

Strain and interdiffusion in semiconductor heterostructures

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It is often suggested that the rate of interdiffusion at semiconductor heterostructure interfaces may be strongly dependent on elastic strain in the structure. Experimental and theoretical results show that strain does not, and should not, affect interdiffusion.

INTRODUCTION

Interdiffusion in semiconductor heterostructures such as quantum wells and superlattices can occur under growth conditions and in subsequent device processing. It changes effective layer thicknesses and compositions, and so both a qualitative and a quantitative understanding is necessary to enable interdiffusion to be avoided or controlled. Many authors have suggested that the grown-in strain in pseudomorphic structures will enhance interdiffusion significantly. Pseudomorphic structures are now used routinely in commercial devices such as strained-layer lasers, and it is timely to review the evidence and consider whether strain-enhanced interdiffusion in semiconductors is indeed a real effect. We conclude that it is not.

Iyer and LeGoues,¹ to our knowledge, first reported strain-enhanced interdiffusion in semiconductors. They found that a Si-SiGe strained interface could interdiffuse at 550°C at a rate which, without strain, would require over 1000°C. They did not consider this result surprising as the effect of strain-enhanced diffusion had long been known in metals.^{2,3} Kuan and Iyer⁴ later reported significant interdiffusion in the Si-SiGe system at a temperature as low as 400°C, which, if due to the intrinsic strain in the structure, would make silicon-germanium pseudomorphic structures technologically very difficult to grow and process.

Other authors do not find a significant effect of strain on interdiffusion. Holländer and co-workers^{5,6} also studied the Si-Si-Ge system, but they found that strain had only a minor effect on interdiffusion compared with concentration. Gillin and co-workers studied the $\text{In}_x\text{Ga}_{1-x}\text{As-GaAs}$ system in detail and found no detectable effect of either strain or concentration.⁷⁻⁹ The picture is therefore unclear. To resolve the question of strain-enhanced diffusion in semiconductors, we show that theoretically strain should not affect interdiffusion significantly, and we consider whether the experimental evidence requires an effect of strain or whether the data can be explained by other known effects.

THEORY

Interdiffusion in the tetrahedral semiconductors is closely related to self-diffusion. It requires the exchange of neighboring atoms, on any lattice site in the elemental Si-Ge system, on the group III sites in the $\text{In}_x\text{Ga}_{1-x}\text{As-GaAs}$ system, and separately on the group III and on the group V sites in a quaternary structure such as $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}\text{-InP}$. The exact mechanism of this exchange is not clear; however, it is thermally activated and described by a diffusion constant $D(T)$ given by

$$D = D_0 e^{(-E_A/kT)}. \quad (1)$$

Quantum wells and superlattices include layers of thicknesses of tens of Ångströms and so this gives a length scale for significant diffusion, with the diffusion length L_D given by a Fick's law analysis as

$$L_D = 2\sqrt{Dt}. \quad (2)$$

The activation energy E_A for the III-V systems is close to 3.7 eV (Refs. 7,10, and 11) with a prefactor D_0 of typically around $0.2\text{--}20\text{ cm}^2\text{ s}^{-1}$, thus requiring temperatures in the range 600°C–1100°C to get significant diffusion within a time scale of hours to seconds. Many factors and perturbations can affect interdiffusion. Any of these which vary with position, such as concentration and strain, invalidate the application of Fick's law and make the definition of a diffusion length imprecise. Experimentally, most perturbations are found^{7,8,12} to affect interdiffusion through the prefactor D_0 rather than through the activation energy, although, because of the limited temperature range over which many experiments test Eq. (1), there is a wide disparity in the values of E_A quoted, and many authors quote changes in E_A as being significant even when they are taken from Arrhenius plots over a temperature range of only 100 K.

Strain, on the other hand, is expected to affect the rate of interdiffusion through the activation energy in Eq. (1). This is because a large atom moving away from a region of compressive strain lowers the energy of the system. It

is, therefore, worthwhile calculating the energy change to predict the effect on the activation energy. A biaxially compressed pseudomorphic layer of strain ϵ_0 has an energy given by

$$E = \int_V \sum_{i,j=1}^3 \frac{1}{2} \epsilon_{ij} \sigma_{ij} dV = \frac{2Y}{1+\nu} \epsilon_0^2 V, \quad (3)$$

where Y is the Young's modulus. For a technologically useful strain of $\epsilon_0 = 0.01$, and using the GaAs elastic constants,¹³ this gives an elastic energy of approximately $1.73 \times 10^7 \text{ Jm}^{-3}$, or about 2.5 meV per atom.

This is a very small energy. If the diffusion event goes from an initial state S_i through a high-energy state S_b , which provides the energy barrier and the activation energy E_A , to the final state S_f , the largest effect of the elastic energy occurs when it raises the energy of S_i without affecting S_b and S_f . In this case, it will reduce E_A from 3.7 to 3.697 eV, which will be completely insignificant.

The strain energy is not, of course, completely relieved by a single diffusion event. For a quantum well width of L , the large atoms must move distances of the order of L if they are to go to a region of significantly lower strain. This implies a number of diffusion events $n \geq L/a_0$, where a_0 is the lattice constant, and a reduction in the activation energy for each event not of 2.5 meV but of $2.5/n$ meV, which is even less detectable experimentally.

Finally, the strain energy is not in fact relieved at all by complete diffusion. In the limit of diffusion to an infinitely dilute alloy, each large atom is at the center of a spherically symmetrical strain field (in an isotropic continuous elastic medium approximation). If we treat the large atom as a sphere of volume $V_0(1+3\epsilon_0)$ where ϵ_0 is the misfit strain, the strain field is

$$\begin{aligned} r > r_0, \quad -\sigma_{rr} = 2\sigma_{\theta\theta} = 2\sigma_{\phi\phi} &= \frac{12B\mu}{3B+4\mu} \epsilon_0 \frac{r_0^3}{r^3}, \\ r < r_0, \quad \sigma_h = \sigma_{rr}(r_0), \end{aligned} \quad (4)$$

where σ_h is the hydrostatic stress within the sphere, r_0 is the radius, B is the bulk modulus, and μ is the shear modulus. The energy of this strain field is readily found, and for a Poisson's ratio of $\nu = \frac{1}{3}$ is

$$\begin{aligned} E &= \int_V \sum \frac{1}{2} \epsilon_{ij} \sigma_{ij} dV = \frac{3}{4} \sigma_h^2 V_0 \left[\frac{2}{3B} + \frac{1}{2\mu} \right] \\ &= \frac{3Y}{2} \epsilon_0^2 V_0, \end{aligned} \quad (5)$$

which is the same energy as the energy of a volume V_0 of the strained layer given by Eq. (3).

This result is perhaps counterintuitive. It means that the energy of the random strain fields of a dilute alloy is the same as the energy of the coherent strain field when the alloying atoms are gathered up into a single layer. Whether the energies remain equal for all dilutions during diffusion is not clear; it is clear that less strain energy is relieved by diffusion than previously supposed.

EXPERIMENTAL EVIDENCE

We consider now the experimental evidence for and against strain-enhanced diffusion. Large effects were re-

ported by Iyer and LeGoues¹ at SiGe-Si interfaces. They compared the diffusion at a pseudomorphic interface, with the full misfit strain and no misfit dislocations, with the diffusion at an interface with a partially relaxed metamorphic layer, with reduced strain and a high dislocation density. They observed much faster diffusion at the pseudomorphic interface and attributed this to the presence of the misfit strain. However, dislocations are observed in other systems to suppress interdiffusion: Mallard *et al.*¹⁴ reported that misfit dislocations suppress interdiffusion for a distance of about 300 μm around the dislocation. This phenomenon, while not understood (it may speculatively be attributed to dislocations acting as sinks for defects such as vacancies), is certainly sufficient to account for the observations of Iyer and LeGoues.

The first reported effects of strain on the interdiffusion of III-V systems were reported by Temkin *et al.*¹⁵ in the $\text{In}_x\text{Ga}_{1-x}\text{As-InP}$ system. They used both TEM and photoluminescence to investigate quantum wells before and after annealing and they suggest that following annealing their quantum wells remain square rather than the error functions one would expect for Fick's law diffusion. In order to explain these effects, they suggest that the compositional driving force for diffusion is opposed by the increase in the lattice strain that diffusion would introduce, and that this resistance to strain adjusts the interdiffusion coefficient to produce a roughly lattice-matched quantum well. However, the conclusions reported in this work are based on a qualitative analysis of both their TEM and photoluminescence results and thus their case for strain-retarded diffusion is far from proven.

Fujii *et al.*¹⁶ have also studied the $\text{In}_x\text{Ga}_{1-x}\text{As-InP}$ system, and have used photoluminescence to determine interdiffusion between 500°C and 640°C. They suggested that the diffusion rate is determined by the diffusion of the group V species across the heterointerface and that this is much lower than the diffusion rate in either the $\text{In}_x\text{Ga}_{1-x}\text{As}$ or in the InP. This they attribute to the diffusion at the interface creating local strain and this strain energy they suggest is sufficient to retard the diffusion. In this work they quote an estimated strain energy of about 1 eV per atom, which they calculated from elastic constants. This strain energy is of the same order as the activation energy for interdiffusion that they determined, and they therefore suggest that strain can have a significant effect upon the diffusion through the exponential term in Eq. (1). However, their strain energy is nearly three orders of magnitude greater than the correct value, from Eq. (3). Furthermore, recent data by Gillin and co-workers^{10,11} have shown that the diffusion coefficients on the group III and group V sublattices in the $\text{In}_x\text{Ga}_{1-x}\text{AsP}$ material system are identical and, therefore, the diffusion of lattice-matched $\text{In}_x\text{Ga}_{1-x}\text{As-InP}$ quantum wells would not introduce any strain into the material.

The Surrey group has reported a large body of work which finds no effect of strain on interdiffusion in the III-V systems $\text{In}_x\text{Ga}_{1-x}\text{As-GaAs}$ and $\text{In}_x\text{Ga}_{1-x}\text{As-In}_z\text{Ga}_{1-z}\text{As}_y\text{P}_{1-y}$.⁷⁻¹² In this work, the structures were designed so that there was a concentration gradient to drive diffusion on only one sublattice so

that the complexities of trying to deconvolute the effects of diffusion on two sublattices simultaneously were avoided. This work relies on the shift of the photoluminescence of a quantum well to deduce the diffusion length L_D and hence the diffusion constant.⁹ A single sample is annealed repeatedly, and a plot of the square of the deduced diffusion length L_D^2 against t , as in Fig. 1, tests the applicability of Eq. (2). A straight line shows that the diffusion constant does not change with time, and therefore does not change either with concentration or with strain since both of these evolve with time. Furthermore, a study of a multiple-quantum-well sample with different indium concentrations in each well and hence different initial strains showed no change in the diffusion constant with strain.⁸

It may be questioned how rigorously the straight-line fit of Fig. 1 tests the applicability of Fick's law and hence the strain independence of the interdiffusion. In order to assess this we have used a finite-element method to solve the diffusion equation for various concentration (i.e., strain)-dependent diffusion coefficients. The diffusion coefficient we used in our calculations was,

$$D = D_A \left[1 + \alpha \frac{x}{x_0} \right], \quad (6)$$

where x_0 is the initial concentration at the well center and α allows us to change the concentration dependence. Using this model, the effects of the orders-of-magnitude enhancement reported by Iyer and LeGoues¹ and by Kuan and Iyer⁴ can readily be assessed. With much higher interdiffusion values in the presence of strain this would be represented in Eq. (6) by $\alpha \gg 1$. We take $\alpha = 9$ to give an order of magnitude increase in diffusion coefficient from $x = 0$ to $x = x_0$. In order to determine

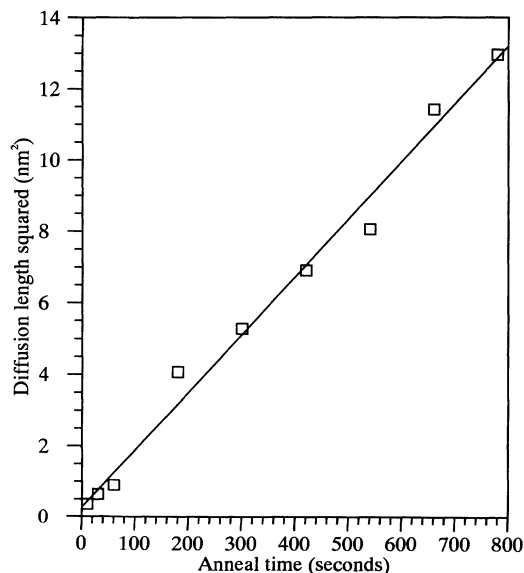


FIG. 1. A plot of diffusion length squared against anneal time for a 10-nm $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ quantum well in GaAs barriers annealed at 900°C. Details of the method used to convert photoluminescence peak shift to diffusion length are given in Refs. 7 and 8.

whether this type of diffusion process could be detected with our experiments, we solved the Schrödinger equation for the well shape determined from the finite-element calculation in order to determine how the photoluminescence transition energy would change as a function of time. These data were then plotted as diffusion length squared against anneal time in the same way as experimental data and the results are shown in Fig. 2. It can be seen that the data in no way resembles a straight line.

Using this technique we have also modeled the effects of strain-suppressed diffusion by setting $\alpha = -0.9$ to give an order-of-magnitude decrease in D from $x = 0$ to $x = x_0$. Again we used the results from the finite-element calculation to determine the expected photoluminescence peak shift with annealing and again we have plotted the calculated diffusion length squared against anneal time data in Fig. 2, which also varies significantly from the straight lines obtained experimentally. From these data we can conclude that the observation of a straight $L_D^2(t)$ characteristic rules out order of magnitude changes of D with concentration or strain.

In Fig. 3 we have plotted the indium concentration profile for the value of α and D_A used in Fig. 2. The profiles for the nonzero α values are calculated at the point where the two curves in Fig. 2 cross while the profile for $\alpha = 0$ is for a diffusion length required to give an identical photoluminescence peak shift. This diagram clearly shows the effects of a concentration dependence of diffusion coefficient on the well shape with the strain-retarded profile losing indium from the well center more slowly and effectively narrowing the width of the quantum well; whereas the strain-enhanced diffusion results in a well profile which is losing indium from the well center much faster and effectively broadening. It is these changes in the effective well width that modify the

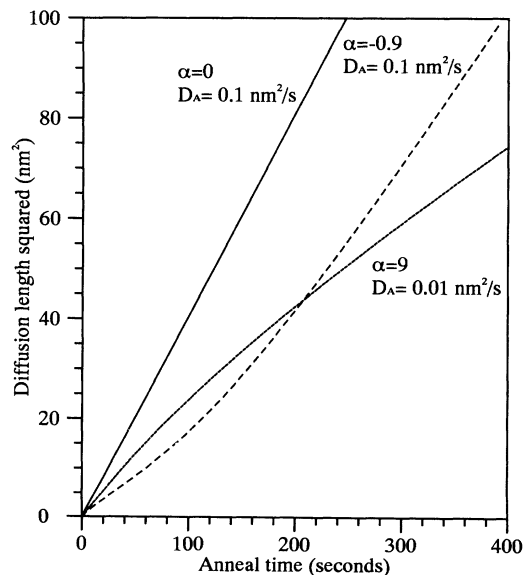


FIG. 2. A plot of the calculated diffusion length squared against anneal time for a concentration-dependent diffusion process. The values of D_A were chosen as a scaling factor such that there would be comparable diffusion.

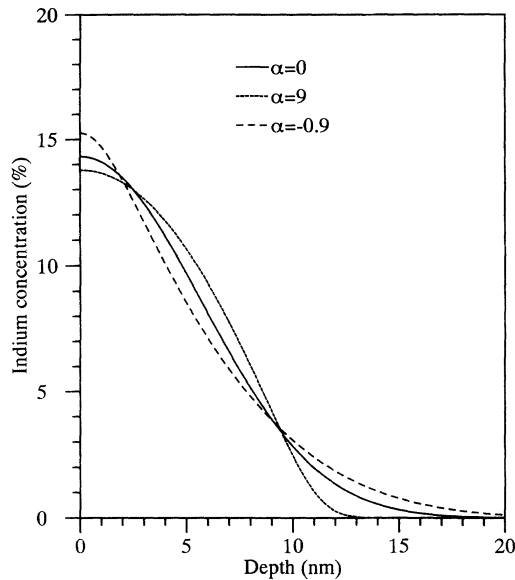


FIG. 3. The calculated indium profiles for three diffusion processes all of which produce the same shift in photoluminescence energy, i.e., the point at which the nonzero α curves cross in Fig. 2. The full profile would be symmetrical about $x=0$, which is at the well center.

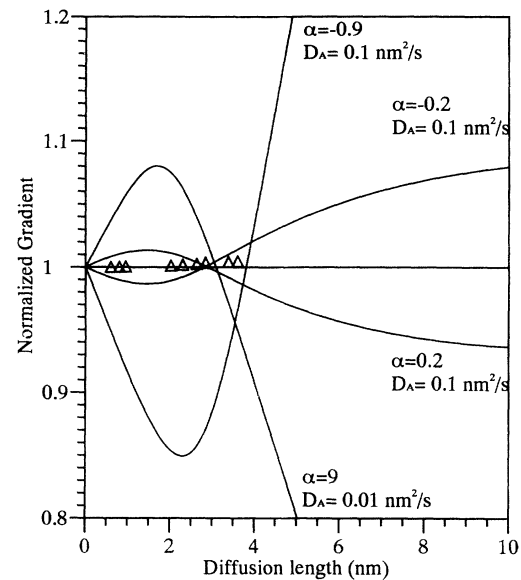


FIG. 4. Calculated plots of the normalized gradient from a $L_D^2(t)$ plot against diffusion length calculated from the photoluminescence peak shift. The triangles are the experimental data presented in Fig. 1, where the data were fitted by the best polynomial fit.

confined states in the well and make optical measurements so useful.

As large changes in D with concentration and strain cause the $L_D^2(t)$ plot to deviate significantly but not greatly from a straight line, it might be thought that small changes in D might be undetectable. As a small change in slope is not easy to see, we have plotted in Fig. 4 the normalized gradient $\{[d(L_D^2)/dt]/[d(L_D^2)/dt \text{ at } t=0]\}$ of the $L_D^2(t)$ plot against diffusion length, which is equivalent to normalized anneal time. From Fig. 4 we can see that our data demonstrate a concentration dependence of less than $\pm 20\%$. This shows that small variations from Fickian behavior can be detected with

sufficiently careful experiments by following the time dependence. It would of course be desirable to measure diffusion to much greater diffusion lengths, however at the present time this is limited by degradation of the encapsulant layer following the repeated thermal cycling.

CONCLUSIONS

We conclude that strain has been shown not to enhance interdiffusion in some materials systems, and that since the strain energy per atom is over three orders of magnitude below the activation energy of diffusion, strain-enhanced diffusion is not in any case expected to be a significant effect in the tetrahedral semiconductors.

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