

GENERAL MODEL FOR THE DIFFUSION OF IMPURITIES IN COVALENT CRYSTALS: INTERSTITIAL OXYGEN IN SI, GE, AND SI-GE CRYSTALS

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Development of theoretical methods of determining the diffusivity of atoms in crystals is of great interest not only from a fundamental, but also from a practical, point of view. It is common knowledge that the diffusion of interstitial oxygen atoms in silicon crystals is of crucial importance in the processes of oxygen agglomeration (formation of thermal donors) and in the gettering of metallic impurities in industrial processing of silicon. Several theoretical efforts have attempted to calculate the diffusion barrier, but different results were obtained. Thus the calculated values of the barrier range from 1.2 eV up to 2.7 eV [1 and ref. in 1]. The complete calculation of the diffusion coefficient should also include calculation of the pre-exponential factor. Unfortunately, in the majority of previously published works the pre-exponential factor was not evaluated at all, and the calculated value in [2] differs from the experimental one by more than an order of magnitude. Thus, despite of major efforts, until the present time the diffusion constant was not calculated with sufficient (experimental) degree of accuracy even for an interstitial atom of oxygen in crystals of silicon. The given situation is characteristic practically for all impurity atoms in silicon crystals.

In the given paper, the simulation of diffusion of interstitial oxygen (O_i) in silicon, germanium and silicon-germanium crystals under normal and hydrostatic pressure (HP) is reported. The activation barrier and pre-exponential factor (Si, Ge) have been calculated and are in excellent agreement with experimental ones. To the best of my knowledge, no simulation of O_i diffusivity in $Si_{1-x}Ge_x$ (O) and effects of HP have been considered yet.

Modelling by the random walk method results in the following general expression for the diffusion constant:

$$D = \frac{d^2 N_{et}}{2d_s} \Gamma, \quad (1)$$

where d is the diffusion jump distance, N_{et} is the number of equivalent trajectories leaving the starting point, d_s is the dimension of space (in our case $d_s = 3$), and Γ is the average frequency of jumps on the distance d . In the case of a system consisting of N atoms, using the reaction-rate theory [3], the value of Γ may be written in the following form:

$$\Gamma = \frac{1}{2\pi} \frac{\prod_{i=0}^N \lambda_i^{(o)}}{\prod_{i=1}^N \lambda_i^{(b)}} \exp\left(-\frac{\Delta E_a}{k_B T}\right), \quad (2)$$

where ΔE_a is the adiabatic potential energy difference between the saddle point and the stable one, $\lambda_i^{2(o,b)}$ are the eigenvalues of the matrix (with respect to mass-weighted internal coordinates) $K_{ij} = \partial^2 U_{eff} / \partial f_i \partial f_j$, $U_{eff}(f_1, \dots, f_m)$ denotes the potential as a function of the internal degrees of freedom. The indices (b) and (o) indicate that the corresponding quantities are evaluated at the saddle point and local minimum, respectively. The calculation of diffusion parameters was performed in a cluster approximation. For comparison with the previous calculations different

methods such as empirical potential (MM2), semiempirical (AM1, PM3, PM5) and ab-initio (RHF, LDA) have been used for the calculation of the cluster total energy. The calculated value of the potential barrier for the rotation of O_i around Si-Si axis equals $\Delta E_\phi \leq 20$ meV (PM5). As ΔE_ϕ is much less than $k_B T$ (at diffusion temperatures) an interstitial oxygen atom jumps on any of six nearest Si-Si bonds and, hence, in Eq. 1 the parameters $N_{el} = 6$ and $d = 1.9$ Å. In the course of transition of O_i atom from one equilibrium configuration to another the breaking of old and formation of new covalent Si-O bonds takes place. The process of reconfiguration of an electronic subsystem will occur in the case when oxygen and neighboring silicon atoms owing to thermal fluctuations get in the region of configuration space G (bounded by the critical surface S_G) where the electronic reconfiguration leads to lowering of the crystal total energy. It is clear that for the given position of the oxygen atom there are many configurations of silicon atoms for which the electronic reconfiguration can occur but all of these configurations differ in the total energy of a crystal. Since the diffusion constant exponentially depends on the diffusion barrier Eq. 2 we should pick the minimal value of $\Delta E_a = \min[E_{cl}(S_G) - E_{cl}(O)]$, where $E_{cl}(S_G)$ and $E_{cl}(O)$ are the total cluster energy on the surface S_G and in local minimum O (equilibrium O_i configuration), respectively. Recently [1] I revealed an important fact for understanding of the diffusion process. $E_{cl}(S_G)$ and hence ΔE_a depends on the number of the silicon atoms (n) nearest to O_i involved in the minimization of the cluster total energy and essentially all O_i atoms overcome the diffusion barrier when only *three* nearest Si atoms are in the optimum configuration, and the diffusion parameters should be calculated for the given reconfiguration (Fig. 1). For this case the following values of the diffusion barrier $\Delta E_a = 2.59 - 2.60$ eV (PM5 method of calculation) have been obtained. Calculated value of the pre-exponential factor equals $D_0 = 0.28 - 0.30$ cm² s⁻¹. On Fig. 2 one can see the excellent agreement between the calculated and experimental temperature dependences of the diffusion coefficient in all temperature range $T = 350 - 1200$ °C. Being based on the procedure described above, the diffusion coefficient of interstitial oxygen in germanium crystals has been calculated also. Calculated values of the activation energy $\Delta E_a(\text{Ge}) = 2.05$ eV and pre-exponential factor $D_0(\text{Ge}) = 0.39$ cm² s⁻¹ are in excellent agreement with experimental ones $\Delta E_{\text{exp}}(\text{Ge}) = 2.076$ eV, $D_{\text{exp}}(\text{Ge}) = 0.4$ cm² s⁻¹ [5]. High hydrostatic pressure (compression) has been found to enhance strongly the oxygen agglomeration at elevated temperatures [6-9]. The origin of this unusual phenomenon has been under debate and remains open. Effective extension of a crystal lattice is observed for the $\text{Si}_{1-x}\text{Ge}_x$ crystals. Investigations of $\text{Si}_{1-x}\text{Ge}_x:(\text{O})$ crystals have revealed the suppression of generation of thermal donors [11,12]. At the same time in $\text{Si}_{1-x}\text{Ge}_x:(\text{O})$ crystals the decrease of the activation energy of the relaxation of stress-induced dichroism of the 9 micron band in $\text{Si}_{1-x}\text{Ge}_x$ crystals has been observed [12]. Calculations have revealed that hydrostatic pressure (compression) leads to a lowering the diffusion barrier $\Delta E_a(P)$ and in the whole investigated interval of pressures ($P \leq 80$ kbar) is described well by the following expression: $\Delta E_a(P)/\Delta E_a(0) = 1 - \gamma P$, where $\gamma = 1.69 \cdot 10^{-3}$ kbar⁻¹, P is the hydrostatic pressure in kbar. The calculated pressure dependence of the O_i diffusivity (without any adjustable parameters) corresponds well to an enhanced growth of the oxygen-related thermal donors (TDs) observed experimentally [8] (Fig. 2). Extension of a crystalline lattice leads to linear increase of a diffusion barrier and the following relation $\Delta E_a(\text{compression}) = \Delta E_a(\text{extension})$ is valid in the investigated interval of variation of lattice constants (see Fig. 3). The given behavior can be explained as follows. Extension (compression) of a crystalline lattice tends to increase (decrease) a distance between initial and saddle points of a diffusion trajectory and hence increases (decreases) value of deformation of covalent Si-O bonds, and consequently a diffusion barrier. But situation is more complicated in the case of $\text{Si}_{1-x}\text{Ge}_x:(\text{O})$. Really, I have simulated a diffusion barrier when an

oxygen atom located in the second and third coordination spheres around Ge atom. In this case the value of a diffusion barrier is changed essentially.

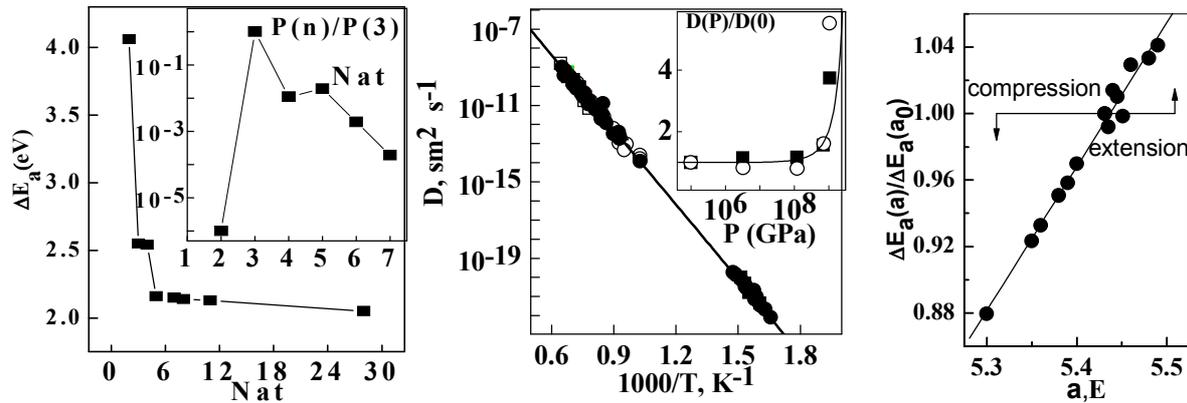


Fig. 1. Diffusion barrier $\Delta E_a(n)$ as a function of the number of Si atoms involved in minimization of the total cluster energy. In the inset the probability $P_{occ}P_{dj}$ of occurrence of an optimum configuration out of n atoms is presented ($\Delta\tau(n)/\tau(n)=0.01$).

Fig. 2. Temperature dependence of diffusion constant of interstitial oxygen atom in silicon. Points – experiment [4], line – theory. In the inset: solid line indicates the calculated pressure dependence of a relative coefficient of diffusion $D(P)/D(0)$, $T = 450^\circ\text{C}$; points are the relative concentration of oxygen thermal donors as a function of pressure (experiment [8]).

Fig. 3. Dependence of relative value of the diffusion barrier $\Delta E_a(a)/\Delta E_a(a_0)$ as a function of the lattice constant. $a_0 = 5.431 \text{ \AA}$.

When a diffusion trajectory is in a plane of Ge-Si bond the value of a barrier changes from $E_a \approx 2.3 \text{ eV}$ (second sphere) to $E_a \approx 2.5 \text{ eV}$ (third sphere). In a case when the atom of germanium does not locate in a plane of a diffusion trajectory the value of a diffusion barrier practically does not change $E_a \approx 2.3 \text{ eV}$. Thus, a germanium atom in a crystalline lattice of silicon essentially changes the value of a diffusion barrier for an interstitial oxygen atom in a region $R \sim 6 \text{ \AA}$ (three coordination spheres). Presence of gradient of a diffusion barrier in a crystal is responsible for diminution of number of equivalent diffusion trajectories N_{et} and decreases a diffusion constant (see Eq. 1). This conclusion agrees with experimental results [10], but for the quantitative comparisons with experimental results more extensive simulations are needed and are in progress.

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