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On the diffusion of lattice matched InGaAs/InP microstructures

F. Bollet and W. P. Gillin[a)]
Department of Physics, Queen Mary, University of London, Mile End Road, London, E1 4NS, United Kingdom

M. Hopkinson
Department of Electronic Engineering, University of Sheffield, Mappin Street, Sheffield, S1 3JD, United Kingdom

R. Gwilliam
School of Electronics, Computing and Mathematics, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

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Photoluminescence and high-resolution x-ray diffraction (HRXRD) studies of the diffusion in lattice matched InGaAs/InP quantum wells show that at high temperatures intermixing can be modeled by Fick's law with an identical diffusion rate for both the group III and group V sublattices. This results in materials that remain lattice matched for all compositions created by the diffusion. At lower temperatures, the photoluminescence shows that the diffusion process changes and HRXRD shows that strained layers are produced within the structure. This may be due to the presence of the miscibility gap within the InGaAsP phase diagram. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Coherency strains arise from the lattice mismatch between domains of different elemental compositions that form a single crystal and are believed to play a significant role in the mechanical properties of some existing structural media. Their control and understanding could potentially open up a design concept for a future generation of materials. Cahn[1] linked the hardening of alloys such as Inconel 80 or Nimonics to the development of coherency strains consecutively to spinodal decomposition, and Kelly[2] suggested that structures alternating thin layers of positive and negative coherency strains could be of interest for high-temperature applications and creep resistance. The underlying principle for the strengthening mechanism resides in the capability of thin domains of alternating strain to smartly control the generation or movement of dislocations through a crystal. It has been shown by high-resolution x-ray diffraction (HRXRD) that superlattices with alternate layers in tension and compression and with a nonzero net strain could maintain this average strain at high temperatures, while comparable homogeneously strained systems relaxed under identical conditions.[3] Furthermore, coherently strained semiconductor epilayers are known to be able to retain their elastic strain even after heat treatments at temperatures reaching 90% of their melting point. Finally, it has also been shown that these inherently brittle semiconductor superlattices display a lower yield stress and an improved plasticity at room temperature.[4] Nevertheless, the interdiffusion of thin layers becomes a significant process at high temperatures and is highly undesirable; with time, a coherently strained structure homogenizes as its free energy tends to be lowered by the entropic nature of diffusion. However, the high positive enthalpy of mixing found in some alloy systems can generate a miscibility gap and this may be used to prevent the homogenization of dissimilar domains. It could also be used for an in situ production of strained layered structures at a high temperature as will be shown in this article.

Alloys of the InGaAsP quaternary system cover a wide range of lattice parameters and band gap energies. They have received much interest from those who conduct semiconductor research for optoelectronic applications, and pseudomorphic crystals of various compositions can be grown. It is an ideal system to study the effect of coherency strains on the mechanical properties of superlattices.[3,4] The InGaAsP phase diagram is also characterized by a miscibility gap, roughly located at its center, having a critical temperature believed to be 808 °C.[5] The present study investigates whether the miscibility gap has any effect on the thermally activated interdiffusion of an InGaAs quantum well and its lattice matched InP barriers. Point defect mediated diffusion is induced by rapid thermal annealing (RTA) and the specimens are subsequently assessed by photoluminescence and HRXRD. Photoluminescence monitors the excitonic recombination of electrons and heavy holes from the $n=1$ quantum well subbands, which is sensitive to variations of composition and quantum well width. Further characterization of the diffusion is conducted by recording and simulating HRXRD rocking curves.

II. EXPERIMENT

A 10 nm lattice matched $In_{0.53}Ga_{0.47}As$ single quantum well (SQW) sandwiched between 100 nm InP barriers, all nominally undoped, was grown on a semi-insulating 001 InP substrate by molecular-beam epitaxy. The wafer was capped

a)Electronic mail: w.gillin@qmul.ac.uk

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with a 50 nm silicon nitride layer (refractive index: 2.19 indicating low oxygen content) deposited by chemical vapor deposition to prevent the loss of group III and V elements and the injection of vacancies through the surface at the elevated temperatures used for the RTA.[6]

Small specimens cut from the wafer were repeatedly annealed at 900, 850, 800, 700, and 600 °C for lengths of time varying from a few minutes to several hours. The anneals were performed in a helium ambient in 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. Linear ramps to the anneal temperature were used with ramp times of 15 s. Each specimen was annealed in the presence of a similar capped InGaAs/GaAs quantum well structure, also characterized for diffusion, and acting as a reference material to detect potential anomalies during RTA sequences.

Photoluminescence spectra were collected at a sample temperature of 80 K and excited using the 514 nm line from an argon ion laser at a power density of ~5 W/cm^2. The luminescence was dispersed in a 1 m grating spectrometer and detected using a liquid-nitrogen-cooled germanium detector.

After each stage of annealing, photoluminescence spectra were collected and the photoluminescence wavelength shift was converted into a diffusion length by using a calibration curve. The calibration curve was constructed by assuming the diffusion on a either sublattice was not concentration dependent and modeling the profiles of composition in the well and barriers with error functions (Fickian diffusion) for each diffusion length. For the simplest case, it was assumed that the diffusion coefficients for group V (As, P) and group III (In, Ga) atoms were identical.[7,8] We have also constructed calibration curves for cases where the relative diffusion on the two sublattices are different, but constant, in order to show how differing degrees of diffusion on the two sublattices can change the magnitude and direction of the peak shift. From the composition profiles, the valance and conduction band profiles could be calculated and the corresponding Schrödinger equation solved with a numerical method to provide the energy of the photoluminescence transition. For the simple case of equal group III and group V diffusion, the Fickian assumption was retrospectively checked by plotting the diffusion length squared against the anneal time to determine if there is a linear relationship,[7,8] and by using x-ray diffraction to look for evidence of strain development. The calibration curves for a range of relative diffusion rates are given in Fig. 1.

HRXRD rocking curves (one-dimensional scans) of the 002, 004, and 224 reflections were collected from the specimens before and after annealing, on a Philips material research diffractometer (MRD). The MRD had a highly collimated monochromatic x-ray beam from the Cu $K\alpha$ radiation produced by using the 220 reflections of a four-crystal Bartels germanium monochromator. The experimental measurements displayed Pendellösung fringes characteristic of the decoupling introduced by the quantum well layer between the x-ray coherent reflections from the InP substrate and the

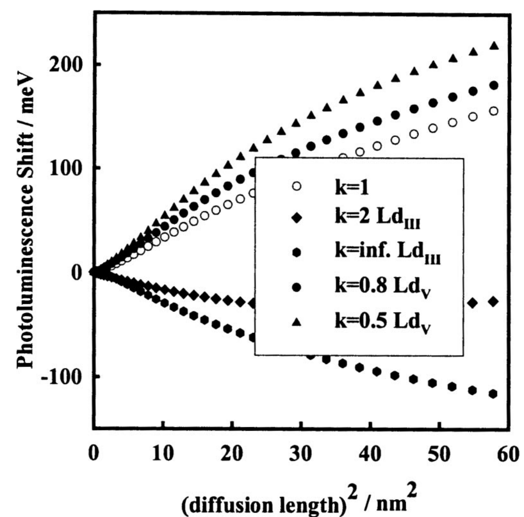

FIG. 1. Theoretical calculations of photoluminescence shift vs diffusion length squared for various values of $k = Ld_{III}/Ld_V$. The abscissa is Ld_{III} for $k > 1$, Ld_V for $k < 1$. A significant redshift is associated with $k > 1$.

top 100 nm InP barrier. The periodicity of the fringes is related to the thickness of the barrier and quantum well layers, while their intensity is essentially modulated by the strain and thickness of the quantum well layer. Subtle or obvious alterations of the Pendellösung fringes occurred as a consequence of annealing the specimens and the measurements were compared with simulations obtained from the Philips X'pert Epitaxy 3.0 software, which can generate, by the dynamical theory of x-ray scattering, a curve from a model pseudomorphic crystal made of layers of uniform composition.

III. RESULTS

A. Photoluminescence

Figure 2 shows the photoluminescence peak shift for InGaAs/InP samples annealed at 600, 700, 800, 850, and 900 °C for various times. It can be seen that for anneal tem-

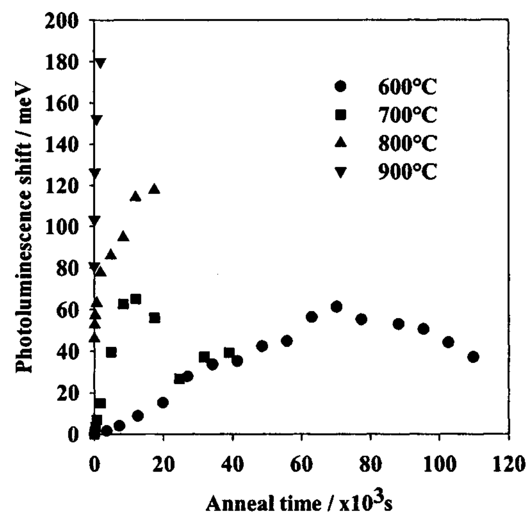

FIG. 2. The photoluminescence peak shift against anneal time for samples annealed at 600, 700, 800, and 900 °C.

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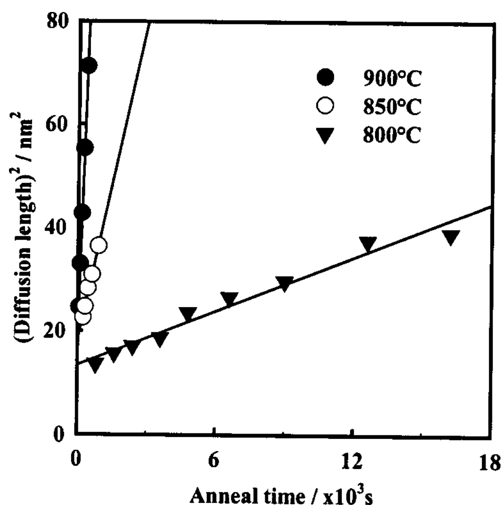

FIG. 3. Diffusion length (L_d) squared vs anneal time (t) at 900, 850, and 800 °C for a 10 nm $In_{0.53}Ga_{0.47}As$ SQW in InP. D is the coefficient of diffusion defined by $L_d^2=4Dt$.

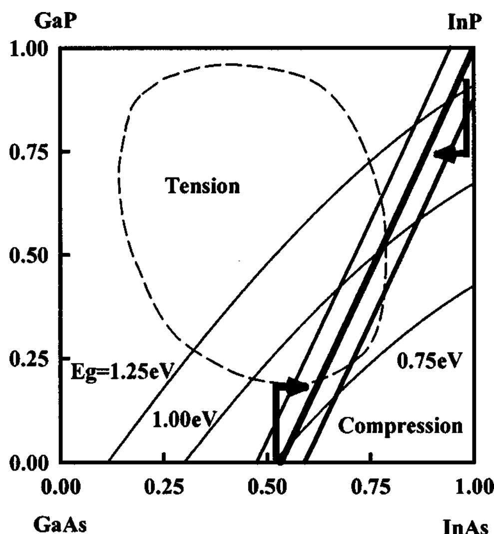

FIG. 4. The thick line joining InP and $In_{0.53}Ga_{0.47}As$ describes the range of compositions that are lattice matched to InP. On either side are displayed the compositions having a 0.4% misfit strain in tension or compression. Constant gap energies are also represented for $E_g=1.25$, 1.00, and 0.75 eV. The dashed line is the binodal isotherm at 677 °C (see Ref. 5).

perature of 800 °C and above, the photoluminescence shifts monotonically with anneal time and peak shifts of greater than 120 meV can easily be achieved. For the 600 and 700 °C annealed samples, very different behavior can be observed, with an initial blueshift of up to ~60 meV whereupon the photoluminescence peak starts to redshift to lower energy. For the 800, 850, and 900 °C annealed samples, the photoluminescence data were converted into diffusion lengths with the calibration curve for equal group III and group V diffusion, Fig. 3. The linear relationship between the square of the diffusion lengths and the anneal times seems to confirm the validity of the Fickian diffusion hypothesis and provides values for the diffusion coefficient of both sublattices of 5.2×10^{-16}, 0.4×10^{-16}, and $0.04\times10^{-16}\,cm^2/s$ at 900, 850, and 800 °C, respectively. The quantum well diffuses readily with the InP barriers at these temperatures, and a diffusion length in excess of 8 nm can be measured.

For experiments conducted at 600 and 700 °C, if the samples had diffused through a Fickian process, as we have modeled the higher-temperature data, some of the alloy compositions formed would lie within the theoretically predicted region of the miscibility gap,[5] Fig. 4. However, it should be stressed that the binodal isotherm shown in Fig. 4 is a calculated value at 677 °C for the incoherent system, which does not take into account any strain in the system. It can, therefore, be seen from the photoluminescence data that the diffusion process changes as the anneal temperature is reduced and that this change is consistent with the miscibility gap having an effect on the diffusion, although it would suggest that the critical temperature for the miscibility gap might be higher than the calculated value.

B. High-resolution x-ray diffraction

Figure 5 shows a 004 HRXRD rocking curve of an as-grown specimen before annealing fitted with a simulated profile. In order to match the experimental profile, thin ternary or quaternary transition layers had to be added at the well/barriers interfaces. The layers are a few angstrom thick on each side of the quantum well, and the top barrier is also slightly (1.2%) contaminated with arsenic over a larger extent (20 nm). Overall, the simulated crystal is close to the intended original specifications and the growth problems of material carry over and phosphorus substitution by arsenic are minimal. The solidity of the simulation is confirmed by the good fits to the experimental data for the 002 and 224 reflections.

The 004 rocking curves collected before and after annealing the quantum well at 900 °C are also shown in Fig. 5. The corresponding photoluminescence data for 30 and 180 s anneal times indicate diffusion lengths of 3.5 and 7 nm, respectively. The rocking curves appear only slightly altered. In contrast, the HRXRD profile is significantly changed after annealing at 600 °C (Fig. 6), and the fringe amplification is, as will be shown, an indication of strain development. The photoluminescence anomalies observed for low-temperature diffusion are, therefore, corroborated by the x-ray data.

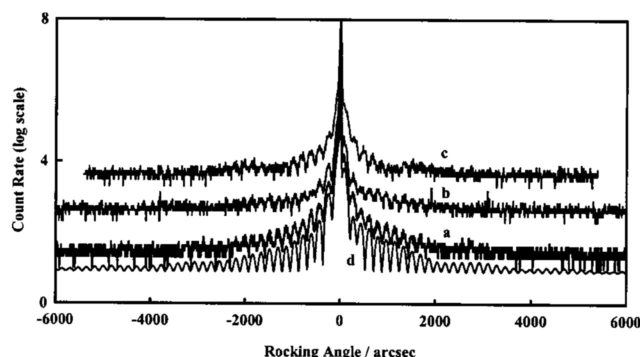

FIG. 5. 004 HRXRD rocking curves for (a) as-received SQW, (b) SQW annealed 30 s at 900 °C ($L_d=3.5$ nm), and (c) SQW annealed 180 s at 900 °C ($L_d=7.0$ nm). (d) A simulation of the as-received specimen. The (b) and (c) profiles show no sign of strain development.

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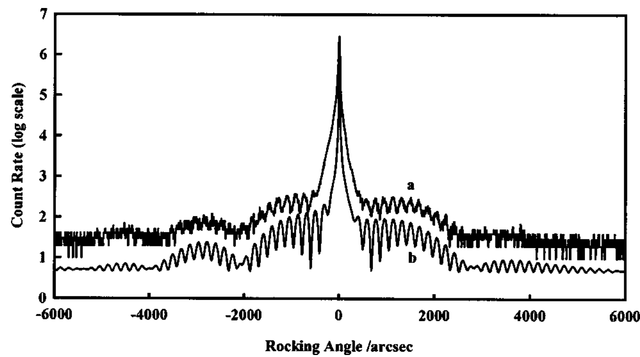

FIG. 6. (a) Experimental 004 HRXRD rocking curve of a SQW annealed for 30 h at 600 °C. The amplifications of the fringes are characteristic of the strains developed in the system. (b) A simulation closely matching (a) (see Fig. 7).

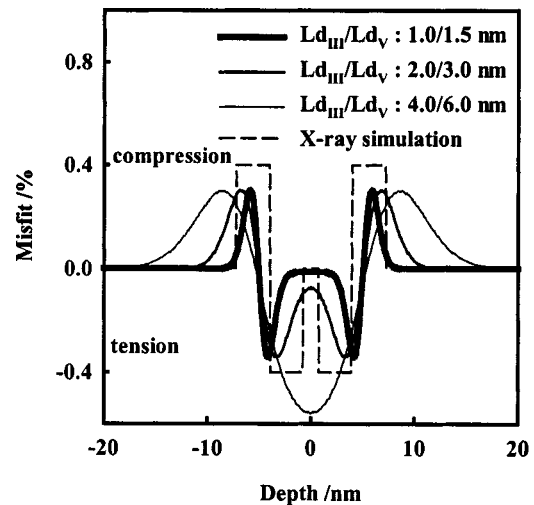

FIG. 7. Calculated strain development for various diffusion lengths in a 10 nm $In_{0.53}Ga_{0.47}As$/InP SQW generated by unequal diffusion of group III and group V atoms. The well center is at 0, $k=0.66$, and diffusion is Fickian. The dashed curve is the strain profile used to generate the rocking curve simulation in Fig. 6.

IV. DISCUSSION

The quantum well/barrier interdiffusion affects the characteristic photoluminescence wavelength by changing the effective width of the well and, therefore, the energy of the confined levels, and also by modifying the well composition and band gap value. The calibration curve used to model this behavior assumes that the Fickian hypothesis is valid, and that group III and V atoms have identical coefficients of diffusion. Under these conditions, the quaternary alloy compositions generated are all lattice matched to the InP substrate (Fig. 1). The fact that the HRXRD shows no evidence for strain introduction with annealing at a temperature of 900 °C, even for the strain sensitive 224 reflection in the grazing incidence configuration. The linear fit to the photoluminescence derived diffusion length data indicates that this assumption is correct. This absence of strain in the diffused sample can only occur if the diffusion process is producing compositions along the tie line between the initial compositions. This can only be achieved if the diffusion coefficients on the two sublattices are identical. For anneal temperatures below 800 °C, it is obvious that we no longer have equal diffusion coefficients on the two sublattices both from the photoluminescence behavior and HRXRD. The photoluminescence data also suggest that the diffusion behavior changes as the anneal time increases with an initial blueshift in the photoluminescence followed by a redshift with further annealing. By adjusting the ratio of the diffusion in the two sublattices, but assuming that the diffusion is still Fickian on each sublattice, we can model how we would expect the diffusion to affect the photoluminescence peak shift if we had differing, but constant, diffusion coefficients on the two sublattices, Fig. 1. The factor k in Fig. 1 is defined as $k=Ld_{\mathrm{III}}/Ld_{\mathrm{V}}$. For $k=0$, there is no group III interdiffusion and for k=infinity, there is no group V interdiffusion. It is clear from Fig. 1 that with the Fickian hypothesis, a significant photoluminescence redshift is associated with indium and gallium diffusing faster than arsenic and phosphorus. While in the early stages of diffusion, where the photoluminescence is blueshifted, we can conclude that we have a diffusion coefficient for the group V sublattice that is larger than or comparable to the group III coefficient. If a concentration dependent diffusion mechanism were used to model the photoluminescence, the same trend in the direction of the peak shift would be observed although the shape of the calibration curves would naturally change. Therefore, from the direction of the photoluminescence peak shift, we can draw information about the large scale changes in diffusion that are occurring between the two sublattices, although the precise mechanism cannot be deduced.

As a direct consequence of different rates of diffusion on the sublattices, the quaternary alloy compositions generated by intermixing in the $In_{0.53}Ga_{0.47}As$/InP system would no longer be lattice matched to the InP substrate, and substantial strains develop rapidly. For $k<1$ (larger diffusion of group V material), Fig. 7 shows that the well would be in tension and the barriers develop compressive strains. Figure 7 shows the strain profile for various diffusion lengths and $k=0.67$. The original undiffused well was lattice matched and 10 nm wide. With increasing diffusion lengths, the strained domain extends. The maximum strain is determined by the k factor and larger magnitudes of strain develop for k smaller than 0.67. Note that higher strains develop in the well after the diffusion fronts from the two barriers have reached the well center. For $k>1$, the well is in compression and the barriers in tension.

Photoluminescence experiments and modeling are not well suited to an accurate evaluation of the ratio of group III to group V diffusion (k in Fig. 1). They simply indicate a dominant interdiffusion of group III atoms in case of a significant redshift. Again, HRXRD can be used to reduce the indetermination on k and model the photoluminescence data. From Fig. 6, the amplitude of the fringes envelope modulations in the rocking curve of the specimen annealed at 600 °C suggested strains of the order of 0.4%, while their widths and positions were indicative of the extent of the strained domains. A simple model was constructed by simulating the quantum well/barrier interphases with two homogeneously strained layers of identical magnitude, but opposite sign. One such simulation is displayed in Fig. 7 and had layers $\pm 0.4\%$

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strained and 3.25 nm wide. This provided the close fit to the rocking curve seen in Fig. 6, in which the left-hand side fringes are only slightly offset from the experimental data. This strain distribution model should not be taken literally, but it provides a good picture of the magnitude and location of the strains present following a long anneal at a low temperature. When compared with the strain profiles generated by a Fickian diffusion, it is fairly close to the $Ld_{\mathrm{III}}=20\,\mathrm{nm}/Ld_{\mathrm{V}}=30\,\mathrm{nm}$ simulation. Although, there is a significant shift of the strained domains toward the well center that suggest that a concentration dependent process occurred at some stage during the anneal. The type of strains measured and the blueshift in the photoluminescence displayed in the early stages of diffusion imply that, possibly due to the influence of the miscibility gap, group V diffusion is favored (Fig. 4). Cohen[10] suggests that such a process is possible as the increase of free energy generated by the well composition entering the miscibility gap is initially compensated by the diffusion of arsenic in the barrier (the free energy is lowered by reducing the group V gradient of concentration) until the total free energy is no longer diminished. Then, a radical diffusion of group III material, as illustrated by the arrows in Fig. 4, is likely to occur, possibly through a spinodal type of decomposition of the alloys within the miscibility gap. Such an increase of group III diffusion could easily be at the origin of the photoluminescence redshifts observed.

The development of strained layers is also consistent with other results. For example, strained layers were imaged by scanning tunneling microscopy in diffused InGaAs/InP superlattices consecutively to a phosphorus implantation in the barrier that probably favour group V diffusion.[9] It has also been predicted by Cohen[10] who considered the effects of different rates of diffusion for group III and group V materials inside and outside the well.

V. CONCLUSION

Photoluminescence and HRXRD studies of diffusion in lattice matched InGaAs/InP quantum wells show that at high anneal temperatures intermixing can be modeled by Fick's laws and an identical rate of diffusion for group III and group V atoms on their respective sublattices. The quaternary alloys generated by the diffusion all have lattice constants close to the lattice matched conditions and no significant strains develop, even for large diffusion lengths. But, at temperatures where the composition of the quaternary alloys developed are within the predicted InGaAsP miscibility gap, an initial blueshift in the photoluminescence occurs but quickly stops and subsequent diffusion results in a subsequent redshift in the photoluminescence data. Furthermore, at these low temperatures, strains are evidenced in HRXRD rocking curves. The photoluminescence blueshift data and the rocking curve modeling imply that strains developed because of a larger intermixing of group V atoms as compared to group III atoms in the early stages of diffusion. The photoluminescence redshift occurs at a later stage and for photoluminescence shifts less than those observed at higher annealing temperatures where the miscibility gap is nonexistent. The photoluminescence redshift is a sign of enhanced diffusion of group III to group V materials. The rocking curve simulation for the specimen annealed at 600 °C suggests that, at least at some point, the diffusion is non-Fickian and probably concentration dependent. It is not clear at this stage whether a spinodal decomposition is taking place or even if new alloy phases are generated on either side of the miscibility gap and, further characterization by transmission and a more detailed HRXRD study at various stages of diffusion is needed. Nevertheless, HRXRD is proven to be a powerful tool in the characterization of the diffusion of very thin layers (10 nm). Finally, the results are consistent with the miscibility gap affecting the diffusion and this opens up the possibility to control diffusion in order to inhibit it by a suitable choice of layer compositions, or to actually develop coherently strained nanostructures.

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