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Thermal expansion behaviour of CdHgTe epitaxial layers on CdZnTe substrates

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Abstract

In order to clarify critical thickness issues for epitaxial layers of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ on $\text{Cd}_{1-y}\text{Zn}_y\text{Te}$ substrates, it is desirable to have accurate data for the difference in thermal expansion between these materials. Based on molecular beam epitaxial samples, we have measured thermal expansion of the two materials simultaneously, over the temperature range 25–110°C, using high-resolution X-ray diffraction. Measured CdHgTe values are corrected for effects of layer strain. Data cover the composition ranges $x = 0–0.7$ and $y = 0–0.05$. Thermal expansion of narrow gap CdHgTe is found to exceed that of lattice matched CdZnTe substrates by approximately 0.3 ppm/K. This can quantitatively account for a previously reported asymmetry in layer relaxation. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Differential thermal expansion can have a significant influence on the strain observed in epitaxial layers at room temperature after high temperature growth. In the case of cadmium mercury telluride ($\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, or CMT) layers on cadmium zinc telluride ($\text{Cd}_{1-y}\text{Zn}_y\text{Te}$, or CZT) substrates, the thermal expansion difference that can be obtained from available reference data is comparable to the scatter in the data [1–7], so that even the sign of the difference remains somewhat

uncertain. It is then difficult to make a proper interpretation of the strain-relaxation behaviour observed at room temperature [8,9], and an accurate determination of the conditions for onset of misfit relaxation remains problematic in this material system.

To overcome the uncertainty inherent in comparing separate measurements of the two materials, we have measured thermal expansion directly on epitaxial CMT/CZT samples, using high-resolution X-ray diffraction, in the temperature range 25–110°C. Simultaneous measurement of the two materials significantly reduces experimental error in the determination of expansion coefficient differences.

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2. Experimental procedure

CMT and HgTe layers were grown by MBE close to Te-rich phase limit conditions on (2 1 1)B oriented CZT substrates. Generally, the MBE layers are compositionally homogeneous and of good crystalline quality. Further details on growth and material properties can be found in Ref. [14]. Layer composition was determined from infrared transmission spectroscopy (see discussion in Ref. [12]), while substrate composition was deduced from the measured lattice constant. For this study, we selected samples with a sufficient lattice mismatch between substrate and layer so that their diffraction peaks were well separated. Some of the layers were relaxed and others unrelaxed. Two samples had a significant variation in the substrate composition, these were characterized in several points with varying lattice mismatch including relaxed and unrelaxed regions. Effects of lattice mismatch are taken into account in the analysis, as discussed below. Two (1 1 1)B oriented CdTe substrates have also been measured, as well as a silicon sample for reference.

The samples were mounted on a temperature controlled sample holder with liquid metal (eutectic Ga/In alloy, melting point 16°C) to ensure good thermal contact while avoiding external stress on the sample. The main part of the holder was a 5 mm thick steel plate, heated by resistive heater elements, on which the samples were mounted. A thermocouple was soldered in a cavity underneath the sample. The sample holder was mounted on a vertical sample stage in the air atmosphere inside the instrument shielding cabinet. The thermocouple temperature was controlled by a PID regulator, and was stable to within $\pm 0.5^\circ$ (some measurements had a somewhat larger fluctuation at high temperatures).

High-resolution X-ray diffraction, using Bond's method [10,11], was employed to measure the lattice constant of the substrate and the apparent lattice constant of the layer. The nearly symmetrical (7 3 3) reflection was used in these measurements. Measurement procedures were similar to those employed in Ref. [12]. Lattice constant measurements were made at several temperatures in the range 25°C (cabinet temperature) to 110°C.

3. Data analysis

As in Ref. [12], diffraction peak positions for substrate and layer are determined by peak fitting. From this, we calculate the substrate lattice constant a_S and the apparent layer lattice constant in the (7 3 3) direction, $a_{(7\ 3\ 3)}$. Small corrections of the lattice parameter values due to refraction and goniometer calibration were not applied here since these have a negligible influence on the measured expansion coefficients.

To interpret the results, elastic deformation of the layer must be taken into account. For an epitaxial layer elastically deformed by lattice mismatch, the measured value $a_{(7\ 3\ 3)}$ is determined by a_S and the unstrained layer lattice constant a_L through a relationship of the form [9,13].

$$a_{(7\ 3\ 3)} = a_L - K(a_S - a_L). \quad (1)$$

For our measurement geometry and sample orientation, a value of 1.009 can be calculated for K from known values of the material elastic constants, in agreement with direct measurement of the elastic deformation behaviour [12].

Fig. 1 shows a typical set of measured lattice constant values for one sample. The data are well fitted by straight lines, and this is the case for all

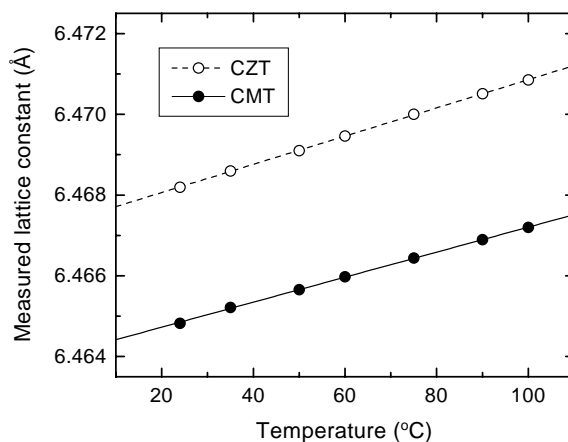


Fig. 1. Measured lattice constants $a_{7\ 3\ 3}$ and a_S for a sample with layer composition $x = 0.22$. Straight lines give excellent fits to the data, and a slight difference in thermal expansion can be seen. The measurement sequence is from low to high to low temperature, and there is no sign of permanent layer deformation.

samples. The slopes of the fitted lines are the substrate expansion coefficient, α_S , and the apparent expansion coefficient for the layer in the (7 3 3) direction, denoted $\alpha_{(7\ 3\ 3)}$. From these we may calculate the expansion coefficient of unstrained CMT

$$\alpha_L = \frac{\alpha_{(7\ 3\ 3)} + K\alpha_S}{1 + K}. \quad (2)$$

(As $K \approx 1$, α_L is effectively the average of α_{733} and α_S for this measurement orientation.) Eq. (2) assumes that K has no strong temperature dependence, i.e. $\Delta K/K \ll 1$ over the temperature interval. This is checked experimentally below.

For relaxed layers, (1) is not valid. For our purposes, relaxation is equivalent to a small and constant offset of the α_S experienced by the layer [16]. Based on this, we have assumed (2) to be valid even for relaxed layers. This has also been checked experimentally.

4. Results and discussion

Fig. 2 shows the measured sets of a_{733} and a_S at two temperatures, for several points on a sample with varying substrate composition. The resulting strain-relaxation characteristic has been discussed elsewhere [9,15]. We note that the shape of the curve is essentially independent of temperature. The slope between the two points on each side of the lattice matching line, which is an estimate of K , is -0.94 at 35°C and -0.97 at 110°C . This small change, as well as the deviation from the nominal value, is attributable to measurement uncertainties [12], and we choose to use the nominal value for the analysis. However, even if the observed variation were a real effect, this amount of change over the temperature interval would have only a small effect on the thermal expansion coefficients calculated according to (2) above.

We have assumed that the expansion coefficients are constant over the temperature range of the measurements. To check this, the data for all samples (such as those in Fig. 1) have been fitted by parabolic functions to estimate their curvature. There is no systematic trend in the sign of the curvature. This is consistent with literature data, in

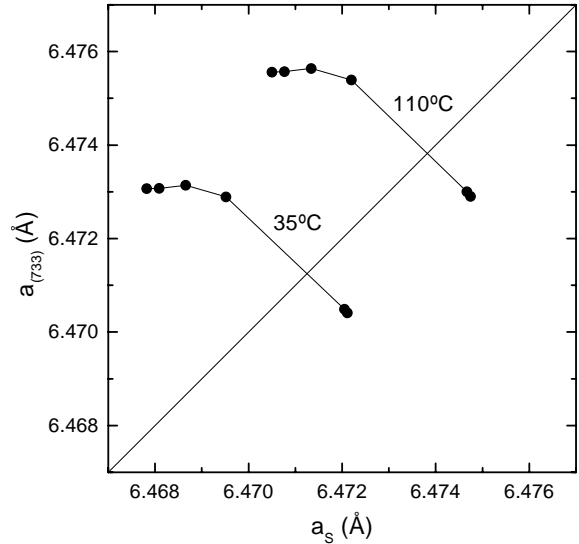


Fig. 2. Measured lattice constants α_{733} and α_S for a sample with layer composition $x = 0.482$ at low and high temperatures. The substrate composition spans a range from compressive plastic deformation (partial relaxation) to tensile elastic deformation. These data demonstrate that the elastic deformation slope K varies insignificantly with temperature, and also illustrate that thermal expansion behaviour is independent of the layer relaxation state.

which thermal expansion coefficients exhibit little temperature dependence beyond 250 K.

The lattice constants measured before and after the heating cycle do not differ significantly for any of the samples. This confirms that none of the layers undergo any strain relaxation or other permanent deformation due to the thermal treatment experienced by the sample during measurement. Thus, it is quite clear that the density of misfit dislocations remains constant in the measurement.

Fig. 3 shows α_L and α_S values obtained in several points on two samples with varying substrate composition, and hence varying degree of layer strain and relaxation. As expected, the relaxation state appears to have no influence on the expansion coefficient. For one of the samples, α_L is practically independent of substrate composition, as expected. For the other sample, α_S and α_L appear to vary with substrate composition. However, this can be explained by a vertical temperature gradient of approximately 1.3 K/cm along the

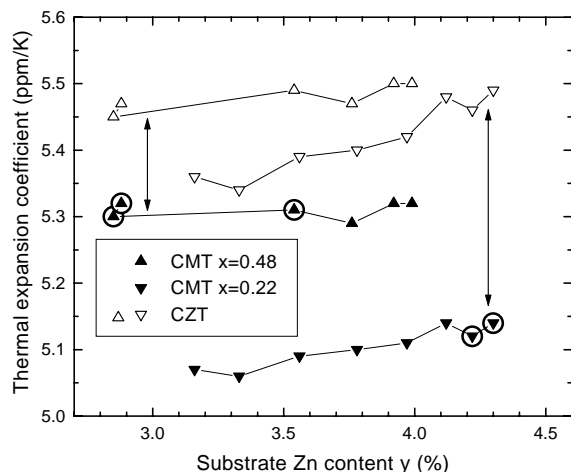


Fig. 3. Thermal expansion coefficient of substrate (open symbols) and layer (closed symbols) for two samples with different x -values as shown, which both have a large span in substrate composition. Unrelaxed points (with only elastic deformation, as determined from plots like Fig. 2) are indicated by circles. Clearly, the relaxation state has no significant effect on the measured expansion coefficient. (These data suggest imperfect control of the sample temperature, as discussed in the text.)

sample while mounted on the holder. This is in good agreement with measurements with a thermocouple attached to a dummy sample, which indicated that a gradient of 1 K/cm was present.

In general, uncertainties related to thermal gradients are expected to dominate the measurement uncertainty, since the lattice constant determinations are quite accurate [12]. The gradients will be approximately proportional to the heater power, which varies nearly linearly with the deviation from cabinet ambient temperature. Thus, the relevant temperature error is the difference between setpoint and sample surface temperature at the maximum measurement temperature. At 100°C, the sample surface was 5° below the setpoint, as measured by a thermocouple attached to a dummy sample. This corresponds to a 6% underestimation of the expansion coefficients. This measurement appears pessimistic, since the thermocouple wires will increase the heat loss at the measured point. However, measurement on a silicon reference sample yields an expansion coefficient of 3.0 ppm/K. This is 8% below the literature value, corresponding to a

temperature error of 6°. The total scatter of the CdZnTe values suggest that variations in thermal contact between sample and holder introduce a temperature uncertainty of some 2° or less, at the highest setpoints. Since temperature errors may vary, setpoint temperatures have been used in the calculation of absolute expansion coefficients here. Considering the observed temperature imperfections, the absolute expansion coefficients may therefore be somewhat *underestimated*, although by less than 10%. This uncertainty is still less than the range of values previously reported, and we note that our results are already in the upper part of this range.

Fig. 4 shows all measured thermal expansion coefficients as a function of composition for CMT and CZT. The figure also shows a number of previously published values. Results for HgTe layers and CdTe substrates agree with data in Ref. [1] within their uncertainties. For CZT, the composition dependence appears consistent with

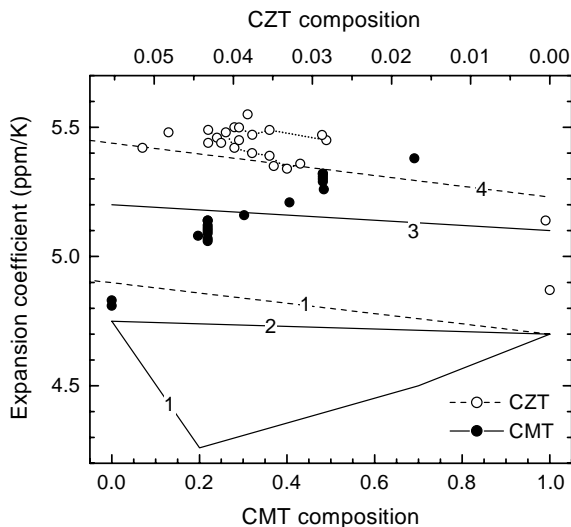


Fig. 4. Thermal expansion coefficient as a function of composition for CMT and CZT. The datasets shown in Fig. 4 are joined by solid lines. Two (1 1 1)-oriented CdTe substrates are included for comparison. As discussed in the text, temperature gradients may lead to some underestimation of expansion coefficients, possibly in the range 5–10%. Straight lines show literature values: lines marked 1 are from Ref. [3], line 2 is from Refs. [4 and 5], line 3 is from Ref. [2] and line 4 is from Refs. [6 and 7], quoted in Ref. [8]. The latter data are for a temperature of 200°C.

previous data, although the values are somewhat higher. For intermediate CMT compositions, there are few literature data to compare with, but we note that the slope is comparable to that observed in Ref. [3] above $x = 0.2$. However, the CMT data do not seem to converge on the measured CdTe value, contrary to expectations. (We note that the CdTe and CZT substrates were from different manufacturers, but this is not expected to have a large effect on thermal expansion.) The apparent inconsistency between high- x CMT and CdTe, about 10% of the mean value, has not been resolved due to lack of suitable CMT (higher x) and CZT (larger y range) samples.

The differential thermal expansion between substrate and layer can be determined to a much better accuracy than the bulk values. Since the sample surface region probed by X-rays is thin, both materials are at the same temperature and the relative errors in α_L and α_S due to temperature gradients are equal. Thus for an error less than 10% in the absolute values, the difference between them will also be determined within 10% (assuming temperature errors to be dominating). This accuracy is significantly better than what can be obtained from previously published data. Fig. 5 shows the difference between the substrate and

layer expansion coefficients as a function of CMT composition for layers grown on substrates with y in the range 0.03–0.05. As expected, this exhibits less scatters than the absolute values. Any effect of CZT composition differences have not been taken into account in the plot, since the variation in y is small and the data in Fig. 4 suggest that variation with CMT composition is the dominating effect.

At $x = 0.25$, the CMT expansion coefficient is about 0.3 ppm/K less than for lattice matched CZT. For an MBE layer grown at 200°C, this gives a non-negligible contribution to the layer strains observed at room temperature, for typical layer thickness used in devices. Thermal expansion can account for much of the asymmetry we observe between compressive and tensile relaxation in our layers [9]. For other growth techniques, using higher growth temperatures, differential thermal expansion becomes correspondingly more important. Fig. 5 shows the value reported by Tobin et al. [8] which would account for their observation of asymmetric relaxation behaviour on LPE-grown material. This coincides very well with our data.

5. Conclusions

We have measured the thermal expansion coefficient for CZT in the composition range $y = 0–0.05$ and for CMT in the composition range $x = 0–0.7$. Thermal gradients cause some uncertainties, which are nevertheless smaller than the range of values found in the literature. The differential thermal expansion between CMT and CZT at the technologically most important compositions has been determined with good accuracy. These data can account for asymmetry in relaxation behaviour reported elsewhere. Our data will aid in the interpretation of misfit relaxation measurements, and will thus eventually help clarify critical thickness issues in the CMT/CZT material system.

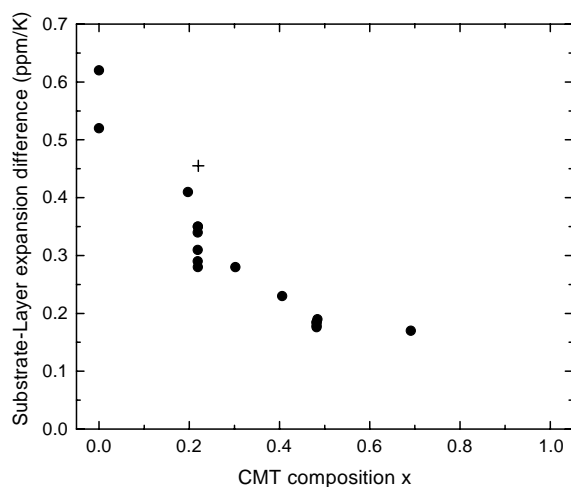


Fig. 5. Difference in thermal expansion coefficient between substrate and layer for all CMT samples. The scatter in these data is small, due to cancellation of temperature errors. The cross indicates the value, which would account for the relaxation asymmetry observed in Ref. [8].

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