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Germanium–hydrogen pairs in silicon

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Abstract

Hydrogen in a dilute SiGe alloy is considered theoretically in comparison with hydrogen in Si and Ge. Structural, vibrational and electronic properties of crystalline alloys containing ~ 1.6 at.% Ge complexed with single hydrogen atoms are considered. The behaviour of bond-centred hydrogen is found to be weakly perturbed, when compared to hydrogen in pure Si.

1. Introduction

Isolated hydrogen was first observed in crystalline silicon by means of channelling [1] and then subsequently studied by several other techniques. Isolated H in Si is a bistable species having a negative electron correlation energy, U . H^0 and H^+ lie at bond centres with a donor level at $E_c - 0.17$ eV [2, 3], but H^- lies near a T-site with a level around mid-gap [4–7]. The positive bond-centre hydrogen has been observed by means of infrared absorption [8], with an A_{2u} stretch mode at 1998 cm^{-1} , while electron paramagnetic resonance [9, 10] has been used to observe the neutral bond-centred (BC) species. Muon studies [11] ‘see’ both diamagnetic (μ^+) and paramagnetic (Mu) environments, with the neutral Mu population subdivided into BC and a less stable tetrahedral site (Td) species. An extensive literature of theoretical calculations on isolated H in Si exists; see [12, 13] for recent reviews.

Isolated hydrogen in crystalline germanium is less represented in the experimental literature. Infrared absorption by a mode due to the A_{2u} vibration of H_{BC}^+ at 1794 cm^{-1} and a degenerate mode due to H^- at 745 cm^{-1} have been observed [14]. Muon studies [15] on Ge reveal a somewhat different picture from Si, where the two paramagnetic forms of Mu at the Td and BC sites are of similar energy, with movement between the two environments at 100 K and above.

The microscopic structure of H in SiGe has not been extensively studied, despite the importance of H in CVD SiGe production. The behaviour of muons in SiGe has been examined [16, 17]. The diamagnetic fraction of H (H^+) is seen to behave similarly to Si,

Table 1. Relative energy, eV, of H near to Ge_s in Si for several structures (see figure 1) and charge states. The shift in energy with respect to the number of Monkhorst–Pack (MP^x) k -points is also shown.

	MP^2			MP^4		
	+	0	–	+	0	–
H_{Td1a}	0.81	0.20	0.17	0.80	0.18	0.18
H_{Td1b}	0.29	0.17	0.13	0.29	0.29	0.13
H_{BC1}	0.00	0.00	0.68	0.00	0.05	0.76
H_{Td2}	0.70	0.00	0.00	0.68	0.00	0.00
H_{BC2}	0.01	0.02	0.71	0.01	0.07	0.78
H_{BC3a}	0.01	0.01		0.01	0.02	
H_{BC3b}	0.01	0.03		0.01	0.07	
Si:H	0.05	0.00	0.07	0.05	0.04	0.08

but the paramagnetic Mu fraction (H^0) shows evidence at low temperatures for not only the Td species, but also several additional forms of Mu_{BC} not seen in Si. Site interchange between the Td and BC populations was not observed, unlike the case for Ge. Vibrational modes characteristic of Si–H, Si– H_2 and Ge–H bonding are all seen in amorphous SiGe [18], with a preference towards Si– H_x bonding over Ge–H, due to the larger enthalpy of formation of Si–H bonding [19].

2. Theoretical technique

A first-principles density functional method [20, 21] is used, in conjunction with 64-atom cubic supercells containing the defects, to determine the energies, electrical levels and vibrational modes of different configurations of Ge–H defects in silicon. The wavefunctions of the defects were represented with a real-space Cartesian–Gaussian basis centred on each atom, with various numbers of independent s, p and d functions. The Hartree and Perdew–Zunger [22] exchange–correlation energies were calculated using a 200 Ryd plane-wave intermediate fit, with a $4 \times 4 \times 4$ Monkhorst–Pack k -point sampling scheme (MP^4) used to integrate over the band structure [23]. This basis set and reciprocal space parameters have previously been successfully used in modelling the computationally more demanding C–H pairs in Si [24].

All atoms were allowed to relax by a conjugate gradient method. The second derivatives of the energy were found for H atoms and immediate neighbours, allowing vibrational modes to be calculated from the dynamical matrix, with additional entries in the matrix constructed from a Musgrove–Pople potential (further details are given in [20]). The energies of the various stable structures considered are given in table 1.

The donor levels of the defects were obtained by use of the bulk ionization method of Jeong and Oshiyama [25, 26], while the acceptor levels were calculated by extending the method to compare the energy of the neutral and negative defects against the energy of a bulk cells in the neutral and negative charge states. The band gap of SiGe alloys is known to change continuously in a near linear fashion as a function of composition between that of Si and that of Ge [27]. Hence, for the concentration of Ge considered in this work, a decrease of the gap of ~ 7 meV is to be expected.

3. Results

The relative energies of the configurations of H around Ge_s , as shown in figure 1, are given in table 1. For the positive charge state, as expected, the bond-centre structures are of low energy compared to those derived from the Td site. All of the bond-centre sites around Ge_s are found

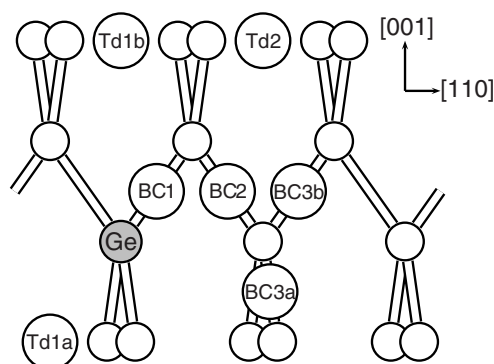


Figure 1. Configurations of H near substitutional germanium (filled grey circle). The hydrogen positions are labelled xy , where x is the type of site, tetrahedral (Td) or BC, and y is the relative distance away from Ge_s . The symmetries of the complexes are given in table 2.

Table 2. Site symmetries and degeneracies for structures in figure 1.

Site	Symmetry	Degeneracy
Td1a	C_{3v}	4
Td1b	C_{2v}	6
Td2	C_{3v}	4
BC1	C_{3v}	4
BC2	C_{1h}	12
BC3a	C_1	24
BC3b	C_{1h}	12

to be degenerate with H_{BC}^+ in bulk Si, to within the error of the calculations. This suggests that below ~ 200 K, when H^+ is not mobile in Si [6–8], there should be complexes between Ge and H formed in a proton-implanted alloy. The H_{Td1b}^+ structure is found surprisingly to be only 0.3 eV higher in energy than the BC population, unlike the case for pure Si. For the neutral hydrogen case, again the BC structures are found to be degenerate in energy with H in Si, but the Td structures are also found to be of similar energy. For the negative charge state of H, the most strongly bound structure is one where the H is at a Td site near to Ge_s , but not adjacent (i.e. structure Td2); this is found to be bound by ~ 0.1 eV compared to isolated H in Si. While such small energy differences are within the typical error margin of density functional theory, this result suggests that the local strain near to Ge_s somewhat compensates that of H at a Td site, leading to a partial cancellation of strain fields [28]. Since Ge expands the nearest surrounding cages (Td1a and Td1b) compared to bulk Si, but contracts the next nearest cage (Td2), this then favours H at this next nearest site.

The calculated shifts in electrical level compared to H in Si are shown in table 3. The donor activity of the low energy BC structures around Ge_s is found to be similar to that of H in Si, while the acceptors are displaced slightly further from the valence band. This then leads to a slight increase in U for these centres compared to the case for isolated H.

Vibrational modes of H^+ near to Ge_s are shown in table 4. The frequency of H_{BC}^+ in Si falls at 2148 cm^{-1} with the current method, which is observed experimentally to be 1998 cm^{-1} [8], while the frequency of H_{BC}^+ in Ge is calculated to be 1857 cm^{-1} , which is observed experimentally to be at 1794 cm^{-1} [14]. The discrepancy can be accounted for by the anharmonicity of the modes, leading to a downward shift, which is not correctly accounted

Table 3. Thermodynamic electrical levels, eV, of H near to Ge_s in Si for several structures shown in figure 1. The shift in levels with respect to the number of Monkhorst–Pack (MP^x) *k*-points is also shown.

	MP ²		MP ⁴	
	0/+	−/0	0/+	−/0
H _{Td1a}	$E_v + 0.04$	$E_c - 0.59$	$E_v + 0.04$	$E_c - 0.50$
H _{Td1b}	$E_v + 0.56$	$E_c - 0.63$	$E_v + 0.56$	$E_c - 0.54$
H _{BC1}	$E_v + 0.86$	$E_c - 0.08$	$E_v + 0.86$	$E_c + 0.09$
H _{Td2}	$E_v + 0.16$	$E_c - 0.76$	$E_v + 0.16$	$E_c - 0.67$
H _{BC2}	$E_v + 0.85$	$E_c - 0.05$	$E_v + 0.85$	$E_c + 0.11$
H _{BC3a}	$E_v + 0.85$		$E_v + 0.85$	
H _{BC3b}	$E_v + 0.84$		$E_v + 0.84$	
Si:H	$E_v + 0.81$	$E_c - 0.69$	$E_v + 0.85$	$E_c - 0.64$

Table 4. Vibrational modes, cm^{−1}, of H⁺ near to Ge_s in Si for several structures (see figure 1) obtained using MP² *k*-point sampling.

	H	D
Ge:H _{BC}	1857	1316
H _{Td1b}	1649	1187
	691, 627	597, 586
H _{BC1}	2120	1507
H _{BC2}	2148	1528
H _{BC3a}	2135	1519
H _{BC3b}	2150	1529
Si:H _{BC}	2148	1528

for in the current calculations. As the BC hydrogen is moved further away from Ge_s, the calculated frequency increases towards the frequency in pure Si.

4. Conclusions

The behaviour of H in a dilute SiGe system has been studied. Compared to Si, H⁺ near to isolated Ge_s is found to be degenerate in energy, suggesting that such complexes are only present at low temperatures where the role of entropy and the migration of H are not relevant. The vibrational modes of these complexes are found to be similar to those of H in silicon, but shifted downwards in frequency by the nearby Ge atom. The effect of Ge on the electrical levels of H is to weakly perturb the acceptor and donor levels compared to those of H in Si. Multiple trapping sites are found for H⁺ near to Ge_s.

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