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Ab Initio Modeling of Defects in Silicon, Germanium and SiGe Alloys

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Understanding the most elemental defects in semiconductors is a fundamental step to grasp the countless solid-state reactions that may occur during crystal growth, device processing and operation stages. The higher carrier mobility in SiGe alloys and germanium, when compared with silicon, and the necessity to a higher K dielectric than SiO₂ makes these semiconductors the most contenders to a new generation of electronic devices. Our aim is to model self and impurity point defects in SiGe alloys and germanium, and compare with their equivalent complexes in silicon. We use density functional theory and pseudopotentials to determine the structural, electronic and vibrational properties. The calculations are performed in a 32 CPU PC cluster, in Physics Department of Aveiro University.

1. Method

- We use a pseudopotential spin density-functional supercell code (AIMPRO)⁸, along with the exchange-correlation parameterization by Perdew and Wang. The pseudopotentials by Hartwigsen, Goedecker, and Hutter scheme were used.
- The wave function was expanded on localized atomic *s*-, *p*- and *d*-like Gaussian orbitals;
- Several standard tests to the method were done. These include calculations of the lattice parameter and bulk modulus of silicon (germanium), 5.39 Å (5.58 Å) and 91.9 GPa (71.9 GPa), respectively, which agree well with the experimental data 5.40 Å (5.65 Å) and 97.8 GPa (75.2 GPa), respectively.
- Defects were introduced in otherwise perfect 64 and 128 Si (Ge or SiGe) atom supercells, or in H-terminated large clusters.
- Full atomic relaxation is performed using Hellmann-Feynman forces.
- Formation energies are obtained for several charge states.
- Electric levels are determined using a marker method⁹.
- Quasi-harmonic Local Vibrational Modes (LVM) were obtained from the second order derivatives of the total energy with respect to the positions of the defect and its neighbors.
- Other measured quantities like piezoelectric constantes, hyperfine parameters and diffusion barrier energies may be calculated.

2. Modeling the Alloy^c

- Alloys are modeled by using randomly generated Si_{1-x}Ge_x supercells, being $x = n/64$ the Ge concentration.
- Topological details, including Si-Si, Si-Ge and Ge-Ge bond lengths were analysed and fitted to the equations:

$$\begin{cases} r_{SS}(x) = r(x) - a(r_{Ge-Ge}^0 - r_{Si-Si}^0)x \\ r_{SG}(x) = [r_{SS}(x) + r_{GG}(x)]/2 + g \\ r_{GG}(x) = r(x) - b(r_{Ge-Ge}^0 - r_{Si-Si}^0)(x-1) \end{cases} \quad (1)$$

where $a=0.79$ and $b=0.74$ are the fitted topological rigidity parameters, and $g=-0.0059\text{Å}$ the fitted bowing parameter, which agrees very well with the experimental value at -0.006Å .

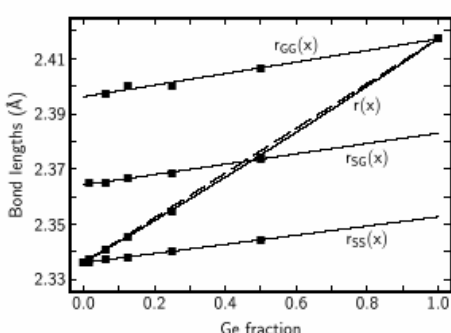


Fig.1 Calculated bond lengths in SiGe alloys (squares) and fitted bond lengths to eqs.(1) (lines).

3. Vacancy in Germanium^d

We used a large H-terminated Ge₃₇₆H₁₉₆ spherical clusters with a vacant site at its center. We have used the marker method to estimate the electrical levels at $E(-/0) = E_v + 0.20\text{ eV}$, $E(0/-) = E_c - 0.50\text{ eV}$, $E(=/-) = E_c - 0.25\text{ eV}$ where E_v and E_c are the top of the valence band and the bottom of the conduction band, respectively.

The main conclusion are:

- The Jahn-Teller instabilities result in a number of a variety of structural relaxations and spin states, depending on the electric charge.
- As opposed to the Si vacancy, the vacancy in Ge is not a donor, being a triple acceptor center, Fig.2.

4. Interstitial Oxygen in Silicon^e, Germanium^e and SiGe Alloys^f

- In agreement with previous reports^{9,10}, in Si (Ge) after atomic relaxation the puckered Si-O-Si (Ge-O-Ge) defect, Fig. 3a, shows a Si-O (Ge-O) bond length 1.63 Å (1.76 Å) forming an angle of 153° (136°). The linear form, Fig. 3b, costs a few tens (hundreds) of meV.
- LVM frequencies and isotope shifts for O_i in Si (Ge) are reported in Table I, and they account for the observations within a 5% error. To access the accuracy of our 'molecular' model we have calculated the dynamical matrix elements considering the nearest Si (Ge) neighbors to the Si-O-Si (Ge-O-Ge) "pseudo-molecules". These are reported within parenthesis in Table I. The results in the two models agree within 1%, and it is clear that a triatomic Si-O-Si (Ge-O-Ge) model is sufficiently accurate for the purpose of this work.
- In SiGe alloys, from energetics, we conclude that oxygen atoms sit only between silicon atoms, i.e., avoid the formation of Ge-O bonds which cost about 0.7 eV each when compared to the formation of Si-O bonds.
- In SiGe, the asymmetric mode frequency of the Si-O-Si defect in SiGe was calculated as a function of the alloy composition. This was accomplished by averaging over the frequencies obtained from abovementioned 15 supercell calculations for each composition, Fig.4. We found that the B mode frequency shifts downwards by 1.7 ± 2.8 , 7.3 ± 4.1 and $10.2\pm 3.4\text{ cm}^{-1}$, for $x=0.25$, 0.50 and 0.75, respectively. These shifts agree very well the experiments, which report red-ripts of the 1136 cm^{-1} band of 4.3, 8.6 and 13.0 cm^{-1} for the same Ge compositions.

Table 1. Calculated LVM's (cm^{-1}) of oxygen interstitial in silicon and germanium and their downward isotopic shifts for the A (symmetric) and B (asymmetric) modes, from the second derivatives of the X-O-Y molecule, being X, Y =Si or Ge atoms (X-O-Y molecule plus X and Y first nearest neighbors). Experimental data from Refs. [g,h].

in Si	Mode	²⁸ Si- ¹⁶ O- ²⁸ Si	³⁰ Si- ¹⁶ O- ²⁸ Si	²⁸ Si- ¹⁶ O- ²⁸ Si	³⁰ Si- ¹⁶ O- ²⁸ Si
Exp.	B	1136.4	3.7	51.4	55.2
	A	618	9.5	≈ 0	
Calc.	B	1075.5	3.4	48.8	52.4
	A	(1076.0)	(3.7)	(48.8)	(52.7)
		602.5	9.3	2.7	8.2
		(606.9)	(9.1)	(2.6)	(11.8)
in Ge	Mode	²⁸ Ge- ¹⁶ O- ²⁸ Ge	³⁰ Ge- ¹⁶ O- ²⁸ Ge	²⁸ Ge- ¹⁶ O- ²⁸ Ge	³⁰ Ge- ¹⁶ O- ²⁸ Ge
Exp.	B	862.91	1.01	43.28	45.45
	A	412.1	7.3		
Calc.	B	812.8	2.0	42.1	44.2
	A	(813.1)	(2.0)	(42.1)	(44.2)
		415.7	5.2	12.6	18.0
		(417.0)	(5.2)	(12.3)	(17.9)

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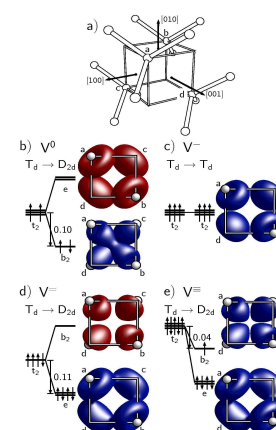


Figure 2. a) Structure of the perfect vacancy in Ge, and b-e) effect of Jahn-Teller effect distortions on the triplet (t_2) gap level for charge states ranging from neutral to triple-negative. Blue and red isosurfaces represent the electron density for the highest occupied and lowest unoccupied Kohn-Sham states. Jahn-teller relaxation energies (eV) for V^0 , V^- and V^{2-} are represented on the right to the downward arrows.

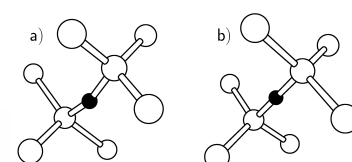


Figure 3. Puckered a), and linear b) forms of an interstitial oxygen defect in silicon and in germanium. Oxygen and Si (Ge) atoms are shown in black and white, respectively.

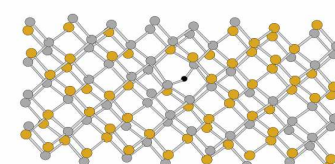


Figure 4 A Si₆₄Ge₆₄O supercell used to simulate the 50% Ge concentration for the SiGe alloy. Small black ball indicates oxygen atom, grey silicon atoms and yellow germanium atoms.