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Interdiffusion of the group-III sublattice in In-Ga-As-P/In-Ga-As-P and In-Ga-As/In-Ga-As heterostructures

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We present the results of a photoluminescence study of interdiffusion on the group-III sublattice in the ternary In-Ga-As/In-Ga-As and the quaternary In-Ga-As-P/In-Ga-As-P systems, both grown off InP substrates. We have shown that the diffusion obeys Fick's law, and that over the temperature range 950 °C–650 °C, the diffusion coefficients of both the ternary and quaternary materials can be described by the equation $D=D_0\exp(-E_A/kT)$, where $E_A=3.4\pm0.2$ eV and $D_0=3.9$ cm^2/s. Within experimental error these values are identical to those previously measured for interdiffusion on the group V in the same material system.

The ability to grow ever more complicated structures, consisting of several layers with atomic dimensions on a single substrate, can be accredited to the two major growth techniques, namely, metal-organic chemical-vapor deposition (MOCVD) and molecular-beam epitaxy. Having this microscopic control over growth demands that we characterize the diffusion of these atoms to a similar level. This is because, during the fabrication of semiconductor devices, high-temperature processes are used which can cause the intermixing of adjacent layers. This can have detrimental effects in, for example, a quantum-well laser where the intermixing of the active region can cause a change in the emission wavelength of the laser from that nominally grown.[1] It has long been thought that it was only the group-V sublattice in the In-Ga-As-P material system that exhibited appreciable diffusion, and thus many groups have designed structures without a change in the group-V concentration from wells to barriers and have seen marked reductions in the emission wavelength following annealing.[2] In this paper we report the results of a quantitative study of interdiffusion on the group-III sublattice in $In_xGa_{1-x}As/In_yGa_{1-y}As$ and quaternary $In_xGa_{1-x}As_yP_{1-y}/In_zGa_{1-z}As_yP_{1-y}$ structures, where the structures were designed so that there was no change in the group-V concentrations from well to barrier so that the diffusion is occurring solely on the group-III sublattice.

The materials used in this work were grown by MOCVD at 650 °C. Two structures were grown, one with a ternary well in ternary barriers and one with a quaternary well in quaternary barriers. For the ternary/ternary (T/T) structure the wafer consisted of a 1-μm InP buffer layer followed by 100 nm of lattice-matched $In_{0.53}Ga_{0.47}As$. On this was grown a 10-nm 1% strained quantum well of $In_{0.67}Ga_{0.33}As$, and on this was a further 100 nm of $In_{0.53}Ga_{0.47}As$, and finally 50 nm of InP. For the quaternary/quaternary (Q/Q) structure the wafer consisted of a 1-μm InP buffer layer followed by 100 nm of lattice-matched $In_{0.66}Ga_{0.34}As_{0.75}P_{0.25}$. On this was grown a 10-nm 1% strained quantum well of $In_{0.79}Ga_{0.21}As_{0.75}P_{0.25}$, and on this was a further 100 nm of $In_{0.66}Ga_{0.34}As_{0.75}P_{0.25}$ and finally 50 nm of InP, which was grown to protect the surface during cooling in the growth reactor. These structures were grown on both sulfur- and tin-doped substrates to look for any effect on the interdiffusion from the substrate type.[3]

After growth all the layers were capped with silicon nitride at 300 °C in a plasma enhanced chemical-vapor deposition system. Annealing was performed in two systems. For anneal temperatures between 950 °C and 700 °C a double graphite strip heater was used in which the samples were placed between two graphite strips which were resistively heated. For anneal temperatures below 700 °C a conventional furnace was used with temperature measurement achieved with a thermocouple.

To remove the effects of any variations in temperature between samples all the samples were annealed together as a batch. A photoluminescence measurement, at 80 K, was performed on each of the samples prior to annealing, and then again following the anneal. Further anneals were then performed on the samples with the low-temperature photoluminescence recorded after each anneal. This was then repeated several times so that the evolution of the diffusion with time could be observed.

In order to determine the diffusion coefficient for intermixing for these materials it is necessary to calculate the well shape after diffusion and then solve the Schrödinger equation for the resulting conduction- and valence-band energy profiles in order to determine the photoluminescence transition energy. Figure 1 shows the theoretical curves of 80-K photoluminescence peak shift with diffusion length calculated for the T/T and Q/Q structures used in this work. From these theoretical data, the measured shift in the photoluminescence with annealing can be converted into a characteristic diffusion length. Full details of the method used are given in Ref. 4.

Figure 2 shows a plot of diffusion length squared against anneal time for the T/T and Q/Q structures annealed at several temperatures. It can be seen that for a given anneal temperature the data points all lie on a straight line. For Fick's law diffusion $L_D^2=4Dt$, therefore the gradient of this line gives the diffusion coefficient and shows that our initial assumption as to the diffusion being concentration independent was correct. From Fig. 2 it can also be seen that the lines do not quite pass through the origin. This may be due in part to there being some interdiffusion during growth.

These measurements were made at temperatures between 950 °C and 650 °C and the results are plotted on an Arrhen-

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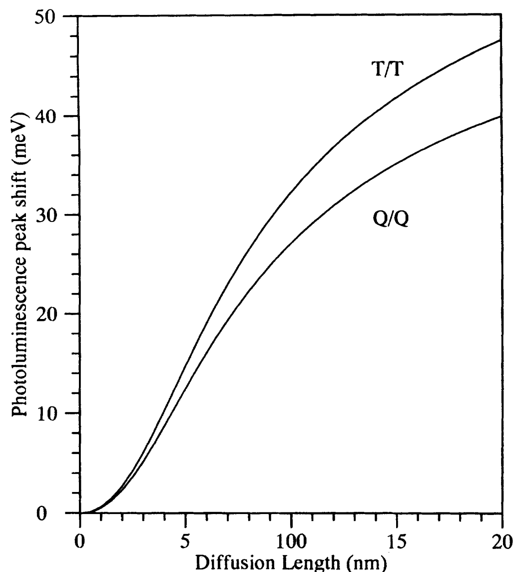

FIG. 1. Calculated change in the 80-K photoluminescence transition energy as a function of diffusion length for both the ternary/ternary (T/T) and quaternary/quaternary (Q/Q) structures used in this work.

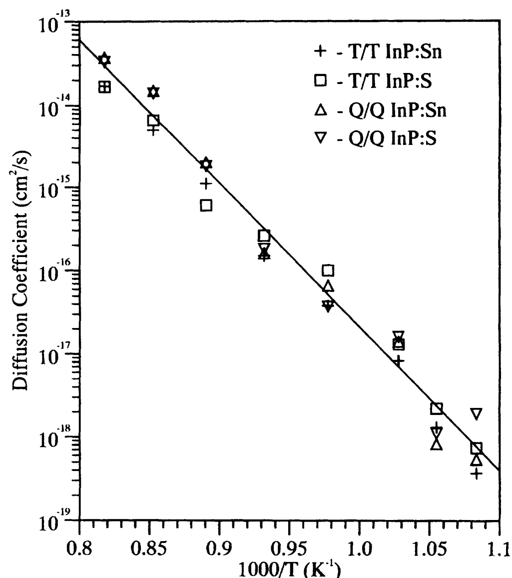

FIG. 3. An Arrhenius plot of the diffusion coefficients for both the ternary/ternary and quaternary/quaternary structures grown on both sulfur- and tin-doped substrates; the solid line is a least-squares fit to the average of all the data at each temperature.

ius diagram in Fig. 3. From Fig. 3 it can be seen that there is some scatter between the data from the four samples; however, there are no systematic differences between either the T/T and Q/Q structure or between the two structures grown on the different substrate types. The line drawn through the data in Fig. 3 is a least-squares fit to the average of all the samples at each temperature. This line gives an activation energy E_A of 3.4±0.2 eV with a prefactor D_0 of 3.9 cm^2/s. Within experimental error this value of E_A is the same as we have previously measured for the interdiffusion on the group-V sublattice in this material system (3.7±0.1 eV).[5]

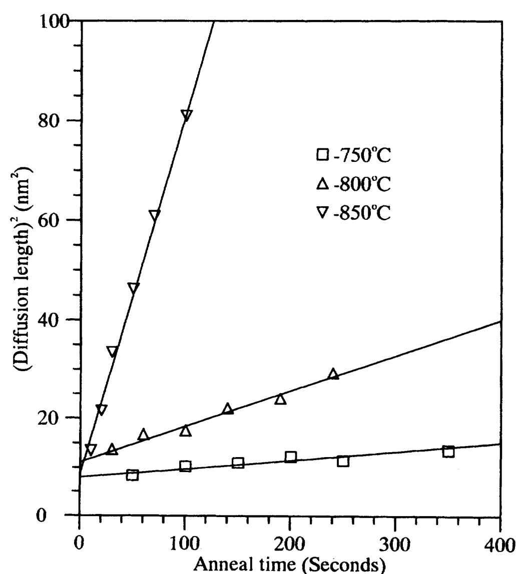

FIG. 2. A plot of the diffusion length squared against anneal time at several temperatures for the ternary/ternary structure showing that Fick's law is being obeyed.

As the measured values of the diffusion coefficient for the group-III and group-V sublattices at any temperature are identical within experimental error the observed differences in prefactors are purely a reflection of the small differences in the least-squares fit to the Arrhenius plot. These experiments show the difficulties present in calculating reliable values of E_A and D_0 from data over a limited temperature range, although the 300 °C temperature range measured in this work is considerably greater than that used in many reports of activation energies.

These data clearly show that in the In-Ga-As-P material system grown off InP substrates the diffusion coefficients for intermixing on the group-III and group-V sublattices are identical, within experimental sensitivity. The observed empirical effects of reduced "blueshift" found in structures where the group-V ratio has been kept constant in both the wells and barriers, and has been attributed to a lower group-III diffusion rate is in fact due to the lower band offsets found in constant group-V structures as opposed to those where changes in the group-V ratio is allowed. As an illustration of this effect we have calculated the change in the room-temperature photoluminescence emission wavelength from the Q/Q structure used in these experiments compared with the structure we used in our earlier work to measure the diffusion coefficient on the group-V sublattice. For equal diffusion lengths of 20 Å on both sublattices the structure with a step in the group-V concentration would exhibit a 22.7-nm change in wavelength compared with 4.6 nm for the Q/Q structure used in this work.

These results explain some empirically observed facts and also show that even in structures which have been engineered to give small changes in emission wavelength with annealing there is still an appreciable diffusion which will result in the structures having graded compositions and

hence graded strain profiles; this fact is rarely appreciated in the modeling of device structures grown in this material system although it may have important implications for device operation.

In conclusion we have shown that the interdiffusion of the group-III sublattice in the ternary In-Ga-As/In-Ga-As and the quaternary In-Ga-As-P /In-Ga-As-P material systems is Fickian with diffusion coefficients equal to those measured for group-V interdiffusion in the same system.

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