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Stress influence on substitutional impurity segregation on dislocation loops in IV–IV semiconductors

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ABSTRACT

The influence of stress on the distribution of slow-diffusing substitutional impurities in the vicinity of a dislocation loop in Si and Ge bulk was theoretically investigated, at the atomic scale, using the Si and Ge Stillinger–Weber potentials via Monte Carlo and kinetic Monte Carlo simulations. The dislocation loop was modeled by an extra atomic plane introduced between two (1 1 1) planes. The calculations were performed at high temperature, for which impurity diffusion was enabled. The influence of atomic size effect on Cottrell atmosphere formation was investigated considering the difference of atomic volume between Si and Ge. The dislocation loop elastic field was found to prevent the accumulation of substitutional atoms in the vicinity of the dislocation. However, the calculations suggest that substitutional impurities can occupy interstitial sites close to the dislocation loop. In this case, the elastic field surrounding the dislocation loop can promote Cottrell atmosphere formation mainly if the impurity exhibits a larger atomic radius than the matrix atoms (Si or Ge).

1. Introduction

The understanding of point defect and extended defect interactions is of great interest in material science in order to improve material properties, such as plasticity in metallurgy technology [1–3], and to prevent material degradation during fabrication processes [4–6] and operations, such as when subjected to irradiations in nuclear energy technology [7–9]. For example, in microelectronics, the understanding of dislocation loops and Si self-interstitial interactions was shown to be crucial to understand dopant diffusion in Si after dopant implantation [10,11], and thus, for dopant distribution engineering [12]. In addition, atom probe tomography (APT) was used to experimentally observe, at the atomic scale, the distribution of different types of impurities such as B, As, P, and Ni in the vicinity of dislocation loops in Si [13–16]. These observations are very important since they provide information as to the effect of dislocation loops on impurity clustering and impurity-Si phase nucleation, which have direct impacts on semiconductor electrical properties. In microelectronic technology, dislocation loops are generally formed in the semiconductor after dopant implantation and activation annealing [17]. Depending on the implantation and annealing conditions, these dislocation loops can be located in (or close to) the doped region [18]. Surprisingly, APT observations showed similar behaviors for interstitial impurities (Ni atoms) diffusing at room temperature (T), and for substitutional impurities (B, P and As) diffusing at $T > 750$ °C. The impurities mainly accumulate at the border of the dislocation loop. In a previous work [19], the Si Stillinger–Weber potential (SW) and Monte Carlo simulations were used in order to investigate the stress distribution surrounding a dislocation loop in the Si lattice on substitutional sites and on interstitial sites, and to simulate the behavior of fast-diffusing interstitial impurities such as Ni. It was shown that in the vicinity of the dislocation loop, the majority of substitutional sites are under compression and preventing atomic accumulation, while interstitial sites located at the border of the dislocation loop exhibit lower pressures and promote atomic accumulation at the edges of the dislocation loop. Thus, fast-diffusing interstitial impurities such as Ni and Cu are expected to accumulate at the edge of Si dislocation loops forming Cottrell atmospheres, as observed experimentally [16]. However, in the case of substitutional impurities such as B and As diffusing at temperatures allowing for precipitation and phase formation in Si, Cottrell atmospheres are not expected to form on Si dislocation loops. Consequently, in the case of substitutional impurities, the experimental observations [13–15] may be explained by either impurity site exchange in the vicinity of the dislocation loop, impurities initially on substitutional sites far from the dislocation occupying interstitial sites close to the dislocation, or by a regular segregation controlled by the difference

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between Si and impurity dangling bond energies, prevailing on elastic energy [20–22]. The calculations also showed that, due to the long-range Coulomb interactions, impurity accumulation on dislocations can occur only if the impurities do not carry the same charge [19]. Thus, fast-diffusing species should not be in their usual ionized states (on interstitial sites [23]) and dopants should not be in their usual activation states (on substitutional sites [24]) when segregating on the dislocation loop.

The goal of the present work is to better understand the behavior at the atomic scale of substitutional impurities in the vicinity of Si dislocation loops. In particular, the simulations aim to investigate (i) whether substitutional impurities can segregate on dislocation loop edges or migrate to interstitial sites in the vicinity of dislocation loops to form Cottrell atmospheres due to elastic energy minimization; and (ii) whether there is a behavior difference between impurities exhibiting a small atomic radius (r) and those exhibiting a large atomic radius compared to the atomic radius of the matrix atoms (size effect). With this aim, it was chosen to study the diffusion of Ge solute atoms in the vicinity of an Si dislocation loop and of Si solute atoms in the vicinity of a Ge dislocation loop. The Si–Ge system corresponds to an ideal solid solution (no compound formation), Si and Ge atoms occupying the substitutional sites of a same diamond lattice over the entire domain of mixing composition. The charge effects can be neglected as Si and Ge atoms have the same valence electron number. Consequently, the energy variations from one atomic site to another are expected to be mainly related to elastic energy variations. In addition, the diffusion kinetics of Si in Ge and Ge in Si are comparable to the diffusion kinetics of substitutional impurities dissolved in Si or Ge. Finally, the SW potential parametrizations for Si and Ge have been investigated in numerous works, allowing for the use of well-known Si and Ge SW potentials that have already been proven reliable in previous calculations. Thus, the Ge–Si system should allow the stress contribution to be investigated independently of the chemical effect also involved in case of dopant segregation on Si (or Ge) dislocation loops. For example, in the case of tetrahedral covalent chemical bonds, B atoms can be considered as 'small' atoms in Si ($r_{Si} \sim 0.117$ nm) with $r_B \sim 0.088$ nm and $\Delta r = r_B - r_{Si} = -0.029$ nm, whereas As atoms can be considered as 'large' atoms in Si with $r_{As} \sim 0.118$ nm[24] and $\Delta r = +0.001$ nm. In addition, the chemical interactions between Si and B or As can be estimated in a simple manner by means of the parameter $V^{AB} = ½(\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB})$, which gives the tendency and the strength of phase separation ($V^{AB} < 0$) and compound formation ($V^{AB} > 0$) between the A and B elements, with ε_{AA}, ε_{BB}, and ε_{AB} being the A–A, B–B, and A–B atomic pair energy, respectively [19,25,26]. Considering the simple model of a random A–B binary solid solution on a diamond lattice, and the experimental formation energy of the compounds SiB_6 (~ -1.254 eV at^{-1} [27]) and SiAs (~ -0.056 eV at^{-1} [28]), one can deduce $V^{SiB} \sim +5.12$ eV at^{-1} and $V^{SiAs} \sim +0.11$ eV at^{-1}. For the Si–Ge system, $\Delta r = +0.005$ nm in the case of Ge atoms ($r_{Ge} \sim 0.122$ nm [24]) diluted in Si and $\Delta r = -0.005$ nm in the case of Si atoms diluted in Ge, with $V^{SiGe} = 0$. Thus, the stress effect investigated in the Si–Ge system is expected to be overestimated compared to both cases, As and B atoms in Si. This is particularly true for B atoms, since the size difference between B and Si atoms is significantly larger than between Si and Ge atoms ($\sim$6 times), while the chemical interactions between B and Si are particularly high ($\sim$50 times the Si–As interactions).

As for a previous work [19], the dislocation loop (DL) was modeled as an additional plane of finite size inserted between two (1 1 1) planes in either the Si or the Ge lattice. The SW potential was used to relax the Si or the Ge lattice with the DL, using the Monte Carlo (MC) technique. After relaxation, the same potentials were used to calculate the energy and the hydrostatic pressure for each atomic site in the crystals. Finally, the calculated energies were used to simulate, by kinetic Monte Carlo (KMC), the diffusion of Ge atoms in the Si lattice and of Si atoms in the Ge lattice, allowing for atomic jumps on substitutional and interstitial sites, using the relaxed lattice containing the DL as a rigid lattice. Compared to the previous calculations that aimed to investigate interstitial impurity accumulation on Si DL [19], in this work: (i) the DL size was increased from 3 nm (61 atoms) to 5 nm (183 atoms) leading to an increase of the simulation cell from 16,189 to 32,768 atoms, (ii) in addition to substitutional (S) and tetrahedral interstitial (TI) sites, the hexagonal interstitial (HI) sites were also considered in the Si and Ge lattices, (iii) the diffusion of substitutional impurities occurring at temperatures for which $T/T_m \sim 0.7$ (with T_m being the melting temperature of Si or Ge) [29], lattice relaxation and impurity diffusion were performed at $T = 1173.15$ K for Si and $T = 873.15$ K for Ge, instead of 10 K in the previous work [19], and (iv) all the atomic interactions were calculated using the Si–Si, Ge–Ge, and Si–Ge SW potentials using the cut-off distance corresponding to the specified potential parametrization, instead of considering first-neighbor atomic pair energies in the case of metallic atom and Si atom interactions in the previous study.

We show that: (i) at high temperature, the pressure distribution on atomic sites surrounding the DL is less uniform, and the range of the DL stress effect on substitutional and interstitial atomic sites is reduced (two to three atomic planes), decreasing the segregation tendency of impurities on the DL, (ii) single S impurities can reach the DL but cannot accumulate on the DL due to high compression stress, (iii) if the impurities can change from S to TI sites, they can accumulate on both the DL plane and the DL edges, (iv) the DL stress effect is more pronounced for atoms having an atomic radius larger than that of the matrix atoms, the accumulation tendency on the DL of impurities occupying TI sites being significantly reduced in the case of 'small' impurities, and (v) despite the well-known overestimation of interstitial atom energy by the SW potential [26], the present calculations show that S impurities can occupy TI sites located at the border of a DL. These results suggest that the experimental observations of As accumulation at Si DLs edges [13,14] could be explained by the formation of Cottrell atmospheres resulting from the change of As atomic site occupancy from substitutional sites (far from the DLs) to interstitial sites in the vicinity of the DLs. However, atom probe tomography observations of B accumulation at Si DL edges [15] appear to be more difficult to explain only by the stress effect, even if B atoms occupy interstitial sites close to the DLs, since 'small' interstitial atoms are expected to be significantly less influenced by the elastic field surrounding Si DLs at high temperatures. Due to the strong Si–B chemical interactions, the reason for B accumulation on Si DL edges could be more easily explained by a regular segregation due to B–Si bonding and/or due to charge effects (Coulomb interactions) between B atoms (acceptors in Si substitutional sites) and the DL, not taken into consideration in the present calculations.

2. Computational procedure

2.1. Si and Ge Stillinger–Weber potentials

The SW potential has been extensively used to model Si, Ge, and SiGe properties at the atomic scale. However, depending on the goal of the calculations, different parametrizations have been proposed [31–40]. In our case, vacancies were not considered since first-neighbor atomic exchanges were performed on a fully occupied and rigid lattice. Thus, as the simulations focused on modeling substitutional and interstitial atom interactions with a DL created as an interstitial plan inserted between two (1 1 1) planes [10,17], the choice of the SW parameters was mainly based on the properties of the simulated interstitial point defects. The formation energies of interstitial defects were calculated using Eq. (1):