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Strain and temperature effects on interdiffusion in InAsP/InP heterostructures

D.J. Tweet, H. Matsuhata, P. Fons, H. Oyanagi, and H. Kamei[a]

Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305

[a]Sumitomo Electric Industries, 1, Taya-cho, Sakae-ku, Yokohama 244

Evidence is presented for large, strain-dependent interdiffusion in $InAs_{1-x}P_x$ layers grown on InP(001) substrates by organometallic vapor phase epitaxy at 620°C. Specifically there are strong indications for the existence of a "critical strain": if the strain is ~1.9% or more much P-As mixing occurs, but for smaller strain the mixing is greatly decreased. The interdiffusion is also highly sensitive to temperature. A set of samples grown at 580°C exhibits a significant decrease in P-As mixing compared to a set grown at 620°C. These results were obtained using X-ray diffraction, AFM, TEM, and energy-dispersive X-ray analysis.

1. INTRODUCTION

$InAs_{1-x}P_x$/InP(001) quantum wells show excellent promise for long-wavelength optoelectronic device applications, such as 1.3 μm laser diodes [1]. However, control of the interface has been a major problem, due to the rather large exchange between P and As atoms [2-4] Usually, several monolayers of interdiffusion are found. Here we argue that, at least for high temperature growth techniques, the amount of strain in the quantum well critically influences the degree of interdiffusion.

We find evidence for large, strain-dependent interdiffusion and for the existence of a "critical strain" in a set of $InAs_{1-x}P_x$ layers grown on InP(001) substrates: if the strain is ~1.9% or more ($x < 0.4$) much P-As mixing between the layer and substrate occurs, but for smaller strain ($x > 0.4$) the mixing is greatly decreased. Specifically, in the higher strain films, initially strong interdiffusion occurs, producing pseudomorphic islands of intermediate composition. As these grow and start to relax, the strain decreases. When it reaches ~1.9% the intermixing suddenly stops and islands of the intended composition begin to appear. Furthermore, both types of islands penetrate deeply into the substrate. The resulting phase separation is thus caused by strain-induced interdiffusion, and is unrelated to that due to spinodal decomposition in other compound semiconductor systems [5,6]. In support of this idea, a set of samples having strain of less than the critical value of 1.9% shows virtually no intermixing, even in the thinnest films investigated. The interdiffusion is also found to be highly sensitive to temperature. Samples grown at 580°C exhibit a significant decrease in P-As mixing compared to an equivalent set grown at 620°C.

2. EXPERIMENTAL

The samples were made by low-pressure organometallic vapor phase epitaxy (OMVPE) using trimethylindium, arsine, and phosphine as source gases. For each sample, a 1000 Å InP buffer was grown on a InP(001) substrate before deposition of a single $InAs_{1-x}P_x$ layer, which was then covered by a 20 Å InP cap. The layers were grown at a rate of about one micron per hour. The intended thicknesses, t, of the layers range from t = 40 to 1000 Å with intended values of x of 0.0, 0.4, or 0.6, corresponding to strains of 3.2%, 1.9%, and 1.3%, with respect to the InP substrate. A sample with just the buffer layer was also prepared, to be used as background for the x-ray data. These were all produced at a substrate temperature of 620°C. Another set with x = 0.4 was grown at 580°C.

The structure of the films was examined using x-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), and energy-dispersive x-ray analysis (EDX). For XRD a MAC Science SRA 18 kW generator with $CuK_{\alpha 1}$ radiation selected by a four-crystal Ge(220) monochromator was used, and the sample set on a Philips MRD goniometer. AFM was done with a Seiko Instruments SFA 300. TEM observations were made with a JEOL JEM-4000FX, while the EDX microbeam analysis was performed using a Topcon 002B with a Philips 9900.

3. RESULTS

3.1. InAs/InP and $InAs_{0.6}P_{0.4}$

The measured XRD intensities near the InP(004) substrate peak for specimens with intended layer composition of x = 0.0 (strain, ε = 3.2%) are shown in Fig. 1. In the thicker films two peaks are visible, corresponding to regions with mixed composition (InAsP), labeled A, and intended composition (InAs), labeled B. Initially there is just region A, which grows only until region B appears. From analysis of the (004) and (115) peaks (not shown) x_A and x_B, the compositions of regions A and B, respectively, were calculated [7,8].

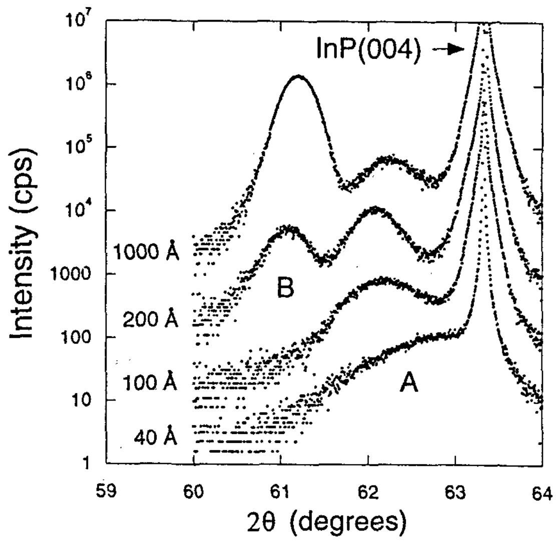

Fig. 1. XRD intensities as a function of scattering angle, 2θ, near the InP(004) substrate peak for specimens with intended composition InAs. The intended layer thickness in Å is indicated for each data scan, which are offset for clarity.

As can be seen from Fig. 1, in the film with intended thickness t = 40 Å only the mixed region (A) appears. Analysis of the XRD data indicate that the film is strained to the InP substrate and has an average P composition of about x_A = 0.8. AFM indicates that islands are starting to form. Cross-sectional TEM confirms that the film, including the islands, is strained to the substrate. TEM also shows that it is noticeably thicker than 40 Å, over 90 Å on average, suggesting interdiffusion of P from the substrate into the InAs. However, the layer/substrate interface is flat and sharp. Details of the TEM analysis will be published elsewhere [9].

In the t = 100 Å film, XRD indicates that still only the mixed region appears, but now with x_A = 0.7. XRD also shows that the sample is partially relaxed, in agreement with TEM which finds numerous dislocations at the interface between the layer and substrate. Islands 800 Å tall are found, which are penetrating into the substrate.

XRD of the t = 200 Å sample shows that the InAs peak (B) has appeared, and that the mixed peak (A) has stopped increasing in intensity, indicating that P has suddenly ceased diffusing into the layer. Region A has relaxed further and has x_A = 0.55, while region B is completely relaxed and has x_B = 0.0. TEM reveals heavily dislocated islands over 1000 Å tall penetrating deeply into the substrate. EDX finds that some regions of these islands are InAs and others are InAsP of varying composition [7-9]. The final structure is quite complex. Analysis of the t = 1000 Å sample indicates that it is basically like the 200 Å one.

In the above analysis, it is important to note that, due to the progressive relaxation of region A, InAs deposited pseudomorphically on this mixed region is strained 3.2% for the t = 40Å sample, 2.7% for t = 100 Å, but only about 1.9% for the t = 200 Å and 1000 Å samples.

XRD of the $InAs_{0.6}P_{0.4}$ (ε = 1.9%) set of films indicates very similar behavior to that of the InAs set [7,8]. In thin samples (<200Å) XRD finds only a mixed peak. In thicker samples, once the intended peak appears, the mixed peak ceases growing.

3.2. $InAs_{0.4}P_{0.6}$

The InAs and $InAs_{0.6}P_{0.4}$ results suggest that an approximately 1.9% value of strain may be important to the unusually large diffusion observed. At higher strains mixing is large and at lower strains mixing stops. To test this idea, a set of samples with intended composition $InAs_{0.4}P_{0.6}$ (ε = 1.3%) was grown. XRD data are shown in Fig. 2. In contrast to the above higher strained systems, the interdiffusion is almost completely gone, with the mixed peak (A) only becoming visible in the thickest films. The oscillations seen on either side of the thinner samples are an interference pattern due to finite thickness. The 50 Å and 100 Å samples are extremely flat allowing their XRD data to be compared to a model calculation. The model indicates that the compositions are as intended, although the thicknesses are 30% higher than expected [10].

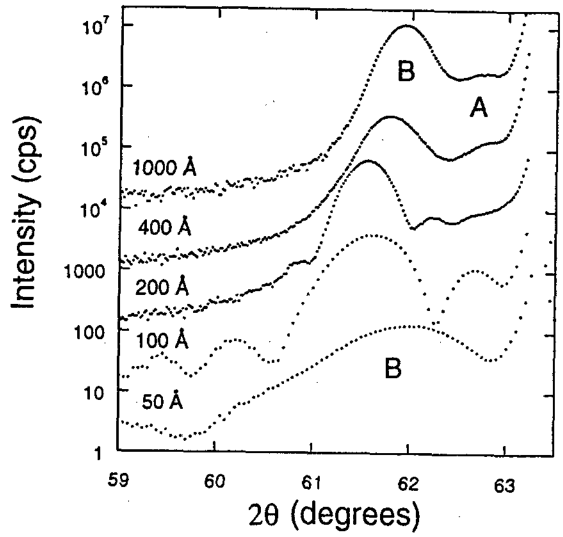

Fig. 2. XRD intensities near the InP(004) substrate peak for specimens with intended composition $InAs_{0.4}P_{0.6}$.

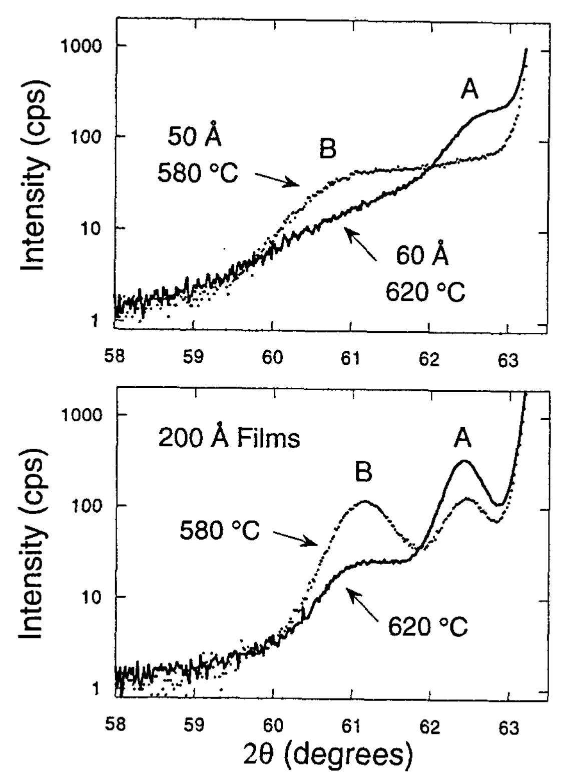

Fig. 3. Comparison of XRD data for $InAs_{0.6}P_{0.4}$ samples grown at 620°C (dots) and 580°C (line).

3.3. $InAs_{0.6}P_{0.4}$ grown at 580°C

To begin testing the effects of temperature, a set of films with intended composition $InAs_{0.6}P_{0.4}$ (ε = 1.9%) was grown at 580°C. Fig. 3 compares two of these samples with corresponding ones from the set with the same composition but grown at 620°C. It is apparent that for the thinnest samples, only the mixed peak is present at 620°C, but at 580°C most of the film has a composition close to the intended value. In the 200 Å films peaks A and B are present at both temperatures, but the mixing is considerably reduced at the lower temperature.

Such a strong suppression of intermixing for only a 40°C drop in growth temperature suggests a large activation energy for the P-As interdiffusion. However, further analysis is required to derive a quantitative result.

4. DISCUSSION

Strain effects on interdiffusion in semiconductor systems have been much debated recently, with some researchers reporting distinct changes [11] and others not [12]. Our results seem to be caused by strain-enhanced mixing, but whether it is a bulk effect or due to growth kinetics is not yet clear. Diffusion coefficients for As-P at 620°C have been reported to be 5.7 x 10^{-21} cm^2/sec for InAs/InP quantum wells (3.2% compressive strain) [13] and about 1.3 x 10^{-19} cm^2/sec for InGaAs/InGaAsP quantum wells (1% compressive strain) [14]. These differ by a factor of over 20, with the diffusion being smaller at higher strain, in contrast to what we find. In either case, the calculated diffusion length for the six minutes it takes to grow a 1000 Å sample is of the order of one angstrom or less. These points suggest that the anomalously large interdiffusion we find is due to growth kinetics. However, since the P-As interdiffusion is occuring at the buried layer/substrate interface, it is hard to imagine that growth kinetics (usually a surface effect) is the controlling factor. More studies are required to discern the cause.

Finally, the observed separation into regions of different compositions does not appear to be related to that commonly observed in III-V ternary and quaternary alloys [5,6]. This is usually attributed to phase separation occurring at the growing surface due to the presence of a miscibility gap, in accordance with calculations. In contrast, none is expected for InAsP [5].

5. CONCLUSION

We have found large, strain-dependent interdiffusion in $InAs_{1-x}P_x$ layers grown on InP(001) substrates by OMVPE at 620°C. Specifically there are strong indications for the existence of a "critical strain": if the strain is ~1.9% or more much P-As mixing occurs, but for smaller strain the mixing is greatly decreased. The interdiffusion is also highly sensitive to temperature.

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