

Defect engineering in germanium

Feature Article

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State of the art nanoelectronic devices are mainly fabricated on silicon (Si). In order to take advantage of the properties of germanium (Ge) in advanced electronic nanodevices all steps of device fabrication must be controlled. This, in particular, concerns the diffusion, doping, and activation of dopants in Ge. In this paper, the mechanism of self- and dopant diffusion in Ge under thermal equilibrium and non-equilibrium conditions are reviewed. Non-equilibrium conditions can, *e.g.*, be realized by irradiation, implantation, and the dissolution of unstable defect

clusters. Defect reactions mediating dopant diffusion and dopant deactivation in Ge under different experimental conditions are discussed. Special attention is paid to the charge states of the involved point defects and their Coulomb interactions that explain numerous results on dopant diffusion and dopant deactivation. Controlling the formation of vacancies *V* and self-interstitials *I* is the key to develop successful defect engineering strategies that are required to achieve the objectives for the fabrication of Ge-based devices.

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1 Introduction Germanium (Ge) as material for microelectronic applications has received renewed attention over the past decade [1–3]. This is due to the advantageous electron and hole mobilities that are higher than those of silicon (Si) [4]. Successful integration of Ge in future nanoelectronic devices requires detailed control on the diffusion of n- and p-type dopants and their electrical activation. In the case of Si, the understanding of the existence and properties of both vacancies (*V*) and self-interstitials (*I*) and their contributions to self- and dopant diffusion (see *e.g.* [5] and references therein) has led to advanced doping strategies that have realized the fabrication of Si-based nanoelectronic devices. Compared to Si, much less research has been conducted on the mechanisms of dopant diffusion in Ge and, in general, on the interaction between native and foreign-atom defects. Recently, some studies on self- and dopant diffusion under thermal equilibrium [6–12] and non-equilibrium conditions [13–17] have been performed to identify the atomic mechanisms of mass transport in Ge and the type of defects involved. In this work experimental studies are reviewed that significantly contribute to our understanding on diffusion, doping, and on defect reactions in Ge. Based on this improved understanding strategies to control the diffusion and activation of dopants in Ge are discussed.

The paper is organized as follows. Section 2.1 reports the properties of native point defects in Ge that act as main vehicle for atomic transport under thermal equilibrium and non-equilibrium conditions. Evidences on their preferred charge states are given. The section also comprises definitive clues on the dominance of either *V* or *I* under specific experimental conditions. The type of dopant-defect pairs that control the diffusion of n- and p-type dopants in Ge is treated in Section 2.2. Section 2.3 discusses the deactivation of dopants due to dopant defect interactions. Finally, strategies to effectively control the diffusion and activation of dopants in Ge are discussed in Section 3 that emerge from our understanding on the type and interaction of defects in Ge.

2 Defects in germanium

2.1 Native point defects Native point defects such as *V* and *I* are the most fundamental defects in a solid. They always exist due to thermodynamic principles and are the main entities that mediate the diffusion of self- and substitutionally dissolved foreign atoms. Accordingly, the characterization of native point defects, *i.e.*, identifying their type, charge state, and thermodynamic properties such as their formation and migration enthalpy and entropy are of pivotal significance to understand atomic transport in solids and the interactions of atomic defects.

First studies on self-diffusion in Ge date back more than 50 years after the invention of the first Ge point contact transistor [18, 19]. The impact of doping and hydrostatic pressure on self-diffusion provided first evidence on the acceptor nature of V in Ge [20]. The excellent agreement between Ge self-diffusion and the V contribution to self-diffusion deduced from copper diffusion in dislocation-free Ge has proved the dominance of V in Ge [21–23]. The interest in Ge as base material for electronic devices decreased with the invention of metal-oxide-semiconductor (MOS) structures based on Si. The low density of electronic states at the oxide/semiconductor fired the development of Si- rather than Ge-based devices. Accordingly, extensive research on defects in Si and their interaction was conducted. The successful interaction of basic research and technology contributed significantly to the increasing performance of Si-based devices that have been fabricated over the past decades. With the improvements of layer deposition systems and the development of novel dielectric materials with high dielectric constants as possible replacement for silicon dioxide, novel Ge-based nanoelectronic devices with advanced properties due to the higher carrier mobilities compared to Si were foreseen to be fabricated [1]. This prospect has awakened the interest in Ge.

The story on the evolution of Si-based electronics illustrates that a successful integration of Ge requires a comprehensive understanding on the type, properties, and interaction of point defects in this material system. In particular, for the fabrication of nanoelectronic devices the diffusion of self- and foreign-atom defects must be controlled within a few nanometer. Since diffusion is a thermally activated process small diffusion lengths can be easily realized by heat treatments at low temperatures. However, low temperatures also favor the formation of defect clusters that can hinder the electrical activation of dopants. Defect clusters usually dissolve at high temperatures but in order to suppress long-range mass transport,

heat treatments for a few milliseconds or even smaller times must be realized. Thus, the heat treatment strongly affects the dopant distribution and activation and must be controlled precisely to attain the desired objective. To control atomic transport in Ge over a wide processing window, the behavior of atomic defects should be known for a wide range of temperatures. Since self-diffusion is the most fundamental process of mass transport, we investigated self-diffusion in Ge down to 429 °C by means of neutron reflectometry [12]. The temperature dependence of Ge self-diffusion D_{Ge} is best described by a single diffusion activation enthalpy (see dashed line in Fig. 1) given by

$$D_{\text{Ge}} = 25.4 \times \exp\left(-\frac{3.13 \text{ eV}}{k_{\text{B}}T}\right) \text{ cm}^2 \text{ s}^{-1}, \quad (1)$$

for temperatures between 429 and 904 °C [12]. This result also comprises former data of Ge self-diffusion [20] and reveals that mainly V determine self-diffusion in Ge, *i.e.*, a contribution of I to self-diffusion is not evident. Additional studies on the impact of n-type doping on Ge self-diffusion demonstrate that V are doubly negatively charged under n-type doping conditions. This was independently verified by Brotzmann et al. [7] and Naganawa et al. [8] by means of dopant diffusion in isotopically controlled Ge multilayers. Recently, the impact of p-type doping on Ge self-diffusion was investigated with homogeneously boron (B) doped Ge isotope structures grown by means of molecular beam epitaxy [25]. Figure 1 shows that self-diffusion under p-type doping is clearly retarded compared to electronically intrinsic conditions. The doping dependence of self-diffusion is best described by two V -related acceptor levels in the band gap of Ge. Assuming these energy levels to be fixed to the valence band maximum (VBM), *i.e.*, $E_{V1-0} = \text{VBM} + 0.28 \text{ eV}$ and $E_{V2-/-} = \text{VBM} + 0.14 \text{ eV}$, the temperature dependence of self-diffusion under p-type doping is accurately described [25]. This is illustrated by the lower



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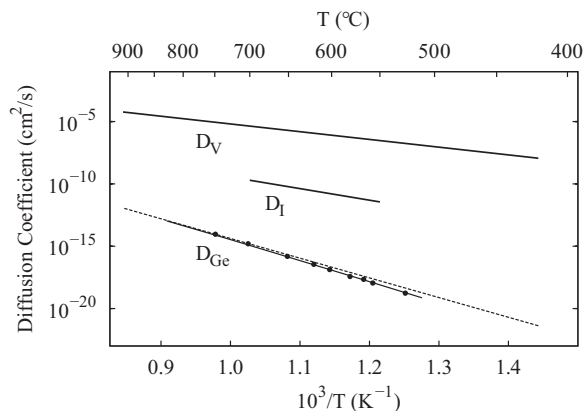


Figure 1 Temperature dependence of self-diffusion in undoped (dashed line: [12]) and boron-doped (solid line with points: [25]) Ge in comparison to the diffusion of vacancies (V) and self-interstitials (I). Data of D_V and D_I are given by Vanhellemon et al. [33] and Schneider et al. [37], respectively.

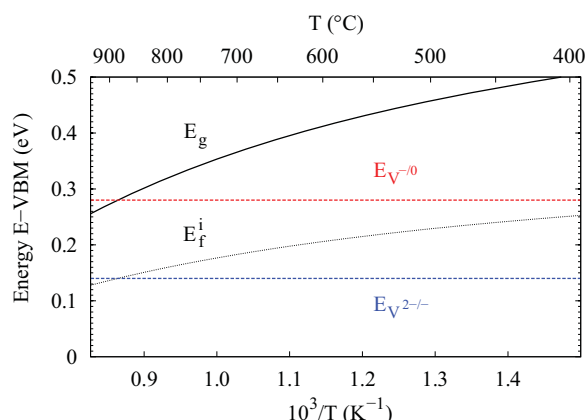


Figure 2 Calculated positions of the energy levels $E_{V-/0}$ (upper dashed line) and $E_{V^{2-}/-}$ (lower dashed line) of V within the band gap of Ge. The expression given by Vanhellemont and Simoen [24] were considered for the temperature dependence of the band gap $E_g(T)$ (solid line) and the position of the intrinsic Fermi level $E_f^i(\approx 0.5E_g(T))$ (short-dashed line). The position of the VBM is used as energy reference.

solid line in Fig. 1. The energy level positions within the Ge band gap are illustrated in Fig. 2. An inverse level ordering is suggested, *i.e.*, the single acceptor state lies above the double acceptor state. The ordering of the energy levels shows the dominance of doubly negatively charged V^{2-} under n-type doping and of neutral V^0 under p-type doping, *i.e.*, singly charged V^- are not expected to control self-diffusion under any doping conditions [25]. The level position considered for the double acceptor state is consistent with recent deep level transient spectroscopy studies of defects introduced in Ge by low-temperature electron irradiation [26]. According to theoretical calculations an inverse level ordering for the first and second V acceptor states cannot be excluded [27].

The activation enthalpy $Q_{Ge} = 3.13$ eV of Ge self-diffusion given by Eq. (1) equals the sum of V formation and migration. Analysis of Cu precipitation in Ge and of thermally induced acceptors after quenching reveal a V formation enthalpy of about 2 eV [28–31]. Although the values deduced for the V concentration in thermal equilibrium seem to be supported by metal diffusion studies [32], they must be considered as an upper bound because other defects formed by transition metal impurities also introduce acceptor levels. Recently, Vanhellemont et al. [33] reviewed experimental as well as theoretical results on the formation and migration enthalpy of V . They suggest a formation and migration energy of (2.35 ± 0.1) eV and (0.6 ± 0.1) eV, respectively, for V in Ge. The temperature dependence of the V diffusion coefficient D_V reported by Vanhellemont is illustrated in Fig. 1. For self-interstitials in Ge formation energies around 3 eV are predicted by theory [33–35] thus supporting their irrelevance under thermal equilibrium conditions compared to V . Calculated migration energies vary between 0.3 and 1.2 eV depending on the charge state of I [36]. For doubly positively charged I^{2+} a migration enthalpy of 1.2 eV is predicted [36]. This

value is in acceptable agreement with the diffusion activation enthalpy obtained from the temperature dependence of I diffusion [37]

$$D_I = 0.67_{-0.64}^{+18.60} \exp\left(-\frac{(1.84 \pm 0.26) \text{ eV}}{k_B T}\right) \text{ cm}^2 \text{ s}^{-1}. \quad (2)$$

Data of D_I were recently deduced from studying the radiation-enhanced self- and B diffusion in Ge [37]. The temperature dependence of D_I is shown in Fig. 1 in comparison to D_V and the Ge self-diffusion coefficient D_{Ge} . The present experimental and theoretical results on native point defects in Ge yield the following picture. Vacancies dominate self-diffusion in Ge and are mainly doubly negatively charged under n-type doping and neutral under p-type doping conditions. Self-interstitials do not significantly contribute to self-diffusion under thermal equilibrium. In the case self-interstitials are formed non-thermally, *e.g.*, by means of irradiation, they are doubly positively charged under intrinsic and p-type doping conditions and likely even under n-type doping. Accordingly, self-interstitials are expected to introduce a donor level in the upper half of the Ge band gap. Such an energy level position for I has been confirmed by perturbed angular correlation spectroscopy of electron irradiated Ge [38]. Haesslein et al. [38] suggested a donor level of I close to the conduction band E_C , *i.e.*, 0.04 eV below E_C . These results indicate that V and I are predominately negatively and positively charged, respectively. The opposite charge states of the two native defects is also supported indirectly by the very efficient recombination of V and I formed by irradiation, implantation, or other processes that introduce non-equilibrium native defect concentrations. For example, even at low temperatures of 400 °C, implantation damage can be removed, I -related

Table 1 Activation enthalpy Q and prefactor D_0 of self-diffusion and of the properties of vacancies V and self-interstitials I in Ge. $H_{V,I}^F$ and $H_{V,I}^M$ denote the formation and migration enthalpy, respectively, of the particular native defect. $E_{V-/0}$, $E_{V^{2-}/-}$, and $E_{I^{2+}/0}$ are the energy levels of the V acceptor and I donor states introduced within the band gap of Ge. The acceptor and donor states are referred to the VBM and conduction band minimum (CBM), respectively.

physical quantity	value	reference	comment
Q	3.13 eV	[12]	experiment
D_0	$25.4 \text{ cm}^2 \text{ s}^{-1}$	[12]	experiment
H_V^F	2.35 eV	[33]	theory
H_V^M	0.6 eV	[33]	theory
H_I^F	~ 3 eV	[33–35]	theory
H_I^M	0.3–1.2 eV	[36]	theory
H_I^M	1.84 eV	[37]	experiment
$E_{V-/0}$	VBM + 0.28 eV	[25]	experiment
$E_{V^{2-}/-}$	VBM + 0.14 eV	[25, 26]	experiment
$E_{I^{2+}/0}$	CBM – 0.04 eV	[38]	experiment

defect clusters dissolve readily, and recrystallization of preamorphized Ge proceeds rapidly [39–42]. This behavior of V and I in Ge is at variance to Si where recombination of the native defects seems to be hindered [43]. This has been related to an entropy barrier against V – I recombination [43] but is also indicative of a less pronounced Coulomb attraction between I and V in Si where both defects are mainly neutral under intrinsic conditions [5]. Thus, the strong Coulomb attraction between V and I in Ge compared to Si gives rise to different characteristics in the annealing behavior of implantation damage. Summarizing this section, a compilation of Ge self-diffusion data and of the properties of V and I is given in Table 1.

2.2 Dopant-defect pairs Dopant-defect pairs are of fundamental significance for dopant diffusion. In the case of Si both dopant- V and dopant- I pairs contribute to dopant diffusion under thermal equilibrium conditions (see *e.g.*, Ref. [5]). In the case of Ge, mainly dopant- V pairs exist in equilibrium because the formation of I is energetically suppressed due to its high formation energy. Information about the charge states of dopant- V pairs in Ge is gained from the shape of the dopant diffusion profiles and the doping dependence of diffusion [44]. Experiments on the diffusion of n-type dopants such as phosphorus (P), arsenic (As), and antimony (Sb) in Ge have revealed the dominance of singly negatively charged dopant- V pairs [9]. The charge state of these pairs is also different to the charge state preferred for these pairs in Si [5]. In Si, dopant- V pairs are mainly neutral. Only for very high doping levels a contribution due to singly negatively charged dopant- V pairs becomes evident in, *e.g.*, P diffusion profiles [5]. This difference in the preferred charged states of dopant- V pairs explains the strong doping dependence of the diffusion of n-type dopants in Ge that increases with the square of the electron concentration [9]. In Si, n-type dopant diffusion mainly increases just with the electron concentration [5]. In summary, the diffusion of n-type dopants $A \in \{P, As, Sb\}$ in Ge is accurately described by the vacancy mechanism with the following defects and charge states involved [7]:



The diffusion of p-type dopants such as Ga and In in Ge does not reveal any significant doping dependence [10, 11]. Analysis of In diffusion in Ge reveal an In diffusivity for extrinsic conditions that is only twice as high as for intrinsic conditions [11]. This demonstrates that the (In V) pair must be singly negatively charged and therewith possesses the same charge state as the In acceptor. Data reported in the literature on Ga diffusion in Ge also indicate a concentration independent diffusion [10]. Accordingly, the (Ga V) pair is likely also singly negatively charged. Small differences in the extrinsic and intrinsic diffusion of Ga like those observed in In diffusion were not recognized by the authors [10]. Presumably, Al in Ge behaves similar [45]. In summary, p-type dopants $A \in \{Al, Ga, In\}$ in Ge diffuse via the vacancy

mechanism with the following defects and charge states involved:



Note, reactions (3) and (4) consider the charge state of V that prevails under the particular doping condition (see Section 2.1). The diffusion of the acceptor dopant B in Ge behaves very different from Al, Ga, and In. Its diffusivity is several orders of magnitude lower than self-diffusion [6] and exhibits a diffusion activation enthalpy of 4.65 eV [46] that clearly exceeds the activation enthalpy of self-diffusion [see Eq. (1)]. This can be explained with a repulsive elastic interaction between B and V as confirmed by theoretical calculations [47, 48]. On the other hand the slow diffusion of B may reflect the contribution of the interstitialcy or kick-out mechanism to dopant diffusion. This contribution is usually covered by the dominance of the vacancy mechanism but could step out due to the repulsive interaction between B and V . Following this interpretation, B diffusion in Ge could be mediated by the interstitialcy mechanism



that considers the acceptor nature of substitutional B and the self-interstitial in its preferred charge state (see Section 2.1). Reaction (5) is equivalent to the kick-out reaction since the BI pair and interstitial B are hardly distinguishable. The charge state of the BI pair is assumed to fulfill the charge neutrality of reaction (5). The reaction predicts that the diffusion of B should increase with the square of the acceptor concentration. This could be verified by B diffusion in Ge with different acceptor background doping levels. To the authors knowledge, such experiments have not yet been performed.

Finally, differences and similarities in the diffusion behavior of dopants in Ge and Si are highlighted. Let us consider again the reaction



where (AX) is the dopant(A)-defect(X) pair. Reaction 6 is representative for the vacancy ($X = V$) and interstitialcy ($X = I$) mechanisms of dopant diffusion. These two mechanisms mainly control the diffusion of dopants in Si and Ge. Relevant dopants possess a high solid solubility and mainly occupy substitutional lattice sites, *i.e.*, the concentration of A in thermal equilibrium is significantly higher than the concentration of V and (AX). The formation of A via reaction (6) is either controlled by the supply of (AX) or the removal of X. In the case of Ge the supply of (AX) always limits the formation of A [6, 7, 9, 11] whereas in case of Si both (AX) and X can control the distribution of A [5]. The two different ways of mediating dopant diffusion are called foreign-atom and native defect controlled mode [44]. In Ge, the foreign-atom controlled mode of dopant diffusion prevails. No exception has been found so far. In Si, the

foreign-atom controlled mode of dopant diffusion prevails for all dopants except for B and P [5]. The diffusion of these dopants is controlled by I , i.e., the diffusion process itself leads to concentrations of I that deviate from thermal equilibrium [5]. Such a diffusion behavior is not operating in Ge where mainly V controls dopant diffusion. But considering V only, a V -controlled mode of dopant diffusion is also not observed in Si. In this respect, dopant diffusion in Si and Ge via V behave very similar.

2.3 Dopant-defect complexes Dopant-defect complexes may form during ion-implantation, during annealing of ion-implanted Ge, and even under equilibrium diffusion conditions. The latter aspect is considered first as this describes the case, where the concentration of native point defects are in thermal equilibrium. By all means, the formation of dopant-defect complexes is highly undesirable during fabrication of electronic devices. It reduces the concentration of electrically active dopants and the mobility of free carriers due to scattering events. Understanding of the mechanisms that lead to dopant deactivation will help to develop strategies for its prevention.

Dopant-defect complexes form in the first case when a dopant-defect pair (AX) gets close to a substitutional dopant A or to an isolated defect X. This is expressed by the reactions



where (A_2X) and (AX_2) are the respective defect complexes consisting of either two dopant atoms A or two native defects X. It is evident from Eq. (3) that the formation of (A_2V) complexes is very favorable for n-type dopants in Ge due to the attractive Coulomb interaction between $(AV)^-$ and A^+ . Indeed, a significant deactivation of n-type dopants becomes evident in the diffusion behavior of P and As at high concentrations [7]. This is accurately described assuming (A_2V) complex formation. On the other hand, (AV_2) complexes are not favored under equilibrium diffusion conditions as a Coulomb barrier exists between $(AV)^-$ and V^{2-} . Considering p-type dopants, the formation of (A_2V) complexes is not very likely due to the Coulomb repulsion between $(AV)^-$ and A^- [see Eq. (4)]. Instead, reaction (8) can cause a successive deactivation of p-type dopants since the formation of both $(AV)^-$ and (AV_2) is not hindered by a Coulomb barrier [see Eq. (4)]. Hence, deactivation of Ga in Ge [49] very likely proceeds via reaction (8). Finally, B in Ge is considered. As already mentioned B diffuses exceptional slowly [46] and is likely mediated by I [15, 17, 37, 50]. In the case the concentration of I increases in Ge that is sufficiently doped with B also the concentration of $(BI)^+$ will increase. With increasing concentration of $(BI)^+$ a deactivation of substitutional B^- is favored like in Si. However, under conventional annealing conditions the concentration of I is too low to initiate B complex formation. However, this

situation changes when I are formed athermally, e.g., by ion implantation and/or irradiation.

Equations (7) and (8) represent the most simple reactions that initiate the formation of dopant-defect complexes. More complicated clusters can evolve when additional mobile defects such as (AX) and X approach the complex. It is beyond the scope of this paper to describe the evolution or dissolution of bigger clusters as this has been performed, e. g., for B-interstitial clusters (BICs) in Si. But it is important to note that the formation of defect complexes and bigger clusters strongly relies on the behavior and stability of native point defects. Since the properties of V and I in Ge differ from those in Si (see Section 2.1) also the evolution of defect clusters will be different. Key for the understanding of cluster formation and dissolution is a physical-based understanding on the properties and the behavior of native point defects in Ge under various experimental conditions. With this information at hand effective defect engineering strategies can be developed to tune the distribution and activation of dopants as desired.

3 Defect engineering

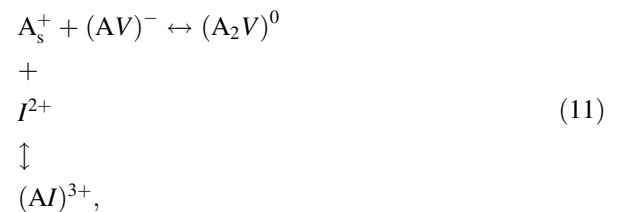
3.1 Basic concepts The previous sections demonstrate that native point defects are involved in all processes that concern dopant diffusion, activation, and complex formation. Accordingly, defect engineering that aims to improve the distribution of dopants and their activation seeks for strategies to control the concentration and distribution of V and I . Only in this case full flexibility exists to alter reaction processes that are dominated by either V or I . Since self-interstitials in Ge are negligible under thermal equilibrium conditions, other strategies are required to introduce I in a controlled way. Ion implantation is known to create both V and I . Different microscopic structures can evolve in the bulk of the implanted material depending on the implantation parameters and sample temperature. Various regimes can be defined such as a low, intermediate, and high temperature regime. At low temperatures the diffusion of native point defects is suppressed and therewith an annealing of the implantation damage. As a consequence, implantation will finally result in an amorphous structure. At high temperatures the native defects are highly mobile. This not only favors dynamic annealing of the implantation damage but also suppresses the formation of defect clusters, whose stability decreases with increasing temperature. At intermediate temperatures the native defects are already mobile but the reduced kinetic energy favors a trapping of the defects at random nucleation sites that may be initiated by the simple complexes introduced in Section 2.3. As a consequence V - and I -related microscopic clusters can evolve that become visible in the electron microscope. The evolution of such microscopic defects is a complex phenomenon whose description involves many model parameters. Although, this intermediate region is often used for the processing of electronic devices it is less appropriate for studying the impact of non-equilibrium defects on dopant diffusion and activation.

3.2 Concurrent annealing and irradiation More defined experimental conditions can be realized by concurrent annealing and irradiation with light particles such as electrons or protons. These particles mainly form isolated Frenkel defects and thus V and I in equal numbers. The effect of proton irradiation on self- and dopant diffusion in Ge has been recently studied by means of isotopically controlled Ge samples and samples doped with P, As, and B [13, 37, 51]. In order to avoid the formation of end-of-range defects at the projected depth of the protons, Ge samples thinner than the projected depth were prepared. In this way complications due to the presence of defect clusters are avoided that can form undefined sinks/sources for native point defects. Instead, only the surface needs to be considered as annihilation side for V and I beside the direct annihilation of the defects. Analysis of self- and dopant diffusion in Ge under irradiation revealed a surprising diffusion behavior. Whereas the diffusion of self- and B-atoms is enhanced compared to thermal equilibrium conditions, the diffusion of n-type dopants such as P and As remains unaffected, *i.e.*, equals the diffusion under thermal equilibrium conditions [13, 37, 51]. In addition, self- and B diffusion does not reveal any depth dependence that is expected in the case the Ge surface acts as efficient sink for native defects. This behavior of self- and dopant diffusion in Ge under irradiation strongly differs from that in Si [52] and, accordingly, must be related to specific Ge properties that differ from Si. First, the striking equilibrium diffusion of As and P under irradiation demonstrates that the V concentration in Ge under irradiation does not significantly deviate from thermal equilibrium. Second, the absence of any depth-dependent broadening in self- and B-atom profiles indicates that the distribution of the native defects must be homogenous. Third, the strongly enhanced diffusion of B shows that B diffusion is not mediated by the same defect that controls the diffusion of P and As. Altogether these characteristics are consistently explained when the Ge surface is considered to be an efficient sink for V but a barrier for I , *i.e.*, V are readily annihilated at the Ge surface but I are reflected. Detailed modeling of self- and dopant diffusion under irradiation demonstrates that this surface property explains the homogenous distributions of V and I with concentrations close to thermal equilibrium and concentrations exceeding thermal equilibrium by several orders of magnitude, respectively [37, 51]. Accordingly, the diffusion of B via reaction (5) is strongly enhanced. Self-diffusion is enhanced due to the enhanced I contribution that is below the V contribution of self-diffusion for equilibrium conditions. The absence of any significant impact of irradiation on the diffusion of P and As in Ge is, on first sight, unbelievable as these dopants may in principle also diffuse via dopant- I pairs. However, the positive charge state of the substitutional donor and the doubly positively state of I hamper the formation of dopant- I pairs. Compared to As and P diffusion under equilibrium conditions, the diffusion of these dopants under irradiation does not provide evidence on dopant deactivation, *i.e.*, the formation of dopant-defect clusters is

suppressed under irradiation. Considering the charge states of (AV) pairs, (A_2V) complexes, and of I , the reactions



describe the preferred formation of the substitutional donor A_s^+ under irradiation. Beside the suppression of the deactivation reaction (10) also the formation of (AV) is hindered via reaction (9). This would lead to a reduced mobility of (AV) , which is, however, at variance with the experimental results. Instead, the diffusion behavior of P and As under irradiation clearly resembles donor diffusion in Ge under equilibrium conditions without formation of inactive (A_2V) complexes [51]. This observation is better described by means of a competitive inhibition reaction [53]. Such reactions are known from biochemical enzymatic reactions. In our case self-interstitials act as inhibitors for the formation of (A_2V) complexes without forming stable (AI) pairs. The inhibitor reaction described by



lowers the rate constant for the formation of the (A_2V) complex, *i.e.*, the formation of A_2V is suppressed by $A_s^+ + I^{2+} \leftrightarrow (AI)^{3+}$. The suppression increases with increasing supersaturation of I . Physically the inhibitor reaction describes the tendency of the substitutional donor A_s^+ to form a pair with I^{2+} that can be favored due to attractive elastic interactions. However, the repulsive Coulomb interaction finally hampers the actual formation of the pair.

The interpretation of the diffusion of self- and substitutional foreign atoms in Ge observed under concurrent annealing and irradiation is directly related to the limited efficiency of the Ge surface to annihilate I . This unusual behavior of the Ge surface is supported by the fact that I could be observed directly after electron irradiation by means of high resolution transmission electron microscopy [54]. This would be hardly possible in the case the Ge surface is a perfect sink. In order to control the diffusion and activation of dopants in Ge it is important to understand the behavior of the Ge surface that controls the balance between V and I . In particular, the following questions should be addressed. What is the physical origin of the Ge surface to repel I ? Is it possible to alter the surface property of Ge in order to control the annihilation of native point defects? It is very likely that both elastic and electrostatic interactions affect the annihilation of I at the Ge surface. As discussed above, the self-interstitial in Ge is positively charged. On the

other hand, electronic states established at the Ge surface or at interfaces are known to pin the Fermi level. This is already known since the pioneering work of Brattain and Bardeen [55] on the Ge point contact transistor. The operation of this transistor relied on the fact that surface acceptor states have pinned the Fermi level near the valence band. As a consequence, an inversion layer of holes is formed near the surface. However, the electric field established within the inversion layer would attract rather than repel positively charged self-interstitials created athermally in the bulk by irradiation. A few years later, Clarke [56] reported that surface acceptor states can be removed by heating in vacuum. Following this line, it is possible that the conditions realized by concurrent annealing and proton irradiation at a vacuum pressure of 2×10^{-5} mbar favor donor-type surface states rather than acceptor states. In this case, the electric field within the inversion layer would hinder positively charged self-interstitials to annihilate at the surface. On the other hand, self-interstitials approaching the Ge surface may also be repelled by a strain field close to the surface. Such a strain field should cause a higher formation enthalpy of I at the Ge surface compared to the bulk. Recent *ab initio* studies of Kamiyama et al. [57] report on lower formation energies of V and I at the surface of Si crystals compared to the bulk due to structural relaxation. Similar, the authors calculated the formation energies of V and I in Ge. Also lower values near the surface than deeper in the bulk [58] were obtained. This suggests concentrations for both types of intrinsic defects that exceed the bulk values. Moreover, Kamiyama et al. [59] considered surface-induced charge states and its interaction with intrinsic defects in Ge. The calculations support a reflection of I due to positively charged surface atoms and positively charged I generated inside the Ge crystal.

The studies on self- and dopant diffusion in Ge under concurrent annealing and irradiation conditions demonstrate the significance of I . For the fabrication of Ge-based electronic devices experimental conditions are advantageous that suppress the deactivation of donors without enhancing their mobility. However, the increased activation leads to an enhanced diffusion due to the strong doping dependence of donor diffusion [9]. Accordingly, the annealing time must be reduced to compensate for the enhanced diffusion. On the other hand, a diffusional broadening of B that is practically immobile under thermal equilibrium conditions can be induced by concurrent annealing and irradiation. However, the temperature and time of annealing and the doping level must be appropriate to avoid the formation of BICs.

3.3 Formation and dissolution of defect clusters Other strategies to alter the diffusion and activation of dopants in Ge relies on the formation and dissolution of defect clusters that, *e.g.*, emit self-interstitials. Under such conditions the concentration of I will increase and therewith the diffusion of dopants mediated by I . Moreover, the formation of dopant- I clusters is favored. Such conditions are, *e.g.*, realized by

Ge oxide nanoclusters (NC) formed in Ge by oxygen implantation and subsequent annealing [60]. An injection of I due to NC formation became evident in the transient enhanced diffusion of B. In a similar approach the impact of fluorine (F) doping on As diffusion in Ge was investigated by Impellizzeri et al. [61]. Coinplantation of Ge with F and As and subsequent annealing demonstrates an enhanced diffusion of As in the layer amorphized by F and As implantation. However, $F_M I_N$ cluster formed next to the end-of-range damaged region give rise to a reduced concentration of V that locally retards the diffusion of As [61]. The concept of forming NC that inject I either during their formation or dissolution is also well suited to alter the balance between V and I . However, ion implantation finally not only causes an amorphization of Ge but also an ion beam mixing that has to be considered to predict the dopant distribution. Moreover, various types of dopant-defect clusters with specific stabilities can form (see *e.g.*, Ref. [62]) that complicate the modeling of the underlying physical processes.

Irrespective of the method used to change the balance between I and V , *i.e.*, either by concurrent annealing and irradiation or by postimplantation annealing, the property of the Ge surface remains the key to the strong I - V imbalance. Certainly, atomistic calculations can help to understand the interaction between I and the Ge surface, but in the end experiments have to prove the concept.

4 Conclusions Summarizing previous and recent results on atomic mass transport in Ge under thermal equilibrium conditions it has been evidenced that acceptor-type vacancies mainly mediate self- and dopant diffusion in Ge, no evidence of Ge interstitials was found. The vacancy in Ge is doubly negatively charged under n-type doping and mainly neutral under p-type doping conditions. In contrast, self-interstitials are likely mainly doubly positively charged even under n-type doping. The charge states deduced for the native point defects and for dopant-defect pairs give rise to specific dopant-defect reactions that favor dopant deactivation via Coulomb interaction. The peculiar behavior of self- and dopant diffusion in Ge under non-equilibrium conditions demonstrates that the Ge surface repels self-interstitials. Depending on the experimental conditions these self-interstitials are formed in the bulk by irradiation, the formation of nanoparticles, or the dissolution of defect clusters. These methods have in common that they change the balance between V and I and thus are applicable to affect the diffusion and activation of dopants in Ge. Overall the strong impact of the Ge surface on the V - I imbalance seems to be the key to control the diffusion and activation of dopants in Ge. The interaction of surfaces and interfaces with intrinsic defects is, in particular, important for the realization of Ge-based nanoelectronic devices. The diffusion and activation of dopants in nanostructures are expected to be different compared to the properties of dopants inside a bulk crystal. The impact of nanostructuring on doping and atomic diffusion will be the subject of future studies.

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