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Formation energy of intrinsic point defects in nanometer-thick Si and Ge foils and implications for Ge crystal growth from a melt

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Formation energies of vacancies and self-interstitials in nanometer-thick Si and Ge foils are calculated by means of Density Functional Theory applying thin film models. Plate models consisting of six to sixteen atomic layers with c(4×2) dimer structures on both surfaces with a vacuum slab are used. The formation energies E_f of the intrinsic point defects of Si and Ge in the middle of the foil and obtained from the twelve layer models, are in good agreement with reported values for bulk material. In all cases, E_f in the middle of the foil decreases with decreasing foil thickness. Using the same twelve or more layers thin plate models for Si and Ge thus also allows compar-

ing the formation energies of intrinsic point defects in the bulk. The thermal equilibrium concentration of Ge self-interstitials near melt temperature is more than one order of magnitude lower than that of Si self-interstitials while the vacancy concentrations are of same order of magnitude. Contrary to Si, the diffusivity of Ge self-interstitials can therefore not recover the unbalance of the thermal equilibrium concentrations during crystal growth, even if the growth rate is reduced to very low values. This is the reason why Ge crystals grown from a melt are always vacancy-rich which results in void formation independent of the crystal growth conditions.

1 Introduction Nanometer-scale ultra-thin Si films are now being applied in next-generation electronic device structures and substrates. Silicon-on-insulator (SOI) substrates consisting of a thin high quality Si layer on an amorphous SiO_2 layer grown on a low cost Si substrate are widely used [1]. A variety of SOI substrate fabrication methods have been been developed [2-5]. A further development is Si films having nothing beneath them, so called silicon-on-nothing (SON) substrates [6]. SOI wafers with a top Si film of only 5 nm will be used in future electronic devices [7]. Germanium on insulator wafers also have been proposed for the same purpose, taking advantage of the higher carrier mobility and of the possibility to grow defect-free epitaxial GaAs layers on the Ge film [8]. FinFETs are studied intensively as candidate for next-generation electronic devices. The heart of the finFETs is a "fin"-shaped Si film of nanometer-scale thickness [9]. Ultra-thin

semiconductor films will thus be key components in future advanced devices as. For such applications a fundamental understanding of the properties of ultra-thin Si and Ge, fin structures or foils is essential.

At the same time, crystal surfaces play an important role in defect engineering of the semiconductor materials and structures [10, 11]. It is usually thought that crystal surfaces are filled intrinsic point defects. In case of Si (100) surfaces, density functional theory (DFT) calculations predict lower formation energies near the surface than deeper into the bulk [12]. Atoms inside ultrathin films having free surfaces on both sides tend to be distorted due to surface reconstruction [13]. The effect of the surface increases when the thickness of the film, fin or foil decreases, and cannot be ignored when it becomes of the order of a few nm. In such ultra-thin film system, intrinsic point defects strongly interact with the surface due to the dangling

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bonds. The influence of the electronic states originating from a dangling bond can even reach deeper than ten layers [14].

In the present paper, the formation energies of intrinsic point defects in a Si or Ge ultra-thin film or foil were calculated using plate-shaped models, called "plate models" in the following. The main features of plate models are: (i) as-is models with no constraint, corresponding to nanometer-thick ultra-thin foils in free space, (ii) the energy gap opens or widens due to the carrier confinement effect [15] without the need to use new type of exchange-correlation potentials like HSE06 [16]. This is in contrast to the bulk Ge calculation case where no energy gap is obtained when using "traditional" exchange-correlation potentials [17, 18]. The obtained formation energy dependence on the thickness of the plate is discussed as well as the different point defect behaviour in Si and Ge crystals grown from a melt.

2 DFT calculation of thin plate models
2.1 Base model aspects It is widely accepted that the c(4×2) dimer structure is the most stable state for both Si and Ge (001) clean surfaces [19, 20], although some unclear points remain such as the observation of a p(2×1) structure below 20 K in Si [21]. Plate models with dimer structures on both surfaces in a vacuum slab (Fig. 1) are therefore often used to examine the effect of a clean Si or Ge surface with c(4×2) structure. In this type of model, the atoms at the centre of the plate are mostly constraint during the geometry-optimization when investigating the surface of bulk crystals [22] in order to minimize the coupling between both dimer surfaces [13]. However, all atoms in the models used in the present study, are left free during the geometry optimization to describe nanometer-thick ultra-thin foils with or without a point defect in a free space.
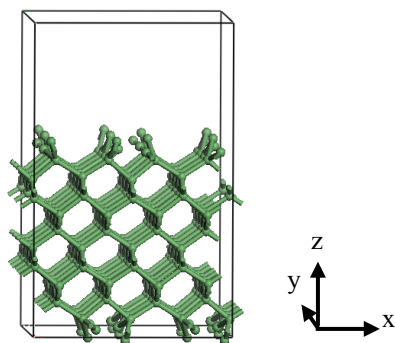

Figure 1 A twelve atomic layers plate model with c(4x2) dimer structures on both surfaces surrounded by vacuum [34].

2.2 Introducing intrinsic point defects A point defect is included in the plate model as described in previous papers [12, 23]. The depth of the intrinsic point defect below the plate surface in each model is expressed by d, the number of atomic layers from the surface. For the uncharged self-interstitial, DFT calculations show that the (110) split dumbbell (DB) model has the lowest energy and is thus the most stable configuration [24, 25].

2.3 Basic calculation conditions The DFT calculations in the present study are based on the local density approximation [26, 27] using the ultrasoft pseudopotential method [28] and plane waves as a basis set for an efficient structure optimization. The standard expression proposed by Hammer et al. [29] was used for the exchange-correlation energy in the generalized gradient approximation (GGA). The *CASTEP* code was used to self-consistently solve the Kohn-Sham equation using a three-dimensional periodic boundary condition [30]. The density mixing method [31] and the BFGS geometry optimization method [32] were used to optimize the electronic structure and the atomic configurations, respectively. Only the neutral charge state of the systems was considered in this study. For the k-point sampling, the 2×2×1 special points of the Monkhorst-Pack grid were used [33]. The cutoff energy of the plane waves was 310 eV.

3 Results for Si and Ge [34]
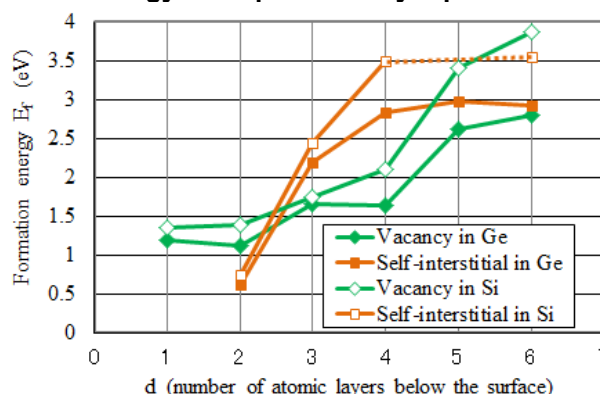**3.1 Dependence of intrinsic point defect formation energy on depth in 12-layer plate models**

Figure 2 Intrinsic point defect formation energy dependencies on the depth below the plate surface for a twelve layer plate model [34].

The formation energies were calculated by using the chemical potential of a Si or Ge atom in a 64 atoms cell with no vacuum slab and using a three dimensional boundary condition, similar to the method used in a previous paper [12]. Figure 2 shows the formation energy dependencies on d. When a vacancy or a self-interstitial moves deeper inside the crystal from the surface, the interaction with the surface through the overlap of wave functions, the transfer of electric charges from the surface, and the relaxation of atom positions by the deformation of surface dimer structures due to the introduction of the point defect become less effective, and the formation energy will be closer to the bulk value. The depth position dependencies for Si and Ge are similar for two aspects: (i) the formation energies of both Si and Ge self-interstitials are lower than that of a vacancy at the top surface. Self-interstitials can thus form easier than vacancies at the surface or, in other words, an isolated atom can move from a melt and become a self-

interstitial as discussed further, (ii) the formation energies of both Si and Ge self-interstitials increase rapidly when moving deeper inside the crystal and become higher than that of the vacancy at the third layer and finally saturate at the fifth layer. The formation energies of both Si and Ge vacancies increase more slowly, and the Si vacancy has a higher energy than that of the self-interstitial starting from the sixth layer.

3.2 Dependence on plate thickness of intrinsic point defect formation energy in the centre of a thin plate The dependence of the intrinsic point defect formation energy on plate thickness expressed by N, the number of atomic layers in the plate is shown in Fig. 3. In this model, the point defect is set at the centre of the film. The thickness dependency of formation energies is similar for Si and Ge, and also similar for vacancy and self-interstitial. It is however interesting to note that the ordering of the formation energies of a vacancy and a self-interstitial is opposite between Si and Ge. This is due to the lower formation energy of a vacancy in Ge than in Si due to the fact that chemical bonds in Ge are weaker than those in Si. Therefore, this trend will continue until the bulk crystal (1/N= 0). The maximum values obtained for the twelve layer models in Fig. 3 (except for the Ge self-interstitial) are close to the bulk values although they start already to be slightly affected by the bandgap narrowing which is an artefact of the DFT calculation with the classical potential The value for the Ge self-interstitial however did not yet saturate even for a sixteen layer model. This is due to that fact that the surface effect reaches even down to the fifteenth layer from the surface in that case [35]. Therefore the formation energy of the Ge self-interstitial is still lower than the bulk value.
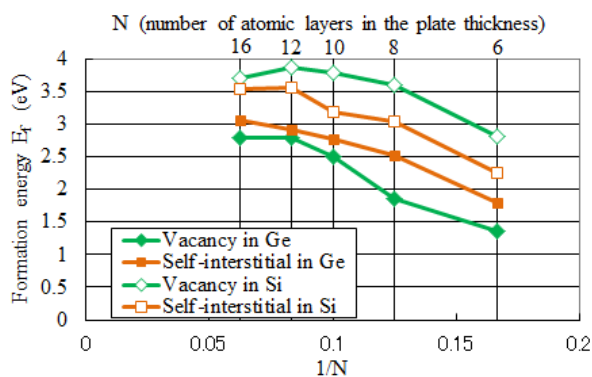

Figure 3 Formation energy as a function of the thickness of the plate, expressed by N, the number of atomic layers in the plate [34].

4 Direct observation of Ge self-interstitials in a ultra-thin foil Isolated Ge self-interstitials have been directly observed by using a sophisticated High Resolution Electron Microscopy (HREM) technique [36]. The analysed regions were thinner than 2.4 nm, which corresponds to about 17 layers thickness in the [001] direction. Most

probably the lower formation energy as illustrated in Fig. 3, due to which Ge self-interstitials will generate more easily in the thinnest parts of a Ge foil plays an important role in this as a sufficient high concentration of isolated interstitials can be created so that they can be observed by HREM.

5 Implications for Ge single crystal growth from a melt [34] The majority of commercial Si and Ge single crystals are grown from a melt using the Czochralski or the floating-zone technique. In the case of Si, it is widely accepted that both vacancies and self-interstitials, are introduced into the crystal at the melt-solid interface and that these defects can be transformed into voids or dislocation loops by agglomeration during crystal cooling. Contrary to Si, only voids are reported as grown-in defects in Ge single crystals [37]. The dependence of the intrinsic point defect formation energy on the distance from the interface should be investigated to understand their generation and the temperature dependence of their equilibrium concentrations. As a first step, the dependence on the distance from the crystal surface can be studied as illustrated in Fig. 2. The region just below the interface tends thus to have a higher concentration of point defects than the equilibrium concentrations inside the bulk crystal at a given temperature. A large fraction of these point defects will diffuse back to the surface or annihilate by mutual recombination when the distance to the melt-solid interface becomes larger due to the crystal growth. Therefore, the thermal equilibrium concentrations in the bulk (and thus also the formation energies in the bulk) are dominant factors in defect free single crystal growth, as Voronkov proposed [38]. The formation energies of intrinsic point defects of Si and Ge obtained from the twelve layer models of Fig. 3 and listed in Table 1 are in good agreement with published bulk values [34]. The relations between thermal equilibrium concentrations of the Si vacancy, the Si self-interstitial, the Ge vacancy and the Ge self-interstitial at the melting points can be approximately written as [34]:

$$C_{eq}^{V_{Ge}} \approx C_{eq}^{V_{Si}}\Big/1.3, \qquad C_{eq}^{I_{Ge}} \approx C_{eq}^{I_{Si}}\Big/36.2 \qquad (1)$$

Thermal equilibrium concentrations of both types of intrinsic point defects in Ge are thus lower than those in Si at the respective melting temperatures. It is especially important to note that the concentration of the Ge self-interstitial is more than one order of magnitude lower than that of the Si interstitial while the vacancy concentrations are quite similar. Regarding Si crystal growth from a melt, the thermal equilibrium vacancy concentration at the melting temperature is about 20~40% higher than that of the self-interstitial and the diffusivity of the self-interstitial is larger than that of the vacancy [39]. This is the reason why it is possible to create a balance between both point defects determined by Voronkov criterion defined by the ratio of the growth rate over the thermal gradient [38]. In the case of Ge, however, such a balance cannot be achieved, simply because there are not enough interstitials available. As the formation energy of the Ge self-interstitial is probably underestimated

as mentioned in Section 3.2, the actual disruption of the balance in the thermal equilibrium concentrations between vacancies and self-interstitials is expected to be even larger than suggested by Eq. (1). This also explains why the temperature dependency of Ge self-diffusivity can be accurately described by a single activation enthalpy and a pre-exponential factor, and that the Arrhenius behaviour implies that vacancy diffusion controls self-diffusion without a noticeable self-interstitial contribution up to the melting temperature [40]. There is no way that the diffusivity of the Ge self-interstitial can recover the unbalance of the thermal equilibrium concentrations even if the growth rate is reduced to very low values. Therefore, moderately doped Ge crystals grown from a melt are always vacancy-rich which results in vacancy cluster formation, independent of the growth condition.

Table 1 Formation energies of the uncharged intrinsic point defects in Si and Ge in the centre of a 12 layer plate model [34].

$E_f^{V_{Si}}$	$E_f^{I_{Si}}$	$E_f^{V_{Ge}}$	$E_f^{I_{Ge}}$
3.87 eV	3.55 eV	2.80 eV	2.92 eV

6 Conclusion Using plate models to describe nanometer-scale thin foils shows that the formation energies of intrinsic point defects decrease with decreasing foil thickness. This is one of the reasons why individual Ge self-interstitials can be observed in situ by HREM in ultra-thin Ge foils.

Using the same models for Si and Ge also allows comparing the bulk formation energies of intrinsic point defects. Near melt temperature, the thermal equilibrium concentration of Ge self-interstitials is more than one order of magnitude lower than that of Si self-interstitials while the vacancy concentrations are of same magnitude. This is the reason why moderately doped Ge crystals grown from a melt are always vacancy-rich resulting in void formation.

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