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Optical properties of BeCdSe/ZnCdMgSe strained quantum well structures

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We report the optical properties of BeCdSe/ZnCdMgSe single quantum well (QW) structures that consist of closely lattice matched ZnCdMgSe barrier layers and a strained BeCdSe QW layer ($\Delta a/a = 1.95\%$) grown on InP substrates. Emission from the red to the green regions of the visible spectrum was obtained from the structures with the QW thickness varying from 95 to 12 Å. Efficient QW emission, dominated by an exciton recombination behavior, was observed. From the Arrhenius plot of the integrated emission intensity as a function of temperature, an activation energy of 61 meV was obtained for a BeCdSe QW structure with a 48 Å thick QW layer. Parameters that describe the temperature dependence of the near band edge emission energy and the broadening of the excitonic emission were evaluated. Our results indicate that the BeCdSe-based QW structures are attractive for application as red light emitters. © *2001 American Institute of Physics.*
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I. INTRODUCTION

In the past few years ZnCdMgSe-based light emitting diodes (LEDs) operating in the visible range of the spectrum have been reported by several research groups.[1,2] These structures were grown lattice matched to InP substrates and utilized high-band gap ZnCdMgSe as a barrier layer material and low-band gap ZnCdSe as a quantum well (QW) material for emission in the yellow, green, and blue regions of the spectrum. An application of the lattice matched low-band gap ZnCdMgSe as a QW layer for LEDs operating in the blue–green range was also explored.[3] For emission in the red, strained ZnCdSe QWs with excess Cd ($\Delta a/a \approx 1.8\%$) had to be used.[4] However, the strain in the lattice-mismatched active layer may enhance the multiplication and diffusion of point defects, decreasing the reliability of LEDs.

We have recently grown high quality $Be_xCd_{1-x}Se$ epilayers with BeSe concentration varying from 5% to 20%. Bright room-temperature (RT) luminescence in the red region of the spectrum was observed from them.[5] Strong RT emission was also demonstrated from BeCdSe/ZnSe QWs grown on GaAs substrates.[6] Due to a high degree of covalent bonding in Be chalcogenides,[7] introduction of BeSe in the QW active layer increases alloy hardness and is expected to decrease the formation of point defects and suppress the propagation of extended defects. Considering this, we propose that BeCdSe can be used as an alternative to the strained ZnCdSe QW layer material for light emitting devices operating in the red region of the spectrum.

In this article we report on optical properties of BeCdSe/ZnCdMgSe structures with strained BeCdSe ($\Delta a/a = 1.95\%$) QWs. A set of structures with nominal QW thickness varying from 95 to 12 Å was grown by molecular beam epitaxy (MBE). Efficient luminescence from the red to the green regions of the spectrum was observed from QW structures that differed only in the QW thickness. Sharp luminescence lines consistent with high quality interfaces were obtained. The temperature and the excitation intensity dependence of the photoluminescence (PL) emission were studied for the structure with a 48 Å thick QW. These studies showed that the QW emission was dominated by exciton recombination processes. From the Arrhenius plot of the integrated intensity as a function of temperature, activation energies for the BeCdSe QW emission and the ZnCdMgSe barrier layer emission were estimated. The temperature dependence of the BeCdSe QW emission energy, an important parameter for design of lasers and light emitters, was investigated and fitted to the Varshni's and Bose–Einstein equations. The broadening of the QW emission linewidth with temperature was studied using a similar Bose–Einstein type equation.

II. EXPERIMENTAL DETAILS

QW structures were grown on semi-insulating epiready (001) InP substrates in a Riber 2300 MBE system. This system consists of III–V and II–VI growth chambers connected by an ultrahigh vacuum channel. The InP substrates were deoxidized in the III–V chamber by heating to 500 °C under an As flux. Then, a lattice matched InGaAs buffer layer (170 nm) was grown. After this, the samples were transferred in vacuum to the II–VI chamber for the QW growth. Prior to the growth of the QW structure, Zn irradiation of the InGaAs surface was performed and a 10 nm thick low-temperature ZnCdSe interfacial layer was grown at 170 °C to optimize the crystalline quality.[8] The substrate temperature was then raised to 270 °C and a 500 nm thick ZnCdMgSe ($E_g \approx 2.9$ eV at 10 K) barrier layer was grown, followed by the $Be_{0.08}Cd_{0.92}Se$ QW layer. Then, a 100 nm thick top ZnCdMgSe barrier layer with the same composition as the bottom one was grown. The structure was capped by a 5 nm thick pseudomorphic ZnCdSe cap layer to protect

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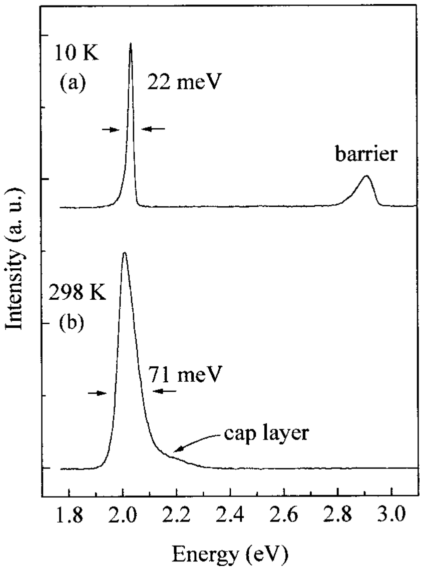

FIG. 1. Photoluminescence spectra for a 48 Å thick BeCdSe/ZnCdMgSe QW at: (a) 10 K and (b) 298 K.

ZnCdMgSe from oxidation by atmospheric oxygen. A series of samples with QWs ranging in thickness from 12 to 95 Å were grown. The ZnCdMgSe barrier layers were nearly lattice matched ($\Delta a/a < 0.15\%$) to InP, and the BeCdSe QW layer was strained with $\Delta a/a = 1.95\%$. The QW mismatch estimate was based on a single crystal x-ray diffraction measurement of a thick BeCdSe layer ($E_g = 2.018\,\mathrm{eV}$ at 10 K) with the same nominal composition as the QW, grown just prior to the QW structures.

The QW structures were characterized by PL measurements using the 325 nm line of a He–Cd laser for excitation. Temperature dependent PL measurements were performed using a liquid helium continuous flow cryostat with a temperature control unit that provided control over a temperature range from 5 to 300 K.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the 10 K PL spectrum of the structure with a 48 Å thick QW layer. The band-edge emission from the ZnCdMgSe barrier layer is at 2.909 eV and that from the QW layer is at 2.078 eV. The absence of a deep level emission is indicative of the high quality of the QW structure. The asymmetric line shape with a tail in the low energy side may be related to the involvement of localized exciton emission, which may be due to composition fluctuations[9] and/or thickness deviations of the well width.[10,11]

The RT PL spectrum for the same sample is shown in the Fig. 1(b). A strong emission at 1.996 eV is obtained from the QW while the emission from the ZnCdMgSe barrier layer is thermally quenched. An increase of the full width at half maximum (FWHM) of the QW emission with increasing temperature is observed (from 22 to 71 meV). A weak shoulder at ≈2.18 eV originates from the top ZnCdSe cap layer.

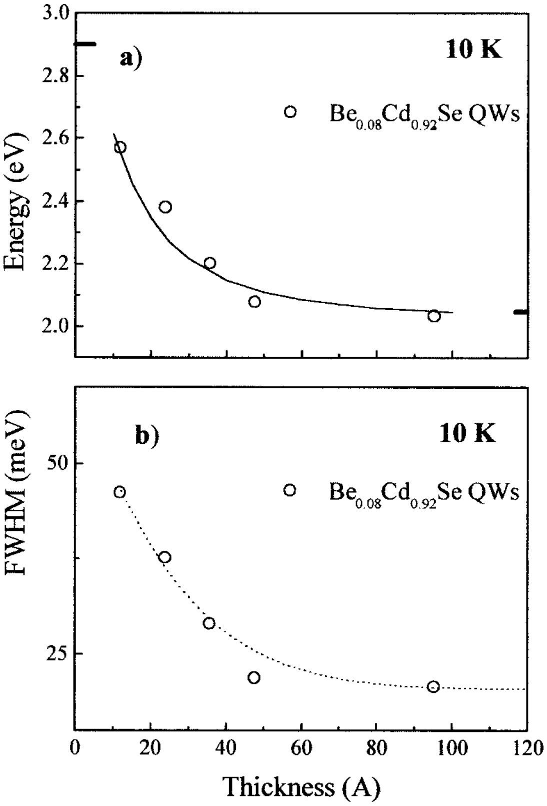

FIG. 2. (a) Emission energy at 10 K as a function of QW width for the BeCdSe/ZnCdMgSe QWs (open circles) grown on InP substrates. The solid line is a fit based on the analytical method of Mathieu *et al.* (Ref. 12). (b) FWHM of the emission lines for the BeCdSe/ZnCdMgSe QWs (open circles) grown on InP substrates. The dashed line is drawn for visualization.

The PL emission energy at 10 K from a series of QW structures is plotted as a function of the QW thickness in Fig. 2(a). Each data point represents a different growth run. The quaternary barrier layers had a band gap at around 2.9 eV, indicated by a bar on the left axis of the plot. The band gap of a thick $Be_{0.08}Cd_{0.92}Se$, which is the composition used in the QW, is 2.018 eV and is marked by another bar on the right axis of the plot.

The fit of the QW emission energy, indicated by a solid line, was performed using the analytical method of Mathieu *et al.*[12] For our calculations, we used the effective mass values of CdSe: $m_c = 0.11m_0$ for electrons and $m_h = 0.44m_0$ for holes.[13] These values were used both for the wells and for the barrier materials. The distribution of the band offsets ($\Delta E_c/\Delta E_v$) was varied, and the best fit was obtained with $\Delta E_c/\Delta E_v = 70/30$.

The $Be_{0.08}Cd_{0.92}Se$-based QW structures presented here can be tuned to a lower energy than those based on $Zn_{0.55}Cd_{0.45}Se$ QWs,[14] reaching an emission energy of 2.1 eV (useful for red light emitters) with a 48 Å thick $Be_{0.08}Cd_{0.92}Se$ QW layer. At this thickness the strained active layer is pseudomorphic and free of misfit dislocations.

From the width of the PL emission lines we can obtain an assessment of the quality of our QW structures. Figure 2(b) shows a plot of the FWHM of the PL emission lines from the BeCdSe QWs as a function of the QW thickness for the same set of samples as those shown in Fig. 2(a). Narrow emission lines ($\mathrm{FWHM} < 25\,\mathrm{meV}$) are obtained for the thick QWs (>40 Å), suggesting that the interfaces of the QWs are smooth and abrupt.

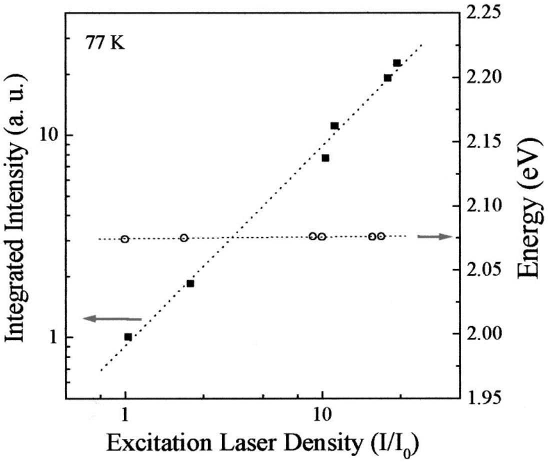

FIG. 3. Dependence of the integrated QW emission intensity (solid squares) and emission energy (open circles) on the excitation laser density at 77 K in a log scale. The dashed lines are linear fits.

As expected, the linewidths increase with the decrease in QW thickness. This is due to the increasing effect of the interface roughness as the QWs become thinner.

Figure 3 shows the dependence of the integrated QW emission intensity on the excitation laser density measured at 77 K in a logarithmic scale. The solid squares represent the experimental results and the dashed line is a linear fit. A linear dependence with a slope of 1.04 is obtained. The QW emission energy as a function of the excitation laser density is shown by the open circles and no energy shift is observed. These results indicate that the QW emission has an excitonic recombination behavior.

The temperature dependence of the PL intensity has also been studied for the structure with a 48 Å thick QW layer. Figure 4 shows an Arrhenius plot of the integrated QW (solid triangles) and barrier (open squares) emission intensity as a function of the inverse temperature. The experimental data can be fitted to the formula

$$I(T)=I_0/(1+C\exp(-E_a/kT)), \tag{1}$$

where I_0 and C are constants, T is the temperature, k is the Boltzmann's constant, and E_a is the activation energy. Activation energies of 61±2 and 30±1 meV were obtained for the QW and barrier layer emissions, respectively. The activation energy obtained for the $Be_{0.08}Cd_{0.92}Se/ZnCdMgSe$ QW emission was comparable to that reported for $Zn_xCd_yMg_{1-x-y}Se/Zn_{x'}Cd_{y'}Mg_{1-x'-y'}Se$ QWs (68 meV)[3] and much higher than that reported for $Zn_{0.5}Cd_{0.5}Se$/ZnCdMgSe (20 meV)[3] and $Zn_{0.8}Cd_{0.2}Se$/ZnSSe/ZnMgSSe (25 meV)[15] QWs with similar thickness. High activation energies indicate high luminescence efficiencies even at high temperatures, which are desirable for the RT operation of light emitting devices. The activation energy obtained for the ZnCdMgSe barrier layer emission was similar to the previously reported values (31 meV).[3]

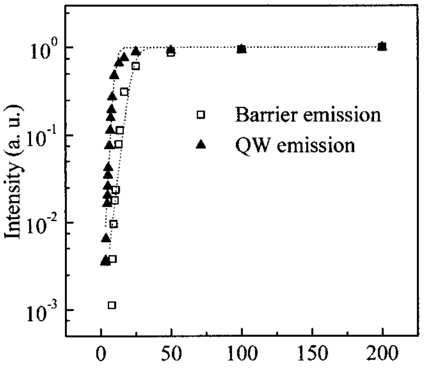

FIG. 4. Arrhenius plot of the QW (solid triangles) and the barrier layer (open squares) emission intensities as a function of the inverse temperature for a 48 Å thick BeCdSe/ZnCdMgSe QW.

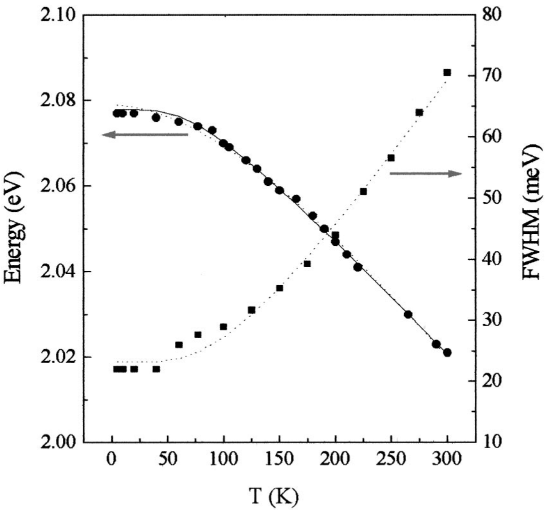

FIG. 5. FWHM (solid squares) and energy (solid circles) of the QW emission as a function of temperature for a 48 Å thick BeCdSe/ZnCdMgSe QW. The dashed lines represent fits based on the electron–LO–phonon coupling model and Varshni's relationship. The solid line represents a fit based on the Bose–Einstein relationship.

We have plotted the luminescence linewidth of the same structure versus temperature in Fig. 5. The measured luminescence linewidth is a sum of an inhomogeneous part Γ_i, which is due to interface roughness, composition fluctuations, alloy scattering, electron–electron interactions, impurities and dislocations, and a temperature-dependent homogeneous part Γ_h. The homogeneous component is dominated by the scattering of longitudinal acoustic (LA) phonons at low temperature and by longitudinal optic (LO) phonons at higher temperatures. By neglecting the contribution from the LA phonons, the value of the electron (exciton) LO phonon (Fröhlich) interaction constant Γ_{LO} and the LO phonon energy $h\upsilon_{LO}$ can be determined by fitting the FWHM of the QW emission to the equations[16,17]

$$\Gamma(T)=\Gamma_i+\Gamma_h, \tag{2}$$

$$\Gamma_h=\Gamma_{LO}/(\exp(h\upsilon_{LO}/kt)-1). \tag{3}$$

The best fit gave us $\Gamma_i=23.3\pm0.7$ meV, $\Gamma_{LO}=82\pm16$ meV, and $h\upsilon_{LO}=26\pm3$ meV. The LO phonon energy, obtained by this fit, is very close to that obtained for bulk CdSe epilayers (25.9 meV).[18,19] This is reasonable, since the BeCdSe QW contains only 8% BeSe. However, the electron–LO–phonon interaction constant is much higher than the reported one for bulk CdSe layers (23 meV).[18] Similar electron–LO–phonon interaction constants have been reported for ZnSe/ZnMgSSe QWs (60–80 meV).[20,21]

We have plotted the QW emission energy versus temperature in Fig. 5. The solid circles are the experimental results and the dotted line is a theoretical fit based on Varshni's relationship:[22]

$$E_V(T)=E_0-\alpha T^2/(\beta+T), \tag{4}$$

where E_0 is the fundamental transition energy at 0 K and α and β are constants, known as Varshni's coefficients. The best fit gave us $E_0=2.079\,\text{eV}$, $\alpha=0.37\pm0.03\,\text{meV/K}$, and $\beta=249\pm39\,\text{K}$.

The data were also fit to the Bose–Einstein relationship (solid line)[23]

$$E_{\text{BE}}(T)=E_0-2a_B/(e^{\theta/T}-1), \tag{5}$$

where E_0 is the fundamental transition energy at 0 K, a_B represents the strength of the electron–average phonon interaction, and θ corresponds to the average phonon temperature. The best fit gave us $E_0=2.078\,\text{eV}$, $a_B=35\pm2$ meV, and $\theta=210\pm8$ K. It should be noted that a_B and θ are close to the values reported for bulk CdSe ($a_B=36\,\text{meV}$ and $\theta=179\,\text{K}$)[18] layers.

The results of the fittings to the Bose–Einstein and Varshni's equations can be compared in the high temperature limit, in which the two equations reduce to

$$E_V\approx E_0-\alpha T,$$

$$E_{\text{BE}}\approx E_0-2a_BT/\theta.$$

From a comparison of these equations it follows that $\alpha=2a_B/\theta$. By substituting the values of a_B and θ obtained from the fitting to the Bose–Einstein equation we obtain $\alpha=0.34\,\text{meV/K}$. This is in good agreement with the value obtained from Varshni's relationship ($\alpha=0.37\pm0.03\,\text{meV/K}$), indicating consistency between the parameters obtained by the two techniques.

IV. CONCLUSION

Quantum well structures having ZnCdMgSe barrier layers and BeCdSe QW layers were grown and their optical properties were investigated. Emission from the red to the green regions of the visible spectrum was obtained from the QW structures by varying only the QW thickness. Efficient luminescence was observed both at 10 K and at room temperature. The PL intensity as a function of the excitation laser density showed a linear dependence with a slope near unity, indicating an excitonic recombination behavior. The temperature dependence of the PL intensity of a structure with a 48 Å thick QW was studied and an activation energy E_a of ≈61 meV was obtained. The LO phonon energy and the electron–LO–phonon interaction constant were estimated and compared with those of other II–VI materials. Also, the temperature dependence of BeCdSe QW emission energy was measured and was fit to the Varshni and Bose–Einstein equations. Parameters that describe the temperature dependence of the QW emission were obtained. Our results indicate that the BeCdSe-based QW structures are attractive for application as red light emitters.

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