# Engineering the free vacancy and active donor concentrations in phosphorus and arsenic double donor-doped germanium

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# Engineering the free vacancy and active donor concentrations in phosphorus and arsenic double donor-doped germanium

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In germanium, donor atoms migrate or form larger immobile clusters via their interaction with lattice vacancies. By engineering the concentration of free vacancies, it is possible to control the diffusion of the donor atoms and the formation of those larger clusters that lead to the deactivation of a significant proportion of the donor atoms. Electronic structure calculations in conjunction with mass action analysis are used to predict the concentrations of free vacancies and deactivated donor atoms in germanium doped with different proportions of arsenic and phosphorous. We find, for example, that at low temperatures, the concentration of free vacancies is partially suppressed by increasing the proportion of arsenic doping, whereas at high temperatures (above 1000 K), the concentration of free vacancies is relatively constant irrespective of the donor species. It is predicted that the free vacancy and active donor concentrations vary linearly with the arsenic to phosphorous ratio across a wide range of temperatures. © *2008 American Institute of Physics*.
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## I. INTRODUCTION

It has been demonstrated experimentally[1] and through supporting density functional theory (DFT)[2,3] calculations that large immobile arsenic-vacancy clusters, such as $As_3V$ and $As_4V$, will form in heavily doped silicon (Si). These clusters lead to the deactivation of As and hence to a degradation in the performance of Si-based devices. In a recent DFT study[4] it was predicted that similar clusters also form in germanium (Ge). Brunco *et al.*[5] observed a phosphorous (P) peak concentration of about $10^{21}$ $cm^{-3}$ in Ge, which was attributed to the formation of P clusters. One of the outcomes of the formation of the clusters is the trapping of a large number of $V$. This is particularly important in Ge where diffusion is primarily $V$ mediated.[6–10] For example, the formation of neutral $P_2V$ was recently proposed to explain the complex P diffusion behavior in Ge at high dopant concentrations.[11] Experimental studies demonstrated that P diffusion in Ge is slower compared to As.[6] The higher activation enthalpy of P diffusion has also been predicted by DFT studies.[9] The $V$ concentration will therefore be important in determining the concentration of immobile P or As clusters (e.g., $P_3V$, $P_4V$, $As_3V$, and $As_4V$) and mobile pairs (e.g., P$V$ and As$V$). Previous studies[11,12] concentrated on the use of carbon (C) codoping to retard donor diffusion in Ge, but the formation of neutral dopant-vacancy complexes could not be hindered. In the present paper we consider double donor doping using both P and As as a tool to control the free $V$ concentration and the formation of the larger complexes.

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## II. THEORETICAL METHODOLOGY

The calculations were performed using the DFT plane-wave code CASTEP[13,14] with a supercell containing 64 diamond structure tetrahedral sites and a 350 eV energy cutoff. The generalized gradient approximation using the exchange-correlation functional proposed by Perdew–Burke–Ernzerhof[15] was implemented in conjunction with ultrasoft pseudopotentials.[16] Brillouin-zone sampling was used with a Monkhorst–Pack[17] grid of $2\times2\times2$ $k$ points. Structural parameters and atomic positions were relaxed, and the calculations were performed at the static limit. Adequate convergence with the present computational approach was demonstrated previously.[10,18–20]

The association between donor atoms and lattice $V$ is quantified through the calculation of binding energies. The binding energy of $x$ P atoms to $y$ As atoms and a $V$ to form a $P_xAs_yV$ cluster in Ge is given by

$$E_b(P_xAs_yVGe_{N-x-y-1}) = E(P_xAs_yVGe_{N-x-y-1}) - xE(PGe_{N-1}) - yE(AsGe_{N-1}) - E(VGe_{N-1}) + (x+y)E(Ge_N), \quad (1)$$

where $E(P_xAs_yVGe_{N-x-y-1})$ is the energy of a $N$ lattice site supercell (here $N=64$) containing $N-x-y-1$ Ge atoms $x$ P atoms, $y$ As atoms, and a $V$; $E(PGe_{N-1})$ [or $E(AsGe_{N-1})$] is the energy of a supercell containing one P (or As) and $N-1$ Ge atoms; $E(VGe_{N-1})$ is the energy of a supercell containing one $V$ and $N-1$ Ge atoms; and $E(Ge_N)$ is the energy of the $N$ Ge atom supercell. A negative binding energy indicates that the defect cluster is stable with respect to its constituent point defect components.

 

TABLE I. Predicted binding energies $E_b$ (eV) of $P_xAs_yV$ clusters with respect to isolated species in Ge.

| P doped (Ref. 12) | | (P+As) doped | | As doped (Ref. 4) | |
|---|---|---|---|---|---|
| $P_2$ | 0.28 | PAs | 0.19 | $As_2$ | 0.17 |
| $PV$ | −0.52 | $PAsV$ | −1.14 | $AsV$ | −0.60 |
| $P_2V$ | −1.06 | $P_2AsV$ | −1.64 | $As_2V$ | −1.22 |
| $P_3V$ | −1.54 | $PAs_2V$ | −1.73 | $As_3V$ | −1.82 |
| $P_4V$ | −2.27 | $P_2As_2V$ | −2.46 | $As_4V$ | −2.62 |
| | | $PAs_3V$ | −2.54 | | |
| | | $P_3AsV$ | −2.37 | | |

## III. RESULTS AND DISCUSSION

The binding energies of $P_nV$ and $As_nV$ clusters in Ge have been presented in recent publications[4,9,12,21] that employed the same computational approach. In the present study we have predicted the binding energies of $P_xAs_yV$ clusters in Ge (see Table I). The energetically favorable $P_xAs_yV$ cluster configurations (see Fig. 1) are analogous to the most stable configurations of $P_nV$ and $As_nV$ clusters.[4,12,21] By comparing the binding energies of $P_xAs_yV$ with the previous studies for $P_nV$ and $As_nV$ clusters, it is observed that they are approximately equal to their mean value. For example $P_2As_2V$ (−2.46 eV, Table I) is only about 1% higher than the mean value of $P_4V$ (2.27 eV, see Ref. 12) and $As_4V$ (−2.62 eV, see Ref. 4). Consequently, due to the higher binding energies exhibited by $As_nV$ clusters compared to the equivalent $P_nV$ clusters,[4,12] mixed clusters have a tendency to be As rich, being more stable as more As are incorporated. Similarly to $P_2$ and $As_2$ pairs,[4,12] the PAs pair has a positive binding energy, 0.19 eV (Table I). Therefore P and As mutually repel one another and PAs pairs that are not stabilized through the addition of a $V$ are energetically unlikely to occur. Of course, this does not necessarily exclude the formation of large donor precipitates under heavy implantation conditions.[22]

Using the DFT results, we have predicted the relative concentrations of $P_xAs_yV$ clusters through mass action analysis.[23] For this analysis the total concentration of P and As substitutional atoms and $V$ is required. The aim of the present study is to explore the equilibrium state of the system after P and As coimplantation. The concentration of a $P_xAs_yV$ complex $[P_xAs_yV]$ relative to [P], [As], and $[V]$ is given by

$$\frac{[P_xAs_yV]}{[P]^x[As]^y[V]} = \exp\left(\frac{-E_b(P_xAs_yV)}{k_BT}\right), \tag{2}$$

where $k_B$ is Boltzmann's constant, $T$ is the temperature, $[V]$ is the concentration of unbound $V$, and [P] and [As] are the concentrations of unbound P and As atoms, respectively. Similar methodology was used to study $As_nV$ clusters in Ge.[4] However, as a word of caution, the mass action framework predicts the equilibrium behavior of defects toward which the system tends to evolve, whereas, in experiments, kinetics can hinder the ability of the system to reach the equilibrium state.

We will consider the situation where the total donor concentration is $10^{19}$ $cm^{-3}$, which is typical of the P or As concentration used experimentally to dope Ge.[24,25] As discussed in previous work,[4] an initial $V$ concentration of $10^{18}$ $cm^{-3}$ is appropriate for donor doped Ge, although this will depend on the experimental conditions (e.g., implantation parameters). In the mass action analysis we considered all the defect clusters that are bound (see Table I), that is, all clusters containing up to four dopant species regardless of type. Clusters that incorporate multiple $V$ were not included as these were previously found to be insignificant for a total $V$ concentration of $10^{18}$ $cm^{-3}$ (see Ref. 4).

Figure 2 presents the temperature dependent free $V$ concentration ($[V]$) in P doped, As doped, and Ge doped with equal concentrations of P and As. At temperatures below 1050 K, the free $[V]$ is a maximum when the donor atom population is composed entirely of P and a minimum when it is composed of only As. This is particularly important, for example, at 800 K where there is about an order of magnitude more free $V$ in P doped Ge than in As doped Ge. This is a direct consequence of the higher binding energy of As-rich clusters.

In Fig. 3 the total concentration of donor atoms trapped in immobile $P_xAs_yV$ clusters ($P_3V$, $P_2AsV$, $PAs_2V$, $As_3V$, $P_4V$, $P_3AsV$, $P_2As_2V$, $PAs_3V$, and $P_4V$) is reported as a function of temperature. Larger clusters containing more than one donor atom have previously been determined to be essentially immobile in Ge.[11] These clusters are also important as they limit the active donor concentration and also trap lattice

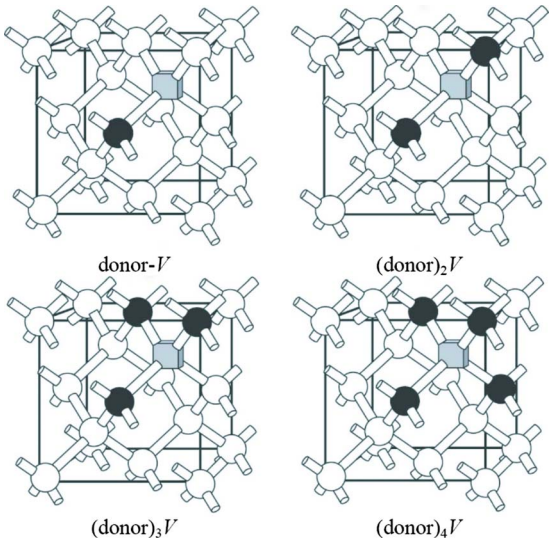


FIG. 1. (Color online) A schematic representation of the $P_xAs_yV$ [donor $V$, (donor)$_2V$, (donor)$_3V$, and (donor)$_4V$] clusters in a unit cell of Ge in which white spheres represent the Ge atoms, black spheres the donor atoms (P or As), and cubes the $V$.

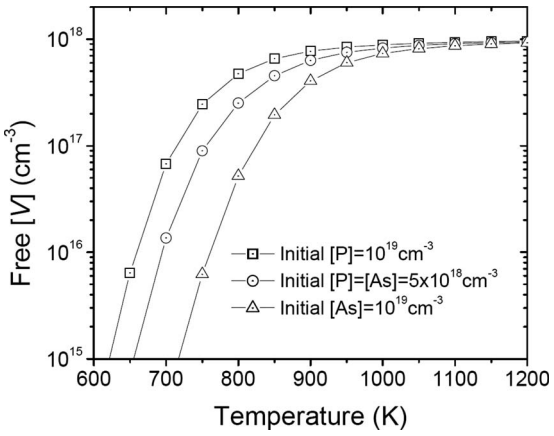


FIG. 2. The temperature dependence of the concentration of free $V$ for an initial donor concentration of $10^{19}$ cm$^{-3}$ and initial $V$ concentration of $10^{18}$ cm$^{-3}$.

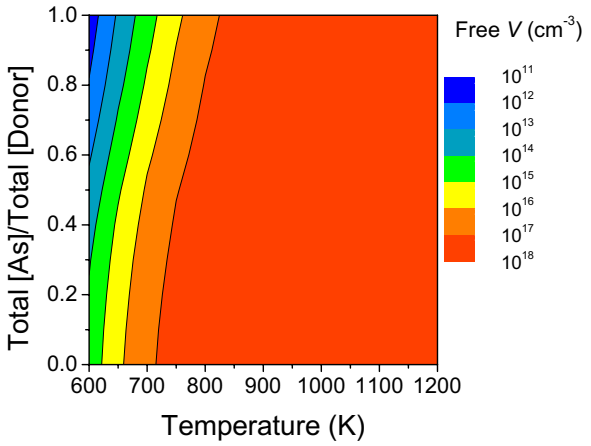


FIG. 4. (Color online) The temperature dependence of the concentration of free $V(\ln[V])$ as a function of the implanted total As content for initial total donor concentration of $10^{19}$ cm$^{-3}$ and initial $V$ concentration of $10^{18}$ cm$^{-3}$ (contour plot based on 143 calculations).

$V$. It can be observed from Fig. 3 that the highest concentration of deactivated donors is realized for As-doped Ge and conversely the lowest for P-doped Ge. This is, again, a direct consequence of the $V$ trapping described above. By codoping, the concentration of deactivated donors will vary between these two extremes depending on the relative concentrations of P to As, which can be quantified as the total As concentration over the total donor concentration. Interestingly, the concentration of donor atoms trapped at the (total As)/(total donor) value of 0.5 (in equal As and P concentrations) is essentially the average of the values in purely P-doped and purely As-doped materials.

Experimentally the two factors that are easily controlled are the total implanted donor concentration and the relative concentration of As with respect to P. Using mass action analysis it is possible to consider the temperature dependent free $V$ concentration as a function of the relative concentrations of As to P (for a given total donor concentration, again here $10^{19}$ cm$^{-3}$). Figure 4 presents such results in the form of a contour plot for a total donor concentration of $10^{19}$ cm$^{-3}$ (so that the $y$-axis shows total As concentration/$10^{19}$). This type of map could be used as a design tool. That is, it indicates the expected free $V$ concentration for a specific mix of P and As dopants at a given temperature. It should be stressed, however, that implantation conditions (e.g., implantation energy and dose) will affect the initial defect concentration and therefore the values for the initial $V$ concentration are bound to change subject to these. Conversely, in Fig. 5, the total active donor concentration is predicted for the same total implanted donor dose $10^{19}$ cm$^{-3}$ and a given initial $V$ concentration of $10^{18}$ cm$^{-3}$ as a function of temperature and relative As to P content. The lowest active donor concentrations are found for low temperature and high As content. This is also where the free $V$ concentration is a minimum. This is a direct result of the higher binding energy of As clusters, which result in both more trapped $V$ and more trapped donors. Thus, at these concentrations, minimizing the free $V$ concentration to reduce diffusion also results in less overall active donors. However, the $V$ concentration is much more sensitive to the relative As content, and one might be able to sacrifice a relatively small fraction of active donor content in order to greatly reduce the free $V$ concentration.

The calculations performed in this work provide the first

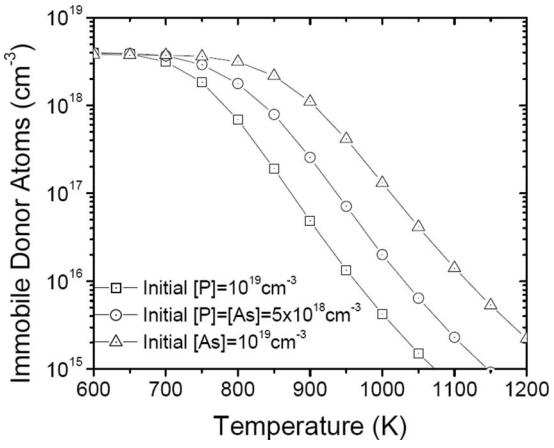


FIG. 3. The temperature dependence of the total concentration of donor atoms trapped in immobile $P_xAs_yV$ clusters ($P_3V$, $P_2AsV$, $PAs_2V$, $As_3V$, $P_4V$, $P_3AsV$, $P_2As_2V$, $PAs_3V$, and $P_4V$) for initial donor concentration of $10^{19}$ cm$^{-3}$ and initial $V$ concentration of $10^{18}$ cm$^{-3}$.

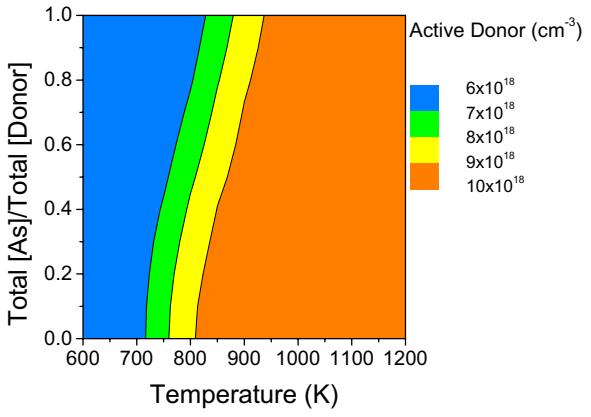


FIG. 5. (Color online) The temperature dependence of the total active donor concentration (ln[donor]) as a function of the implanted total As content for initial total donor concentration of $10^{19}$ cm$^{-3}$ and initial $V$ concentration of $10^{18}$ cm$^{-3}$ (contour plot based on 143 calculations).

insights into the interplay between defect reactions taking place when Ge is doped with As and P. The higher binding energy between As-vacancy clusters compared to P-vacancy and to mixed dopant-vacancy clusters suggests that $V$ could be trapped in As-doped Ge. This would result in a reduced P diffusion compared to P diffusion under similar extrinsic conditions. Whether this approach is appropriate to reduce the enhanced diffusion of P and its deactivation specifically via the formation of $P_2V$ complexes[11] has to be checked experimentally. Such experiments are presently in progress.

## IV. CONCLUSION

We have investigated the possibility of controlling the concentration of free $V$ in P and As double donor doped Ge. It is predicted that the free $[V]$ increases linearly with the proportion of P in the initial donor concentration across a wide range of temperatures. In other words, more donor atoms are trapped and deactivated in larger clusters given an increasing proportion of As in the initial donor concentration. By varying the relative concentration of the donor species and equilibrium temperature, it is possible to engineer a target free $V$ or active donor concentration. Another way to control the enhanced diffusion and deactivation of $n$-type dopants could be engineering the concentration of free Ge interstitials. Whether this approach is applicable remains unsolved, although in most cases, it is not possible to optimize both quantities simultaneously.

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