COMMUNICATIONS

Intermixing in GaAsSb/GaAs single quantum wells

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Photoluminescence coupled with repetitive thermal annealing has been used to study the interdiffusion process in a 10 nm $GaAs_{1-x}Sb_x$/GaAs single quantum well. The diffusion equations and the Schrödinger equation were solved numerically to obtain the composition profile and the $n=1$ electron to heavy-hole transition energies in the intermixed quantum well, respectively. The intermixing process was shown to obey Fick's second law. © *1998 American Institute of Physics.*
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Lattice-mismatched heterostructures of III–V compound semiconductors, such as GaAsSb/GaAs and InGaAs/GaAs, are of considerable interest because of their potential application in optoelectronic devices. The ability to incorporate strain into low-dimensional structures allows not only the novel physics of valence-band engineering to be exploited, but also a wider range of material systems to be grown. If these systems are to be used in real devices, a knowledge of how they behave during typical semiconductor processing is essential. Because the composition is changed at an atomic scale in quantum well and superlattice structures, even quite modest anneals can cause broadening of the interface and in some structures this mixing, if selectively enhanced, can be vital to the final device.

The GaAsSb/GaAs system is particularly promising for electronic and optical devices because of its high carrier mobilities and band-gap tailorable over a wide energy range. Very few studies of the thermal stability of this strained system can be found in the literature. Indeed, there exist only a few studies on the diffusion of the group-V sublattice of GaAs in general. In-diffusion of radioactive arsenic isotopes into GaAs have been performed to obtain arsenic self-diffusion data.[1,2] These experiments led to estimates of the self-diffusion coefficient of arsenic in GaAs and indicated that arsenic self-diffusion is governed by a vacancy diffusion mechanism.

Contrary to diffusion on the gallium sublattice,[3,4] diffusion on the arsenic sublattice was reported by Homewood *et al.*[5] and Gillin *et al.*[6] to be nonlinear. Furthermore, the authors reported that doping to a concentration of 10^{17} cm^{-3} with either Si or Be retarded the interdiffusion. This finding is the opposite to that claimed to be the case by some authors for group-III diffusion and is in contradiction to the studies of group-III diffusion by Jafri and Gillin[7] who see no effect of dopants on diffusion, except at very high concentrations. Recently, Egger *et al.*[8] reported on the interdiffusion on the group-V sublattice in GaAs. Superlattices of either GaAsP/GaAs or GaAsSb/GaAs were studied. In both cases the diffusion process was found to be linear. The authors explained their results by an interstitial–substitutional type of diffusion mechanism. It is clear that very few studies of the diffusion on the group-V sublattice can be found and these studies often contradict each other.

In this article we use photoluminescence (PL) coupled with repetitive thermal anneals to quantitatively study the interdiffusion process on the group-V sublattice for single quantum wells of $GaAs_{1-x}Sb_x$/GaAs grown by molecular beam epitaxy (MBE). The potential profile of the interdiffused GaAsSb/GaAs was calculated using the error function approach. The Schrödinger equation was then solved numerically, by the shooting method, to determine the confined energy levels (the $n=1$ electron to heavy-hole transition) in the interdiffused quantum well.

The samples used in this study were grown by MBE on a semi-insulating (100)-oriented GaAs substrate. All the samples were single GaAsSb quantum wells of 10 nm thickness with a nominal concentration of 12% Sb, placed 30 nm

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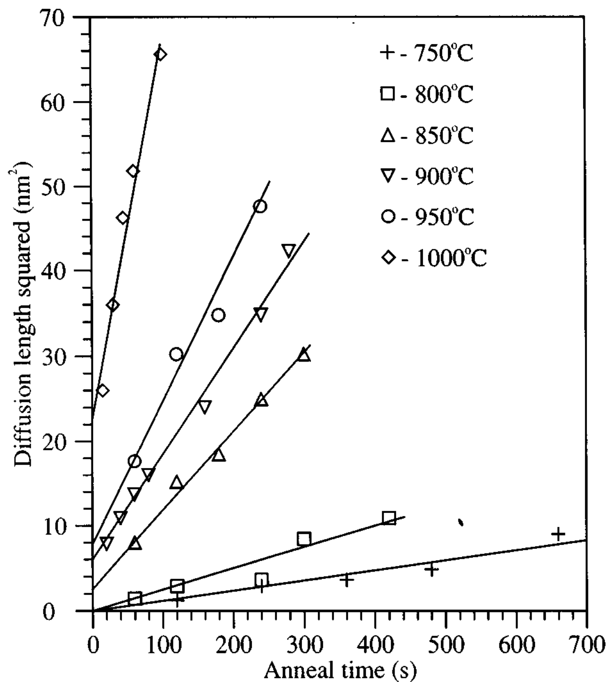

FIG. 1. A graph of diffusion length squared as a function of anneal time calculated from the photoluminescence peak shift for samples annealed at various temperatures. The solid lines are the least-square fit.

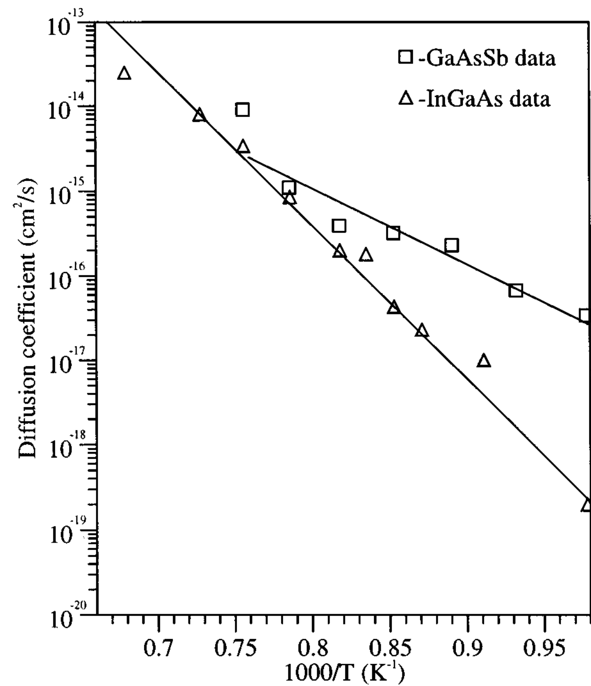

FIG. 2. An Arrhenius plot of GaAsSb/GaAs interdiffusion coefficients for temperatures between 750 and 1050 °C (squares), with an activation energy of 2±0.2 eV. The triangles are the diffusion coefficients of InGaAs/GaAs.

below the sample surface. Photoluminescence was used to follow the diffusion with annealing and details of the experimental procedures used can be found in Refs. 3 and 4.

We used a standard solution to Fick's law to determine the antimony concentration profile following diffusion.[3,4] Having obtained an antimony profile for a given diffusion length, the conduction-band minimum and the valence-band maximum at each point in the calculated profile were determined from an empirical relationship between the strained band gap (E_g in eV) and the antimony composition x obtained by Prins *et al.*[9] from high-pressure photoluminescence, and is given by

$$E_g = 1.519 - 1.908x + 1.2x^2, \tag{1}$$

where x is the antimony composition in the well. The band offset ratio between the conduction and valence bands was taken to be 50:50.[9] The electron effective mass was linearly interpolated between values of GaAs (0.067) and GaSb (0.063). The heavy-hole effective mass was taken to be that of GaAs with a value of 0.35.[9] Once the band structure across the diffused well is known, the Schrödinger equation can be solved using the shooting method for both the conduction- and valence-band wells to give the confined energy levels, and thus, the photoluminescence transition energy. Thus, we were able to construct a graph of photoluminescence energy as a function of diffusion length.

Photoluminescence (80 K) spectra from a sample before and after annealing were collected. The shift in the PL emission wavelength was monitored as a function of thermal anneal time and temperature. The thermal anneal process leads to a shift in the band-gap emission wavelength of the material in the well through the diffusion of antimony atoms to the barrier regions and a modification in the electron and heavy-hole subband energies from an initially square-well potential to a gradually graded potential profile. The full width at half maximum of the quantum well emission was found to increase with anneal time. This broadening is due to variations in the quantum well thickness and a reduction of the quantum confinement due to the intermixing process.

The shifts in the PL after annealing were recorded and the calculated shift in photoluminescence against diffusion was used to convert the observed shifts in the PL luminescence into diffusion length. Using this, we have been able to plot the diffusion lengths squared against anneal time for temperatures ranging from 750 to 1050 °C. These data are presented in Fig. 1. The data points for samples annealed at a given temperature were found to lie on a straight line indicating that the quantum well was diffusing with a constant diffusion. These results contradict earlier results reported by Homewood *et al.*[5] and Gillin *et al.*,[6] who showed a nonlinear diffusion process in GaAsSb/GaAs single quantum well samples. The nonlinear diffusion process reported in our earlier papers could be due to an initial fast diffusion which may be due to poor quality growth; this could have resulted in high concentrations of point defects being present in the samples. Since the diffusion coefficient of point defects, for example, vacancies, have been reported to be very high,[10,11] then we would expect samples having high concentration of point defects to diffuse faster at early anneal times. As the annealing progresses the diffusion coefficients would reduce to an intrinsic value as the point defects diffuse away, which in turn will result in a reduction in the diffusion coefficient. Indeed, this effect has been observed in the InGaAs/GaAs system, where a low-temperature InGaAs layer was intro-

duced to act as a source of vacancies.[10] However, in our present experiments we saw no such effect as the plot of L_D^2 against the anneal time, for all the temperatures used, resulting in data points lying on a straight line passing through the origin. Figure 2 shows an Arrhenius plot of the calculated diffusion coefficients of our samples of GaAsSb/GaAs (squares) for temperatures between 700 and 1050 °C and the InGaAs/GaAs system (triangles).[10] From Fig. 2 it can be seen that for temperatures above 950 °C the diffusion coefficients for GaAsSb/GaAs intermixing are very similar to those for InGaAs/GaAs intermixing. This is similar to the behavior of group-III and group-V interdiffusion in InGaAsP-based materials grown on InP substrates[4] where it was observed that the two sublattices diffuse with identical activation energies and prefactors.

However, for temperatures below 950 °C there is a growing divergence in the diffusivities of the antimonides and InGaAs materials with there being a two order of magnitude difference at 750 °C. As there is no real evidence for there being two diffusion processes (considering the scatter in the data and the limited number of data points which follow the InGaAs data), we have calculated an activation energy for the whole data set and obtain a value of 2.0±0.2 eV, which is considerably smaller than the measured value for As/P interdiffusion in either InP- (Ref. 4) or GaAs- (Ref. 8) based materials.

Given the evidence, it can be seen that group-III interdiffusion is controlled by a nonequilibrium concentration of vacancies and that the measured ~3.5 eV activation energy in the InGaAs/GaAs system is solely the diffusion energy for these vacancies.[10] We have argued that the group-V diffusion in InP-based InGaAsP materials, where we measure an identical activation energy, is controlled by a similar process.[4] As the activation energy for the antimonide diffusion is less than this value it is difficult to explain a mechanism for this diffusion without resorting to speculation. We do not believe that the diffusion is controlled by an interstitial process. For intermixing to occur, and to leave the material with good optical quality, an interstitial mechanism would have to operate via the creation of Frenkel pairs and the subsequent diffusion of the interstitial and recombination of the pairs. This would need both a creation and a diffusion term in the activation energy, which seems inconsistent with the low value measured. It may be possible that like the InGaAs and InGaAsP systems the antimonide diffusion is controlled by nonequilibrium vacancies. But then we would need to account for the large difference in the activation energies for vacancy diffusion in the different materials as well as the large difference in the prefactors. We, therefore, feel that more experiments are needed before any definite conclusions as to the mechanism can be made.

In summary, we have used photoluminescence coupled with repetitive thermal annealing to measure the interdiffusion coefficient on the group-V sublattice for the GaAsSb/GaAs single quantum wells. A linear diffusion process was demonstrated confirming that Fick's second law is obeyed. We determined an activation energy of 2.0±0.2 eV for the diffusion.

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