

Intrinsic point defect properties and engineering in silicon and germanium Czochralski crystal growth

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Abstract

In the present paper, the intrinsic point- and extended-defects properties and behaviour in silicon and germanium are reviewed both from an experimental and theoretical point of view. It is shown that they behave quite similar at the same temperature normalised with respect to the melt temperature. Some differences exist however which have important implications for extended defect formation during crystal growth and device processing and also for other physical processes during important device processing steps.

Introduction

Defects in Si have been studied for more than half a century now and a tremendous database and know how has been established. Only a limited number of loose ends remain today. For Ge the situation is quite different as most research activities stopped or were strongly reduced end of the sixties of the previous century when it became clear that Si had won the battle to be the substrate of preference to prepare electronic devices.

Nowadays the use of Ge as active device layer in advanced devices is receiving a lot of interest due to the fact that Si is reaching its limits in nano-electronic (and high frequency) devices and a significant gain can be expected from the much higher carrier mobility in Ge combined with the fact that Ge processing is compatible with the Si process. For that reason an increasing number of academic and industrial research groups are exploring the possibilities and limitations of Ge [1]. Also the development of large diameter Ge wafers has made tremendous progress during the last years culminating in the commercial availability of 200 mm Ge wafers and the demonstration of 300 mm wafers fulfilling the ITRS wafer specifications [2].

A lot can indeed be gained from using the experiences obtained during the Si material and process development obtained during the last decades. Although very similar in many respects, Ge sometimes behaves unexpected and special attention should be given especially to properties of point defects such as solubility, diffusivity, pair formation [3-6].

Intrinsic Point Defect Solubility and Diffusivity in Si and Ge from experiment

In Si the most reliable quantitative data on the solubility and diffusivity of intrinsic point defects were obtained on the basis of metal diffusion experiments and of intrinsic point defect cluster formation during Czochralski crystal growth. Originally the data obtained from both approaches differed considerable in part due to the very different temperature window which was used. Recently Voronkov et al. [7] made an attempt to unify the results from both approaches and proposed expressions for the vacancy V and interstitial I diffusivity $D_{V/I}$ and solubility $C_{V/I}^{eq}$, respectively.

For Ge, mainly three approaches have been used to directly study intrinsic point defect properties [8], i.e. quenching from high temperatures followed by annealing at lower temperatures, plastic deformation at high temperatures and irradiation at low temperatures in order to create Frenkel pairs and individual point defects. In addition, the study of the diffusion and/or precipitation of fast diffusing dopants such as Cu and Zn can provide indirect information on intrinsic point defects. Finally, also ab initio calculations can shed more light on the formation and migration energy and the electrical activity of the intrinsic point defects.

The quenching technique has been very successful in the assessment of vacancy properties in metals and has therefore initially also been used extensively for Ge revealing that quenching of n-type Ge from temperatures above 800°C could result in p-type material, pointing to the creation of quenched-in acceptors with concentrations up to 10^{15} cm^{-3} depending on the starting temperature and quenching rate. Annealing at 500°C recovered the original n-type, indicating the out-diffusion/annihilation of the acceptors assumed to be related to quenched-in vacancies. It was soon realized however that many of the early experiments suffered from copper contamination, whereby substitutional copper is a triple acceptor. Further-more it soon became clear that quenching experiments can only yield indirect (and incomplete) information on single vacancies as diffusion is so fast that vacancy clustering during quenching is difficult to avoid.

Self-diffusion in Si and Ge is the slowest diffusion process and provides direct evidence of the existence of an equilibrium concentration of intrinsic point defects. Giese et al. [9] showed that in contrast to Si, the self-diffusion coefficient D_{Ge} in Ge is dominated by vacancies and that in the temperature interval which they studied the transport capacity $C^{eq}_I D_I$ of interstitials is at least one order of magnitude smaller than that of vacancies. This is quite different from the behavior in Si where there is an important interstitial contribution to the self-diffusion which at temperatures close to the melt temperature even can become dominant.

Figure 1 illustrates that the self-diffusivity in Si and Ge is very similar when plotted as a function of the temperature normalized to the melt temperature T_m . A significant difference is however observed between the vacancy transport capacity in both materials which is due to the important interstitial contribution to the self diffusion in Si while in Ge it can be neglected [4,5]. For the thermal solubility of the vacancy shown in the right of Figure 1, a large spread is observed in the published Si data. For Ge only very limited experimental data are available mainly based on quenching experiments.

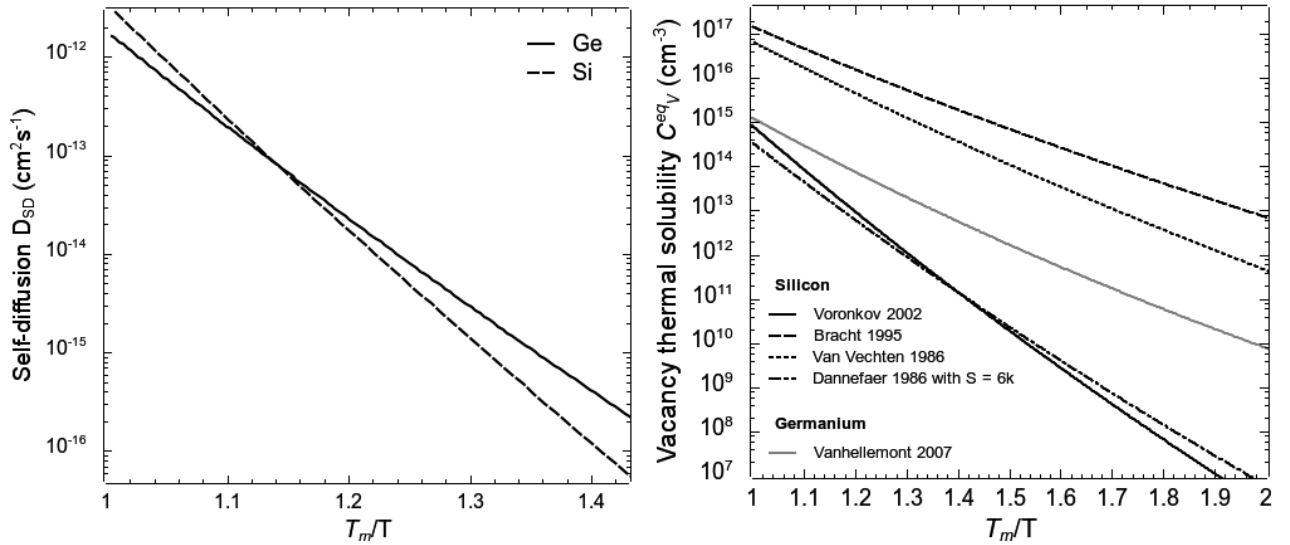


Figure 1: Self-diffusion coefficient $D_{Si,Ge}$ (left) and vacancy solubility C^{eq}_V (right) in Si and Ge as a function of the temperature T normalized with respect to the melt temperature T_m [10 and references therein]. No experimental data are available for the self-interstitial solubility in Ge.

Simulation of Intrinsic Point Defect Properties

As reliable experimental data for intrinsic point defects in Ge are still lacking to a large extent especially for the self-interstitial, atomistic simulations and comparison with results obtained for Si can yield useful information [11,12].

The formation energy $E_f(V^q)$ of the vacancy in charge state q can be calculated as a function of the Fermi level using [13]

$$E_f(V^q) = E^{N-1}(q) - (N-1)/N \times E^N(0) + q[E_F + E_{vm} + \Delta V], \quad (1)$$

where $E^{N-1}(q)$ is the total energy of a relaxed supercell containing one vacancy with charge state q , and $E^N(0)$ is

the total energy of the perfect neutral cell containing N atoms. E_F is the Fermi level in the band gap, with respect to the valence band maximum E_{vm} . The presence of an intrinsic point defect in the supercell strongly affects the band structure. Therefore, one cannot simply use E_{vm} as calculated before for calculating the defect containing supercell and several corrections have to be performed [12,15].

The formation energy $E_f(I^q)$ of the interstitial in charge state q can be calculated as a function of the Fermi level using [13]

$$E_f(I^q) = E^{N+1}(q) - (N+1)/N \times E^N(0) + q[E_F + E_{vm} + \Delta V]. \quad (2)$$

$E^{N+1}(q)$ is the total energy of a relaxed supercell containing N neutral atoms and one self-interstitial with charge state q . $E^N(0)$ is the total energy of the perfect neutral cell containing N atoms. E_F is the Fermi level in the band gap, with respect to the valence band maximum E_{vm} .

Figures 2 and 3 shows the formation energy of the vacancy V and the self-interstitial I for different charge states, as a function of the position of the Fermi level in the bandgap, for Si [11] and for Ge [12,15], respectively.

The results for Si are obtained in the frame of the local density approximation (LDA) using the ultra-soft pseudopotential method, plane waves as a basis set for efficient structure optimization and the generalized gradient approximation (GGA) [11]. The cutoff energy of the plane waves is chosen at 310 eV. The *CASTEP* code is used to solve the Kohn-Sham equation self-consistently with three-dimensional periodic boundary condition. The results can be summarized as follows [11]. In intrinsic Si, V^0 is the most stable vacancy state while in p-type Si, V^{2+} is the most stable one and in n-type, V^{2-} . Without the energy correction for the T site, I^{2+} at T site is the most stable in intrinsic Si. I^0 at the [110] D site is considered to be the most stable interstitial state if the energy correction for the T site is performed [16]. On the other hand, I^{2+} at the T site is the most stable in p-type Si. In positively charged state, the energy barrier between the T and the H site disappears, and the I atom moves to the T site from the H site during geometry optimization. I^{+1} is not the most stable in the whole region of the band gap.

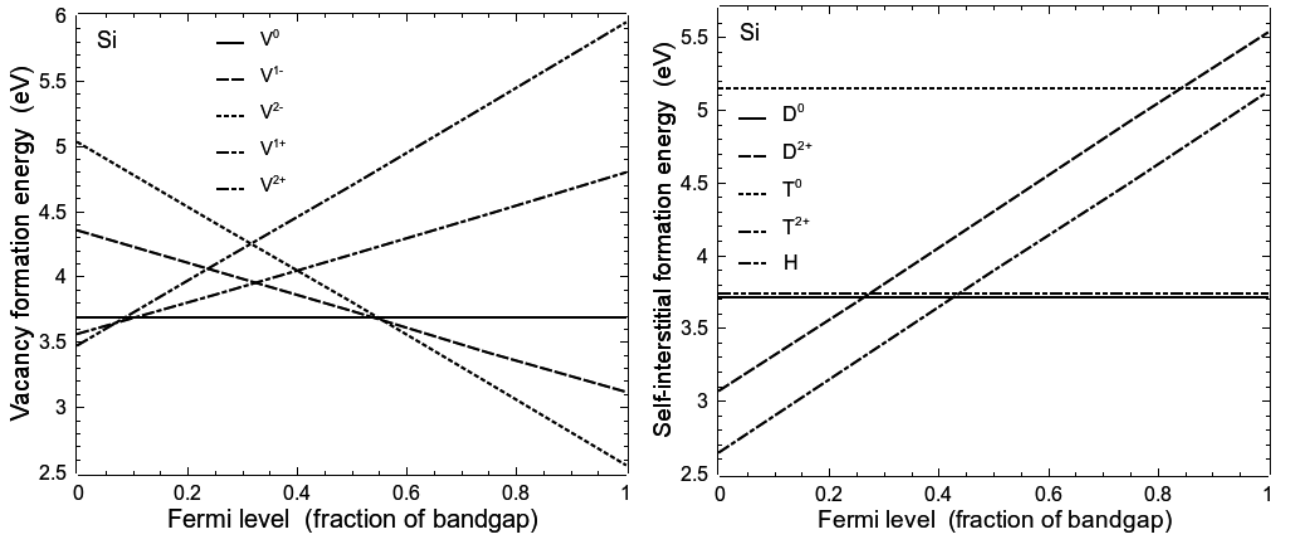


Figure 2: Formation energy of the vacancy (left) and the self-interstitial (right) in Si as a function of Fermi level and charge state calculated with CASTEP and GGA [11].

The calculations for Ge shown in Figure 3 were performed in the framework of the density functional theory (DFT), using the pseudopotential method with the projector augmented wave (PAW) potentials with d states treated as valence as implemented in the VASP code [12,15]. For the exchange-correlation energy, the local density approximation (LDA) is used with a cut-off energy of 400 eV. Brillouin-zone integrations are carried out using the Monkhorst–Pack scheme with a regularly spaced mesh of $4 \times 4 \times 4$ points in the reciprocal unit cell shifted from the origin at the Γ point. Symmetry reduces this to a set of points in the irreducible part of the Brillouin zone. To calculate the properties of the intrinsic point defects, periodic supercells of atoms are used with a computed equilibrium lattice constant \AA to be compared with the experimental value of 5.6569 \AA .

With these parameters the system converges for the supercell size and k-point sampling which are used. A closing

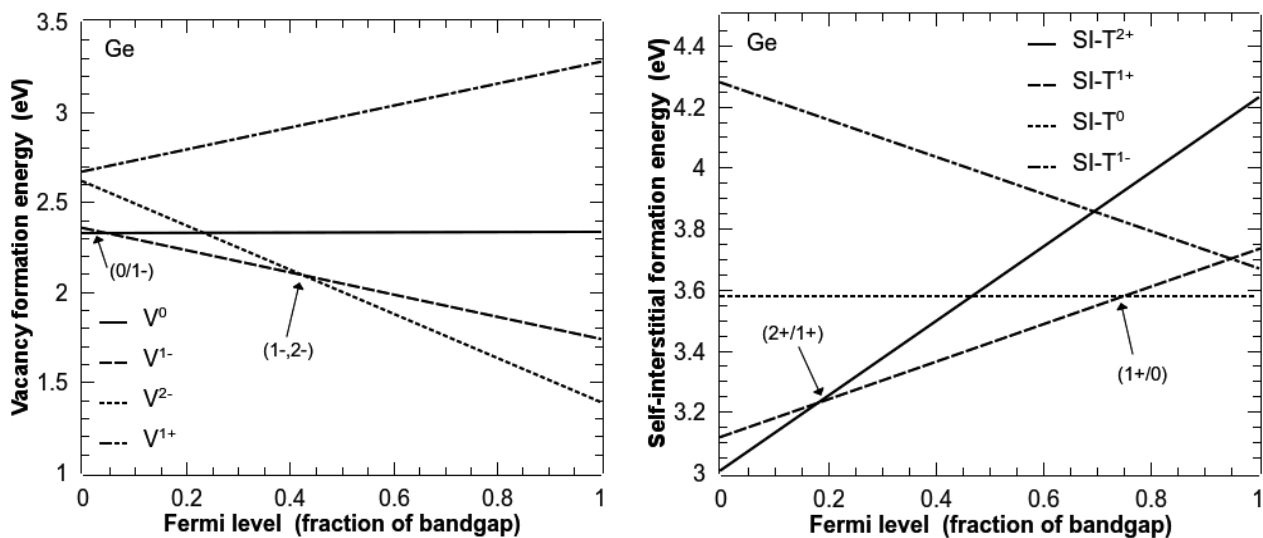
of the band gap is however observed, predicting a metallic ground state. This is due to the strong electronic interaction by the localized (strongly correlated) d electrons in germanium. These strong Coulomb interactions are not adequately described by the DFT-LDA approach. For the opening of the band gap, the LDA+U method was implemented [12], whereby the on-site Coulomb interaction U accounts for the strong electronic interaction by adding an orbital-dependent term to the LDA potential. The idea of the LDA+U method is to separate the valence electrons in two subsystems: localized d electrons for which the Coulomb d-d interaction (repulsion U) should be taken into account via a Hartree-Fock like approach, and delocalized s and p electrons for which the LDA description is based on an orbital-independent one-electron potential.

In order to find out the energetically most stable structure for the neutral Ge self-interstitial defects three different atomic arrangements, i.e. the $\langle 110 \rangle$ dumbbell (D), the tetrahedral (T), and the hexagonal (H) positions are examined. The hexagonal position is unstable in the present calculations and transforms in the $\langle 111 \rangle$ distorted hexagonal (H_d) position during relaxation. This is due to the fact, that the hexagonal configuration is the saddle point in the migration path of the self-interstitial from the tetrahedral to the adjacent tetrahedral position. The D position has a 0.40 eV lower energy than the T position, 0.49 eV lower than the H position, and 0.42 eV lower than the H_d position. The formation energies of the self-interstitials in the D (SI-D) and T (SI-T) configurations are calculated using the LDA+U approximation [15] and are shown in Figure 3 (right) for different charge states as a function of the Fermi level in the band gap.

The formation energy of the germanium vacancy in $2-$, $1-$, 0 , and $1+$ charged states, i.e., V^{2-} , V^{1-} , V^0 , and V^{1+} is shown in Figure 3 (left) as a function of the Fermi level in the bandgap obtained from the LDA+U

approximation. For intrinsic Ge (Fermi level at mid bandgap), the calculated formation energies for V^{2-} , V^{1-} , and V^0 are 2.00, 2.05, and 2.33 eV, respectively, in good agreement with the values estimated from quenching experiments [17].

Figure 3: The formation energy of the vacancy (left) and the self-interstitial (right) formation energy in Ge as a function of Fermi level and charge state calculated on the basis of LDA+U [12,15].



A similar result is obtained by using an alternative approach based on the CASTEP code, which yields a slightly overestimated effective energy bandgap, resulting, however, in a similar dependence of the formation energies on Fermi level position [11]. The ionization levels of the vacancy with respect to the valence band maximum correspond to the Fermi level where the formation energies of two different charge states become equal (intersections in Figure 3). The calculations suggest that the (0/1-) level is at 0.02 eV above the valence band, while the (1-/2-) level lies at 0.26 eV, which are both in excellent agreement with the results of Hall measurements.

Frenkel pairs and recombination of vacancies and self-interstitials

In processes such as crystal pulling, plastic deformation and ion implantation, both types of intrinsic point defects are generated and/or coexist. An important parameter controlling the concentration of both point defects is the recombination factor k_{IV} which is given by the well-known expression

$$k_{IV} = 4\pi a_c (D_V + D_I) \exp[-\Delta G_{rec}/kT], \quad (3)$$

with a_c the capture radius of the order of 1 nm and ΔG_{rec} the free energy barrier against recombination.

Assuming an Arrhenius-type behavior, (3) can also be written as [18]

$$k_{IV} = k_m \exp[-(E_{rec}/kT_m)(T_m/T - 1)]. \quad (4)$$

k_m is a constant and E_{rec} the activation energy for recombination.

Applying (3) and (4) for data obtained from grown-in defect distributions in floating zone and Czochralski grown Si crystals [19,20] yields the k_{IV} dependence on the temperature normalized to the melt temperature as shown in Figure 4. It is clear that a large uncertainty still exists with respect to the value of k_{IV} and that it strongly depends on the model that is used to simulate the crystal growth process. For Ge, data for the self-interstitial are still lacking making it very difficult to estimate the recombination factor.

Void Formation in Czochralski-Grown Crystals

In most cases, the vacancy is the dominant intrinsic point defect in dislocation free Cz Si and Ge crystals. In some cases the excess of vacancies that is created during cooling of the crystal can lead to the formation of larger agglomerates that are visible as crystallographic pits on the polished wafer surface which are observed by light scattering based wafer surface inspection tools and were historically called “COP’s” (Crystal Originated Particles) [21,22].

The formation mechanism can be explained as follows. During the solidification process, thermal equilibrium concentrations of both intrinsic point defects are introduced at the melt/solid interface. They are transported axially by thermal diffusion due to the thermal gradient G and by the crystal itself that is moving away from the melt with the pulling speed v . These two transport mechanisms and the recombination of the intrinsic defects (controlled by k_{IV}) determine the dominant intrinsic point defect in the cooling crystal and thus, also the type of extended defects formed by point defect clustering. Si crystals pulled with a v over G ratio larger than a critical value are vacancy-rich, while below the critical value the crystal is interstitial-rich.

Already in 1957, Tweet [23] reported the occurrence of surface pits on Ge samples with a pit size depending on the thermal growth history of the Ge crystal. He observed a pit density reduction when pulling slower or by reducing the temperature gradient thus keeping the crystal longer at high temperatures or by post-heating the crystal in the puller. The observed pit density reduction was accompanied by an increase of size of the remaining pits. The observations were explained by a vacancy clustering mechanism. Four decades later, similar ideas were used to reduce the number of grown-in intrinsic point defect clusters in large diameter Cz Si crystals [24].

Figure 5 shows results of the simulation of void distributions formed in Si and Ge crystals during Czochralski pulling, using the software developed by Sinno [25]. The figure illustrates the impact of pulling speed on the grown-in void size/density distribution [21, 26]. Although the size and density of the voids is quite different for both materials, the total amount of vacancies incorporated is quite similar and of the order of 10^{14} cm^{-3} .

The larger void/COP sizes in germanium are due to the higher diffusivity of vacancies which is controlling the growth of the clusters during crystal cooling. The good agreement between measurement and simulation is

illustrated in Figure 6.

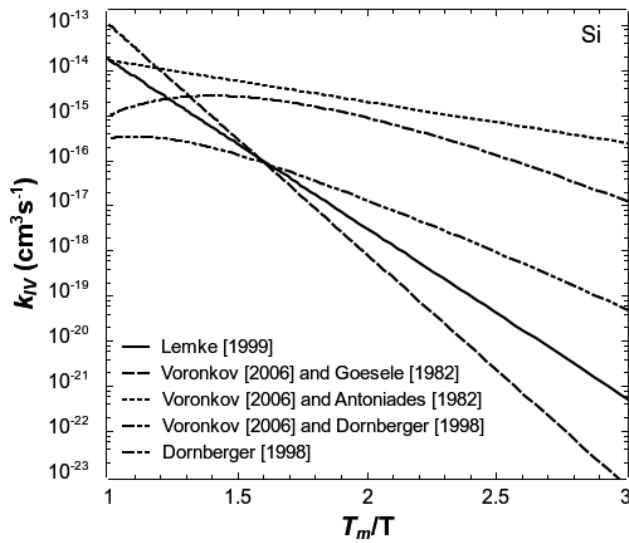


Figure 4 : k_{IV} in Si as a function of the temperature normalized with respect to the melt temperature [10].

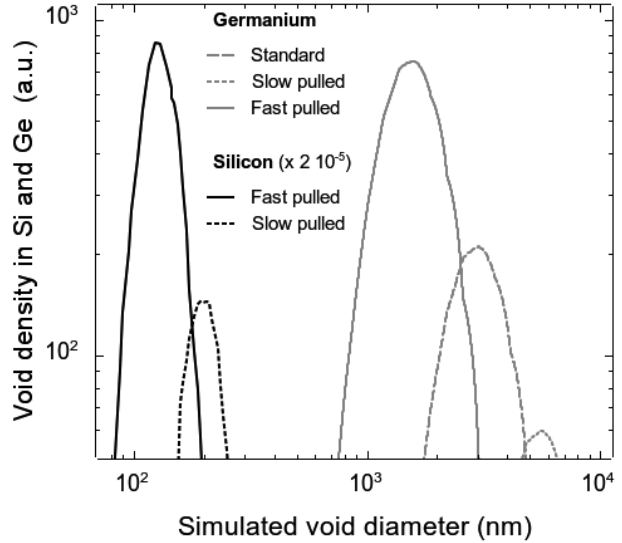


Figure 5: Simulated void size/density distributions in Si and Ge, illustrating the impact of crystal pulling speed [10].

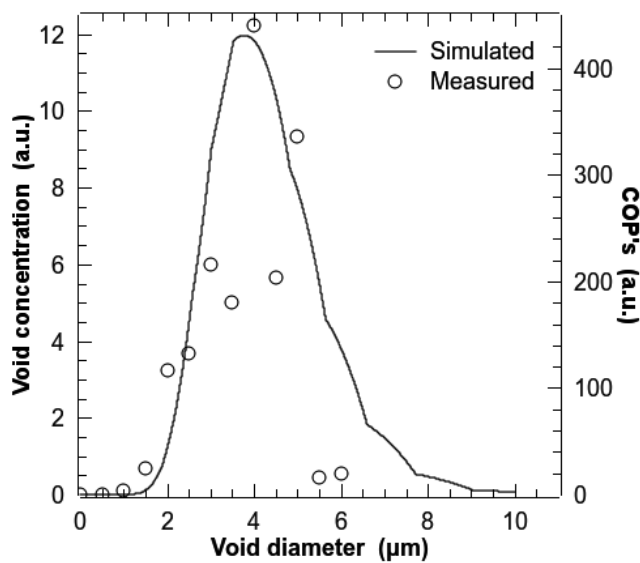


Figure 6: Simulated distribution of voids formed during cooling of a Ge crystal [4]. The COP distribution is measured with a confocal review station [21,22].

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