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E-beam irradiation effect on CdSe/ZnSe QD formation by MBE: deep level transient spectroscopy and cathodoluminescence studies

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Abstract

CdSe/ZnSe structures containing 1 or 15 thin (3–5 monolayers) CdSe layers were studied by cathodoluminescence (CL) and deep level transient spectroscopy (DLTS). The DLTS spectra consisted of peaks from deep levels (DLs) and an additional intense peak due to electron emission from the ground quantized level in the CdSe layers. Activation energy of this additional peak correlated with an energy of the CdSe-layer emission line in the CL spectra. Electron-beam irradiation of the structure during the growth process was found to influence the DLTS and CL spectra of the CdSe layers, shifting the CdSe-layer emission line to the long-wave side. The obtained results are explained using the assumption that e-beam irradiation stimulates the formation of quantum dots of various sizes in the CdSe layers.

1. Introduction

In recent years, interest in CdSe/ZnSe QD structures has increased. Structures containing thin CdSe layers in a crystal ZnSe matrix are used as modelling objects in QD research in II–VI compounds. They can also be used as an active area of semiconductor lasers radiating in the visible part of the spectrum [1]. To date there have been many articles devoted to research into the structural and optical properties of CdSe/ZnSe QD structures and their dependence on growth conditions. However, some problems connected with the determination of electronic levels in QDs and the efficiency of charge carrier capture by these levels remain unsolved.

Deep level transient spectroscopy (DLTS) is a very informative method of low-dimensional structure characterization. For example, DLTS allows us to measure the band offset in QW structures [2, 3], which is important information for structure applications. In [4] the height of an energy barrier for charge carrier capture into InAs/GaAs QDs was determined by using

Table 1. Parameter of CdSe/ZnSe QD structures.

No. of sample	Quantity of QDs layers	Thickness of each CdSe layer (ML)	Barrier layer thickness (nm)
278	1	3.5	—
279	1	5	—
281	15	3	200
283	15	3	12
284	15	5	50

DLTS together with photoluminescence. The DLTS method was also used to research the influence of deep levels (DLs) located around InGaAs QDs on charge carrier capture [5]. However, such a method has not been used for detailed investigation of QD structures based on II–VI compounds.

In this work we represent results of MBE-grown CdSe/ZnSe-structure research by DLTS and cathodoluminescence (CL) methods. We use the current relaxation mode of the DLTS (CDLTS) because the structures studied were high-resistance. Special attention was given to compare the CDLTS and CL spectra received from the e-beam irradiated area of the structure with similar spectra from other parts. The irradiation was carried out during epitaxy using RHEED diffraction. We found a difference in the CDLTS spectra of irradiated and radiation-free areas that correlated with those in the respective CL spectra. The e-beam irradiation effect on QD formation had previously been found by CL [6].

2. Experiment

The studied structures were grown on n^+ -GaAs(100) by MBE and contained 1 or 15 CdSe layers separated by ZnSe barriers (see table 1). The thicknesses of the layers were evaluated from RHEED oscillations during the growth. First a 1 μm thick ZnSe buffer layer was grown at $T = 280^\circ\text{C}$ and a VI/II flux ratio of 3:1. The CdSe layer was deposited at a lower temperature $T = 230^\circ\text{C}$. After deposition of each CdSe layer, the Cd flux was blocked and the structure was heated up to $T = 340^\circ\text{C}$ and then cooled to $T = 280^\circ\text{C}$ under Se flux. The time durations of the temperature increase and decrease were 4 and 5 min respectively. After each procedure the next ZnSe barrier or a 100 nm thick cap layer was grown. The e-beam for RHEED supervision was switched on before each deposition of CdSe and was switched off before the next ZnSe layer was grown. The e-beam had the following parameters: the current was 0.2 mA, the electron energy was 12 keV, the diameter of the e-beam spot on the growing surface was 0.5 mm and the angle between the e-beam and the growing surface was 3° . The structure area irradiated by RHEED electrons represented a strip 1.5–2 cm in length and 0.5 mm in width. Below it is referred to as a trace.

CL spectra were measured at $T = 14$ and 300 K, electron energy $E_e = 10$ and 30 keV and current density $j_e = 0.1 \text{ mA cm}^{-2}$. Thermal evaporation of In on the back side of the GaAs substrate and Ni on the ZnSe cap layer was used to prepare diode-like structures for CDLTS measurements. Schottky diodes based on sample Nos 278 and 279 were formed outside the e-beam trace. On structure No. 284 Schottky contacts overlapped the e-beam trace but were larger than the trace area. On the basis of samples Nos 281 and 283 two diode-like structures were made with and without the e-beam trace between the contacts. We applied the CDLTS method [7] based on a relaxation of the electrical current through the structure because samples were compensated and have high specific resistance ($10^5 \Omega \text{ cm}$).

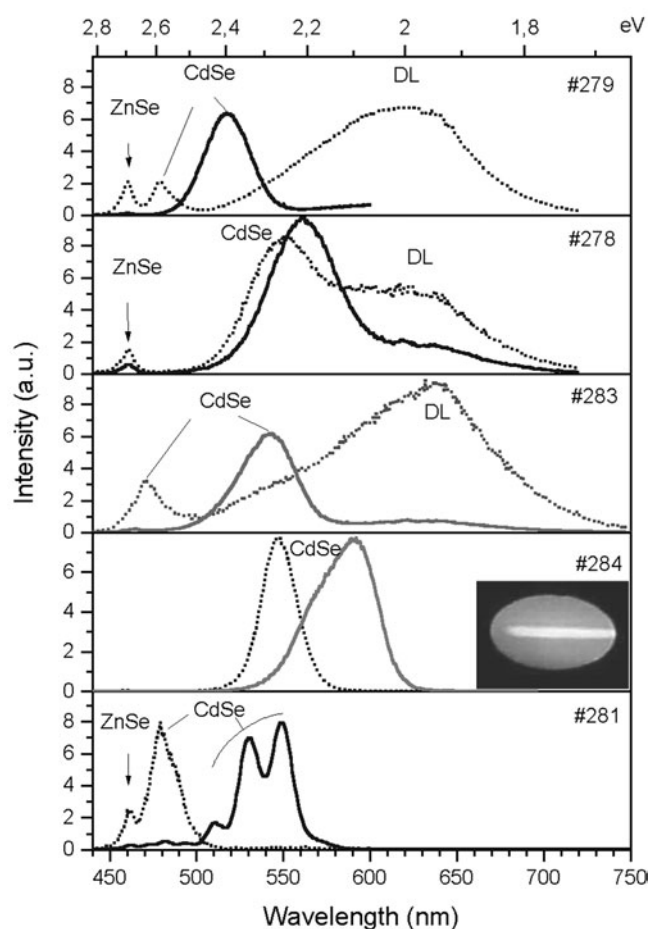


Figure 1. CL spectra of CdSe/ZnSe structures at $T = 300$ K and $E_e = 10$ keV for the area with the trace (solid curves) and without one (dashed curves). The inset shows the CL image of a small area of the multi-CdSe-layer structure with the RHEED e-beam trace.

3. Results and discussion

3.1. Cathodoluminescence study

CL spectra of the CdSe/ZnSe structures measured at $E_e = 10$ keV and $T = 300$ K are presented in figure 1. Solid curves correspond to structure areas inside the e-beam trace whereas dashed curves correspond to areas outside the trace. In the inset, the CL image of a small area of structure No. 284 with the RHEED e-beam trace is shown. The oval green spot (dark grey on the inset) is an area excited by the CL e-beam of 5 mm in diameter. The yellow stripe (light grey on the inset) is the trace from the e-beam used at RHEED observation during epitaxy. The image is a visual demonstration of the strong difference in CL emission from within the trace area and outside it.

The CL spectra contain a weak emission line from the buffer layer or barrier ZnSe layers, a wide peak due to DLs with a maximum close to 2 eV (630 nm) and an intense line from the CdSe layer. If the area outside the trace increases, with the CdSe layer

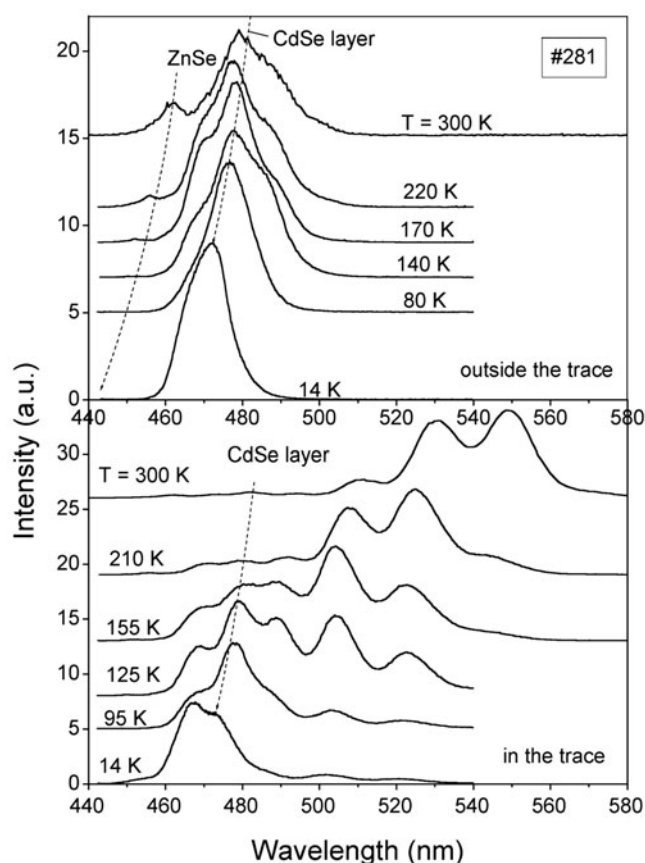


Figure 2. CL spectra of CdSe/ZnSe structure (sample No. 281) at different temperatures from 14 to 300 K.

thickness increasing from 3.5 up to 5 ML (sample Nos 279 and 278), then this results in a widening of the CdSe-layer emission line and its strong long-wave shift from 2.57 up to 2.25 eV. A similar effect has been observed by many scientific groups [8, 9]. They explained it by a QD formation at the indicated CdSe-layer thickness range. For all samples, the CdSe-layer emission line for the radiation-free area was at larger energies than that for the trace area. Based on the mentioned long-wave shift with increasing CdSe layer thickness, it may be supposed that the actual thickness of the CdSe layer outside the trace is less than within the trace. The e-beam irradiation is likely to increase the concentration of atomic Se on the growth surface and hence decrease the probability of Se desorption that results in an increase in the average thickness of the Cd layer. Furthermore the defect concentration in the trace is reduced. The decrease of the DL emission intensity points to this. For the sample No. 281, the CdSe-layer emission spectrum for the trace area consists of several lines. Apparently these lines are due to light interference caused by reflection from the upper and interior surfaces of the structure.

CL spectra of sample No. 281 at various temperatures from 14 up to 300 K inside and outside the trace are represented in figure 2. The maximum of the CdSe-layer emission line from the area outside the trace shifts to the long-wave side with increasing temperature approximately as the ZnSe layer emission line. The CdSe-related line has some shoulders that

are seen better at medium temperatures. The reason for this spectrum modulation is the light interference on the structure thickness mentioned before. The spectra from the trace consist of two parts. The first part is similar to the spectrum for the area outside the trace. The second long-wave part has a greater temperature dependence. A similar temperature dependence of photoluminescence spectra was observed in [10]. Following this work we assume that in structures Nos 279, 281 and 283 the CdSe layer outside the trace is partially diluted by zinc and has varied thickness and composition along the layer. In the whole structure, such a layer behaves in CL spectrum as a QW with localization of charge carriers depending on composition and thickness inhomogeneity. This localization reduces transport of excitons or charge carriers along a layer at low temperatures.

In the trace, three-dimensional formations of CdSe are also formed. Their electronic spectrum is determined by quantization in all three directions. Such formations behave as QDs in the CL spectrum. The ground energy levels for charge carriers in CdSe QDs depend on their sizes. In our structures, to all appearances, QD sizes change over a wide range, as in the structures studied in [10]. The density of such QDs is lower than the density of the located states in the CdZnSe layer. Therefore at low temperature when transport of excitons and charge carriers along a layer is ineffective, the CdSe QDs in CL spectra are seen weakly. Charge carrier capture by QDs directly from ZnSe layers is difficult also because of the presence of an energy barrier for such a capture, as has been found out for InAs/GaAs QDs [4]. The barrier is formed due to elastic strains in ZnSe layers around CdSe QDs because of a lattice mismatch. With increasing temperature, the transport of carriers along the CdZnSe layer and the efficiency of their capture in the QDs is increased. Besides, the capture efficiency directly from barrier layers is also increased. It is obvious that QDs of smaller size will be filled first. They radiate in a shorter wave spectral range. This explains the temperature dependence of the observed CL spectra.

In structures Nos 278 and 284, the CdSe-layer emission line from the area outside the trace may be interpreted as an emission due to QDs. However, the temperature shift of this line is close to that for the ZnSe layer. This is possible if the QD density is very high and the redistribution of carriers on the QD ensemble occurs effectively enough and only weakly depends on temperature. In this case it is difficult to distinguish the QD ensemble from a strong nonuniform CdZnSe layer. However, in the trace of these structures, CdSe QDs of larger size are formed and their surface density is small enough. Their properties are described as for structures Nos 279, 281 and 283.

3.2. DLTS study

CDLTS spectra of structures Nos 281 and 284 are presented in figures 3 and 4 respectively. They contain peaks from electronic traps with deep energy levels E_2 , E_3 and E_4 registered in the ZnSe buffer early [11] and peaks E_1 , E_1^* and H_1 in the low-temperature range. The basic parameters of the DLs are indicated in table 2 for particular values of filling voltage V_f and depletion voltage V_r . We registered the peak E_1^* in samples with 15 CdSe layers in the trace area. The activation energy of peaks E_1 and E_1^* correlates with the CdSe-layer emission line energy in CL spectra for different samples. We suppose that the peaks E_1 and E_1^* are connected with electron emission from ground quantized levels in the CdSe layers. The apparent broadening of these peaks is due to nonuniformity of CdSe-related QWs or QDs. Obviously the temperature standing of peak E_1 or E_1^* is determined by what QDs are filled under those or other filling conditions. The dependence of peaks E_1 and E_1^* on filling conditions is represented in table 3. For samples Nos 281, 283 and 284, increasing V_f at constant V_r leads to moving the peaks E_1 and E_1^* to the high-temperature side. The activation

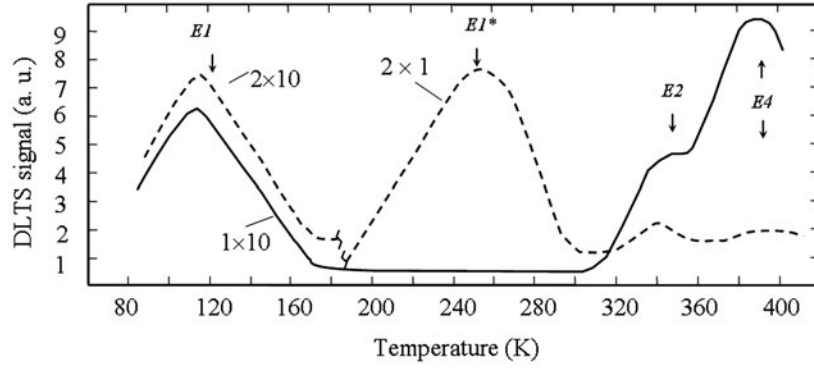


Figure 3. CDLTS spectra (sample No. 281) without the trace (curve 1) and with the trace (curve 2) at $V_r = -1$ V and $V_f = 0$ V, emission time constant $\tau = 133.8$ μ s and filling pulse wide $t_p = 10$ μ s.

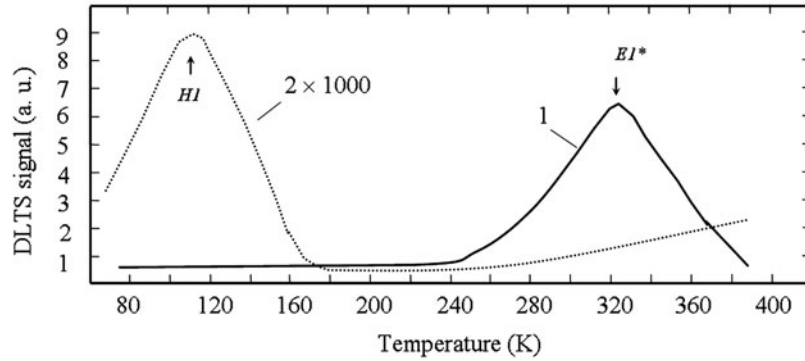


Figure 4. CDLTS spectra (sample No. 284) at $V_r = -1$ V and $V_f = 0$ V, $\tau = 11$ ms, $t_p = 3$ ms (curve 1) and $V_r = -1$ V and $V_f = 1$ V, $\tau = 15.99$ μ s, $t_p = 3$ μ s (curve 2).

energy of $E1$ and $E1^*$ increases; however, the sheet concentration (concentration of traps per 1 cm^2 of one CdSe layer) practically does not change. Such a dependence may be explained by the influence of DLs located around the QD on charge carrier capture by it [12]. However, another explanation is also possible. At $V_f = 0$ V only the QDs with quite low energy barriers for electron capture are effectively filled. The peak $E1^*$ in this case corresponds to electron emission averaged on an ensemble of QDs previously filled. With increasing V_f , the probability of infill of the QDs with more deep electronic levels, which have an accordingly higher initial barrier for electron capture, increases and this results in an increase of the average value of the activation energy for electron emission from an ensemble of the QDs filled.

To estimate a potential barrier height for electron capture in QDs we explored the dependence of the $E1$ and $E1^*$ amplitudes for structure No. 281 on the relaxation time as described in [4, 5, 13]. These examinations allow us to determine a temperature dependence of capture cross section $\sigma(T)$ as [4]: $\sigma_n(T) = \sigma_\infty \exp(-E_\sigma/k_B T)$ where σ_∞ is a constant independent of temperature, E_σ is the capture barrier, k_B is the Boltzmann constant. The results of such an approximation are $\sigma_\infty = 3.2 \times 10^{-13} \text{ cm}^2$, $E_\sigma = 24 \text{ meV}$ and $\sigma_\infty = 1.8 \times 10^{-13} \text{ cm}^2$, $E_\sigma = 150 \text{ meV}$ for $E1$ and $E1^*$ respectively. Obviously more DLs have higher capture barriers than has been supposed.

Table 2. Parameters of DLs obtained by CDLTS at $V_f = 0$ V, $V_r = -1$ V (level $H1$ was detected when $V_f > 1$ V). E_a is activation energy; σ is capture cross section; ρ is sheet concentration.

No. of sample	Deep level	E_a (eV)	σ (cm ²)	ρ (cm ⁻²)
278	$E1$	0.282 ± 0.02	1.6×10^{-14}	1.1×10^9
	$E3$	0.72 ± 0.03	4.1×10^{-15}	4.3×10^9
279	$E1$	0.105 ± 0.02	5.4×10^{-16}	2.2×10^8
	$E3$	0.72 ± 0.03	2.7×10^{-15}	3.9×10^9
281	$E1$	0.154 ± 0.02	3.9×10^{-15}	6.3×10^8
	$E2$	0.589 ± 0.05	9.6×10^{-14}	4.5×10^8
	$E4$	0.84 ± 0.03	1.9×10^{-12}	9.2×10^8
281, trace	$E1$	0.161 ± 0.02	3.0×10^{-15}	7.3×10^8
	$E1^*$	0.377 ± 0.03	4.2×10^{-15}	7.3×10^9
	$E2$	0.626 ± 0.04	8.9×10^{-14}	2.1×10^9
	$E4$	0.84 ± 0.03	8.3×10^{-13}	1.8×10^9
283	$E1$	0.134 ± 0.01	3.7×10^{-16}	9.1×10^9
	$E2$	0.536 ± 0.03	1.3×10^{-17}	5.4×10^9
	$E3$	0.714 ± 0.03	4.2×10^{-15}	7.7×10^9
283, trace	$E1$	0.139 ± 0.01	4.7×10^{-16}	1.2×10^9
	$E1^*$	0.287 ± 0.02	1.0×10^{-13}	2.4×10^9
	$E3$	0.721 ± 0.03	9.6×10^{-15}	5.3×10^9
284, trace	$H1$	0.124 ± 0.01	1.9×10^{-15}	8.9×10^8
	$E1^*$	0.627 ± 0.03	3.5×10^{-15}	6.7×10^{11}

Table 3. Parameters of DLs $E1$, $E1^*$ (samples Nos 281, 283 and 284). E_a is activation energy; ρ is sheet concentration; $V_r = -1$ V; $\tau = 133.8$ μ s, $t_p = 10$ μ s (samples Nos 281 and 283); $\tau = 11$, $t_p = 3$ ms (sample No. 284).

V_f (V)	E_a (eV)					ρ (cm ⁻²)				
	No. 281		No. 283		No. 284	No. 281		No. 283		No. 284
	$E1$	$E1^*$	$E1$	$E1^*$		$E1$	$E1^*$	$E1$	$E1^*$	
0	0.154	0.377	0.134	0.287	0.627	6.3×10^8	7.3×10^9	9.1×10^9	2.4×10^9	6.7×10^{11}
0.5	0.164	0.391	0.141	0.292	0.650	6.4×10^8	6.9×10^9	8.7×10^9	2.3×10^9	3.9×10^{11}
1	0.188	0.445	0.166	0.310	0.687	5.1×10^8	7.7×10^9	7.0×10^9	2.1×10^9	4.4×10^{11}

The peak $H1$ was registered in sample No. 284 at amplitude V_f more than 1 V (table 2, figure 4), which appears obviously due to hole emission from a ground quantized level in the QD. Indeed the $H1$ peak was observed only at positive impulses of filling when hole injection from the metal contact occurred. In sample No. 284, only peaks $E1^*$ and $H1$ were registered. Against a background of huge peak $E1^*$, peaks from others DLs become indistinguishable due to their smaller concentration.

4. Conclusion

In this work it has been found that electron-beam irradiation of MBE-grown CdSe/ZnSe structures during the growth process influences both the DLTS and CL spectra of the CdSe layers. This observation should be taken into account when one compares PL, DLTS or other data with the CdSe layer thickness estimated from RHEED oscillation measurements. On the other hand, this phenomenon may be used for intentional stimulation of CdSe QD formation during epitaxy.

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