

# Evaluation of Low-Temperature Interdiffusion Coefficients in Hg-Based Superlattices by Monitoring the $E_1$ Reflectance Peak

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We show that variations of the  $E_1$  reflectance peak in Hg-based superlattices can be used to probe low-temperature interdiffusion by monitoring the shift of the  $E_1$  peak with time over extended periods. Little evidence of interdiffusion was detected for a number of HgTe/CdTe and HgCdTe/CdTe superlattices stored at room temperature for approximately two years. Two HgTe/CdTe superlattices and one HgCdTe/CdTe superlattice were subsequently annealed in a dry nitrogen atmosphere at 100°C for approximately six months, and then at 150°C for 24 days. During these intervals, the superlattices were periodically removed from the anneal for reflectance measurements to assess the extent of the interdiffusion. Comparison of these results with calculations of superlattice bandgaps and interdiffusion profiles has led to an evaluation of the low temperature interdiffusion coefficients. These extend previous results to lower temperatures and confirm that the degradation of Hg-based superlattices devices due to thermal interdiffusion under normal processing, storage, and operating conditions should not be an issue of concern.

**Key words:** HgTe-CdTe superlattice,  $k \cdot p$  calculation, low temperature interdiffusion, molecular beam epitaxy

## INTRODUCTION

HgCdTe heterojunctions and multi-layer structures continue to be of interest for infrared light detection and emission.<sup>1</sup> However, in the context of practical devices, an issue of ongoing concern has been the long-term stability of compositional profiles under typical processing, storage, and operating conditions. Reliable predictions of what will occur at the interfaces over extended time periods depends on a detailed knowledge of the compositional interdiffusion coefficients for HgCdTe at low temperatures. As pointed out in the recent review by Shaw,<sup>2</sup> there is good agreement for values of the interdiffusion coefficients above 400°C, but poor agreement below 400°C. This is

clearly indicated by the temperature- and composition-dependent interdiffusion coefficients measured by various groups<sup>3-16</sup> as displayed in Fig. 1. In particular, previous data are quite sparse for the region below 200°C, which is most relevant to device considerations.

In general, reflectance peaks occurring above the bandgap in a semiconductor have a monotonic correlation with the bandgap energy, and hence with the composition. Such a dependence has been used previously to determine compositions in HgCdTe.<sup>17</sup> We recently reported that a similar relationship exists between the bandgap and the  $E_1$  reflectance peak for HgTe/CdTe superlattices.<sup>18</sup> Using this relationship, changes in the position of the  $E_1$  reflectance peak can be used to probe for changes in the layer compositions resulting from interdiffusion. While similar information can be determined from infrared photolumines-

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cence or low temperature infrared absorption measurements, both are more complicated to perform. In addition, absorption measurements give an average of the entire sample, and thus may miss surface diffusion. Similarly, if depth-dependent interdiffusion is taking place, the resulting photoluminescence (PL) from the interdiffused region may be too broad to easily indicate a small change. We previously demonstrated<sup>18</sup> that reflectance measurements can detect depth-dependent interdiffusion occurring near the front surface of a HgTe/CdTe superlattice, and so have chosen this technique for our study. In this paper, we report the results of long-term monitoring of the  $E_1$  reflectance peaks for various HgTe/CdTe and HgCdTe/CdTe superlattices which allows us to estimate the magnitude of the interdiffusion coefficient at low temperatures.

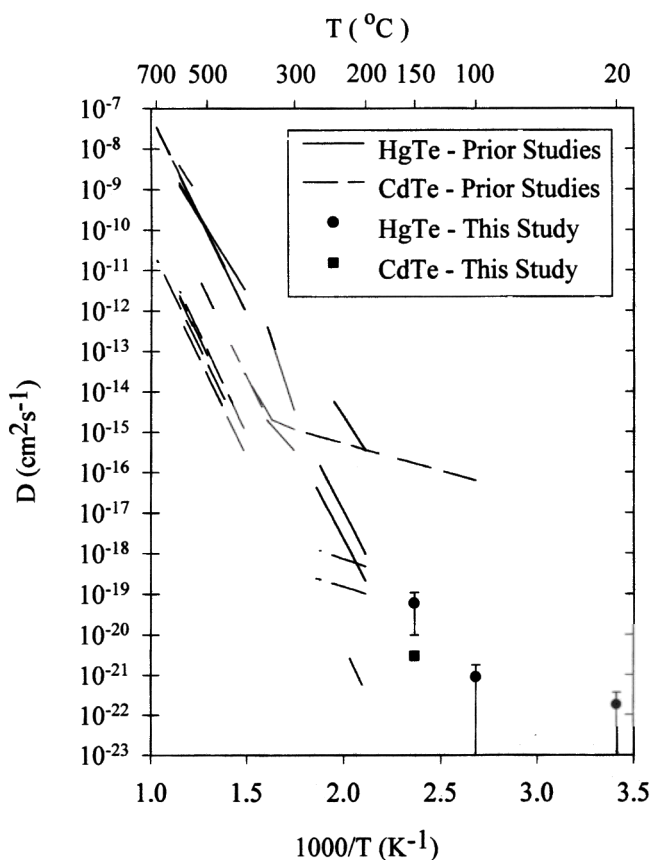


Fig. 1. Summary of interdiffusion coefficients<sup>3-16</sup> for the HgCdTe system. Shaw<sup>2</sup> has presented an excellent review of this information which details the individual studies.

## EXPERIMENTAL AND THEORETICAL DETAILS

During this study, reflectance measurements were made on six (211)B HgTe/CdTe and one (211)B HgCdTe/CdTe superlattices grown by molecular beam epitaxy (MBE) at Lockheed-Sanders Electronics Laboratory (Syracuse, NY), and three (211)B HgCdTe/CdTe superlattices grown by metalorganic MBE at the Physical Sciences Laboratory at Georgia Tech Research Institute. The epilayers were of high quality, as determined by transmission electron diffraction, Hall effect, and double crystal x-ray diffraction measurements. Reflectance measurements were made at room temperature using an Olis-14 dual-beam spectrophotometer. The measured reflectance was referenced to a calibrated sapphire window. The bandgap energies reported for the various superlattices were determined by infrared photoluminescence measurements.

The superlattices were stored at room temperature for over two years, with no special care taken to minimize exposure to the atmosphere. Three of the superlattices from Lockheed-Sanders, labeled SL1, SL2, and SL3, were also annealed at elevated temperatures in an isothermal oven. The pertinent parameters of these superlattices are listed in Table I. During annealing, the superlattices were exposed to a dry nitrogen atmosphere maintained at one atmosphere pressure to simulate conditions encountered in processing and long-term storage.

It has long been recognized that interdiffusion in the HgCdTe system is a nonlinear process<sup>7,10,11</sup> which is best approached by a numerical solution of Fick's second law. Following previous treatments,<sup>10,11</sup> we assume that the interdiffusion coefficient has a strong compositional dependence of the form

$$D(x) = D(\text{HgTe})\exp[-\alpha x]$$

where  $x$  is the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloy composition. The parameter  $\alpha$  is related to the energy of formation for defects,<sup>19</sup> and ranges in value from 3 to 14 for reported interdiffusion coefficients (see again Fig. 1). Since  $D(x)$  is at least 50 times larger near  $x = 0$  than near  $x = 1$ , the interdiffusion in a HgTe/CdTe superlattice is driven primarily by the HgTe rate. This implies the maintenance of relatively sharp interfaces, with the CdTe barriers becoming progressively thinner while the Cd diffuses rapidly through the HgTe wells to form a HgCdTe layer with relatively constant concen-

Table I. Summary of Superlattice Parameters

Layer	Well Composition (x-value)	Well Thickness (Å)	Barrier Composition (x-value)	Barrier Thickness (Å)	CdTe Capping Layer (Å)	$E_0$ Energy at 80K (eV)	$E_1$ Peak at RT (eV)
SL1	0.0	42	0.9	45	None	0.108	2.296
SL2	0.3	100	0.9	50	200	0.305	2.391
SL3	0.0	39	0.9	36	200	0.140	2.313

tration.<sup>10</sup> A small compositional gradient does exist throughout the well, however, becoming more pronounced near the interface.

Numerical integration of Fick's second law was performed to generate compositional profiles for a wide range of values. The change in bandgap energy for the superlattice will, to first order, be related to the change in average well composition. Thus, the simulations could be used to estimate the times required for specific average compositional changes in the wells. Since the calculated profiles were driven primarily by the fast ( $x \approx 0$ ) interdiffusion component, we derive only about a factor-of-three difference between the times required for a given average composition change for any value of  $\alpha$  ranging between 2 and 14.

Since a full multi-band calculation of the bandgaps in superlattice structures with continuously varying composition profiles is difficult, we performed eight-band calculations assuming that the CdTe removed from the barriers (which became correspondingly thinner) was evenly redistributed throughout the wells, leading to wider HgCdTe layers. This closely approximates the interdiffusion profiles discussed above, and allows a reliable approximation of expected changes in the bandgap energies. Band structures for both the original and the "diffused" superlattices were calculated using an eight-band transfer matrix  $\mathbf{k} \cdot \mathbf{p}$  algorithm<sup>20</sup> which includes strain and accounts for the (211) crystal orientation. The valence band offset between HgTe and CdTe was taken to be 350 meV,<sup>21</sup> although for this orientation the barriers are assumed to have an  $x$ -value of 0.9. The results of these calculations indicated the change in bandgap associated with a given change in well composition due to interdiffusion of a specific superlattice structure.

## RESULTS AND DISCUSSION

In order to extract interdiffusion coefficients from the positions of the reflectance peaks, a monotonic relationship must exist between the  $E_1$  position and bandgap (and hence compositional) changes. As reported earlier,<sup>18</sup> both theoretical modeling and experimental data indicate such a trend exists. Figure 2 illustrates the reflectance spectrum for a HgTe/CdTe superlattice (SL3) with a 200Å thick CdTe capping layer. Both the  $E_1$  and  $E_1 + \Delta_1$  peak of the superlattice are present, along with the  $E_1$  peak of the CdTe capping layer.

Figure 3 summarizes the  $E_1$  peak energies measured for six HgTe/CdTe and four HgCdTe/CdTe superlattices, plotted as a function of their 80K bandgap energies as determined from infrared photoluminescence measurements. While there is scatter in the data, the monotonic trend is clearly apparent. Also shown for comparison is the same correspondence for HgCdTe alloys, derived from expressions by Raccah<sup>17</sup> and Hansen et al.<sup>22</sup> Interestingly, both the magnitude and the variation of the  $E_1$  peak energies in the superlattices closely track those for the alloy. This trend allows us to correlate the magnitude of the

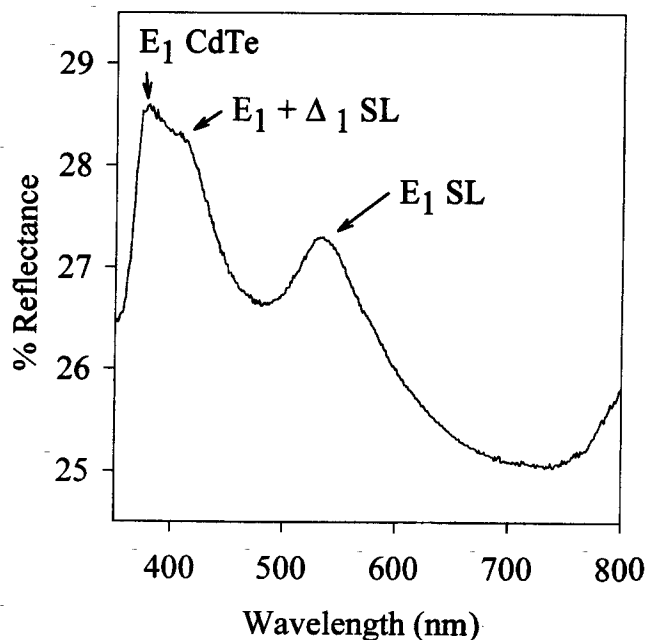


Fig. 2. Reflectance spectrum for SL3.

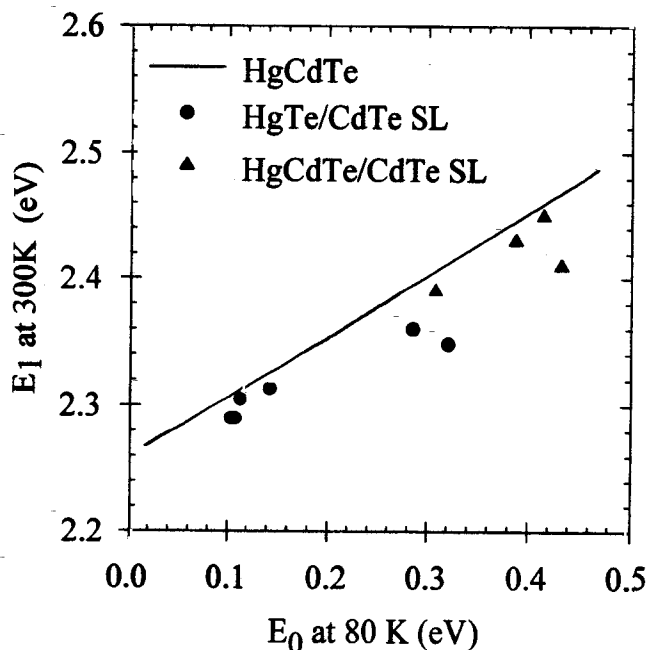


Fig. 3. Measurements of the  $E_1$  reflectance peak energy plotted against the bandgap energy of various Hg-based superlattices. The solid line represents the relationship observed for the HgCdTe alloy system.

expected peak shift for a given change in the bandgap energy in a superlattice structure. Conversely, given a shift in the  $E_1$  peak energy, one can infer a specific change in the superlattice bandgap, for example due to compositional interdiffusion. The  $E_1$  features measured for the superlattices were typically not as well-resolved as those observed for alloy samples, leading to a measurement uncertainty of about  $\pm 1$  nm. This corresponds to a minimum detectable change in bandgap of about 8 meV if we assume a linear dependence derived from a fit to the data in Fig. 3. While

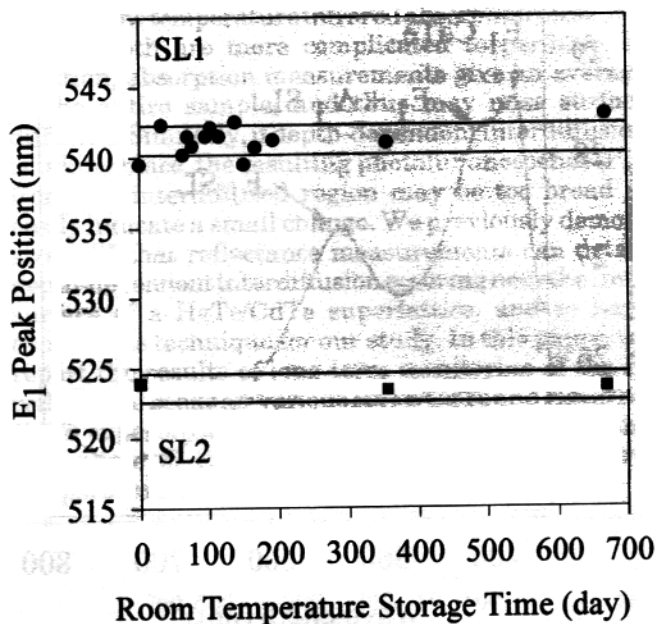


Fig. 4.  $E_1$  peak wavelength as a function of time at room temperature for SL1 and SL2. The solid lines represent  $\pm 1$  nm intervals about the mean  $E_1$  value, representing the uncertainty in our determination of the  $E_1$  peak.

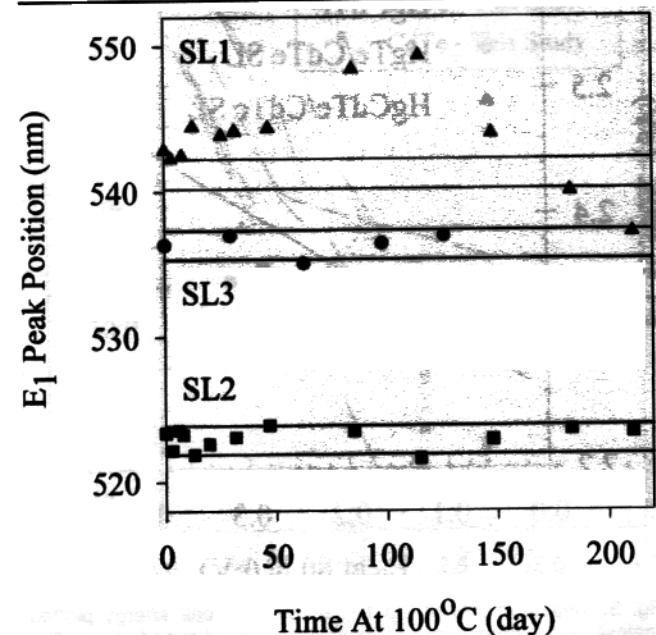


Fig. 5.  $E_1$  peak wavelength as a function of time at 100°C for SL1, SL2, and SL3.

sample-to-sample scatter in the data contribute a somewhat larger uncertainty of about 40 meV in the absolute correlation between  $E_0$  and  $E_1$ , this should not affect the conclusions concerning the shift of the gap in a given sample.

While a shift in the  $E_1$  energy can indicate that a change is occurring in the superlattice, a linkage must be established between compositional changes and the bandgap if interdiffusion coefficients are to be estimated. Use of the eight-band transfer matrix  $\mathbf{k} \cdot \mathbf{p}$  calculations described above provides this linkage.

Calculations were performed for a 40Å/40Å HgTe/CdTe superlattice to mimic both SL1, and SL3, and for a 100Å/50Å  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ /CdTe superlattice to mimic SL2. The calculations yield  $\Delta E_1/\Delta x \approx 400$  meV (where  $\Delta x$  is the change in well composition following interdiffusion) for the 40Å/40Å HgTe/CdTe superlattice, while  $\Delta E_1/\Delta x \approx 800$  meV for the 100Å/50Å  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ /CdTe superlattice for small ( $\Delta x < 0.05$ ) changes in well composition. This establishes the minimum detectable change in well composition expected from an observable shift in the  $E_1$  peak energy, which corresponds to  $\Delta x \approx 0.02$  for the 40Å/40Å HgTe/CdTe superlattice and  $\Delta x \approx 0.01$  for the 100Å/50Å  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ /CdTe superlattice.

Interdiffusion profiles resulting from  $\Delta x \approx 0.02$  for the 40Å/40Å HgTe/CdTe superlattice and  $\Delta x \approx 0.01$  for the 100Å/50Å  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ /CdTe superlattice were calculated by numerical integration of Fick's second law as discussed above, also assuming that  $x = 0.9$  in the barriers. Results were obtained for a range of values. Once the total time required to obtain a detectable shift in the  $E_1$  peak energy for a given HgTe/CdTe superlattice has been determined experimentally, comparison with these calculations allows an estimation of the interdiffusion coefficient for the fast (HgTe) component. Furthermore, comparison between this time and the time required for an observable shift in the  $E_1$  peak energy for the  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ /CdTe superlattice then allows an estimation of the parameter  $\alpha$ . This is admittedly an indirect approach, and the resulting values should be considered to be uncertain by roughly an order-of-magnitude. However, since extrapolation of the results shown in Fig. 1 leads to values for the fast component spanning more than four orders-of-magnitude, a measurement of  $D$  to within a factor-of-ten is quite useful. At the very least, the observed times provide an empirical indication of the stability of the superlattice structures.

Figure 4 summarizes results of monitoring of  $E_1$  reflectance peaks for SL1 and SL2 as a function of time during storage at room temperature for nearly two years. Also shown for reference are lines bracketing the mean peak position by our  $\pm 1$  nm confidence intervals. Within the uncertainty of the measurement, clearly no detectable change in the  $E_1$  position resulted from the room-temperature storage. This allows us to infer an upper bound on the interdiffusion coefficient at 300K, which is included on Fig. 1.

Figure 5 shows results for all three superlattices as a function of time during the anneal at 100°C. Again, SL2 exhibited no change for the time monitored. SL1, on the other hand, showed a significant change almost immediately. However, the trend observed for SL1 was opposite what was expected for interdiffusion, namely to longer  $E_1$  wavelengths which indicates a smaller bandgap! Then, after about 180 days at 100°C, the trend in  $E_1$  reversed itself. This particular superlattice had been etched to remove about 0.5  $\mu\text{m}$  of material as discussed previously.<sup>18</sup> We believe that the resulting "exposed" surface allowed Hg-

outdiffusion and subsequent degradation to occur since the  $E_1$  position moved toward what has been observed for Te-rich HgCdTe alloy samples grown by one of us (THM) previously. To check this assertion, annealing studies at 100°C were next performed on a second HgTe/CdTe superlattice (SL3) with a similar bandgap. This sample had a 200Å CdTe capping layer, which should inhibit surface degradation. Although monitored for a shorter period of time, no change in the  $E_1$  peak position was observed for that superlattice. The corresponding upper-limit for the fast interdiffusion coefficient at 100°C is again indicated in Fig. 1.

Figure 6 displays the results measured for SL2 and SL3 at 150°C. By 48 h, a detectable shift in the  $E_1$  peak wavelength had already occurred for SL3. On the other hand, SL2 did not exhibit an appreciable shift until about 380 h had elapsed at 150°C. The longer time required for SL2 is consistent with the expectation that the low temperature interdiffusion coefficient should decrease rapidly with increasing Cd content in the wells (see Fig. 1). However, this finding contradicts the conclusion of at least one previous study.<sup>12</sup> Correlating our times for a measurable shift in  $E_1$  with the results of the numerical interdiffusion simulation gives a value of about  $6 \times 10^{-20}$  cm<sup>2</sup>/s for the interdiffusion coefficient in HgTe at 150°C. The data for SL2 then provide a corresponding estimate of  $\alpha \approx 3$ , which falls near the bottom of the range indicated by previous high temperature results and implies an interdiffusion coefficient of about  $3 \times 10^{-21}$  cm<sup>2</sup>/s for CdTe at 150°C. Both values are included on Fig. 1. The HgTe value appears quite reasonable when compared to extrapolations from the previous higher temperature data and are consistent with the high resolution transmission electron microscopy measurement of sharp interfaces for HgTe/CdTe superlattices by Otsuka et al.<sup>23</sup> and Millien et al.<sup>24</sup> Both studies could not detect any difference in interface abruptness between the initial and final HgTe/CdTe interfaces of thick (4 to 5 μm) superlattices and observed no evidence of interdiffusion. Detailed analysis indicated that the interface roughness corresponded to about one monolayer. If this roughness is taken as an indication of interdiffusion, it indicates an upper bound on the fast interdiffusion coefficient of about  $5 \times 10^{-20}$  cm<sup>2</sup>/s between 175 and 190°C. The CdTe value we report also appears to be consistent with the values obtained from extrapolations from higher temperature data.

We should note the possibility that some type of degradation could be taking place in addition to simple interdiffusion. Defects created by such degradation would then lead to faster interdiffusion. Since our anneals were not performed under an appropriate Hg-overpressure to give equilibrium conditions, the derived values for  $D(x)$  should be regarded as upper limits.

## SUMMARY AND CONCLUSIONS

The  $E_1$  reflectance peak in Hg-based superlattices

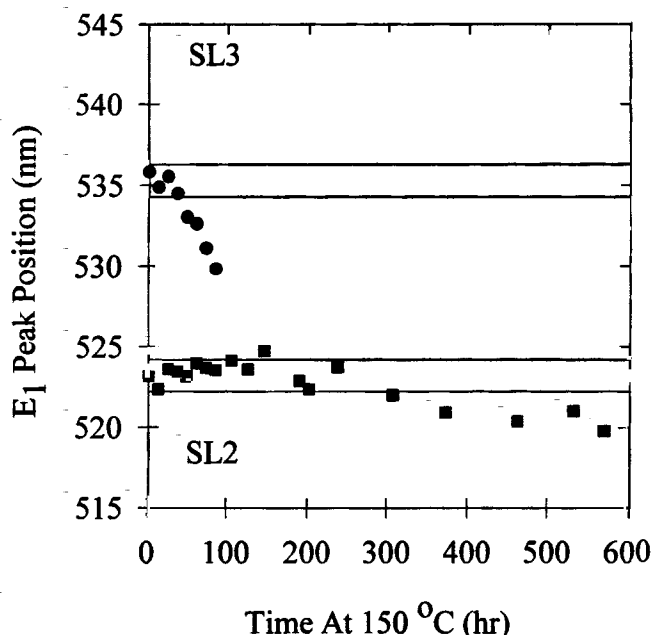


Fig. 6.  $E_1$  peak wavelength as a function of time at 150°C for SL2 and SL3.

has been shown to vary with bandgap energy in such a fashion that this peak can be used to probe interdiffusion. Both the magnitude of  $E_1$  and the shape of  $E_1$  vs  $E_0$  (Fig. 3) is found to be quite similar to that of the alloy. The  $E_1$  reflectance peaks of selected superlattices were monitored for extended periods of time to assess the low temperature interdiffusion. Little evidence of interdiffusion was detected for HgTe/CdTe and HgCdTe/CdTe superlattices stored at room temperature for approximately two years, resulting in an upper bound on the HgTe interdiffusion coefficient of about  $2 \times 10^{-22}$  cm<sup>2</sup>/s. While a superlattice without a CdTe capping layer almost immediately exhibited changes believed to be associated with degradation when annealing was carried out at 100°C, a CdTe-capped superlattice with similar structure showed no signs of change for the period monitored. This led to an upper bound on the HgTe interdiffusion coefficient at that temperature of about  $9 \times 10^{-22}$  cm<sup>2</sup>/s.  $E_1$  peak shifts were observed for the remaining two superlattices at 150°C, resulting in estimated interdiffusion coefficient values of  $6 \times 10^{-20}$  cm<sup>2</sup>/s for HgTe and  $2 \times 10^{-21}$  cm<sup>2</sup>/s for CdTe.

Our findings, that Hg-based superlattices can survive for periods of at least two years at room temperature and six months at 100°C without any measurable  $E_1$  shift, indicate that stability with respect to thermal compositional interdiffusion should not be a problem for most Hg-based multi-layer structures under typical processing, storage, and operating conditions. However, a CdTe or other passivation layer may be required to prevent degradation.

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