

Self interstitial–hydrogen complexes in silicon

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Abstract

The vibrational properties of interstitial silane $(\text{SiH}_4)_i$ and silyl $(\text{SiH}_3)_i$ molecules in crystalline silicon are calculated using a first-principle, cluster based, spin-polarised local-density method. The Si-H stretch modes are found to be red-shifted by $\sim 300 \text{ cm}^{-1}$ from those of the isolated molecule which lie around 2200 cm^{-1} . These results refute recent suggestions that modes observed around 2200 cm^{-1} , and previously assigned to hydrogenated vacancy defects, are due to these interstitial molecules.

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I. INTRODUCTION

The behaviour of hydrogen as an impurity in crystalline silicon has been of widespread interest, due to the large range of effects on the electronic and structural properties of the material.¹ Numerous infrared absorption lines associated with hydrogen have been observed by various experimental groups,² with those related to complexes of native defects with hydrogen being particularly common in irradiated and proton implanted material.

A large number of infrared absorption lines have been observed in the range 1800 – 2300 cm^{-1} after proton implantation, which shift downwards in frequency by $\sim \sqrt{2}$ in deuteron implanted material. This implies that the modes are due to the stretch in covalent bonds between hydrogen and silicon, since this frequency range is near to that of the Raman active A_1 mode at 2187.0 cm^{-1} and the IR and Raman active T_2 mode at 2190.6 cm^{-1} of the isolated silane molecule.³

One particular infrared line observed at 2210 cm^{-1} in room temperature measurements, but rising to 2222 cm^{-1} on cooling to 10 K, has been a source of dispute within the literature. Different workers have assigned this line (and subsequently a class of related defects) to two distinct types of native defects: namely either to a fully hydrogenated lattice vacancy, VH_4 , or to a Si interstitial bonded to four interstitial hydrogen atoms as in the molecule Si_4 which has been trapped within the Si lattice.

Early infra-red absorption studies² on irradiated Si containing both H and D, found that the 2222 cm^{-1} line was consistent with a defect of T_d symmetry and containing four H atoms bonded to Si. It was also suggested that, as this mode was close to those of the silane (Si_4) molecule, the defect consisted of this molecule lying at the T_d interstitial site.⁴ Confirmation that the defect had T_d symmetry came from uniaxial stress measurements.⁵

Subsequent *ab initio* calculations were consistent with an assignment of the 2222 cm^{-1} mode to the fully hydrogenated vacancy, VH_4 . The calculated T_2 stretch frequencies obtained by two different groups^{5,6} at 2319 and 2334 cm^{-1} respectively lie within 120 cm^{-1} of the observed line. Moreover, the calculations were able to predict that the infra-red inactive,

but Raman active A_1 mode lies *above* the T_2 mode. This was confirmed by observation of an infra-red active mode for the VH_3D defect lying above 2222 cm^{-1} .⁵ Indeed, assuming this assignment, infra-red⁷ and electron paramagnetic studies⁸ on low temperature proton implantation experiments have indicated that VH_n ($n < 4$) and V_mH_n , $m > 1$, are readily formed. Naturally, the lattice damage caused by proton implantation creates both vacancies and interstitials and both defects contain unsaturated Si bonds which would be expected to complex with H. Further studies, both theoretical⁹ and experimental,¹⁰ did indeed reveal that a bonded interstitial Si atom can complex with H. Moreover, the evidence that lines at 1986.5 and 1989.4 cm^{-1} and assigned to a $[100]$ oriented split-interstitial which has trapped two H atoms is overwhelming as the effect of uniaxial stress, and the effect of isotopic substitution, leads to a detailed model entirely consistent with the *ab initio* theory. There is then no evidence from these studies that absorption lines arising from $(SiH_4)_i$ are present.

However, the assignment of the 2222 cm^{-1} mode to VH_4 has recently been questioned by Suezawa.^{11,12} IR studies on Si grown in a H-atmosphere reveal the 2222 cm^{-1} band whose integrated intensity increases with B, C and Au doping. These elements are assumed to lead to an increase in the production of Si_i which could then lead to increased concentrations of $(SiH_4)_i$. It is known that interstitial related A- and B-swirl defects are produced during the growth of Si doped with C and B while vacancy related D-defects are suppressed.¹³ Specifically, in float-zone samples with $[C] = 5 \times 10^{16}\text{ cm}^{-3}$ or $[B] = 1.5 \times 10^{16}\text{ cm}^{-3}$, the intensity of the 2222 cm^{-1} band was enhanced relative to material doped with $5 \times 10^{18}\text{ cm}^{-3}$ Sn. Although, this is consistent with the idea that the 2222 cm^{-1} band is interstitial related, this does not provide irrefutable evidence. It is known that both B and C react with interstitials via a kick-out mechanism, moving from substitutional sites to interstitial positions themselves^{14,15} and so removing interstitials from the lattice. Similarly, Sn can trap vacancies below $180\text{ }^\circ\text{C}$ ^{16,17} and this then might prevent VH_4 being formed in the Sn-doped material. It is more difficult to understand whether gold-doping should act to remove interstitials from the lattice, since Au normally sits at substitutional sites in the lattice, and so would be expected to remove vacancies from the lattice instead of interstitials.

Moreover, arguments about $(\text{SiH}_4)_i$ rather than VH_4 being produced in Si containing impurities with smaller covalent radii than Si must be treated with reservation. It is known that VH_4 , unlike the vacancy, compresses the surrounding lattice since VH_4 is 67% larger than the vacancy.⁵ Such an expansion can be argued to favour the production of VH_4 in material doped with elements with small atomic radii such as B or C.

Further work by Suezawa^{18,19} demonstrates that there is a growth in the intensity of the 2222 cm^{-1} band around 180°C which is correlated with a decrease in the intensity of the 0.34 eV optical transition²⁰ due to V_2^- . The suggestion is made that Si interstitial clusters break up around this temperature releasing interstitials which are trapped by either divacancies or hydrogen leading to $(\text{SiH}_4)_i$ defects. Such experiments once again are capable of alternative interpretations, where divacancies are thermally dissociated releasing vacancies which are subsequently trapped by hydrogen forming VH_4 .

In addition to the controversy in the assignment of the 2222 cm^{-1} line, the center responsible for the 2190.3 and 2166.1 cm^{-1} lines – previously assigned to VH_3 ^{5,7} – has been reassigned by Suezawa¹⁸ to SiH_3 .

II. CALCULATIONAL METHODS

Given these contrary viewpoints, there is a clear need to investigate theoretically the structure and vibrational properties of the interstitial silane and silyl molecules to ascertain whether assignment to the 2222 and 2166 cm^{-1} modes is credible. This is accomplished in the present paper by carrying out density-functional cluster calculations using the AIMPRO code.²¹

The defect molecules were each inserted into a $\text{Si}_{84}\text{H}_{64}$ cluster centered on the tetrahedral interstitial site. The wave-function basis consisted of independent s and p Gaussian orbitals, with four different exponents, sited at each Si site and three at each H atom of the molecule. A fixed linear combination of two Gaussian orbitals was sited on the terminating H atoms. In addition, single Gaussian functions were placed at each Si–H bond of the molecule and every

Si–Si bond center. The charge density was fitted with five independent Gaussian functions with different widths on each Si atom, and four (three) on the central (terminating) H atoms. Two extra Gaussian functions were placed at each bond center. All atoms, except the terminating H ones, were allowed to relax by a conjugate gradient method. The second derivatives of the energy were found for the atoms of the interstitial molecule. Further details of the method can be found in Ref. 21.

As a preliminary to calculating the vibrational properties of *interstitial* silane, the isolated molecule in free space was simulated using the same type of basis. The calculated quasiharmonic modes are shown in table I. It is worth noting that whilst the one-dimensional A_1 modes match experiment well (within $\sim 5 \text{ cm}^{-1}$) in the isotopically pure cases, the higher dimensional (T_2 and E) modes and those of the isotopically mixed molecules are of poorer agreement ($\sim 60 \text{ cm}^{-1}$). This leads to an incorrect ordering of some of the vibrational levels, when compared with experiment.

There are two forms of interstitial $(\text{SiH}_4)_i$ with T_d symmetry, with the four Si–H bonds aligned either towards the four nearby hexagonal sites, or alternately towards the four neighbouring Si atoms. The first configuration is calculated to be 9.3 eV lower in energy than the second. This is due to strong interaction between the molecular hydrogen atoms and the nearby silicon atoms in the surrounding cage, which are forced close together in the second configuration.

To test the convergence of the molecular properties with respect to cluster size, the lower energy structure was re-calculated in a cluster with all of the atoms, including the surface terminating hydrogen allowed to relax. In a cluster of this size, the fixed-surface relaxation could be expected to give an unphysically rigid surrounding to the molecule, and the relaxed surface cluster would give an excessively flexible model for the surrounding crystal, hence the two types of simulation will give results lying on either side of the true defect properties. Similarly, to test for effects of increasing the basis, the calculations were repeated in the 148 (plus defect) atom cluster with fixed surface, but with a larger basis using eight different exponents sited at each Si atom for both the wavefunction and charge density, in addition,

a second Gaussian was placed between every bonded pair of atoms. The effects on the molecular vibrational frequency of these changes are shown in table II, the frequency is seen to be converged to within $\sim 100 \text{ cm}^{-1}$ with respect to both cluster size and basis.

III. RESULTS

The calculated quasiharmonic vibrational modes of the low energy form of interstitial silane are shown in table I, and compared with the experimental XH_4 defect modes⁷. The calculated frequencies for the interstitial molecule differs from experimental values by $> 300 \text{ cm}^{-1}$ for all modes, which is large enough to be reasonably confident in ruling out Si_4 as being the defect species responsible.

To further test the assignment of the 2222 cm^{-1} to interstitial Si_4 , the energy of this defect was compared against that of two experimentally known defects with an equivalent stoichiometry. The previously identified hydrogen saturated split-interstitial¹⁰ and the interstitial hydrogen molecule²² were chosen as obvious candidates for competing defects in the material. The calculated energy difference, using the same basis as the interstitial-hydrogen complexes, between $(\text{IH}_4)_i$ and $(\text{IH}_2)_i + (\text{H}_2)_i$ (with an infinite separation between the components) is 2.74 eV in favour of $(\text{IH}_2)_i + (\text{H}_2)_i$.

We consider next the assignment of the 2190.3 and 2166.1 cm^{-1} lines to $(\text{SiH}_3)_i$. There are four possible structures for trigonal interstitial silyl SiH_3 molecules with C_{3v} symmetry. The calculated, relaxed forms of these are shown in figure 1. Structure A has the three equivalent hydrogen atoms aligned towards three of the the nearby hexagonal sites, with the molecular dangling bond pointing towards the fourth hexagonal site. Structure B has the dangling bond pointing instead towards the nearby silicon atom in the opposite direction from the hexagonal site. Structures C and D are similar to A and B respectively, but rotated about the molecular three-fold axis so that the hydrogen atoms approach nearby Si-Si bonds closely. The relative energies and quasiharmonic modes of the four structures, relaxed in the positive, neutral and negative charge states are shown in table III.

The calculated vibrational modes for the interstitial silyl molecule, for both of the degenerate low-energy A and B structures and in all three charge-states, differ from experiment by at least 300 cm^{-1} . Similarly for the intermediate energy ($\sim 1.6\text{ eV}$ above ground state for all charges) C structures, again all vibrational modes do not match the experimental values. Only the high energy ($\sim 4.2\text{ eV}$ above the lowest energy structures for the three charge states) D structure has modes that are close to the experimental values, but due to the high energy of this structure, it must be discounted as a possible candidate for the defect.

So for both the silane and silyl molecules, the calculated vibrational frequencies differ from the experimental observed spectra by more than 300 cm^{-1} for all structures, with the exception of the very high energy D structure. Taken together, these results rule out Si_4 and SiH_3 molecules as the candidates for the defects responsible for the 2222 cm^{-1} and $2190.3/2166.1\text{ cm}^{-1}$ groups of lines.

The large downward shifts in the H stretch frequencies for the interstitial molecules compared with free molecules are reminiscent of the 540 cm^{-1} red-shift found for the stretch mode of the interstitial H_2 molecule.²³ This is believed to arise from the screening of the molecular proton-electron attraction by the lattice charge distribution partially filling the molecular anti-bonding orbitals, leading to a weakened H–H bond. A similar mechanism may operate in the present case and suggests a universal effect.

IV. CONCLUSION

In conclusion, the *ab initio* calculations offer no support to the idea that the 2222 cm^{-1} line originates from an interstitial Si_4 molecule. The frequency of the interstitial silane molecule is found to lie around 1800 cm^{-1} . As far as we are aware, there are no modes in this region due to tetrahedral defects and hence we conclude that such interstitial molecules do not exist in detectable concentrations.

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TABLES

	Si ₄ (<i>T_d</i>)	SiH ₃ D (<i>C_{3v}</i>)	SiH ₂ D ₂ (<i>C_{2v}</i>)	SiHD ₃ (<i>C_{3v}</i>)	SiD ₄ (<i>T_d</i>)
<i>Isolated</i>					
(SiH ₄) _g	2190 (2187.0) <i>A</i> ₁	2174 <i>A</i> ₁	2156 (2198) <i>A</i> ₁	2138 (2182) <i>A</i> ₁	1549 (1545) <i>A</i> ₁
	2123 (2190.6) <i>T</i> ₂	2122 <i>E</i>	2121 (2183) <i>B</i> ₂	1546 (1573) <i>A</i> ₁	1541 (1597) <i>T</i> ₂
		1546 <i>A</i> ₁	1545 (1587) <i>A</i> ₁	1542 (1598) <i>E</i>	
			1544 (1601) <i>B</i> ₁		
<i>Trapped</i>					
Theoretical	1812 (<i>A</i> ₁)	1809 (<i>A</i> ₁)	1806 (<i>A</i> ₁)	1803 (<i>A</i> ₁)	1312 (<i>T</i> ₂)
(SiH ₄) _i	1802 (<i>T</i> ₂)	1801 (<i>E</i>)	1801 (<i>B</i> ₂)	1313 (<i>E</i>)	1281 (<i>A</i> ₁)
		1306 (<i>A</i> ₁)	1314 (<i>B</i> ₁)	1313 (<i>A</i> ₁)	
			1297 (<i>A</i> ₁)	1289 (<i>A</i> ₁)	
Experimental	2221.9 (<i>T</i> ₂)	2250.4 (<i>A</i> ₁)	2243.5 (<i>A</i> ₁)	2236.1 (<i>A</i> ₁)	1616.6 (<i>T</i> ₂)
XH ₄	NIR (<i>A</i> ₁)	2223.5 (<i>E</i>)	2225.4 (<i>B</i> ₁)	1636.1 (<i>A</i> ₁)	NIR (<i>A</i> ₁)
		1620.3 (<i>A</i> ₁)	1628.3 (<i>A</i> ₁)	1615.6 (<i>E</i>)	
			1614.6 (<i>B</i> ₂)		

TABLE I. Calculated quasi-harmonic frequencies (cm⁻¹) for the fundamental vibrational transitions of isolated, non-rotating, silane molecules (experimental frequencies^{3,24} are shown in brackets), and the low energy form of trapped interstitial silane at the T_d site, as compared with observed frequencies for the tetrahedral XH₄ defect⁷ (*note*: the two entries marked NIR are infrared inactive modes).

mode	Fixed Surface	Relaxed Surface	Increased Basis
A_1	1812	1861	1877
T_2	1802	1755	1829

TABLE II. Effect of allowing free-relaxation of the surface or increasing basis size on the higher frequency modes of interstitial silane, as described in the text.

<i>Calculated</i>	A	B	C	D
+1				
Energy	0.21	0.00	1.84	4.37
SiH ₃ modes	1853 (<i>E</i>)	2045 (<i>E</i>)	1643 (<i>A</i> ₁)	2373 (<i>A</i> ₁)
	1551 (<i>A</i> ₁)	1949 (<i>A</i> ₁)	1194 (<i>A</i> ₁)	2239 (<i>E</i>)
			1067 (<i>E</i>)	1155 (<i>A</i> ₁)
0				
Energy	0.00	0.04	1.61	4.29
SiH ₃ modes	1668 (<i>E</i>)	1849 (<i>E</i>)	1844 (<i>A</i> ₁)	2317 (<i>A</i> ₁)
	1371 (<i>A</i> ₁)	1629 (<i>A</i> ₁)	1369 (<i>A</i> ₁)	2162 (<i>E</i>)
			1228 (<i>E</i>)	
			1161 (<i>E</i>)	
-1				
Energy	0.00	0.00	1.48	4.16
SiH ₃ modes	1390 (<i>E</i>)	1032 (<i>E</i>)	1971 (<i>A</i> ₁)	1873 (<i>A</i> ₁)
	1188 (<i>A</i> ₁)	1006 (<i>A</i> ₁)	1519 (<i>A</i> ₁)	1271 (<i>E</i>)
			1513 (<i>E</i>)	
			1401 (<i>E</i>)	
<i>Experimental:</i>	2190.3 (<i>A</i> ₁)	2166.1 (<i>E</i>)		

TABLE III. Relative energies (eV) and modes (cm⁻¹) of the four *C*_{3*v*} configurations of interstitial SiH₃ in the +1, neutral and -1 charge states, and the experimental frequencies of XH₃

FIGURES

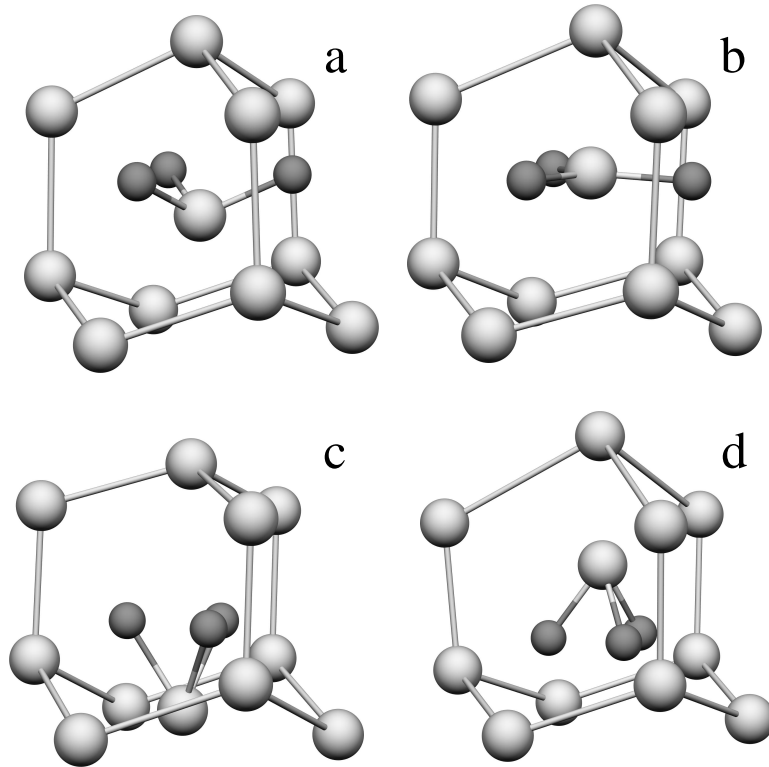


FIG. 1. Relaxed structures for the neutral form of the four distinct C_{3v} configurations of *interstitial* SiH_3

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