysis, solar energy conversion, projection television, fluorescence microscopy[1]. The nanostructures of Zinc Selenide (ZnSe), in particular, have attracted considerable attention. ZnSe is an important II–VI semiconductor due to its promising optoelectrical and electrical properties of direct wide band gap 2.68 eV at 300 K. The ZnSe nanoparticles can be obtained through chemical reduction[2] vapor synthesis[3], or laser ablation method[4].

Actually, the PLD technique has several advantages for the deposition of nanoparticles thin films for instance stoichiometric transfer of material from the target to the substrate. Comparatively low substrate temperature and less demanding in vacuum technology with respect to other more expensive deposition techniques like molecular beam epitaxy and metalorganic chemical vapour deposition. The structural and optical properties of deposited films are pointedly affected by the deposition parameters. One of the important parameter is the laser fluence because it controls the deposition rate, the number of particulates, which are usually present in PLD layers[5]. Generally, crystalline ZnSe exhibits two structural phases, that is, zinc blende and wurtzite[6]. However, the studies on wurtzite phase ZnSe nanoparticles are few[7][8][9] owing to that the wurtzite structure is

thermodynamically unstable in ambient environments and requires the critical growth conditions. In this work, we have achieved a new method to transform the structure phase of ZnSe zinc blend to Wurtzite crystal structure by PLD technique. Moreover, PL is dependence on the laser fluence.

Experimental method

ZnSe target fabricated from Zn and se elements to formation alloy. The powder of ZnSe was investigated by X-ray diffraction with cubic phase structure by orientations (111), (200), and (311) respectively as shown in Figure 1. A pellet of target produced by pressing squeeze at (13) ton, and sintering ZnSe target under vacuum at 1000K. Dimensions of target about (2 cm x 0.1 cm), it is a suitable target for PLD technique, it is dense and flat, enabling uniform energy transfer to its surface and the absence of voids keeps large particles being ejected from the surface. ZnSe target fixed to a holder that located at 2 cm with 45^{o} to the substrate surface. The PLD was carried out by using a Q-switched Nd-YAG laser with wavelength (1064 nm), laser fluences (4.77, 5.57 and 5.97 J/cm^2) and laser spot with diameter (d=4mm). The repetition rate was 5 Hz. The target and substrate rotated with 6 rpm, by using DC motor to avoid the drilling effect. The chamber of deposition system evacuated to a pressure about 10^{-5} mbar. The substrate temperatures (T_s) of samples were (373K). The thickness created after deposition by 1500 pulses was found to be 50 nm.

Results and discussions

The crystalline structure could be unambiguously observed through x-ray diffraction patterns. From the X-ray diffraction θ-2θ scans, all the diffraction peaks in this pattern (Figure 1) can be indexed to the hexagonal structure according to the JCPDS card no.80-0008 for ZnSe (a = b = 3.974 Å, c = 6.506 Å). It clearly shows that the crystalline structure of ZnSe NPs transformed from the ZnSe cubic phase with (111) and (220) into ZnSe hexagonal phase with (100), (101), (102) at different laser fluence (4.77 , 5.57 and 5.97 eV).The particles size can be estimated from Scherrer's equation, which is expressed as:

$$D = 0.89\lambda/\beta \cos\theta \quad (1)$$

where D is the particle diameter, λ is the wavelength of X-ray, θ is the diffraction angle, β is the FWHM of diffraction peak and K is Scherrer's constant (0.89).

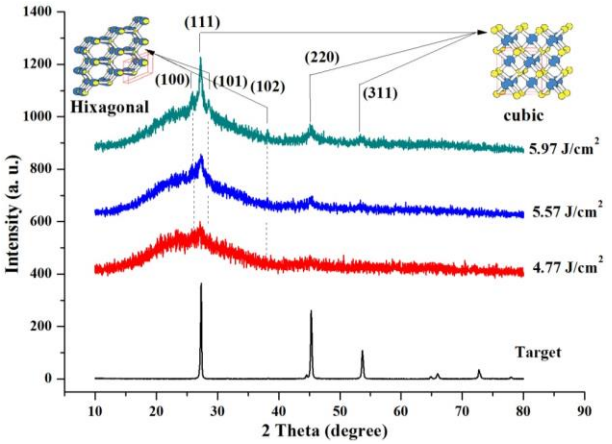

Figure 1: The XRD pattern of ZnSe NPs thin films grown under different laser fluence at 373K.

The obtained of (D) values for ZnSe nanoparticles thin films are about 6.2, 9.7 and 11.4 nm for the laser fluences (4.77, 5.57 and 5.97 eV), respectively as shown in Figure 2.

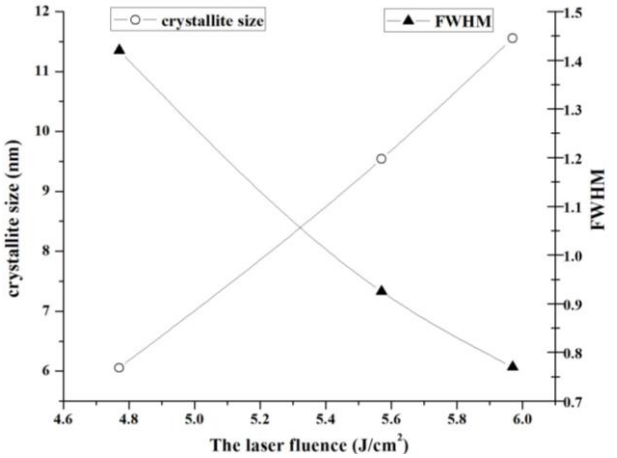

Figure 2: Crystallite size Vs FWHM of ZnSe NPs thin films prepared by increasing laser flounce (4.77, 5.57 and 5.97 J/cm^2).

In Figure 2, we observed the crystallite size of ZnSe nanoparticles becomes larger as increasing the laser fluence. Figure 3 shows the typical AFM images for studied samples.

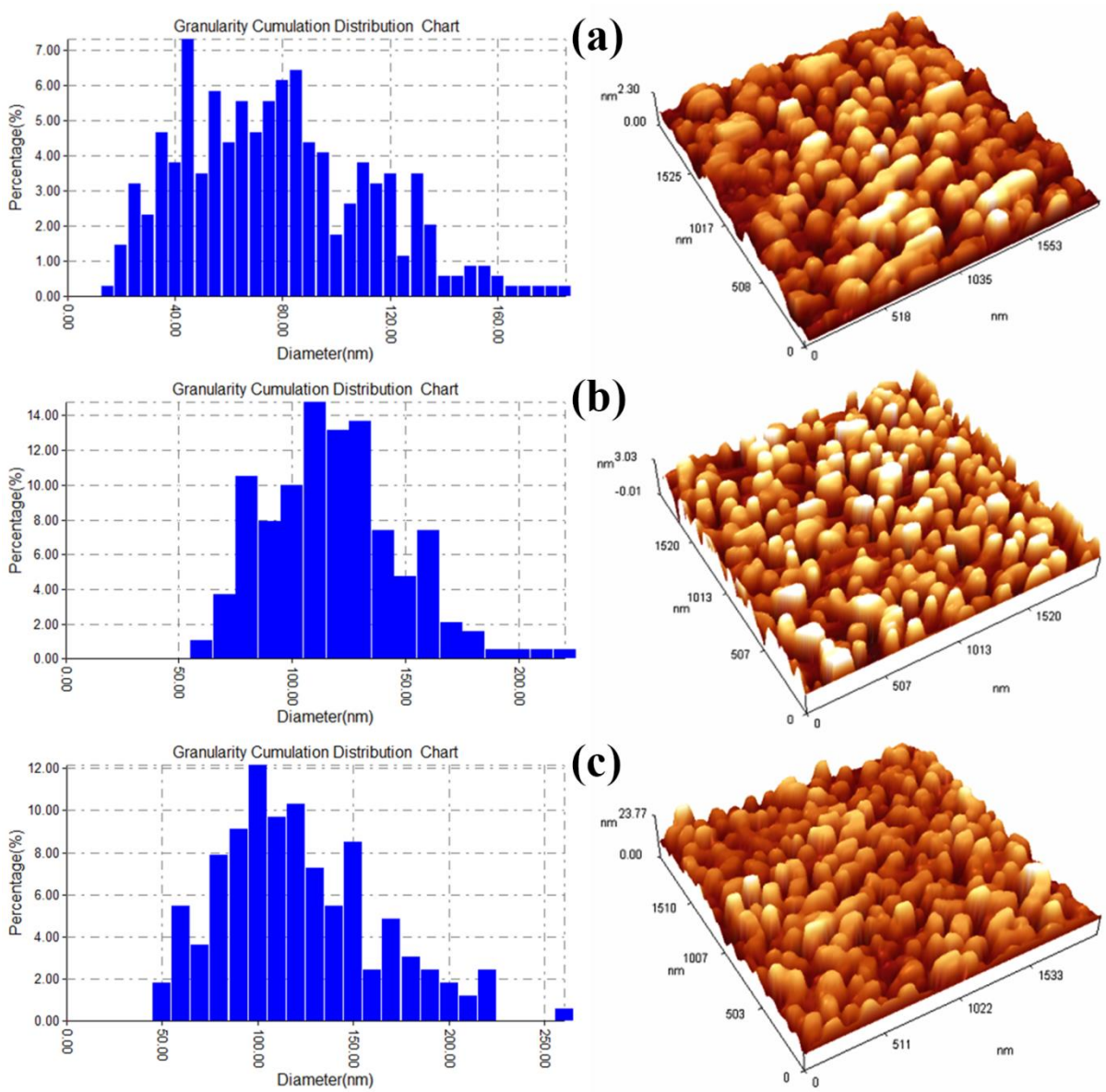

Figure 3: The AFM images of ZnSe NPs thin films prepared by increasing laser flounce (a-4.77, b-5.57 and c-5.97 J/cm^2).

The AFM images provide some quantitative data about the surface roughness (R), the average particle size (D_a) and the maximum height of the studied thin films, as shown in the Table 1.

Table 1: some quantitative data of AFM measurements at various laser fluence of ZnSe NPs thin films.

Laser fluence (J/cm^2)	Average particle size (D_a) (nm)	Roughness (R) (nm)	Max. height (nm)
(a) 4.77	77.73	0.433	2.3
(b) 5.57	113.49	0.679	3.02
(c) 5.97	116.53	3.59	10.9

In the Figure 4, we have observed the TEM images of ZnSe nanoparticles with average particle size about (45, 64 and 95 nm) at various laser fluences (a) 4.77, (b) 5.57 and (c) 5.59 J/cm^2, respectively.

Additionally, the hexagonal structure of ZnSe nanoparticles is clearly identified from the selected-area of TEM in Figure 5. It indicates that the hexagonal structure does exist in the ZnSe nanoparticles fabricated by the Nd-Yag laser deposition. This interesting phase transition from the cubic structure of ZnSe single crystal target to the hexagonal structure

of ZnSe nanoparticles is caused by the increasing of laser fluencies lead to great ablation pressure of the sudden high-energy injection.

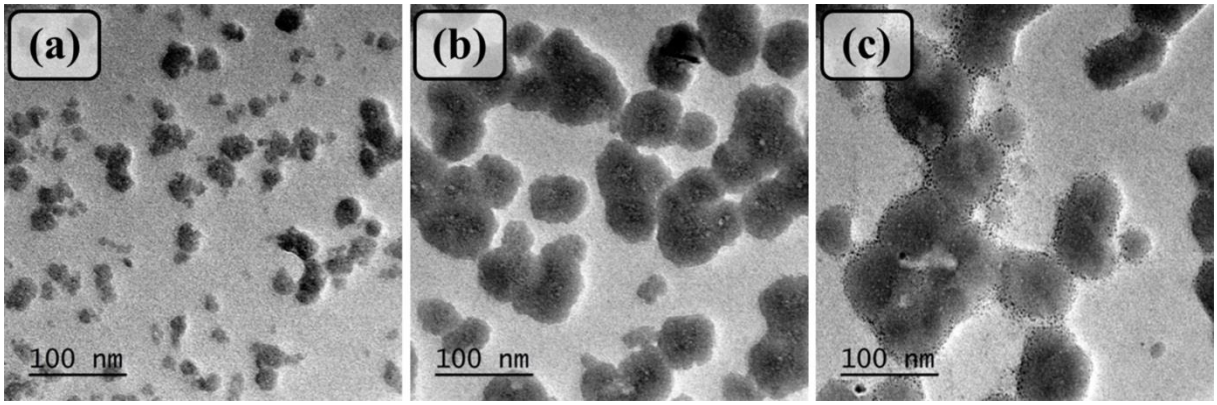

Figure 4: TEM images of ZnSe nanoparticles thin films at different laser fluencies (a, b and c) for (4.77, 5.57 and 5.97 J/cm^2), respectively.

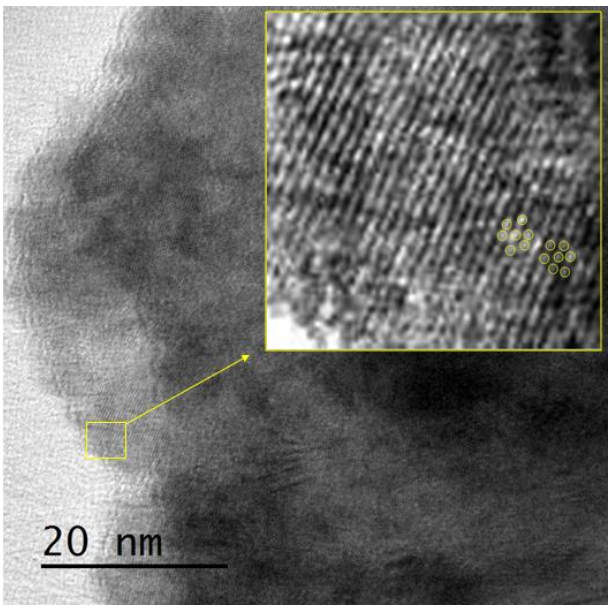

Figure 5: TEM image of the hexagonal structure does exist in the ZnSe nanoparticles fabricated by the Nd-Yag laser deposition films at laser fluencies (5.97 J/cm^2).

Optical transmission and absorption spectra (in the wavelength range from 190 nm to 1100 nm) were performed by subtracting the absorption of the glass substrate, which was taken as a reference and recorded using a single beam spectrophotometer (T 60) as shown in Figure 6.

The values of absorption coefficient (α) are calculated in the region of strong absorption using the Tarey's and Raju's relation[10]:

$$\alpha = -(1/t)ln(T) \qquad (2)$$

where T is the transmission in % and (t) is the film thickness nm. The optical band gap E_g has been calculated using Tauc's formula[11]:

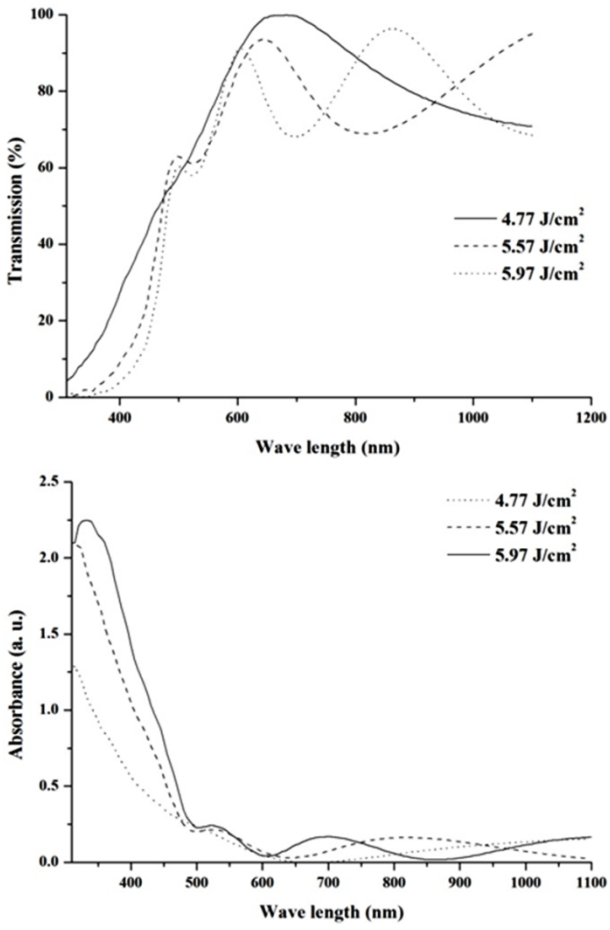

Figure 6: Transmittance and absorbance spectra of ZnSe NPs thin film at different laser fluence (4.77, 5.57 and 5.97 J/cm^2).

$$(\alpha h\vartheta)^{1/n} = A(h\vartheta - E_g) \quad (3)$$

where α is absorption coefficient, $h\vartheta$ is incident photon energy, A is a constant, and the exponent n depends on the type of transition. n may have values 1/2, 2, 3/2, and 3 corresponding to the allowed direct and allowed indirect transitions. Since ZnSe is a direct band-gap material, the corresponding Eg is obtained with n = 1/2.

The values of optical band gap for ZnSe NPs are 3.08, 2.868 and 2.776 eV were laser fluence increased with values 4.77, 5.57 and 5.97 J/cm^2 as shown in Figure 7. The observed values of E_q are higher than the value of bulk optical gap (E_q=2.7 eV) of ZnSe due to quantum confinement in the ZnSe nanoparticles.

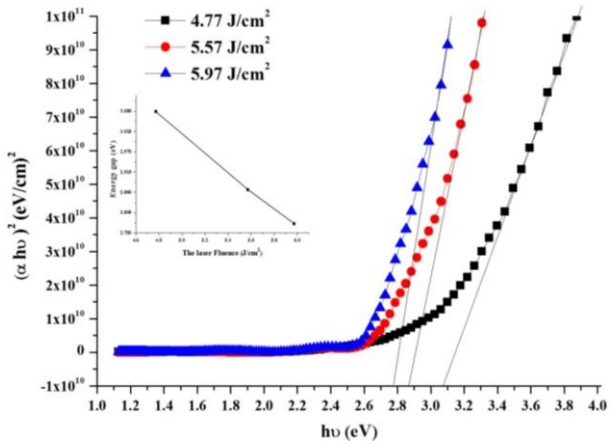

Figure 7: The typical variation of $(\alpha h\upsilon)$ as a function of photon energy$(h\upsilon)$ of ZnSe NPs thin films at different laser fluence (4.77, 5.57 and 5.97 J/cm^2).

PL spectra of the three films measured at 300K. All films were excited by wavelength about 440 nm are shown in Figure 8.

Optical excitation is achieved below band gap, in order to investigate the defect and impurity luminescence. Actually, we have observed a centered emission at 522 nm (2.379), 521 nm (2.3838) and 520 nm (2.3882 eV) for the laser fluence (4.77, 5.57 and 5.97 J/cm2), respectively. However, the intensity of this green luminescence (GL) depends on the deposition conditions. In particular, we found the PL intensity to decrease with increasing the laser fluence. Such a behavior is caused by the rise of the deposition rate with the laser fluence: a more disordered deposition process and, then, a larger number of non-radiative recombination centers appear.

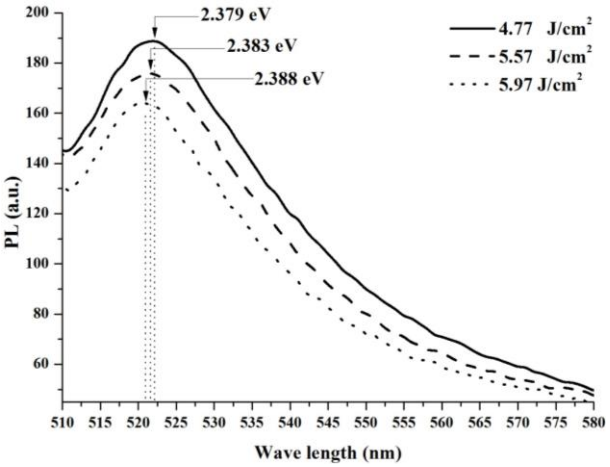

Figure 8: PL emission for ZnSe NPs thin films was carried out at 300K. PL measurements were Excited at 440 nm at different laser fluence (4.77, 5.57 and 5.97 J/cm^2).

Conclusion

PLD technique has been employed to deposition thin films of ZnSe with varying the laser fluences. The increase in laser flunce has led to increased grain size approximately to 95 nm. All the deposited films exhibit a large emission band in the visible region, whose PL efficiency decreases with increasing the laser fluence. This study demonstrated the laser fluence dependent quenching behavior of photoluminescence emissions. These results are promising in order to optimize the growth parameters for a possible optoelectronic application of materials deposited by PLD technique. In conclusion, the Nd-Yag laser deposition method is a useful method for fabricating the hexagonal ZnSe NPs thin films.

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