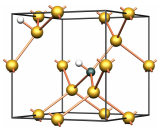
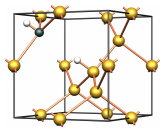


EVIDENCE FOR H_2^* TRAPPED BY CARBON IMPURITIES IN SILICON



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Abstract

Local mode spectroscopy and *ab initio* modelling are used to investigate two trigonal defects found in carbon rich Si into which H had been in-diffused. Isotopic shifts with D and ^{13}C are reported along with the effect of uniaxial stress. Ab-initio modelling studies suggest that the two defects are two forms of the CH_2^* complex where one of the two hydrogen atoms lies at an anti-bonding site attached to C or Si respectively. The two structures are nearly degenerate and possess vibrational modes in good agreement with those observed.

Background

Several IR absorption lines in the ranges of 790–820 cm^{-1} and 1900–2250 were observed in FZ-Si crystals which were grown in a hydrogen atmosphere [1, 2].
Positions of these lines, except a few ones, are different from those found in proton-implanted Si samples, but coincide with those found in FZ- and Cz-Si crystals, (the lines were especially pronounced in C-rich samples) which were subjected to high-temperature treatments in H2 gas ambient [3].
Carbon seems to play an important role in formation of these new defects [4]. A combined stress and IR absorption study of carbon-rich FZ-Si crystals, which were subjected to high-temperature treatments in H_2 or/and D_2 ambient has been carried out. Observed modes are compared against the results of first-principle simulation.

Experimental Details

- Samples FZ-Si:P (B) crystals enriched with carbon; [O]$\leq 2\times10^{16}$ cm^{-3}, [C]=(1.5–3.0)$\times10^{17}$ cm^{-3}
- Hydrogenation of samples in sealed quartz ampoules with H_2 or/and D_2 gas; T = 1200–1350 °C; P = 1.0 or 1.5 atm.; Fast cooling by plunging the ampoules into water
- FT-IR: Brucker IFS 113v and Bomem DA3.8 spectrometers, T_{meas}=10 K; Resolution : 0.1 – 0.5 cm^{-1}
- Uniaxial stress measurements on samples 10×3×2 mm^3

Theoretical Details

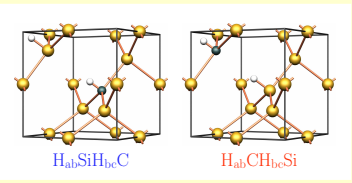
Supercell, spin-polarised–LDF calculations using the AIMPRO code [5, 6]

- Si_{64} cubic supercells
- Cartesian Gaussian basis
- 200 Ry planewave intermediate fit for Hartree and exchange-correlation energies
- BHS pseudopotentials [7]
- All atoms allowed to relax by conjugate gradient
- Second derivatives of C & H atoms and neighbours found
- Stress/energy B-tensor evaluated directly

Summary of Experimental Results

1. Lines at 792.0, 1921.8, and 2752.3 cm^{-3} in hydrogenated Si:C crystals originate from the same centre.
2. Lines at 665.3 and 2210.4 cm^{-3} in hydrogenated Si:C crystals originate from the same centre.
3. Downward shift in hydrogen characteristic frequencies (2210.4 and 1921.8 cm^{-3})with a factor of about $\sqrt{2}$ after substitution of hydrogen by deuterium for both defects.
4. 2752.3 cm^{-3} mode typical for C–H bonds.
5. Small splitting of the lines in samples co-doped with hydrogen and deuterium indicates that both sets of lines originate from defects containing a pair of weakly interacting hydrogen atoms.
6. Uniaxial stress measurements showed that the 2210.4 cm^{-1} line represents an A_1 mode of a trigonal centre.
7. Uniaxial stress measurements showed that the 792.0 cm^{-1} line represents an E mode of a trigonal centre.

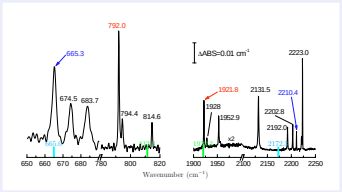
Proposed Defects Based on H_2^* Trapped at Carbon



The calculated energies for $H_{ab}SiH_{bc}C$ and $H_{ab}CH_{bc}Si$ are degenerate. For these trigonal defects, the stress/energy B-tensor is $\frac{1}{2}B_{11} = -B_{22} = -B_{33}$ with B_{11} being 7.69 ($H_{ab}CH_{bc}Si$) and 11.15 ($H_{ab}SiH_{bc}C$) eV per unit strain.

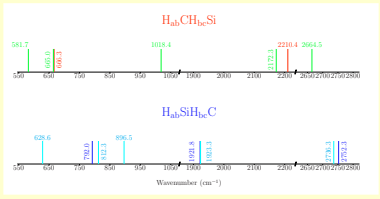
Observed Spectra

Fragments of infrared absorption spectrum of a carbon-rich ([C]=2 × 10^{17} cm^{-3}) FZ-Si sample, which was treated in H_2 gas at 1350 °C for 30 min. Modes that share annealing characteristics are colour coded. The calculated modes for $H_{ab}SiH_{bc}C$ and $H_{ab}CH_{bc}Si$ are also shown.



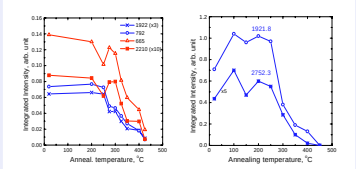
Calculated and Measured Vibrational modes

Only the $^{12}CH_2^*$ isotope is shown, other isotopic modes also match well (see associated paper).



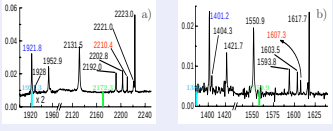
Annealing

The isochronal annealing temperature dependence of the integrated absorption intensity of the bands at 792.0, 1921.8, and 2752.3 cm^{-1} and the modes at 665.3 and 2210.4 in a C-rich FZ-Si sample which was treated in H_2 gas ambient at 1350 °C for 30 min. IR absorption measurements were carried out at 10 K with a resolution of 0.5 cm^{-1}.



Isotopic Substitution – H/D

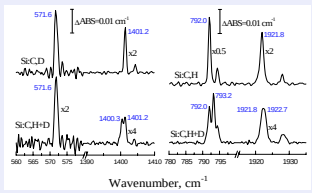
Fragments of infrared absorption spectrum of a carbon-rich ([C] = 2.7 × 10^{17} cm^{-3}) FZ-Si sample, which was treated in H_2 (a) or D_2 (b) gas at 1350 °C for 30 min. The calculated modes for $H_{ab}SiH_{bc}C$ and $H_{ab}CH_{bc}Si$ are also shown.



Conclusions

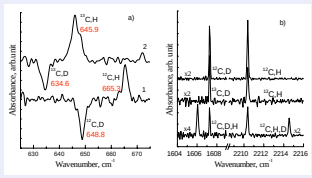
1. The lines at 792.0, 1921.8 and 2752.3 cm^{-1} are assigned to Si–H bend and stretch modes, and a C–H stretch mode of a CH_2^* ($H_{ab}SiH_{bc}C$) complex with C_{3v} symmetry.
2. The lines at 665.3 and 2210.4 cm^{-1} are assigned to a C–H bend mode and an Si–H stretch mode of a CH_2^* ($H_{ab}CH_{bc}Si$) complex with C_{3v} symmetry.
3. The calculated modes are in good agreement with those observed for both defects.

Isotopic Substitution – mixed H/D



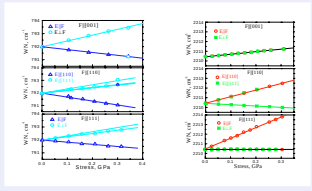
Isotopic Substitution – $^{12}C/^{13}C$

Isotopic shifts with carbon, showing the modes characteristic of a) carbon-related stretch modes, and b) silicon-hydrogen related modes.



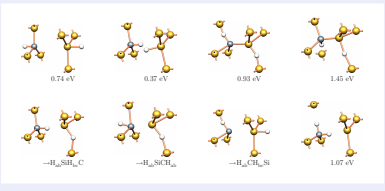
Stress

The effect of uniaxial stress on the 792.0 and 2210.4 cm^{-1} mode. **F** is the force and **E** is the electric-field vector of the incident light. The splitting pattern is found to be consistent with the assignment of E and A_1 character.



Other Possibilities

A number of other structures consisting of C_s + 2×H were investigated, but all other forms were found to be at least $\gtrsim$ 0.4 eV higher in energy.



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