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L. Wang, L. Hsu, E.E. Haller, J.W. Erickson,
A. Fischer, K. Eberl, and M. Cardona
Materials Sciences Division
Center for Advanced Materials

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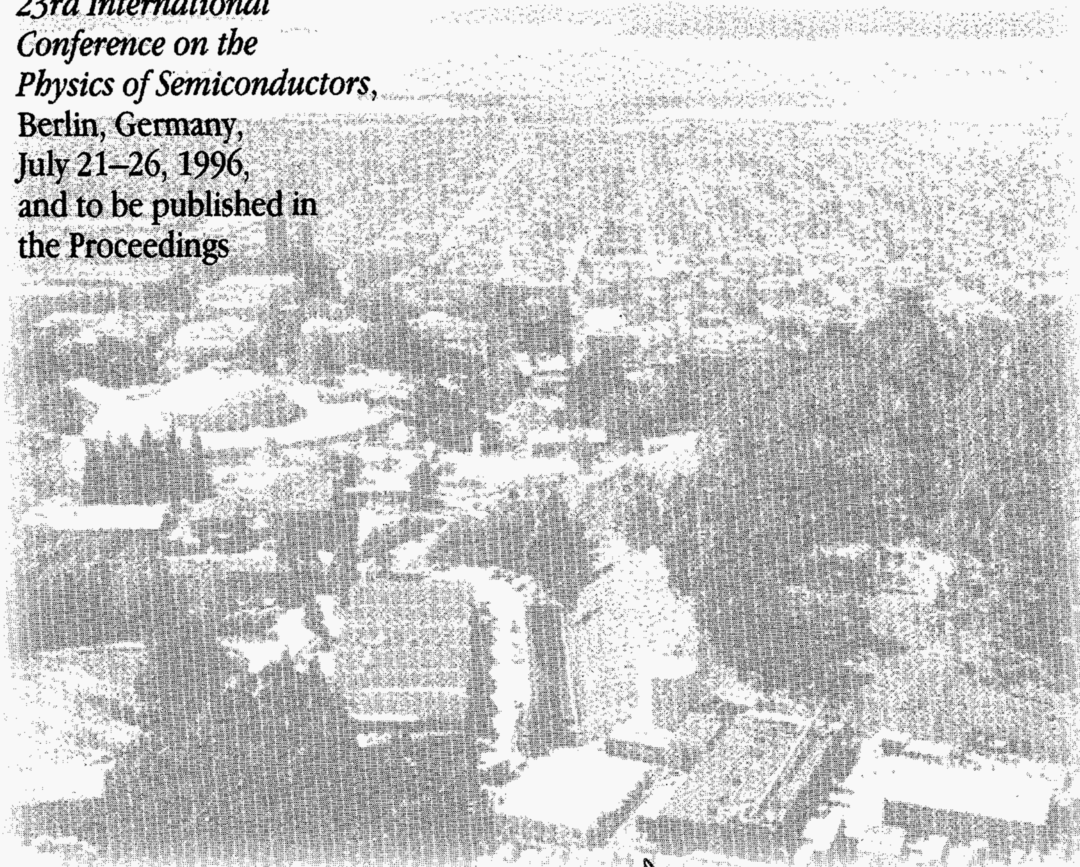

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Lei Wang, L. Hsu, and E.E. Haller

Materials Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

J.W. Erickson

Charles Evans & Associates
Redwood City, California

A. Fischer, K. Eberl, and M. Cardona

Max-Planck-Institut
Stuttgart, Germany

September 1996

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GALLIUM SELF-DIFFUSION IN GALLIUM ARSENIDE: A STUDY USING ISOTOPE HETEROSTRUCTURES

LEI WANG, L. HSU, and E. E. HALLER
University of California at Berkeley and Lawrence Berkeley National Laboratory
1 Cyclotron Road, MS 2-200, Berkeley, CA 94720, USA

J. W. ERICKSON
Charles Evans & Associates, California, USA

A. FISCHER, K. EBERL, and M. CARDONA
Max-Planck-Institut, Stuttgart, Germany

Ga self-diffusion has been studied with secondary-ion mass spectroscopy (SIMS) in ^{69}GaAs/^{71}GaAs isotope heterostructures grown by molecular beam epitaxy (MBE) on GaAs substrates. Our results show that the Ga self-diffusion coefficient in intrinsic GaAs can be described accurately with $D = (43 \pm 25\ \mathrm{cm^2s^{-1}}) \exp(-4.24 \pm 0.06\ \mathrm{eV}/ k_BT)$ over six orders of magnitude between 800 °C and 1225 °C under As-rich condition. The experimental results combined with theoretical calculations strongly suggest gallium vacancy being the dominant native defect controlling the diffusion. No significant doping effects were observed in samples where the substrates were doped with Te up to 4×10^{17} cm^{-3} or Zn up to 1×10^{19} cm^{-3}.

1. Introduction

The diffusive motion of the constituent atoms of a solid, the so-called self-diffusion, is one of the most fundamental dynamic processes. The process can be studied via the diffusion of isotopes monitored with radioactivity analysis or mass spectroscopy. Self-diffusion studies yield information on intrinsic point defect properties and dynamics including their concentrations, diffusivities, charge states, and annihilation probabilities. The knowledge is pivotal to understanding almost all diffusion processes since they are most certainly mediated by defects.

Compared to metals where self-diffusion has been successfully investigated employing the radioactive isotope tracer method [1], the process in semiconductors is significantly more complex due to the richer spectrum of intrinsic defects and to the much larger effects of small concentrations of defects on the properties of the materials [2,3]. The situation is further complicated by the short half-life of radioactive isotope tracers in semiconductors (e.g. 2.6 hours for ^{31}Si).

Recently a new approach to studying self-diffusion in semiconductors has been developed in which stable isotopes are used. The samples consist of epitaxial layers of isotopically enriched semiconductors grown by molecular beam epitaxy (MBE). The concentration profiles of the isotopes can be measured with secondary ion mass spectroscopy (SIMS) to relatively high spatial resolution. Since the diffusion of the isotopes takes place at the epitaxial interfaces inside the crystal, it is not directly affected by surface effects encountered in the conventional technique.

Tan *et al* performed the first such experiment in GaAs [4]. They studied Ga self-diffusion using a ^{69}GaAs/^{71}GaAs isotope superlattice. Unfortunately, their data analysis was complicated by heavily Si-doped substrates.

In our investigation, we grew a ^{69}GaAs/^{71}GaAs double-layer isotope heterostructure and determined accurately the self-diffusion enthalpy H^{SD} and estimated the associated entropy S^{SD}. An excellent agreement was found between our results and that of recent theoretical work. The effects of substrate doping were also examined.

2. Experiment

The GaAs isotope layers were MBE-grown at 580 °C on GaAs substrates of natural isotopic composition (^{69}Ga:^{71}Ga = 60.2:39.8). ^{71}GaAs and ^{69}GaAs layers each of 200 nm thick were grown. The nominal isotope purity in the epilayers is 99.6%.

The samples were annealed in sealed quartz ampoules evacuated to ~10^{-6} Torr with solid arsenic and crushed GaAs powder to preserve the surfaces. Details about cleaning procedure and annealing conditions have been reported earlier [5].

In the SIMS analysis, 3.3- and 5.0-keV Cs^+ ions formed the primary beam. $GaCs^+$ molecules were detected as secondary species.

3. Results and Discussion

Fig. 1 (a) and (b) show the SIMS depth profiles of ^{69}Ga and ^{71}Ga in both as-grown samples and in a sample annealed at 974 °C for 55.4 minutes. A resolution of 3.5 nm/decade

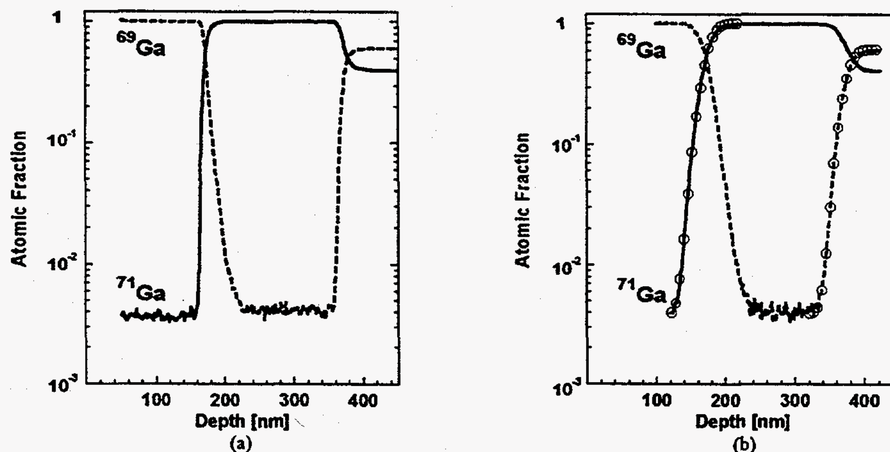

Figure 1. SIMS profiles of Ga isotopes in (a) as-grown GaAs isotope heterostructure and (b) a sample annealed at 974 °C for 55.4 min. The circles are theoretical fits.

can be achieved for the rising concentration edges at the as-grown interfaces (Fig. 1(a)).

The diffusion profiles in Fig. 1(b) can be fitted with solution to the Fick's equation, assuming the self-diffusion coefficient D is homogeneous in the region of interest:

$$C(x) = \frac{C_1 + C_2}{2} - \frac{C_1 - C_2}{2} erf(\frac{x}{R}) \qquad (1)$$

where $x = 0$ at the isotope heterostructure interface, C_1 and C_2 are the initial isotope concentrations at the left and right side of the interface, respectively, and $erf(y)$ is the error function. The characteristic diffusion range $R = 2(Dt)^{1/2}$ and t is the annealing time.

Excellent fits were obtained for both Ga isotope profiles with R as the only adjustable parameter. The fit validates the assumption made in arriving Eq.(1) and demonstrates that the sample surface is well preserved and introduces no anomalous effects.

If one assumes that only one type of intrinsic defect dominates the self-diffusion process, then the diffusion coefficient D can be written as [2]

$$D = D_0 \exp(-\frac{H^{SD}}{k_B T}) \qquad (2)$$

where H^{SD} is the self-diffusion enthalpy and D_0 the pre-exponential factor. D_0 can be expressed as

$$D_0 = fga^2 \nu_0 \exp(\frac{S^{SD}}{k_B}) \qquad (3)$$

where S^{SD} is the self-diffusion entropy, f is the correlation factor in the jump process, g is a geometry factor for the crystal lattice, a is the lattice constant, ν_0 is the frequency of the highest vibrational mode in the crystal, and k_B is the Boltzmann constant.

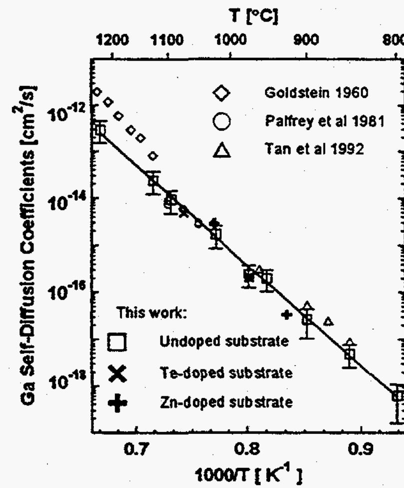

Figure 2. Arrhenius plot of Ga self-diffusion coefficient in GaAs.

Fig.2 is an Arrhenius plot of D. Between 800 °C and 1225 °C, the data points follow a straight line over six orders of magnitude in D values, verifying Eq.(2) applies in this self-diffusion process. From the plot we derived $H^{SD} = 4.24$ eV and $D_0 = 43$ cm^{2}s^{-1}. Also shown in Fig.2 are the results of self-diffusion studies in other groups. The results of Palfrey *et al.* [6] and Tan *et al.* [4] are consistent with ours while that of Goldstein's [7] early study leads to a higher H^{SD}.

The self-diffusion entropy S^{SD} is found to be $8k_B$ using Eq.(3), assuming $f \bullet g \sim 1$, $a = 0.54$ nm, $\nu_0 = 8\times10^{12}$ Hz. This is a reasonable value in comparison with $S^{SD} \approx 9k_B$ in Ge and $S^{SD} \approx 5\sim12k_B$ in Si [2].

The migration enthalpy H^M for the gallium vacancy has been estimated to be 1.5 eV[8] in low-temperature-grown As-rich GaAs, which is confirmed by Dabrowski and Northrup's calculation [9]. The formation enthalpy of Ga vacancy H^F has been calculated by Zhang and Northrup [10] to be $H^F = 2.5 \sim 2.8$ eV in As-rich GaAs, depending on the charge state. Therefore, $H^{SD} = H^M + H^F = 4.0 \sim 4.3$ eV according to the theory, which agrees excellently with our data, if Ga vacancy is the mediating defect in Ga self-diffusion process. An *ab initio* molecular dynamics study of Ga vacancy diffusion by

Bockstedte and Scheffler [11] found the formation entropy $S^F = 8k_B$. Since the migration entropy S^M is not known, it is difficult to compare our experimentally determined S^{SD} (= $S^F + S^M$) with this value. If we accept the calculated S^F, our result of $S^{SD} \approx 8k_B$ would lead to a very small S^M while the previously proposed $S^{SD} \approx 32k_B$ [3] lead to a huge S^M. Considering S^M is approximately equal to logarithm of the number of equivalent migration path for the defect, our estimate makes more physical sense.

We have also deliberately tested the influence of doping by annealing samples with Te- or Zn-doped substrates. No significant effects are observed (Fig. 2) in these samples (Te: $4x10^{17}$ cm^{-3}; Zn: $1.5x10^{19}$ cm^{-3}).

4. Conclusions

We have studied Ga self-diffusion in GaAs employing stable isotope heterostructures grown by MBE combined with SIMS analysis. We have found that diffusion profiles of both ^{69}Ga and ^{71}Ga in intrinsic GaAs can be fitted with simple error functions. An Arrhenius plot of the self-diffusion coefficient D yielded a straight line over six orders of magnitude in D, strongly indicating that a single defect mechanism is operative in the process. Our determination of $H^{SD} = 4.24$ eV and $S^{SD} \approx 8k_B$ agrees excellently with the result of the state-of-the-art calculations, assuming gallium vacancies being responsible for the process. The effect of doped substrates were also examined and found to be insignificant.

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