SPECTRAL DEPENDENCE OF THE PHOTOLUMINESCENCE
OF CdS$_{1-x}$Se$_x$ NANOCRYSTALS EMBEDDED IN SILICATE GLASS

L. Grigoryan$^1$, M. Ghulinyan$^2$, P. Petrosyan$^1$, and H. Petrosyan$^1$

$^1$Yerevan State University, ppetros@ysu.am,
$^2$University of Trento, Trento, Italy

1. Introduction

Semiconductor CdS$_{1-x}$Se$_x$ quantum dots embedded in a silicate glass matrix have attracted considerable attention over the last years because of their novel optical and dynamic properties associated with the quantum confinement effects [1-3]. The optical properties of silicate glasses containing semiconductor nanocrystals are controlled by the nanocrystal size and size distribution. Such an approach, to our opinion, is not satisfactory. The studies made by us show that during a heat treatment the final formation of the CdS$_{1-x}$Se$_x$ nanocrystal structure does not occur at once. At the first stage of the heat treatment, a formation of controlled structure takes place, but the crystal lattice is not completely formed at that stage. It takes the crystal lattice a long-term heat treatment to be completely formed. It is shown that the nucleus of crystal formed at a high temperature (560°C) and subjected to further heat treatment at 450°C during which the diffusion growth of the nucleus of crystal is missing, undergoes structural changes. These structural changes occurring during the heat treatment can affect the photoluminescence (PL) properties of the samples.

The aim of this work is to study the effect of structural changes in semiconductor CdS$_{1-x}$Se$_x$ nanocrystals occurring during their heat treatment on the PL properties of silicate glasses containing them.

2. Experimental results and discussion

The samples have been grown using the method described in [4, 5].

Two of the studied samples differ from each other by the time-period of their heat treatment at 560°C (Ut5–3 minutes, Ut4–22 minutes, and the third sample Ut–6 was subjected to 1.5 hour heat treatment at 450°C after three-minute heat treatment at 560°C).

PL measurements on the samples have been performed using the 488 nm line of the Ar laser (continuous) in the wavelength range from 500 to 900 nm. Different pump powers checked 0.7 mW to 12 mW, without any essential change in the PL shape. Simultaneously the optical spectra of the samples have been measured (Fig. 1). Fig. 2 gives the PL spectra of silicate glasses
containing semiconductor CdS$_{1-x}$Se$_x$ nanocrystals obtained by different regimes. As seen from the obtained results, PL is very weak at the first stage of the nucleus formation.

![Graph 1](image1)

**Fig. 1**

![Graph 2](image2)

**Fig. 2**
This is because of the fact that the crystal lattice is not completely formed yet at the first stage and the recombination is non-raying in these conditions. The heat-treatment of the same samples at a lower temperature (Ut6) in which, as we have already mentioned, the formation of the crystal lattice grows to perfection caused the increase in the PL intensity by one order of magnitude. More intensive is the photoluminescence of the samples subjected to longer heat-treatment at 560°C. In the PL spectrum two maxima are observed around 550 nm and 760 nm. The studies of the PL spectra of the semiconductor CdS_{1-x}Se_{x} nanocrystals of different sizes show that two maxima ranges can be distributed in the spectrum. One maximum is localized at the absorption edge which corresponds to the recombination of the charge carriers between the lower energy levels or shallow traps. The PL spectra study at 77 K is a proof of this. The temperature decrease leads to about a similar shift of the absorption edge and the first maximum to the short-wave range. The second maximum is much broader and is shifted to the long-wavelength range. The band gap energy of the studied semiconductor nanocrystals cannot be smaller than 1.8 eV, and the size quantization can only lead to an increase in the energy. In the PL spectrum intensive luminescence is observed in the range 650-850 nm which we think to be connected with the defects that are made either in the semiconductor nanocrystals which are being formed or on the nanocrystal – matrix interface. The PL in this range can be conditioned by the recombination of the charges on the shallow traps and the opposite charges that are in the deep traps. It is known [6] that the carriers are most likely trapped in the states localized at the semiconductor-matrix interface or outside the nanocrystal in the surrounding matrix. The surface traps can be associated with Cd^{2+}, S^{2-}, and Se^{2-} vacancies, dangling bonds, or external adatoms. The electric charge of the trapped carrier can also change electronic states and wave functions in the nanocrystal. When the optical properties during the heat treatment process are studied, the influence mentioned above usually is not taken into consideration. This influence can become essential if we take into account the fact that during the heat treatment the ray intensity in the second range of the PL spectrum can be changed by one order of magnitude. As the latter, according to the studies, is associated with the concentration of the deep traps, it can be assumed that such a change in the trap concentration will have noticeable effect on the energy spectrum of nanocrystals.

3. Conclusions

We have studied the PL of the silicate glasses containing semiconductor CdS_{1-x}Se_{x} nanocrystals at the different pump powers. The studies of the spectrum have shown that two maxima ranges can be distributed in the spectrum. One maximum corresponds to the recombination of the charge carriers between the lower energy levels or shallow traps. The other
maximum is associated with the recombination of the charges on the shallow traps and the 
opposite charges that are in the deep traps. It is shown that with the help of heat treatment the PL 
intensity is possible to increase more than one order of magnitude.

REFERENCES

4. L. Grigoryan, P. Petrosyan, and V. Bellani. The fifth International Conference, 
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