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ORIGINAL ARTICLE

Determination of Optimum Zn Content in $Cd_{1-x}Zn_xS$ Quantum Dots

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Abstract: CdZnS quantum dots (QDs) QDs containing concentrations of 0.25, 0.5, 1, 3 and 5% Zn were synthesized at room temperature by chemical precipitation method and then incident photons to current efficiency (IPCE) measurements were performed to determine optimum Zn concentration in CdZnS QDs. Moreover, Zn_2SnO_4, a ternary compound semiconductor, was used instead of TiO_2 as counter electrode for the first time. As a last part of the study, the structural and optical properties of CdZnS QDs containing optimum Zn content were investigated, respectively. Consequently, it appears that CdZnS QDs have a higher efficiency than CdS and that Zn doping plays an important role in this increase.

Keywords: Characterization, doping, photovoltaic, quantum dots, zinc

1. Introduction

Semiconductors in their unique properties have received a great deal of attention in recent years. II-VI compounds and their alloys, which are one of the different semiconducting materials, have been extensively explored since they are used in many areas such as the production of solar cells and opto-electronic devices [1-3]. CdS, which has a wide band gap of 2.42 eV is one of the II-VI compound semiconductors and is considered as a suitable material for many applications such as photo catalysis and gas sensors for lasers and infrared solar cells [4-5].

When CdS is doped with Zn and CdZnS is obtained, the band gap of CdS is increased because of fact that the band gap of ZnS semiconductor is 3.6 eV. Owing to this feature, substituting CdZnS for CdS has been identified as an alternative method [6]. Kumar et al [7] have synthesized CdZnS quantum dots (QDs) containing different concentrations of Zn by solid state reaction technique and then precipitated on the substrates to produce CdZnS thin films with different Zn concentrations. In a study by Burton et al [8], it was observed that the resistance of the material obtained when CdS is doped with Zn content, is higher than that of CdS. In addition, Zn plays an important role in reducing the absorption losses at window layer in the CdS. This leads to an increase in the short circuit current and the open the circuit voltage in the hetero-junction structures. Due to the Zn content, the spectral response of CdZnS is greater than that of CdS. Due to this feature, it is expected that the efficiency of CdZnS based solar cells will be high and the CdZnS will be used as a convenient material for producing p-n junctions [9-11].

Bedir et al [12] reported that the crystal size of CdZnS is reduced by increasing the Zn concentration. Moreover, they found that the degree of preferential orientation decreases when the samples were annealed in vaccum at 6000C. Due to Zn doping, the absorption wavelengths of CdS based materials have been observed to be shifted to lower wavelengths (blue-shifted). Besides this, it was found that the lattice constant of CdZnS is lower than that of CdS. Studies [13-14]

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have shown that the synthesized CdZnS QDs have a cubic structure, in other words the Zn doping process does not alter the structure of CdS. Contrary to the structure of CdZnS QDs, XRD studies have indicated that CdZnS thin films have a hexagonal structure and a strong orientation along the (002) plane. The effects of Zn doping on optical absorption, energy band gap and transmittance were investigated by Hossain et al. [15]. The optical properties of CdZnS QDs were investigated by Alehdaghi et al [16]. According to the results obtained, the absorption spectrum of CdZnS is shifted to the shorter wavelengths as compared to CdS. In addition to investigating the effect of Zn doping on the structural and optical properties of CdS in the work done [17-18], it is necessary to search in detail the photovoltaic properties of CdZnS materials.

In this study, the CdZnS QDs containing concentrations of 0.25, 0.5, 1, 3 and 5% Zn were synthesized at room temperature by chemical precipitation method and then incident photons to current efficiency (IPCE) measurements were performed to determine optimum Zn concentration in CdZnS QDs. Moreover, Zn_2SnO_4, a ternary compound semiconductor, was used instead of TiO_2 as counter electrode for the first time. As a last part of the study, the structural, elemental and optical properties of CdZnS QDs containing optimum Zn content were investigated, respectively. Consequently, it appears that CdZnS QDs have a higher efficiency than CdS and that Zn doping plays an important role in this increase.

2. Experimental Details

2.1 Chemicals

Cadmium acetate dehydrate [Cd $(CH_3COOH)_2$. $2H_2O$] as Cd source, zinc acetate dehydrate [Zn $(CH_3COOH)_2$. $2H_2O$] as Zn source and Na_2S as S source were used to synthesize the CdZnS QDs containing concentrations of 0.25, 0.5, 1, 3 and 5% Zn at room temperature using the chemical precipitation method. 1-Thioglycerol was used as capping agent to obtained nice QDs. All chemical sources were purchased from Sigma Cooperation.

2.2 Synthesis of QDs

In typical chemical precipitation method; in the first beaker; 0.1M of Cd $(CH_3COOH)_2$. $2H_2O$ was dissolved in 100 ml of aqueous solution. In the second beaker: 0.1M of Na_2S was dissolved in 100 ml of aqueous solution. After dissolving process, two solutions were transferred to third beaker. The obtained solution in third beaker was stirred 1 hour to get homogeneous CdS mixture. During stirring process, 0.5 ml of 1-Thioglycerol was added on the solution. The precipitated sample was separated from the solution by a filter paper. The obtained orange colour sample was washed three times with de-ionized water and 2 times ethanol to get rid of the unwanted compounds. The final step in the chemical precipitation method is to heat sample in the oven at 80 ^{0}C for 24 h.

To synthesize CdZnS QDs containing concentrations of 0.25, 0.5, 1, 3 and 5% Zn; 0.00025M, 0.0005M, 0.001M, 0.003M and 0.005M of Zn $(CH_3COOH)_2$. $2H_2O$ was added into first beaker, separately then same procedure as mentioned above was followed.

2.3 Characterization

Incident photons to electron conversion efficiency (IPCE) measurements were performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator. For IPCE measurements, fluorine doped tin oxide (FTO, $13\Omega.sq^{-2}$) conductive glass substrates were used as the photo electrodes. The Zn_2SnO_4 nanowires (NWs) were coated on the FTO substrates using the doctor blade method, and then sintered at 450 ^{0}C for 45 minutes. A suspension of CdS and CdZnS QDs containing concentrations of 0.25, 0.5, 1, 3 and 5% Zn were dropped on the FTO substrates with the Zn_2SnO_4 NWs. The substrates were dried with N_2 gas and secured against Cu_2S counter electrodes

containing polysulfide electrolytes. Structural properties of CdZnS and Mn-doped CdZnS QDs were characterized by X-ray diffraction (XRD) on a Rigaku x-ray diffractometer with Cu K_α (λ= 154,059 pm) radiation. Optical characterization was performed by ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectroscopies on a Perkin-Elmer Lambda 2 and a Perkin-Elmer LS 50B, respectively.

The measurements were performed in ambient atmosphere. Output and transconductance characteristics of the device are measured using Keitheley SM-4210, where voltage is the source and current is the measured quantity. Constant gate bias in control gate is applied from another sourcemeter source and corresponding gate-current was measured with the same to ensure that the gate current remains a small fraction of the drain current.

3. Results and Discussions

3.1 Photovoltaic Properties

3.1.1 Incident Photons Current Efficiency (IPCE) Measurement

The main goal of this study is to determine the optimum Zn content that yields the best efficiency in CdZnS QDs containing different Zn concentrations by performing IPCE measurements. Therefore, this study is unique. In addition, the Zn_2SnO_4 was used as counter electrode instead of TiO_2. The IPCE spectrum of CdS and CdZnS QDs containing different Zn concentrations is shown in Figure 1.

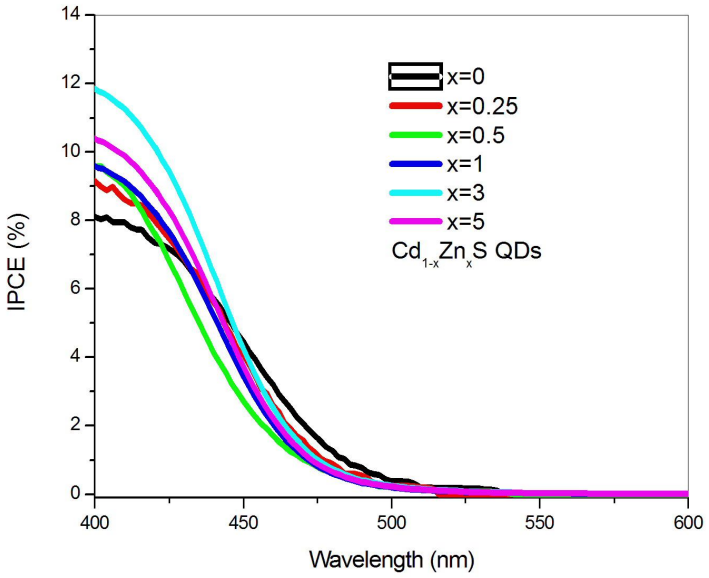

Figure 1: IPCE spectra of CdS and CdZnS QDs with different Zn concentrations attached on the Zn_2SnO_4 NWs.

As can be seen from the Figure 1, it was determined that the maximum percentage IPCE value (12%) obtained belongs to Cd1-xZnxS (x=3%) QDs. Thus, the optimum Zn concentration which provided the best efficiency for CdZnS was found as 3%. Another noteworthy observation is that the IPCE value of CdS increases when it is doped with Zn. In other words, the doping of Zn can be suggested as a suitable method to enhance the efficiency of CdS-based solar cells.

The structural, optical and elemental properties of Cd1-xZnxS (x=3%) QDs were investigated after determining the optimum Zn concentration in the CdZnS QDs yielding the best solar cell efficiency by IPCE

measurements.

3.2 Structural Properties

3.2.1 X-ray Diffraction (XRD) Measurement

XRD measurements were carried out on both samples to determine the structure of CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs and calculate their crystal size. Figure 2 indicates the XRD patterns for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs.

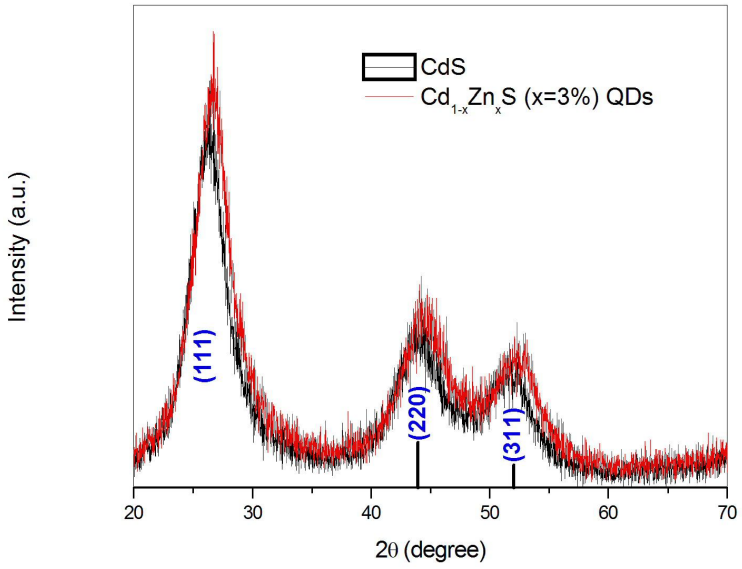

Figure 2: XRD patterns for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs

Three broad diffraction peaks corresponding to (111), (220) and (311) planes were obtained for both samples and it was determined that the obtained result agrees with standard data (JCPD No: 65-2887). Based on the Bragg`s diffraction angle corresponding to the plane (111), the lattice constant for both sample is calculated using the equation given below.

$$a = \frac{\lambda}{2sin\theta}\sqrt{h^2 + l^2 + k^2} \qquad (1)$$

Where, a is lattice constant, λ is the wavelength of XRD used, (hkl) is Miller indices and θ is Bragg`s diffraction angle. The obtained value of a is demonstrated in Table 1.

Table 1: Calculated lattice constant (a) values for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs

Samples (QDs)	a (Å)
CdS	5.92
$Cd_{1-x}Zn_xS$ (x =3%)	5.81

The lattice constant of $Cd_{1-x}Zn_xS$ (x=3%) QDs was found to be lower than that of CdS in the data presented in Table 1. The probable reason is that the ionic radius of Zn is less than the radius of Cd. This situation leads the distortion in the CdS lattice.

Another effect of Zn doping on the CdS QDs is that the crystal size changes. It is expected that the produced sample sizes will be small due to the broad XRD patterns. By using the Debye-Scherrer relation given in Equation 2, the crystal size of both samples was calculated.

$$d=0.9\,\lambda / (\beta \cos\theta) \quad (2)$$

Where d is the mean size of the QDs, λ is the wavelength of x-ray, β is the broadening measured as FWHM in radians, and θ is Bragg's diffraction angle. The crystal size of CdS QDs was calculated as 2.2 nm while this value for $Cd_{1-x}Zn_xS$ (x=3%) QDs, was 2.19 nm. As can be seen the results obtained, Zn doping has an active role in changing the crystal size of CdS QDs.

3.3 Optical Properties

3.3.1 Optical Absorption Measurement

Investigation of optical properties such as energy band gap and characteristic absorption of semiconductor materials is important for the use of these materials in optoelectronic fields. The optical absorption spectrum obtained for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs as result of measurements performed at room temperature in the range of 350 to 600 nm, is indicated in Figure 3.

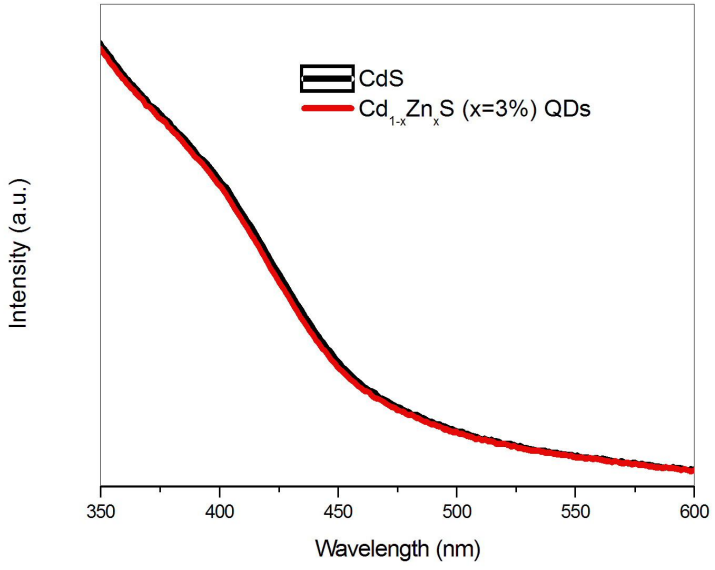

Figure 3: UV-VIS absorption spectrums of CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs.

As shown in Figure 3, a slight blue shift was observed in the absorption shoulder of $Cd_{1-x}Zn_xS$ (x=3%) QDs compared to CdS. The reason of this shift is that Zn^{2+} ion, which causes the crystal size to decrease, resides instead of Cd^{2+} ion. This also confirms the existence of quantum confinement effect.

The presence of a shift in the absorption shoulder indicates the energy gap of CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs will be different. To calculate the band gap energy for each of the two samples, Tauc relation, referred to in Equation 3, are used.

$$\alpha h\upsilon = C(h\upsilon - Eg)^n \quad (2)$$

Where α is the absorption coefficient, n=1/2 or 2 for direct or indirect allowed transition, respectively, C is the characteristic parameter for respective transitions, hυ is photon energy and Eg is energy band gap. Figure 4 demonstrates $(\alpha h\upsilon)^2$ versus hυ for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs.

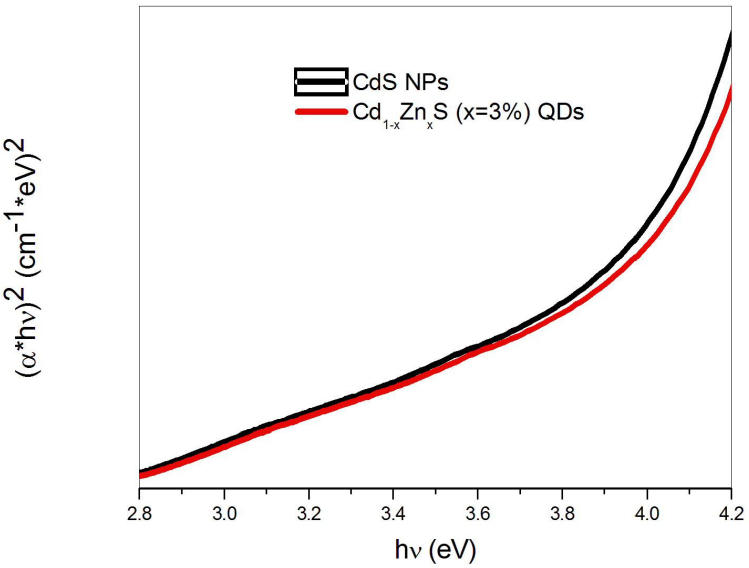

Figure 4:Plots of $(\alpha h\upsilon)^2$ versus hυ for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs.

The energy band gap values obtained for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs are 3.82 and 3.85 eV, respectively. The energy band gap of both samples is higher than the band gap of the bulk CdS (2.42 eV). This is an indication that the crystal sizes of the samples will be at the nanometer range. Consequently, this change in band gap values has occurred since Zn doping play an effective role in adjusting the band gap of CdS.

3.3.2 Photoluminescence (PL) Measurement

Photoluminescence (PL) measurements, another optical analysis, were carried out at room temperature and under 310 nm excitation wavelengths to study the luminescence properties of both samples. Figure 5 reveals the PL spectra of CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs.

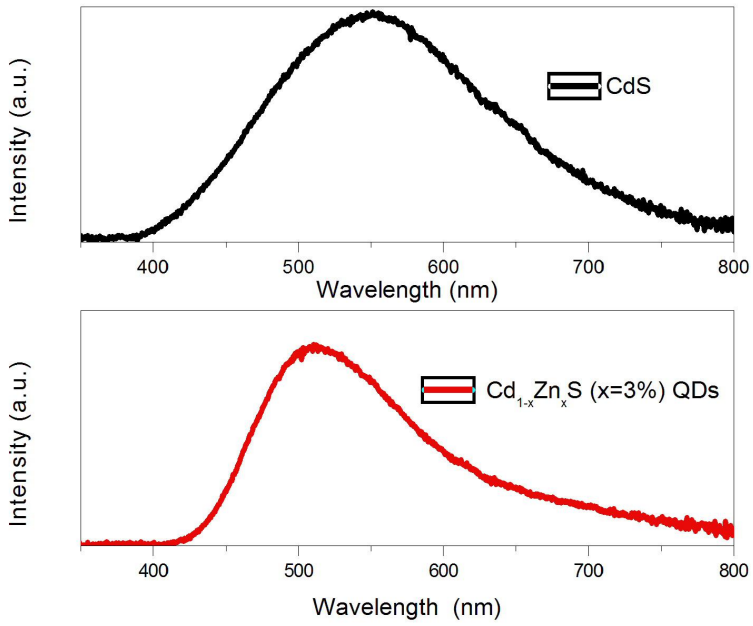

Figure 5: The room temperature PL excited with a wavelength of 310 nm for CdS and $Cd_{1-x}Zn_xS$ (x=3%) QDs.

A wide luminescence peak at 550 nm belonging to CdS QDs was observed. This luminescence band is attributed to the radiation transition of surface defects. Compared to CdS QDs, the PL spectrum (509 nm) of $Cd_{1-x}Zn_xS$ (x=3%) QDs, show a shift towards shorter wavelength. The reason for this shift is explained as follows:

In CdS QDs, electrons are caught by defects existing in the band gap when they are excited from the valence band (VB) to conduction band (EB). When these QDs are doped with Zn, these surface defects are modified. This satiation broadens the band gap of CdS. In other words, it results in a shift towards the short wavelength in the PL spectrum.

4. Conclusions

CdS and CdZnS QDs containing concentrations of 0.25, 0.5, 1, 3 and 5% Zn were successfully synthesized at room temperature by chemical precipitation method. The main aim of our current study is to determine the Zn content that yields the best efficiency by taking IPCE measurements of CdZnS QDs containing Zn at different concentrations. The IPCE results show that CdS QDs have 12% efficiency when Zn is doped at 3%. This result indicates that the optimum Zn concentration, which gives the best efficiency, is 3%.

Structural and optical analyzes of $Cd_{1-x}Zn_xS$ (x=3%) QDs were performed after determining that the optimum Zn concentration was 3%. Based on the XRD measurements, it was observed that the crystal size of $Cd_{1-x}Zn_xS$ (x=3%) QD is lower than CdS. In the absorption spectrum obtained to this XRD result, the energy band gap of $Cd_{1-x}Zn_xS$ (x=3%) QD was found to be larger than that of CdS. This situation is explained by the quantum confinement effect. In other words, as the energy band gap increases, the crystal size of the QDs decreases.

Consequently, $Cd_{1-x}Zn_xS$ (x=3%) QDs can be promising materials that can be used in solar cell application, as the increase in solar cell efficiency is observed when CdS QDs are doped with Zn content.

Acknowledgements

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