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Theoretical investigation of Cottrell atmosphere in silicon

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Abstract

The distribution of fast-diffusing interstitial impurities (Ni, Cu, etc.) in the vicinity of a dislocation loop in Si bulk is theoretically investigated, at the atomic scale, using the Si Stillinger–Weber potential via Monte Carlo and kinetic Monte Carlo simulations. The Si dislocation loop is modeled by an extra Si plane introduced between two Si(1 1 1) planes. Interstitial impurities are shown to gather on the dislocation loop edges only, in interstitial sites of minimum pressure. These results are in agreement with experimental atom probe tomography observations related to Ni accumulation on Si dislocation loops, and can be interpreted as a Cottrell atmosphere.

Keywords: Silicon; Dislocation; Segregation; Cottrell atmosphere; Simulation

1. Introduction

Impurity segregation has been extensively studied on metallic surfaces [1–3] and metal grain boundaries (GBs) [4]. At the surface, three major driving forces have been shown to pilot the segregation of an impurity A in a matrix made of B atoms [3]:

(i) The strongest force is the dangling bond (or surface) energy difference between the pure elements A and B, promoting the segregation of the lower energy element.
(ii) The second force controlling segregation is the tendency of the A–B binary system to form homoatomic or heteroatomic chemical bonds between neighboring atoms, which can be quantified using the parameter $V = ½\ (\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB})$, with ε_{AA} the A–A pair energy, ε_{BB} the B–B pair energy and ε_{AB} the A–B pair energy ($\varepsilon_{ij} < 0$): if $V > 0$ the A–B system promotes the formation of ordered A–B compounds (heteroatomic chemical bonds), while if $V < 0$ the A–B system promotes phase separation between A and B (homoatomic bonds), and impurity segregation is promoted in the case of $V < 0$ (phase separation).
(iii) The last force controlling impurity segregation is related to the size mismatch between A and B atoms, a larger impurity in a matrix of smaller atoms segregates; however, segregation is less promoted in the case of a small impurity within a matrix of bigger atoms.

In addition, the stress field has an important effect on atomic segregation. For example, Monte Carlo simulations of solute segregation in grain boundaries showed that highly stressed regions are more likely to be occupied by atoms exhibiting lower elastic moduli [5]. Consequently, the segregation energy of an impurity in a given matrix is composed of two terms, a chemical term grouping both the effects of dangling bond energy and of phase separation, and an elastic term due to atomic size-mismatch and possible stress field influence, atomic segregation being mainly controlled by chemical bond (or dangling bond) energy.

Following these considerations, the segregation of small atoms exhibiting weak interactions with the matrix atoms

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should not be promoted at the surface. However, the situation can be more subtle at grain boundaries [5,6]. Accumulation of small interstitial impurities on defects such as dislocations was first predicted [7], and then recently observed thanks to atom probe tomography (APT) [8–14]. This phenomenon was explained by Cottrell and Bilby in the late 1940s [7] (before it was actually observed at the atomic scale) considering only the influence of the elastic field surrounding the defect. Cottrell and Bilby introduced the concept of "atmosphere" to describe the tiny clouds of interstitial impurities that can be found decorating dislocations in crystals. Cottrell atmosphere is specifically used to describe the behavior of interstitial C and N in the vicinity of Fe dislocations, which has a significant effect on the mechanical properties of iron, since it was predicted to be able to pin dislocations, leading to a decrease of the metal plasticity.

Cottrell atmosphere modeling has been mainly performed in metals, generally using continuum models to describe dislocation's elastic field [15–18]. Its application in the metallurgy industry is of crucial importance, since its control allows the production of various steels, exhibiting various mechanical properties. Recently, thanks to the development of laser-assisted APT, the accumulation of impurities on dislocations has been also observed in semiconductors [12–14]. However, despite the authors' assertion [12,14], the accumulation of some of the impurities on Si dislocations does not appear to be related to Cottrell atmosphere. For example, B [14], As [12,13] and P [13] do not occupy interstitial sites in Si, but instead are substitutionally dissolved in Si. Their diffusion coefficients in Si are among the slowest (compared to other impurities such as Au or Cu), as their diffusion mechanism is not direct interstitial [19], and their interaction with Si is attractive (compound formation, $V > 0$) [20]. Consequently, their accumulation on Si dislocation loops can be due to conventional segregation, mainly piloted by atomic chemical bond energy (phase formation occurs at diffusion temperatures). In contrast, the observations of Hoummada et al. [21], concerning Ni accumulation on Si dislocation loops at room temperature, can correspond to Cottrell atmosphere, since Ni occupies interstitial sites and uses the direct interstitial diffusion mechanism in Si. Ni diffusion in Si is ~10 orders of magnitude faster than Si self-diffusion [22], which allows the interactions between the interstitial Ni atoms and the lattice Si atoms to be neglected.

Ni Cottrell atmosphere in Si can be of significant influence during the fabrication process of Si-based transistors, since it has been shown that the formation of Cottrell atmospheres (usually at low T) precedes phase nucleation (higher T) on defects [15,23]. Indeed, Ni is a common contaminant in Si-based microelectronics (as it is used for contact fabrication [24], and has a non-negligible diffusion at room temperature: diffusion length $\sim 6\ \mathrm{nm\ h^{-1}}$ [25]), and Si doping is performed via atomic implantation, involving the formation of defects such as dislocation loops [21,26,27]. For example, the encroachment phenomenon, which is related to the uncontrolled formation of Ni-silicide clusters in the transistor's channel, is a current problem for low-dimension (<45 nm) transistor production [28].

The goal of the present work is to study, theoretically, at the atomic scale, the distribution of fast-diffusing interstitial impurities (such as H, Ni, Fe, Cu, Mn, Cr and Co) in the vicinity of a dislocation loop in Si bulk, and to compare the theoretical results with the experimental APT measurements. With this aim, a dislocation loop was modeled as an additional plane of finite size inserted between two (1 1 1) planes in the Si diamond lattice. The Si Stillinger–Weber (SW) potential [29] was used to relax the Si lattice with the dislocation loop, using the Monte Carlo (MC) technique. After relaxation, the same potential was used to calculate the energy of each lattice and interstitial site in the crystal, and the hydrostatic pressure on each of these sites was calculated. Finally, the calculated interstitial site energies were used to simulate the diffusion of an interstitial impurity, thanks to the kinetic Monte Carlo (KMC) technique, using the relaxed lattice containing the dislocation loop as a rigid lattice. We show that interstitial atoms decorate only the edges of the dislocation loop, forming a ring-shape distribution as observed experimentally for interstitial Ni. This distribution is in agreement with the pressure variations located in the vicinity of the dislocation loop, and thus corresponds to a Cottrell atmosphere: high pressure regions are free of interstitial impurities, while diffusing atoms gather in low pressure regions. In contrast, chemical interactions between interstitial atoms are shown to promote impurity accumulation on both sides of the dislocation plane. The elastic field surrounding the dislocation loop is not symmetrical along the direction perpendicular to the dislocation plane, and expands up to 4–5 atomic planes on the interstitial lattice in this direction. The interstitial sites located on both sides of the dislocation plane exhibit a high compression stress, which drives interstitial atoms away from the dislocation, preventing the impurities from clustering on the dislocation plane, and leading to the formation of a shell free of impurities all around the dislocation loop. In contrast, in the direction along the dislocation plane, the elastic field is symmetrical, and its effect vanishes rapidly from the dislocation edge. It is from this location that interstitial atoms can reach the dislocation plane by diffusion, and thus decorate the dislocation edges.

2. Computational procedure

2.1. Si dislocation loop relaxation

Dislocation loop formation in Si bulk is known to result from self-interstitial atom precipitation, especially during Si recrystallization following atom implantation [21,26,27]. These dislocation loops are generally made of one or two extra atomic planes located between two Si(1 1 1) planes of the diamond lattice [26,27]. In order to match as closely as possible transmission electron microscopy [21,26,27] and APT experimental observations [21]