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Two Photon Absorption in Nanostructure Wide Band Gap Semiconductor CdS Using Femtosecond Laser

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Abstract

Strong nonlinear absorption in CdS nanoparticles of dimensions in the range 4 - 50 nm when irradiated with a femtosecond pulsed laser at 800 nm is observed. The CdS nanoparticles sizes were controlled by changing the reaction time of aqueous solutions of thiourea and cadmium chloride. The structure of the prepared CdS nanoparticles were tested and their optical properties were investigated and the nonlinear absorption coefficients were measured using a fully computerized z-scan unit. It is found that the formation of the CdS nanostructuresfor are responsible for the observation of the strong tow photon absorption.

Keywords: Cadmium Sulfide, Nanostructure, Multiphoton Absorption

1. Introduction

Nanoparticle semiconductor materials with large nonlinear coefficients have attracted much attention in recent years [1-5]. This is interest due to their unique optical properties when their size decreased from bulk to few nanometers. Such unusual properties may have technological applications such as optical switching devices, Q-dot lasers, and there is great potential in biophotonics [6,7]. The linear optical properties of the semiconductor nanoparticles depends strongly upon the particle size [8]. The nonlinear optical properties, the absorption and refractive index, were observed in nanoparticles semiconductor CdS material [9-11]. The dynamic of the CdS excited state have been studied by femtosecond laser and by the photoluminescence (PL) analysis [12-14]. In this study, a CdS nanofilm was deposited using a simple and low cost spray pyrolysis technique. A fully computerized Z-Scan setup with femtosecond laser was used to investigate the effect of surface state formation in CdS nanoparticles on the nonlinear dynamics parameters.

2. Experimental

The CdS nanofilm was prepared by mixing an 0.1 M aqueous solution of thiourea (NH_2CSNH_2) and an 0.2 M aqueous solution of Cadmium Chloride ($CdCl_2$) as starting solution. They were mixed and dissolved in distilled water in the ratio of 3:2. The solution was mixed thoroughly and the final solution was sprayed onto a heated substrate kept at a temperature of 300˚C. Spray pyrolysis is a useful alterative to the traditional methods for obtaining cadmium sulfide nanofilms, because of its simplicity, low cost and minimal waste production. The spray pyrolysis process allows the coating of a large surface and it is easy to include in an industrial production line. With spray pyrolysis, the solution is sprayed directly onto the substrate. A stream of nitrogen gas can be used to help the spraying of solution through the nozzle.

In the study, a CdS nanofilm was deposited by the spray pyrolysis technique on a glass substrates. The flow rate of the solution experimentally was 5 ml/min and the substrate temperature was held constant at 300˚C. The nozzle to substrate distance was 28 cm and the diameter of the nozzle was 0.8 mm. The number of sprays was 15. The spraying time was controlled by solenoid valve. The heated substrate was left for 10 s after each spraying run to give time for the deposited CdS layer to be dry and also to prevent excessive cooling of the substrate. This yielded a uniformly grown CdS film on the substrate. The schematic representation of the spray system is given in **Figure 1**. When the solution is sprayed the following reaction takes place at the surface of the heated substrate.

$$CdCl_2 + (NH_2)_2 CS + 2H_2O \rightarrow \downarrow CdS + \uparrow 2NH_4Cl + \uparrow CO_2$$

During the chemical reaction gas and water vapor is

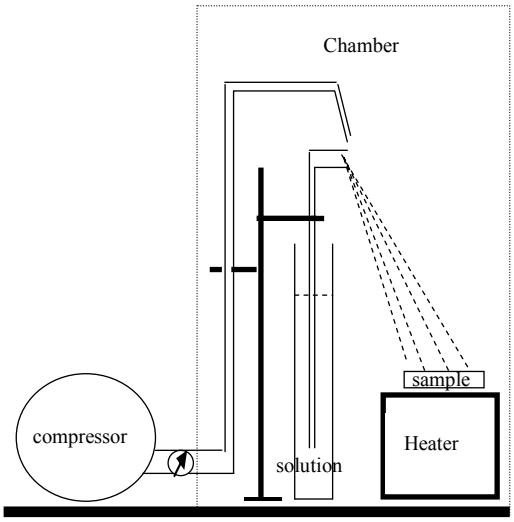

Figure 1. Schematic representation of the spray system.

obtained from this reaction due to the high temperature of the substrate. At the end of the reaction a yellow precipitates remains as a nanofilm of CdS material.

After deposition the film, the material was cooled to room temperature gradually. There are several experimental parameters which are control the homogeneity and the thickness of the nanofilm. These parameters are the spraying time, the height of the atomizer and the pressure of the nitrogen gas carrier. The topography of the prepared nanofilm was studied using Scanning Electron Microscopy (SEM) type ULTRA 55 with different magnifications; as shown in **Figure 2**. The figures show nanocrystals of size ~4 - 50 nm. The sample was scanned in all zones before the picture was taken. The micrographs reveal that the particles were hexagonal in shape. The X-ray diffraction (XRD) pattern of the CdS nanofilm was recorded using an XRD 2000 system. The X-ray diffractometer used a copper tube radiation line with a wavelength of 1.54 Å and a 2θ range from 20˚ to 60˚. Scan rate was 1 deg/min. The UV-VIS absorption and transmission spectra of the sample were recorded by a Hitachi U-4100 spectrometer covering 200 - 1100 nm. The photoluminescence (PL) spectrum was studied using an SL1174 spectrophotometer in the range 300 - 900 nm. The nonlinear absorption study at the near resonant regime was carried out using the single-beam femtosecond open aperture z-scan technique (OA). The z-scan setup is illustrated by the schematic diagram shown in **Figure 3**. A femtosecond laser with a pulse duration of 51 fs and average power of 351 mW was used as a laser source. The pulse duration was measured using an autocorrelatior and the energy was measured using a pyroelectric energy probe of model type (PDA36A), covering the wavelength range 350 - 1100 nm from THORLABS. The beam profile was adjusted using a spatial filter, leading

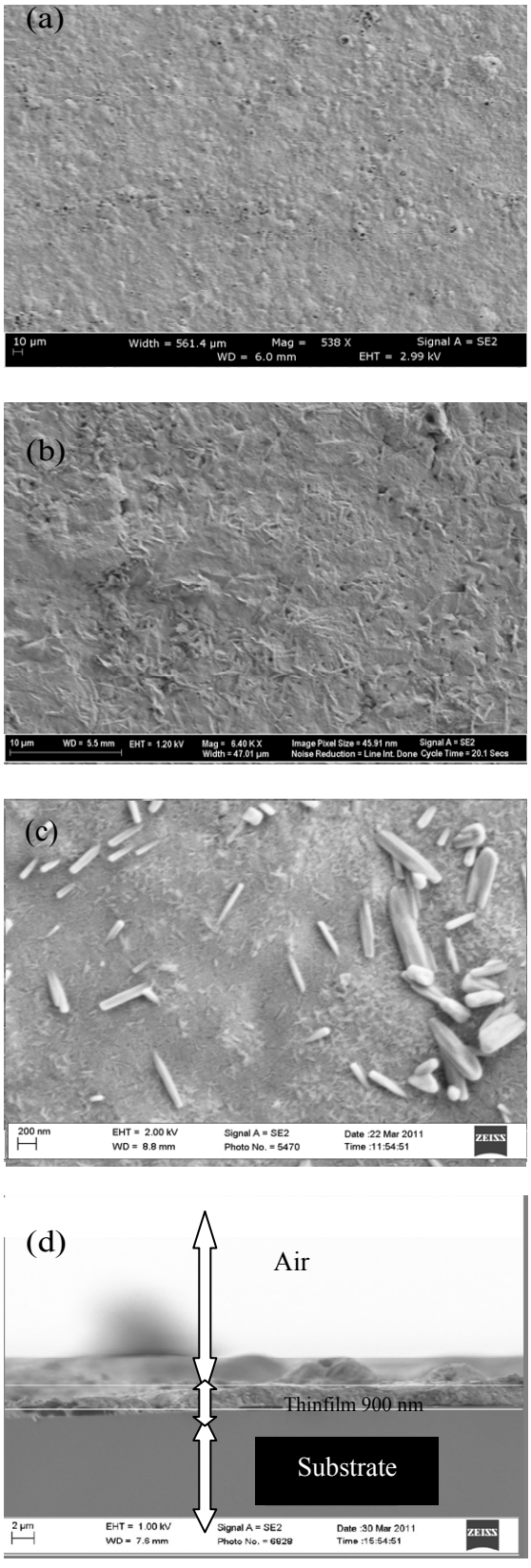

Figure 2. Top-view SEM images of CdS nanofilm at different magnification powers (a)-(c) and cross-section (d).

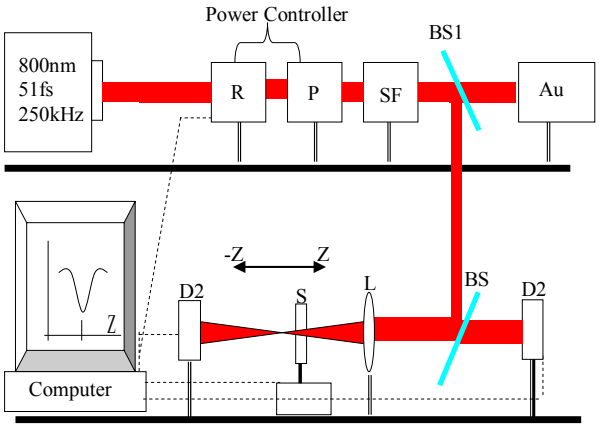

Figure 3. Schematic of the z-scan setup recording the nonlinear absorption, R—Rotator, P—Polarizer, SF—Spatial filter, BS1, BS2—Beam Splitter, Au—Autocorrelation, D1, D2—Detectors, L—Lens, S—Sample.

to spatial intensity profile that was near-Gaussian with beam quality of $M^2 \approx 1.36$. The laser beam was focused by a lens with 15 cm focal length to produce a waist of 32.7 μm. The sample was translated along the beam axis (z-axis) through the Rayleigh distance 4200 μm.

3. Results and Discussion

The topography study of the prepared film shows the formations of the CdS nano structure and the film thickness was in the range of 0.5 - 2 μm. The XRD pattern was recorded for the nanofilm CdS spray-deposited film as shown in **Figure 4**. The spectrum through $2\theta = 20^\circ$ to $2\theta = 60^\circ$ indicates that the CdS nanofilm has a polycrystalline structure. The observed values of the XRD peaks are compared with American Society for Testing and Materials (ASTM) data for hexagonal CdS. The figure shows broad peaks which give evidence of the formation of the nanostructure. Using the width of the (002) peak which appears at an angle of 26.8˚ on the 2θ scale in Scherrer's formula [15]:

$$d = 0.94\lambda/\beta\cos\theta \qquad (1)$$

where d is the average crystalline grain size, λ is the wavelength, β represents the full width at half maximum (FWHM) in redian that equal 0.0087 and θ is the Bragg diffraction angle in degree, the size of the formed nanoparticles was found to be about 50 nm. The absorption spectrum of the CdS nanoparticles film is shown in **Figure 5**. The film is highly absorbing at wavelength below 500 nm.

The energy band gap of CdS film was estimated using Tauc relation which can be written as [16]:

$$(\alpha hv) = A(hv - Eg)n \qquad (2)$$

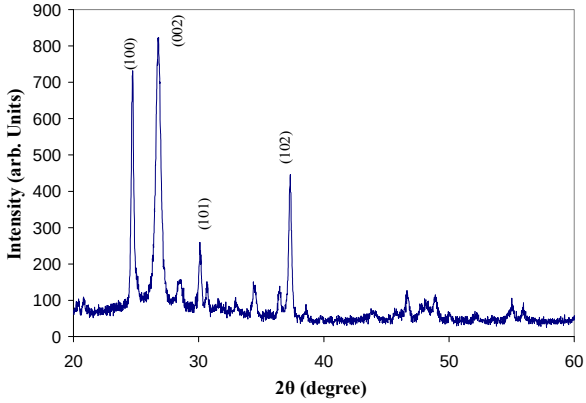

Figure 4. XRD pattern of CdS nanofilm deposited on a glass substrate at 300˚C.

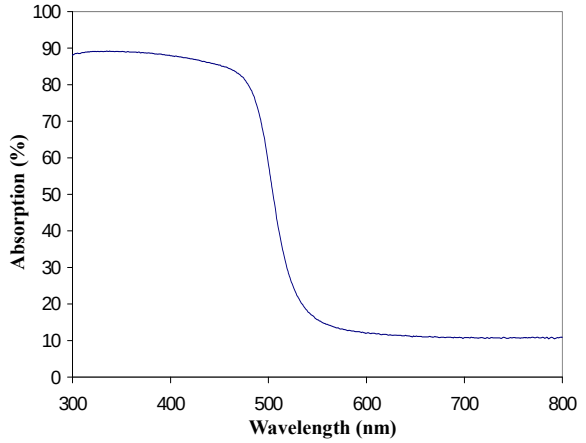

Figure 5. Optical absorption spectra of CdS nanofilm.

where A is a constant, α absorption coefficient, hv the photon energy (Eg) the band gap, $n = 1/2$ for the direct transitions.

Referring to the data extracted from the absorption spectrum, the absorption coefficient was calculated as function of wavelength. Assuming an allowed transition, direct band gap transition, the dependence of $(\alpha hv)^2$ on hv is plotted in **Figure 6**.

The extrapolation of the linear part of the plot to $(\alpha hv)^2 = 0$ gives rise to an estimate the energy gap value of the CdS nanoparticles which was found to be 2.7 eV. This value is comparable to the values found by the other workers [17]. The optical transmittance spectrum of the CdS nanofilm is shown in **Figure 7**.

The transmittance is high in the visible region with a sharp increasing beyond the 520 nm, this indicates that the CdS nanofilm has high absorption below this value because of the occurrence of the linear and nonlinear absorption. The (PL) emission spectrum of CdS nanoparticles excited by a 350 nm line is shown in **Figure 8**.

The spectrum shows a peak at 485 nm which can be re-

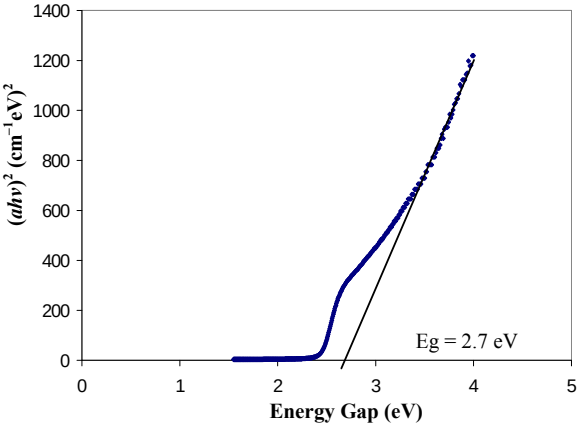

Figure 6. $(\alpha hv)^2$ versus enrgy gap.

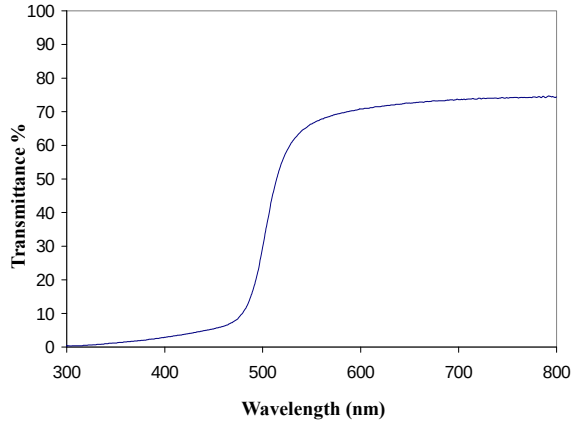

Figure 7. Transmission spectrum of CdS nanofilm.

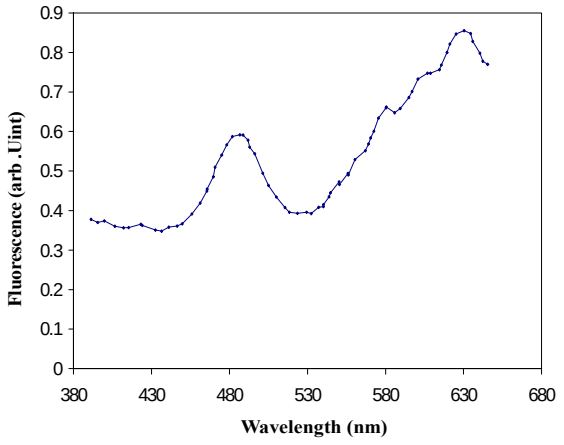

Figure 8. Photoluminescence emission spectrum of CdS nanofilm.

ferred to the direct band gap transition and two peaks around 580 and 630 nm which are attributed to the formation of surface states. The observation of surface states in the photoluminescence spectrum of the CdS nanoparticles has been reported by many authors [18,19]. The nanocrystals synthesized with elemental sulfur have more surface defects which act as traps on the nanocrystals surface [20].

The z-scan transition curves for different laser intensities incident on the CdS nanofilm are presented in **Figure 9**. The normalized transmittance of the open aperture z-scan is given by [21]:

$$T(z)=\frac{1}{\pi^{1/2}q_o}\int_{-\infty}^{\infty}\ln\left[1+q_o\exp\left(-x^2\right)\right]\mathrm{d}x \qquad (3)$$

where, $q_o=\beta I_o L_{eff}$, $I_o=I_\infty\Big/\left(1+z^2/z_o^2\right)$ is the excitation intensity at the position z, $z_o=\pi\omega z_o^2\Big/\lambda$ where z_o is the Rayleigh range, ω_o is the minimum beam waist at focal point (z = 0), λ is the laser free-space wavelength, L_{eff} = [1-exp(-$\alpha_o L$)]/α_o is the effective sample length for 2PA processes; L is the sample length and α_o is the linear absorption coefficient. The open aperture z-scan graphs are always normalized to linear transmittance *i.e.*, transmittance at large values of $|z|$. The 2PA coefficient can be extracted from the best fit between Equation (3) and the experiment (OA) z-scan curve.

If q_o < 1 Equation (3) can be expanded in a Taylor series as [21]:

$$T=\sum_{m=0}^{\infty}(-1)^m\frac{q_o^m}{(m+1)^{3/2}} \qquad (4)$$

Furthermore, if the higher order terms are ignored, the transmission as a function of the incident intensity is given by [21,22]:

$$T=1-\frac{\beta I_o L_{eff}}{2^{3/2}} \qquad (5)$$

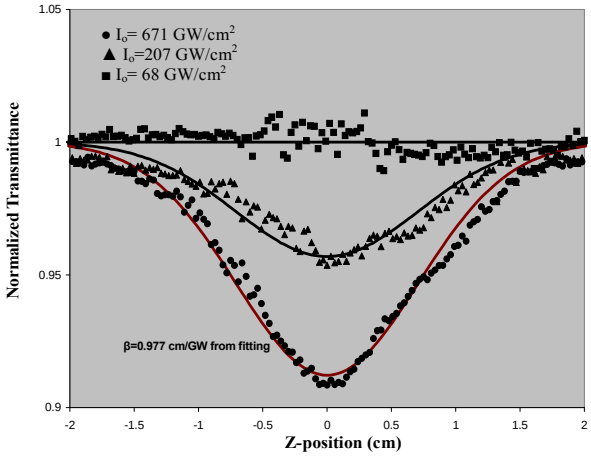

Figure 9. OA z-scan curves measured with different excitation irradiance at a wavelength of 800 nm and a pulse duration 51 fs and repetition rate of 250 kHz. The solid lines are the fitted curves by employing the z-scan theory, described in the text, on 2PA.

The sold curve in **Figure 9** is the best fit for Equation (5). The Equation (5) shows clearly that the depth of the absorption dip is linearly proportional to the 2PA coefficient β, but the shape of the trace is primarily determined by the Rayleigh range of the focused Gaussian beam. The fitted value of β is on the order of 50 cm/GW. This value is ten times of magnitudes higher than the value observed with bulk CdS sample. This results is in a good agreement with values mentioned in [23]. The natural logarithm of the (1-T) values are plotted as a function of the natural logarithm of the incident intensity I_o in **Figure 10**. The curve can be reasonably fitted with a straight line with a slope of 0.97. This indicates that the 2PA was occur in CdS pump by 800 nm laser source of 51 fs pulse duration as shown in **Figure 10**.

The formation of surface defects may contribute to the absorption mechanism of the prepared film due to small increase in the linear absorption cross section [24]. The formation of the surface defects in CdS and in the other sulfur compound increase the nonlinear scattering leading to decreasing in the nonlinear absorption coefficient. This was observed by viewing the transmittance light through IR camera.

4. Conclusions

A CdS nanocrystalline film was prepared by the chemical spray pyrolysis technique. The nonlinear absorption coefficient was measured by fully computerized the z-scan technique. The measurements show that the nonlinear absorption coefficient for the nanocrystallites is one order of magnitude higher than that of the bulk CdS material. This increase in the nonlinear responsivity when the crystalline size approaches nano-scale dimensions may be attributed to collimating of the incident intensity of the pumped laser which led to improve the nonlinear dynamic of the CdS nanocrystallite.

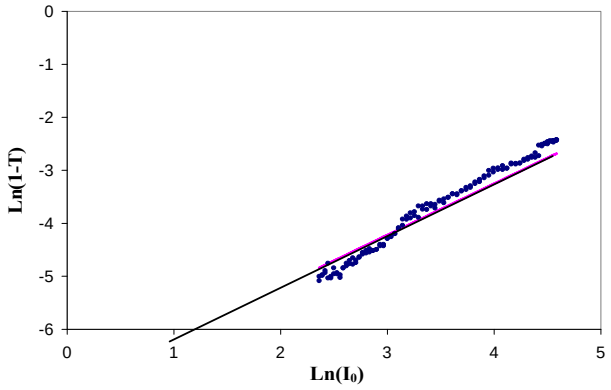

Figure 10. Plot of Ln(1-T) vs. Ln(I_o) at 800 nm wavelength, the solid line is the example of the linear fit at 800 nm with slope s = 0.97.

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