Ab-initio Calculations to Predict Stress Effects on Boron Solubility in Silicon

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Abstract

Stress effects on dopant diffusion and activation are of critical interest in current and future CMOS devices. Since experiments are very difficult to perform, we utilized *ab-initio* calculations to predict the effect of stress on B solubility. We find strongly enhanced solubility under compressive biaxial stress, whereas tensile biaxial stress leads to a reduction. In contrast to other work the enhancement/reduction is primarily due to the size effect of substitutional B. We compared our calculated B strain relaxation effect with various x-ray diffraction data, which shows excellent agreement. Measurements in different SiGe alloys also support our predictions.

1 Introduction

As ULSI devices enter the nanoscale, steep doping gradients and hetero-interfaces induce large stresses. On top of this, stress is induced purposefully to enhance carrier mobility [1]. The effect of stress on both dopant diffusivity and dopant activation are of major importance. Since experiments are difficult and in the case of boron (B) diffusion even lead to contradictory results [2], we utilize *ab-initio* calculations to predict B solubility under arbitrary strains, which is an extension of our previous work on stress effects on formation and migration of point-defects and B diffusion [3]. Our analysis extends beyond simple hydrostatic activation volumes [4] in order to predict anisotropies associated with more complex stress states.

The diffusion and clustering behavior of B in unstrained silicon has been studied extensively in the past. There exists broad agreement that B-I clusters (BICs) play an important role in the diffusion and activation behavior of B. The key to understand B behavior is to determine the energetics of these clusters. In addition to inverse modeling studies, *ab-initio* calculations have been conducted to determine the structure and formation energies of $\mathrm{B}_n\mathrm{I}_m$ clusters [5]. Multiple *ab-initio* calculations and inverse modeling results conclude that $\mathrm{B}_3\mathrm{I}$ is a key cluster which controls BIC kinetics (see [5]), while $\mathrm{B}_{12}\mathrm{I}_7$ is reported experimentally to be the building block of the SiB_3 phase [6]. Thus, we focus on the stress dependence of these clusters. Earlier work by Sadigh *et al.* [7] reports large B solubility enhancements under compressive biaxial stress primarily attributed to changes of the intrinsic Si carrier concentration n_i. However their analysis implicitly assumes non-degenerate Si, which is not a valid assumption in the B solubility limit. Under such high doping conditions an impurity band gets formed and Si becomes a degenerated semiconductor. In our analysis we assume the Fermi level to be at the valence band edge, which is a valid assumption for heavily B-doped Si.

2 Model

To predict stress effects on boron activation in current CMOS devices, the effects on intrinsic B diffusion, B transient enhanced diffusion (TED) and BIC kinetics need to be calculated. Previous work addressed the stress effects on B diffusion and TED [3]. In this paper we predict B solubility in silicon based on three key B complexes: B_s, $\mathrm{B}_3\mathrm{I}$, and $\mathrm{B}_{12}\mathrm{I}_7$ (see Fig. 2 (left)). In local equilibrium C_B can be expressed as a function of C_B^{tot} and the solubility can be predicted as $C_{ss} \approx C_\mathrm{B}$ for large enough C_B^{tot}. This solubility model depends only on the formation energies of the different $\mathrm{B}_n\mathrm{I}_m$ clusters and can be extended to arbitrary stress states once the stress effect on the formation energy is known. Following the methodology of Ref. [3], the energy of a $\mathrm{B}_n\mathrm{I}_m$ clusters in an arbitrary strain state can be written as a function of the elasticity tensor and induced strain:

$$E_{\mathrm{B}_n\mathrm{I}_m}(\vec{\epsilon}) = E_{\mathrm{B}_n\mathrm{I}_m}(0) + \frac{\Omega}{2}\left(\vec{\epsilon} - x\Delta\vec{\epsilon}_{\mathrm{B}_n\mathrm{I}_m}\right)\left(\mathbf{C}_\mathrm{Si} + x\Delta\mathbf{C}_{\mathrm{B}_n\mathrm{I}_m}\right)\left(\vec{\epsilon} - x\Delta\vec{\epsilon}_{\mathrm{B}_n\mathrm{I}_m}\right), \quad (1)$$

where Ω is the volume of the super-cell, $x = C_{\mathrm{B}_n\mathrm{I}_m}/C_S$ denotes the relative complex concentration, $\Delta\vec{\epsilon}_{\mathrm{B}_n\mathrm{I}_m}$ is the induced strain, and $\mathbf{C}_\mathrm{Si} + x\Delta\mathbf{C}_{\mathrm{B}_n\mathrm{I}_m}$ is the elasticity tensor of the super-cell. In this work, $x = 1/64$ since our super-cell contains 64 Si lattice sites. Thus, once the elastic constants and induced strains for a given equilibrium structure are known, the change in formation E_f can be calculated, which leads directly to modified equilibrium concentrations. For our calculations, we used the density functional theory (DFT) code VASP [8] with ultra-soft Vanderbilt type pseudo-potentials [9]. All calculations were performed in generalized gradient approximation (GGA) with a 64 atom super-cell, a energy cut-off of 340 eV and 2^3 Monkhorst-Pack **k**-point sampling. The rather large cut-off is necessary to reach convergence for B systems. All structures were fully relaxed to a maximal force of less than 0.005 $\mathrm{eV}/\text{Å}$ per atom. Convergence was tested for the B_s system. Further increasing the cut-off to 360 eV or increasing the **k**-point sampling to 3^3 lead to a change in $\Delta\epsilon$ less than 4%. In general convergence seems to be more sensitive to the cut-off selection than on the **k**-point sampling.

3 Results

Our calculated formation energies of $\mathrm{B}_3\mathrm{I}^-$ and $\mathrm{B}_{12}\mathrm{I}_7{}^=$ in unstrained Si are -0.58 eV and -5.88 eV respectively. These energies are in reference to B_s^- and pure Si. We assume $E_\mathrm{F} = E_\mathrm{V}$ as appropriate for heavily B-doped Si. We define the formation energy of a $\mathrm{B}_n\mathrm{I}_m$ clusters as $E_f^{\mathrm{B}_n\mathrm{I}_m} = E_{\mathrm{B}_n\mathrm{I}_m} - nE_\mathrm{B} - \left((n-1) - \frac{m}{N}\right)E_\mathrm{Si}$, where Si and B have N atoms, whereas $\mathrm{B}_n\mathrm{I}_m$ has $N + m$ atoms in the super-cell. To account for the change in formation energy due to stress, the elasticity tensors $\mathbf{C}$ and induced strains $\Delta\vec{\epsilon}$ are calculated for B_s, $\mathrm{B}_3\mathrm{I}$, and $\mathrm{B}_{12}\mathrm{I}_7$. Figure 1 (left) shows the energy vs. hydrostatic and uniaxial strain for the complexes of interest. Table 1 lists the extracted parameters. Substitutional B exhibits a rather large induced strain of -0.316. Due to this induced strain, the Si lattice parameter is a strong function of the B concentration. Figure 1 (right) shows a comparison of various experimental data with this work. Our calculated value agrees well with the experimental measurements. In the dilute limit, the change in formation energy of the various clusters can be derived using Eq. 1 as:

$$\Delta E_f^{\mathrm{B}_n\mathrm{I}_m} = -\Omega_0\left(\Delta\vec{\epsilon}_{\mathrm{B}_n\mathrm{I}_m} - n\Delta\vec{\epsilon}_{\mathrm{B}_s}\right)\mathbf{C}_\mathrm{Si}\vec{\epsilon} + \frac{\Omega_0}{2}\vec{\epsilon}\left(\Delta\mathbf{C}_{\mathrm{B}_n\mathrm{I}_m} - n\Delta\mathbf{C}_{\mathrm{B}_s} - m\mathbf{C}_\mathrm{Si}\right)\vec{\epsilon}. (2)$$

For small strains the linear strain term is dominant; however at 1% strain the quadratic term gives rise to contributions on the order of 15% of the linear term for large clusters

like $B_{12}I_7$. Equation 2 also indicates that large strain effects are expected for B rich clusters due to the relative induced strain $\Delta\vec{\epsilon}_{\mathrm{B}_n\mathrm{I}_m} - n\Delta\vec{\epsilon}_{\mathrm{B}_s}$. A similar effect also exists for the quadratic term due to $\Delta\mathbf{C}_{\mathrm{B}_n\mathrm{I}_m} - n\Delta\mathbf{C}_{\mathrm{B}_s} - m\mathbf{C}_{\mathrm{Si}}$.
In summary, our calculations predict strongly enhanced activation for compressive biaxial stress, while tensile biaxial stress reduces the B solubility and this increases sheet resistance. Figure 2 (right) shows the boron solubility as a function of biaxial strain for different temperatures. There is experimental evidence that B solubility is enhanced in compressively strained SiGe on Si films with increasing Ge content [10] in agreement with our calculations. This paper suggests that stress effects play a major role in modifying B solubility/segregation in SiGe in comparison to Si.

Complex	$\Delta\epsilon$	ΔC_{11} [GPa]	ΔC_{12} [GPa]
B_s	-0.316	-1371	621
B_3I	-0.299	-1517	681
$B_{12}I_7$	-0.236	-1308	793

Table 1: Induced strain $\Delta\epsilon$ and ΔC_{ij} for B_s, B_3I, and $B_{12}I_7$ extracted from Fig. 1 (left), assuming $C_{11}^{\mathrm{Si}} = 155$ GPa and $C_{12}^{\mathrm{Si}} = 55$ GPa for pure Si.

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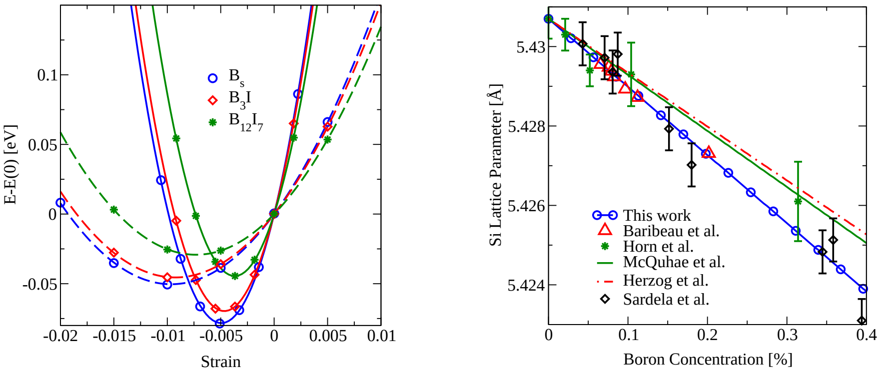

Figure 1: **Left:** Energy vs. hydrostatic (solid lines) and uniaxial strain (dashed lines) for B_s, B_3I, and $B_{12}I_7$. All energies are reported with respect to their values in unstrained Si. Due to the symmetry of the complexes ($x = y = z$) the induced strain $\Delta\epsilon$ is the shift of the minimum from $\epsilon = 0$ (unstrained Si) under hydrostatic strain. ΔC_{11} and ΔC_{12} are determined from the curvatures. The data shown corresponds to a 64 atom super-cell calculation. $\epsilon = 0$ response to the GGA Si lattice constant $a_{\mathrm{Si}} = 5.4578$ Å. The extracted values are listed in Table 1. **Right:** Comparison of experimental data [11] with our *ab-initio* results for the Si lattice parameter as a function of B concentration. Theoretically the Si lattice constant can be expressed in terms of the induced strain $\Delta\epsilon$ (see Table 1) of substitutional B and the fractional B concentration $x = C_{\mathrm{B}}/C_S$ as $a = (1 + x\Delta\epsilon)a_{\mathrm{Si}}$, where a_{Si} is the lattice parameter of bulk Si. $\Delta\epsilon = -0.316$ corresponds to a lattice contraction coefficient $\beta = 6.32 \cdot 10^{-24}$ cm^3. Sardela *et al.* report $\beta = (6.3 \pm 0.1) \cdot 10^{-24}$ cm^3 based on active B concentration. For other experiments, cluster formation at high B concentration may lead to lower strain levels.

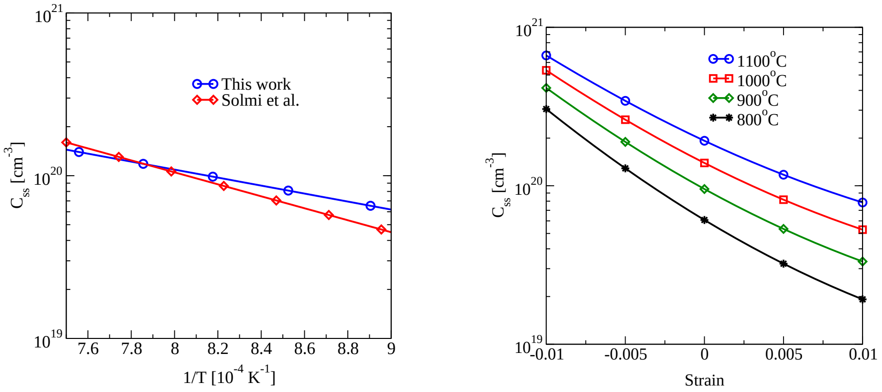

Figure 2: **Left:** Comparison of the boron solubility in unstrained Si as determined experimentally by Solmi *et al.* [12] with the simple solubility model used in this paper. Entropy factors were not calculated for the complexes in the model. To match the data at 1000°C an small entropy factor of $\Delta S = -1.17k$ was added. The temperature dependence of C_{ss} is matched well. **Right:** Predicted boron solubility as a function of biaxial strain for various temperatures. Positive strains are tensile.