

THE NATURE OF OPTICAL TRANSITION IN THE CdS_xSe_{1-x} SEMICONDUCTOR NANOCRYSTALS

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1. Introduction

Semiconductor nanoparticles have been studied extensively for a quarter century due to their potential applications in semiconductor lasers, nonlinear optical devices, photovoltaic cell, thin film transistors, display devices and gas sensors [1-3]. Nanometer –sized crystals have distinctive optical properties due to the confinement of charged particles in all three space dimensions. The band gap can be modified to optimize the optical properties of the nanostructure by controlling its size. CdS_xSe_{1-x} semiconductor nanocrystals in glass have been most widely studied in a model system for quantum-confinement effects through optical methods [4,5]. In this work, we analyze the nature of optical transition in the CdS_xSe_{1-x} semiconductor nanocrystals, which are in different stages of formation.

2. Experiment

The CdS_xSe_{1-x} nanocrystals in silicate glass were fabricated using the procedure of [6]. The samples differ from each other by mean sizes of nanocrystals and degrees of perfection of crystal lattice. The formation of semiconducting nanocrystals corresponded to a thermal treatment temperature of 530⁰C. The temperature of the heat treatment is reached over one hour, then the samples are stored at a constant temperature (sample T₁ is not thermally processed and the processing times of samples T₂–T₈ at a temperature of 530⁰C are t₂=5 min, t₃=15 min, t₄=35 min, t₅=65 min, t₆=125 min, t₇=245 min and t₈=425 min). The transmission spectra studied in the wavelength interval 300-900 nm using Ocean optics USB-4000 spectrometers.

On the spectral dependence of the absorption coefficient can distinguish the fundamental absorption region, which corresponds to electron excitation from the valance to conduction bands. The fundamental absorption region can be used to determine the nature and value of the optical band gap (E_g). The optical band gap has been calculated using Tauc's formula [7].

$$(\alpha h\nu)^{1/m} = A(h\nu - E_g), \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is a constant dependent on the nature of the optical transition, and m indicates the nature of optical transition in the material. For bulk semiconductors the value of m is $1/2, 2, 3/2$, and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions [7] respectively. As CdS_xSe_{1-x} is a direct band gap material, $m = 1/2$ for the allowed transition. The band gaps has been calculated by extrapolating the linear region of the plots $(\alpha h\nu)^2$ vs. $h\nu$. In samples that are in the initial stage of formation is not always possible to select a linear region, that makes it difficult to determine the value of the energy gap. In such samples, E_g can be determined from the relationship $\frac{d\{\ln(\alpha h\nu)\}}{d(h\nu)}$ vs. $h\nu$. Now Eq.(1) can be written as follows:

$$\frac{d\{\ln[\alpha(h\nu)]\}}{d(h\nu)} = \frac{m}{(h\nu - E_g)} \quad (2)$$

So, there should be a discontinuity in $\frac{d\{\ln[\alpha(h\nu)]\}}{d(h\nu)}$ vs. $h\nu$ plot at the bandgap energy. In fact, the value of the bandgap energy can be considered energy $h\nu$ in which dependence $\frac{d\{\ln[\alpha(h\nu)]\}}{d(h\nu)}$ vs. $h\nu$ is a maximum. In order to construct the mentioned plot, dependence $\ln(\alpha h\nu) = f(h\nu)$ was fitted to polynomial form. Further, the mathematical equation describing the dependence is derived by $h\nu$. A few examples depending $\frac{d\{\ln[\alpha(h\nu)]\}}{d(h\nu)}$ vs. $h\nu$ are shown in Fig. 1. It is seen that maximum is relatively weak at the initial stage of the annealing, which can be due to the absence of the perfect crystal lattice. When the heat treatment time increases the degree of perfection of the lattice increase and the maximum become more expressed. Fig. 2 shows the dependence of the bandgap, which were determining two different ways vs. heat treatment time. As can be seen the value of bandgap are close enough. Reducing the value of the band gap of the heat treatment time is

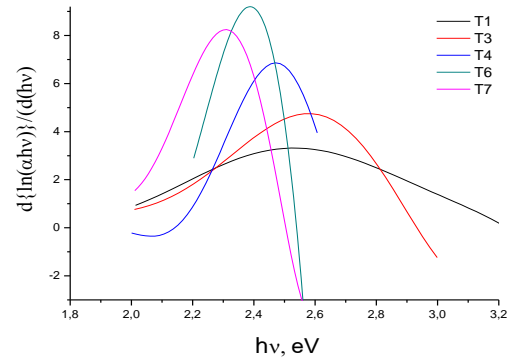


Fig.1. Plot of $\frac{d\{\ln[\alpha(h\nu)]\}}{d(h\nu)}$ vs. $h\nu$.

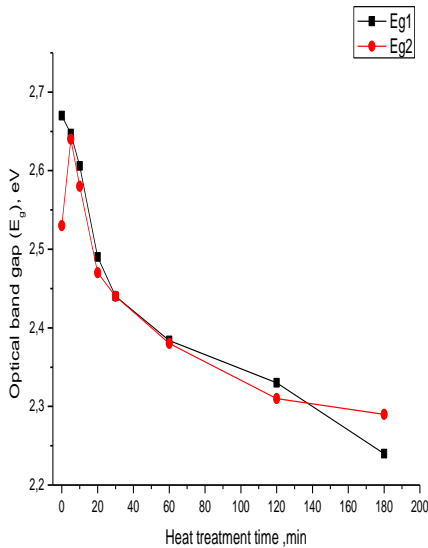


Fig.2. Dependence of the bandgap vs. heat treatment time.

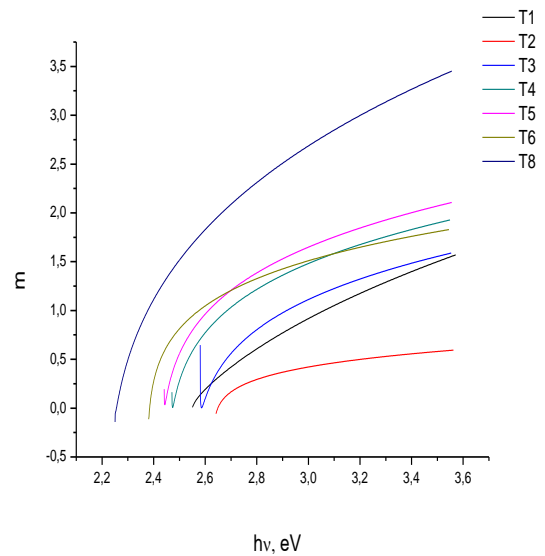


Fig.3 The spectral dependence of the coefficient m in the strong absorption region.

due to the increasing size of the nanocrystals.

The dependence of the coefficient m from the incident photon energy, contains important information about changes in the nature of the optical transitions in nanocrystals. Using the value of bandgap energy, we can determine the value of m . Again, from Eq. (2) we can get

$$\ln(\alpha h\nu) = \ln A + m \ln(h\nu - E_g) \quad (3)$$

The value of m was determined from the slope of $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_g)$.

To determine the spectral dependence of the m was previously plotted $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_g)$. Dependence $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_g)$ was fitted to polynomial form. It was shown that this dependence is well described by a fourth-order polynomial. Further, the mathematical equation describing the dependence is derived by $\ln(h\nu - E_g)$. Figure 3 shows the spectral dependence of the coefficient m in the strong absorption region. As can be seen from the resulting dependency value m increases monotonically in the range (0 ÷ 3). This behavior m indicates that depending on the photon energy changes the nature of optical transition. If at the initial stage of formation of nanocrystals value of m is in the range of 0.5, which corresponds to the allowed direct transitions, further approaching to 3/2, which corresponds to the forbidden direct transitions. In order to get the law of change m vs. $h\nu$ the experimentally obtained dependence was approximating expression $m = K(h\nu - E_g)^c$. The experimental dependence is well described by this expression and the coefficient c for different samples varied within (0.36 ÷ 0.7).

3. Conclusions

Thus, by means of optical transmission spectra investigated the nature of optical transition in the $\text{CdS}_x\text{Se}_{1-x}$ semiconductor nanocrystals, which are in different stages of formation. It is shown that the initial stage of formation of nanocrystals predominate the allowed direct transitions, further the forbidden direct transitions.

References

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