The kinetics of intermixing of GaAs/AlGaAs quantum confined heterostructures

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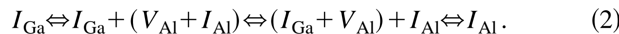
An atomic-scale model for the kinetics of intermixing of GaAs/AlGaAs, quantum confined heterostructures is presented. It quantifies the effects of the statistical nature of defect diffusion through heterostructures on the Ga/Al interdiffusion across such an interface. The model has been validated by successfully predicting the observed amounts of quantum well intermixing induced by a hydrogen plasma induced defect layer intermixing process. Agreement within 30% of the measurements was obtained for values of the surface release velocity>1 μm s[1]. © *1997 American Institute of Physics.* [S0003-6951(97)02646-6]

Intermixing of quantum confined heterostructures is an attractive alternative to regrowth and overgrowth techniques for realizing photonic and optoelectronic integrated circuits. To date the majority of research has been directed at experimental investigations of the processes. Although quantum well intermixing (QWI) was first reported in 1981,[1] no comprehensive mechanism of the process was presented until 1988.[2] A limited amount of modelling has followed; however this was mostly either incomplete or only described trends rather than relating the measurements to the physics involved.[3,4] A comprehensive qualitative model would permit further process optimization and predict the limits of this technology. Such a model would not only result in improved control of existing processes such as impurity free vacancy disordering (IFVD) in GaAs based semiconductors, but also is necessary for extending the technology to more complicated semiconductor systems, such as IFVD in InP based semiconductors. The model described here allows an initial, nonequilibrium group III vacancy concentration in a GaAs/AlGaAs heterostructure to be related to the amount of intermixing induced during subsequent annealing. The model can be generalized to any intermixing process.

Initially the physical assumptions underlying the model will be highlighted. Compositional intermixing, and hence Al and Ga interdiffusion in GaAs/AlGaAs heterostructures, is either carried out directly through diffusion of group III vacancies, V_{III}, as described by the equation,

$$V_{\mathrm{Ga}} \Leftrightarrow V_{\mathrm{Ga}} + (V_{\mathrm{Al}} + I_{\mathrm{Al}}) \Leftrightarrow (V_{\mathrm{Ga}} + I_{\mathrm{Al}}) + V_{\mathrm{Al}} \Leftrightarrow V_{\mathrm{Al}}, \qquad (1)$$

or is assisted by the formation of group III Frenckel defect pairs, through the diffusion of group III interstitials, I_{III},



$$I_{\mathrm{Ga}} \Leftrightarrow I_{\mathrm{Ga}} + (V_{\mathrm{Al}} + I_{\mathrm{Al}}) \Leftrightarrow (I_{\mathrm{Ga}} + V_{\mathrm{Al}}) + I_{\mathrm{Al}} \Leftrightarrow I_{\mathrm{Al}}. \qquad (2)$$

Group III point defects can be introduced by various processes, such as impurity induced disordering, IID,[4] implantation defect induced disordering,[5] plasma induced defect layer intermixing (PIDLI),[6] IFVD,[7] and by lasers.[8] During the thermal processing stage, the point defects, V_{III} and I_{III}, acquire thermal energy and diffuse either out of, or into, the sample, depending on their initial concentration profile. The vacancy diffusion length, L_D, can be viewed as a result of a random walk which consists of a certain average number of lattice hops, determined by the hop rate, and hence by the diffusion coefficient of the vacancies, as illustrated in Fig. 1. For an AlAs/GaAs heterostructure, on each occasion that a V_{III} crosses the plane of the quantum well, a Ga atom moves one lattice site out of the well into the barrier. A subsequent crossing would then assist one Al atom to move one lattice hop towards the well. In other words, every two crossings of the barrier/QW interface by a particular V_{III} allows one Al atom from the barrier to exchange with one Ga atom from the quantum well. Thus, the parameter, N_{IC}, which corresponds to the total number of lattice sites available for the Al/Ga interdiffusion can be calculated from

$$N_{IC} = \frac{1}{2} \int_0^t f . w_v . N_v(d_{\mathrm{QW}}, t) dt, \qquad (3)$$

where f is the proportion of V_{III} with a direction of motion in the plane perpendicular to the QW. For a three-dimensional (3D) lattice, considering equal probabilities of movement in all directions, f is equal to 1/6. w_v is the vacancy hop rate at

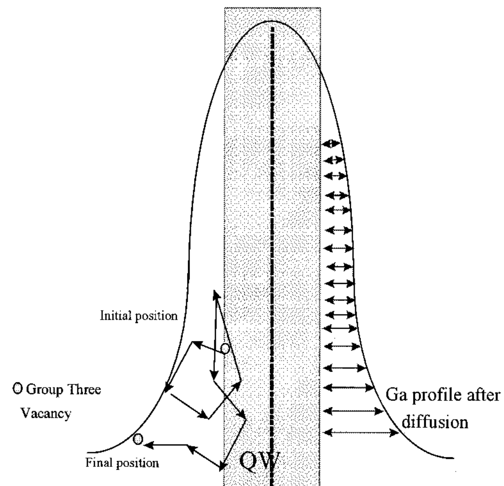


FIG. 1. Schematic diagram of the lattice hops comprised in Ga outdiffusion from the quantum wells, illustrating the random walks associated with the group three vacancy diffusion.

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the anneal temperature (directly related to the vacancy diffusion coefficient), and $N_v(d_{QW},t)$ is the time dependent V_{III} concentration at the barrier/QW interface. It should be noted that the statistical motion of defects is represented by the mean hop rate in any allowed crystal direction of the vacancies at the barrier/QW interface, whereas f ensures that only the vacancies which cross the interface plane are taken into account. Calculations of N_{IC} will now be performed for the H_2 plasma induced defect layer disordering process.

The H_2 plasma process introduces Frenckel defect pairs into the GaAs/AlGaAs structures using bombardment by H_2 ions, in a reactive ion etching machine.[6] After exposing the semiconductor to the plasma, the samples are thermally processed to initiate point defect diffusion. The defect profile induced in such structures during dry etching using a similar H_2/CH_4 process has been measured previously.[9] In the referenced work, the defects studied were deep level traps. The concentration of group III defects is expected to have the same functional dependence as that of the deep level defects, since they are both created by hydrogen ion bombardment.[10] Consequently the same parameters measured in the referenced work have been adopted in our calculations. The sheet density of induced defects can be described by[9]

$$C_{\text{defects}}(z)=5.6\times 10^{12}\exp[-z/30]\text{cm}^{-2}, \tag{4}$$

where z is the depth of the sample from the surface in nanometers.

Vacancies and interstitials will be created in equal numbers during plasma exposure. Although a fraction of these will recombine instantaneously, the diffusion coefficient of interstitials is sufficiently large, even at room temperature,[11] to allow them to diffuse into the bulk of the sample, leaving behind a vacancy profile given by Eq. (4). It should be noted that diffusion of interstitials alone does not lead to significant intermixing, as can be seen in Eq. (2). At elevated temperatures, the vacancies' behavior will be primarily governed by their diffusion into the semiconductor and by their annihilation at the semiconductor surface. Because of the large concentration gradient immediately below the surface, the preferential direction of diffusion will be towards the surface rather than towards the substrate. At the surface, vacancies have a surface release velocity v, which is directly related to the probability that a vacancy recombines at the surface. A high surface release velocity implies that all vacancies recombine upon reaching the surface.[6] The diffusion equation governing the behavior of the vacancies and the appropriate boundary conditions, can be expressed as

$$D_{\text{vac}}\frac{\partial^2 C_{\text{vac}}}{\partial z^2}=\frac{\partial C_{\text{vac}}}{\partial t}, \tag{5}$$

where the boundary conditions at $t=\{0,\infty\}$ is $C_{\text{vac}}=\{C_{\text{defects}}(z),0\}$, and at the surface $\nu C_{\text{vac}}=D_{\text{vac}}(\partial C_{\text{vac}}/\partial z)$. The diffusion equation is a form of standard Sturm-Liouville theory, which can be solved by expanding the concentration profile as a series of orthogonal trigonometric functions. The predicted number of lattice hops for Ga in the quantum wells for the given vacancy profile, N_{IC}, can thus be obtained using the vacancy diffusion coefficient data of Kahen *et al.*[11]

The PIDLI process was applied to a 5 nm undoped GaAs quantum well 37 nm below the surface with a 2 nm AlAs layer to the side of the structure surface, and $Al_{0.37}Ga_{0.63}As$ barriers. The wafer used was a *pin* structure grown on an n-type GaAs substrate. Samples were annealed for different times at 875 °C. Photoluminescence (PL) spectra from the samples were then measured. From the measured band gap shift, the Al/Ga diffusion length can be obtained by solving the diffusion equation for Ga/Al atoms in the wells/barriers, in conjunction with Schrödinger's equation for the bound electronic states in the wells. Such calculations allow the change in the e1→1h1 transition of the wells to be related to the Ga/Al diffusion length,[12] giving diffusion lengths of 0.38–0.7 nm for intermixing shifts of 18–46 meV. The square of the diffusion lengths are then plotted versus the anneal time. The slope of the line joining the measured points in the plot is constant, implying a time independent diffusion coefficient for the time spans and temperatures studied, and D_{Ga} the diffusion coefficient of Ga in the well was found to be $1.8\times 10^{-16}\ \text{cm}^2\,\text{s}^{-1}$. From the calculated diffusion coefficient, together with the concentration of the Ga in the GaAs quantum well, $6.3\times 10^{14}\ \text{cm}^{-2}$, the number of lattice hops needed to achieve the observed intermixing profile as a function time can be obtained as follows. Before intermixing, the QWs are assumed to have a square profile. During the subsequent thermal processing Al/Ga interdiffusion takes place, with an exchange between Al and Ga atoms in the vicinity of the well, giving rise to error function concentration profiles.[3] The profile of the diffused Ga arises from a number of random lattice hops; the number of lattice hops can be found by integrating the spatial parameter over the Ga profile out of the well boundary, as illustrated in Fig. 1, and then normalizing with respect to the lattice hop length:

$$N_{\text{Ga}}=\frac{1}{a_0/2}\int_0^{C_{\text{Ga}}(L_z/2)} z(C_{\text{Ga}})\,d(C_{\text{Ga}}), \tag{6}$$

$$z(C_{\text{Ga}})=2\sqrt{D_{\text{Ga}}t}\cdot \text{erfc}^{-1}\left(\frac{2C_{\text{Ga}}}{C_0}\right), \tag{7}$$

where C_{Ga} is the profile of outdiffused gallium atoms, C_0 is their initial concentration in the well, L_z is the quantum well thickness, z is the spatial depth parameter, a_0 is the GaAs lattice constant, and N_{Ga} is the number of lattice hops carried out by the Ga atoms outdiffusing from the quantum well. The number of Ga lattice hops in the z direction should be the same as the number of lattice crossings carried out by the V_{III}. The validity of the model will be confirmed below by direct comparison with experimental results.

The predicted number of lattice hops contributing to the interdiffusion, N_{IC} is plotted in Fig. 2 along with the number of lattice hops obtained experimentally N_{Ga}. The latter is calculated by numerically evaluating the integral in (6) using the D_{Ga} measured for the process. Agreement between both is very close—within 30%—for values of ν exceeding $1\ \mu\text{m s}^{-1}$. As can be seen in Fig. 2 a negligible change of N_{Ga} is observed for values of ν exceeding $1\ \mu\text{m s}^{-1}$. This is consistent with a high probability of surface recombination,[13] as might be expected at a free damaged surface. Lower values of ν might be expected from passivated surfaces, and even generation of vacancies when SiO_2 caps are used. The

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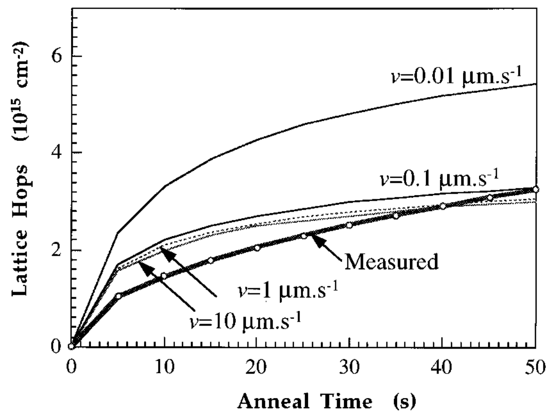

FIG. 2. Plot of the number of lattice hops needed to obtain the measured amounts of intermixing, and the number predicted from the model for the given defect profile produced by PIDLI. Plots for various values of the surface recombination velocity are shown.

results plotted in Fig. 2 are for annealing spans within the vicinity of the anneal times used to calculate D_{Ga}.

Starting from first principles, we have developed an atomic-scale model for the kinetics of intermixing of GaAs/AlGaAs quantum confined heterostructures. The model hypothesis has been validated by successfully predicting the amounts of observed quantum well intermixing induced by a hydrogen plasma induced defect layer intermixing process. The predictions were within 30% from the measurements for values of the surface release velocity $>1\ \mu\mathrm{m\ s}^{-1}$.

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