

Boron Diffusion in Strained $\text{Si}_{1-x}\text{Ge}_x$ Epitaxial Layers

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(Received 3 May 1993)

B diffusion in $\text{Si}_{1-x}\text{Ge}_x$ strained layers on Si was studied as a function of annealing temperature and Ge content and is shown to be characterized by lower diffusivity as compared to unstrained Si. The influence of the Ge content on the dopant diffusion was also measured, demonstrating that the diffusivity of the B atoms is reduced with increasing Ge fraction in the strained layer. The reduced diffusivity of B in the strained $\text{Si}_{1-x}\text{Ge}_x$ relative to the dopant diffusivity in unstrained Si is attributed to the change in the charged point-defect concentration caused by band-gap narrowing. We find good agreement between the measured and simulated diffusivity using the known band-gap for the strained layers.

PACS numbers: 68.35.Fx, 61.66.Dk

Diffusion in solids is a fundamental material process which shows extraordinary variation in value and complexity depending on the atomic system of interest. Diffusion of dopants in crystalline Si and Ge is an example where well-controlled experiments in pristine material have led to complex, phenomenological models. These models, although limited in their absolute predictions of diffusivity, do provide a guide for predicting the change of diffusivity with certain materials parameters. The underlying concept in these models is that substitutional dopants diffuse by interacting with native point defects. The concentration of these point defects, which may be in various charge states, is strongly influenced by the electronic properties of the semiconductor, Fermi level, band gap, etc. These models have had considerable success, particularly in explaining the concentration-dependent diffusion coefficients reported by early investigators.

The advent of the growth of high-quality $\text{Si}_{1-x}\text{Ge}_x$ strained films on Si, with controllably variable x , now provides another medium to test and explore the parameterization of the accepted diffusion theory in Si. In this paper we report measurements of boron diffusivity in $\text{Si}_{1-x}\text{Ge}_x$ as a function of temperature and $x < 0.5$. In agreement with other recent reports [1] we find a reduced boron diffusion in the strained alloy. This is in contrast to an intuitive expectation based on the fact that the boron diffusion in pure Ge is greater than that in pure Si over the temperature range used [2]. We show that our diffusion values can be quantitatively understood by including the modified $\text{Si}_{1-x}\text{Ge}_x$ band gap and the corresponding change in the point-defect concentration in the model for Si. The fact that this perturbation approach to boron diffusion in $\text{Si}_{1-x}\text{Ge}_x$ works so well is surprising, since it assumes that defect formation and migration enthalpies are similar in $\text{Si}_{1-x}\text{Ge}_x$ and in bulk Si.

Strained 15 nm thick $\text{Si}_{0.7}\text{Ge}_{0.3}$ layers were grown at 630°C by rapid thermal chemical vapor deposition (RTCVD) on 400 nm thick Si epitaxial buffer layers on top of Si substrates. Sharp boron distributions with a peak concentration of 8×10^{19} B atoms/cm³ and full width at half maximum of 5 nm were introduced during the growth in the middle of the strained $\text{Si}_{0.7}\text{Ge}_{0.3}$ layers. Thin Si cap layers were deposited on top of the strained

films. Both the cap and the buffer layers were doped to about 10^{18} cm⁻³ boron to avoid any electric field effects during the diffusion. Control structures were also grown with no Ge in the boron-doped region.

Annealing was carried out in a rapid thermal annealing system (RTA) in the temperature range 800–1000°C for 10 to 600 sec in dry N₂. Si control samples were annealed simultaneously with the $\text{Si}_{0.7}\text{Ge}_{0.3}$ material. Diffusivities of the dopant atoms in furnace annealed (N₂) control samples were also measured in the temperature range of 800–850°C. Values of the boron diffusion coefficient of these Si control samples were close to the literature values, indicating that no anomalous material effects influence the diffusion of boron in the RTCVD grown material, in agreement with other reports [3].

A separate multilayer structure, grown by molecular beam epitaxy (MBE) at 500°C, contained five $\text{Si}_{1-x}\text{Ge}_x$ layers with Ge content in the range of 10% to 50%, separated by 50 nm intrinsic Si space layers. Thin boron-rich regions (~5 nm) were introduced in the center of each $\text{Si}_{1-x}\text{Ge}_x$ layer. This structure was used for the study of the boron diffusion as a function of the Ge content in the strained material annealed at 975°C.

A primary ion beam of 2–3 keV O₂⁺ was used for optimal secondary ion mass spectroscopy (SIMS) depth profiling of the as-grown and diffused boron distributions. Boron implanted standards of $\text{Si}_{1-x}\text{Ge}_x$ and Si were used for calibration. The B⁺ secondary ion yield and sputter rates changed by less than 10% between the Ge containing alloys and the elemental Si.

The diffusion process was simulated using the well accepted model for boron diffusion via multicharged point defects [4]. Diffusion parameters for boron in Si were taken from Ref. [5]. The as-grown boron distributions were used as the initial condition for the calculations, and the best fits to the experimental result after annealing were obtained by varying a single parameter and neglecting an interfacial effects.

Diffusion of dopants in semiconductors is sensitive to the band gap and dopant concentration. Since these are functions of the semiconductor composition and layer strain, it is necessary to establish these parameters in the materials of interest.

The strain of the $\text{Si}_{0.7}\text{Ge}_{0.3}$ layers due to the lattice mismatch between the grown material and the underlying Si was confirmed by high-energy He⁺ particle channeling (1.8 MeV) along the $\langle 111 \rangle$ principle lattice direction, both prior to the annealing and after the high-temperature treatments. In all cases, the strain measured in the $\text{Si}_{0.7}\text{Ge}_{0.3}$ layers was in close accordance with the expected values for 30% Ge [6].

The electrical activity of the incorporated boron atoms was measured by high resolution stripping Hall measurements [7] and was compared to the atomic concentration of the dopant as measured by SIMS. Greater than 90% electrical efficiency was achieved in the as-grown material. $^{11}\text{B}(p,\alpha)^8\text{Be}$ channeling experiments were also performed in order to investigate the B incorporation in the strained lattice. More than 80% of the boron atoms occupy substitutional lattice sites, very close to the limits of detection for the specific experimental conditions (considering the damage induced by the high energy, 650 keV, proton beam and a total dose of $10^{15} p^+/\text{cm}^3$) [8].

High resolution transmission electron microscopy (TEM) showed excellent lattice arrangement; misfit or threading dislocations were undetected as expected for these below critical thickness strained layers.

The stability of the $\text{Si}_{1-x}\text{Ge}_x$ layers was investigated along with the boron diffusion experiment between 800 and 1000°C. Clear evidence for Ge interdiffusion into the Si epitaxial layers was observed for temperatures above 950°C for 30 sec. Thus the amount of Ge in the layers varies slightly from the as-grown Ge fraction at the end of the most drastic heat treatments. This increases the uncertainty in the exact composition of the strained alloys to less than 10% of the total Ge content in the layer.

These material characterization results allow us to apply the diffusion analysis with confidence that the investigated layers are indeed strained $\text{Si}_{1-x}\text{Ge}_x$ of known composition and that the boron is electrically active, as assumed in the diffusion analysis.

(a) *Diffusion in $\text{Si}_{0.7}\text{Ge}_{0.3}$ strained layers.*—Boron profiles were analyzed using a standard, one-dimensional diffusion analysis with the initial profile given by the measured, as-grown structure. We analyze the diffusion data with two different forms of the concentration-dependent diffusion coefficient.

In the first case we treat the data in the standard format used to analyze boron diffusivity in Si under extrinsic conditions. The diffusion coefficient in this case is given by [4]

$$D = D_i^{(0)} + D_i^{(+)} \frac{p}{n_i} \quad (1)$$

Here p is the spatially varying hole concentration and n_i is the intrinsic electron concentration; $n_i = \sqrt{N_c N_v} \times e^{-E_g/2kT}$ with E_g the band gap of pure Si, N_c and N_v are the density of states in the conduction and valence band, respectively, and k is the Boltzmann constant. In the above expression $D_i^{(0)}$ is the diffusion coefficient of

the *boron-neutral-point-defect* pairs and $D_i^{(+)}$ is the diffusion coefficient of the *boron-positively-charged-point-defect* pairs under intrinsic conditions. The explicit defect mediated diffusion mechanism need not be specified in the expression given above [4]. The intrinsic diffusivity is usually defined as $D_i = D_i^{(0)} + D_i^{(+)}$ and is characterized by an Arrhenius behavior for the case of boron diffusion in pure Si with an activation energy of 3.46 eV for both $D_i^{(0)}$ and $D_i^{(+)}$ and a preexponential factor $0.76 \text{ cm}^2/\text{sec}$ for D_{i0} (see, for instance, Ref. [9]). Our data for $\text{Si}_{0.7}\text{Ge}_{0.3}$ show an Arrhenius behavior (Fig. 1). Using Eq. (1) we get $E_a = 4.4 \text{ eV}$ and $D_{i0} = 1440 \text{ cm}^2/\text{sec}$ for the boron diffusion in the $\text{Si}_{1-x}\text{Ge}_x$ system.

We now consider an alternative approach to understand the dopant diffusion process in the strained material relative to pure Si. We generalize the treatment of Fair [5] who took into account the changes in both n_i and the point-defect concentrations that can occur in a crystalline environment due to a strain from dopant atoms. In our formulation we extend this concept to the change in band gap that occurs from a strain and modified composition in the epitaxial strained $\text{Si}_{1-x}\text{Ge}_x$ layers.

The applicable expression for the diffusion coefficient for a p -type layer under extrinsic conditions and assuming an ionized-point-defect level close to the middle of the band gap is [5]

$$D^S = D_i^{(0)} + D_i^{(+)} \frac{p}{n_i} e^{\Delta E_g/2kT}, \quad (2)$$

where ΔE_g is the change in the band gap and the superscript S denotes the band-gap-modified condition. The factor $\exp(\Delta E_g/2kT)$ in the above expression arises from two sources: (a) the changes in n_i ($[n_i]^S = n_i \times \exp(-\Delta E_g/2kT)$) and the free carrier concentration p ($[p]^S = p \exp(-\Delta E_F/kT)$ with ΔE_F , the difference between the Fermi levels of the extrinsic semiconductor with and without the band-gap change) and (b) the change in the point-defect concentration due to the band-gap modification [proportional to $\exp(\Delta E_F/kT)$]. In this approach the band-gap modification is considered as a perturbation on the standard Si diffusivity. Therefore we use the values of the activation energy E_a and the preexponential factor D_{i0} applicable to boron diffusion in

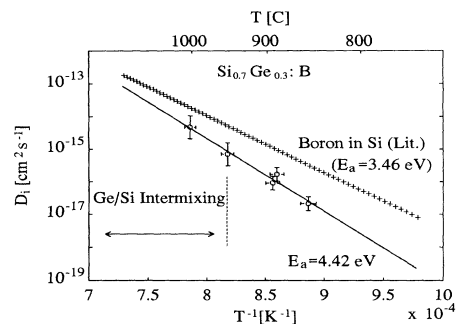


FIG. 1. Extracted intrinsic diffusivity (assuming the Si parameters) as a function of the reciprocal temperature (see text).

pure Si and determine the best fit values of ΔE_g that result from the experimental data. The best fit values of ΔE_g , according to the above model, are shown in Fig. 2(a) for diffusion profiles at various temperatures. The horizontal line represents the average value for ΔE_g and is close to the expected value based on published reports of the 90 K band gap in $\text{Si}_{0.7}\text{Ge}_{0.3}$ strained layers [10]. Also shown is an example of a fit to the experimental data [Fig. 2(b)], as obtained by the simulation program based on the modified diffusivity expression [Eq. (2)] for $\Delta E_g = 0$ and $\Delta E_g = -0.34$ eV.

The factor $\exp(\Delta E_g/2kT)$ ($\Delta E_g < 0$) also explains the relative weak dopant concentration dependence of the dopant diffusivity in $\text{Si}_{1-x}\text{Ge}_x$ reported in the first part of Ref. [1]. The reduced value of the second term in Eq. (2) results in a reduced sensitivity to the actual dopant concentration.

These results indicate that the diffusivity of boron in $\text{Si}_{0.7}\text{Ge}_{0.3}$ can be quantitatively described by the diffusivity of boron in Si taking into account the modified band gap and the corresponding changes in the charged-point-defect concentrations which directly affect the diffusion process. Note, however, that this treatment contains the strong assumptions that the preexponential factor and activation energy appropriate to B diffusion in

Si apply to $\text{Si}_{0.7}\text{Ge}_{0.3}$.

Reliable formation enthalpies for point defects in semiconductors are not yet available from experiment or theory. Thus no direct estimation of point-defect formation energies in the alloy can be derived as compared to the elemental materials. However, assuming a 20% difference between the point-defect formation enthalpy in Si and Ge [11] only a small average change is expected in the intrinsic diffusivity of $\text{Si}_{1-x}\text{Ge}_x$ ($x < 0.3$) material and is thus neglected here. It should also be noted that the smaller values for point-defect formation enthalpies in Ge as compared to Si [12] are expected to *enhance* the dopant diffusion, in contrast to our experimental results.

Since the driving force for the diffusing species is related to the gradient of the respective chemical potential, no direct influence of a homogeneous strain field is expected on the dopant redistribution in the alloy. Obviously, differences exist between the elastic tensors of the strained material and the unstrained crystal [13], and hence differences in the intrinsic diffusivity expression [14] are possible. Nevertheless, the good agreement between the measured and calculated diffusivity suggests that these effects are small.

(b) *Dependence on Ge content.*—In Fig. 3(a) we show the SIMS boron profiles in the multilayer structure before and after the heat treatment (975 °C, 30 sec). A clear retardation of the dopant redistribution is seen for the strained layers with increasing Ge content.

As for the case of the diffusion analysis in the $\text{Si}_{0.7}\text{Ge}_{0.3}$ layers we have simulated the diffusion profile using both the standard approach [Eq. (1)] and the band-gap modified diffusivity expression [Eq. (2)]. The intrinsic diffusivities [Eq. (1)] or band-gap change [Eq. (2)] were assumed to be different at each layer with different Ge content. The relative diffusivities in the different layers, derived by using the standard approach, are shown in Fig. 3(b). This illustrates the strong dependence of the dopant redistribution on the Ge content in the strained alloys. In Fig. 3(c) we show the band-gap change required to fit the experimental profiles to the simulated boron diffusion in Si using Eq. (2). In this plot we have normalized the diffusivities to the 30% Ge content RTCVD layer at the relevant annealing temperature. The corresponding band-gap narrowing theoretically calculated [10] and experimentally verified [15] for strained $\text{Si}_{1-x}\text{Ge}_x$ with $x = 0.1-0.5$ is also shown. The Ge dependence of the band-gap change extracted from the diffusion is in good agreement with the established strain-induced band-gap narrowing. Note, however, that the band-gap narrowing values quoted from Ref. [15] correspond to the values at 90 K while the diffusion analysis is carried out at temperatures above 1000 K. Assuming a similar temperature dependence of E_g for Si and $\text{Si}_{1-x}\text{Ge}_x$, the 90 K values may be as much as 30% smaller than shown in Fig. 3(c).

In conclusion, we have demonstrated that the boron diffusion in strained $\text{Si}_{1-x}\text{Ge}_x$ thin layers is smaller than

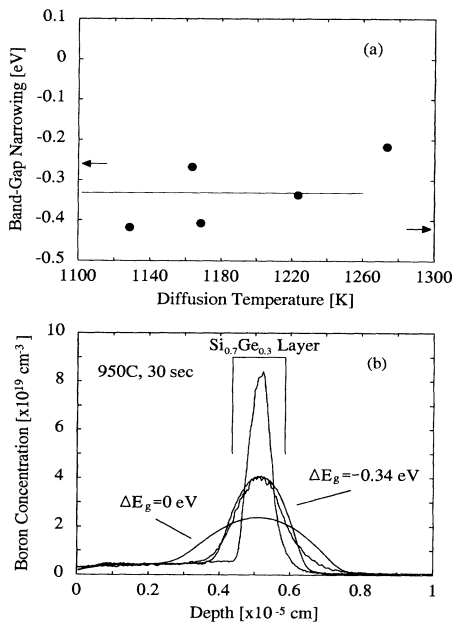


FIG. 2. (a) The energy band-gap narrowing values extracted from the diffusion experiments as a function of the annealing temperature based on the strain-induced diffusivity expression [Eq. (2) in the text]. The arrows at 0.26 and 0.41 indicate the band-gap narrowing for $\text{Si}_{0.7}\text{Ge}_{0.3}$ at 90 K [15] and pure Ge at room temperature, respectively. (b) An example for a simulation fit of the experimental boron profiles obtained by applying the multicharged-point-defect model for the case of the diffusion in the strained $\text{Si}_{1-x}\text{Ge}_x$ system with $\Delta E_g = -0.34$ and without the strain effect ($\Delta E_g = 0$).

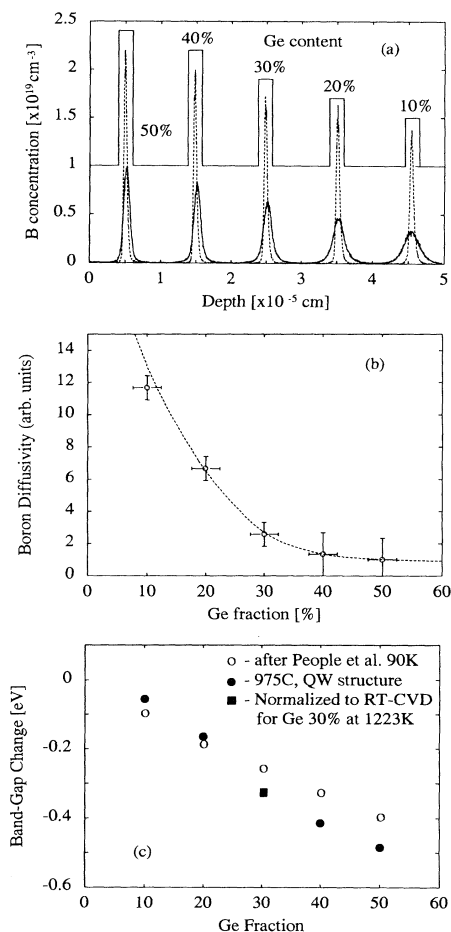


FIG. 3. (a) Boron concentration in a MBE grown multilayer structure with different Ge content in each layer before (dashed line) and after (solid line) annealing at 975°C for 70 sec. (b) Relative dependence of the extracted intrinsic diffusivities as a function of the Ge fraction in the MBE grown multilayer structure with different Ge content in each layer. (c) Normalized band-gap-change values extracted from the diffusion experiments as function of the Ge content in the MBE grown strained multilayer structure. Also shown are the band-gap values as a function of Ge content from Ref. [10].

in pure Si in the temperature range $800\text{--}1000^\circ\text{C}$. Based on the parameters for boron diffusion in Si, we have shown that the process can be characterized by an activation energy of 4.4 eV and a preexponential factor of $1440 \text{ cm}^2 \text{ sec}^{-1}$ for $\text{Si}_{0.7}\text{Ge}_{0.3}$.

An alternative approach to describe dopant diffusion in Si-based strained layers is applied to boron diffusion in $\text{Si}_{1-x}\text{Ge}_x$ thin layers. This approach is based on the band-gap-induced modification of the concentration of point defects which assist the diffusion process. The band-gap narrowing required to explain the experimental results is found to be in good agreement with known values for strained $\text{Si}_{1-x}\text{Ge}_x$.

The authors would like to acknowledge the kind help of

Dr. A. Katz for his helpful assistance in this work and Dr. C. Rafferty and Dr. H. J. Gossmann for useful discussions.

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