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Vacancy diffusion kinetics in arsenic-rich nonstoichiometric AlAs/GaAs heterostructures

S. Balasubramanian and S. W. Mansour
Department of Physics, Purdue University, West Lafayette, Indiana 47907-1396

M. R. Melloch
School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907-1285

D. D. Nolte
Department of Physics, Purdue University, West Lafayette, Indiana 47907-1396

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Transient-enhanced intermixing is known to occur in arsenic-rich nonstoichiometric AlAs/GaAs quantum wells grown at a low substrate temperature around 300 °C. The intermixing is attributed to a supersaturated concentration of group-III vacancies and is enhanced by several orders of magnitude relative to diffusion in stoichiometric structures grown at ordinary substrate temperatures. In this paper we establish that the decay of the excess vacancy concentration satisfies second-order decay kinetics at a confidence level of 80%.

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Transient-enhanced diffusion occurs in semiconductor crystals when self-diffusion is augmented by nonequilibrium conditions. When a crystal is grown under nonequilibrium conditions, as in many epitaxial forms of growth, a supersaturated concentration of vacancies can be temporarily frozen into the crystal. The enhanced concentration of vacancies enhances substitutional diffusion, which is most noticeable in heterostructures that experience enhanced intermixing at elevated temperatures relative to the intermixing observed in similar structures under equilibrium conditions. The vacancy primarily responsible for vacancy-mediated diffusion in GaAs is the Ga vacancy,[1] or more generally the group-III vacancy in alloys such as AlGaAs. In heterostructures of AlGaAs, the group-III vacancies cause originally abrupt interfaces between layers with different concentrations to intermix during sustained annealing.

An important class of AlGaAs crystal grown under nonequilibrium conditions is low-temperature-grown (LTG) epilayers and heterostructures grown by molecular beam epitaxy (MBE). These materials are rich in arsenic with up to 2% of excess arsenic. They have a supersaturated concentration of group-III vacancies, which enhance intermixing over equilibrium conditions. Furthermore, the vacancy concentration decays during annealing, leading to transient time-dependent effects.[2,3] The role of supersaturated vacancy concentrations in interface intermixing was studied in several AlAs/GaAs heterostructures by Lahiri *et al.*[4] Further work was done by Guersen *et al.*[2] on the kinetics of the transient-enhanced diffusion. It was found at that time that both first-order and second-order decay kinetics agreed equally well with the diffusion data obtained from isochronal and isothermal rapid thermal annealing (RTA). Both of these kinetics require a thermally activated annihilation enthalpy. It was found that the annihilation enthalpy H_a for the decay was between 1.4 and 1.6 eV, which was comparable to the migration enthalpy $H_m = 1.8$ eV for vacancy diffusion.[5] For the strongest annealing the diffusion length approaches the self-diffusion values observed in isotopic superlattices of stoichiometric GaAs.[5]

In this paper we reanalyze the data of Guersen *et al.*[2] from RTA LTG AlAs/GaAs multiple quantum wells (MQW's). To determine the exciton position even more accurately we plot the derivative of the photomodulated signal vs energy and perform a standard χ^2 analysis by fixing the migration enthalpy of the vacancy to be $H_m = 1.8$ eV and allowing the annihilation enthalpy H_a to vary. The fitting parameters are obtained from the minimum χ^2 values for each decay order. We have obtained results that are consistent with second-order vacancy decay kinetics. This is expected because the sites that trap the vacancies also anneal away during the annealing process.

The sample structure was a MBE LTG AlAs/GaAs MQW grown using an As_4 source. Contact and stop-etch layers of *n*-type materials were grown on an n^+ GaAs substrate at 600 °C. This was followed by a LTG (310 °C) MQW layer consisting of a 150-period superlattice of 100 Å GaAs wells and 35 Å AlAs barriers. A 2000 Å *p*-type $Al_{0.3}Ga_{0.7}As$ ($1 \times 10^{18}\,cm^{-3}$) layer followed by a 2000 Å top *p*-type GaAs ($1 \times 10^{19}\,cm^{-3}$) layer were grown at 450 °C on top of the LTG layers. The 450 °C growth temperature for the *p*-doped layers acts as a weak *in situ* anneal of the previously grown LTG layers and results in the formation of As precipitates in the MQW region. The samples were isochronnally and isothermally annealed in a RTA furnace for a matrix of annealing temperatures and annealing times.

The experiments were carried out using phase-shifted photomodulation spectroscopy.[2] The modulation of the heterostructure is provided by a low-power cw laser diode (15 mW) at a wavelength of 690 nm. Our quantum well structures are *p-i-n* diodes and have a built-in electric field. Photomodulation spectroscopy involves the generation of free carriers by above-band-gap light. These carriers screen the electric field, producing a flat-band condition in the quantum wells, thereby causing a blueshift of the Stark-shifted excitons back to their zero-field energy. The spectroscopy was performed in transmission to minimize sensitivity to surface band-bending effects. The transmitted probe beam light signal is detected 90° out of phase with the optical excitation.

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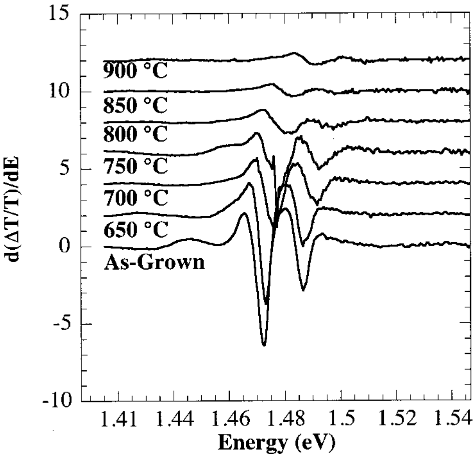

FIG. 1. First derivative of $\Delta T/T$ with respect to energy for rapid thermally annealed samples. The samples were annealed for 30 s.

An example of the derivative of the photomodulated spectra with respect to energy is shown as a function of energy in Fig. 1 for 30 s annealings at a variety of temperatures. Similar plots were obtained for the other annealing times.

The theory for transient-enhanced diffusion can be formulated on the basis of first- or second-order decay kinetics. In first-order kinetics, the vacancy-trapping site or annihilation site concentration is assumed to remain independent of annealing. The supersaturated vacancy concentration leads to a nonequilibrium diffusion constant that decays with the time constant τ_a:

$$D_1(t)=D_1\exp(-H_m/k_BT)\exp(-t/\tau_a), \tag{1}$$

where H_m is the migration enthalpy and the decay time constant is given by

$$1/\tau_a=\nu_a\exp[-H_a/k_BT]. \tag{2}$$

Here ν_a is the attempt frequency for annihilation and H_a is the annihilation enthalpy. The total time-dependent diffusion coefficient is given by

$$D(t)=D_0\exp[-(H_f+H_m)/k_BT] + D_1\exp(-H_m/k_BT)\exp(-t/\tau_a). \tag{3}$$

This has two terms, one of which is a time-independent term that depends on the formation enthalpy of the vacancies, and the other the time-dependent term from Eq. (1). The time-dependent diffusion coefficient leads to a time-dependent diffusion length, given by

$$L_D^2(t)=D_0t\exp[-(H_f+H_m)/k_BT] + D_1\tau_a\exp(-H_m/k_BT)[1-\exp(-t/\tau_a)] \tag{4}$$

for an annealing time t.

The more likely decay kinetics for the decay of the supersaturated vacancy concentration are second-order decay kinetics because the sites that trap the vacancies also anneal away. The time dependence of the diffusion length and the decay of the transient-enhanced diffusion for second-order kinetics is given by

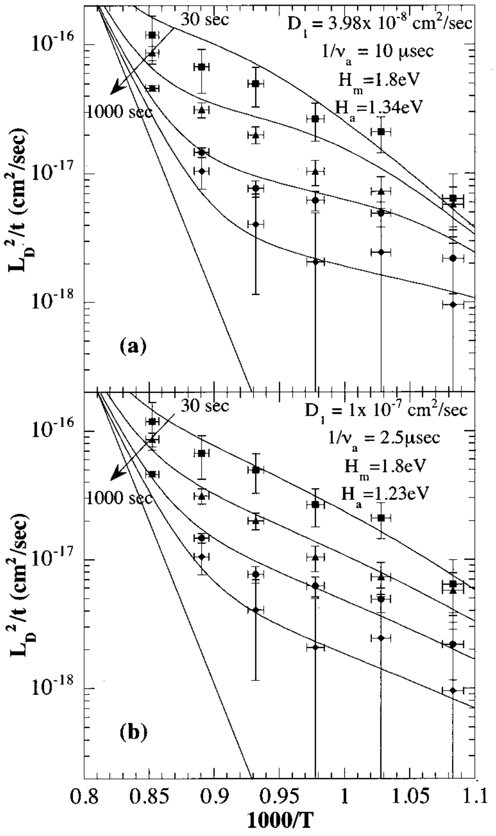

FIG. 2. Square of the diffusion length divided by annealing time as a function of annealing temperature for rapid thermally annealed samples. The fit assumes (a) first-order kinetics from Eq. (4), and (b) second-order kinetics from Eq. (7).

$$\frac{dL_D^2}{dt}=D_0\exp[-(H_f+H_m)/k_BT] + D_1\exp(-H_m/k_BT)y(t), \tag{5}$$

where $y(t)$ is the relative excess in the vacancy concentration, satisfying

$$\frac{dy}{dt}=-\nu_a\exp(-H_a/k_BT)y^2. \tag{6}$$

The analytical solution to the second-order differential equations is

$$L_D^2(t)=D_0t\exp[-(H_f+H_m)/k_BT] + D_1\tau_a\exp(-H_m/k_BT)\left[\ln\left(1+\frac{t}{\tau_a}\right)\right]. \tag{7}$$

We perform a χ^2 analysis of the data by considering individual contributions to the total error. In the case of RTA samples there are several sources of error, such as the errors associated with the oven in which the samples are annealed. All our samples were annealed in an oven that has fast ramp-up times, and in an arsenic atmosphere to prevent out-diffusion. The annealings were done under a ramp-up rate of

100 °C/s. To ensure that the temperature remains fairly uniform across the sample the ramp-up rate was reduced to 4 °C/s for the final 20 °C of the annealing temperature. After the annealing the samples cooled at 80 °C/s. We assume that the nominal annealing temperature for observing significant enhanced diffusion is 550 °C.[6] From this information we calculate the error contributions due to the annealing time using the relationship

$$\left\{\Delta\left[\ln\left(\frac{L_D^2}{t}\right)\right]\right\}^2 = 2\left(\frac{\Delta L_D}{L_D}\right)^2 + \left(\frac{\Delta t}{t}\right)^2, \tag{8}$$

where we have calculated the error in the logarithm. Other contributions to the total error are the error in temperature, obtained due to a temperature fluctuation of ±7 °C in the oven, and the error in obtaining the excitonic energy shift from the derivative spectra, which was estimated to be around 1.4 meV.

The χ^2 was minimized using a simplex-type algorithm. The migration enthalpy of the vacancy was fixed to be $H_m = 1.8\,\mathrm{eV}$ and the annihilation enthalpy H_a, the time-dependent diffusion coefficient D_1, and the annihilation attempt frequency ν_a were all allowed to vary. A minimum χ^2 of 1.75 per degree of freedom (DOF) was obtained for the first-order decay kinetics. This translates to only a 2% confidence in the goodness of fit for 20 DOF's (23 data points minus three varying parameters). The square of diffusion length divided by annealing time is plotted against annealing temperature in Fig. 2(a) for rapidly thermally annealed LTG AlAs/GaAs MQW's with a first-order decay kinetics fit. The high-temperature-annealing asymptote to the equilibrium values was obtained by Wang *et al.*[5]

For the second-order decay kinetics, a minimum χ^2 of 0.70 per DOF was obtained. This translates to an 80% confidence in the goodness of fit. Figure 2(b) shows a plot of the square of diffusion length divided by annealing time against annealing temperature for second-order decay kinetics. In the figure, the second-order decay kinetics fit the data noticeably better than first-order decay. This is reasonable because the concentration of sites that annihilate isolated vacancies (such as other vacancies, antisites, or precipitates) is also known to decay in time. The annihilation enthalpy that one obtains from minimization for the second-order decay kinetics is $H_a = 1.23 \pm 0.3\,\mathrm{eV}$. This somewhat smaller value of H_a when compared to $H_m = 1.8\,\mathrm{eV}$ could be attributed to experimental uncertainty or to a suppression in the migration enthalpy, as has been reported in LTG materials.[7–9] The similarity between H_a and H_m weighs against any interstitial mechanism,[10] and lends support for the vacancy-dominated enhanced diffusion process. In summary, we have shown in this work that second-order decay kinetics provide a better fit to the transient-enhanced diffusion in RTA LTG AlAs/GaAs MQW's than first-order decay kinetics. The minimization of the χ^2 function gives us an 80% to 2% comparison in the confidence levels for the two decay orders. It must be noted that, despite the high degree of confidence in second-order decay kinetics, further work needs to be done in fine-tuning the error contributions to improve the minimum χ^2. Nonlinear diffusion also must be addressed because it could have a quantitative effect on the annihilation enthalpy H_a.

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