PHOTOLUMINESCENCE OF ZnSe EPILAYERS ON GaAs UNDER HYDROSTATIC PRESSURE

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ABSTRACT

The near bandgap photoluminescence of ZnSe epilayers grown on GaAs substrates is measured for pressures up to ~25 kbar using a diamond anvil cell at T = 9 K. The bandgap changes with pressure, dE/dp, for pseudomorphic and nonpseudomorphic films are obtained, and are compared with results for bulk crystalline ZnSe.

INTRODUCTION

Commensurate growth of ZnSe on GaAs has been achieved for thicknesses up to ~0.15 μm [1-3]. Elastic strain due to the lattice mismatch (0.25% at room temperature) is accommodated until the critical thickness is obtained. For larger thicknesses misfit dislocations lower the total energy of the system and incommensurate growth ensues. Previous studies have demonstrated the relation of this strain to epilayer thickness, with its concomitant effect on the density of misfit dislocations [2,4]. Moreover, photoluminescence (PL) studies have demonstrated the effect of this strain on band-edge emission [4-6].

The presence of biaxial strain in very thin films is also expected to alter the effect of applied hydrostatic pressure (p) on the band-edge photoluminescence relative to its effect on the PL from bulk material. Previous reports have determined dE/dp, the change in bandgap energy with pressure, to be in the range 6.0 – 7.5 meV/kbar for bulk ZnSe at room temperature down to 77 K [7-9]. The current study determines dE/dp for ZnSe epilayers of contrasting thickness, grown by MBE on GaAs, and compares these values with the bulk crystalline value, which is also measured here. All measurements are made at 9 K.

Mat. Res. Soc. Symp. Proc. Vol. 161. ©1990 Materials Research Society

EXPERIMENTAL PROCEDURE

Photoluminescence measurements were made on 0.1 and 2.1 µm-thick ZnSe epilayers grown on GaAs by MBE and on bulk ZnSe grown by zone melting. The "thin" epilayer was commensurately grown, while the "thick" layer was thicker than the critical thickness for commensurate growth. Experiments were conducted at a temperature of T = 9 K and at pressures up to ~25 kbar. The GaAs substrate was initially ~300 µm thick, and was thinned down to ~50 µm by mechanical polishing.

High pressure measurements were made in a gasketed Merrill-Bassett diamond anvil cell (DAC) [10,11], contained within a closed cycle refrigerator (9 K). The ZnSe sample was loaded with ruby chips in a liquid argon bath within the DAC to obtain near-hydrostatic pressure conditions at low temperature [12]. ZnSe and ruby photoluminescence were excited using the 4067 Å line from a krypton ion laser, and were detected using a 0.85 m double spectrometer and a cooled PMT. Photon counting electronics were interfaced to an IBM AT for A/D data conversion, storage, and analysis.

The pressure in the DAC was determined using the calibration scale for ruby fluorescence vs. pressure [13]. This was in turn calibrated using the 6929.468 Å line from a neon discharge lamp, together with the 6965.430 Å line from an argon lamp. The pressure determination is accurate to < 0.15 kbar, and energy measurements for the ZnSe photoluminescence are accurate to < 0.6 meV. The resultant uncertainty in the values of dE/dp is less than 0.21 meV/kbar.

RESULTS

Near band-edge PL spectra are shown for the three samples at ambient pressure (1 bar) and T = 9 K, as the lower spectra in each of the three parts of Figure 1. For the bulk crystalline sample in Fig. 1a, the dominant feature at 2.7973 eV (I_{2O}) is associated with a neutral bound donor exciton, attributed to either an In or Ga impurity. A neutral bound acceptor accounts for the exciton feature at 2.7924 eV (I_1). The feature at 2.7829 eV (I_1^{DEEP}) is due to a deep level acceptor, commonly attributed to Cu. The phonon replica, $I_1^{DEEP-LO}$, is found 31.6 meV lower in energy than I_1^{DEEP}. Finally, the two weak features higher in energy than I_{2O}, are due to the excited state (n=2) of a donor bound exciton at 2.8014 eV (I_{2D}) and the free exciton transition at 2.8039 eV (FE).

Identification of the PL peaks is less certain for the epilayers. For the "thick" film in Fig. 1b, the ambient pressure peak at 2.8009 eV (FE) is attributed to the ground state free exciton peak. The red shift from the bulk value may be due to a slight tensile strain [3]. The peak at 2.7958 eV (I_{2O}) is associated with an exciton bound to a neutral donor and

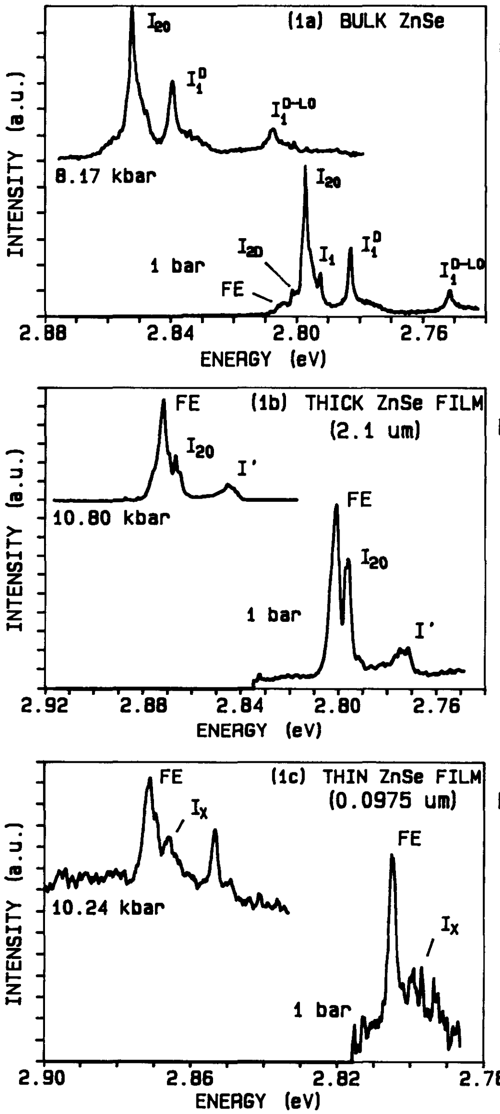

Figure 1. Photoluminescence spectra at T = 9 K.

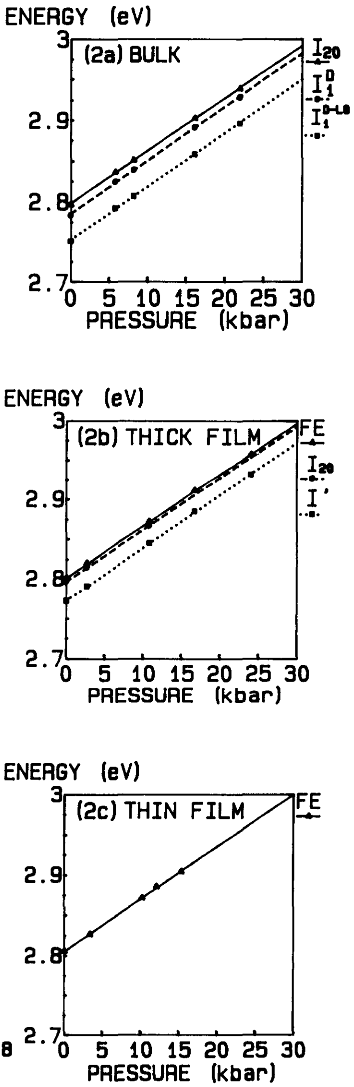

Figure 2. Plots of energy vs. pressure for the various exciton peaks.

the peak at 2.7728 meV (I') is as yet unidentified. For the "thin" film in Fig. 1c, one large peak is obtained. This corresponds to the ground state free exciton transition with energy 2.8055 eV (FE). The blue shift from the bulk value corresponds to an in-plane compressive strain due to a lattice mismatch at 9 K of ~0.23%. A very small peak is found near 2.7998 eV (I_x), which is usually attributed to a neutral bound exciton.

The photoluminescence is monitored with increasing pressure for all three samples. A representative plot for each sample at a higher pressure is provided by the upper spectra in the three parts of Figure 1. For the "thick" epilayer, the I_{20} peak intensity decreases with increasing pressure and disappears altogether at approximately 16 kbar. At approximately the same pressure, a new feature begins to grow at 2.9170 eV, which is 6.4 meV higher in energy than the FE peak. As pressure is increased the exciton energies I_{20}, I_1^{DEEP}, and $I_1^{DEEP\text{-}LO}$ are monitored for bulk ZnSe, the FE, $I_{20}^{Cl,In,Ga}$, and I' peaks are monitored for the "thick" sample, and the free exciton transition (FE) is monitored for the "thin" sample. The resultant plots of energy vs. pressure are shown in Figure 2. Least square lines are plotted for these data, yielding values for dE/dp. For bulk crystalline ZnSe, a value of dE/dp = 6.64 ± 0.12 meV/kbar is obtained for the dominant I_{20} peak, with dE/dp = 6.59 ± 0.12 meV/kbar for I_1^{DEEP} and 6.58 ± 0.15 meV/kbar for $I_1^{DEEP\text{-}LO}$. For the "thick" sample, dE/dp = 6.50 ± 0.13 meV/kbar for the dominant free exciton (FE) peak, 6.54 ± 0.13 meV/kbar for I_{20}, and 6.67 ± 0.15 meV/kbar for I'. For the "thin" sample, dE/dp = 6.48 ± 0.21 meV/kbar (FE).

ANALYSIS

The effect of hydrostatic and uniaxial pressure on a semiconductor is to shift the conduction and valence band edges by changing the volume and crystal symmetry. For ZnSe with its direct bandgap at Γ_1, the conduction band is only subject to hydrostatic components of strain. However, in addition to the effect of hydrostatic strain on shifting the valence bands (Γ_8), tetragonal distortion splits the degeneracy of the four-fold $P_{3/2}$ multiplet into heavy hole (hh: $J = 3/2$; $m_J = \pm 3/2$) and light hole (lh: $J = 3/2$; $m_J = \pm 1/2$) bands. The effect of biaxial stress due to lattice mismatch may therefore be separated into hydrostatic and nonhydrostatic components [14,15], which when considered together with externally applied hydrostatic pressure may be shown to affect energy bandgap shifts, according to:

$$\Delta E_g = -(a_c - a_v)\frac{3p}{C_{11} + 2C_{12}} + \left[2(a_c - a_v)\left(1 - \frac{C_{12}}{C_{11}}\right) \mp b\left(1 + \frac{2C_{12}}{C_{11}}\right)\right]\varepsilon_{xx}^{ZnSe}(T,p) \quad [1]$$

The first term is the hydrostatic pressure component, while the first component of the second term is due to the hydrostatic portion of the strain and the second component is due to tetragonal deformation, with – for heavy holes and + for light holes. Spin-orbit splitting has been included in the overall bandgap term. Here, a_c and a_v are the hydrostatic deformation potentials for the conduction and valence bands respectively, b is the uniaxial deformation potential for a strain of tetragonal symmetry, and C_{11} and C_{12} are elastic constants for ZnSe. The strain $\varepsilon_{xx}^{ZnSe}(T,p)$ is evaluated for a given temperature and pressure and has the form:

$$\varepsilon_{xx}^{ZnSe}(T,p) = \frac{a'_x(T,p_0)}{a_x(T,p_0)}\left(\frac{1 - \frac{p}{C'_{11} + 2C'_{12}}}{1 - \frac{p}{C_{11} + 2C_{12}}}\right) - 1 \qquad [2]$$

where $a_x(T,p_0)$ is the lattice constant for ZnSe at temperature T and ambient pressure (p_0 = 1 bar), and the primed quantities correspond to the respective parameters for GaAs.

The resultant shift in bandgap energy with pressure for a strained layer may be related to $(dE/dp)_{bulk} = -\{3(a_c - a_v)/(C_{11}+2C_{12})\}$ for bulk material by:

$$\left(\frac{dE}{dp}\right)_{\substack{hh\\lh}} = \left(\frac{dE}{dp}\right)_{bulk} - \left[2(a_c - a_v)\left(1 - \frac{C_{12}}{C_{11}}\right) \mp b\left(1 + \frac{2C_{12}}{C_{11}}\right)\right] \frac{a'_x(T,p_0)}{a_x(T,p_0)} \left[\frac{1}{C'_{11} + 2C'_{12}} - \frac{1}{C_{11} + 2C_{12}}\right] \qquad [3]$$

The variation of the exciton binding energy with applied hydrostatic pressure is not significant here.

The values for dE/dp may be evaluated using C_{11} = 929 kbar, C_{12} = 562 kbar, C'_{11} = 1221 kbar, C'_{12} = 566 kbar [16,17], $a_x(298\ K,p_0)$ = 5.6676 Å, and $a'_x(298\ K,p_0)$ = 5.6533 Å [5,17]. The elastic constants are for T = 77 K. For 9 K, the elastic constants are estimated to be 940, 570, 1234, and 577 kbar, respectively, extrapolating from the constants at 77 and 300 K by using an exponential fit. A wide range of deformation potential values are reported in the literature. The values $(a_c - a_v) = -4.17$ eV and b = – 1.20 eV [3,18] can be used as reference parameters. Then the expected values of dE/dp are 6.09 meV/kbar for bulk crystalline ZnSe, and 6.05 and 5.72 meV/kbar for the hh and lh bands for strained layer ZnSe on GaAs, using the elastic constants at 77 K. At 9 K, the respective values are 6.01, 5.98, and 5.65 meV/kbar. Using the previously determined experimental values [6] as a second reference, $(a_c - a_v) = -4.87$ eV and $b = -1.05$ eV, the three expected values for dE/dp are 7.11, 7.02, and 6.73 meV/kbar, respectively at 77 K, and 7.02, 6.93, and 6.64 meV/kbar at 9 K. The value of $(a_c - a_v)$ determined here is -4.60 eV, using dE/dp measured for the I_{20} peak in bulk crystalline ZnSe and using the elastic constants estimated for 9 K.

The heavy hole band is higher in energy than the light hole band for compressed films, while for films under tensile stress the light hole band is higher. However, since dE/dp for hh is greater than that for lh, increasing the pressure will cause the bands to cross. Thus films initially under compressive stress, such as "thin" ZnSe films, will become tensile beyond some pressure, and the value of dE/dp will change from the hh to the lh value. The "thick" films, on the other hand, are always either relaxed or under tensile stress, and will therefore follow the lh value throughout.

Low temperatures (9 K) will affect the film strain and the relative energies of the valence bands. Specifically, for ZnSe films on GaAs, a temperature decrease relaxes the compressive strain due to lattice mismatch, since the thermal expansion coefficient for ZnSe is larger than that for GaAs [15]. Nonetheless, the "thin" films here remain compressively strained even at low temperature for $p \lesssim 41$ kbar, so that the heavy hole band will therefore always be at the higher energy. Hence, the model suggests that dE/dp for the "thin" film hh excitons and for excitons in the bulk should be within 0.1 meV/kbar of each other. Within experimental uncertainty, this is seen here.

The "thick" ZnSe films, however, are always under tensile stress, since it is assumed that the compressive strain has been completely relaxed at room temperature. As a result, dE/dp for these films is expected to be the lh value which, according to the model, is ~0.3-0.4 meV/kbar lower than the bulk and "thin" film values. Within experimental error, this is consistent with the reported measurements.

CONCLUDING REMARKS

The experimental value obtained for dE/dp for bulk crystalline ZnSe falls within the range of values determined in previous experiments. Moreover, the values of dE/dp obtained for the ZnSe epilayers grown on GaAs are indistinguishable from the bulk result. Work is continuing on examining the effect of pressure on ZnSe films, including potential causes of strain relaxation in films with the application of high pressure.

ACKNOWLEDGMENTS

This work was supported at Columbia by the Joint Services Electronics Program Contract DAAL03-88-C-0009 and at Purdue by the Office of Naval Research Contract

N00014-82-K0563. The authors would like to thank Chris Berzins, Rob Scarmozzino, and Tom Licata for their assistance in data processing, and K. Shahzad for valuable discussions.

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