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Ab initio analysis of a vacancy and a self-interstitial near single crystal silicon surfaces: Implications for intrinsic point defect incorporation during crystal growth from a melt

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The microscopic model of the Si (001) crystal surface was investigated by first principles calculations to clarify the behavior of intrinsic point defects near crystal surfaces. A $c(4 \times 2)$ structure model was used to describe the crystal surface in contact with vacuum. The calculations show lower formation energy near the surface and the existence of formation energy differences between the surface and the bulk for both types of intrinsic point defects. The tetrahedral (T)-site and the dumb-

bell (DB)-site, in which a Si atom is captured from the surface and forms a self-interstitial, are found as stable sites near the third atomic layer. The T-site has a barrier of 0.48 eV, whereas the DB-site has no barrier for the interstitial to penetrate into the crystal from the vacuum. Si atoms in a melt can migrate and reach at the third layer during crystal growth when bulk diffusion coefficient is used. Therefore, the melt/solid interface is always a source of intrinsic point defects.

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1 Introduction Grown-in defects in Czochralski (CZ) and Floating Zone (FZ) Si single crystals have been investigated intensively during the last decades, focusing on the behavior of intrinsic point defects in view of their importance with respect to device and crystal quality. It is widely accepted that the type and concentration of the dominant intrinsic point defect after crystal growth depends on the ratio V/G , where V is the crystal pulling rate and G is the longitudinal temperature gradient near the melt/solid interface. This model was proposed by Voronkov in a study on defect formation during FZ crystal growth [1]. A distinct difference between the grown-in defect type and distribution inside and outside the so-called stacking fault ring (R-OSF) region was observed in CZ Si single crystals [2]. Considering the Voronkov model, it is also widely accepted that vacancy-related defects are distributed inside the R-OSF while self interstitial-related defects are formed outside the R-OSF. Grown-in defects nucleate and grow in a narrow temperature range of about 30 °C around 1100 °C due

to a rapid agglomeration and diffusion of vacancies [3]. Several critical values of V/G obtained experimentally and theoretically have been reported [4–6]. By optimizing the design of the hot zone in the crystal puller and by controlling the axial and radial V/G within a critical range during crystal growth, “perfect silicon” polished wafers, containing no measurable grown-in defects due to clustering of intrinsic point defects have been developed [7]. Nowadays, perfect silicon wafers of 200 and 300 mm diameter are widely used in industry. During these improvements of crystal quality, macroscopic (or continuum) simulation models that calculate the nucleation and growth of void defects or dislocations during crystal growth were developed [8–10].

Recently, the validity of the Voronkov model is being re-examined by considering also the source of intrinsic point defects during crystal growth. In the macroscopic simulations based on the Voronkov model, there has indeed always been a difficulty to determine the concentrations of the intrinsic point defects at the growing crystal surface. As

boundary condition, the local concentration of vacancies was always considered to be higher than that of Si interstitials. These concentrations were usually obtained by fitting them as parameters to adjust the predicted defect behavior to the observed as-grown defect distributions after crystal growth [11]. Nevertheless, the origin of the intrinsic point defects was not considered in detail. From a crystallographic view point, vacancies and interstitials were thought to be generated at the surface, and to diffuse from there into the bulk but the detailed mechanism was unclear. Hence, these values were also interpreted as the “thermal equilibrium bulk values at the melting point”. Abe assumed that a vacancy source was dominant at the melt/solid interface, based on crystal detaching experiments in which the anomalous oxygen precipitation (AOP) was always found near the melt/solid interface during subsequent thermal treatments [12]. Oppositely, it was quantitatively demonstrated that compressive stress can move the balance of point defects toward a dominance of the self-interstitial [13]. These two examples illustrate the lack of quantitative models describing the generation of point defects at the melt/solid interface on a microscopic scale.

In the previous paper [14], the properties of vacancies and self-interstitials near Si (001) surfaces were studied using first principles calculations. In these calculations, only the interaction of point defects with the Si single crystal surface in contact with vacuum was considered. For self-interstitials, the possible paths of a Si atom from the vacuum into the surface region of the Si single crystal were investigated. For the different possible paths, both the stability in each site for different depths below the surface and the barrier height for point defect diffusion were calculated. Then, the vacancy and interstitial formation energies were estimated to evaluate the possibility to form them at the surface/interface.

Based on these results, an actual scheme of the incorporation of point defects near the melt/solid interface during crystal growth will be proposed in this paper. The key issue is to compare crystal growth rate and migration velocity in the transient layers near the melt/solid interface.

2 Finding paths for a Si atom from the surface As a starting model, a model of the Si (001) surface was constructed consisting of $c(4 \times 2)$ structures as shown in Fig. 1(a). In this model, the bulk part of the crystal is cut at the 12th atomic layer from the surface, and the dangling bonds of atoms in that layer are terminated by hydrogen atoms. The detailed conditions for the calculation were described in a previous paper [14]. After the geometrical optimizations, possible paths for a Si atom from the vacuum above the surface into the bulk of the crystal were explored, thus simulating the creation and movement of a self-interstitial. Taking the symmetry of the model in consideration, only a limited region shown as dotted line in Fig. 1(b) was considered. This region of about

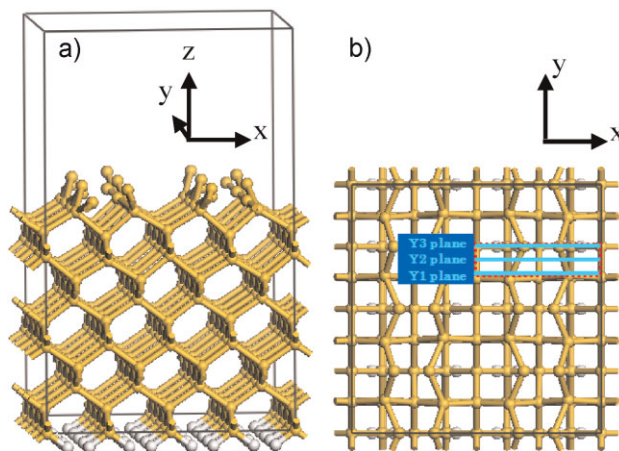


Figure 1 (online colour at: www.pss-a.com) A model of the $c(4 \times 2)$ structure of the Si (001) surface used in this study. The bulk region is cut at the 12th atomic layer from the surface, and the dangling bonds of the Si atoms in that layer are terminated by hydrogen atoms (white colour); (a) Bird's-eye view, (b) XY-plane view.

$5.82 \text{ \AA} \times 9.70 \text{ \AA} \times 1.34 \text{ \AA}$ was divided into $8 \times 3 \times 16$ by each coordinate. For each of the possible positions of the starting model, a trial Si atom was added and the total energy was calculated. Then, three Y-planes were drawn (Y1, Y2, and Y3 as shown in Fig. 1(b)) with energy maps to determine the lower energy paths. The geometrical optimizations were performed again for the models with a Si atom in the obtained positions.

The tetrahedral (T)-site and the dumbbell (DB)-site, in which a Si atom is able to be captured from the surface to form a self-interstitial, were found as stable sites near the third atomic layer [14]. The T-site has a barrier of 0.48 eV, whereas the DB-site has no barrier for the interstitial to penetrate into the crystal from the vacuum [14].

3 Point defect formation near the surface Using the starting model, mono vacancy models were constructed by removing one Si atom from each layer [15]. Then, geometrical optimizations were again performed and calculated the total energy $E(\text{Surf} + V \text{ at } N_{\text{th}})$ for each mono vacancy model. As to self-interstitial models, DB sites were also examined as an initial position for geometry-optimization to seek stable positions in deeper regions than the third layer, after which the total energy $E(\text{Surf} + I \text{ at } N_{\text{th}})$ was calculated.

4 Estimation of vacancy and self-interstitial formation energies near the crystal surface To estimate the formation energy of a vacancy in the near surface region shown in the surface model of Fig. 1, the total energy of a 64 Si cell (bulk model) $E(\text{Si}_{64})$ was calculated to estimate the self-energy of a Si lattice atom. Consequently, using the total energy of the surface model $E(\text{Surf})$, the

formation energy of the vacancy in the N_{th} atomic layer $E_f^{Surf,V at N_{th}}$ can approximately be written as

$$E_f^{Surf,V at N_{th}} = [E(Surf + V at N_{th}) - E(Surf)] + \frac{1}{64}E(Si_{64}). \quad (1)$$

This can be interpreted as the energy needed for the transfer of a vacancy from the 64 Si cell to the near surface. If the self-energy is calculated at a finite temperature (T), in particular at the melting point of Si, this formation energy will become an indicator of the degree of ease to form a vacancy at the melt/solid interface when pulling a crystal. $E(Si_{64})$ is also calculated by first principle molecular dynamics (MD) in a normal temperature and pressure ensemble condition for a finite temperature.

In case of the self-interstitial, the formation energy of an interstitial in the N_{th} layer $E_f^{Surf,I at N_{th}}$ is also approximately written as

$$E_f^{Surf,I at N_{th}} = [E(Surf + I at N_{th}) - E(Surf)] - \frac{1}{64}E(Si_{64}). \quad (2)$$

The second term in (1) and (2), is about -107.35 eV at $T = 0$ K, -107.20 eV at $T = 1700$ K, -106.70 eV at $T = 2000$ K, and -106.30 eV at $T = 5000$ K, which are the energies obtained after 200 MD cycles. After this number of MD cycles, the energy of the cell is not yet stable, but is stable enough to obtain a rough estimate of the correction of the self-energy for a finite temperature around the melting point. Using (1), (2), and these corrections, the dependence of formation energy of point defects on the depth are shown in Fig. 2(a) and (b), respectively.

5 Discussion The most important result in Fig. 2 with respect to Si crystal growth from a melt is the existence of formation energy differences between the surface and the deeper region for both types of point defects. This supports a macroscopic model whereby the recombination of a vacancy and a self-interstitial is a much more important process deeper than the fourth layer into the bulk of the crystal than closer to the surface and that the near surface layers thus act as a reservoir/source of intrinsic point defects. Although the melt/solid interface is most probably quite different from the crystal surface on which the results so far were obtained, one can assume that boundary conditions for the point defect concentrations at the interface for crystal growth from the melt in continuum simulations can be set at fixed values like “thermal equilibrium values at the melting point”. When discussing “thermal equilibrium” values of intrinsic point defect concentrations, one should therefore take into account the contribution from the melt/solid interface, as explained below.

Figure 2 illustrates the lower formation energy of the vacancy and the self-interstitial at the surface, too. Hence, the thermal equilibrium concentrations of intrinsic point

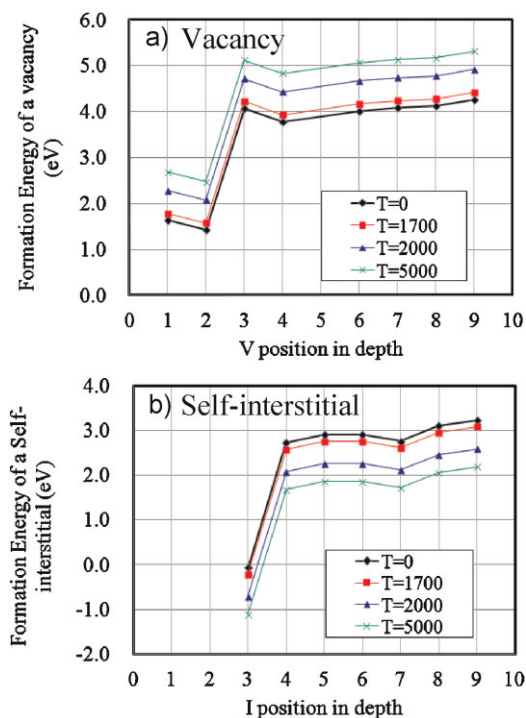


Figure 2 (online colour at: www.pss-a.com) Estimated formation energy of point defects in each layer for various temperatures of 64 Si cell in MD simulation [14].

defects near the surface are expected to be higher than in the bulk. The microscopic mechanism which lowers the formation energy of a vacancy is the decrease of the number of dangling bonds by moving and binding of atoms with dangling bonds. At the free surface in contact with vacuum, the atoms can move easily even at $T = 0$ K, compared with atoms in a bulk. A similar phenomenon will most probably also occur at the melt/solid interface. Once a vacancy is formed in the first layer, it can easily transfer to the second layer as there is no diffusion barrier between the two layers [14]. In some cases, a vacancy in the first layer does not transfer to the second layer but annihilates with an interstitial coming from the melt or from the bulk of the crystal.

A vacancy in the second atomic layer will be transported to the bulk automatically when the crystal growth continues and extra Si atoms supplied from the melt form an additional crystal layer at the top surface (which becomes a new first layer). The region just below the surface tends thus to have a higher concentration of vacancies than the equilibrium concentration inside bulk crystals at a given temperature. Many vacancies, which were transported to go up the energy slope or released in the bulk by crystal growth, diffuse back to the surface due to the formation energy slope in Fig. 2(a) or annihilate by recombination with a self-interstitial. According to the same mechanism, a self-interstitial transported to go up the energy slope or released in the bulk by crystal growth will also diffuse back to the surface or annihilate by recombination. This is, however, the

Table 1 Diffusion parameter comparisons of self-interstitial.

pre-factor (cm ² /s)	activation energy (eV)	diffusion coefficient <i>D</i> (cm ² /s)	ref.
6.55×10^{-2}	0.84	2.07×10^{-4}	[13]
2.37×10^{-1}	0.94	3.86×10^{-4}	[16]
6.63×10^{-3}	0.55	1.53×10^{-4}	[11]

only case when the self-interstitial atoms can reach at the T or DB-site of the third layer after going through the first and second layers. If the Si atoms coming from the melt pile up at the space for interstitial atoms around the first and second layers, they will disturb the normal stacking of atoms in the growing crystal and may lead to dislocation nucleation. Piled-up mono-vacancies in the first or second layer on the other hand will not lead to dislocation formation because there are sufficient bonds available at the atoms surrounding the vacancy to accommodate the next arriving Si atom in its appropriate position in the growing crystal. The formation energies of self-interstitials at the first or the second layer are expected to be as low as that of the third layer, however, the Si atoms coming from the melt cannot stay there and go through quickly. This Si atom diffusion and growth of the crystal must actually occur in parallel. Hence, one has to compare the migration velocity with the growth rate to understand the behavior of self-interstitials close to the melt/solid interface.

We used the bulk diffusion parameter sets in Table 1 to analyze the behavior of self-interstitials close to the melt/solid interface during crystal growth. A wide range of pre-factors and activation energies of the diffusion can be found in literature, however, the diffusion coefficient *D* at the melting point is in the range of $1.5\text{--}4.0 \times 10^{-4}$ cm²/s. A migration time for three layers (0.41 nm) is estimated at 9.2×10^{-14} min, even if minimum bulk diffusion coefficient is used. Assuming even an unrealistic crystal growth rate of 100 mm/min., the number of growing layer within this span is much smaller than one atom layer ($\sim 6.7 \times 10^{-4}$). A Si atom can reach at third layer and melt can be always a source of intrinsic point defects.

6 Conclusions Vacancies and self-interstitials have lower formation energies near the free surface. The existence of formation energy differences between the surface and the bulk for both types of intrinsic point defects supports a

macroscopic model in which the recombination of vacancies and self-interstitials is more important inside the bulk than at the surface. This also supports the idea that boundary conditions of the point defect concentrations at the surface in simulations can be set at fixed values, which used to be considered as bulk thermal equilibrium values. Si atoms can migrate and reach at the third layer during crystal growth from a melt when bulk diffusion coefficient is used. Therefore, melt can be always a source of intrinsic point defects.

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