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Mismatch-tuning by applied pressure in ZnSe epilayers: Possibility for mechanical buffering

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The effect of applied hydrostatic pressure on mismatch-generated strain in semiconductor epilayers is measured for ZnSe films on [001]-oriented GaAs and calculated for several common systems. We observe that pseudomorphic behavior persists in a 775-Å ZnSe epilayer until at least 60 kbar. In agreement with theory, the biaxial strain changes from compressive to tensile at 21±2 kbar, where exact lattice matching occurs. Our work suggests a "mechanical buffering" method for enhancing coherent growth of thick mismatched heterostructures.

Internally strained epitaxial heterostructures are of wide interest and importance because of the varied electronic and optical properties arising from lattice mismatch.[1] External hydrostatic pressure can tune this mismatch-generated strain[2-4] for constituents with sufficiently different elastic constants. At room temperature the tuning range may, in principle, exceed the dislocation limit that restricts pseudomorphic growth. In this paper we investigate the extent that pseudomorphism can be preserved under pressure tuning (at 300 K) for ZnSe overlayers on GaAs. Raman evidence is presented for pressure-induced lattice matching in this system, and matching pressures are calculated for several other epilayer-substrate combinations. Hydrostatic pressure tuning is shown to be a method for creating mechanically metastable interfaces of potential importance for the study of dislocation kinetics. The possibility of applying *biaxial* strain to assist coherent epitaxial growth in situations where chemical buffering is inadequate or unavailable is discussed.

The strain in a pseudomorphic epilayer under applied hydrostatic pressure is easily calculated for high-symmetry growth orientations by minimizing the elastic energy.[4,5] The total linear strain is taken to be the sum of a pressure-induced component, and a constant term due to the 1-bar lattice mismatch. For substrate and epilayer materials labeled by superscripts s and e, respectively, let B_0^s and B_0^e be the 1-bar bulk moduli, and $f_0 = (a_0^s - a_0^e)/\bar{a}_0$ the usual 1-bar misfit strain. We consider explicitly [001]-grown films and refer the strain tensor ϵ_{ij}^e to the cubic axes. Then, the $i \neq j$ terms vanish, and, at all pressures P, the constraint of pseudomorphism in the film plane requires

$$\epsilon_{11}^e = \epsilon_{22}^e = f_0 - \frac{P}{3B_0^s} , \tag{1}$$

while the condition for mechanical equilibrium normal to the film gives

$$\epsilon_{33}^e = -\eta \left[f_0 + \left(\frac{1}{B_0^e} - \frac{1}{B_0^s} \right) \frac{P}{3} \right] - \frac{P}{3B_0^e} . \tag{2}$$

Here one has $\eta = 2C_{12}^e/C_{11}^e$. To first order the expression in square brackets is the pressure dependent misfit $f(P)$.

These strain components will induce a frequency shift of the zone-center (Γ) optic phonons, which can be calculated for zinc-blende semiconductors using a theory originally developed to treat applied uniaxial stress.[6] For a [001]-grown epilayer studied in backscattering, the shift of the singlet LO(Γ) mode is

$$\left(\frac{\Delta\omega}{\omega_{\rm LO}} \right)^e = \frac{\tilde{K}_{11}^e}{2} \epsilon_{33}^e + \frac{\tilde{K}_{12}^e}{2} (\epsilon_{11}^e + \epsilon_{22}^e) . \tag{3}$$

Here the $\tilde{K}_{ij}^e$ denote first-order strain derivatives of the LO(Γ) spring constant in the epilayer material. These coefficients are known for many bulk semiconductors from various uniaxial and hydrostatic stress experiments; a collection of values and cited sources is presented in Ref. 7.

Evaluating Eqs. (1)–(3) using the reported $\tilde{K}_{ij}$ (Ref. 7) and C_{ij} (Ref. 8), we calculate the LO(Γ) pressure coefficients for pseudomorphic epilayers belonging to 14 different epilayer-substrate combinations of general interest. The results are listed in Table I along with the corresponding coefficients for each epilayer material in its bulk (superscript b) form. We see that for many substances these theoretical pressure shifts can differ by ±10% or more between epilayer and bulk. The last column of Table I gives the calculated pressures P_m at which the LO(Γ) frequencies become equal in an epilayer and the corresponding bulk material. Since this happens only when the biaxial strain in the epilayer vanishes, P_m is also the pressure of exact lattice matching for a given epilayer-substrate combination, and P_m must satisfy $f(P_m)=0$.

The ZnSe/GaAs system is a particularly interesting candidate for our hydrostatic pressure investigation. At

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TABLE I. Calculated linear pressure coefficients at 300 K for the LO(Γ) frequencies in some common epilayer (e) – substrate (s) combinations. The second and third columns pertain to the e material coherently bonded to the given substrate, and the same e material in bulk (b) form, respectively. The fourth column gives the lattice-matching pressure P_m for each system; asterisks mark cases where matching occurs before a phase transition (see text).

Samples e/s	$\left(\frac{\partial\omega}{\partial P}\right)^e$ (cm^{-1}/kbar)	$\left(\frac{\partial\omega}{\partial P}\right)^b$ (cm^{-1}/kbar)	P_m (kbar)
ZnSe/GaAs*	0.330	0.378	22.8
GaAs/Si	0.424	0.477	396.0
Ge/Si	0.396	0.448	394.5
InAs/Si	0.351	0.416	537.9
GaP/Si*	0.465	0.491	103.1
InAs/GaAs	0.383	0.416	679.5
GaP/GaAs	0.540	0.491	553.1
GaAs/GaP	0.443	0.477	553.1
InAs/InP	0.389	0.416	380.7
AlSb/InAs	0.563	0.573	668.1
AlSb/GaSb	0.590	0.573	−221.1
InAs/GaSb	0.431	0.416	128.4
InAs/ZnTe*	0.451	0.416	67.5
GaSb/ZnTe*	0.525	0.503	20.2

1 bar the room-temperature mismatch of ZnSe relative to GaAs is 0.0153 Å.[9] Hence, a ZnSe [001]-grown epilayer on GaAs is under biaxial compression with f_0=−0.27%. However, the bulk modulus of ZnSe [595 kbar (Ref. 8)] is smaller than that of GaAs [755 kbar (Ref. 8)], so that according to Eq. (2), applied pressure should reduce and eventually reverse the ZnSe strain from biaxial compression to biaxial tension. From Table I, this is expected to occur at 22.8 kbar (room temperature).

To study these effects, high-pressure Raman measurements are performed on two ZnSe epilayers, a 775-Å-thick film and a 2-μm-thick film, both grown by molecular-beam epitaxy on (001) GaAs substrates.[10] For comparison a melt-grown (bulk) ZnSe specimen is also measured. The epilayer samples are characterized at 1 bar by standard x-ray diffraction and low-temperature reflectivity techniques.[10] Since the *measured* critical thickness h_c for coherent ZnSe overgrowth on GaAs is ~ 1500 Å,[9] only the thinner epilayer sample should be pseudomorphic. Consistent with this, the reflectivity data for the 775-Å film show the predicted (i.e., for f_0=−0.27%) 12-meV heavy-hole–light-hole splitting of the ZnSe band edge.[1,10] However, no splitting is observed for the 2-μm ZnSe film, indicating complete strain relief due to threading dislocations.[11]

Raman spectra are excited with 488.0- and 520.8-nm laser lines, and recorded at room temperature in the backscattering geometry using a double monochromator with microscope foreoptics and an intensified-diode-array detector. The incident laser power is less than 15 mW, well below laser heating levels. Further details of the apparatus are reported elsewhere.[12]

Hydrostatic pressures up to 80 kbar are generated in this work using a ruby-calibrated diamond-anvil cell (DAC) with 4:1 methanol-ethanol mixture as the pressure medium. Specimen preparation for the DAC requires careful thinning and cleaving by established techniques that minimize damage to the epilayers.[12] Raman measurements at 1 bar verify that the epilayer spectra are unchanged before and after preparation, indicating no appreciable increase in dislocation density. A chip of bulk ZnSe is always loaded into the DAC alongside of the particular epilayer under study. Hence, precise comparison between the two is possible independent of the ±1-kbar pressure calibration uncertainty. Sufficient multiplexing and integration (~30 min total counting time) are employed to achieve ~ ±0.2-cm^{-1} accuracy in determining the Lorentzian-fit LO(Γ) peak frequency. This margin is confirmed by repeated observations at the same pressure. Overall, our statistics allow the pressure coefficient of the LO(Γ) frequency to be measured to ± 5% in each specimen.

Figure 1 compares the LO(Γ) Raman peak of the 775-Å ZnSe epilayer to that of the bulk ZnSe chip at three different pressures. Trace (a) shows that the 1-bar LO(Γ) frequency in the epilayer is higher than in bulk ZnSe. This is as expected, since the epilayer is biaxially compressed by its GaAs substrate. Under applied pressure, the LO(Γ) peaks in both specimens exhibit the normal shift to higher frequency. However, the rates of shift are different, so that near 21 kbar [Fig. 1(b)] the two peaks coincide, while at still higher pressure [Fig. 1(c)] their frequency order is reversed. Based on this behavior, we conclude that the biaxial strain in the 775-Å epilayer changes from compressive to tensile as the applied pressure exceeds this value.

In Fig. 2 we plot the measured and calculated pressure

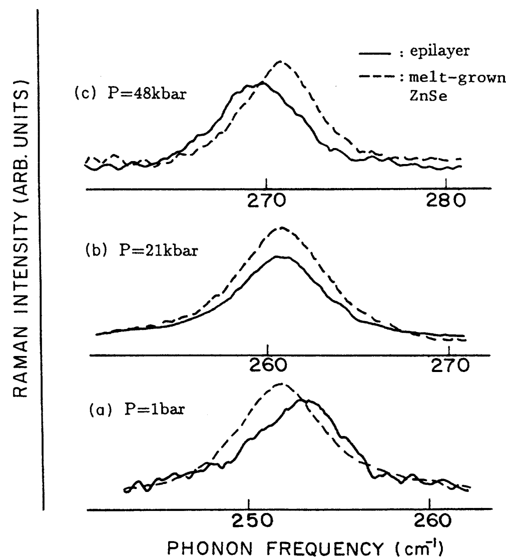

FIG. 1. Comparison between the LO(Γ) Raman peaks of the 775-Å ZnSe epilayer (solid curve) and melt-grown ZnSe (dashed curve) at three different pressures. The two samples are loaded side-by-side in the DAC pressure chamber. Note the reversal in relative separation between the peaks. The frequency axis is shifted by ~ 10 cm^{-1} in each trace.

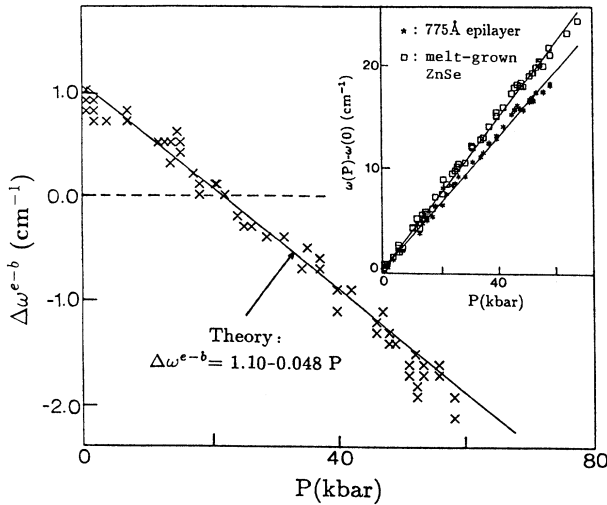

FIG. 2. Pressure response of the difference ($\Delta\omega^{e-b}$) between the LO(Γ) frequencies of the 775-Å ZnSe epilayer and the melt-grown ZnSe sample. The inset plots the corresponding pressure shifts of each sample's LO(Γ) frequency. The solid lines (and displayed formula for $\Delta\omega^{e-b}$) are calculated as described in the text, and are not fitted to the data points.

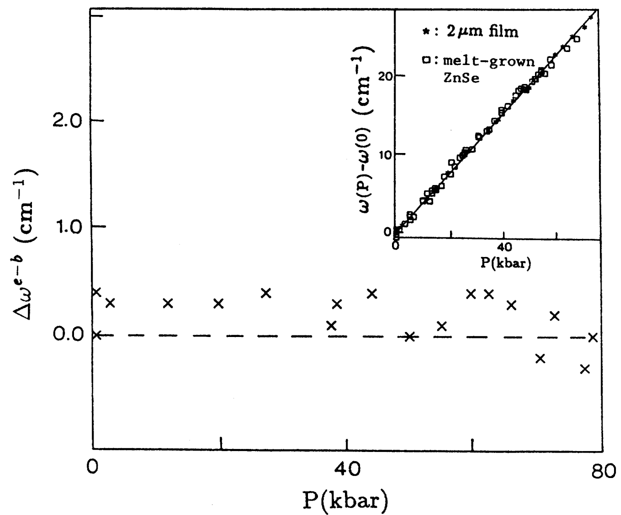

FIG. 3. Effect of pressure on the difference between the LO(Γ) frequencies of the 2-μm ZnSe film and melt-grown ZnSe, similar to Fig. 2. Again the two samples are measured in the same DAC run. They exhibit the same experimental pressure response. The solid line in the inset is calculated for bulk ZnSe.

dependences of the LO(Γ) frequencies in the 775-Å epilayer and the bulk ZnSe sample. The figure inset shows the pressure response of the separate LO(Γ) frequencies, and the difference between these frequencies $\Delta\omega^{e-b}$ is plotted over the same pressure range in the body of the figure. The solid lines are calculated for pseudomorphic behavior using Eqs. (1)-(3), and are not least-square fits. It is clear beyond experimental uncertainty that the LO(Γ) peaks in the two specimens do not exhibit the same response to hydrostatic pressure. Of particular interest, the zero crossing of $\Delta\omega^{e-b}$ is found to occur at 21±2 kbar, close to the predicted result P_m=22.8 kbar (see Table I) for exact lattice matching to the GaAs substrate. The excellent agreement of the data with the calculated lines in Fig. 2 is strong evidence that the 775-Å ZnSe epilayer remains pseudomorphic under applied pressure up to 60 kbar. Hence, we find that interface coherence is sustained in this sample to at least a tension twice as large as the initial (as-grown) biaxial compression. Epilayer data could not be recorded above 60 kbar due to loss of resonance with the available laser-excitation lines.

A similar plot for the 2-μm-thick ZnSe film is displayed in Fig. 3. In this case, the separate pressure shifts of the film and bulk LO(Γ) frequencies both fall along the line calculated for bulk material. (See inset.) Accordingly, $\Delta\omega^{e-b}$ now exhibits no significant pressure response, and, in this regard the 2-μm film behaves like bulk ZnSe. This is to be expected since the film thickness is ten times larger than the known 1-bar critical thickness. The contrast between Figs. 2 and 3 demonstrates that pressure-Raman measurements can clearly distinguish between coherent and incoherent interfaces in the ZnSe/GaAs system.

Let us try to estimate the highest applied pressure P_c under which pseudomorphism could be sustained in the 775-Å ZnSe epilayer. This is easily done by using either the model of Matthews and Blakeslee[11] or that of People and Bean[13] to calculate the misfit strain f_c corresponding to a 775-Å critical thickness, and relating f_c to pressure via the bracketed expression in Eq. (2). Of the two critical-thickness models, the nonequilibrium scheme of Ref. 13 is probably more appropriate here because, unlike the growth process at 320 °C,[10] the room-temperature condition of our experiments should severely hinder dislocation motion. It is instructive, however, to make both estimates in order to establish a realistic range for P_c. Given the ~1500-Å critical thickness measured for f_0 =−0.27% at 1 bar,[9] we find by simple scaling that for a 775-Å epilayer f_c has the values 0.46% and 0.35%, yielding P_c=61 and 52 kbar, for the approaches of Refs. 11 and 13, respectively.[14]

According to the above estimates, one expects that the magnitude of $\Delta\omega^{e-b}$ for the 775-Å epilayer will decrease in the 50–60-kbar range as dislocations form and act to relieve interface strain. However, the data in Fig. 2 exhibit no tendency to bend upward at these pressures. If anything, there is a slight deviation in the opposite direction. We speculate that this behavior is basically of kinetic origin, reflecting, for preexisting lattices at room temperature, an increased difficulty to surmount barriers created during layer-by-layer growth at 320 °C. In effect, our pressure-Raman measurements suggest that the 775-Å epilayer can be compressed into a mechanically metastable state. Thermal studies of interface-dislocation kinetics can clearly benefit from the wide range of mismatch available via hydrostatic pressure tuning.

An interesting method for enhancing the epitaxial growth of thick lattice-mismatched layers follows from

these results. If one directly applies *biaxial* strain to a substrate *during growth* (using a piezoelectric transducer or a bending harness), it should be possible to reduce or even eliminate mismatch with the material (or heterostructure) being deposited. This would increase the effective critical thickness for coherent overgrowth. After deposition is complete, the specimen can be removed to room temperature before releasing the strain, thereby exploiting frozen-in barriers in order to hinder formation and motion of dislocations. By such "mechanical buffering" (with or without chemical buffering), it may be possible for growth to exceed normal critical-thickness limits.

Several factors control the practical value of this method. For many epilayer-substrate combinations the strain needed to significantly reduce lattice mismatch is sufficient to bring about the α-β phase transition(s) in one or both of the constituents. We have considered this in Table I, and find that only the four combinations marked by an asterisk could attain (or even approach) complete matching before a phase change occurs. In addition, the applied biaxial strain must be small enough to avoid fracturing the substrate. This can be gauged from reported behavior under applied uniaxial stress. For example, GaAs often fractures under a [001] compressive stress of 12 kbar, corresponding to a normal (Poisson's) strain of 0.44%.[15] Since this far exceeds $|f_0|=0.27\%$ for ZnSe/GaAs, it seems that mechanical buffering should be practical in the ZnSe/GaAs system. More generally, for many alloy systems of current interest, mechanical *and* chemical buffering could be combined to increase critical thickness. Of course, if growth beyond normal thickness limits is attainable, the longevity of the resulting metastable structures would have to be studied. It is hoped that the present work will stimulate further research in this area.

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