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_m) 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_m on the pressure P, or in other words, the pressure dependence of the formation energy (E_f) and the relaxation volume (v_f), 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 dependences 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 $I0_{crit}$ 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 5×10^{15} 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_f, 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^I at the [110] dumbbell site (most stable). For self-interstitials, H_f^I and H_m^I are given by $H_f^I = 3.425 - 0.057\times P_h$ (eV) and $H_m^I = 0.981 - 0.039\times P_h$ (eV), respectively, with P_h given in GPa. Fig. 1(below) shows the calculated formation enthalpy H_f^V for Jahn-Teller distortion (*h*-JT, most stable) of vacancies V. The calculated H_f^V and H_m^V dependencies on P_h given by $H_f^V = 3.543 - 0.021\times P_h^2 - 0.019\times P_h$ (eV) and $H_m^V = 0.249 + 0.018\times P_h^2 - 0.037\times P_h$ (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_{in}, Fig. 2 shows the changes in formation enthalpies ΔH_f^I for D-site (most stable) and T-site (transition state) of self-interstitials I, and ΔH_f^V for Jahn-Teller distortion (*h*-JT, most stable) and split-V (transition state) of vacancies V due to internal pressure P_{in}. We found that the H_f^I of I increases while the H_f^V of V decreases with the increase in P_{in}. The calculations lead to the dependencies of H_f^I, H_m^I and H_f^V, H_m^V on P_{in} given by $H_f^I = 3.425 + 0.070\times P_{in}$ (eV) and $H_m^I = 0.981 - 0.038\times P_{in}$ (eV), respectively, with P_{in} given in GPa. The calculated H_f^V and H_m^V dependencies on P_{in} given by $H_f^V = 3.543 - 0.160\times P_{in}$ (eV) and $H_m^V = 0.249 - 0.026\times P_{in}$ (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.

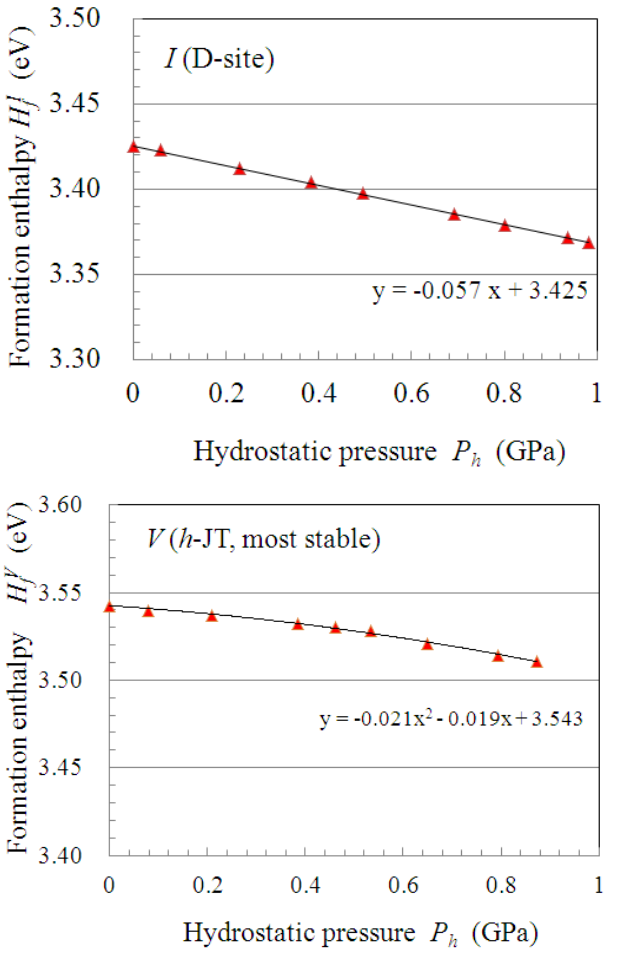

Fig.1 Dependence of formation enthalpy H_f^I for D-site (above) and H_f^V for *h*-JT (below) on the hydrostatic pressure P_h.

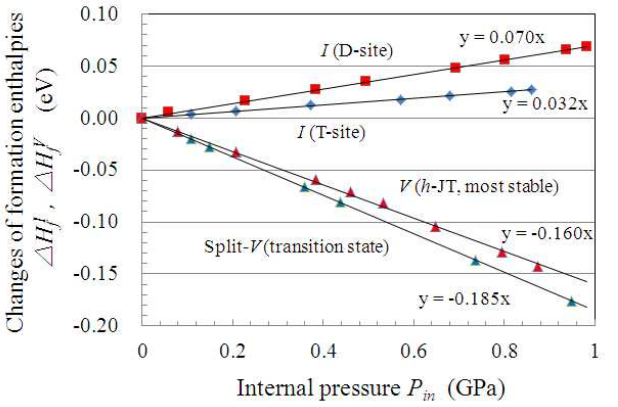

Fig. 2 Changes in formation enthalpies ΔH_f^I for D-site (most stable) and T-site (transition state), ΔH_f^V for Jahn-Teller distortion (*h*-JT, most stable) and split-*V* (transition state) due to internal pressure P_{in}.

The obtained result for internal pressure was used to more accurately describe the impact of thermal stress on Voronkov criterion [1] $\Gamma 0_{crit}$ than the estimates under hydrostatic pressure as shown in Fig. 3. A nearly linear relation between $\Gamma 0_{crit}$ (in 10^{-3} $cm^2min^{-1}K^{-1}$) and the thermal stress at the melt/solid interface $\sigma 0$ (in MPa) was obtained, described by $\Gamma 0_{crit} \approx 1.509–0.023\sigma 0$. The impact of thermal stress on $\Gamma 0_{crit}$ makes the growing Si crystal more *V*-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.

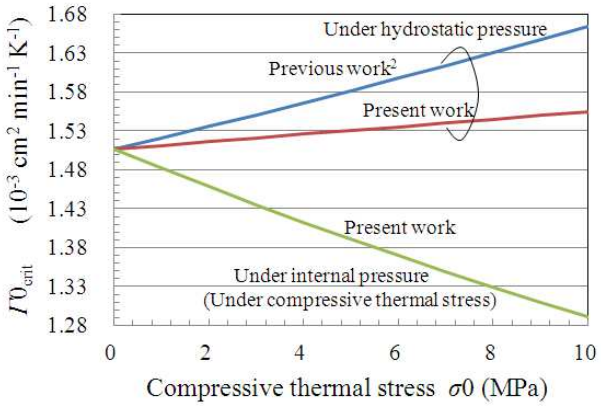

Fig. 3 Variations in critical *v*/*G* (*v*: pulling speed, *G*: temperature gradient) ratio $\Gamma 0_{crit}$ with thermal stress $\sigma 0 = P_{in}$. Results obtained by using values for H_f and H_m under hydrostatic pressure P_h are also given.

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- 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^I 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 $\Gamma 0_{crit}$ than the estimates under hydrostatic pressure. A nearly linear relation between $\Gamma 0_{crit}$ (in 10^{-3} $cm^2min^{-1}K^{-1}$) and $\sigma 0$ (in MPa) was obtained, described by $\Gamma 0_{crit} \approx 1.509–0.023\sigma 0$. The impact of thermal stress on $\Gamma 0_{crit}$ 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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