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Enhancement of CdSSe QD exciton luminescence efficiency by hydrogen RF plasma treatment

V.P. Kunets, N.R. Kulish, V.V. Strelchuk, A.N. Nazarov, A.S. Tkachenko, V.S. Lysenko, M.P. Lisitsa

Institute of Semiconductor Physics, NAS of Ukraine, 45 prospect Nauky, 03028 Kyiv, Ukraine
Phone: +38 (044) 2656282; Fax: +38 (044) 2658342; E-mail: vl_kunets@yahoo.com

Abstract. We report an enhancement of exciton luminescence in CdS_xSe_{1-x} QD embedded into borosilicate glass matrix and then treated by the low-temperature hydrogen RF plasma. Results clearly confirm the essential crushing of the surface levels that have a high nonradiative recombination efficiency.

Keywords: quantum dots, photoluminescence, surface passivation, RF plasma treatment.

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1. Introduction

Since the pioneering works by G. Bret [1], V. Borodulin [2] and M. Lisitsa [3], CdSSe-doped glasses have been extensively studied in two directions. Besides investigations of the quantum confinement effects in CdSSe QDs, they were widely tested as the nonlinear-optical materials that can be employed in optical devices. That is why during the early years much interest had been focused on measurements of the absorption saturation threshold (I_s) [4], the Kerr susceptibility $\chi^{(3)}$ [5] and the carrier *lifetime* τ [6] that are the basic parameters in the field. Meanwhile, the experimental data on the *lifetime* seem to be inconsistent and sometimes contradictory varying from 10 ps to 10 ns and even more. The following investigations were then directed on the *lifetime* size dependence [7], and the reasonable explanation based on the role of the surface traps was proposed [8]. On the other hand, the exciton luminescence efficiency does not exceed several percents in these glasses, which is obviously caused by a high nonradiative recombination efficiency of the surface levels. The thermal annealing at high temperatures ($\sim 700^\circ\text{C}$), which is usually used to anneal the deep levels in composite structures can not be used to modify QD surface, because it stimulates the growth of QDs producing the new dangling bonds and the surface traps for the carriers. Therefore, to use the CdSSe-doped glasses in the nonlinear optical devices [9], one should have the low temperature method to modify the surface states con-

trolling the *lifetime* and the exciton luminescence. In this paper, we report the results about the low temperature hydrogen RF plasma treatment of CdSSe-doped glasses that clearly evidence the crushing of the surface levels rising the exciton *lifetime* and luminescence efficiency.

2. Experiment

CdSSe-doped glasses with different QD's composition were studied at room temperature. The samples were excited with a CW Ar⁺ laser ($\lambda = 488.0$ nm, $P < 100$ mW). The PL light was monitored with DFS-24 spectrometer equipped with a photomultiplier and a photon counting system. First order Raman LO spectra were used to control QD composition. The luminescence spectra were measured using the samples prepared by the typical heat-treatment procedure [10] and the same samples but after their RF plasma treatment. The reactor of the diode type (the pressure in the chamber was 5×10^{-2} Torr, the frequency was 13.6 MHz) was used. The RF treatment with the power at 1.5 W/cm² and additional heating of the sample up to 200°C for 30 min has been performed. These power and additional heating correspond to the sample temperature of about 300°C [11]. This temperature was chosen to avoid the QDs growth. At these regimes the hydrogen atoms diffuse into the dioxide layer down to 400 nm [12]. Thus, we can suggest that in the CdSSe-doped glasses with QD concentration up to 10^{14} – 10^{15} cm⁻³ the distance of hydrogen penetration will have a similar order, which

is sufficient for PL measurements. In fact, the borosilicate glass matrix has the so-called “free” or “vacant” volume, which is associated with its porous structure and can consist of 0.01÷0.10 for various glasses. Thus, we think the real hydrogen penetration depth is greater (about several microns), because the hydrogen ions can diffuse along the porous surfaces in this case.

3. Results and discussion

Fig. 1 shows the PL spectra of CdS_xSe_{1-x} QDs before (curve 1) and after (curve 2) RF plasma treatment. All spectra were recorded at the same experimental conditions. The rise of the signal is clearly observed all over the investigated spectral region. Any valuable shift of the maximum was no observed. The halfwidth of the luminescence band was also remained practically invariable in the range of the measurement accuracy. The plasma stimulated enhancement of the PL signal was determined to be about several dozens of percents and could rise in some cases up to 70%. All the experimentally observed data are summarized in Table 1.

The relatively wide PL peaks in Fig. 1 are attributed to the direct electron-hole recombination in CdS_xSe_{1-x} QDs, which is also confirmed by the superlinear PL signal dependence on the excitation intensity. The short wavelength shift of the peaks is attributed to both the composition and the confinement of the electrons and holes in QDs. In Fig.1 the exciton peaks are only presented. The large halfwidth of the peak is particularly explained by the size dispersion of QDs. The average radius \bar{r} of QD's in our samples were less than the Bohr exciton radius in the bulk ($a_B \sim 3\div 5$ nm). In this strong confinement regime (the confinement energy was 150 to 200 meV), the electron-hole pair in QD (“squeezed pair” or “exciton”) is considered as the elementary electron QD excitation. The short wavelength laser excitation (488.0 nm) was used to excite the low-energy confined states in QDs and to avoid the photoionization effects [13]. In general, PL intensity is described by the formula:

$$I_{PL} = I_0 [1 - (1 - R)^2 \exp(-Kd)] \eta^* \eta_{in}, \quad (1)$$

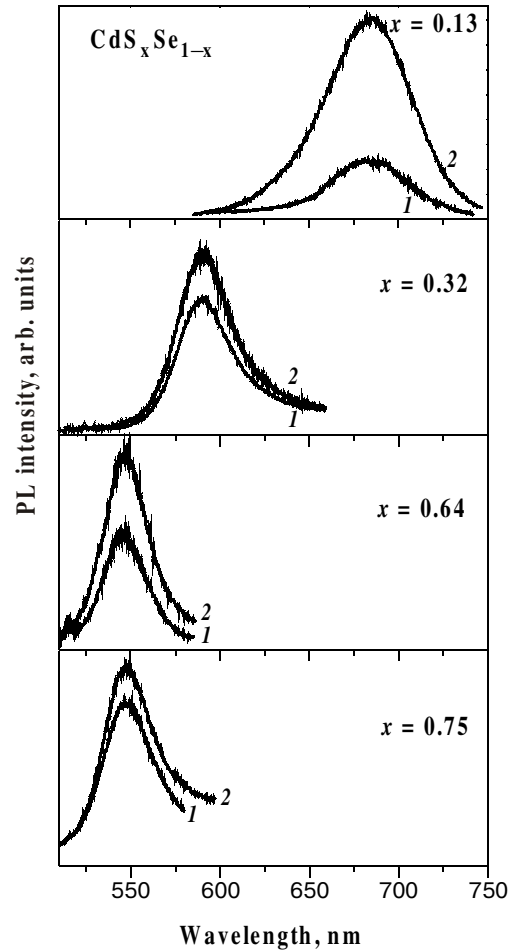


Fig. 1. Exciton PL spectra of CdS_xSe_{1-x} QDs at room temperature before (1) and after (2) RF plasma treatment.

where R is the reflection coefficient, K is the absorption coefficient, d is the sample thickness, η_{in} is the internal luminescence quantum yield, η^* describes the luminescence losses in the structure due to the light scattering, reabsorption, etc. The value η_{in} is related to the carrier lifetime or radiative recombination time τ_R by the following formula:

Table 1. Sample and PL spectra parameters for four compositions.

Parameter	Composition							
	CdS _{0.13} Se _{0.87}	CdS _{0.32} Se _{0.68}	CdS _{0.64} Se _{0.36}	CdS _{0.75} Se _{0.25}				
Average radius, \bar{r} , nm	7.80 [10]	2.50 [10]	2.35 [10]	2.65 [10]				
QD concentration, N , cm ⁻³	$\sim 10^{15}$ [10]	$5.3 \cdot 10^{13}$ [10]	$2.8 \cdot 10^{14}$ [10]	$\sim 10^{13}$ [10]				
PL spectra parameters	before RF-treat.	after RF-treat.	before RF-treat.	after RF-treat.	before RF-treat.	after RF-treat.	before RF-treat.	after RF-treat.
PL max., nm	685.0±0.5	684.5±0.5	589.4±0.5	589.9±0.5	546.5±0.5	546.8±0.5	546.1±0.5	547.1±0.5
PL halfwidth, eV	0.192	0.190	0.131	0.131	0.147	0.148	0.121	0.123
PL intensity, arb.un.	1.00	1.70	1.00	1.24	1.00	1.18	1.00	1.39

$$\eta_{in} = \tau_S / (\tau_R + \tau_S) \approx \tau_S / \tau_R, \quad (2)$$

where τ_S – is the carrier *lifetime* determined by the nonradiative recombination processes. It is taken into account in (2) that usually in QDs $\tau_S \ll \tau_R$. This fact is clearly confirmed by both the data on the absorption saturation [9] and the low external PL quantum yield ($\eta_{in}\eta^* \sim 1\%$). For the “exciton” luminescence

$$\eta_{in} \approx \tau_S / \tau_{EX} = Bn / \sigma_S \nu N_S, \quad (3)$$

where $\tau_{EX} = 1/Bn$ is the exciton lifetime or radiative exciton recombination time, B is the coefficient of the bimolecular recombination, n is the exciton concentration, $\tau_S = 1/\sigma_S \nu N_S$, σ_S is the cross section for the carriers captured by the surface traps, ν is the thermal velocity of the carriers, and, finally, N_S is the concentration of the surface traps that are the effective non-radiative recombination levels for the electron or holes in these small QDs [9].

The B coefficient does not depend on the excitation intensity and describes the probability of the bimolecular recombination. As a rule, B , σ_S and ν do not also depend on N_S . On the other hand, only two possible ways can be considered to increase of η_{in} (see, formula (3)): the increasing of the exciton concentration (n) which recombine radiatively, while fixing N_S value, or the decreasing of N_S value at the same excitation conditions. In our case, we intentionally tried to change the value of N_S using the RF plasma treatment of the samples and measuring the PL spectra under the same conditions. This allowed us to rise drastically the η_{in} (see, formula (3)) and, finally, the external luminescence yield $\eta_{in}\eta^*$ at the constant losses η^* that is experimentally observed as the enhancement of the exciton PL intensity. In general, we realize that the non-radiative recombination efficiencies for electrons and holes are quite different, and that the surface modification drastically changes τ_S value probably for one type of the carrier only. Meanwhile, the photoionization of QD which modifies the charge of the E_1^- -centers in the glass matrix near the QD surface [13] can also effect on τ_S . To develop the model of the CdS_xSe_{1-x} QD surface modification by the RF plasma treatment one should perform additional investigations. At the same time, we also realize that the effect is, one as the matter of fact, more strong than we've visually observed. Indeed, the glass thickness modified by the hydrogen atoms is smaller than the absorption light depth. In this case, the PL signal is formed by the whole excited region of the glass, while the thin hydrogen riched layer of the glass gives only to the effect.

4. Conclusions

We prepared CdSSe QD with the modified surface using the low temperature RF hydrogen plasma treatment. In these samples, we have observed the enhancement of the

exciton luminescence in comparison with the non-treated samples. Using the simple idea about the mechanism of the exciton luminescence in QDs, we have concluded that such treatment decreases the quantity of the nonradiative recombination centers on QD surface. This result clearly demonstrates the possibility of the effective QD surface modification in these composite materials.

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