Interdiffusion: A probe of vacancy diffusion in III-V materials

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We have used the interdiffusion of a multiple quantum well sample due to a thin source of vacancies, as a probe, to simultaneously measure the interdiffusion coefficient, diffusion coefficient for group III vacancies in GaAs and the background concentration of these vacancies in a single experiment. We have shown that the interdiffusion at all temperatures is governed by a constant background concentration of vacancies in the material and that this background concentration is the concentration of vacancies in the substrate material. The measured vacancy concentration is around 2×10^{17} cm^{-3}. This result shows that the vacancy concentrations in GaAs are not at thermal equilibrium concentrations as has been widely assumed. Rather it has value which is ''frozen in,'' probably at the GaAs crystal growth temperature. The activation energy found for the intermixing of InGaAs/GaAs is shown to be governed solely by the activation term for vacancy diffusion which is calculated to have an activation energy of 3.4 ± 0.3 eV. [S0163-1829(97)05724-X]

I. INTRODUCTION

There has been a considerable literature during the past 20 years on the diffusion of impurities in semiconductors, self-diffusion, and the interdiffusion of heterostructures. Although there are many techniques available for measuring diffusion processes they all give information only on the diffusivity of the species that is being measured and usually give no information about the mechanisms responsible for the diffusion process. This mechanism is only inferred from the behavior of the system as various parameters are changed. This approach has led to widely accepted mechanisms postulated for a number of diffusion processes. With the interdiffusion of III-V heterostructures, for example, it is now believed that the diffusion process is governed by the diffusion of vacancies on a given sublattice [second nearest neighbor hopping (2NNH).[1,2] The diffusion of these vacancies are also considered important for a number of other diffusion processes, such as some impurity diffusion[3] and may be important for the formation of extended defects.[4] However, despite the importance of knowing the diffusivities and concentrations of these point defects there is very little quantitative data in the literature, and that which does exist provides scant information on the thermal behavior of those defects.

In this paper we use measurements of the interdiffusion of multiple quantum wells of InGaAs each with a different indium concentration, as probes for the diffusion of vacancies. As a source of vacancies a quantum well of InGaAs grown at a temperature, 470 °C, which is just below the temperature needed for good quality InGaAs was used. This material is known to be arsenic rich following growth,[5] this produces group-III vacancies which are then free to diffuse.

II. EXPERIMENTAL DETAILS

The sample used in this work was grown by molecular beam epitaxy (MBE) in a Vacuum Generators V80H reactor on (100) orientated GaAs. The sample consisted of seven quantum wells of $In_xGa_{1-x}As$ where x was varied between 0.1 and 0.21. These wells were each separated by 50 nm of GaAs. The first of these quantum wells was grown at a substrate temperature of 470 °C which is known to produce As rich GaAs. Following the growth of this layer the substrate temperature was raised and the rest of the structure was grown. This structure provided a photoluminescence spectra in which all of the quantum well emissions could be easily distinguished (Fig. 1), although the emission from QW7, the well grown at low temperature, is weak as would be expected from poor quality material.

Following growth the wafer was capped on both the front and back surfaces with ~30 nm of silicon nitride. The cap was grown at 300 °C in a plasma enhanced chemical vapor deposition (PECVD) system. The nitride used ($n=2.1$) has been found to give the lowest diffusion coefficient for intermixing in the layers below (i.e., the lowest injection of vacancies). Following capping the wafer was cut into 5×5 mm^2 squares for the annealing experiments.

Annealing was performed in a helium ambient using a resistively heated graphite strip heater. The sample was placed between two graphite strips and the temperature measured an controlled using an Accufiber thermometry system. The annealing furnace was calibrated against the melting points of gold and silver and found to be accurate to ±1 °C. Photoluminescence was excited using the 488 nm line of an argon ion laser, and spectra were collected at a sample temperature of 80 K using a liquid nitrogen cooled Ge detector.

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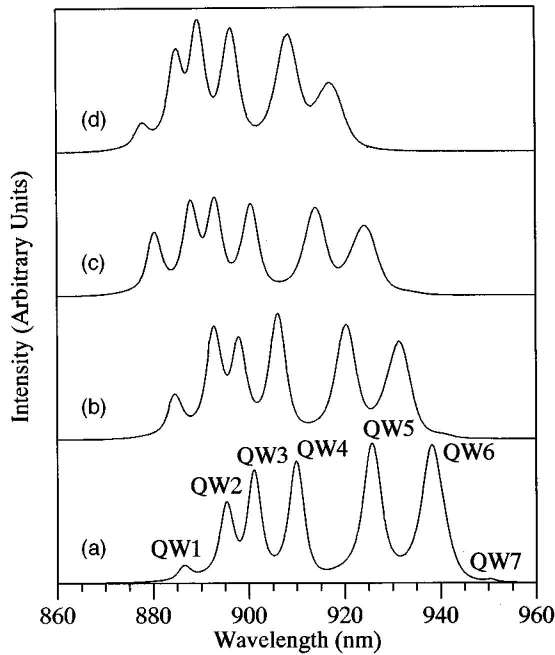


FIG. 1. Photoluminescence spectra of the sample before (a) and after annealing at 900 °C for 30, 60, and 120 s, respectively, (b)–(d).

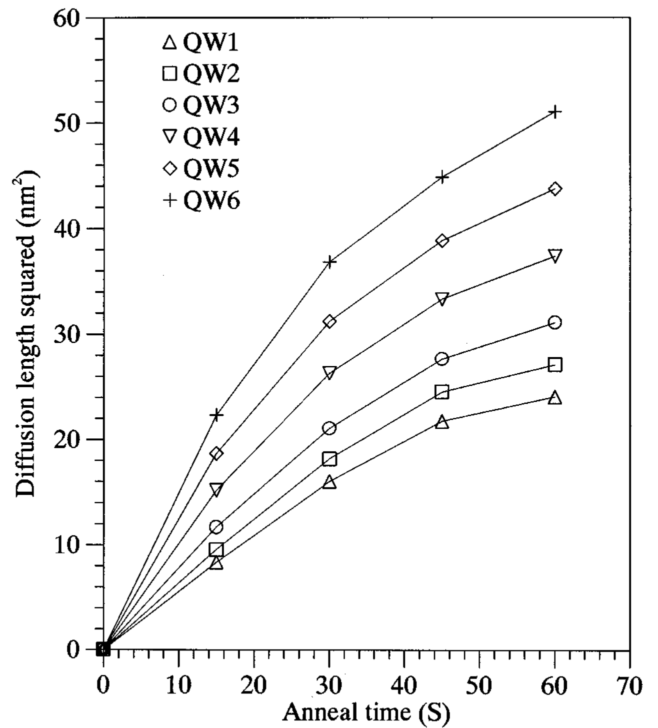


FIG. 2. A graph of the diffusion length squared for all of the quantum wells, calculated from the photoluminescence peak shift, as a function of anneal time for a sample annealed at 950 °C. The lines joining the point are only a guide to the eye.

In order to measure the diffusion coefficient for intermixing a single sample was repeatedly annealed at a given temperature and the photoluminescence spectra recorded after each anneal. As the quantum well diffuses there is a shift in the photoluminescence peak position to higher energies (Fig. 1), this is caused by the quantum wells effectively narrowing in the early stages of diffusion and subsequently by the reduction in the indium concentration at the well center. By assuming that Fick's law is being obeyed with a constant diffusion coefficient, which can be proven from the analysis, it is possible to model the shift in the peak position and consequently to calculate the diffusion length for interdiffusion after each anneal. If the square of the diffusion length determined from this analysis is plotted against the anneal time the diffusion coefficient for the intermixing can be determined from the gradient of the graph. This procedure is now well established and is presented in more detail in Ref. 6.

III. RESULTS AND DISCUSSION

Typical photoluminescence (PL) spectra from a sample before and after annealing are presented in Fig. 1. Figure 1(a) is the PL spectra of the as-grown sample. The seven peaks are the $n=1$ electron to heavy-hole transitions corresponding to the seven quantum wells in the structure. Figures 1(b)–1(d) are the PL spectra from the same sample after it was annealed at 900 °C for 30, 60, and 120, respectively. The peaks are labeled QW1 to QW7, where QW1 is the well nearest to the surface and QW7 is the well that was grown at low temperature. From Fig. 1 it can be seen that the peak intensity from QW7 is very low for the unannealed sample and rapidly disappears with annealing.

Using the method described earlier and in Ref. 6 we can convert the measured shift in the photoluminescence peak position for each well into a diffusion length. Figure 2 shows a graph of diffusion length squared as a function of anneal time for the sample annealed at 950 °C. As $L_D{}^2=4Dt$, where L_D is the diffusion length, D is the diffusion coefficient and t is the anneal time, if the wells were diffusing with a constant diffusion coefficient then we would expect to see the data points for each quantum well lying on a straight line passing through the origin. However, from Fig. 2 it can be seen that there is a larger gradient at short times which indicates a higher diffusion coefficient. As the annealing progresses this diffusion coefficient reduces to an intrinsic value. It can also be seen from Fig. 2 that the amount of extra interdiffusion in the wells is a function of the distance of the well from the initial source of vacancies, with greater interdiffusion closer to the source, QW7. For all the wells, however, the diffusion coefficient is tending towards a constant value as annealing proceeds (i.e., the slopes are converging), the plots becoming parallel at longer anneal times.

Using the data presented in Fig. 2 we can take a snapshot of the diffusion process as a function of depth in the sample at a given time. It is known that the diffusion coefficient for intermixing is the product of the concentration of the diffusing point defects and their diffusivity. If we assume that the interdiffusion is governed solely by vacancies then this can be written as

$$D=D_V N_V, \tag{1}$$

where D is the interdiffusion coefficient, D_V is the diffusion coefficient for the vacancies, and N_V is the ratio of vacancies

to the number of sites present. As the diffusion length for intermixing is given by $L_D=2\sqrt{Dt}$ then, if the concentration of vacancies as a function of time is known, we can express the total diffusion length after a given anneal as

$$L_D^2=4D_V\int_0^t N_V\,dt. \quad (2)$$

For a layer of vacancies at the position of QW7 in our samples the time evolution of their diffusion with annealing can be expressed as the common double error function solution,

$$N_{VS}(x,t)=\frac{N_0}{2}\left\{\mathrm{erf}\left(\frac{d/2-x_0}{2\sqrt{D_V t}}\right)+\mathrm{erf}\left(\frac{d/2+x_0}{2\sqrt{D_V t}}\right)\right\}, \quad (3)$$

where $N_{VS}(x,t)$ is the vacancy concentration due to the source at QW7 as a function of depth and time, N_0 is the initial concentration of vacancies in the layer, d is the thickness of the vacancy layer, x_0 is the depth of the layer from the surface, t is the anneal time, and D_V is the diffusion coefficient for the vacancies. This equation may not give a completely accurate description of the concentration profile near the surface of the sample as it assumes an isolated source in infinite barriers. However, as we do not know the barrier conditions for the vacancies at the surface it is the best approximation that we can use. In addition to this vacancy source we also need to take into account the background vacancy concentration, N_{VB}, which may be a temperature activated term caused by the formation of Frenkel pairs. Thus in Eq. (2) $N_V=N_{VS}+N_{VB}$.

We fit our data, with this model, using three variables for the fitting. If we only fitted the data taken at a single anneal time (i.e., L_d^2 as a function of depth), Fig. 3, we find no unique solution for the three variables but a range of combinations of D_V, N_0, and N_{VB} all give reasonable fits to the data (however, all have D_V and N_{VB} varying by less than an order of magnitude). However, when we then used these values to calculate the time dependence of L_d^2 for the different wells we find that only one of the solutions can fit to the time evolution of the diffusion for all the wells.

Figure 3 shows the depth dependence of the diffusion length squared, after the first anneal, for several temperatures and shows the theoretical fits to the data. Figure 4 shows the time evolution for QW6 and QW1, being the wells nearest and furthest from the source of vacancies, respectively, again at several anneal temperatures. Whilst we used 10 nm as the thickness of the vacancy source layer in these calculations this may not accurately reflect the actual distribution of vacancies in the source layer, as following growth of this layer the temperature of the substrate was ramped up to normal growth temperatures before the next well was grown and consequently there might be some GaAs next to QW7 which is also arsenic rich. However, for the model used this does not affect the results, because the diffusion lengths for the vacancies are large in comparison to the initial thickness of the source layer so only the thickness concentration product affects the results. This will however have the effect of increasing the error in the calculated initial concentration of vacancies. For example, if the vacancy source were 20 nm rather than 10 nm then the vacancy concentration would be a factor of 2 lower. The values of the initial vacancy concentration, background vacancy concentration, and vacancy diffusion coefficient as a function of temperature are given in Table I.

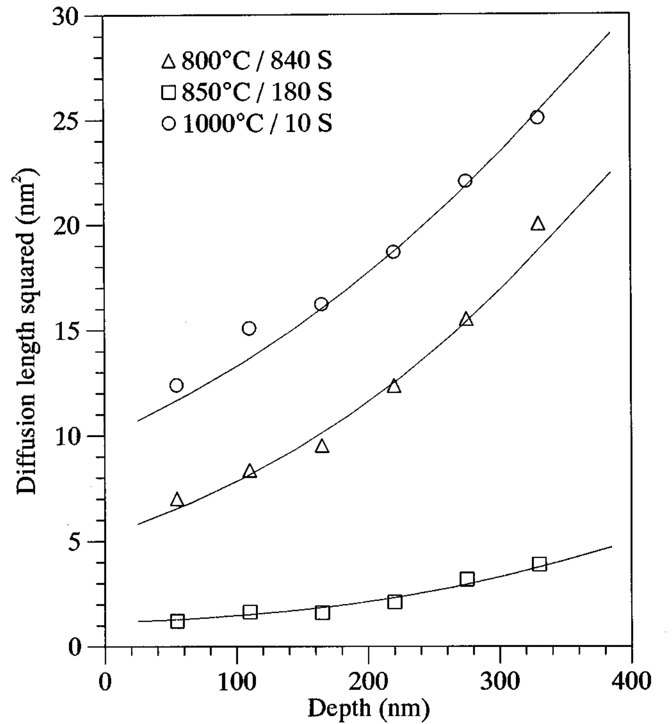
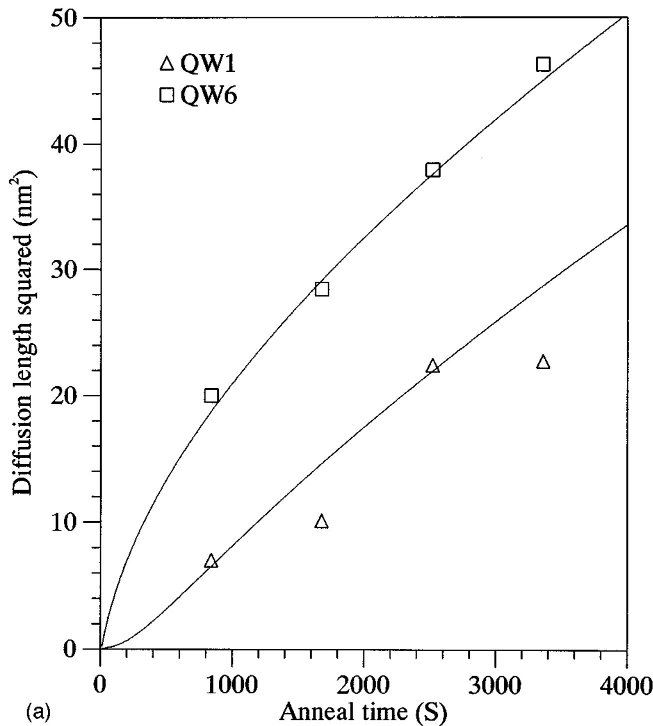


FIG. 3. A graph of the diffusion length squared as a function of depth in a single sample after an anneal at several temperatures. The solid lines through the data points are the results of the simulations using the values given in Table I.

The most notable thing that can be seen from Table I is that the background concentration of vacancies in our samples is not a function of temperature but remains constant at $\sim 10^{-5}$. As the concentration of group-III sites in GaAs is 2.2×10^{22} cm^{-3} this gives a background concentration of group-III vacancies of $\sim 2\times 10^{17}$ cm^{-3}.

This result is in contradiction to what many people have thought about the diffusion processes in GaAs. It has often been assumed that the activation energy for interdiffusion in these systems was made up of both a creation and a diffusion term for the vacancy and that the system was in thermodynamic equilibrium during a diffusion experiment. Indeed such thermodynamic arguments have been used by a number of authors in order to try and explain trends that they have seen in their data. This result strongly suggests that the concentration of vacancies present in the material is grown in and is much higher than the equilibrium concentration. Indeed as we have measured the interdiffusion coefficient in InGaAs/GaAs up to a temperature of 1200 °C (Fig. 5) and we see no evidence of a higher activation energy term we can conclude that this background concentration is controlling the interdiffusion up to at least this temperature.

This background concentration of vacancies is, however, comparable to that measured by Dannefaer *et al.*[7] in commercial semi-insulating GaAs at temperatures up to 600 °C, using positron lifetime spectroscopy. Our measurements, however, were made on layers grown by MBE so it is worth



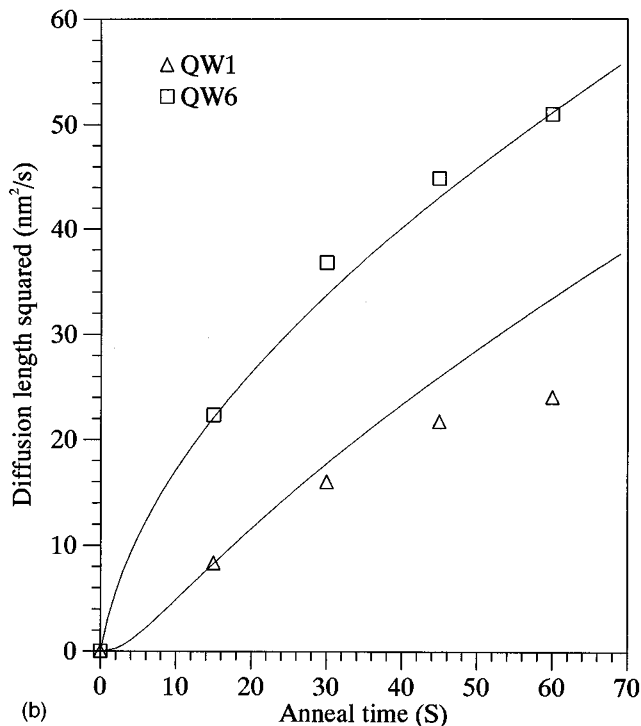


FIG. 4. A graph of the diffusion length squared, for QW1 and QW6, as a function of anneal time for samples annealed at 800 °C (a) and 950 °C (b). The solid lines are the results of the simulations using the values given in Table I.

determining whether our background vacancy concentrations should be comparable to those in GaAs wafers. With the measured diffusion coefficient of 5×10^{-11} cm^2/s at 950 °C after an anneal of one minute the vacancies would have a diffusion length of ~ 1 μm. If this measured vacancy concentration was only in the epilayer and the underlying GaAs had a much lower vacancy concentration then we would expect to see a thin epilayer reach an equilibrium with the substrate very quickly at this temperature and hence show a marked reduction in the measured interdiffusion of a quantum well with annealing. We have performed such measurements on quantum wells grown in epilayers between 50 nm and 2 μm thick and seen no such effects which seems to suggest that the vacancy concentration in the epilayer is the same as that in the substrate. It is also worth noting that we have measured interdiffusion coefficients and activation energies for InGaAs/GaAs samples produced by a number of different laboratories and grown using both MBE and MOVPE and in all cases we have measured the same activation energy and prefactor for the diffusion. Due to the very

TABLE I. The calculated values for the vacancy diffusivity, D_V, background vacancy concentration, N_{VB}, and the vacancy concentration in QW7, N_{VS}, as a function of temperature. The vacancy concentrations are the ration of the number of vacancies to the number of group-III sites.

Temperature (°C)	$D_V\times10^{-12}$ (cm^2/s)	$N_{VB}\times10^{-5}$	$N_{VS}\times10^{-3}$
800	0.70	0.8	3.8
850	1.60	0.8	1.0
900	14.5	1.0	1.0
950	50.0	0.5	4.0
1000	90.0	1.0	3.8

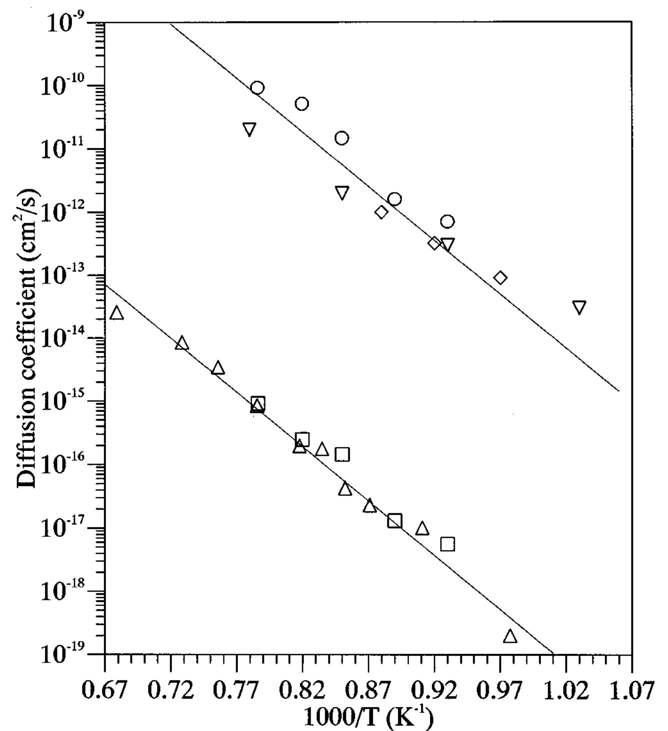


FIG. 5. An Arrhenius plot of InGaAs/GaAs interdiffusion coefficients for temperatures between 750 °C and 1200 °C (triangles). The squares are the $D_V N_V$ values calculated from Table I. Also plotted are our measured vacancy diffusion coefficients (circles) and those of Chang *et al.* (inverted triangles) (Ref. 9) and Tsang *et al.* (diamonds) (Ref. 8).

different nature of MBE and MOVPE growth this is again suggestive that the background concentration is determined by the substrate material used. During these experiments the biggest difference between samples that we found was a factor of ~ 2 in the prefactor. These prefactor changes had been measured by us on samples which were grown sequentially in the same growth reactor on the same day and from these results are probably a reflection of differences in the substrate materials.

As we have shown that the substrate vacancy concentration can reach equilibrium with the epilayer during growth one would expect any vacancies present in QW7 also to have diffused during the sample growth. This has evidently not happened from the photoluminescence measurements made after growth. In order to explain this we suggest that at growth temperatures there are not any excess vacancies only excess arsenic. It is only during the subsequent annealing that this arsenic dissolves on to the GaAs lattice producing the group-III vacancies which are then free to diffuse.

As the diffusion coefficient for intermixing is given by $D_V N_V$ we can calculate the steady state diffusion coefficient for intermixing that we would expect in our samples. These theoretical values are plotted on an Arrhenius plot in Fig. 5 along with our experimental data between 750 °C and 1200 °C collected from a single quantum well of InGaAs/GaAs, the straight line is a least squares fit to the experimental data. It can be seen that there is an excellent agreement. From this data we can calculate the activation energy for interdiffusion in InGaAs/GaAs as 3.4 ± 0.3 eV. In Fig. 5 we have also plotted our data for the vacancy diffusion coefficients along with those obtained by Tsang *et al.*[8] and Chang *et al.*[9] Using a least squares fit to each of these data sets we calculate activation energies for each of the three data sets as 3.1 ± 0.7 eV, 2.3 ± 1.4 eV, and 2.3 ± 0.6 eV, respectively. These values are the same within the experimental errors. It should be noted how large these errors in the activation energy are when a proper least squares analysis to the data is performed, and this highlights the importance of collecting large data sets over a wide temperature range in order to make meaningful comparisons of activation energies. Using all of the vacancy diffusion data presented in Fig. 5 we can calculate an activation energy of 2.8 ± 0.4 eV this value is, within experimental error, the same as that calculated for the InGaAs/GaAs interdiffusion. As there is no temperature dependence to the vacancy concentration this is to be expected and thus we can state that the activation energy for interdiffusion measured in InGaAs/GaAs samples, 3.4 ± 0.3 eV, is the activation energy for vacancy diffusion in this material. In Fig. 5 we have put a line through the vacancy diffusion data using this activation energy and it can be seen to provide a good fit to the data. Although we have been able to determine the activation energy with a reasonable degree of accuracy we cannot determine the prefactor for the diffusion to within even an order of magnitude. The result of using the Arrhenius plot for the InGaAs/GaAs interdiffusion (shifted by 10^5 to place it on the vacancy diffusion data) gives us a prefactor of $e^{(7.8 \pm 2.9)}$ cm^2/s. Thus all we can say about the prefactor is that it is likely to lie in the range 134 to 46027 cm^2/s. The size of this potential error, even when we are using data collected over a 450 °C temperature range, highlights the difficulties in correlating experimental D_0 values with theoretical predictions.

These results also have implications for interdiffusion in other III-V material systems. The diffusion coefficients and activation energy for interdiffusion that we measure for InGaAs/GaAs interdiffusion are very similar to those that we have determined for the AlGaAs/GaAs system.[10] If the background concentration of vacancies in these epilayers is indeed determined by the concentration of vacancies in the GaAs substrates then this is not surprising and would mean that differences in the activation energy for AlGaAs/GaAs interdiffusion compared to InGaAs/GaAs interdiffusion are a direct measure of differences in the activation energy of vacancy diffusion in the two systems.

Similarly we have measured the interdiffusion of InGaAs/InGaAs samples grown on InP substrates.[11] This material has an activation energy for interdiffusion which is the same as that measured for InGaAs/GaAs grown on GaAs, within experimental error, but it has a prefactor which is more than an order of magnitude greater. As the material through which the vacancies are diffusing in these two systems are very similar it is unlikely that the prefactor for the vacancy diffusion is the cause of this difference and suggests that it is a high concentration of vacancies in the poorer quality InP substrate material which is the source of the larger prefactor. Further experiments need to be performed on this material system to confirm this, but if true then the thermal stability of InP based materials could be improved by improvements in the substrate quality.

From Table I we can see that there are some variations in the vacancy concentration in QW7 in the different samples, although there is no trend with temperature. It may be that these differences are an indication of our measurement accuracy or that they may reflect real changes in the vacancy concentration in QW7 due to the position of the sample with respect to the wafer. It is known for example that in MBE growth the beams have a roughly Gaussian shape and the intensities are usually lower at the edge of the wafer than at the center. This is usually manifest as a nonuniformity in the grown wafer. Differences in the overlap of the three sources may slightly affect the stoichiometry across the wafer and result in changes in the vacancy incorporation in QW7. At normal growth temperatures where the species are mobile this may not cause a serious problem but at the low temperature used to grow QW7 these effects could be more pronounced. This is only speculation at the present time but this is an area in which we plan to perform more experiments in order to clarify the cause of these changes. However, it can be seen from Table I that the changes are only a factor of ~ 4. From the values given in Table I for the vacancy concentration ratio in QW7 we can calculate the actual concentration of vacancies in the well to be at most $\sim 8 \times 10^{19}$ cm^{-3}. This is the value if the source of the vacancies is 10 nm. As stated earlier a wider source layer will result in a corresponding decrease in this value.

IV. CONCLUSIONS

We have used the interdiffusion of a multiple quantum well sample to measure the diffusion coefficient for group-III

vacancies in GaAs and the background concentration of these vacancies in a single experiment. We have shown that the interdiffusion of this material is governed by the background concentration of vacancies present in the material and that this background concentration is probably the concentration of vacancies in the substrate material. This background vacancy concentration is temperature independent and this proves that the vacancy concentration is not at a thermal equilibrium value as has been widely assumed in the literature. We obtain vacancy concentrations of around 2×10^{17} cm^{-3}.

The activation energy for intermixing of InGaAs/GaAs is shown to be governed solely by the activation term for vacancy diffusion which is calculated to have an activation energy of 3.4 ± 0.3 eV.

These results suggest that in order to improve the thermal stability of heterostructures over that which can be achieved using good surface encapsulation it will be necessary to either reduce the concentration of vacancies grown in to the substrate material or provide some means of blocking their movement in to the epilayer during growth. This latter approach however, would still be reliant on epitaxial growth being able to provide lower vacancy concentrations in the epilayers.

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