The activation energy for GaAs/AlGaAs interdiffusion

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We present data of the interdiffusion coefficient of AlGaAs/GaAs over the temperature range 750–1150 °C, and obtain E_A and D_0 values of 3.6 ± 0.2 eV and 0.2 (with an uncertainty from 0.04 to 1.1) cm^2/s, respectively. These data are compared with those from the literature taken under a wide range of experimental conditions. We show that despite the range of activation energies quoted in the literature all the data can be described using a single activation energy. Using this value of E_A to fit the published data and then determining D_0 for each data point we find that the published data fall into two clusters. One, for samples annealed under a gallium rich overpressure and a second for As rich or capped anneals. This result can be explained by the diffusion in all cases being governed by a single mechanism, vacancy-controlled second-nearest-neighbor hopping. © *1997 American Institute of Physics.* [S0021-8979(97)03822-X]

INTRODUCTION

The interdiffusion of III–V heterostructures, in particular the GaAs/AlGaAs system, has been studied now for ~20 years. During this time there have been numerous measurements of the diffusion coefficient for intermixing under a wide range of sample conditions, using a range of experimental techniques. These measurements have produced widely varying estimates of both the diffusion coefficient at a given temperature and more significantly the activation energy for intermixing. This latter term has been quoted in the literature as having values between 0.32 eV[1] and 7.34 eV.[2] In many cases these differences in activation energy have been used by authors as evidence for different mechanisms for the interdiffusion process. However, it is extremely unlikely that mechanisms with such a wide range of activation energies would be observed for a process, and hence it is important to investigate the role of experimental error in these determinations.

Many of the measured activation energies are determined from small data sets. It is not unusual for papers to present diffusion data measured at three or four temperatures over 100 °C temperature range, while a least squares analysis on such a small data set may provide a data set which can be well fitted. The value measured and its statistical uncertainty may not be very reliable.

In our earlier work we have extensively studied the InGaAs/GaAs system[3–5] and developed the technique of performing many anneals on a single sample coupled with photoluminescence as a means of measuring interdiffusion in a sample as a function of time. This technique has the advantage of not only giving a larger data set for each measured value of the diffusion coefficient, but also reducing the errors in individual values of D. It also has the advantage that it allows one to see whether there are any time dependent diffusion processes occurring, such as may be due to poor surface encapsulation causing the injection of diffusion-mediating point defects from the surface. For example, we have shown using this technique that gallium implantation, which is often quoted as enhancing interdiffusion, plays no role in the steady state diffusion of InGaAs/GaAs heterostructures but rather that the damage created during implantation causes a very rapid intermixing which if only a single anneal were performed would be mistaken for an enhanced D.

This article presents the results of a study of the interdiffusion of GaAs/AlGaAs using repetitive annealing and photoluminescence which has been performed over a temperature range of 750–1150 °C. Using these data we calculate an activation energy for GaAs/AlGaAs interdiffusion. We then compare our data with those presented in the literature. These literature data have been collected using a range of experimental techniques and with a range of surface conditions. We show that all the literature data can be described by a single activation energy.

EXPERIMENTAL METHOD

The samples used in this work were grown by either molecular beam epitaxy (MBE) in a Vacuum Generators V80H reactor or by metal organic chemical vapor deposition (MOCVD) on (100) oriented GaAs. The samples consisted of a single quantum well of 10 nm of GaAs with 100 nm barriers of $Al_{0.2}Ga_{0.8}As$ both above and below the well. On the surface an additional 5 nm of GaAs was deposited to protect the AlGaAs from oxidation.

Following growth, the wafers were 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, and for interdiffusion on InP based materials we have shown that this capping gives inter-

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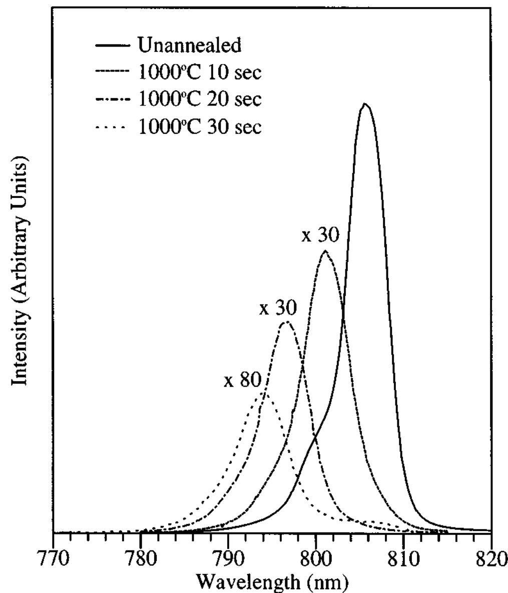

FIG. 1. The photoluminescence spectra for a 10 nm GaAs quantum well in $Al_{0.2}Ga_{0.8}As$ barriers before and after annealing at 1000 °C for 10, 20, and 30 s.

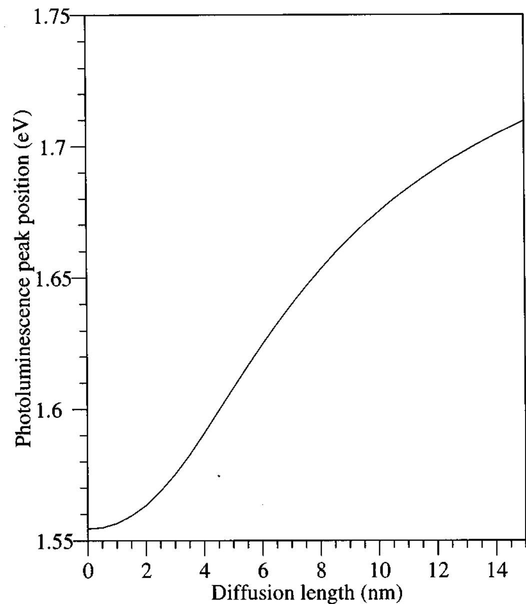

FIG. 2. The calculated variation in photoluminescence peak position with diffusion length for a 10 nm GaAs quantum well in $Al_{0.2}Ga_{0.8}As$ barriers.

diffusion coefficients identical to those for uncapped samples annealed under growth conditions in a MOCVD reactor.[3] The composition of this nitride is crucial for diffusion experiments, and we have found that nitrides grown with a refractive index of less than 2 showed at least an order of magnitude increase in D at all temperatures (i.e., a change in D_0). Following capping the wafer was cut into 5 mm×5 mm squares for the annealing experiments.

Rapid thermal annealing (RTA) was performed in a helium ambient using a resistively heated graphite strip heater. The use of helium in the RTA system ensured the fastest heating rate for the sample due to its high thermal conductivity. The sample was placed between two graphite strips and the temperature measured and 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. This system was used to perform anneals with a duration between 15 s and 30 min. 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.

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 increase in the aluminium 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 Refs. 4 and 5.

We used the empirical value for the 80 K $Al_xGa_{1-x}As$ band gap, E_g, in electron volts given by Bosio *et al.*[6]

$$E_g = 1.516 + 1.36x + 0.22x^2, \tag{1}$$

where x is the aluminium mole fraction, and a band offset ratio of 60:40.

RESULTS AND DISCUSSION

Figure 1 shows the photoluminescence spectra for a single quantum well sample which has been annealed at 1000 °C for 10, 20, and 30 s. It can be seen that the photoluminescence shifts to higher energy as predicted and this shift in the photoluminescence peak position can be converted in to a diffusion length for Ga–Al interdiffusion using the calculated curve given in Fig. 2.

For our earlier work on InGaAs/GaAs interdiffusion[3–5] we were able to measure the peak shift with annealing and convert it to a percentage of the total shift from the unannealed quantum well emission to the GaAs band edge emission. This variation of this percentage shift with diffusion length for the InGaAs/GaAs system is independent of the initial indium concentration in the well (provided the initial indium concentration is less than 25% and the well thicknesses were identical) and thus we were able to use a single calculated curve for all our samples. This method worked because the barrier emission energy, to which the diffused quantum well emission was tending, was well defined, being the GaAs band edge. For the GaAs/AlGaAs system, where the ternary system is in the barriers, and hence not well defined, this approach cannot be used and we were forced to

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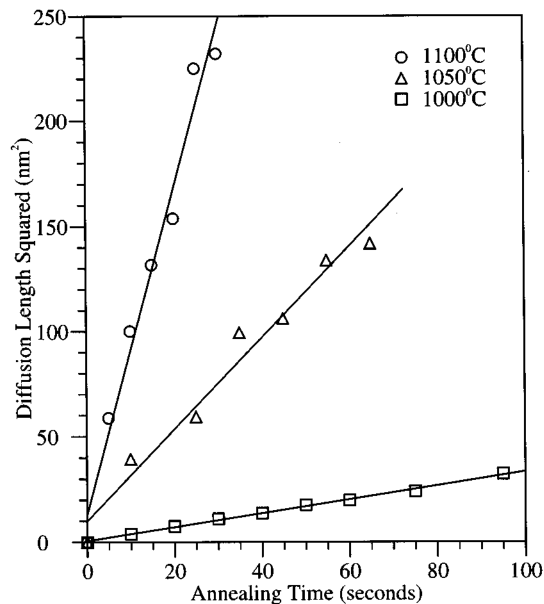

FIG. 3. The diffusion length squared plotted against anneal time for a 10 nm GaAs quantum well in $Al_{0.2}Ga_{0.8}As$ barriers after annealing at 1000, 1050, and 1100 °C. The diffusion lengths were determined from the photoluminescence spectra using Fig. 2.

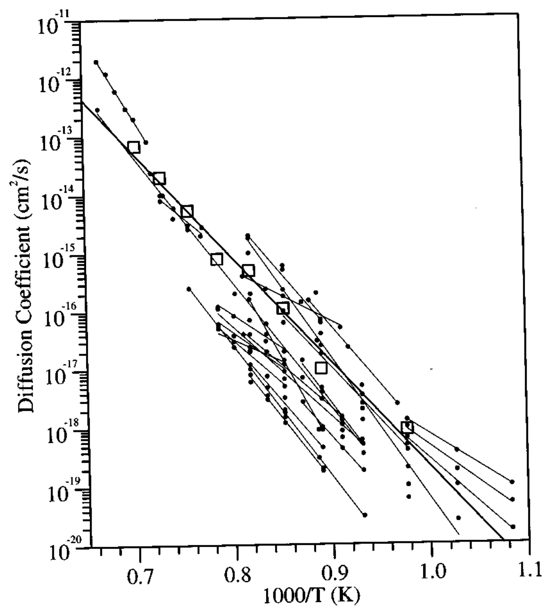

FIG. 4. An Arrhenius plot of our GaAs/AlGaAs interdiffusion data (squares) and much of the data form the literature (dots) the solid line is the least squares fit to our data, and the light lines are the least squares fits to all the other data sets. They literature data comes from Refs. 1 and 7–20.

measure the aluminium concentration in the barriers of each of our samples and calculate a theoretical curve of photoluminescence peak shift against diffusion length for each sample. The curve given in Fig. 2 is for a $Al_{0.2}Ga_{0.8}As$ barrier layer with a 10 nm GaAs well.

The graphs of diffusion length squared against anneal time at several anneal temperatures are shown in Fig. 3. From Fig. 3 it can be seen that over our range of anneal times we obtain a straight line fit to the data and as $L_D^2 = 4Dt$ the gradient of the straight line directly gives the diffusion coefficient, D. This straight line also shows that there is no dependence of D on the aluminium concentration, as the aluminium concentration in the well center will have increased from 0% to $>10\%$ during some of these experiments with no change in D.

In addition to proving that Fick's law is being obeyed, measuring the time dependence of the diffusion has two other advantages over performing single measurements. First, one gets statistically better data as we are in effect averaging a number of measurements, and second by following the time dependence we can look for unexpected variations in D. For example, we have had samples where after a number of anneals the encapsulant has started to fail. In these cases before the failure had been severe enough to quench the photoluminescence it caused an increase in the diffusion coefficient, presumably by the injection of vacancies from the surface. These effects are generally not noticed when only a single anneal is performed but are clear from the time dependence.

The results of these experiments are plotted on an Arrhenius plot in Fig. 4 (squares). The dots in Fig. 4 are Al–Ga interdiffusion and Ga self-diffusion data taken from Refs. 1 and 7–20 and the light lines are the least squares fits to each of those data sets. The slopes of those lines give E_A values, with their uncertainties, ranging from 1.5 ± 0.5 eV[7] to 6.2 ± 0.2 eV.[8] The first thing to notice from Fig. 4 is that there appear to be two clusters of data points. The first cluster which covers a temperature range of 650–1229 °C and includes our data can be very well fitted by a least squares fit to our data set ($E_A = 3.6\pm0.1$ eV and $\ln[D_0/(\mathrm{cm}^2/\mathrm{s})] = -0.7\pm1.3$). This value is significantly different from the value of 6 eV, which was obtained by Tan and Gösele,[21] and which is widely quoted in the literature, although in later work[22] they quote an activation energy which is, within experimental uncertainty, the same as the value we quote here. The second cluster which is below our data can be equally well fitted by our activation energy but with a prefactor which is an order of magnitude lower. This is despite the fact that the data in Fig. 4 includes the results from experiments with the samples annealed in both As rich and Ga rich ambients or with silicon nitride or silicon dioxide.

This result is significant because many authors collect data under different annealing conditions and measure different activation energies which are then either left without comment or used to suggest that there are different active diffusion mechanisms. One of the most common of these is the Fermi level model of Tan and Gösele.[21] You *et al.*,[2] for example, have stated that ''...prevalent opinion concerning the point defect species governing Ga self-diffusion and Al–Ga interdiffusion is that they are dominated by the triply negatively charged Ga vacancies under intrinsic and n-doping conditions at high P_{As_4} values, and by the doubly positively charged Ga self-interstitial under intrinsic conditions at low P_{As_4} values... .'' They go on to estimate activation energies of 6–7.34 eV for the vacancy mediated process and 3.37–4.71 eV for the interstitial process. It should also

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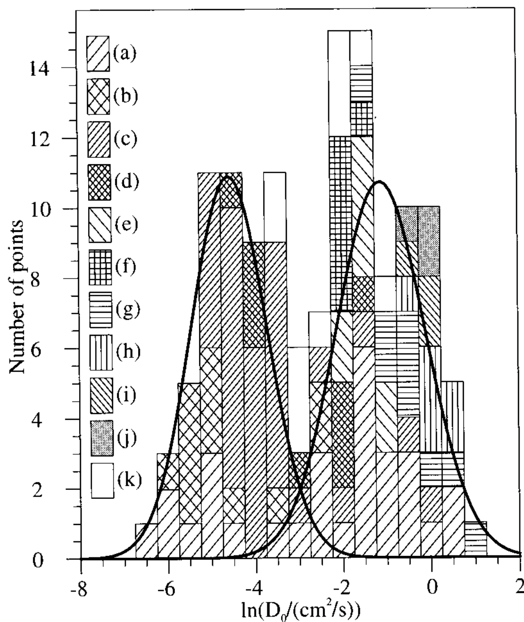

FIG. 5. A histogram of the $\ln[D_0/(\mathrm{cm}^2/\mathrm{s})]$ values for each of the data points plotted in Fig. 4 having been fitted by our activation energy. The data points marked (a) are taken from Refs. 10 and 17, (b) are from Ref. 8, (c) from Refs. 2, 7, and 18 and are all from one laboratory, (d) from Refs. 12 and 14, (e) this work, (f) from Ref. 13, (g) from Ref. 9, (h) from Ref. 16, (i) from Ref. 11, (j) from Ref. 15, and (k) from Ref. 20.

be noted that these activation energies require prefactors ranging from $\sim 10^{-4}$ to $\sim 10^{12}$ cm^2/s although no mention is given to the physical significance of this range of prefactor. From Fig. 4 it is clear that by selecting a small data set from those available it is very easy to measure a large range of E_A values. However, the large amount of data now available on interdiffusion should be looked at in it's entirety. Indeed if we perform a least squares fit to all the data presented in Fig. 4 we obtain an activation energy of 3.4 ± 0.2 eV, while if we take only the data in the cluster around our data we get an activation energy of 3.5 ± 0.2 eV and similarly if we only take the data in the cluster below our data we get an activation energy of 3.5 ± 0.2 eV. Consequently, it is very difficult to argue anything other than a single activation energy for all experiments with a value of ~ 3.5 eV.

In order to highlight the fact that the data can be grouped in two clusters with a single E_A but differing D_0 values we have used our activation energy to fit a straight line through every data point on Fig. 5 and then determined the D_0 value that this fit produces. It should be noted that although we have used the activation energy obtained from the least squares fit calculate the D_0 values in Fig. 5, the distribution obtained is not dependant on the absolute value of E_A used. These results are plotted in Fig. 5 as a histogram, where the height of each column is the number of data points giving a $\ln(D_0)$ value in a given range. Also plotted in Fig. 5 are two Gaussians which are a fit to the data obtained using a χ^2 minimization routine.[24] From this diagram it can be seen that there are two distributions, one centered on a $\ln(D_0)$ value of about -1.12, $\sigma = 1.4$ and the second centered around a $\ln(D_0)$ value of about -4.6, $\sigma = 1.2$.

Suggesting that there is a single diffusion mechanism describing all the data in the literature, we will now discuss how to account for the observed variations in D_0. In our earlier work on InGaAs/GaAs interdiffusion[3–5] we have observed that two different wafers of quantum well material, which were grown sequentially in the same MBE reactor, capped at the same time with silicon nitride and annealed together can easily show differences in D_0 of a factor of 2.[5] At that time we attributed it to differences in the substrate materials. This factor alone could account for much of the random scatter seen in the data. If this were coupled with the experiment variations one would expect to see differences between different groups such as in furnace calibration, in the treatment of ramp times, surface passivation (c.f. our earlier comment on the dependence of diffusion on the refractive index of a silicon nitride cap), etc., then the spread in the data is to be expected. What is more interesting is the presence of the two clusters in the data. Hsieh *et al.*[8] demonstrated that annealing in a Ga rich environment resulted in a lower interdiffusion coefficient than an As rich environment. Their small temperature range produced an apparent change in E_A from 4 to 6 eV. Olmsted *et al.*[10,17] performed a more detailed study in 1993 of the effect of annealing in both Ga rich and As rich conditions. Their original data showed that under both annealing conditions they get essentially the same activation energy but with D_0 values approximately two orders of magnitude different, again with the Ga rich annealing producing the lower diffusion coefficients. Another paper which presents results of similar experiments was that of You *et al.*[2] Their results also show no significant change in E_A with annealing ambient, although in contradiction to the results of Hsieh *et al.*[8] and Olmsted *et al.*[10,17] they seem to find that the Ga rich anneals give higher diffusion coefficients. This work was performed in collaboration with Holonyak[18] from the University of Illinois at Urbana-Champaign. The groups of Major *et al.*[7] and Guido and Holonyak[18] are responsible for most of the other data which lie in the second cluster consisting of approximately half of the data. This work is significant in that it contains a large amount of data obtained on samples which have been annealed with a silicon dioxide cap as well as some results with silicon nitride caps and some with As overpressure annealing. The results of Major *et al.*,[7] like many other workers, show that an SiO_2 encapsulant enhances interdiffusion compared with Si_3N_4. Their results however have diffusion coefficients which are nearly two orders of magnitude below those obtained under similar conditions by other groups (e.g., Ralston *et al.*[15]). The reasons for this large discrepancy are not clear. Also included in Figs. 4 and 5 are the data of Wang *et al.*[20] who studied Ga self-diffusion in GaAs using isotope heterostructures. Their results, collected over a large temperature range of 800–1225 °C, produce an activation energy which, within experimental uncertainty, is identical to that which we have calculated.

In some of our recent experiments, Khreis *et al.*[23] have highlighted a possible mechanism to explain how annealing in a Ga rich ambient could reduce D_0 without affecting E_A. These experiments used the interdiffusion of a InGaAs/GaAs quantum well stack to measure the diffusion of vacancies

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from a quantum well of material grown slightly below the standard InGaAs growth temperature. These experiments allowed us to determine in a single sample both the gallium vacancy diffusion coefficient and the background concentration of vacancies, both as a function of temperature. These results showed that, contrary to commonly held beliefs, the vacancy concentration in III–V materials is not at a thermal equilibrium value but rather has a constant value of $\sim 10^{17}/\text{cm}^3$ for all temperatures. These results also showed that the activation energy for the vacancy diffusion is the activation energy for interdiffusion. This result provides an explanation not only for the differences in interdiffusion coefficients measured on different wafers (differences in the background vacancy concentrations in the wafers) but also provides a mechanism to explain the reduced diffusion coefficients measured under Ga rich conditions. This could be explained because the excess Ga in the ambient in effect acts as a sink for arsenic vapor leaving the surface during annealing. This will result in a surface which is very gallium rich. Some of this excess gallium at the surface can then react with gallium vacancies causing them to annihilate through the reaction

$$I_{\text{Ga}} + V_{\text{Ga}} \Leftrightarrow 0. \quad (2)$$

Thus the gallium rich ambient can reduce the gallium vacancy concentration responsible for the intermixing and hence reduce D_0 without changing E_A.

CONCLUSIONS

We present data on the interdiffusion of AlGaAs/GaAs over the temperature range 750–1150 °C, and obtain E_A and $\ln[D_0/(\text{cm}^2/\text{s})]$ values of 3.6 ± 0.2 eV and -1.5 ± 1.6, respectively. These are much lower than the widely quoted value of Tan and Gösele. These data are compared with those from the literature taken under a wide range of experimental conditions. We show that despite the range of activation energies quoted in the literature all the data can be described using a single activation energy, the published data falling into two clusters: one for samples annealed under a gallium rich overpressure and a second for As rich or capped anneals. This result can be explained by the diffusion, in all cases, being governed by a single vacancy-controlled mechanism, involving second-nearest-neighbor hopping, where the gallium vacancy concentration can be altered by the surface conditions. This result is in contradiction to the widely published theory that interdiffusion and self-diffusion are controlled by vacancy concentrations which are at thermal equilibrium values.

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