

## Multilayers as Microlabs for Point Defects: Effect of Strain on Diffusion in Semiconductors

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We describe how a systematic variation of experimental parameters can turn multilayers into microscopic laboratories for point defects. The effects of composition, doping, and strain on point defect diffusion and interdiffusion can thus be separated. This approach also allows one to determine the nature and the charge state of the mediating defect. More specifically, our results show interdiffusion in the model system InAlAs is mediated by a double-acceptor, vacancylike defect, with an activation energy of 4.0 eV in  $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ . This activation energy changes by 51 meV per % strain.

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When two stable solids differing in composition are placed in contact, the resulting system is often metastable. Scientifically, the approach of such systems to the stable (e.g., intermixed) state is of interest, because it involves intrinsic point defects, which are the elementary excitations of the solid. Technologically, the nature of this relaxation is important, because it influences the stability of solid-state devices, some of which now exploit strain to optimize performance (see, e.g., [1]). The route to stability is determined by a combination of parameters, some of which are characteristic of the bulk solids (such as composition, doping, strain), and others that are due to differences between the two solids (e.g., differences in composition, vacuum level, lattice parameter) [2]. This allows one to use multilayers to investigate properties of point defects in ways that are difficult to realize in bulk solids. For example, lattice mismatch can be used to generate strains in thin layers that can be achieved in bulk solids only by the diamond anvil. The systematic exploitation of such possibilities constitutes an approach in which multilayers are viewed as microscopic laboratories for the study of point defect properties. For this to achieve its full potential, one must establish the way experimentally accessible variables affect the fundamental variables, and how the point defect properties may be measured by systematic manipulation of these fundamental variables. This is important because, in multilayers, changing one experimentally accessible variable often changes a number of fundamental variables (see Fig. 1).

This Letter has three goals. First, it describes a set of experiments in which the fundamental variables are systematically manipulated to explore the chemical relaxation of inhomogeneous solids in the most general case. Second, it develops a framework for extracting from such experiments the parameters controlling point defect diffusion. Third, it analyzes the experimental data within this framework to determine separately the effects of composition, Fermi level, and strain on the diffusion properties of intrinsic point defects. Specifically, we determine the composition-dependent activation energy, the charge state, and the activation volume of the intrinsic defect me-

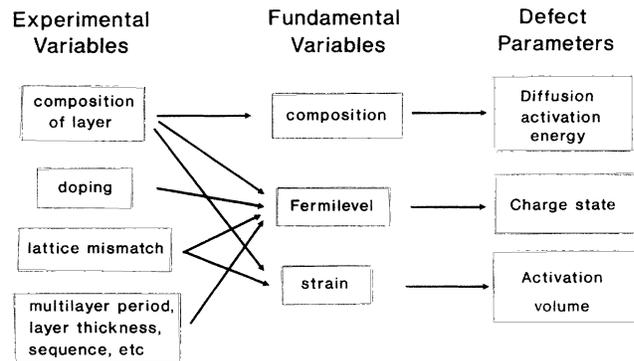


FIG. 1. Schematic illustration of the connection between accessible variables, fundamental variables, and defect parameters controlling diffusion in the general case.

diating the relaxation of compositional inhomogeneities in the model system InAlAs. Our results can be summarized as follows: (a) The activation enthalpy of the mediating defect is strongly composition dependent, changing from 6.8 eV in AlAs to 1.3 eV in InAs. (b) The mediating defect is doubly negatively charged during diffusion. (c) Strain changes the diffusion activation enthalpy by 51 meV per % strain. The fundamental parameters we measure provide a comprehensive description of the diffusive properties of intrinsic point defects in the most general case (see Table I). They also allow one to separate and rank the effects of composition, Fermi level, and strain on diffusion and interdiffusion. Remarkably, the effect of strain on the diffusion activation energy (51 meV per % strain) can still be measured in the presence of the huge changes due to composition (5.5 eV from AlAs to InAs) and the Fermi level ( $\sim 1$  eV as the material is changed from intrinsic to extrinsic).

To use multilayers as microlabs for point defects, one injects the defect of choice by annealing in an appropriate environment [3,4], and varies the experimental variables so as to bring about systematic changes in the fundamental variables (Fig. 1). We use  $\text{In}_x\text{Al}_{1-x}\text{As}$  as a model system, because it can be grown in tension

TABLE I. Fundamental parameters controlling diffusion and interdiffusion. Referred to intrinsic material at  $P_{As_4} = 1$  atm.

Parameter	Symbol (unit)	Value
Activation enthalpy ( $x = 0.52$ )	$H(x_0)$ (eV)	$4.0 \pm 0.3$
Composition dependence of enthalpy	$\Delta'H^i(x_0)$ (eV)	$5.5 \pm 0.6$
Strain dependence of enthalpy (per % strain)	$\Delta'H^i(\varepsilon)$ (meV)	$51 \pm 20$
Composition dependence of entropy	$\Delta'S^i(x_0)$ ( $k_B$ )	$54 \pm 7$
Preexponential factor	$D_0$ ( $\text{cm}^2/\text{s}$ )	$8.7 \times 10^5$
Charge state of defect	$m$	-2

or compression by a suitable choice of substrate and layer composition. This allows one to alternate the sign of strain to grow stacks of highly strained, pseudomorphic layers, with zero net strain after each period. In this way, we use molecular beam epitaxy to grow (at 490 °C) samples that allow us to explore a wide range of compositions and strain. In the following, we denote each layer by its indium content  $x$  and thickness (in Å). To vary the strain, samples consisting of five periods of 0.76(40 Å)/0.52(60 Å)/0.27(40 Å) layers, doped with  $5 \times 10^{18}$  Si/cm<sup>3</sup>, were deposited on substrates matched to  $x = 0.52$  or 0.76 (Fig. 2). The former substrates are readily obtained by depositing In<sub>0.52</sub>Ga<sub>0.48</sub>As on InP. The latter substrates were prepared by growing a 2 μm thick, graded InAlAs buffer, with a superlattice dislocation filter every 0.5 μm, capped with a fully relaxed, 2 μm thick 0.76 layer, resulting in a dislocation density <math> < 10^6 \text{ cm}^{-2}</math>. Pseudomorphic growth of several 0.76/0.52/0.27 periods on this (highly mismatched) substrate requires the deposition of strain-compensating layers, shown dotted in Fig. 2(b). Each sample was capped with a 2000 Å thick In<sub>0.52</sub>Ga<sub>0.48</sub>As layer. To vary the Fermi level, a third sample containing two identical, three-period 0.76(40 Å)/0.52(60 Å)/0.27(40 Å) stacks was grown on a substrate matched to 0.52. The first stack was doped with 10<sup>18</sup>, the second with 2 × 10<sup>18</sup> Si/cm<sup>3</sup>. Interdiffu-

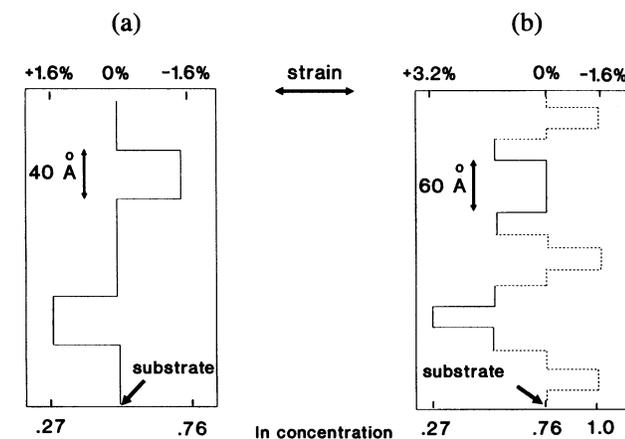


FIG. 2. Schematic diagram of a period of the multilayers used. Strain was changed independently of composition by growth on different substrates. Solid lines represent the parts of the multilayers where diffusion measurements were made.

sion was induced by annealing bulk samples at temperatures between 550 and 725 °C in 0.5 atm. As ambients in evacuated sealed quartz ampoules. <math> < 100 </math> cross-sectional samples for transmission electron microscopy were prepared by subsequent mechanical polishing and etching in a Br: methanol solution. High resolution composition profiles of as-grown and annealed layers were obtained by quantitative chemical mapping, as described elsewhere [5].

Figure 3 shows the composition profiles before and after anneals at different temperatures, for layers grown on different substrates to change the strain, and on the same substrate with different doping concentrations to move the Fermi level. Altogether 30 such profiles were obtained by varying the temperature from 550 to 725 °C, the composition  $x$  from 0.27 to 0.76, the strain from -1.6% to +3.2%, and the Fermi level from 0.304 to 0.514 eV (with respect to the intrinsic level in In<sub>0.76</sub>Al<sub>0.24</sub>As). Qualitative inspection of these profiles (e.g., Fig. 3) leads to the following conclusions: (a) The interdiffusion process is nonlinear, depending strongly on (at least) composition. This is evident from the grossly different effects of the anneals on the layers with  $x = 0.27$  and 0.76 [6]. (b) Changes in the substrate strongly affect

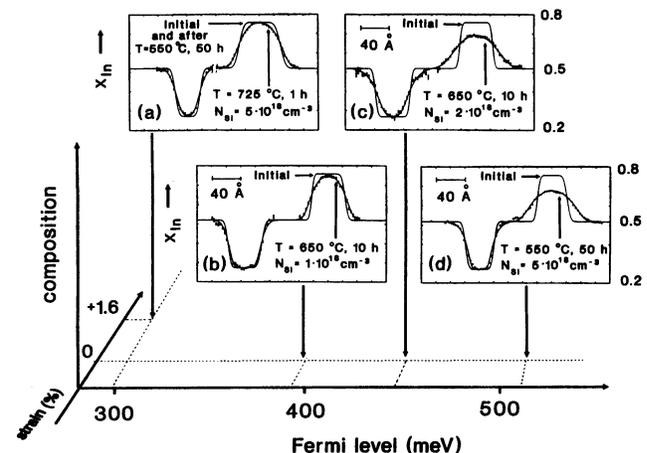


FIG. 3. Schematic representation of parameter phase space explored. Panels show experimental concentration profiles before and after annealing for different values of strain (for In<sub>0.52</sub>Al<sub>0.48</sub>As) and Fermi level. Dots are data points; curves are solutions of the nonlinear diffusion equation [Eq. (6)].

the intermixing behavior: When identically doped layers are deposited on different substrates, their intermixing behavior is strongly modified [compare panels (a) and (d) in Fig. 3]. It is tempting to assign this to the influence of strain. However, we will show that this is primarily due to changes in the position of the Fermi level, caused by the presence of the strain compensating layers, and strain-induced changes in the band structure. (c) Moving the Fermi level by doping strongly influences the intermixing [compare panels (b) and (c) in Fig. 3]. This indicates the interdiffusion to be mediated by a (multiply) charged point defect.

We now outline the framework needed to extract the fundamental parameters controlling point defect diffusion in the general case. Our strategy is to develop a local equilibrium formalism, which includes all significant effects to first order. We begin by assuming that the elementary interdiffusion process (an In  $\rightarrow$  Al exchange) is mediated by a point defect, such as a vacancy or interstitial, whose local concentration is determined by a spatially uniform electrochemical potential, set by the ambient, the electron reservoir (Fermi level) and strain. (We believe our formalism is applicable even in the absence of an equilibrium concentration of point defects, with the caveat that the intermixing *rate* would not be characteristic of the equilibrium case [7]. This formalism is in essence equivalent to that of Hu [2] for the case when the electrochemical potential for the mediating defect is spatially uniform.) The defect concentration is controlled by a formation free energy [4,8,9]:

$$G^f(x, E_f, \varepsilon, P, T) = G_{i0}^f(x, P, T) + m[E_f(\varepsilon, T) - eV_{bb}] + \Delta G_i^f(\varepsilon). \quad (1)$$

$x$  is the composition,  $T$  the temperature,  $G_{i0}^f(x, P, T)$  the formation (free) energy in intrinsic, unstrained material of composition  $x$ , in equilibrium with an (As) ambient at pressure  $P$ , and  $m$  is the charge state of the defect.  $E_f(\varepsilon, T)$  is the Fermi level in the doped, strained multilayer, measured from the Fermi level in the intrinsic, unstrained multilayer.  $\varepsilon$  is the strain,  $V_{bb}$  the (position-dependent) band bending.  $\Delta G_i^f(\varepsilon)$  is the change in the defect formation energy in intrinsic material due to strain.

$G_{i0}^f(x, P, T)$  is the energy cost of creating a charged (mediating) point defect in unstrained, intrinsic  $\text{In}_x\text{Al}_{1-x}\text{As}$ , in equilibrium with the ambient. The effect of an  $\text{As}_4$  ambient is explicitly given by an additive term  $\pm 1/4k_B T \ln(AT^{-5/2}P)$ , where  $P$  is the  $\text{As}_4$  pressure [4,9] and  $A$  is a constant. The minus sign holds for vacancies, the plus for interstitials. The variation of the formation energy with composition  $x$  is in general unknown. We retain terms up to first order in a Taylor expansion of  $G_{i0}^f(x, P, T)$  about the composition  $x_0 = 0.52$ . Thus,  $G_{i0}^f(x, P, T) = G_{i0}^f(x_0) + (x - x_0)\Delta^i G_{i0}^f(x_0) \pm 1/4k_B T \ln(AT^{-5/2}P)$ , where  $\Delta^i$  is the appropriate derivative in the Taylor expansion [10].

When the Fermi level is raised from its intrinsic, unstrained position to  $E_f(\varepsilon)$ , the energy gain in transferring  $n$  electrons from the Fermi reservoir to the mediating defect is increased by  $nE_f(\varepsilon)$ . When uniformly doped layers with different band gaps are placed in contact, the resulting Fermi level and band bending are characteristic of the multilayer *as a whole*, and can be different for identically doped samples with different layers and/or strains [see Fig. 3, panels (a) and (d)]. We calculate the position of the Fermi level and the band bending in each of our samples by iterative, self-consistent solution of the Poisson and Schrödinger equations [11].

The change in the defect formation energy  $\Delta G_i^f(\varepsilon)$  due to strain has two parts: one electronic, the other mechanical. Here, we argue that to first order, each part and hence the sum  $\Delta G_i^f(\varepsilon)$  vary linearly with strain. The electronic part results from strain-induced shifts in the electronic states of the mediating defect [12]. The magnitude of this shift is in general unknown, but a simple argument suffices to establish its functional dependence on strain. When pressed together, bonding states lower their energy, while antibonding states rise in energy. Thus, if the defect state responds to strain at all, the "leading term" in its response must depend on odd powers of strain. The mechanical contribution to  $\Delta G_i^f(\varepsilon)$  arises from the work done on a crystal by the hydrostatic component of the strain  $p$ , making the creation of a defect more expensive by  $pV^*$ , where  $V^*$  is the activation volume of the defect. Since  $p \propto$  strain, for a given defect type, the leading term in the "mechanical" contribution to  $\Delta G_i^f(\varepsilon)$  also varies linearly with strain.

The concentration of mediating defects  $C$  and the interdiffusion coefficient  $D$  at a point with composition  $x$  are given by

$$C(x, E_f, \varepsilon, P, T) = e^{-G^f/kT}, \quad (2)$$

$$D(x, E_f, \varepsilon, P, T) = d_0 C(x, E_f, \varepsilon, P, T) e^{-G^m/kT}, \quad (3)$$

where  $G^m$  and  $d_0$  are the migration energy and preexponential factor of the mediating defect. Defining the activation free energy  $G = G^f + G^m$ , and breaking the free energy into its enthalpy and entropy parts  $H$  and  $S$ , the explicit expression for the interdiffusion coefficient becomes

$$D(x, E_f, \varepsilon, P, T) = D_0 [P_{\text{As}_4} AT^{-5/2}]^{\pm 1/4} e^{-Q/kT}, \quad (4)$$

$$Q = H^i(x_0) + (x - x_0)[\Delta^i H^i(x_0) - T\Delta^i S^i(x_0)] + (x - x_{\text{sub}})[\Delta^i H^i(\varepsilon)] + m(E_f - eV_{bb}). \quad (5)$$

$D_0$  is the activation preexponential factor,  $x_0$  refers to the midpoint composition ( $x = 0.52$ ),  $x_{\text{sub}}$  denotes the strain free composition in each sample, and the superscript  $i$  indicates starting from an intrinsic multilayer in a (perhaps fictitious) strain-free state.

The appropriate equation to describe composition-dependent interdiffusion in the presence of strain is

$$\frac{\partial x}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial x}{\partial z} + \frac{xD}{kT} F \right), \quad (6)$$

where  $x$  is the composition, and  $z$  is the spatial (depth) coordinate. The force  $F$  describing the effect of strain on the interdiffusion, i.e., the In  $\rightarrow$  Al exchange, is given by the gradient of the strain energy  $U$  per atom:  $F = -\partial U/\partial z$ .  $U$  can be expressed in terms of the elastic modulus  $E$ , the Poisson ratio  $\nu$ , and the volume change per In  $\rightarrow$  Al atom exchange  $\beta$  [12]:  $U = E\beta^2(x - x_0)^2/2(1 - \nu)$ .

To summarize the formalism section, the In  $\rightarrow$  Al interdiffusion coefficient  $D$  is mediated by an intrinsic point defect, whose local concentration is determined by equilibrium with the ambient, and depends on composition, Fermi level, band bending, and strain. This interdiffusion coefficient enters the (nonlinear) equation governing In  $\rightarrow$  Al exchange under the driving forces due to the composition gradient and strain. Thus the strain enters twice: once through its effect on the local concentration of the intrinsic point defect mediating the In  $\rightarrow$  Al exchange (vacancies, for example, are scarce in regions of high compression), and a second time through its influence on the In  $\rightarrow$  Al exchange itself (the larger indium atoms try to move away from regions of high compression). This formalism links the experimental variables (composition, strain, and doping) to the fundamental defect parameters (composition- and strain-dependent activation energies, and charge state). The results obtained from our first-order expansion of the formalism are clearly most accurate close to the midpoint composition  $x_0 = 0.52$ .

To extract the fundamental parameters controlling diffusion, we numerically solve Eq. (6) and fit our 30 experimental profiles simultaneously, with  $D_0$ ,  $H(x_0)$ ,  $\Delta'H^i(x_0)$ ,  $\Delta'S^i(x_0)$ ,  $\Delta'H^i(\epsilon)$  and  $m$  as free parameters. The charge state of the defect  $m$  was fixed to be  $-1$ ,  $-2$ , or  $-3$ . Fits were performed separately for the positive and negative signs of the  $\text{As}_4$  pressure dependence. This affects the results by less than 10%, which is well within our error bars. The values extracted for the fundamental parameters controlling diffusion are listed in Table I for a positive sign of the  $\text{As}_4$  overpressure in Eq. (4). The error bars were obtained by a Monte Carlo procedure to simultaneously fit randomly picked subsets of eight profiles, with each profile corresponding to a different set of experimental conditions. Our results indicate the mediating intrinsic defect to be a double acceptor ( $m = -2$ ); changing  $m$  to  $-1$  or  $-3$  increases  $\chi^2$  by 30%.

The effect of strain on the activation energy in intrinsic material  $\Delta'H^i(\epsilon)$  amounts to only  $51 \pm 20$  meV per % strain. It seems remarkable that such a small change can be measured in the presence of the large changes in the activation energy due to composition and Fermi level. We note, however, that for a system with 3.5% strain, the effect of strain changes the diffusion coefficient at 650 °C by an order of magnitude. Separating the effect of strain  $\Delta'H^i(\epsilon)$  into its electronic and mechanical parts requires information about the shift in the electronic states of the defect with strain, which is not available.

However, since the defect is a double acceptor, it may be reasonable to assume that its electronic states follow the valence band edge (for details see [13]). This leads to an activation volume  $V^* = 21 \text{ \AA}^3$  for the mediating intrinsic defect, compared with  $25 \text{ \AA}^3$  for an unrelaxed vacancy. Taken together with the double-acceptor nature of the defect, [8,14] the sign and magnitude of the activation volume provide an intriguingly strong indication that a vacancylike defect is involved in the In  $\rightarrow$  Al exchange process.

We now summarize. First, we have outlined the experimental approach and the theoretical formalism needed to exploit multilayers as microlabs for point defects. Second, we have succeeded in clearly separating the effects of composition, Fermi level, and strain on diffusion in the general case. Finally, we have shown how doping and strain may be used in conjunction to gain insight into the nature of the intrinsic defects involved in key solid-state processes. These possibilities may offer new approaches to long standing riddles, such as the nature of the intrinsic point defects mediating dopant diffusion in Si. And they may herald the systematic use of multilayers to study point defects, in the way quantum wells were exploited to investigate charge carriers in solids.

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