

Aluminium-vacancy complexes in $\text{Ge}_{1-x}\text{C}_x$

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A brief review on the potential importance of $\text{Ge}_{1-x}\text{C}_x$ for electro-optic applications and *ab initio* calculations of the aluminium-vacancy complexes are presented. The stability and geometry of aluminium-vacancy complexes has been examined within the frame of density functional theory and the use of the pseudopotential plane-wave method. The predictions highlight the preference of the cluster geometry on the energetics in $\text{Ge}_{1-x}\text{C}_x$ and the effect of carbon concentration on the stability of clusters.

Представлен краткий обзор потенциально важных $\text{Ge}_{1-x}\text{C}_x$ для применения в электрооптике и расчеты *ab initio* алюминий-вакансионных комплексов. Устойчивость и геометрия алюминий-вакансионных комплексов исследована в рамках функциональной теории плотности и с применением метода псевдопотенциальной плоской волны. Полученные прогнозы свидетельствуют о предпочтительности кластерной геометрии для энергетического состояния $\text{Ge}_{1-x}\text{C}_x$ и влияние концентрации углерода на устойчивость кластеров.

The demand for improved performance of microelectronic devices has led to the dramatic progress in development of the silicon (Si) based metal-oxide-semiconductor field effect transistor (MOSFET) in the past decades [1]. An alternative route to higher performance is the use of materials of superior carrier mobilities such as silicon-germanium ($\text{Si}_{1-x}\text{Ge}_x$) or germanium carbide ($\text{Ge}_{1-x}\text{C}_x$) Group IV alloys. In the past material issues associated with the formation of insulator layers have established Si as the mainstream material due to its superior oxide (silicon dioxide). Silicon dioxide (SiO_2) seems to become insufficient for the future generation of devices. In synergy development, in high- k dielectric materials have eliminated the need to use SiO_2 . Consequently, the Group IV alloys or materials such as germanium (Ge) can now be actively pursued.

$\text{Ge}_{1-x}\text{C}_x$ is considered to be a promising material for photovoltaic and electro-optic

applications because the addition of carbon (C) in Ge results in the increase of the band-gap and reduces the lattice parameter of Ge [2]. The reduction of the lattice parameters allows for the ordered growth on Si substrates. There are few previous experimental and theoretical studies on $\text{Ge}_{1-x}\text{C}_x$ [2, 3]. It is to note that the solubility of C in Ge is very low. Nevertheless, high C concentrations in Ge can be introduced using techniques, such as molecular beam epitaxy (MBE). In recent studies, it has been demonstrated experimentally that arsenic (As) diffusion in Ge is retarded by the presence of C [4]. This is important as it implies that defect engineering with C can control the concentration profile of As in Ge. It should be noted that the precise arrangement of dopants in the semiconductor substrates is critically important as devices are becoming smaller and smaller.

The incorporation of aluminium (Al) into $\text{Ge}_{1-x}\text{C}_x$ decreases the crystallinity but en-

hances the absorption of photons and is therefore important for the optoelectronic properties of the material. Atomic scale simulations can provide useful information concerning the structure and defect chemistry of materials (for example [5, 6] and references therein). The aim of the present study is to investigate the structure and binding energies of aluminium-vacancy pairs in $\text{Ge}_{1-x}\text{C}_x$ using density functional theory (DFT). To explore the nature of binding of aluminium-vacancy clusters with C, a range of Al_2V and AlV_2 clusters have also been considered.

In this study, the ground state total energies are predicted using the plane-wave DFT code CASTEP [7, 8]. The plane-wave basis set has been expanded to an energy cut-off of 350 eV and the k -point set is based on a $2 \times 2 \times 2$ Monkhorst-Pack grid. The generalized gradient approximation (GGA) of density functional of Perdew, Burke and Ernzerhof (PBE) [9] is used to describe the exchange-correlation interactions combined with ultrasoft pseudopotentials [10]. A periodic cell with 64 lattice sites has been used to model the system under zero pressure conditions. The atomic sites and unit cell parameters are allowed to relax using an energy minimization approach. This methodology has successfully described the structures and energetics of semiconductors [11, 12] and other systems such as hydroxide minerals [13].

The interaction between point defects is quantified by calculating binding energies, E_b , that are defined by

$$E_b = E_{\text{defect-cluster}} - \left(\sum_{\text{components}} E_{\text{isolated-defects}} \right), \quad (1)$$

where a negative binding energy implies that the defect cluster is stable with respect to its constituent point defect components.

For example, based on equation 1, the binding energy of a substitutional (at a Ge site) Al defect to a Ge vacancy (V) in $\text{Ge}_{N-n}\text{C}_n$ is given by

$$E_b(\text{AlVGe}_{N-n-2}\text{C}_n) = E(\text{AlVGe}_{N-n-2}\text{C}_n) - (2) \\ - E(\text{AlGe}_{N-n-1}\text{C}_n) - E(\text{VGe}_{N-n-1}\text{C}_n) + E(\text{Ge}_N\text{C}_N),$$

where $E(\text{AlVGe}_{N-n-2}\text{C}_n)$ is the energy of a N lattice site supercell containing $N-n-2$ Ge atoms, n carbon atoms, a vacancy and an Al atom. Based on this equation, the binding energy of an AlV pair in Ge is given by setting $n = 0$.

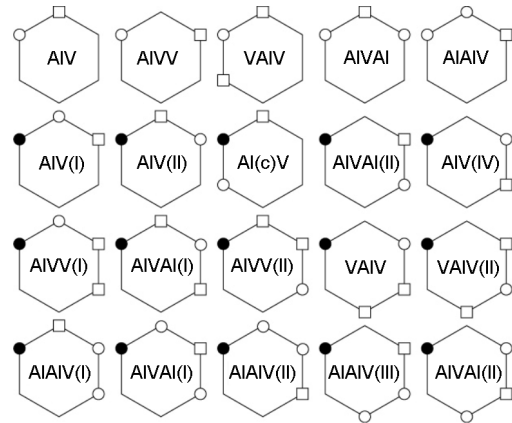


Fig. The most important clusters considered in this study projected onto the (111) surface of Ge and $\text{Ge}_{0.984}\text{C}_{0.016}$. White circles represent Al substitutional atoms, black circles, the C host atoms and squares the vacancies.

The most important cluster configurations considered in this study are presented in Fig. 1. AlV pairs are important in Ge as previous studies indicate that the vacancy mechanism of diffusion is important (see, e.g., [12, 14] and references therein). In Ge, the V is predicted to be bound to an Al substitutional atom with 0.40 eV (Table). Furthermore, the binding energy of AlAl pair is -1.42 eV in Ge (Table). On the contrary, the binding energies for $\text{Ge}_{0.984}\text{C}_{0.016}$ predict that the AlAl pair will not be bound and that the binding of the AlV pair will be insignificant (Table).

In Ge, the AlVV complex (Figure) is more stable than the VAIV complex by -0.58 eV (Table). In $\text{Ge}_{0.984}\text{C}_{0.016}$, the AlVV complex is more stable by -0.33 eV as compared to VAIV. It should be noted that a number of different configurations were calculated in $\text{Ge}_{0.984}\text{C}_{0.016}$ and the most energy favorable AlVV and VAIV complexes were the ones that had the C atom at a nearest neighbor site to the Al and the V, respectively. The binding

Table. Binding energies (eV) of the complexes considered in Ge and $\text{Ge}_{0.984}\text{C}_{0.016}$

Defect cluster	E_b Ge	E_b $\text{Ge}_{0.984}\text{C}_{0.016}$
AIV	-0.40	-0.02
AlAl	-1.42	0.04
VAIV	-0.29	-0.05
AlVV	-0.87	-0.38
AlAIV	-0.40	0.29
AlVAI	-0.38	0.29

energy to associate a single V to an existing AIV pair is given by the subtraction of the binding energy of the AIV pair from that of the AIVV cluster. For Ge, this energy difference is -0.47 eV which is almost identical to the divacancy (VV) binding energy (-0.48 eV). Consequently, a similar concentration of VV and AIVV complexes after the annealing of Ge samples containing AIV pairs should be expected.

When an Al atom binds to an AIV pair, there are two possible nearest neighbor configurations (Fig.). In Ge, the AIAIV and AIVAl complexes have almost the same binding energy (Table). Again, for $\text{Ge}_{0.984}\text{C}_{0.016}$, a number of different nearest neighbor configurations have been calculated for the AIAIV and AIVAl complexes, none of which was stable.

The study of the stability of Al-vacancy and related complexes in Ge and $\text{Ge}_{0.984}\text{C}_{0.016}$ provides an insight into the similarities and differences in the defect chemistry of the two materials. For both materials, the AIVV is the most stable configuration of an Al substitutional and two vacancies. On the contrary, clusters containing 2 Al atoms and a V were stable only in Ge.

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Алюміній-вакансійні комплекси у $\text{Ge}_{1-x}\text{C}_x$

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Подано короткий огляд потенційно важливих $\text{Ge}_{1-x}\text{C}_x$ для застосування в електрооптиці та розрахунки *ab initio* алюміній-вакансійних комплексів. Стабільність та геометрію алюміній-вакансійних комплексів досліджено у рамках функціональної теорії густини та з застосуванням методу псевдопотенціальної плоскої хвилі. Одержані прогнози посвідчують перевагу кластерної геометрії для енергетичного стану $\text{Ge}_{1-x}\text{C}_x$ та вплив концентрації вуглецю на стабільність кластерів.