



Diffusion and Dopant Activation in Germanium: Insights from Recent Experimental and **Theoretical Results**

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Abstract: Germanium is an important mainstream material for many nanoelectronic and sensor applications. The understanding of diffusion at an atomic level is important for fundamental and technological reasons. In the present review, we focus on the description of recent studies concerning *n*-type dopants, isovalent atoms, *p*-type dopants, and metallic and oxygen diffusion in germanium. Defect engineering strategies considered by the community over the past decade are discussed in view of their potential application to other systems.

Keywords: germanium; dopants; diffusion; defect engineering; electronic materials

1. Introduction

For over a decade, Ge has been actively considered for many nanoelectronic and sensor applications, as it has a number of material property advantages over Si or alternative materials such as silicon–germanium ($Si_{1-x}Ge_x$) alloys. The main properties include its superior carrier mobilities, low-dopant activation temperatures, and smaller band-gap [1–3]. A main advantage of Ge-technology is its compatibility to existing Si processes and this may be an important factor as industrial inertia may delay the introduction of more exotic materials, unless, of course, they provide a clear breakthrough as compared to present technologies. The second determining factor for the consideration of Ge is the development of high-k gate dielectric materials. This, in turn, eliminates the need for a good-quality native oxide for the semiconducting material. The poor quality of germanium dioxide as compared to silicon dioxide in Si-technology plagued Ge-technology in the early days of the semiconductor industry [1].

Defects in semiconductors cannot be avoided in device processing (for example, implantation and diffusion). Essentially, understanding their properties is key to comprehend diffusion and can lead to devices with improved characteristics. For example, diffusion issues are important as the characteristic dimensions of devices are presently only a few nanometers. This necessitates the control of *p*- and *n*-type dopants to form efficient Ge-based *p*- and *n*-channel metal oxide semiconductor field effect transistors (MOSFETs) for advanced complementary metal-oxide semiconductors (CMOSs). There have been numerous studies on Ge over the past decade; however, research on Ge was limited for many decades with most being published over the last decade [4–25].



Vacancies (*V*) and self-interstitials (*I*) are the intrinsic point defects which act as vehicles mediating diffusion and as such understanding of their properties is critical to control the diffusion and/or electrical activation of dopants [26–40]. The dominance of *V* is established experimentally [28] and is important as it mediates the diffusion of most dopants in Ge [5,41,42]. Concerning donor atom diffusion, previous studies have established that *n*-type dopants such as P, As, and Sb diffuse in Ge via a vacancy mechanism at a rate that is faster than self-diffusion [41–45]. It should be considered that the relatively fast transport of *n*-type dopants is not appropriate for the formation of ultra-shallow donor profiles.

It is established that *p*-type dopants (for example Ga, In, B) diffuse at a lower rate as compared to *n*-type dopants [36]. The diffusion of the *p*-type dopants is similar to self-diffusion; however, in the case of B, it is significantly lower [46–49]. This slow diffusion of the *p*-type dopants is advantageous for the formation of ultra-shallow and well-defined acceptor doped regions in Ge.

The most common isovalent dopant in the Czochralski-grown group IV semiconductors is C [50–52]. Other dopants such as Sn or lead Pb have been used in defect engineering strategies to contain the fast diffusion of *n*-type dopants in Ge [20,36,53,54]. The interest in isovalent doping stems also from the interest to employ group IV binary (for example Si_{1-x}Ge_x, Sn_{1-x}Ge_x) and/or ternary (for example Si_{1-x-v}Ge_xSn_y) alloys in devices [55].

In Czochralski-grown semiconductors such as Ge or Si, there is a non-negligible concentration of oxygen [1,56–60]. Oxygen is mainly incorporated in the lattice via the growth process and its impact has been mainly investigated in Si and to a far lesser extend in Ge. Notably, most Ge crystals are pulled in graphite crucibles, leading to a lower oxygen content than in Czochralski-grown Si. At any rate, the introduction of oxygen is important as it can lead to further extended defects, which can degrade the performance of devices.

Metallic diffusion in semiconductors such as Ge is both scientifically and technologically important [30,61–65]. For example, Giese et al. [30] have studied the diffusion of nickel and copper in Ge to derive information regarding the vacancy-mediated Ge self-diffusion coefficient and the concentration of vacancies with respect to temperature. From a technological viewpoint metals such as copper, nickel, and palladium are used as crystallization inducers in the metal-induced lateral crystallization (MILC) method which is an efficient way to produce large grain crystals [64].

The methodological advances in the past years and their wide spread (for example, density functional theory (DFT) and time of flight secondary ion mass spectrometry (ToF-SIMS)) have enabled the better understanding of materials at an atomistic level [66–80]. In particular, these methods can resolve the energetics of atomic diffusion, provide evidence of the diffusion mechanism, the formation of clusters, and other electronic and mechanical properties. Therefore, they are useful tools to devise defect engineering strategies.

The present review is mainly focused on the diffusion of technologically important dopants and impurities. The review considers self-diffusion, the diffusion of *n*-type dopants, *p*-type dopants, and metallic diffusions. The latter is mainly concerned with recent results on Pd diffusion, which recently calculated a very low migration energy barrier of Pd interstitial (Pd_i) diffusion.

2. Self-Diffusion

The studies by Werner et al. [28] determined that V is the prevalent intrinsic point defect mediating self-diffusion in Ge under conditions of equilibrium. Werner et al. [28] determined that there are no I under thermal equilibrium conditions. The dominance of V is strengthened by recent DFT calculations that exhibit a lower formation energy for V as compared to I. Bracht et al. [81] proposed proton irradiation to generate a supersaturation of Ge self-interstitials, and thus, to better control the concentration of vacancies. This is an important method as vacancies mediate the fast diffusion of n-type dopants in Ge, and therefore, need to be controlled [36,70,82]. Conversely, the generation of self-interstitials can enhance the boron diffusion in Ge via an interstitial mechanism that requires the formation of boron-self-interstitial pairs [83].

3. *n*-Type Dopants

Interestingly, although Ge shares the same crystal structure to Si, its defect properties are distinctively different. A key issue in Ge is the excessive *n*-type dopant diffusion. This in turn poses a technological difficulty to form well-defined *n*-type doped regions for devices. It has also been established that donor atoms such as arsenic can form clusters with vacancies (As_nV defect clusters, refer to Figure 1) [4]. The community aims to confront these issues by considering defect engineering strategies that can address both the fast diffusion and the clustering of the donor atoms. It should be noted that, in the past, a common defect engineering strategy was to introduce co-dopants in the material [84–88]. The purpose is that the co-dopants will act competitively, attracting native point defects (such as vacancies) and in that respect, will allow the annihilation and/or control of the dopants and their clusters. Experimental and theoretical investigations used isovalent C or Sn to co-dope *n*-type doped Ge (refer to Reference [36] and references therein). It was determined that isovalent co-doping will impact the diffusion of the donor atoms; however, it did not affect the deactivation of the donor profile [41,44]. In essence the picture is that the isovalent atoms associate with the migrating vacancies and (or donor-vacancy pairs) effectively immobilizing a proportion of them. These in turn, are not available to associate with the donor atoms and facilitate their migration, hence, less donor atoms will migrate, and this leads to a decline in their diffusivity [44]. The association, however, of the isovalent atoms with the donor-vacancy pairs results in defect clusters which still lead to the deactivation of the donor atoms [44]. Therefore, although isovalent co-doping solves the fast diffusion of the donor profile issue, it does not impact the deactivation issues [36,41,44].



Figure 1. A schematic of the arsenic-vacancy $(As_n V)$ defect clusters in Ge. Black circles represent the As atoms, white circles the Ge atoms, and cubes the vacancies [4].

To address both these issues concurrently, double-donor doping and doping with aliovalent dopants was considered [2,89]. Double-donor doping is the process where a second *n*-type dopant is introduced in the lattice aiming to impact the electronic properties and defect-dopant processes [89–94]. Tsouroutas et al. [90] investigated the diffusion and activation of P and as co-doped Ge using conventional thermal annealing (600–750 °C). It was determined using Secondary Ion Mass Spectrometry (SIMS) that As diffusion was retarded, whereas P diffusion remained unaffected or even somewhat enhanced [90]. Additionally, double-donor doping was not beneficial concerning the level of activation [90]. Stathopoulos et al. [92] considered P and N co-doping but with millisecond non-melt laser annealing. It was determined that co-doping with N reduces the diffusion of P but with a lower activation level [92]. Therefore, the conclusions for double-donor doping are similar to those for isovalent doping: fast diffusion is reduced but there is no benefit concerning the activation of the donor

atoms. At any rate it should be considered that in other classes of materials (for example oxides), these defect engineering strategies are effective [95,96]. In these systems the key is the relaxation manipulation offered by the two co-dopants, whereas here electronic effects are also important.

To the best of our knowledge the primary study that considered the impact of F on donor dopants in Ge was the DFT study by Chroneos et al. [97] nearly a decade ago. The promising DFT results motivated a series of experimental studies to determine the impact of F on the electrical activation of P and As in Ge [2,98–104]. The introduction of F in Ge was inspired by analogous experimental and theoretical work of F in Si, where it was employed to control the transient diffusion of B [105-107]. The host lattices are different; however, the key feature of the highly electronegative F in Si and Ge is that it can passivate the dangling bonds formed by vacancies. In essence, as the F atoms saturate the dangling bonds (formed by the vacancies) they concurrently solve the low activation and high diffusion of donor atom problems in Ge [97]. This is because the donor atom diffusion is vacancy mediated, whereas they are also necessary for the formation of the large donor atom-vacancy clusters that deactivate the donor profile. In the DFT study by Chroneos et al. [97], it was calculated that F captures vacancies to form $F_n V_m$ clusters, in effect depriving these vacancies from the donor atoms. Although this early study employed relatively crude mass action analysis arguments, it inspired experimental work to investigate the interaction of F with defects in Ge. Interestingly, Sanson et al. [104] used X-ray absorption near edge structure (XANES) spectroscopy to study the local structure of ion-implanted F-doped Ge and determined that $F_n V_m$, and in particular $F_6 V_2$ clusters, form in agreement with the DFT results [97]. Considering the diffusion of donor atoms in the presence of F, Impellizzeri et al. [2] determined that F retards As diffusion in Ge (refer to Figure 2). Jung et al. [100] determined that F implantation passivates vacancies at around 500 °C, and this is linked to the enhancement in Ge-MOSFET performance.



Figure 2. The determined arsenic concentration profiles with respect to depth for arsenic-doped (blue line 3×10^{13} As/cm² with 50 keV implantation energy) and fluorine + arsenic-co-doped (red line As: 3×10^{13} As/cm² with 50 keV implantation energy; F: 1×10^{15} F/cm² with 35 keV implantation energy) germanium [38].

It should be stressed that the search for efficient defect engineering strategies in the case of *n*-type doped Ge is a good example of the compatibility and complementary information that can be achieved when utilizing experiment and DFT calculations.

4. *p*-Type Dopants

In Ge, the diffusion of B is slow, and this is a consequence of its very high diffusion activation enthalpy, which is higher than the activation enthalpy of self-diffusion by more than 1 eV [46]. As the dominant intrinsic defect is the Ge vacancy with the higher activation energy of the B atom as compared to the vacancy self-diffusion indicates that it is not bound to a vacancy when it migrates. This is also confirmed by the DFT calculations, which show that the boron atom repels the vacancy [36]. This is the opposite picture to the donor atoms where diffusion is facilitated by vacancies with the donor–vacancy pairs being highly bound [36]. For B in Ge, the interstitial-mediated diffusion mechanism is proposed,

and this is consistent with the DFT investigations of Janke et al. [48] and by the enhanced diffusivity of B under irradiation (where there is a self-interstitial supersaturation) [83].

Conversely, the diffusion of *p*-type dopants such as Al, Ga, and In is mediated by vacancies. These *p*-type dopants have a higher activation enthalpy of diffusion as compared to *n*-type dopants [36,42]. The main difference between the acceptor and donor atoms is that the latter have a higher attraction to the vacancies (i.e., Coulombic attraction of the positively charged *n*-type dopants to the negatively charged vacancies) and this is, in turn, reflected in the activation enthalpies of diffusion [18,42–44]. For example, Kube et al. [18] determined that indium diffusion in germanium is vacancy mediated but with a relatively high activation enthalpy of diffusion of 3.51 eV (under intrinsic conditions).

It has been determined that for high-dopant concentrations (i.e., at $\sim 10^{20}$ cm⁻³), there is a formation of dopant-defect clusters [44]. These clusters in turn will impact *p*-type dopant diffusion as in the case of analogous clusters for *n*-type dopants (refer to Figure 1 and References [4,44]); however, the impact on the activation enthalpy of migration has not been calculated using advanced computational methods.

5. Isovalent Dopants

Tetravalent or isovalent atoms can be introduced in the Ge lattice mainly as substitutional atoms. Apart from C, which is mainly introduced during the processing (although at smaller concentration as compared to Si lattices) [1], isovalent atoms are considered in Ge as co-dopants that will be useful to constrain A-centers (or other oxygen-related defects) and reduce the diffusivities of *n*-type dopants (also refer to Section 3 above).

Considering oxygen-related defects in Ge [108–113] (refer to Section 7 for what follows), the main benefit for introducing isovalent dopants is to anchor or attract the lattice vacancies, which would otherwise bind with the oxygen atoms [39,112]. In DFT calculations, it was calculated that the SnV defect is more bound compared to the VO defect by 0.2 eV [112], and thus, if there is enough Sn in the lattice (i.e., more than the existing oxygen) most vacancies will be trapped by the Sn atoms limiting the concentration of the VO pairs. This is analogous to the defect engineering strategies employed using isovalent dopants to minimize the formation of the deleterious oxygen-vacancy defects in Si [86]. A difference between Si and Ge as host lattices is that in the latter, the concentration of oxygen is far lower [1]. Therefore, smaller oxygen-vacancy clusters are likely to form.

For *n*-type dopants, the co-doping with isovalent atoms again aims to control the behavior of the *n*-type dopant by depriving it from vacancies. In that respect, previous studies have considered the co-doping with large isovalent dopants such as Sn and Hf which relax (and thus are bound) near lattice vacancies [54]. In particular, the DFT studies by Tahini et al. [54] showed that the SnV and HfV defects are strongly bound. The interaction with these large isovalent atoms does effectively increase the activation energy of diffusion of *n*-type dopants and thus succeeds in decelerating (and constraining) *n*-type dopants in the Ge lattice (refer to Figures 3 and 4) [54]. This effect is more significant for the larger isovalent dopant (i.e., Hf). As discussed in Section 3 above, the introduction of isovalent dopants fails to deal with the deactivation issues, and thus, other defects engineering strategies such as co-doping with F should be more efficient.



Figure 3. Diffusion of the PV pair via the ring mechanism of diffusion in the presence of an oversized dopant atom. Reproduced by permission from the PCCP Owner Societies [54].



Figure 4. Diffusion of the PV in the presence of (**a**) Sn and (**b**) Hf significantly increases the migration energy barrier. Reproduced by permission from the PCCP Owner Societies [54].

6. Metal Atom Diffusion

Metals have been previously used in Si and Ge as they can lead to the increase of the rate of crystallization leading to large grain materials (via the MILC process). Typical crystallization inducers are copper, nickel, and palladium with the Ge growth taking place on a thin film of the metal that initiates crystallization.

In a recent study, Tahini et al. [64] employed hybrid density functional theory calculations to investigate the diffusion of a number of metals (Ag, Pt, Li, Pd, Au, and Cu) in Ge. In that investigation, Tahini et al. [64] considered all the possible diffusion mechanisms (for example, the dissociative or Frank–Turnbull mechanism, the kick-out mechanism, and the ring mechanism); however, the direct interstitial process, $Pd_i \leftrightarrow Pd_i$, (refer to Figure 5) was the lowest energy way for a Pd atom to diffuse in the Ge lattice. The migration energy for this process is only 0.03 eV, which is one of the lowest energies ever calculated for mass transport in a crystalline material [64]. In this order of magnitude are the migration energies of helium in tungsten and the self-diffusion of silver in α -AgI [64].



Figure 5. The calculated, by Tahini et al. [64], minimum migration energy mechanism is the direct interstitial process $Pd_i \leftrightarrow Pd_i$. Copyright 2015 Royal Society of Chemistry [64].

The question is what is driving an oversized metallic atom such as palladium to diffuse through the crystalline germanium lattice so fast? In fact, the migration energy is far smaller compared to the *n*-type dopants which are considered to be relatively fast diffusing atoms in a semiconductor lattice [2,36]. To facilitate comparison Tahini et al. [64] considered the diffusion with the direct interstitial process of another five metals (Li, Cu, Ag, Pt, and Au) in Ge (refer to Figure 6). These metals have low migration energies (0.14–0.54 eV) but still comparatively lower than that of Pd [64]. Considering that it is not an atomic size effect and in this case the focus was on doping. In essence, diffusion may be visualized as a sequence of bond breaking and forming steps. Typically, in this picture at the saddle point (highest energy step), the migrating atom has broken all (or most) of its bonds with its neighboring host atoms. What is distinctly different in the metals considered by Tahini et al. [64], is that they still have bonding

states at the saddle point and in essence throughout the diffusion process. For Pd, these bonding states are more pronounced as compared to the other metal atoms, and this could be the key for its extremely low migration energy of diffusion [64]. At any rate these concepts should be investigated further as their applicability in energy materials where diffusion processes are important (for example solid-oxide fuel cells and batteries) could lead to significant improvements in device performance.



Figure 6. The migration energy barriers for metals (**a**) Ag, Pt, Li and (**b**) Pd, Au, and Cu in Ge through the direct interstitial mechanism. Copyright 2015 Royal Society of Chemistry [64].

7. Oxygen Diffusion

It is well established that oxygen in Si and in particular Czochralski-grown Si is present at concentrations that can impact the defect process and in turn the applicability and performance of the material in devices (for example, see References [26,27,32,51,52,56,76] and references therein). Commonly in Si and Ge, oxygen can be introduced through the growth process. As in most defects and processes, oxygen in silicon has been thoroughly investigated, whereas there are only limited studies in germanium. It has been established that the concentration of oxygen in germanium substrates is lower as compared in silicon [1]. Nevertheless, the solubility of oxygen can be up to 10¹⁸ cm⁻³, whereas there exist alternative routes for its introduction in germanium (Ge/oxide interfacial diffusion) [1,108–110]. Considering one of the most fundamental defects in semiconductors, the oxygen interstitial (O_i), it is deemed to be electrically inactive in Ge [1]. At any rate though, it can bind with vacancies to form oxygen-vacancy defects known as A-centers (refer to Figure 7). These in turn, can influence the electronic properties and/or lead to more extended defects (as in the case of Si, see References [26,27,32,51,52,56,76] and references therein) and need to be investigated in more detail.



Figure 7. The A-center. The red sphere is the O atom and the white circle the vacancy. Reproduced by permission from the PCCP Owner Societies 2014 [113].

There is still ground for more work on the defect processes of oxygen in germanium. It should be stressed that analogous work is still performed in silicon and silicon germanium, although the introduction of oxygen in these materials has been studied for numerous decades.

8. Summary

In the present review we considered defect processes and in particular diffusion in Ge. This is of interest as there is renewed interest in Ge for nearly two decades now, as its main disadvantages as compared to Si have been overcome by technological progress. Additionally, methods such as DFT and ToF-SIMS that were not available in the early days of the microelectronics era can now be widely used to investigate the defect processes on Ge at an atomic scale. In essence, DFT calculations provide insights that are supportive and complementary to experiment. For diffusion, DFT can help clarify the dominant diffusion mechanism and the formation or not of clusters that can hinter or aid the migration processes.

Although, *p*-type doping in Ge can be facilitated, it did emerge that *n*-type doping can be problematic particularly when the dopant concentration is high. This led the community to consider defect engineering strategies such as the inclusion of co-dopants. Isovalent atoms such as carbon were determined to retard the donor atom diffusion; however, they did not resolve the clustering and deactivation issues. An interesting field for future work will be the investigation of the conditions under which clustering occurs and how this degrades the performance of the devices. The key issue that needs to be controlled (to avoid clustering and the rapid diffusion of *n*-type dopants) is the vacancy concentration.

Obviously, no review can consider all the references related to such a technological issue and many key contributions have not been discussed (for example, References [114–120]). Additionally, from an experimental viewpoint, the diffusion and activation of dopants can be further complicated by parameters such as the thermal budget, particularly when considering non-equilibrium techniques (e.g., laser, flash, and microwave annealing) [121,122].

The recent studies on Ge can be used as a paradigm in other semiconductor systems such as group IV binary (for example, $Si_{1-x}Ge_x$, $Sn_{1-x}Ge_x$), ternary (for example $Si_{1-x-y}Ge_xSn_y$) alloys, and even advanced 2D materials [123–127]. Many defect processes in random binary and ternary alloys remain undetermined, and thus, offer ground for research. The defect engineering strategies presented here should inspire further experimental work in these systems. Finally, thermodynamic models such as the cB Ω model by Varotsos and Alexopoulos [128,129] can be employed in synergy with experimental and computational methods to study the defect process of electronic materials such as Ge [128–143].

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