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Doping strategies to control A-centres in silicon: insights from hybrid density functional theory

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Hybrid density functional theory is used to gain insights into the interaction of intrinsic vacancies (V) and oxygen-vacancy pairs (VO, known as A-centres) with the dopants (D) germanium (Ge), tin (Sn), and lead (Pb) in silicon (Si). We determine the structures as well as binding and formation energies of the DVO and DV complexes. The results are discussed in terms of the density of states and in view of the potential of isovalent doping to control A-centres in Si. We argue that doping with Sn is the most efficient isovalent doping strategy to suppress A-centres by the formation of SnVO complexes, as these are charge neutral and strongly bound.

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I. Introduction

Group IV semiconductors, particularly Si and Ge, are important both as bulk and in their two-dimensional forms (e.g. silicene or germanene) for numerous nanoelectronic, photovoltaic, and sensor applications.¹⁻³ However, a detailed understanding of defect-dopant interactions that can affect the host material properties is not well established.⁴⁻⁷ The interactions are important given that the characteristic dimensions of devices are on the nanometer scale. Oxygen (O) is introduced in Czochralski-Si during crystal growth with significant concentrations. Oxygen interstitials (O_i) bind to vacancies (V) to form VO pairs,⁸ namely A-centres, which are electrically and optically active. The formation of A-centres is enhanced in space as the radiation environment with high speed particles, such as protons and neutrons, causes lattice displacement damage and supersaturation of vacancies. Therefore, the concentration of A-centres will also be increased, which has a strong impact on Si-based imaging and spectroscopy sensors, in particular complementary metal-oxide-semiconductors, sensors and chargecoupled device sensors in space, so it is technologically important to suppress their formation.

Previous studies have established that large isovalent codopants can affect the dopant–defect interactions in group IV semiconductors.^{9–12} Experimentally, impurities such as Ge, Sn, and Pb can impact the formation processes of V_nO_m complexes in

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Si, see ref. 11 and the references therein. For example, in a recent study an increased concentration of Sn was used to suppress the formation of the deleterious A-centres by the formation of SnVO defects.¹⁰ This was justified through binding energy arguments as the oversized isovalent atoms benefit from the space provided by the A-centre voids, so that the lattice atoms surrounding them relax. The high binding energies ensure that the A-centres are anchored to the isovalent atoms, forming DVO defects (D = Ge, Sn, and Pb), and thus cannot diffuse to form larger members of the $V_n O_m$ family (e.g. VO_2). DVO stands for a defect which consists of a dopant atom, a V, and an O interstitial atom. A full understanding of the structures, formation energies, and electronic properties of the DVO and DV defects is still missing. Using hybrid density functional theory, the aim of the present investigation is to characterize and assess isovalent doping strategies to the control A-centres in Si from the electronic point of view.

II. Methodology

All calculations use the Vienna Ab initio Simulation Package¹³ with pseudopotentials generated by the projector augmented wave method.¹⁴ We employ a Monkhorst–Pack¹⁵ $3 \times 3 \times 3$ k-grid and a plane-wave cutoff energy of 400 eV for a 64 Si atom supercell. The total energy is converged to an accuracy of 0.01 eV with carefully tested technical parameters. Since the PBEsol¹⁶ functional provides lattice constants close to those of very expensive hybrid Heyd– Scuseria–Ernzerhof (HSE) calculations,^{17,18} it is used for the structure optimization. The pristine Si lattice constant is kept for each charged defect and the atomic positions are relaxed with a force criterion of 0.01 eV Å⁻¹. Then the HSE calculations are conducted for the optimized structures with a screening parameter



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of 0.206 Å⁻¹. For correcting artificial interaction between the charged defects in finite size supercell calculations, the approach of Freysoldt and coworkers^{19,20} is employed.

The formation energy of charged DVO and DV defects, as a function of the Fermi energy, is given by

$$\Delta H_{\mathrm{D},\mathrm{q}}(\mu_{\mathrm{e}},\mu_{\alpha}) = E_{\mathrm{D},\mathrm{q}} - E_{\mathrm{H}} + \sum_{\alpha} n_{\alpha}\mu_{\alpha} + q\mu_{\mathrm{e}} \qquad (1)$$

where $E_{\rm D,q}$ and $E_{\rm H}$ are the total energies of the defective cell with charge q and the Si cell without defect, respectively. Furthermore, n_{α} are the numbers of atoms added to or removed from the defective cell and μ_{α} denotes their chemical potentials. Finally, $\mu_{\rm e}$ is the Fermi energy measured from the valence band maximum (VBM) with values between $E_{\rm VBM}$ and $E_{\rm VBM} + E_{\rm gap}$. The O, Ge, Sn, and Pb chemical potentials, respectively, are calculated using α -quartz SiO₂ [($E({\rm SiO}_2) - 3\mu_{\rm Si}$)/6], α -Ge, α -Sn, and pristine Pb.

The energetics of point defect association can be addressed by calculating the binding energies of the formed clusters. For instance, the binding energy of a dopant atom to VO to form a DVO defect is given by

$$E_{b}(\text{DVOSi}_{N-2}) = E(\text{DVOSi}_{N-2}) - E(\text{VOSi}_{N-1}) - E(\text{DSi}_{N-1}) + E(\text{Si}_{N})$$
(2)

where $E(\text{DVOSi}_{N-2})$ is the energy of an *N* site supercell (here N = 64) with N - 2 Si atoms, one dopant atom, and one O atom. Moreover, $E(\text{VOSi}_{N-1})$ is the energy of a supercell containing one V and one O atom, $E(\text{DSi}_{N-1})$ is the energy of a supercell in which one Si atom is substituted by a dopant, and $E(\text{Si}_N)$ is the energy of an N atom Si supercell. With this definition a negative binding energy corresponds to a complex which is stable with respect to its constituent defects.

III. Results and discussion

The structure of the VO defect is shown in Fig. 1 illustrating that an O interstitial atom does not occupy the Si vacancy site in excellent agreement with previous experimental evidence.8 Optimized structures highlighting the atomic chain along the (10-1) direction are depicted in Fig. 2 for various systems. In pristine Si the calculated nearest neighbour distance is 2.35 Å, which increases to 2.40 Å due to the vacancy in this chain in the DVO and DV structures. The oversized species Sn and Pb in group IV semiconductors typically occupy the space between two semi-vacant lattice sites (split-vacancy configuration).²¹ In the present DV structures the Sn and Pb atoms in fact relax to this configuration. Although this does not happen in the SnVO and PbVO structures, as the O atom prevents Sn and Pb from shifting toward the vacancy, the distance between the two Si atoms next to the vacancy in the (10-1) chain reduces from 3.21 Å in the VO structure to 2.99 Å and 3.05 Å in SnVO and PbVO, respectively. GeVO and GeV almost maintain the geometries of the structures without the Ge dopant because the size of the Ge atom is close to that of the Si atom.

Fig. 3 shows the formation energy for different charge states of the DVO and DV defects as a function of the Fermi energy.



Fig. 1 Crystal structure of the VO defect. Medium blue spheres are the Si atoms and the small red sphere is the O atom. The Si chain along the (10-1) direction is highlighted.

GeVO transits from charge neutral to charge -2 at 0.47 eV, similar to previous findings for the VO defect,²² where the formation energy of the charge neutral VO defect is 4.3 eV. SnVO and PbVO show similar trends of the formation energy, where the charge neutral state is favourable in a wide Fermi energy range. This means that these two defects do not like to accept electrons so they will not affect the charge carrier concentration in an n-type doped system. The GeV defect has charge +1 for low Fermi energy and charge -2 otherwise. This may be due to the four dangling bonds left by the vacancy that can accept electrons. The transition levels of the charged GeV defect are concentrated in a small energy range. Besides the -2 charge state, SnV and PbV have charge +2 in the low Fermi energy range, indicating that these defects can donate electrons. The transition levels between the charge states are summarized in Table 1.

Total DOSs of the charge neutral DVO and DV defects are shown in Fig. 4. The area filled by red colour represents the charge required by the dangling electrons of the dopant and Si atoms adjacent to the vacancy for pairing. For DVO the two dangling bonds introduced by the vacancy are saturated by the O atom. The defect states of SnVO and PbVO appear at higher energy as compared to GeVO. According to Fig. 2, Sn and Pb approach O and Si at the broken site of the (10-1) chain more than Ge. Thus, the defect states slightly spread over the neighbours of the dopant and shift to higher energy, so the -1 and -2 charge states of SnVO and PbVO are not energetically favourable. The fact that Sn moves deeper into the vacancy than Pb corresponds to the higher energy of the defect states in this case. The DOS of the GeV defect is very similar to bulk Si with a single vacancy, because the atomic size of Ge hardly distorts the local geometry. However, the states (red colour) required for pairing of the four dangling electrons spread over wider energy ranges for the SnV and PbV defects. This corresponds to the split-vacancy configuration, which delocalizes the defect states over the surrounding atoms. As parts of the defect



Fig. 2 The chain along the (10–1) direction in (a) GeVO, (b) SnVO, (c) PbVO, (d) GeV, (e) SnV, and (f) PbV. Big spheres are the isovalent atoms, medium blue spheres the Si atoms, and small red spheres the O atoms. The distances are given in Å.



Fig. 3 Formation energies as a function of the Fermi energy for different charge states of DVO and DV (D = Ge, Sn, and Pb) defects.

Table 1 Transition levels (eV) between charge states of the DVO and DV defects (D = Ge, Sn, and Pb)

Transition level	GeVO	SnVO	PbVO	GeV	SnV	PbV
+/0	_	0.17	0.03	0.15	0.31	0.42
++/0	_	0.19	0.03	0.06	0.25	0.39
+/++	—	0.22	0.04	_	0.21	0.37
0/-	0.48	_	_	0.16	0.44	0.52
0/	0.47	_	_	0.16	0.49	0.59
_/++	—	0.57	0.38	0.10	0.32	0.44
_/	0.45	_	_	0.16	0.57	0.65
+/	0.05	0.75	0.54	0.15	0.36	0.47
+/	0.19	0.93	0.77	0.16	0.43	0.53
++/		0.75	0.59	0.11	0.38	0.49

 Table 2
 Binding energies (eV) of the DVO and DV defects (D = Ge, Sn, and Pb)

PBEsol	HSE
-0.21	-0.23
-0.89	-0.98
-1.17	-1.26
-1.65	-2.21
-1.60	-2.18
-1.21	-1.69
-1.18	-1.66
-0.25	-0.26
-1.33	-1.50
-1.64	-1.80
	$\begin{array}{r} -0.21 \\ -0.89 \\ -1.17 \\ -1.65 \\ -1.60 \\ -1.21 \\ -1.18 \\ -0.25 \\ -1.33 \\ -1.64 \end{array}$

states in SnV and PbV have lower energy than in SnVO and PbVO, the former two cases can host -1 and -2 charge states.

The binding energies calculated by the PBEsol and HSE functionals are summarized in Table 2, showing a similar behaviour. Because of the higher accuracy we discuss in the following the HSE findings in detail. However, the PBEsol functional would give the same principle picture. The binding energies of Sn + VO and Pb + VO are much higher than that of

Ge + VO, implying that the system gains more energy by the formation of SnVO and PbVO, so Sn and Pb dopants trap the A-centre more easily than Ge. This result agrees with the experimental finding that the production of VO defects in samples doped by Sn or Pb is much lower than for Ge doping.²³ Interestingly, the energy difference between trapping a VO pair by a Pb atom and by a Ge atom is more than 1 eV. This implies not only that doping with Pb will lead to more stable DVO



Fig. 4 Total DOS of pristine Si (gray) and the DVO and DV (D = Ge, Sn, and Pb) defects in the charge neutral state (red). States left of the red dotted line are occupied. Red filled areas highlight the unoccupied states resulting from the dangling bonds.

clusters but also that the region of influence of Pb will extend further as compared to Ge. We find that the A-centre has the highest binding energy of -2.21 eV. The Ge dopant slightly affects the association between V and O, while the Sn and Pb dopants weaken the bond as indicated by the smaller values for SnV + O and PbV + O because Sn and Pb tend to split the V. For DV both Sn and Pb yield much higher binding energies than Ge. The trend is similar to that observed for DVO, but Sn and Pb bind more strongly to the vacancy than to VO. The reason is that Sn and Pb form split-vacancy configurations when there is no interstitial O atom. In addition, the binding energies of the D + VO and DV + O reactions, see Table 2, show significant differences, because the energy gain in the former case mainly arises from the local lattice relaxation due to the dopant, whereas it is larger in the latter case because of the association of V and O in which O saturates two dangling bonds.

Considering that the isovalent dopant must be introduced at concentrations of the same order of magnitude or higher than the A-centre concentration to make an impact, it is necessary to introduce at least 10^{18} cm⁻³.¹⁰ Previous reports have determined that the introduction of high concentrations of Pb in Si leads to the formation of Pb precipitates.^{24,25} Additionally, given that the -2 charge state of GeVO dominates under n-type conditions, see Fig. 3, doping with Ge can be problematic. It is therefore Sn doping and the formation of SnVO complexes that is ideal for the suppression of A-centres in Si, due to the strong binding and the fact that Sn is more soluble in Si than Pb. Recent studies¹⁰ have determined that Sn can be incorporated in Si at concentrations up to near 10^{19} cm⁻³ without the formation of precipitates.

IV. Conclusions

In conclusion, we have used hybrid density functional theory to study the impact of oversized isolated dopants on the A-centres and vacancies in Si. The calculated formation energies show that the charge states of the GeVO defect are similar to those of the A-centre.²² The fact that SnVO and PbVO defects prefer to be charge neutral is explained by the higher energy of the defect states as compared to GeVO. In addition, GeV defects are favourable to be charged so that they can trap charge carriers. We have demonstrated that SnV and PbV defect states appear in a wider energy range, which is connected to the split-vacancy configuration resulting, in essence, from the larger radii of the Sn and Pb atoms. The high binding energies obtained for SnVO and PbVO suggest that doping of Sn and Pb can be an efficient strategy to restrain the concentration of A-centres. Isovalent dopants may have to be introduced at concentrations exceeding their solubility limit, which can be achieved by implantation. Insight into the kinetics of the processes and the study of other isovalent dopants such as hafnium and zirconium can lead to further optimizations. The present work will act as a stimulus for further exertions regarding research on the effect of isovalent doping in Si and especially of Pb and the possible

experimental determination of the PbV and PbVO centres. The present study is consistent with previous studies employing oversized isovalent atoms as a means to control the concentration and diffusion of V-related defects in group IV semiconductors. In Si the key is to control the V from the A-centre, whereas in Ge, for example, the key is to control the V from the E-centre (*i.e.* P–V pair). Isovalent doping is an efficient defect engineering strategy and transferable to other host materials.

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