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Photoluminescence and x-ray diffraction studies of the diffusion behavior of lattice matched InGaAs/InP heterostructures

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Photoluminescence and high resolution x-ray diffraction (HRXRD) were used to follow the diffusion of a lattice matched InGaAs/InP heterostructure at various annealing temperatures. At 900 °C no strain was observed by HRXRD and this indicated that the two sublattices in the sample diffused at an equal rate and only compositions on the tie line between the two initial compositions were formed. At lower annealing temperatures strain was observed in the wells and barriers, the signs of which changed during the annealing process. This is indicative of the diffusion rates of the two sublattices changing during the annealing process. It is suggested that these effects may be due to the presence of the miscibility gap in the InGaAsP system. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1586975]

I. INTRODUCTION

The InGaAsP system has attracted considerable interest due to the wide range of band gaps that can be produced from its alloys using the commercially important GaAs and InP substrates. Materials grown on InP are particularly important due to their use in telecommunications lasers operating at both the 1.3 and 1.55 μm wavelengths. Despite commercial interest in these materials there are still relatively little data on the diffusion behavior of materials that utilize the lattice matched InGaAs/InP system.

In recent years the InGaAsP material system has found use as a model system for understanding of the role of coherency strain on the structural properties of materials. In 1995 Kelly suggested that structures with alternating thin coherently strained layers in tension and compression could be of interest for high temperature applications.[1] Two years later it was demonstrated using the InGaAsP semiconductor system that superlattices with alternate layers in tension and compression and with a nonzero net strain could maintain this average strain at high temperatures, whereas comparable homogeneously strained systems would relax under identical conditions.[2] Although these results show the potential benefit of pseudomorphic strain-balanced structures for structural materials, a potential problem of the approach would be thermal interdiffusion of the structure at high temperature. Thus stability with regard to diffusion is necessary to help prevent the homogenization of the modulated strain field and to extend the durability of the mechanical properties under prolonged exposure to high temperatures. The positive enthalpy of mixing that exists in alloy systems with a miscibility gap might provide a controlled way in which to generate and conserve such thermally stable inhomogeneous structures.

The InGaAsP quaternary system is characterized by a miscibility gap with a calculated critical temperature of 808 °C.[3] Photoluminescence and high resolution x-ray diffraction (HRXRD) characterization of the intermixing of a 10 nm lattice matched InGaAs/InP quantum well at various temperatures[4] clearly showed that the miscibility gap had no noticeable effect on the diffusion at a temperature of 900 °C. But at 600 °C, the HRXRD rocking curves showed that strain had developed in the annealed specimen. The strain was consistent with the larger diffusion length of group V atoms (As, P) at completion of the experiment. The photoluminescence data, which showed an initial blueshift followed by a subsequent redshift back towards the initial photoluminescence peak position, suggested that if group V atoms had initially diffused at a faster rate than group III (In, Ga) ones, the diffusion would have reversed at a later stage of annealing with predominant interdiffusion of indium and gallium. The miscibility gap was suggested to alter diffusion and generate strained layers.

In this article, additional HRXRD measurements were taken upon completion of long anneals at various temperatures and a more systematic study showing the history of the development of strain according to the anneal time is also presented. The data confirm previous results that suggest that the miscibility gap alters diffusion at higher temperatures than were previously expected.

II. EXPERIMENT

10 nm $In_{0.53}Ga_{0.47}As$ single quantum well (SQW) specimens, lattice matched to 001 InP substrates, were grown by molecular beam epitaxy (MBE). They consisted of an InP buffer layer ($\sim$300 nm), the quantum well, and a 100 nm InP barrier layer. A 50 nm silicon nitride cap layer was subsequently deposited by plasma enhanced chemical vapor deposition (PECVD) to prevent surface decomposition of the specimens during annealing.

The samples for the annealing experiments were typically 7×5 mm^2 and were cut from two nominally identical wafers, referred to as A and B in this article. HRXRD rocking curves of the original wafers coupled with simulations

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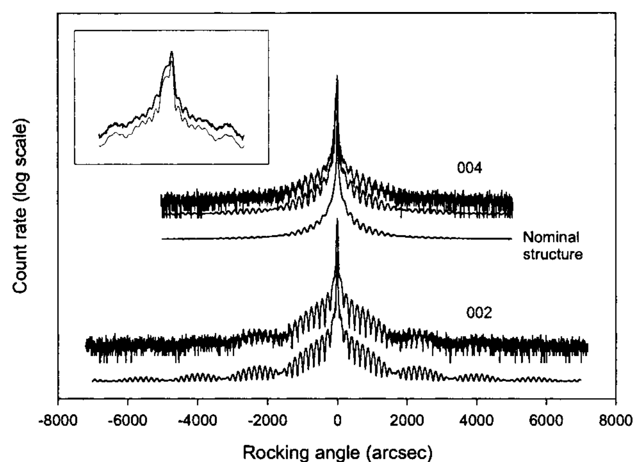

FIG. 1. Experimental and simulated 002 and 004 x-ray rocking curves for as-received wafer B. The simulations are for the structure given in Table I although the 004 simulation of the nominal structure is shown for comparison. The inset is an enlarged view of the 004 rocking curve around the substrate peak.

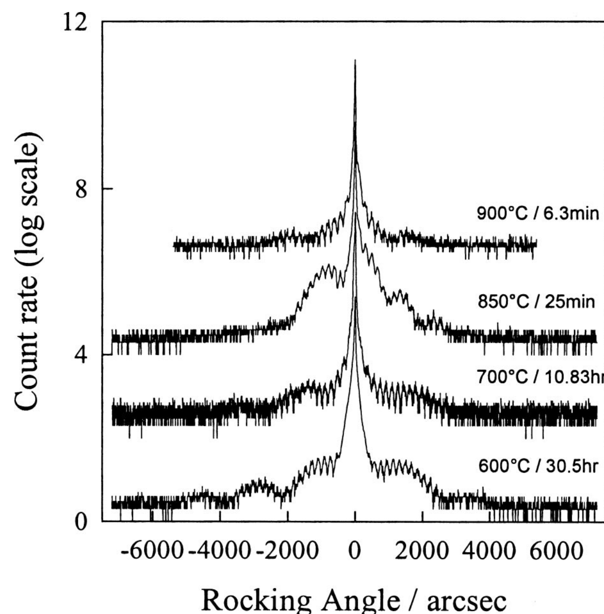

FIG. 2. Experimental 004 x-ray rocking curves for samples following annealing at different temperatures. The samples annealed at 600 and 700 °C show the well in tension whereas the sample annealed at 850 °C shows the well in compression. The sample annealed at 900 °C is unstrained.

showed that wafer A had thin, ~1 monolayer, strained layers between the wells and barriers. It was also observed that the top barrier was slightly (1.2%) contaminated with arsenic over a larger extent (~20 nm). Figure 1 shows the 004 and 002 HRXRD experimental rocking curves of as-grown wafer B. The x-ray profile fits were calculated for 002 and 004 reflections using Philips X'Pert EPITAXY 3.0 software. The software calculates rocking curves by the dynamical theory of x-ray scattering from a model virtual crystal made of layers of uniform composition. The prominent shoulder measured on the substrate peaks and the high frequency structure visible in the enlarged window of the experimental 004 rocking curve were unexpected and signaled the presence of a large layer (generating high frequency features) with slight compressive strain (slightly offset by the layer peak to the left of the substrate peak). All those features could be matched by including a background concentration of 0.5% of arsenic in the epitaxially grown InP buffer layer and barrier, suggesting persistent As contamination throughout the crystal growth. Details of the model structure used to produce the fits in Fig. 1 are given in Table I. The strained interphases arise during MBE growth when the group III sources are closed and the group V sources switched, leading to substitution on the anionic sites grown last. No exact composition is given for the second interphase Table I because all the quaternary compositions between $In_{0.12}Ga_{0.88}As$ and $In_{0.60}Ga_{0.40}P$ with a misfit value of −2.86% provide the same curve fits. A phosphorous rich phase would nevertheless be expected since the arsenic would tend to be substituted, and the indium/gallium ratio should be very close to the well values. Note that $In_{0.531}Ga_{0.469}As_{0.145}P_{0.855}$ would suit the −2.86% strain value and In:Ga ratio. These strained interphases account for the large amplitude of the fringes observed in the experimental measurements compared to in simulation of the nominal structure (Fig. 1).

The samples were subjected to rapid thermal annealing (RTA) in helium ambient using a triple graphite strip heater with the temperature controlled by an Accufibre optical thermometry system. The system was calibrated against the melting point of silver and was found to be accurate to ± 1 °C. Anneals were performed at temperatures between 600 and 900 °C for various times and the SQW diffusion was characterized by HRXRD and low temperature (80 K) photoluminescence measurements. To reduce the scatter in the data a single sample was repeatedly annealed and measurements taken after each anneal.

The low level of arsenic contamination and the thin interphases were not thought to significantly affect the diffusion experiments.

TABLE I. Thicknesses and compositions used to model HRXRD of as received wafer B.

	Composition	Thickness (nm)	Misfit (%)
Substrate	InP		
Buffer layer	$InP_{0.995}As_{0.005}$	298.5	0.016
Interphase 1	$InP_{0.013}As_{0.987}$	0.15	3.20
Well layer	$In_{0.531}Ga_{0.469}As$	9.85	
Interphase 2	InGaPAs	0.15	−2.86
Barrier layer	$InP_{0.995}As_{0.005}$	101.0	0.016

III. RESULTS

HRXRD measurements conducted on lattice matched specimens of type A or B after the completion of long diffusion experiments qualitatively demonstrate various states of strain for annealing temperatures as high as 850 °C; Fig. 2. Strain is only expected to develop if the diffusion rates of the group III and group V sublattices are different. In the case of faster intermixing of the group V sublattice, the quaternary compositions on the well side of the interface are in tension

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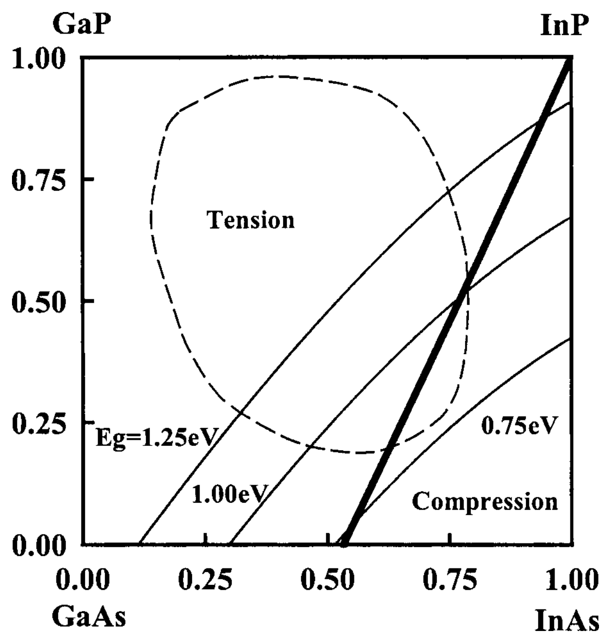

FIG. 3. Compositional map of the InGaAsP system schematically showing the calculated bimodal isotherm at 677 °C (dashed line) (from Ref. 3). The thick line that joins InP and $In_{0.53}Ga_{0.47}As$ describes the range of compositions that are lattice matched to InP. Constant gap energies are also represented for $E_g = 1.25$, 1.00, and 0.75 eV.

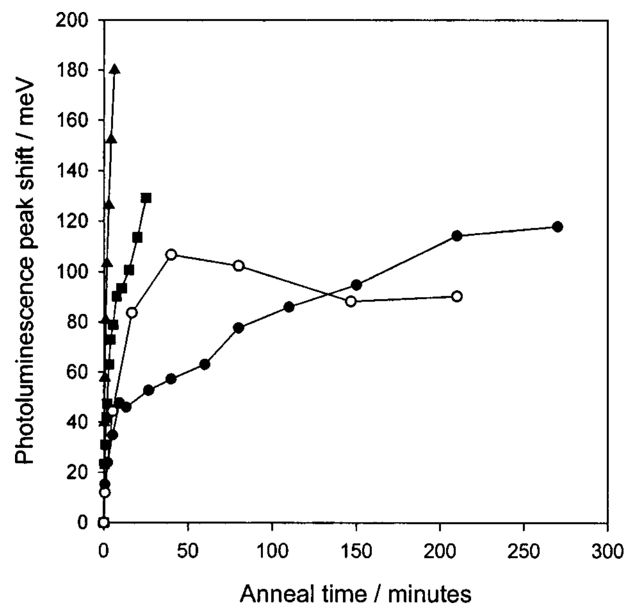

FIG. 4. Shift of the photoluminescence peak vs the annealing time for samples annealed at 800 (circles), 850 (squares) and 900 °C (triangles). The samples from wafer A are shown by closed symbols while those from wafer B are shown by open ones.

whereas those on the barrier side are in compression. If the group III sublattice diffuses faster, the strain takes an opposite sign.

A. Photoluminescence

Annealing a sample from wafer A at 900 °C leads to intermixing of the SQW and barriers along the line of compositions lattice matched to InP (Fig. 3). No strain is evident by HRXRD, and the blueshifts in photoluminescence can be modeled by a Fickian diffusion process where the group III and group V diffusion coefficients are equal and concentration independent. However, it should be stressed that other, e.g., concentration dependent, mechanisms could possibly fit all the data, provided that the rates of diffusion in the two sublattices remain equal at all times so that the compositions that formed remain on the lattice matched tie line. At annealing temperatures below 850 °C, specimens from wafers A and B display an initial blueshift of the photoluminescence. However, with subsequent annealing the rate of the blueshift falls and eventually for the lower temperature anneals the photoluminescence starts to redshift towards the initial photoluminescence peak position. Figure 4 shows shifts of the photoluminescence peak for the different wafers (A+B) as a function of the annealing time for temperatures between 800 and 900 °C. The results for temperatures below 800 °C are shown in Fig. 5. In comparing the photoluminescence shifts in Figs. 4 and 5, diffusion for specimen type B appears to have a stronger temperature dependence. Although it is generally believed that vacancies are the main vector of diffusion, the exact mechanism is not known. Differences in the quality of the substrate wafers and slightly different growth conditions for wafers A and B, such as the arsenic contamination in wafer B, can reasonably account for the variation in concentration and type of point defects in the two crystals, hence the slight alteration of the temperature dependence and rate of interdiffusion. Overall, however, there is no significant qualitative difference in behavior between the two specimens. As will be shown, they both display consistent strain and photoluminescence shifts.

Except for anneal temperatures of 850 and 900 °C, the photoluminescence shifts follow the same trend: an initial blueshift that reaches a maximum, followed by redshifting towards the initial photoluminescence peak position. Figure

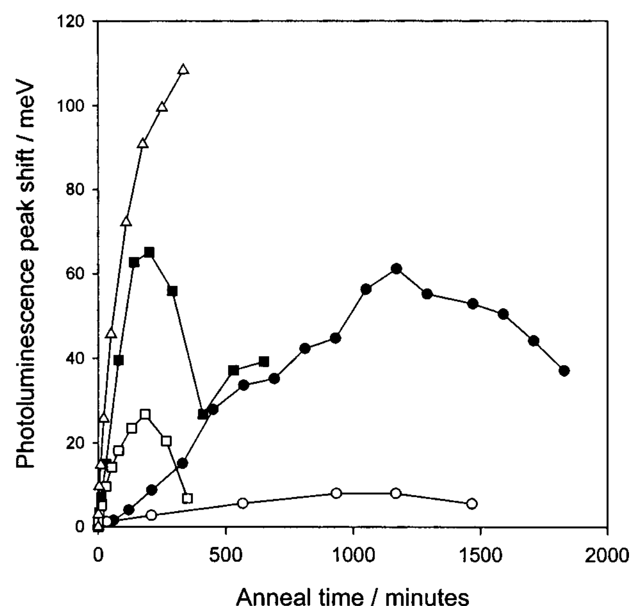

FIG. 5. Shift of the photoluminescence peak vs the annealing time for samples annealed at 600 (circles), 700 (squares) and 750 °C (triangles). The samples from wafer A are shown by closed symbols while those from wafer B are shown by open ones.

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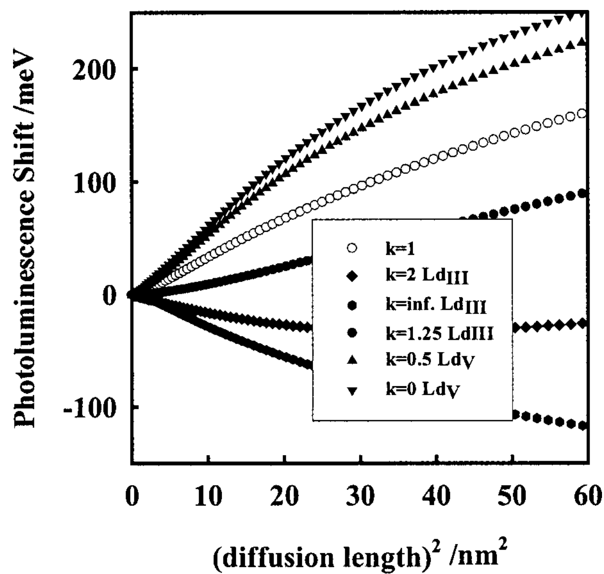

FIG. 6. Simulations of the shift of photoluminescence vs the diffusion length squared for various values of $k=Ld_{III}/Ld_V$. The abscissa is Ld^2_{III} for $k>1$ and Ld^2_V for $k<1$. Note that the abscissa scale is linear with anneal time. A significant redshift is associated to $k>1$. The calculations assume a constant diffusion coefficient for each sublattice.

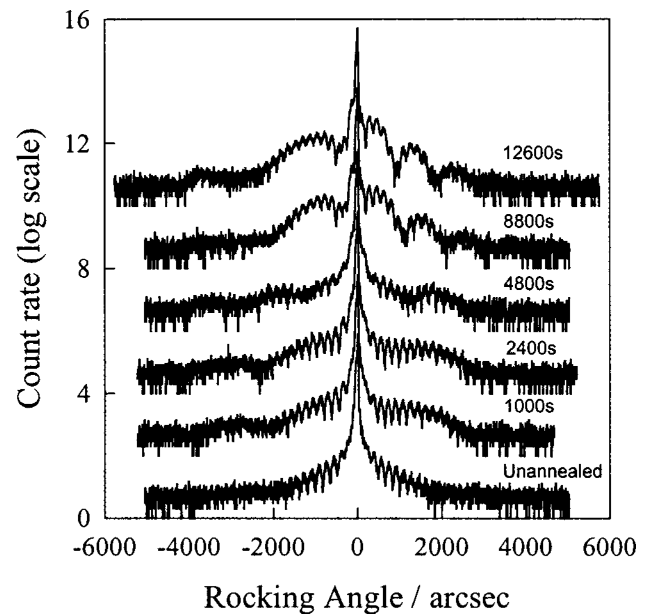

FIG. 7. Experimental 004 x-ray rocking curves for a sample from wafer B annealed at 800 °C for various times. From qualitative modeling of HRXRD the broad feature to the right of the substrate peak for samples annealed for 1000 and 2400 s is indicative of tensile strain in the well. The shift of the broad feature to the left of the substrate peak for the sample after it was annealed 8800 s or longer is indicative of compressive strain in the well.

6 shows the calculated photoluminescence peak shifts for a 10 nm lattice matched InGaAs/InP well as a function of the square of its diffusion length. The calculations assume that the diffusion follows Fick's law and the factor k, defined as $k=Ld_{III}/Ld_V$, measures the ratio of the diffusion length of the two sublattices. Essentially, $k=0$ if there is no group III interdiffusion, $k=$ infinity if there is no group V interdiffusion, and $k=1$ for identical diffusion rates. The quantum confinement effects and the well/barriers composition gradient are both taken into account in calculation of the photoluminescence shift.[5,6] In the case of $k\neq 1$, the diffusion length used on the abscissa in Fig. 6 is relevant to the fastest diffusing species. It should be noted that, with these Fickian conditions, the square of the diffusion length varies linearly with the annealing time at constant temperature, so the abscissa is a normalized time axis. It is clear from these calibration curves that the significant photoluminescence redshift is associated with indium and gallium diffusing faster than arsenic and phosphorus.

B. Strain buildup

The 800 °C data from the wafer B specimen displayed in Fig. 4 are typical of the photoluminescence behavior described. At each annealing step, a HRXRD measurement was also conducted to correlate the changes in photoluminescence according to the strain induced in the specimen by the interdiffusion process. Figure 7 shows the set of resulting experimental 004 rocking curves. The specimen is initially unstrained; following annealing for up to 2400 s it develops tensile strained layers within the well and compressive strained layers in the barrier. These are qualitatively consistent with a higher rate of diffusion of group V atoms. The next measurement, for a total anneal time of 4800 s, shows lower levels of strain, although with the same arrangement of compressive and tensile layers. The final two rocking curves (8800 and 12 600 s) are qualitatively consistent with larger intermixing of group III atoms with the sign of the strained layers being reversed and the well having compressive layers and the barriers being tensile. HRXRD measurements of the specimens annealed at lower temperature and whose photoluminescence peak shift is shown in Figs. 4 and 5 are given in Fig. 2. The strain evidenced by the rocking curves implies greater group V diffusion in specimens from wafer A at 600 °C for 30.5 h and from wafer B at 750 °C for 10.83 h, greater group III diffusion in wafer A at 850 °C for 25 min and no strain in wafer A at 900 °C for 380 s.

IV. DISCUSSION

As illustrated by the data for specimen B at 800 °C, Figs. 4 and 7, there is confirmation that, for low temperature anneals, arsenic/phosphorus interdiffusion is initially favored but with subsequent annealing group III diffusion becomes dominant. The initial photoluminescence blueshift, coupled with the development of strain seen by HRXRD, is consistent with greater group V diffusion; it is then followed by a regime where strain appears to relax and the photoluminescence trend is inverted towards a redshift. Finally dominant group III diffusion characterized by the subsequent redshift and strain inversion is observed.

For the specimen from wafer A at 850 °C, strain inversion has occurred without a photoluminescence redshift. This seems to imply that the difference in diffusion rates in the two sublattices is small and could be compared using Fig. 6 to the case where k is slightly larger than 1 (e.g., $k=1.25$) and does not generate a significant redshift. In Ref. 4 it was stated that for these samples annealed at 800, 850, and

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900 °C the photoluminescence data seem to confirm that the samples were diffusing in a Fickian manner at these temperatures. However, given the HRXRD data here that show the development of strain, it is obvious that this is not the case for the 800 and 850 °C annealed samples and demonstrates that it is not possible to solely use photoluminescence data, even as a function of the annealing time, as proof of a Fickian diffusion process. Given that the HRXRD data presented in this work show that the two sublattices diffuse at different rates at all temperatures below 900 °C the diffusion lengths quoted in Ref. 4 cannot be correct.

The fact that inversion of the photoluminescence peak shift tends to appear at earlier stages of diffusion with lowering of the annealing temperature reinforces the argument that the miscibility gap is responsible for alteration of the diffusion process observed at 900 °C.

This result is in contrast to calculated binodal isotherms in the literature since strain is still generated at 850 °C, a temperature at which the miscibility gap should have shrunk from the lattice matched compositions[7] or even disappeared.[3,8] Chu *et al*.[9] questioned the validity of these models by noting some phase instability in quaternary alloys grown by vapor phase epitaxy at compositions and temperatures outside the calculated miscibility gap. Currently, there is still some controversy about the origin of composition modulation in epitaxially grown layers.[10] The miscibility gap has often been blamed despite the calculated critical temperatures (especially coherent spinodal calculations) being too low to justify it, and surface instability during epitaxial growth, which has higher critical temperature, provides an alternative explanation.

Our findings are nevertheless consistent with a bulk diffusion mechanism; the alternated strain domains modeled rule out the possibility that strain could have developed through a type of macroscopic bending of the specimens during annealing, and the strain inversion and photoluminescence data are consistent with alteration of the ratio of anionic to cationic diffusion rates.

This result is not entirely unexpected because similar diffusion related strain build up has already been observed. For example, strained layers were imaged by scanning tunneling microscopy (STM) in initially lattice matched InGaAs/InP superlattices which were thermally diffused following phosphorus implantation into the barrier region.[11] Mallard *et al*.[12] found, using compositional energy dispersive x-ray microanalysis, greater interdiffusion of group V atoms in an initially lattice matched $In_{0.53}Ga_{0.47}As/In_{0.79}Ga_{0.21}As_{0.45}P_{0.55}$ multiple quantum well (MQW) structure which had been annealed for 2 h at 750 °C. Dark field transmission electron microscopy micrographs showed diffused interfaces and HRXRD displayed amplification of the satellite peak consistent with the development of strain. Ryu *et al*.[13] also noticed strain buildup caused by a larger anionic diffusion rate in lattice matched InGaAs/InP superlattices annealed at 800 °C, and they quantified the coefficients of diffusion in the two sublattices by modeling the diffusion and interpreting photoluminescence and HRXRD measurements. Yu *et al*.[14] characterized the interdiffusion of InGaAs/InP superlattices from their Raman spectra and inferred the presence of small tensile strain in the wells for smaller diffusion lengths and compressive strain for the largest.

V. CONCLUSION

HRXRD characterization of isothermal interdiffusion in 10 nm lattice matched InGaAs/InP SQW shows that for temperatures up to 850 °C strain develops in the well/barrier interface region. The HRXRD and photoluminescence data modeling are consistent with unequal diffusion rates in group III and group V sublattices, with the anions diffusing faster at early stages of annealing, while cationic intermixing dominates at a later stage. Because no strain is observed at 900 °C and the differences in diffusion rate appear to be more significant with a decrease in the annealing temperature, the data are consistent with the presence of a miscibility gap in the InGaAsP quaternary system at temperatures as high as 850 °C.

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