HYDROSTATIC PRESSURE STUDIES OF OPTICAL TRANSITIONS IN THE PHOTOLUMINESCENCE SPECTRA OF $Zn_{1-x}Cd_xSe$ THICK EPILAYERS AND $Zn_{1-x}Cd_xSe$/ZnSe STRAINED LAYER MULTIPLE QUANTUM WELLS

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The effects of hydrostatic pressure (0-110 kbar) on the energy levels of bulk $Zn_{0.86}Cd_{0.14}Se$ in the form of a 1 μm thick epilayer and a six period multiple quantum well comprised of 30 Å wells of $Zn_{0.79}Cd_{0.21}Se$ and 400 Å barriers of ZnSe (both of which are grown on GaAs substrates by molecular beam epitaxy) are studied together in the same diamond anvil pressure cell at a temperature of 14 K, enabling us to accurately determine and compare the first and second order pressure coefficients for direct gap ZnCdSe transitions in the two samples. Theoretical calculations to determine the energy levels for the quantum well sample in the presence of interlayer strain and hydrostatic pressure are carried out using the finite element method in the eight-band **k·p** model, clearly showing the necessity of including a pressure dependent shear deformation potential. The photoluminescence (PL) intensity is irreversibly quenched in both samples by a structural phase transition occurring in ZnCdSe around 105 kbar. The effects of hydrostatic pressure on the lattice vibrational modes in the Raman spectra of bulk ZnCdSe are also studied.

Stimulated by applications in optoelectronic devices with a response in the blue such as light emitting diodes and lasers,[1,2] extensive studies have been conducted on the electronic and vibrational properties of epilayers and quantum wells of wide band gap II-VI materials.[3] In addition, they offer the possibility of tuning the valence band via interlayer strain.[4-6] In this paper we discuss and compare the confined transitions in the PL spectra from a ZnCdSe/ZnSe quantum well sample and a bulk ZnCdSe sample under hydrostatic pressures between 1 bar and 110 kbars and at 14 K. Both samples were grown by MBE on <100> GaAs. The quantum well sample consisted of a 1.0 μm buffer layer of ZnSe, followed by the pseudomorphic growth of six alternate layers of 400 Å ZnSe barriers and 34 Å of $Zn_{0.79}Cd_{0.21}Se$ wells, capped by a 1000 Å ZnSe layer. The bulk sample consisted of a 1.0 μm free-standing $Zn_{0.86}Cd_{0.14}Se$ epilayer.

Because the lattice constant of ZnCdSe is larger than that of ZnSe in the normal bulk form, the initial biaxial strain due to lattice mismatch is compressive in nature. However, under hydrostatic pressure a biaxial tensile strain develops due to the larger bulk modulus of ZnSe. The biaxial strain gives rise to a heavy hole / light hole splitting of the valence band; but only the lower energy heavy hole transition can be seen, since the binding energy of the light hole is not sufficiently deep for its localization in the quantum well. We have also obtained Raman spectra of the ZnCdSe LO phonon as a function of pressure in the bulk sample; but in the Raman spectra of the multiple quantum well the ZnCdSe and ZnSe LO phonon modes were not resolved.

Both samples were loaded together in the same pressure cell, thus avoiding any ambiguity or uncertainty in the pressure measurement between them, and allowing for a point by point comparison of energies/intensities of their respective transitions. A knowledge of the transition energies in bulk ZnCdSe then allows for a calculation of the energy offsets due to interlayer strain and quantum confinement for the heavy hole transition energy in the quantum well.

In order to clearly exhibit the difference in pressure-dependent behavior between these two

samples, we plot in Fig. 1 the major peak in the PL spectra (the heavy hole exciton) for each sample as a function of pressure at selected pressure values between 1 bar and 102 kbars. The spectra from the bulk sample are shown in the top panel and those from the quantum well sample in the bottom panel. From this figure, it can be seen that the major transition energy in the quantum well first lies below that of the bulk, coincides with it at a crossover pressure of 76 kbars, and then lies above it at still higher pressures. This is due to the larger sublinearity of the transition energy as a function of pressure in the bulk sample as compared to that of the quantum well. Note that the linewidths of these PL peaks exhibit only a very slight broadening across the pressure range, with the majority of the broadening taking place in the last 20 kbars, indicating a high degree of pressure homogeneity inside our DAC. The broadening within the last few kbars could in part be attributed to the approaching structural phase transition.

The PL signals from both samples are abruptly quenched beyond 105 kbars, due to a structural phase transition in ZnCdSe from the normally luminescent zincblende semiconductor structure to a metallic non-luminescent rocksalt structure.

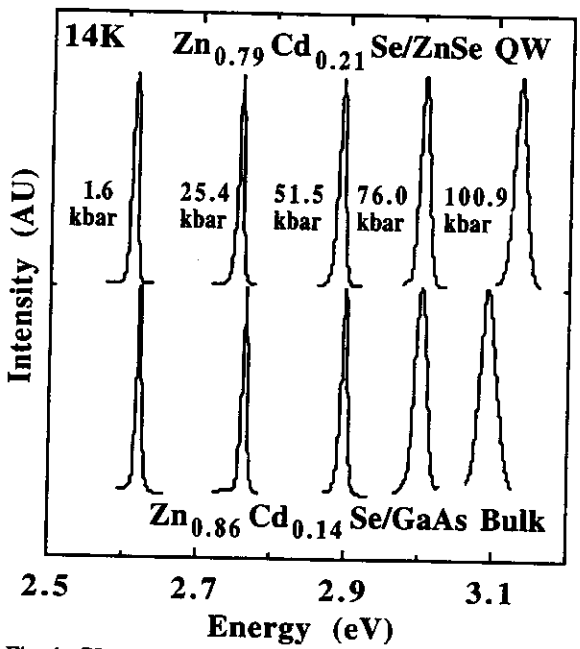

Fig. 1. PL spectra of the heavy hole exciton in the quantum well and bulk samples at several pressures.

This is accompanied by a dramatic color change in the samples from red to black, due to the presence of the GaAs substrate. The phase transition would be expected to occur at a relatively lower pressure in the quantum well than in the bulk due to the 7% higher Cd concentration in this sample. For example, pure ZnSe undergoes a structural phase transition[7] at approximately 137 kbar while pure CdSe undergoes a structural phase transition[7] at only 29 kbar. One would therefore expect that $Zn_{0.79}Cd_{0.21}Se$ undergoes a phase transition about 7 to 8 kbar before $Zn_{0.86}Cd_{0.14}Se$ does. The fact that these two samples undergo the structural phase transition at approximately the same pressure indicates that the presence of the thick ZnSe layers surrounding the extremely thin $Zn_{0.79}Cd_{0.21}Se$ pseudomorphic layers causes these thin layers to hold their present structure to pressures beyond the predicted phase transition pressure in the bulk or free-standing case. Such an effect has also been previously observed in GaAs/AlAs[8] and CdTe/ZnTe[9] multiple quantum well systems. Beyond 105 kbars, an extremely weak ZnSe PL signal can still be obtained from the cap region of the quantum well sample.

We now present in Fig. 2 the results of a fit calculated for the heavy-hole bound exciton transition energy of the ZnCdSe/ZnSe multiple quantum well sample. This calculation was carried out using an eight-band **k·p** model in the framework of the finite element method. The calculation of the transition energies included the effects of interlayer strain within the framework of the Bir-Pikus deformation theory[10], (using experimental values of the deformation potentials) and the effects of the quantum confinement under pressure (through the well widths and depths, barrier widths and heights, effective masses and other material parameters). Details will be discussed in a forthcoming publication[11]. The open squares in Fig. 2 are the experimental data points from the PL spectra for the heavy-hole transition energy in the quantum well sample. The solid line through the open triangles is an empirical second order fit,

$$E(P) = E(0) + \alpha P + \beta P^2$$

where E(P) is the energy of the bound exciton as a function of pressure (in kbar) in bulk

$Zn_{0.86}Cd_{0.14}Se$. The parameters obtained from this fit are $\alpha = 6.40 \pm 0.03$ meV/kbar and $\beta = -0.016 \pm 0.0003$ meV/kbar^2. This line predicts the degenerate energy of the heavy hole and light hole related bound excitonic transitions in the quantum well material after correction for Cd concentration and in the absence of interlayer strain or quantum confinement. The dotted line in this figure has then been calculated from the bulk $Zn_{0.79}Cd_{0.21}Se$ transition energies by including the effects of the quantum confinement energy and the interlayer biaxial strain (which includes the biaxially compressive initial lattice mismatch strain between the ZnSe and ZnCdSe layers, and the pressure generated biaxially tensile strain) on the heavy-hole transition energies. Values of the hydrostatic (a_{cv}) and shear (b) deformation potentials used for the calculation of the strain-dependent energy were obtained from an interpolation between those tabulated for ZnSe[4] and CdTe[5] (which should have deformation potentials which are approximately the same as those of CdSe in the zincblende structure), since none are available for ZnCdSe of any Cd concentration or for CdSe. Although this dotted curve is seen to fit the data well at lower pressures (through approximately 45 kbars), it fails in the higher pressure range, which we believe is due to the assumption of a pressure *independent* shear deformation potential b.

As was observed to be the case in experiments on pseudomorphic layers of ZnTe/InAs[6] and ZnSe/GaAs,[4] the shear deformation potential b is itself pressure dependent, and this pressure dependence cannot be ignored in higher pressure ranges (although it was not a noticeable effect at low pressures, as in CdTe/InSb[5]). This pressure dependence of b gives rise to a *super*linear heavy hole / light hole splitting with pressure, even though the interlayer strain is predicted to be somewhat *sub*linear with pressure by the Murnaghan[12] equation of state, which was used to calculate the strain in this fitting routine. The incorporation of a pressure dependent shear deformation potential [$b(P) = b_0 + b'P$] into the calculation and fitting of the heavy hole bound exciton energy (dashed line), using the values measured ZnSe[4], $b_0 = -1.14$ eV and $b' = -0.017$ eV/kbar (since no b' has been measured for either CdTe or CdSe) removes most of the sublinearity in the fit (dotted line) which used a pressure-independent shear deformation potential. The solid curve can now be seen to fit the experimental data quite well at all pressures, and comparison to the dotted curve demonstrates the absolute necessity of including the pressure dependence of the shear deformation potential for calculated fits, especially in the higher pressure ranges. This is definitive proof in yet another material of a pressure-dependent shear deformation potential. It should also be noted in Fig. 2 that the superlinear heavy hole / light hole splitting explained by a pressure dependent shear deformation potential is exactly the effect that gives rise to the smaller sublinearity in the quantum well as compared to the bulk for the heavy hole bound excitonic transition.

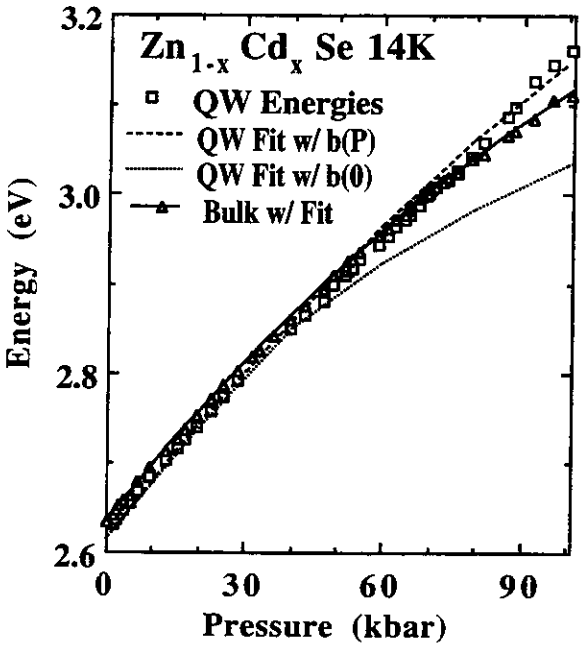

Fig. 2. Energies of the heavy hole exciton in the quantum well (squares, x = 0.21) and bulk (triangles, x = 0.14) as a function of pressure. The solid line through the triangles is a second order fit to the energy (see text). The dotted line is a theoretical calculation for the quantum well energies using eight band **k.p** theory, including the effects of strain and quantum confinement as a function of pressure, but excluding the pressure dependence of the strain deformation potential b. The dashed line includes the pressure dependence of b, $b = b_0 + b'P$.

Finally, in Fig. 3, we plot the frequency shift of the LO phonon lattice vibrational mode in the Raman spectra as a function of pressure between 1 bar and 70 kbars for the thick epilayer sample of

ZnCdSe. The violet 4579 Å line from our 5 W argon ion laser was used to excite the Raman spectra. The Raman frequency shift can be fit with a first order polynomial in pressure with slope ($d\omega/dP$) of 0.395 ± 0.013 cm^{-1} / kbar and an intercept ω_o of 255.1 cm^{-1}. Using the bulk modulus of ZnSe[7] at 14 K of 638.7 kbar, we calculate the longitudinal optical (LO) phonon mode Grüneisen parameter for bulk $Zn_{0.86}Cd_{0.14}Se$ to be $\gamma_{LO} = 0.99 \pm 0.03$, which is in good agreement with the previously calculated (0.88) and experimentally measured (0.90) values for bulk ZnSe.[7] Knowledge of this parameter is essential when relating the Raman frequency shift to the amount of strain present in a material, and we have obtained this parameter to a high degree of precision with our experiment. In addition, this parameter can now be used, along with the experimentally determined mode Grüneisen parameter for bulk ZnSe quoted above, to interpolate and predict the value of the mode Grüneisen parameters for other concentrations of Cd in ZnCdSe samples.

In summary, our experiment and calculations have effectively demonstrated the pressure dependence of the shear deformation potential in the II-VI materials, and have measured and predicted accurate pressure coefficients and mode Grüneisen parameters for ZnCdSe of various Cd concentrations.

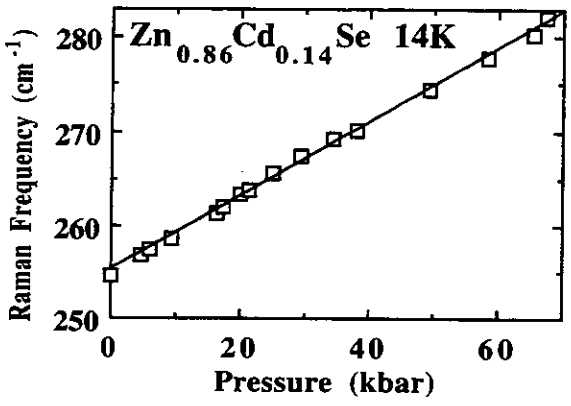

Fig. 3. The energy of the LO phonon in bulk $Zn_{0.86}Cd_{0.14}Se$ under hydrostatic pressure.

ACKNOWLEDGEMENTS

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