Temperature dependence of strain in ZnSe(epilayer)/GaAs(epilayer)

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A study of biaxial strain as a function of temperature in a ZnSe epilayer grown on a GaAs substrate is presented. The strains are determined by measuring the heavy- and light-hole related excitonic transitions via photomodulated spectroscopy. The strain is found to increase with increasing temperature. The data are compared with a calculation using a previously determined elastic constant and thermal expansion coefficients. The temperature dependence determined here allows a comparison of various other optical measurements performed at different temperatures. © 1995 American Institute of Physics.

I. INTRODUCTION

The growth of II–VI materials in combination with III–V materials is a particularly appealing recent development. This combination promises a method of producing high-quality wide-band-gap optoelectronic devices by molecular beam epitaxy (MBE). Due to the lattice mismatch between the epilayer and the substrate, accommodation of strains is limited by a critical thickness of the epilayer. The compressibilities and/or coefficients of thermal expansion (α) of the materials comprising these combinations are usually quite different. As a function of pressure and/or temperature, the lattice constants of these materials may change differently, modifying the in-plane strain in the structure, thereby changing the electro-optical properties of the system.

It has recently been demonstrated that one can measure the strains in the ZnSe/GaAs system as a function of pressure by various methods.[1–3] In these experiments, a ZnSe epilayer which is pseudomorphically grown on a GaAs substrate is placed in a diamond anvil cell (DAC) and by optical spectroscopies, the strains in the ZnSe/GaAs system are observed to be modified by the applied pressure. In all the experiments, the ZnSe goes from a biaxially compressively strained epilayer to one in which a tensile strain is seen. All of these experiments are performed on similar samples, but at different temperatures (See Table I). In this article, we present a study of the strains in the same system as a function of temperature in the 10–300 K range. The strain is monitored by the observation of the excitonic signatures in the photomodulated reflectivity spectrum. The biaxial compressive strain increases in magnitude as a function of decreasing temperature. The strain-free condition under hydrostatic pressure should thus depend on the temperature. A calculation based on this data allows a comparison with the pressure experiments at different temperatures and gives an understanding of the behavior of interlayer strains due to growth temperature.

II. EXPERIMENT

The sample under study is a 0.1 μm epilayer of ZnSe grown on the (001) surface of a 1.5-μm-thick GaAs homoepitaxial epilayer by MBE at a growth temperature of 300 °C employing a [Zn]:[Se] flux ratio of 1:1. The high-resistivity ZnSe was grown in a chamber separated from that in which the GaAs epilayer was grown; the transfer was implemented under high vacuum. The lattice mismatch at room temperature is 0.25%. Cross-sectional transmission electron microscopy measurements show no dislocations or stacking faults in the film and its interface.[4] This lack of dislocations is characteristic of a "pseudomorphic" growth in which the lattice mismatch is accommodated for by the deformation of the lattice constant of the epilayer while maintaining registry between successively grown layers. For the ZnSe/GaAs system, the limit of pseudomorphic growth has been shown to be about 0.15 μm.[5,6] For epilayer thickness above 1 μm, the dislocations relieve the strains in the epilayer at growth. However, it has been shown that when the sample is cooled below the growth temperature the ZnSe epilayers suffer two-dimensional tensile stress due to the strains produced by the difference in the thermal contraction between ZnSe and GaAs.[7]

The photomodulated reflectivity spectrum is measured using a 1 m single grating (1200 gr/mm, 300 nm blaze) McPherson monochrometer set to a dispersion of 2 Å. The sample is attached to a cryostat and cooled using liquid helium, or nitrogen. The lowest attainable temperature was 8 K. The modulation was provided by a chopped HeNe laser (632.8 nm) with a power of about 0.2 mW on a spot size of 5 mm×5 mm. This was determined by Rockwell *et al.*[1] to be a modulation of the ZnSe/GaAs interface region during a high pressure measurement by also using the 514.5 nm line of an Ar$^+$ laser and noting the disappearance of the modulated reflectance signal as the GaAs substrate became transparent to the 630 nm line of the HeNe laser. Signals were obtained up to about 250 K, the peak positions taken from a least-squares fit to the functional form discussed later.

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TABLE I. ZnSe/GaAs pressure experiments.

Author	Method	Temperature (K)	Crossover pressure (kbar) (Meas.)	Crossover pressure (kbar) (Calc.)
Tuchman et al.[a]	Photoluminescence	10	29.0	33.0
Rockwell et al.[b]	Photomodulated reflectance	80	36.2	32.5
Cui et al.[c]	Raman scattering	300	21.0	35.0

[a]See Ref. 3.
[b]See Ref. 1.
[c]See Ref. 2.

III. THEORETICAL CONSIDERATIONS

The strains in the ZnSe epilayer due to the lattice mismatch are characterized by the following relationships:[1,3]

$$\epsilon = \epsilon_{xx} = \epsilon_{yy} = \frac{a_s - a_e}{a_e}, \tag{1a}$$

$$\epsilon_{zz} = \frac{2s_{12}}{s_{11} + s_{12}}\,\epsilon = \frac{-2c_{12}}{c_{11}}\,\epsilon, \tag{1b}$$

$$\epsilon_{xy} = \epsilon_{yz} = \epsilon_{zx} = 0, \tag{1c}$$

where a_s and a_e are the lattice constants of the substrate and epilayer, respectively, for a given temperature and pressure. s_{11} and s_{12} are the elastic compliance constants, c_{11} and c_{12} the elastic stiffness constants for the epilayer. The **z** direction is taken to be the same as the direction of growth. We refer to the biaxial strain in the epilayer as ϵ_{xx} and ϵ_{yy}.

The effect of strain on the direct (**k**=0) band of zinc-blende semiconductors[8,9] is to "split" the normally degenerate maxima of the heavy- and light-hole valence bands. A biaxial strain will shift the location of the normal band gap by an amount given by

$$\delta E_h = 2a_{cv}\left[\frac{c_{11} - c_{12}}{c_{11}}\right]\epsilon = 2a_{cv}\left[\frac{s_{11} + 2s_{12}}{s_{11} + s_{12}}\right]\epsilon \tag{2a}$$

and splits the normal band gap by an amount given by

$$\delta E_s = -b\left[\frac{c_{11} + 2c_{12}}{c_{11}}\right]\epsilon = -b\left[\frac{s_{11} - s_{12}}{s_{11} + s_{12}}\right]\epsilon. \tag{2b}$$

The actual heavy- and light-hole band gaps are given by the following two relationships:

$$E_g^{hh} = E_g + (\delta E_h + \delta E_s), \tag{3a}$$

$$E_g^{lh} = E_g + (\delta E_h - \delta E_s) - \frac{2(\delta E_s)^2}{\Delta}, \tag{3b}$$

where δE_h and δE_s are the hydrostatic and the shear contributions of the gap energy, respectively. Δ is the energy separation of the spin–orbit split Γ_6 valence-band maximum from the Γ_8 valence-band maximum. a_{cv} is the combined hydrostatic deformation potential for transitions between the conduction and valence bands, **b** is the shear deformation potential constant characterizing the splitting of the Γ_8 valence band for tension or compression along [001]. In the case of ZnSe/GaAs, the lattice constant of ZnSe is larger than that of the GaAs substrate (see Table II for 300 K values). This

gives a biaxial strain which is compressive. The band gap is therefore associated with the heavy-hole transition, the light-hole transition becoming one of a larger energy gap. Notice that the strain (ϵ) as defined in Eq. (1a) is negative for compressive strains.

A change in temperature will change the lattice constants of both the epilayer and the substrate. The elastic constants in Eqs. (2a) and (2b) also change as a function of temperature. The strain in the epilayer depends on the difference in lattice constants in the two materials as seen in Eq. (1a). Also, the heavy- and light-hole transition energies depend on both this strain and the elastic constants in the ZnSe. The difference in energies is given by

$$E_g^{hh} - E_g^{lh} = 2\,\delta E_s + \frac{2(\delta E_s)^2}{\Delta}. \tag{4}$$

Elastic constants and coefficients of thermal expansion have been measured as a function of temperature in previous experiments.[10–13] We have used these data to predict how the strain evolves as the temperature varies. We have calculated the lattice constants for ZnSe and GaAs as a function of temperature using the coefficient of thermal expansion data. Then we also allow all elastic constants to become temperature dependent according to the measurements made by Lee[10] and determine heavy- and light-hole splitting according to Eqs. (2a), (2b), and (4). These calculations can be compared with our photomodulated reflectance data. Although there is some discrepancy in the values of these elastic constants, one would expect the general trend as a function of temperature to hold essentially true. The discrepancy is reflected by the

TABLE II. Material data at 300 K.

	ZnSe	GaAs
a (Å)	5.6676[a]	5.653 25[a]
c_{11} (kbar)	859[b]	1184[c]
c_{12} (kbar)	506[b]	537.2[c]
B_0 (kbar)	624	753
B_0'	4.77[d]	4.67[e]
$\alpha(\times 10^{-6}/\ K)$	7.2[d]	5.60[e]

[a]See Ref. 18. [d]See Ref. 11.
[b]See Ref. 10. [e]See Ref. 13.
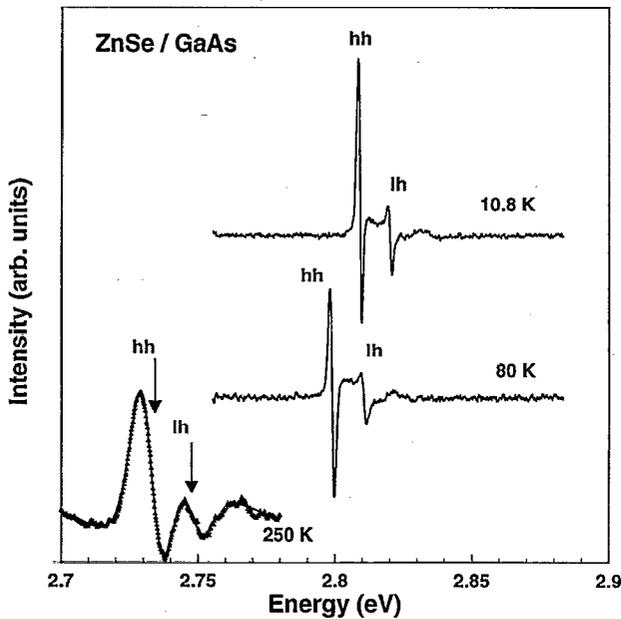[c]See Ref. 12.

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FIG. 1. Photomodulated reflectivity (PR) spectra of a 0.1 μm pseudomorphic ZnSe epilayer on GaAs at 10.8, 80, and 250 K. The heavy- and light-hole related transitions are marked. At 250 K a fit to the functional form given by Eq. (5) is included. Note that the transitions shift to lower energies as the temperature is increased.

uncertainty in the values in **b** reported by various experiments,[1,14] and in the predicted strain-free pressure conditions as discussed in Sec. VI.

IV. RESULTS AND DISCUSSION

Figure 1 shows the photomodulated reflectivity spectra for the ZnSe/GaAs epilayer under study at 10.8, 80, and 200 K. As indicated in the 10 K spectrum, the prominent signature at 2.809 eV corresponds to the exciton associated with the heavy-hole valence-to-conduction-band transition. The signature at 2.820 eV is due to the light-hole exciton. The intensity of the latter is approximately one-third that of the first, which is expected. For temperatures below 100 K, the peak positions can be determined accurately by the three-point method[15] which, at lower temperatures, agrees with fitting to the functional form[16]

$$\frac{\Delta R}{R}(E) = \sum_j \text{Re}[C_j e^{i\theta_j}(E - E_j + i\Gamma_j)^{-n}], \qquad (5)$$

where C_j and θ_j are the amplitude and asymmetry of the line shape, and E_j and Γ_j are the energy and width of the transitions. The exponent n is characteristic of the type of critical point. We have used $n=2$, which simulates two-dimensional excitonic line shapes. At higher temperatures, peak positions and relative intensities, along with linewidths, are obtained from a least-squares fit to the functional form[16] of Eq. (5).

As the temperature increases, these peaks move down in energy as shown in Fig. 2. The fit shown is according to the Varshni[17] semiempirical relationship

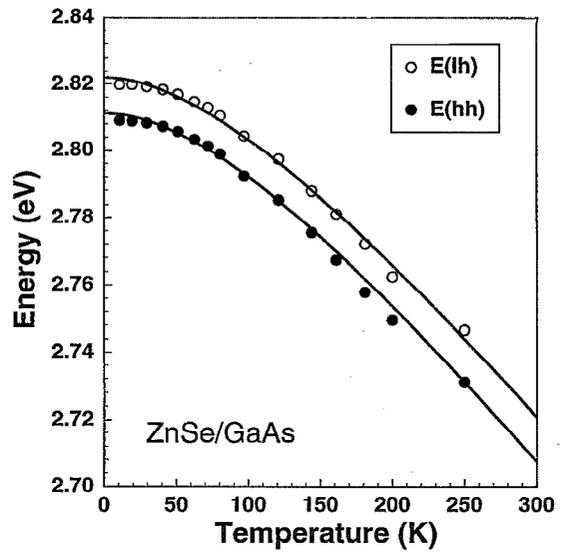$$E(T) = E(0) - [\alpha T^2/(\beta + T)]. \qquad (6)$$

FIG. 2. Variation of ZnSe epilayer transition energies as a function of temperature. The solid line is a fit to the Varshni semiempirical formula in Eq. (6).

The values obtained were 5.9×10^{-4} eV/K for α and 197 K for β corresponding to the heavy-hole related transition, and 5.6×10^{-4} eV/K for α and 196 K for β corresponding to the light-hole related transition.

The energy difference between the heavy- and light-hole transitions is observed to become larger with higher temperatures as shown in Fig. 3. The solid line in the figure is from a calculation utilizing the previously mentioned temperature dependence of elastic constants and lattice parameters in Eqs. (1)–(4). The shear deformation potential (**b**) was taken to be -1.17 eV as given by Ref. 1. The **b** was also assumed to be temperature independent. The error bars for the experi-
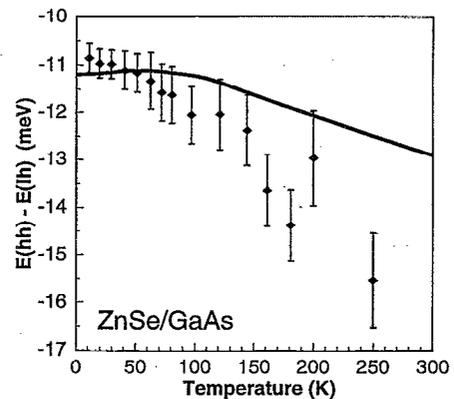

FIG. 3. The energy difference between the heavy- and light-hole ZnSe transitions. The solid line in the figure is from a calculation utilizing the temperature dependence of elastic constants and lattice parameters. The shear deformation potential **b** was taken to be -1.17 eV as given by Ref. 1. The **b** was also assumed to be temperature independent. The error bars for the experimental data are given and increase somewhat at higher temperatures due to the thermal broadening of the spectral features. The measured and calculated biaxial strains increase in magnitude with temperature as reflected in the increased splitting of light- and heavy-hole signatures.

mental data are shown and increase somewhat at higher temperatures. This is due to the thermal broadening of the spectral features. The measured and calculated strains increase with temperature as reflected in the increased splitting of light- and heavy-hole signatures.

One can compare the change in interfacial strains in our pseudomorphic ZnSe epilayer as a function of temperature, with the magnitude of the induced strains due to the cooling of ZnSe epilayers exceeding the crtical thickness for pseudomorphic growth. For a 1.5 μm (i.e., nonpseudomorphic) ZnSe epilayer, Stoher et al.[7] observe a light/heavy-hole splitting of 6.1 meV due to a *tensile* strain induced due to cooling from 600 to 10 K. Stoher's epilayer is above the critical thickness, indicating a strain relaxation at growth. Our data predicts a "tensile" component of strain with a splitting of roughly 10 meV when the substrate is cooled from 600 to 0 K as extrapolated in Fig. 3. The calculation in Fig. 3 would yield approximately 5 meV. Tuchman et al.[18] also observe a tensile component of strain in a thick epilayer. All of these observations are consistent with the trend of increasing magnitude of compressive biaxial strain with increasing temperature as shown in Fig. 3.

The application of hydrostatic pressure will decrease the lattice constant of a semiconductor. Because various semiconductors have different compressibilities, a pressure-induced strain will occur in an interface between two of these differing materials.[1] One can easily see this effect by considering Eq. (1) along with the Murgnahan equation[19] which gives the relationship between the lattice constant of an elastic solid and the hydrostatic pressure applied:

$$a(P) = a_0 \left[1 + \frac{B_0'}{B_0} P \right]^{(-1/3B_0')}, \tag{7}$$

where a_0 refers to the lattice constant at zero pressure. The B_0 is the zero pressure bulk modulus for the material, and B_0' is the pressure derivative of the bulk modulus. This equation is derived from the assumption that the bulk modulus obeys the linear relationship

$$B(P) = B_0 + B_0' P. \tag{8}$$

Since the ZnSe epilayer of the sample under consideration here is more compressible than the GaAs substrate, the lattice constant of the GaAs will eventually "match" that of ZnSe at some given pressure and temperature. For example, Rockwell et al.[1] have measured this condition to be at 36 kbar at 80 K.

In order to compare various pressure experiments, we have made a calculation which simulates and predicts the temperature dependence of the strain-free condition under hydrostatic pressure. Using Eq. (7) to determine lattice constants under pressure, we begin with initial temperature-dependent lattice constants (given by thermal expansion data) and find the pressure at which both ZnSe and GaAs, in bulk form, would have identical lattice constants at a given temperature. This should be the "crossover pressure" or the pressure at which light- and heavy-hole valence bands become degenerate. There are three experiments which determine this pressure in similar ZnSe samples, shown in Table I,

along with our calculated values. The calculation predicts variations of less than 3 kbar in the 0–300 K temperature range, and an increase in the crossover pressure at higher temperatures. The 9 K photoluminescence and 80 K photomodulated reflection data follows this trend while the 300 K Raman scattering experiment indicates a change of 12 kbar in the *wrong* direction. We conjecture that the discrepancy may lie in the method of the experiment for the 300 K Raman experiment which compares a Raman shift in a ZnSe pseudomorphic epilayer with that of a bulk ZnSe crystal. One might guess that this method may be overly reliant on the bulk properties of the melt-grown ZnSe crystal. In this study, the phonon frequency of the epilayer and the bulk differ by 1 cm^{-1} at 300 K. A small shift of a fraction of the linewidth of the phonon in the bulk ZnSe sample, used for reference, which might occur due to sample-dependent effects such as impurities, could alter the crossover pressure drastically.

V. CONCLUSIONS

This work demonstrates how one can determine the temperature dependence of biaxial strain in a heterostructure using photomodulated reflectance techniques. The general trend in the ZnSe/GaAs system is that of increasing interlayer biaxial strain with increasing temperature as illustrated by our measurements, and by straightforward calculation. The epilayer strain can be monitored effectively until the spectral features from heavy- and light-hole related transitions can no longer be resolved. This temperature-dependent splitting provides a method of comparison of hydrostatic pressure experiments performed at differing temperatures. Also we hope to have illustrated the importance of including the temperature dependence of the many parameters needed for analysis of such experiments.

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