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

H. Wang,[1] A. Chroneos,[2,3,a)] C. A. Londos,[4] E. N. Sgourou,[4] and U. Schwingenschlögl[1,b)]

[1] *PSE Division, KAUST, Thuwal 23955-6900, Saudi Arabia*
[2] *Engineering and Innovation, The Open University, Milton Keynes MK7 6AA, United Kingdom*
[3] *Department of Materials, Imperial College, London SW7 2AZ, United Kingdom*
[4] *University of Athens, Solid State Physics Section, Panepistimiopolis Zografos, Athens 157 84, Greece*

Abstract

Hybrid density functional theory is used to gain insights into the interaction of intrinsic vacancies (*V*) and oxygen-vacancy pairs (*V*O, 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 D*V*O and D*V* complexes. The results are discussed in terms of the density of states and in view of the potential of isovalent doping for controlling 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 Sn*V*O complexes, as these are charge neutral and strongly bound.

[a)] Alex.Chroneos@open.ac.uk ; [b)] Udo.Schwingenschlogl@kaust.edu.sa

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, 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 in 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-centers, which are electrically and optically active. The formation of A-centers is enhanced in space as the radiation environment with high speed particles, such as protons and neutrons, causes lattice displacement damage and a supersaturation of vacancies. Therefore, the concentration of A-centers will also be increased, which has a strong impact on Si-based imaging and spectroscopy sensors, in particular complementary metal-oxide-semiconductor, sensors and charge-coupled device sensors in space, so that 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.[10-12] Experimentally, impurities such as Ge, Sn, and Pb can impact the formation processes of V_nO_m complexes in 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_nO_m family (e.g. VO_2). DVO stands for a defect which consists of a dopant atom, V, and O interstitial. 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 the characterization and assessment of 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 Package[13] with pseudopotentials generated by the projector augmented wave method.[14] We employ a Monkhorst-Pack[15] 3×3×3 k-grid and a plane-wave cutoff energy of 400 eV for a 64 Si atoms supercell. The total energy is converged to an accuracy of 0.01 eV with carefully tested technical parameters. Since the PBEsol[16] 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. Then the HSE calculations are conducted for the optimized structures with a screening parameter 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 D*V*O and D*V* defects, as a function of the Fermi energy, is given by

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

where $E_{D,q}$ and E_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, μ_e is the Fermi energy measured from the valence band maximum (VBM) with values between E_{VBM} and $E_{\mathrm{VBM}} + E_{gap}$. The O, Ge, Sn, and Pb chemical potentials, respectively, are calculated using α-quartz SiO_2 [(E(SiO_2)-3μ_{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 *V*O to form a D*V*O defect is given by

$$E_b(DVOSi_{N-2}) = E(DVOSi_{N-2}) - E(VOSi_{N-1}) - E(DSi_{N-1}) + E(Si_N) \qquad (2)$$

where $E(DVOSi_{N-2})$ is the energy of an N site supercell (here $N = 64$) with $N-2$ Si atoms, one dopant atom, and one O atom. Moreover, $E(VOSi_{N-1})$ is the energy of a supercell containing one V and one O atom, $E(DSi_{N-1})$ is the energy of a supercell in which one Si atom is substituted by a dopant, and $E(Si_N)$ 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 *V*O 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 (1 0 -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 *DV*O 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 Sn*V*O and Pb*V*O structures, as the O atom prevents Sn and Pb to shift toward the vacancy, the distance between the Si two atoms next to the vacancy in the (1 0 -1) chain reduces from 3.21 Å in the *V*O structure to 2.99 Å and 3.05 Å in Sn*V*O and Pb*V*O, respectively. Ge*V*O and Ge*V* almost maintain the geometries of the structures without Ge dopant because the size of the Ge atom is close to that of the Si atom.

Figures 3 shows the formation energy for different charge states of the D*V*O and *DV* defects as

function of the Fermi energy. Ge*V*O transits from charge neutral to charge -2 at 0.47 eV, similar to previous findings for the *V*O defect,[22] where the formation energy of the charge neutral *V*O defect is 4.3 eV. Sn*V*O and Pb*V*O 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 that they will not affect the charge carrier concentration in an *n*-type doped system. The Ge*V* 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 Ge*V* defect are concentrated in a small energy range. Besides the -2 charge state, Sn*V* and Pb*V* 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 I.

Total DOSs of the charge neutral *DV*O 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 *DV*O the two dangling bonds introduced by the vacancy are saturated by the O atom. The defect states of Sn*V*O and Pb*V*O appear at higher energy as compared to Ge*V*O. According to Fig. 2, Sn and Pb approach O and Si at the broken site of the (1 0 -1) chain more than Ge. Thus, the defect states slightly spread over the neighbours of the dopant and shift to higher energy, so that the -1 and -2 charge states of Sn*V*O and Pb*V*O 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 Ge*V* 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 than for the Sn*V* and Pb*V* defects. This corresponds to the split-vacancy configuration, which delocalizes the defect states over the surrounding atoms. As parts of the defect states in Sn*V* and Pb*V* have lower energy than in Sn*V*O and Pb*V*O, 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 II, showing a similar behaviour for the binding energies. 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+*V*O and Pb+*V*O are much larger than that of Ge+*V*O, implying that the system gains more energy by the formation of Sn*V*O and Pb*V*O so that Sn and Pb dopants trap the A-centre more easily than Ge. This result agrees with the experimental finding that the production of *V*O defects in samples doped by Sn or Pb is much lower than for Ge doping.[23] Interestingly, the energy difference between trapping a *V*O 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 D*V*O clusters but also that the region of influence of Pb will extend further as compared to Ge. We find that the A-center has the largest 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 bound as indicated by the smaller values for Sn*V*+O and Pb*V*+O because Sn and Pb tend to split the *V*. For *DV* both Sn and Pb yield much larger binding energies than Ge. The trend is similar to that observed for *DV*O, but Sn and Pb bind stronger to the vacancy than to *V*O. 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* + *V*O and *DV* + O reactions, see Table II, 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 Ge*V*O dominates under *n*-type conditions, see Fig. 3, doping with Ge can be problematic. It is therefore Sn

doping and the formation of Sn*V*O 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 studies[10] have determined that Sn can be incorporated in Si in 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 Ge*V*O defect are similar to those of the A-centre[22]. The fact that Sn*V*O and Pb*V*O defects prefer to be charge neutral is explained by the higher energy of the defect states as compared to Ge*V*O. In addition, Ge*V* defects are favourable to be charged so that they can trap charge carriers. We have demonstrated that Sn*V* and Pb*V* 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 large binding energies obtained for Sn*V*O and Pb*V*O 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 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 Pb*V* and Pb*V*O 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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Table I. Transition levels (eV) between charge states of the *DV*O and *DV* defects (*D* = Ge, Sn, and Pb).

Transition level	Ge*V*O	Sn*V*O	Pb*V*O	Ge*V*	Sn*V*	Pb*V*
+/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 II. Binding energies (eV) of the *DV*O and *DV* defects (*D* = Ge, Sn, and Pb).

Reaction	PBEsol	HSE
Ge + *V*O → Ge*V*O	-0.21	-0.23
Sn + *V*O → Sn*V*O	-0.89	-0.98
Pb + *V*O → Pb*V*O	-1.17	-1.26
V + O → *V*O	-1.65	-2.21
Ge*V* + O → Ge*V*O	-1.60	-2.18
Sn*V* + O → Sn*V*O	-1.21	-1.69
Pb*V* + O → Pb*V*O	-1.18	-1.66
Ge + *V* → Ge*V*	-0.25	-0.26
Sn + *V* → Sn*V*	-1.33	-1.50
Pb + *V* → Pb*V*	-1.64	-1.80

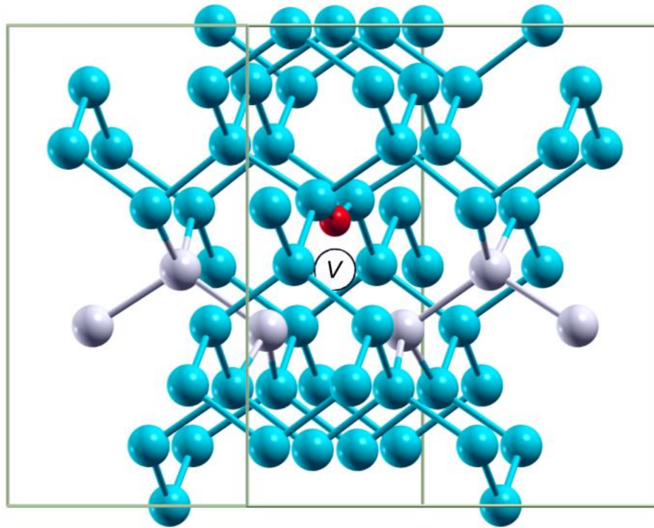

Fig. 1. (Color online) Crystal structure of the *V*O defect. Medium blue spheres are the Si atoms and small red sphere is the O atom. The Si chain along the (1 0 -1) direction is highlighted.

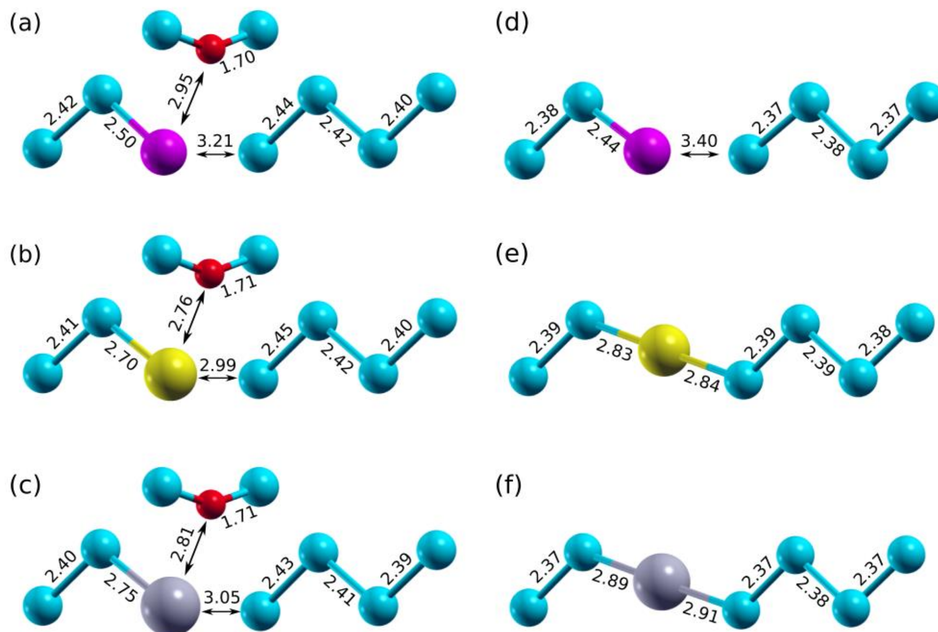

Fig. 2. (Color online) Chain along the (1 0 -1) direction in (a) Ge*V*O, (b) Sn*V*O, (c) Pb*V*O, (d) Ge*V*, (e) Sn*V*, and (f) Pb*V*. Big spheres are the isovalent atoms, medium blue spheres the Si atoms, and small red spheres the O atoms. The distances are given in Å.

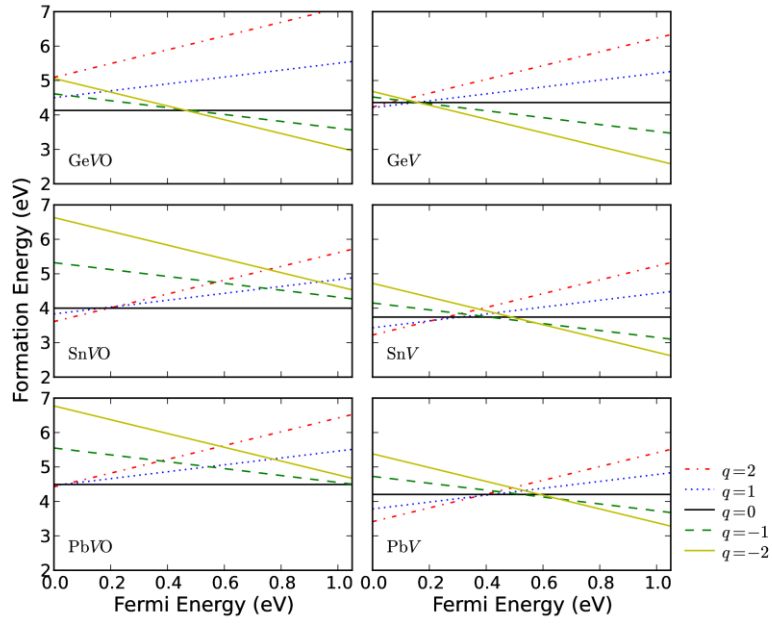

Fig. 3. (Color online) Formation energies as a function of the Fermi energy for different charge states of *DV*O and *DV* (*D* = Ge, Sn, and Pb) defects.

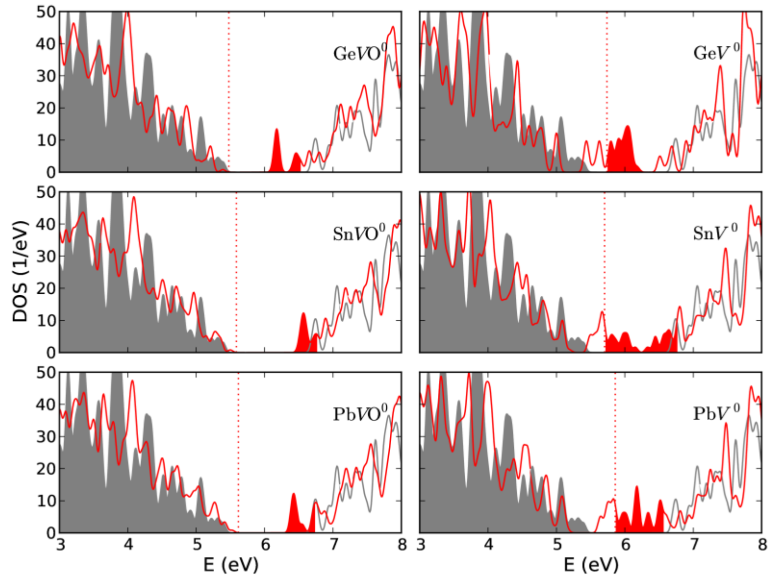

Fig. 4. (Color online) Total DOS of pristine Si (gray) and the *DV*O and *DV* (*D* = Ge, Sn, and Pb) defects in the charge neutral state (red). States left of the red dotted line are occupied. Red filled areas highlight the unoccupied states resulting from the dangling bonds.