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## FAST TRACK COMMUNICATION

# Theoretical investigation of Hf and Zr defects in c-Ge

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Online at [stacks.iop.org/JPhysCM/21/012206](http://stacks.iop.org/JPhysCM/21/012206)**Abstract**

The introduction of high-permittivity gate dielectric materials into complementary metal oxide semiconductor technology has reopened the interest in Ge as a channel material mainly due to its high hole mobility. Since HfO<sub>2</sub> and ZrO<sub>2</sub> are two of the most promising dielectric candidates, it is important to investigate if Hf and Zr may diffuse into the Ge channel.

Therefore, using *ab initio* density functional theory calculations, we have studied substitutional and interstitial Hf and Zr impurities in c-Ge, looking for neutral defects. We find that

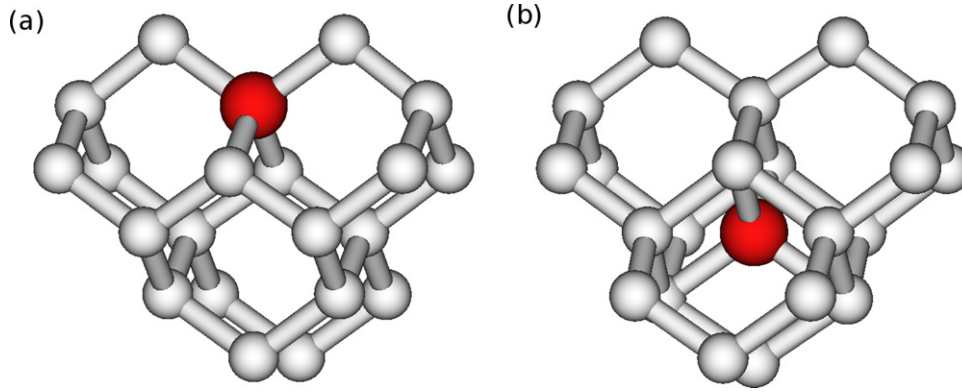
- (i) substitutional Zr and Hf defects are energetically more favorable than interstitial defects;
- (ii) under oxygen-rich conditions, neither Zr nor Hf migration towards the channel is likely to occur;
- (iii) either under Hf- or Zr-rich conditions it is very likely, particularly for Zr, that defects will be incorporated in the channel.

The continued scaling down of Si-based complementary metal oxide semiconductor (CMOS) technology has required, in recent years, an intense search for high-permittivity gate dielectric materials that can replace the more conventional gate insulator SiO<sub>x</sub>N<sub>y</sub>. The performance of a metal oxide semiconductor field effect transistor (MOSFET) is limited by the quality of the interface between the high-*k* material and the channel material, as much as by the properties of the channel material itself. Recent searches for high-permittivity dielectrics have reopened the door to Ge as a channel material [1]. Germanium has been a promising candidate for future MOS technology, in particular for p-type devices since its hole mobility is not only larger than that of Si but is also larger than that for all III–V materials [1, 2].

Among the high-*k* dielectrics, HfO<sub>2</sub> and ZrO<sub>2</sub> are two of the most promising ones. However, for the successful integration of these high-*k* materials with the Ge-based MOSFET technology there are still a number of fundamental issues that must be solved, such as the low interface trap

density of states to enable effective control of MOS channel conductivity, and the low scattering of carriers in the channel by, for example, charged impurities. Even though Ge has higher mobility than Si, the possible presence of Hf and Zr impurities in the Ge channel could lead to a device performance degradation. The solubility of Hf in Si is very low, characterized by a high formation energy [3] (of the order of 2.5 eV for both neutral substitutional and interstitial configurations, under Hf-rich growth conditions). Thus, in Si-based MOS devices the insertion of Hf in the channel is not usually observed. However, for Ge, which has a larger lattice constant than Si, there might be a large reduction in the value of the formation energy. This is, therefore, an important question to address, especially since these impurities, if present, will most likely lead to many charge states in the gap [3].

Here we investigate, using state-of-the-art first-principles calculations, the possible Hf and Zr impurity defects in Ge. Our results show that under equilibrium conditions Hf and Zr atoms have a significantly larger solubility in Ge, as



**Figure 1.** Schematic geometries of defects in c-Ge. Atomic structure of (a) a substitutional defect and (b) a tetrahedral interstitial. The smaller spheres represent Ge atoms and larger spheres represent Zr (or Hf) atoms.

(This figure is in colour only in the electronic version)

evidenced below by the relatively low formation energies. We also find that, for both the Zr and the Hf defects, the substitutional configuration is energetically more favorable than the interstitial configuration.

In this work, we have calculated the formation energies of different Hf and Zr impurity defects in c-Ge, through first-principles calculations, based on the Density Functional Theory (DFT) [4]. In particular, we study Hf and Zr at substitutional ( $X_{\text{Ge}}$ , where  $X = \text{Hf}$  or  $\text{Zr}$ ) and interstitial sites. For interstitial  $X$  defects, we have studied three different configurations: (i)  $X$  at tetrahedral sites ( $X_I^T$ ); (ii)  $X$  at hexagonal sites ( $X_I^H$ ); and (iii)  $X$  at dumbbell sites ( $X_I^D$ ). For all three cases we considered only the neutral charge state. The DFT calculations were performed using ultrasoft Vanderbilt pseudopotentials [5], and a generalized gradient approximation (GGA) for the exchange–correlation potential [6], as implemented in the VASP code [7–9]. In order to study the interstitial and substitutional defects in Ge, we have used 129 atoms (128 Ge atoms and 1  $X$  atom) and 128 atoms (127 Ge atoms and 1  $X$  atom) supercells, respectively. The supercell is built from a primitive FCC Ge cell (2 Ge atoms) via a  $4 \times 4 \times 4$  repetition along the primitive FCC vectors. Our GGA lattice parameter for c-Ge turned out to be 5.445 Å, as expected, a little bit larger than the experimental lattice parameter of 5.431 Å. We have used a plane-wave-cutoff energy of 151 eV. In all calculations the lattice parameter was kept fixed at the calculated value, whereas the atoms were allowed to relax until the atomic forces were smaller than  $0.025 \text{ eV } \text{Å}^{-1}$ .

The formation energy for a substitutional defect is calculated as

$$E_f(X_{\text{Ge}}) = E_t(D) - \frac{127}{128}E_t(\text{c-Ge}) - \mu_X, \quad (1)$$

whereas for the interstitial defects it is calculated as

$$E_f(X_I) = E_t(D) - E_t(\text{c-Ge}) - \mu_X. \quad (2)$$

In the above expressions,  $E_t(D)$  are the total energies of the fully relaxed supercells with the substitutional or interstitial defect  $D$ , and  $E_t(\text{c-Ge})$  is the total energy of the supercell

**Table 1.** Distances between the Zr or Hf atom and the Ge nearest neighbor atoms (in Å), for substitutional and tetrahedral impurities.

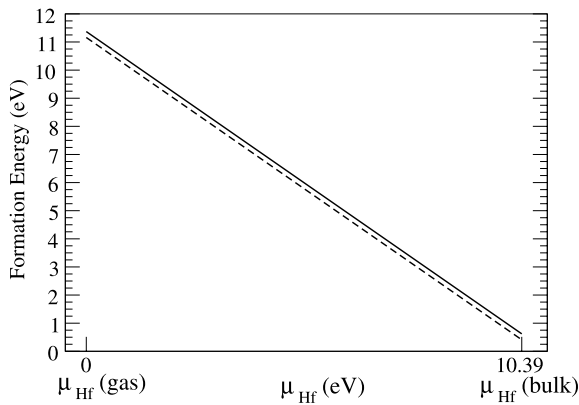
Label	$d_1$	$d_2$	$d_3$	$d_4$
$\text{Hf}_{\text{Ge}}$	2.61	2.61	2.61	2.61
$\text{Hf}_I^T$	2.64	2.64	2.64	2.64
$\text{Zr}_{\text{Ge}}$	2.62	2.62	2.62	2.62
$\text{Zr}_I^T$	2.65	2.65	2.65	2.65

for the perfect crystal of c-Ge;  $X$  can be Hf or Zr atoms. We have considered the bulk c-Ge to be the source of the Ge atoms. The value for the  $X$  chemical potential,  $\mu_X$ , depends on the growth conditions. We will consider the limits of  $X$ -rich conditions and  $O$ -rich conditions in the same way as in our previous work [3, 10].

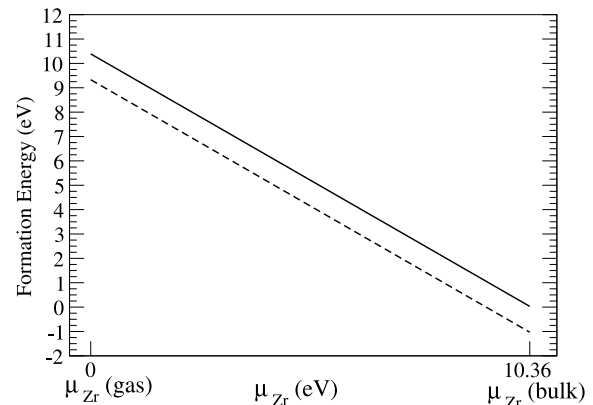
We find that both the hexagonal and the dumbbell interstitial sites are unstable, and after relaxation they converge to the tetrahedral configuration. Thus, in figures 1 a and b, we present the final configuration of a Zr substitutional defect and a Zr tetrahedral interstitial in Ge, respectively. The final configurations for Hf atoms are basically the same.

In table 1 we present the analysis of the interatomic distance between Zr or Hf and the nearest neighbor Ge atoms. Here we can see that there is an outward relaxation of the Ge atoms which are adjacent to the substitutional impurities, resulting in final Hf–Ge (Zr–Ge) bond lengths of 2.61 Å (2.62 Å), that should be compared to the Ge–Ge bond length of 2.49 Å in the bulk. A similar behavior can be observed for Ge atoms neighboring the tetrahedral interstitial impurities, i.e., those having Hf–Ge (Zr–Ge) bond lengths of 2.64 Å (2.65 Å).

In figure 2 we present the formation energies for the substitutional and interstitial Hf defects, calculated according to equation (1) and equation (2), respectively. As mentioned above, we have considered two limits for  $\mu_{\text{Hf}}$ , one corresponding to the Hf-rich growth condition, having the bulk metal as a reference, and the other corresponding to oxygen-rich conditions in such a way that the removed hafnium remains always in equilibrium with the gaseous oxygen. In this case  $\mu_{\text{Hf}}(\text{gas})$  can be written as  $\mu_{\text{Hf}}(\text{gas}) = \mu_{\text{HfO}_2} - \mu_{\text{O}_2}$ , with  $\mu_{\text{HfO}_2}$  being the energy per unit formula for the



**Figure 2.** Formation energy as a function of the Hf chemical potential for a Hf defect at a substitutional (dashed curve) and tetrahedral interstitial (solid curve) site in c-Ge.



**Figure 3.** Formation energy as function of the Zr chemical potential for a Zr defect at a substitutional (dashed curve) and tetrahedral interstitial (solid curve) site in c-Ge.

monoclinic bulk hafnium oxide, and  $\mu_{\text{O}_2}$  being the energy of an isolated oxygen molecule (obtained via the DFT total energy calculation for an  $\text{O}_2$  molecule inside a cubic supercell of 15 Å side). Comparing the interstitial and substitutional defects, we see that  $\text{Hf}_{\text{Ge}}$  is slightly more stable than  $\text{Hf}_i^{\text{T}}$ , by approximately 0.21 eV. Our results indicate that under oxygen-poor growth conditions the presence of Hf substitutional impurities (and most likely interstitials as well, given the small difference in formation energies) in the Ge channel would be likely for  $\text{HfO}_2$  deposited on top of Ge. This could be detrimental since these defects would probably introduce charge levels in the gap [3]. Experimental studies made by Forment and co-workers [11] have introduced Hf atoms by ion implantation in n-type Ge followed by annealing at 500 °C. The experimental results show the appearance of a new level in the Ge gap, located at 0.29 eV below the conduction band.

Figure 3 shows the formation energies for the substitutional and interstitial Zr defects, calculated according to equations (1) and (2), respectively. We also considered two limits for the Zr chemical potential in a similar way to that for Hf as described above. These results show the same behavior as Hf, i.e., the Zr substitutional defect is more stable than the  $\text{Zr}_i^{\text{T}}$  by 1.06 eV. Experimental studies [12] with diffusion of Zr atoms in n-type Ge have shown the presence of Zr-related acceptor states (0.10 eV above the valence band) as well as donor states (0.22 and 0.31 eV below the bottom of the conduction band) in the band gap.

We find that under oxygen-rich conditions, both Zr and Hf migration towards the channel is unlikely to occur. However, the possible formation of a Ge oxide in this case should be considered. On the other hand, under Zr-rich conditions,  $\text{ZrO}_2$  grown on top of Ge has a high probability of having Zr incorporated as defects in the channel. Even though previous experimental works have reported the stable growth of  $\text{ZrO}_2$  on Ge [13], it seems that they have not investigated the possible

presence of Zr in the channel. Moreover, the existence of a thin Ge-oxide layer may have an impact on the Zr migration, a topic that deserves further investigation. Finally, non-equilibrium growth conditions may also alter these conclusions given that our results provide trends for equilibrium situations but kinetic effects have not been considered. For Hf migration towards the channel, under Hf-rich conditions, the presence of Hf at the  $\text{HfO}_2/\text{Ge}$  interface may be a problem, and we suggest that further experimental studies should investigate this issue.

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