A study on density functional theory of the effect of pressure on the formation and activation enthalpies of intrinsic point defects in growing single crystal Si

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1 Introduction

In 1982, Voronkov presented a model describing point defect behavior during the growth of single crystal Si from a melt and derived an expression to predict if the crystal was vacancy- or self-interstitial-rich [1]. Recently, Vanhellemont claimed that one should take into account the impact of compressive stress introduced by the thermal gradient at the melt/solid interface by considering the hydrostatic pressure dependence of the formation enthalpy of the intrinsic point defects [2]. To evaluate the impact of thermal stress more correctly, the pressure dependence of both the formation enthalpy ($H_f$) and the activation enthalpy ($H_a$) of the intrinsic point defects should be taken into account. Furthermore, growing single crystal Si is not under hydrostatic pressure but almost free of external pressure (generally in Ar gas under reduced pressure).

In the present paper, the dependence of $H_f$ and $H_a$ on the pressure $P$, or in other words, the pressure dependence of the formation energy ($E_f$) and the relaxation volume ($v_r$), is quantified by density functional theory calculations. Although a large number of ab initio calculations of the properties of intrinsic point defects have been published during the last years, calculations for Si crystals under pressure are rather scarce [3].

For vacancies $V$, the reported pressure dependencies of $H_f^V$ are inconsistent [4,5].

The thermal stress in growing single crystal Si is compressive, and is not external but internal stress. Therefore, the point defects are under internal pressure. To estimate the impact of thermal stress on intrinsic point defects in growing Si, the differences in the formation volumes of point defects under hydrostatic pressure and under internal pressure should be considered [6]. Taking this into account, we estimated the impact of thermal stress on $V_{0,m}$ by using DFT results.

2 Calculation Details

In the present work, DFT calculations were performed within the generalized gradient approximation (GGA) for electron exchange and correlation, using the CASTEP code [7]. The wave functions were expanded with the plane waves, and the ultra-soft pseudo-potential method was used to reduce the number of plane waves. The cutoff energy was 340 eV. The expression proposed by Perdew et al. [8] was used for the exchange-correlation energy in the GGA. Periodic boundary conditions were used with cubic supercells of 216 atoms for calculations of perfect and defect-containing Si crystals. k-point sampling was performed at 2×2×2 special points in a Monkhorst-Pack grid [9].

The reference point in this study was the perfect Si crystal. The pressure $P$ in cubic cells with different volumes was determined by fitting the total energy for different volumes to a Birch-Murnaghan equation of state [10]. The pressures $P$ in cubic cells with different volumes were also obtained analytically with the method by Nielsen and Martin [11].

Similar calculations were performed with cubic supercells containing point defects. In single crystal Si, the thermal equilibrium concentrations of self-interstitials $I$ and vacancies $V$ even near melt temperature, are well below $5 \times 10^{17}$ cm$^{-3}$. For such low concentration, the calculation cells should be surrounded by perfect cells. These perfect Si crystals should deform isotropically under the hydrostatic pressure. Therefore, we imposed the cubic shape for the defect-involving calculation cell. In each case, the supercells were set at a particular cubic volume and the ionic coordinates were fully relaxed to build up a list of energy-pressure-volume data points by using the analytically obtained $P$. In the present study only neutral point defects were considered.

For the self-interstitial, the two lowest energy configurations, i.e. the [110] dumbbell (D) and the tetrahedral (T) sites were calculated. It is well known that, for neutral $I$, the [110] D-site is the lowest-energy configuration while the T-site is the transition state. A vacancy was introduced by eliminating one Si atom located around the center of each supercell. Further details of the point defect configurations considered in this study will be commented on later. The energy-pressure-volume data of perfect and defect-involving cubic cells were used to find the relationship between pressure $P$ and (1) formation energy $E_f$, (2) relaxation volume $v_r$, and (3) formation enthalpy $H_f$.

3 Results and discussion

In case of the hydrostatic pressure $P_h$, Fig. 1 above shows the calculated formation enthalpy $H_f^H$ at the [110] dumbbell site (most stable). For self-interstitials, $H_f^I$ and $H_f^D$ are given by $H_f^I = 3.425 - 0.057xP_h$ (eV) and $H_f^D = 0.981 - 0.039xP_h$ (eV), respectively, with $P_h$ given in GPa. Fig. 1 below shows the calculated formation enthalpy $H_f^1$ for Jahn-Teller distortion (h-JT, most stable) of vacancies $V$. The calculated $H_f^D$ and $H_f^I$ dependencies on $P_h$ given by $H_f^D = 3.543 - 0.019xP_h$ (eV) and $H_f^I = 0.249 + 0.018xP_h - 0.037xP_h$ (eV), respectively. These results indicate that, when assuming that the pre-factors in the Arrhenius equation are not influenced, hydrostatic pressure up to 1 GPa leads to a slight increase of the thermal equilibrium concentration and diffusion of vacancies but this increase is much smaller than that of self-interstitials.

In case of the internal pressure $P_m$, Fig. 2 shows the changes in formation enthalpies $\Delta H_f^H$ for D-site (most stable) and T-site (transition state) of self-interstitials $I$, and $\Delta H_f^I$ for Jahn-Teller distortion (h-JT, most stable) and split-V (transition state) of vacancies $V$ due to internal pressure $P_m$. We found that the $H_f^I$ of $I$ increases while the $H_f^D$ of $V$ decreases with the increase in $P_m$. The calculations lead to the dependencies of $H_f^I$, $H_f^D$, and $H_f^I$ on $P_m$ given by $H_f^I = 3.425 + 0.070xP_m$ (eV) and $H_f^D = 0.981 - 0.038xP_m$ (eV), respectively, with $P_m$ given in GPa. The calculated $H_f^I$ and $H_f^D$ dependencies on $P_m$ given by $H_f^I = 3.543 - 0.160xP_m$ (eV) and $H_f^I = 0.249 - 0.026xP_m$ (eV), respectively. These results indicate that compressive thermal stress leads to increases in the equilibrium concentration and diffusion of $V$ and to a decrease in the equilibrium concentration of $I$. By the recombination between $V$ and $I$, compressive thermal stress makes Si crystals more V-rich.
σ accurately describe the impact of thermal stress on Voronkov internal pressure distortion (Fig. 1 Dependence of formation enthalpy for D-site (most stable) and T-site (transition state), and as shown in Fig. 3. A nearly linear relation between formation energies $E_f^h$ and $E_f^v$ for pressures up to 1 GPa. For the relaxation volume, $v_f^h$ is almost constant while $v_f^v$ decreases linearly with increasing pressure $P$. The dependencies of formation enthalpies $H_f^h$ for D- and T-sites, $H_f^v$ for h-JT (most stable) and split-V (transition state) on internal pressure $P_{in}$ were obtained. We found that the $H_f^h$ of $I$ increases while the $H_f^v$ of $V$ decreases with internal pressure $P_{in}$.

The results we obtained were used to more accurately describe the impact of thermal stress on formation volumes of point defects in prefect crystal Si.

4 Conclusion

The dependences of the formation enthalpy ($H_f$) and the activation enthalpy ($H_m$) of the self-interstitial $I$ and the vacancy $V$ on the hydrostatic pressure $P_h$ and on the internal pressure $P_{in}$ were calculated by calculating the formation energy ($E_f$) and relaxation volume ($v_f$).

The neutral $I$ and $V$ are found to have quasi constant formation energies $E_f^I$ and $E_f^V$ for pressures up to 1 GPa. For the relaxation volume, $v_f^I$ is almost constant while $v_f^V$ decreases linearly with increasing pressure $P$. The dependencies of formation enthalpies $H_f^I$ for D-site and $H_f^V$ for h-JT (most stable) and split-V (transition state) on internal pressure $P_{in}$ were obtained. We found that the $H_f^I$ of $I$ increases while the $H_f^V$ of $V$ decreases with internal pressure $P_{in}$.

The obtained result for internal pressure was used to more accurately describe the impact of thermal stress on Voronkov criterion $I_{0_{crit}}$ than the estimates under hydrostatic pressure as shown in Fig. 3. A nearly linear relation between $I_{0_{crit}}$ (in $10^{15}$ cm$^{-2}$ min$^{-1}$ K$^{-1}$) and the thermal stress at the melt/solid interface $\sigma_0$ (in MPa) was obtained, described by $I_{0_{crit}} = 1.509 - 0.023\sigma_0$. The impact of thermal stress on $I_{0_{crit}}$ makes the growing Si crystal more vacancy-rich. The results illustrate that it is important to take into account the impact of stress on the generation of intrinsic point defects in developing future large diameter defect-free crystals.

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References

[7] The CASTEP code is available from Accelrys Software Inc.