

Temporal evolution of resonant Raman-scattering in ZnCdSe quantum dots

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We investigated ZnCdSe/ZnSe quantum-dot structures which include planar and coherently strained three-dimensional islands with different sizes. Optical excitation of these islands well below the ZnSe band gap leads to a resonant enhancement of the Zn_{0.7}Cd_{0.3}Se longitudinal-optical (LO) phonon-scattering efficiency and makes the 2LO and 3LO multiphonon emission observable. Resonant excitation with a power density of about 1.3 MW/cm² using a micro-Raman setup results in an exponential decrease of the 1LO, 2LO, and 3LO intensity with irradiation time. This decay behavior is not observed for pure ZnSe crystals and can be avoided for the ZnCdSe/ZnSe structures using much lower excitation densities. The decrease in intensity is accompanied by a shift of the LO mode to higher frequencies resulting from a lower cadmium concentration in the alloy. From these experimental findings, we conclude that resonant excitation at a certain power density leads to cadmium out-diffusion from the planar quantum dots, which shifts the resonance away from the excitation energy. © 2000 American Institute of Physics. [S0003-6951(00)03619-6]

Semiconductor heterostructures of reduced dimensionality have attracted much attention over the past few years.¹ Particularly, quantum-dot (QD) structures based on II–VI compounds are of interest, since they are candidates for the development of laser diodes in the green and blue-green spectral range.² The formation of self-organized QDs during Stranski–Krastanow³ and fractional monolayer growth^{4,5} was recently reported.

In this letter, we report on Raman-scattering and photoluminescence investigations of ZnCdSe/ZnSe structures. Our results show that resonant Raman scattering can be used to investigate the stability of such structures under conditions of resonant excitation of the QDs. It was reported that resonant Raman scattering can be applied to the ZnSe material system to distinguish between the phonons of ZnSe and the ZnSe-like longitudinal-optical (LO) phonons of Zn_{0.8}Cd_{0.2}Se/ZnSe quantum wires.⁶

The ZnCdSe/ZnSe samples under investigation were grown by molecular-beam epitaxy (MBE) and have the following structure. A pseudomorphically strained ZnSe-buffer layer of 45 nm thickness was grown on a (001)-oriented GaAs substrate followed by 2.6 ML of CdSe and capped by 45 nm of ZnSe. Details of growth are given elsewhere.⁷ The sample includes three-dimensional islands formed in the Stranski–Krastanow (SK) growth mode as well as smaller planar quantum dots with a cadmium concentration of 30%.⁸ The cadmium concentration of the SK quantum dots is much higher (>70%) compared to the planar QDs, whereas it is around 15% in the wetting layer.⁸ For comparison, a 4- μ m-thick sample of pure ZnSe on a GaAs substrate was investigated. The photoluminescence (PL) experiments were carried out in a He-flow cryostat providing temperatures between 4.2 and 300 K. The 325 nm line of a cw He–Cd laser was used for excitation. The Raman-scattering experi-

ments were performed in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge-coupled device detector. The microscope optics used provides a spot diameter of about 0.7 μ m. With the 488 nm line of an Ar⁺Kr⁺ mixed-gas laser, we achieved a maximum excitation power of 5 mW at the sample surface, resulting in a power density of 1.3 MW/cm². The Raman shifts were determined with an accuracy of 0.5 cm⁻¹.

Figure 1 shows the temporal evolution of Raman spectra under the described excitation conditions. The spectrum at the beginning of the experiment ($t=0$ s) exhibits three modes at 246.4, 493.5, and 741.8 cm⁻¹. With increasing frequency, the full width at half maximum of these structures increases strongly. The mode at 246.4 cm⁻¹ corresponds to the ZnSe-like longitudinal-optical phonon of Zn_xCd_{1-x}Se with $x=(70\pm 5)\%$. The alloy composition is derived from the data given in Ref. 9, which were measured for Zn_xCd_{1-x}Se epilayers on a GaAs substrate grown by MBE. Local strain and confinement effects may also influence the phonon frequency, but are minor effects and have opposite sign.¹⁰ Therefore, the cadmium concentration of 30% is a good estimate of the Zn_xCd_{1-x}Se alloy, which is the origin of the resonantly enhanced Raman modes. This cadmium concentration matches the value for the planar QDs determined by transmission electron microscopy.⁸

The other two structures in the Raman spectra of Fig. 1 are the two (2LO) and three LO (3LO) multiphonon emissions which are known to appear under resonant excitation conditions.¹¹ A resonance in the Raman-scattering cross section occurs, if the energy of an incoming or outgoing photon (or both) matches the energy difference of electronic states in the material, since in that case the denominator in the expression for the Raman cross section tends to zero.¹² We observe that the intensity of the 1LO, 2LO, and 3LO modes decreases strongly with irradiation time on a time scale of hundreds of seconds. Second, the luminescence background

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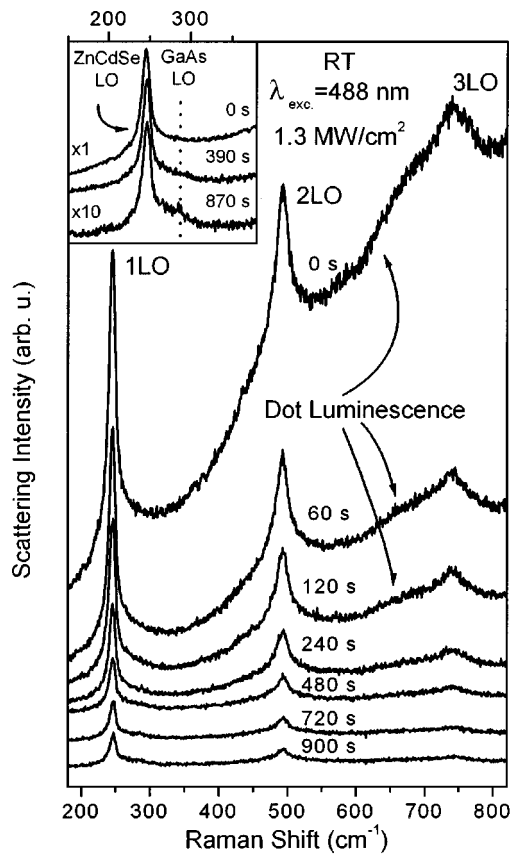


FIG. 1. Room-temperature Raman spectra of a ZnCdSe/ZnSe structure under excitation with 488 nm and 1.3 MW/cm² at different times. The recording time for each spectrum was 10 s. One observes up to 3LO phonon modes. With increasing time the luminescence background and the phonon intensities decrease. The inset shows spectra at three times in the vicinity of the 1LO mode. The high-energy shoulder originates from Raman scattering with phonons from the GaAs substrate.

from the QDs disappears with increasing time. Furthermore, we observe a hardening of the 1LO frequency with irradiation time, as can be seen in the inset of Fig. 1. The high-energy shoulder of the 1LO mode originates from inelastic light scattering with phonons from the GaAs substrate. The Zn_xCd_{1-x}Se 1LO mode is shown as function of irradiation time in Fig. 2 and exhibits a hardening with increasing time. The frequency at the end of the experiment is 1.7 cm⁻¹ higher than at the beginning without an apparent saturation.

Figure 3 shows the scattering intensity of the 1LO, 2LO, and 3LO mode versus irradiation time. The decrease in intensity can be fitted by an exponential decay function using decay times between 141 and 150 s for the different multi-LO scattering processes. The first part of the experiment ended after 900 s. Five minutes after stopping the irradiation and a further 20 min later, the intensity did not recover, but rather remained at the value at the end of the continuous 900 s irradiation, i.e., the underlying process is irreversible. For comparison, the behavior of the 1LO ZnSe phonon of the 4-μm-thick ZnSe sample is shown as well as the 1LO intensity for the ZnCdSe/ZnSe structure when the excitation power was reduced by a factor of 25. Here, the scattering intensity stayed constant within experimental accuracy.

To investigate the origin of the electronic states which are responsible for the resonance behavior, we performed

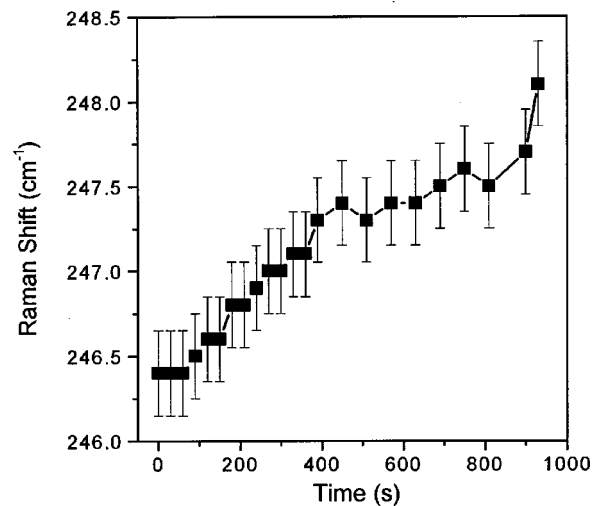


FIG. 2. Frequency of the Zn_xCd_{1-x}Se 1LO mode vs irradiation time (line: guide to the eye).

temperature-dependent PL and micro-Raman experiments. The results are shown in Fig. 4; in the upper part, the PL energy at maximum intensity is plotted versus temperature. Up to 160 K the PL spectrum is mainly determined by the emission of the planar QDs. Due to thermalization the SK dot PL dominates at higher temperatures, but the electronic levels of the planar QDs still exist and are known to have a ZnSe-like temperature behavior.^{8,13} Exciting with 476 nm, a maximum in 1LO intensity appears at 40 K. At this temperature the excitation energy is about 30 meV (energy of 1LO phonon) higher than the PL, i.e., we observe an outgoing resonance. Using the 488 nm line for excitation, no Raman modes are observable up to 140 K. At higher temperatures the scattering intensity strongly increases, having the maximum at room temperature. Note that this is not the temperature effect of the Stokes scattering, since all values were normalized with $n(\omega) + 1$, with $n(\omega)$ being the Bose factor. At room temperature, the excitation energy is 170 meV be-

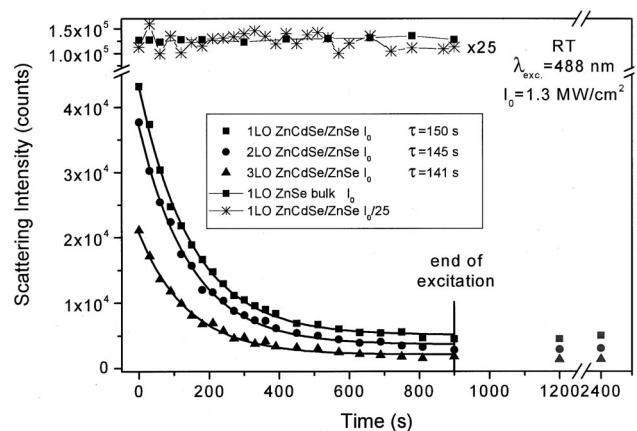


FIG. 3. Phonon mode intensity plotted as function of irradiation time for different data sets. The data for the 1LO, 2LO, and 3LO modes of the ZnCdSe/ZnSe structure were fitted by a single-exponential decay. To check if the observed process is reversible, the intensities for the 1LO, 2LO, and 3LO modes were determined again 5 and 25 min after ending the excitation. The intensity of the 1LO mode of pure ZnSe under the same excitation conditions and the 1LO mode of the ZnCdSe/ZnSe ($\times 25$) structure applying an excitation density attenuated by a factor 25 stay constant over the observation time of 900 s. Here, the lines are a guide to the eye only.

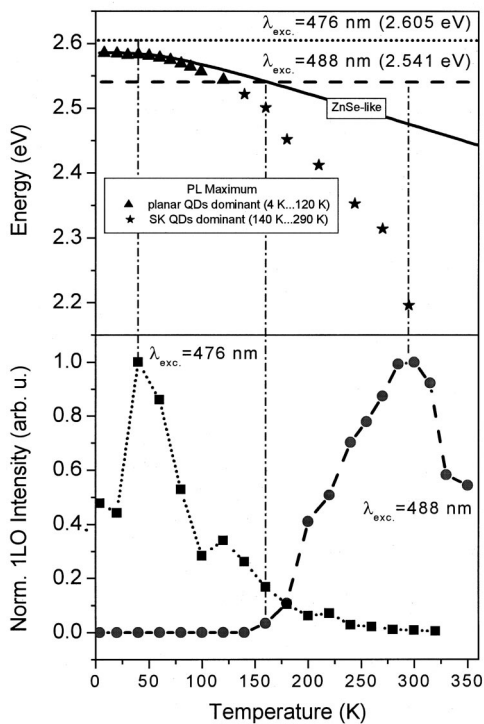


FIG. 4. In the upper part the energy of the PL maximum vs temperature is shown as well as the ZnSe-like temperature behavior of the planar QDs states (using the function given in Ref. 13). The two different excitation energies are indicated by dotted (2.605 eV) and dashed (2.541 eV) lines. The normalized 1LO intensity is plotted as function of temperature for the different excitations in the lower part of the figure. The values are Bose normalized and the maximum is set to be unity.

low the ZnSe band gap and more than 300 meV higher than the energy of the SK dots.

We thus conclude from the results of the temperature-dependent measurements that the electronic states of the planar QDs with a cadmium concentration of about 30% are the origin of the resonance in the Raman-scattering cross section. A similar resonance behavior of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ islands in ZnCdSe/ZnSe structures was reported in Ref. 14. The exponential decrease of the phonon intensities with irradiation time under high-excitation conditions can thus only be explained by a cadmium out-diffusion from the planar $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{Se}$ islands, thus shifting the resonance energy away from the excitation energy and leading to a much lower Raman-scattering efficiency at the end of the experiment.

We suggest the following mechanism. Due to the high absorption coefficient of the $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{Se}$ QDs under excitation with 488 nm strong local heating occurs, which leads to a diffusion of cadmium. Recently, it was shown that metal components diffuse via group-II lattice sites already at temperatures below 500 °C in ZnSe-based quantum-well structures.¹⁵ The cadmium diffusion also explains the hard-

ening of 1LO frequency, since a lower cadmium concentration in the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ alloy leads to a frequency shift towards the value of the LO phonon of pure ZnSe.⁹

In conclusion, we have performed temperature-dependent PL and Raman-scattering experiments on ZnCdSe/ZnSe structures. We found a resonant excitation and an exponential decrease in Raman-scattering intensity of the ZnCdSe-like 1LO, 2LO, and 3LO modes under excitation with 488 nm and 1.3 MW/cm². This behavior is explained by a shift of the resonance energy due to cadmium out-diffusion from the planar QDs. The observed effect is irreversible, but is not the typical degradation mechanism in II–VI semiconductor compound devices, which is widely accepted to result from dislocation spreading in the material. To further investigate the underlying mechanism, it would be useful to compare results of structural investigations, such as high-resolution transmission electron microscopy, before and after irradiation. Our method may be used to destroy selectively one type of dots with specific resonance energies, leaving those with much different energies unaffected.

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