Enhanced diffusion in nonstoichiometric quantum wells and the decay of supersaturated vacancy concentrations

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(Received 18 April 1996; accepted for publication 1 May 1996)

Enhanced superlattice disordering in nonstoichiometric AlAs/GaAs quantum wells exhibits weak temperature dependence because of the decay of the supersaturated concentration of group-III vacancies. We present a formalism for transient enhanced diffusion in nonstoichiometric materials with which we can extract migration enthalpies H_m by assuming that the vacancy decay is thermally activated with an enthalpy H_a. By analyzing the electroabsorption from the quantum-confined Stark effect for a set of isochronal and isothermal anneals, we extract a migration enthalpy $H_m=(1.8\pm0.2)$ eV for group-III vacancies, as well as an activation enthalpy $H_a=(0.7\pm0.2)$ eV for vacancy annihilation. © *1996 American Institute of Physics.* [S0003-6951(96)01628-2]

Nonstoichiometric superlattices grown by molecular beam epitaxy (MBE) at low substrate temperature contain excess arsenic that gives these materials several advantageous properties. Under weak anneals, these superlattices demonstrate simultaneous ultrafast lifetimes and sharp excitonic features,[1] which are crucial ingredients for photorefractive dynamic holographic devices,[2] electroabsorption sampling,[3] ultrafast striplines, low-dark-current photodetectors,[4] and electroabsorption modulators. However, some of these advantageous properties degrade with high temperature anneals caused by pronounced interface intermixing and roughening.[5] Previous work[5,6] on low-temperature-grown (LTG) superlattices, utilizing only isochronal anneals and an equilibrium analysis, resulted in extremely small and unphysical effective migration enthalpies. In this letter, we present a transient enhanced diffusion formalism[7,8] using both isochronal and isothermal anneals that allows us to extract physically relevant diffusion enthalpies, including for the first time an activation enthalpy for vacancy annihilation.

The samples used in our experiments were grown by MBE using a flux of As_4. The structures were LTG MBE AlAs/GaAs multiple quantum wells (MQWs) grown on n^+ GaAs substrates. Contact and stop-etch layers of n-type materials were grown on the n^+ GaAs substrate at 600 °C, followed by a LTG (310 °C) MQW layer consisting of a 150 period superlattice of 100 Å GaAs wells and 35 Å AlAs barriers. The low temperature growth at 310 °C results in approximately 0.2% excess arsenic in the MQW. A 2000 Å p-$Al_{0.3}Ga_{0.7}As$ (1×10^{18} cm^{-3}) layer followed by a 2000 Å top p-GaAs (1×10^{19} cm^{-3}) layer were grown at 450 °C on top of the LTG layers. Gold contacts were made to the top p-GaAs. The samples were epoxied to glass and the substrate was removed using standard techniques. A final gold contact was made to the exposed n-$Al_{0.5}Ga_{0.5}As$ stop-etch layer after substrate removal. Isothermal and isochronal anneals were performed on multiple samples at 600, 750 and 900 °C for 30, 90, and 270 s. Low field (2.5 V/μm) electroabsorption characterization was performed under reverse bias to find the excitonic transition energy as a function of anneal condition.

The intermixing of Al and Ga at the AlAs/GaAs interface is quantified by measuring the change in energy of the lowest quantum-confined exciton and matching the transition energies to calculations of interdiffused interfaces, assuming linear diffusion.[5] To support this assumption we performed Monte Carlo simulations of nonlinear diffusion in the special case of a supersaturated vacancy concentration. Monte Carlo simulations take as input only bond energies, and automatically incorporate deviations from linear diffusion, such as position-dependent vacancy concentrations, vacancy segregation, or concentration-dependent diffusion mobilities. We found that while nonlinear diffusion is known to be important for some cases of intermixing of stoichiometric superlattices,[9] the strong supersaturation of vacancies in the nonstoichiometric case studied here does not significantly alter the diffusion profiles from the linear case, other than producing large enhancements in the intermixing. The simulations do show that the process of vacancy segregation, caused by concentration-dependent migration enthalpies, can inhibit intermixing, which is opposite to the trend observed experimentally. Details of these simulations will be published in a succeeding paper. We are therefore able to calibrate the diffusion length L_D vs exciton transition energy, which is used to obtain the experimental diffusion length as a function of anneal condition. The experimentally determined transition energy shifts are shown in Fig. 1.

The diffusion length squared divided by the anneal time is shown as a function of anneal temperature in Fig. 2. For equilibrium diffusion, this quantity is equal to the diffusion constant. However, for nonequilibrium diffusion, this quan-

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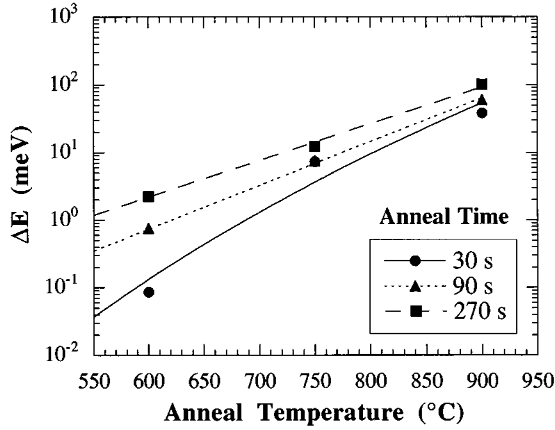

FIG. 1. Changes in the exciton transition energy as a function of anneal temperature and time in nonstoichiometric AlAs/GaAs quantum wells. The changes in energy, ΔE are measured with respect to the *in situ* annealed samples.

tity is time dependent and cannot be related simply to long-time diffusion constants, and cannot be used to extract true migration enthalpies. For instance, the effective migration enthalpy for the nonstoichiometric superlattices is $H^{\text{eff}} = (1.0 \pm 0.2)$ eV. This effective enthalpy is smaller than the migration enthalpy of 1.7 eV attributed to Ga vacancy diffusion,[10,11] but is close to the activation energy of 0.9 eV attributed to arsenic precipitate coarsening[12] in LTG GaAs. Also shown in Fig. 2 is the data obtained by Beernink *et al.*[13] based on photoluminescence energy shifts in stoichiometric superlattices. They obtain an activation enthalpy of 4.5 eV for Al–Ga interdiffusion, which is consistent with other values.[14] It should be noted that this value corresponds to the case of equilibrium linear diffusion, in which the activation enthalpy is the sum of the formation enthalpy and the migration enthalpy for group-III vacancies.

The effective enthalpy of 1 eV obtained in the present analysis is significantly larger than the effective enthalpy of 0.3 eV observed in our earlier work[5,6] on nonstoichiometric

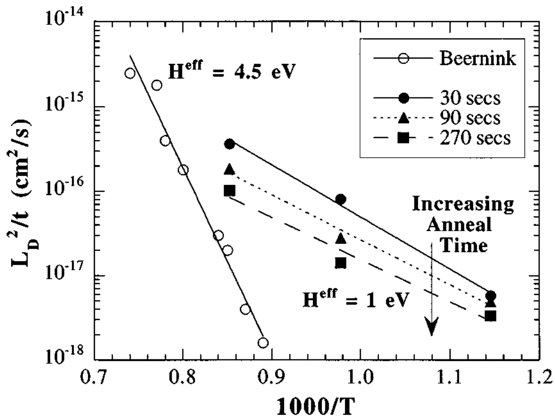

FIG. 2. Square of the diffusion length divided by anneal time for different anneal temperatures showing nonequilbrium linear diffusion in nonstoichiometric AlAs/GaAs quantum wells. Also shown is the data obtained by Beernink *et al.* (Ref. 13) for equilibrium linear diffusion in stoichiometric $Al_{0.4}Ga_{0.6}As$/GaAs quantum wells.

quantum wells. This apparent discrepancy is a simple consequence of different decay rates for the squared diffusion length divided by the anneal time, depending on the initial concentration of supersaturated group-III vacancies. Therefore, the apparent enthalpies obtained using an equilibrium analysis are not unique, and are sensitive to initial growth conditions. To obtain true enthalpies from nonequilibrium diffusion, it is necessary to explicitly include the time dependence of the group-III vacancy concentrations.

We use a simple formalism which utilizes both isochronal and isothermal anneals to recover true migration enthalpies for cases of nonequilibrium diffusion. In this analysis we assume linear diffusion, but with a time-dependent diffusion coefficient caused by the thermal annealing (annihilation) of group-III vacancies. The decay rate of $1/\tau$ of the supersaturated group-III vacancy concentration is assumed to have an activated nature given by

$$1/\tau = v_0 \exp[-H_a/k_B T], \tag{1}$$

where H_a is an activation enthalpy for vacancy annihilation. Vacancy annihilation, although an exothermic chemical reaction, can possess an activation barrier characterized by H_a that must be overcome prior to annihilation at a surface or at a defect complex. The time-dependent diffusion ''constant'' $D(t)$ is given by

$$D(t) = [D_0 \exp(-H_f/k_B T) + D_1 \exp(-t/\tau)] \times \exp[-H_m/k_B T], \tag{2}$$

where H_f and H_m are the formation energy and migration enthalpy respectively for the group-III vacancies. The equilibrium diffusion coefficient is given by the D_0 term. The supersaturated concentration of group-III vacancies contributes the D_1 term, which dominates in the nonstoichiometric material.

The time-dependent diffusion coefficient yields a time- and temperature-dependent diffusion length L_D, given in its most general form by

$$L_D^2(t) = D_1 \tau \exp[-H_m/k_B T][1 - \exp[-t/\tau]]. \tag{3}$$

For annealing times long compared with τ, the effective migration enthalpy is given by the difference in enthalpies

$$H_m^{\text{eff}} = H_m - H_a, \tag{4}$$

which can explain the anomalously small effective enthalpy measured in our previous experiments.[5,6]

For general isochronal and isothermal anneals, the most general form in Eq. (3) can be used with a least squares fit to obtain the important parameters that describe vacancy diffusion, including the respective enthalpies H_m and H_a. The least squares fit to the diffusion length are shown as the solid curves in Fig. 3. The resulting migration enthalpy is $H_m = 1.8 \pm 0.2$ eV, and the resulting annihilation enthalpy is $H_a = 0.7 \pm 0.2$ eV. Using the fit parameters, the time- and temperature-dependent diffusion length in nonstoichiometric quantum wells can be calculated, which show that the diffusion length saturates for long times, with larger asymptotic diffusion lengths at higher temperatures.

The migration enthalpy $H_m = 1.8$ eV obtained from the nonequilibrium analysis is in excellent agreement with the

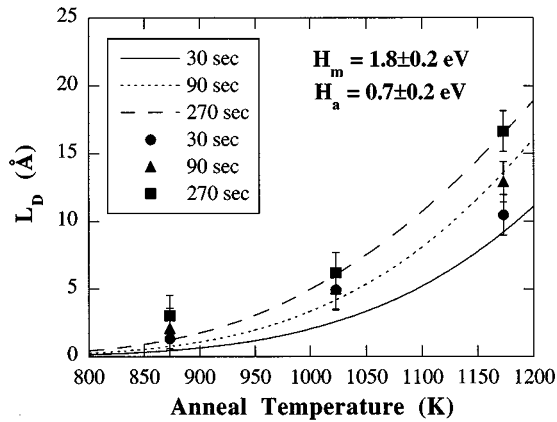

FIG. 3. Diffusion length, L_D as a function of anneal temperature for different anneal times. The solid lines are a least squares fit to the data which yields a migration enthalpy of (1.8±0.2) eV, consistent with V_{Ga} diffusion. The enthalpy for V_{Ga} annealing was found to be (0.7±0.2) eV.

accepted value of 1.7 eV for vacancy migration in bulk GaAs.[15] It is significant that the migration enthalpy in the nonstoichiometric quantum well does not differ significantly from the value in GaAs. This suggests that neither the nonequilibrium defect concentrations of the material nor the aluminum concentration significantly affects the migration enthalpy of the group-III vacancy. This result is important because it makes it possible to use unperturbed bulk values for vacancy migration in the nonstoichiometric quantum well structures.

The annihilation enthalpy $H_a = 0.7$ eV obtained from the nonequilibrium analysis is presented here for the first time. In previous diffusion studies[14] of stoichiometric growth, this annihilation enthalpy could not be isolated from the formation or migration enthalpies. The strong nonequilibrium vacancy supersaturation, combined with AlAs barriers as ''markers,'' present a unique opportunity to isolate the effects of group-III vacancy migration. The existence of an activation enthalpy for vacancy annihilation introduces an interesting new feature to the problem of diffusion in semiconductors. The existence of an energy barrier to vacancy annihilation makes this system susceptible to dynamical time-dependent effects. These dynamical effects can produce confusing behavior if the activated character of the reaction is not explicitly taken into account. This may explain earlier results attributed to vacancy diffusion in semiconductors.[16]

In conclusion, we have applied a general nonequilibrium diffusion analysis to the intermixing of nonstoichiometric quantum wells, based on a matrix of isochronal and isothermal anneals. The resulting migration enthalpy $H_m = 1.8$ eV is in excellent agreement with accepted values for vacancy migration in stoichiometric GaAs. The activation enthalpy for vacancy annihilation $H_a = 0.7$ eV is presented here for the first time. The ability to extract the annihilation enthalpy is made possible by the supersaturation of vacancies combined with ''marker''' layers of AlAs that make it possible to track the effects of vacancy diffusion. The existence of an energy barrier to vacancy annihilation should have important ramifications in the problem of diffusion in semiconductors.

Helpful discussion with E. R. Weber and C. Kisielowski are acknowledged. This work was supported in part by the MRSEC Program of the National Science Foundation under Award No. DMR-9400415. D. D. Nolte acknowledges support by the NSF Presidential Young Investigator program. M. R. Melloch acknowledges support from the US Air Force Office of Scientific Research under Grant No. F49620-93-1-0031. W. Walukiewicz acknowledges support from the US Department of Energy.

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