Interfacial Segregation in Strained Heterostructures: Boron in $Si_{0.8}Ge_{0.2}/Si$

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Using a neutral atom mass spectrometry we have measured the value and temperature dependence of the boron segregation coefficient at the strained $Si/Si_{0.8}Ge_{0.2}$ interface. Segregation coefficients of 0.4 to 0.8 (Si/SiGe) are observed in the temperature range of 900 to 1200 K. The activation energy for the dopant segregation is measured to be 0.3 eV.

The basic nature of dopant diffusion in almost all semiconductor material combinations is insufficiently understood for current applications, providing challenges in fundamental and applied research [1–3]. Of special importance is the thermally activated dopant redistribution through semiconductor heterostructure interfaces [4–7]. From a theoretical point of view, the problem requires a detailed knowledge of all contributions to the free energy of the local subsystem and the minimization of this energy, with respect to the system degrees of freedom, at thermodynamic equilibrium. The control of dopant interfacial segregation from one region to another in a heterostructure based device is a key issue for the device performance. Recent theoretical work by Hu *et al.* revealed a close correlation between the driving forces for interfacial dopant segregation in a strained heterostructure [4–6] and the electronic properties of the system including the conduction and valence band density of states. The approach of Hu *et al.*, which takes into account both structural and electronic contributions, as well as strain field effects, to the total free energy, yields single expressions for the segregation coefficient for the two limiting doping regimes, far above or below the intrinsic carrier concentration at the diffusion temperature.

In this Letter, we present experimental measurements of boron segregation coefficients through strained $Si_{0.8}Ge_{0.2}/Si$ interfaces as a function of temperature. A sputter profiling technique combined with neutral atom detection is used to avoid experimental ambiguities involving charged species at the material interface. Values for the segregation coefficient between 0.4 and 0.8 are observed in the temperature range of 900 to 1200 K. An activation energy of 0.3 eV is extracted for the segregation process. Based on Hu's original formalism, we extract the valence band density of states in the strained SiGe to be a factor of 15 smaller than in unstrained Si at the experimental temperature range.

Strained, 35 nm thick $Si_{0.8}Ge_{0.2}$ layers were grown at 630 °C by rapid thermal chemical vapor deposition (RTCVD) on 400 nm thick Si epitaxial buffer layers, on top of $\langle 100 \rangle$ Si substrates. *In situ* boron deposition was obtained throughout the strained alloy with a homogenous distribution of 5×10^{19} cm^{-3}. All buffer layers were

intentionally boron doped to about 1×10^{18} cm^{-3} to eliminate electric field effects at the interfaces during the diffusion process. Strain values were obtained by ion channeling experiments (1.8 MeV He$^+$) at an off-growth direction and were verified to match the expected values for the Ge content in the strained alloy, as measured by Rutherford backscattering [8]. Thermal annealing treatments were carried out in the temperature range between 630 (growth temperature) and 875 °C, in flowing Ar, for times of 1 to 5 h, in order to approach thermodynamic equilibrium. Note that both interfacial broadening and strain relaxation may occur during the long time, high temperature annealing process. Nevertheless, Ge profiles show only little intermixing in this temperature range, and no strain relaxation could be detected after heat treatment.

Semiconductor dopant profiles are usually measured via secondary ion mass spectrometry (SIMS). The ion emission process is, however, subject to changes in the apparent profile during depth profiling across an interface, i.e., matrix effects [9]. Obviously, this is unacceptable in measuring the segregation coefficient, which requires the true concentration ratio at the interface. Therefore, we have used high resolution, neutral mass spectroscopy (RIMS) [10,11] to record boron distributions across the $Si_{0.8}Ge_{0.2}/Si$ interface. This method, which uses a tunable laser to ionize sputtered neutral atoms, is particularly suitable for such measurements due to its insensitivity to matrix effects while depth profiling through heterostructure interfaces [12]. The actual profiling was obtained by using 2 keV primary Xe$^+$ beam and 0.5 nm step intervals between data points. In separate experiments we have verified that sputtering rates, which can, in principle, differ between the two materials, are the same to within 5%. Total boron content was obtained by $^{11}B(p, \alpha)^8Be$ nuclear reaction experiments [13] and was used to calibrate the boron concentration profiles.

Figure 1 shows boron profiles at the strained $Si_{0.8}Ge_{0.2}/Si$ interface (a) after 5 h at 630 °C (growth temperature), (b) after 750 °C for 5 h, and (c) after 875 °C for 50 min. The boron concentration discontinuity at the SiGe/Si interface can clearly be seen in all measured profiles. Consideration was given to possible segregationlike
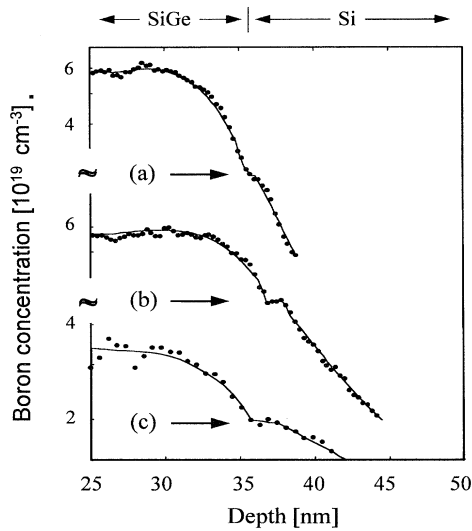
FIG. 1.   Boron distribution profile at the $Si_{0.8}Ge_{0.2}$/Si interface at 630 °C (growth temperature) for 5 h (a), after 750 °C for 5 h (b), and 875 °C for 50 min (c). Solid lines are to guide the eye.

features resulting from the different dopant diffusivities in the two materials [14,15]. However, no interface discontinuities could be simulated under the assumption of a segregation coefficient of unity using the reported diffusivities of the materials. We therefore relate the observed effect to interfacial dopant segregation.

The temperature dependence of the segregation coefficients, defined as the ratio of the boron concentration in the Si to the boron concentration in the SiGe across the mismatched interface (see Fig. 1), is shown in Fig. 2. Also shown is the experimental data point from Ref. [4]. For the dopant segregation from the strained SiGe alloy to the unstrained Si, we observe an increase of the boron segregation coefficient with increasing annealing temperature.
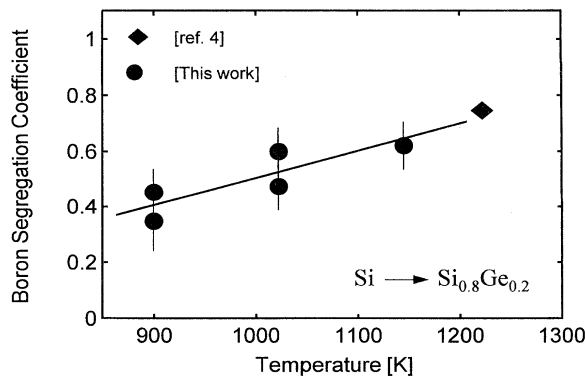
FIG. 2.   Boron segregation coefficient through Si/SiGe interface as a function of annealing temperatures.

We now review the theoretical treatment of Hu et al. for the interfacial dopant segregation. Following the arguments given in Ref. [5] we calculate the relevant changes in the Gibb's free energy upon the introduction of a dopant atom into the solid and the resulting changes in the electronic energy configuration of the system. The derivative of the total free energy is then taken, with respect to the dopant concentration at each side of the interface, to obtain the electrochemical potential which, under thermodynamic equilibrium, is equal across the interface. This yields a segregation coefficient, k_{seg},

$$k_{seg} \equiv \frac{N_1^I}{N_1^{II}} = \frac{N_L^I}{N_L^{II}} \exp\left(-\frac{\Delta H_1 - Z_1 \Delta E_1}{kT}\right). \quad (1)$$

Here N_1^I, N_1^{II} are the respective dopant concentrations in the Si and SiGe sides of the interface, $\Delta E_1 = E_1^I - E_1^{II}$ is the difference in the dopant energy levels, $N_L^{I,II}$ are the respective lattice sites concentrations, and Z_1 is the dopant charge state.

For the SiGe/Si system

$$\Delta H_1 \equiv \Delta E_{1b} - Z_1 \Delta W_i - \theta \beta_1 \beta_2 N_2^{II}, \quad (2)$$

with ΔE_{1b} the difference of the dopant bond energies and ΔW_i the difference between the ideal work function of the two sides of the heterostructure [5]. The term $\theta \beta_1 \beta_2 N_2^{II}$ represents the direct strain gradient effect on the segregation, with β_1 the contraction factor for the boron atoms, β_2 the expansion factor for Ge, θ a geometrical parameter representing the elastic state of the strained material, and N_2^{II} the Ge content in the SiGe. Note that the above expression [Eq. (1)], although most general, is still dopant-concentration dependent via the band offsets of the heterostructure that are determined by the common Fermi-level position across the interface.

Upon the assumption of a shallow acceptor state in the band gap (on both sides of the interface), ΔE_1 may be approximated by the difference between the respective valence band maxima. It can be shown that for highly extrinsic doping levels [5]

$$k_{seg} = \frac{N_1^I}{N_1^{II}} = \sqrt{\frac{N_V^I}{N_V^{II}}} \exp\left(-\frac{\Delta H_1}{2kT}\right), \quad (3)$$

where N_V^I and N_V^{II} are the valence band effective density of states in the two materials, respectively.

A least squares fit of the experimental measurements by the above expression yields preexponential values of 3.8 ± 1.5 and activation enthalpy for the segregation of 0.3 ± 0.1 eV [16]. The interpretation of the preexponential factor according to Hu's theory yields a ratio of approximately $\frac{1}{15}$ for the valence band density of states in the strained $Si_{0.8}Ge_{0.2}$ to Si, at the experimental temperature range. Theoretical estimates of the density of states for a purely strained SiGe alloy have previously predicted reduced values [18,19]. For the conduction band,

the sixfold degeneracy of the Δ symmetry point is lifted, splitting into a fourfold in-plane and two out-of-plane states, and leads to an expected $\frac{2}{3}$ reduction of the density of states as compared to unstrained Si. Strain-induced changes of the valence band density of states are more complicated due to the highly distorted and nonparabolic characteristic of the valence bands [18,19], splitting between heavy (hh), light (lh), and spin-orbit split-off (sso) bands and a substantial modification of the band structure due to the strain and Ge content. Theoretical calculations of the change between hh and lh effective valence band mass density of states in strained $Si_{1-x}Ge_x$ on Si ($x < 0.3$), at room temperature, have recently shown a drastic reduction compared to unstrained Si [19,20]. Additional estimates, based on device modeling of strained $Si_{0.9}Ge_{0.1}$/Si heterostructure bipolar transistors (HJBT) at room temperature, have been used to extract the ratio of $N_V N_C$ [21,22] and suggest a small value for the product (of the order of 0.2) in accord with our results. Although no similar calculations are available for the high temperature regime addressed here, our findings are in qualitative agreement with these predictions. It is interesting to note that the dopant segregation effect is large and in the direction to confine boron in the SiGe alloy in a structure used in HJBT's devices.

In conclusion, we have measured the boron segregation coefficient through the strained $Si/Si_{0.8}Ge_{0.2}$ interface as a function of temperature and obtained both the net segregation enthalpy for the process and the preexponential factor. We show the process to be thermally activated, with an activation energy of 0.3 eV and a tendency for boron to segregate preferentially to the SiGe in the SiGe/Si heterostructure. Based on a theoretical approach, given originally by Hu *et al.*, which relates the segregation coefficient to a function of the valence band density of states in the heterostructure system, we estimate the ratio between the valence band density of states in the strained alloy, relative to unstrained Si, to be in the range of 15 at high temperatures.

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