STABLE HYDROGEN PAIR TRAPPED AT CARBON IMPURITIES IN SILICON

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Local mode spectroscopy and *ab initio* modeling 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 modeling 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 experimentally. The defects are energetically favourable in comparison with separated C_s and H_2 in Si and may represent aggregation sites for hydrogen.

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I. INTRODUCTION

Hydrogen and carbon are common interstitial and substitutional impurities respectively in silicon[1,2]. The single hydrogen defect is highly mobile and is easily trapped by impurities and lattice defects. One prominent defect found in proton implanted Si, or Si containing H which has been *e*-irradiated, is the trigonal H_2^* center which contains two inequivalent H atoms. One H atom lies at a bond centered site and the other at a neighboring anti-bonding site[3]. It might be expected that dilated Si-Si bonds due to the strain field surrounding substitutional carbon atoms will be trapping sites for H. However, the greater binding energy of H with C rather than Si[4] suggests that H will attach directly to C. Examples of defects where H bonds to Si rather than C are given in ref. 5 while ref. 6 exemplifies the second defect type. In other cases, it is not clear which type is present[7,8].

FIG. 1: The two degenerate C_{3v} structures for CH_2^*. a) shows $SiH_{bc}CH_{ab}$, and b) displays $CH_{bc}SiH_{ab}$. Relevant bond-lengths and angles are shown where appropriate.

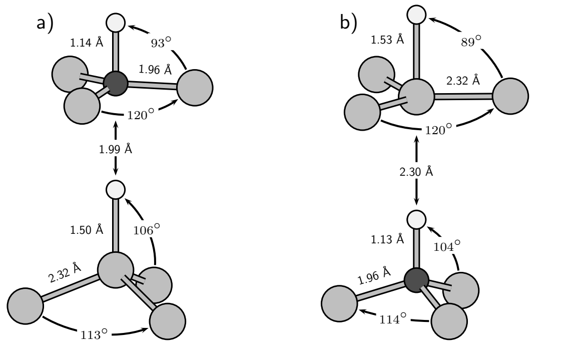
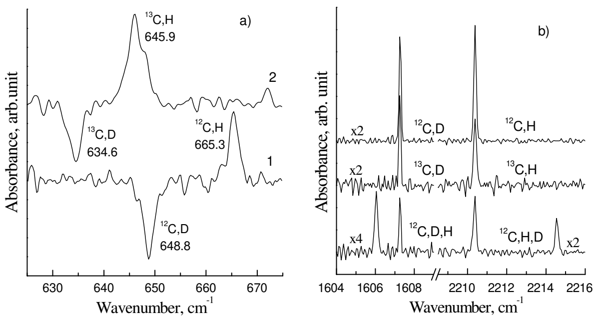


FIG. 2: a) Difference absorption spectra measured at 10 K with a resolution 0.5 cm^{-1} for 1) a Si:^{12}C sample doped with hydrogen and 2) a Si:^{13}C sample doped with hydrogen (spectra of a Si:^{12}C sample and a Si:^{13}C sample doped with deuterium were used as reference spectra for spectra 1) and 2), respectively); b) Details of infrared absorption spectra, measured at 10 K with a resolution 0.1 cm^{-1}, on ^{12}C-rich and ^{13}C-rich Fz-Si samples, which were doped with hydrogen, deuterium and H+D mixture (50% + 50%). Multiplication factors for different parts of the spectra are indicated. All the samples were treated in H(D) gas ambient at 1350 °C for 30 min with a gas pressure of about 1.5 atm.



Recently, several local vibrational modes (LVMs) were observed in carbon-rich Si samples treated in a hydrogen ambient at high temperatures[9–11]. Some arise from a trigonal complex containing one carbon and two hydrogen atoms[9,11]. The LVMs of this defect, labeled $(C\text{-}H_2^*)_2$,

TABLE I: Calculated (observed) LVMs, cm^{-1}, for the $(C\text{-}H_2^*)_2$ trigonal defect ($CH_{bc}SiH_{ab}$).

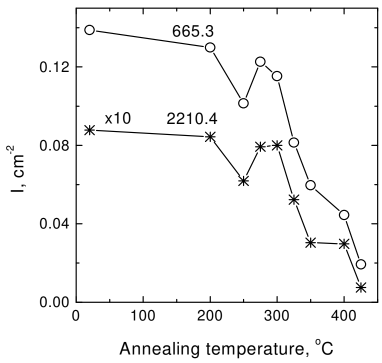
Suggested LVM assignment	$^{12}CH_{bc}SiH_{ab}$		$^{12}CD_{bc}SiH_{ab}$		$^{12}CH_{bc}SiD_{ab}$		$^{12}CD_{bc}SiD_{ab}$		$^{13}CH_{bc}SiH_{ab}$		$^{13}CD_{bc}SiD_{ab}$	
A_1 (C-H stretch)	2736.3	(2752.3)	2007.2	(—)	2736.3	(—)	2006.3	(—)	2728.7	(2745.1)	1995.3	(—)
A_1 (Si-H stretch)	1923.3	(1921.8)	1922.5	(1922.7)	1383.0	(1400.3)	1383.0	(1401.2)	1923.3	(1921.8)	1383.0	(1401.2)
E (C-H wag)	896.5	(—)	708.6	(—)	895.9	(—)	709.1	(—)	892.7	(—)	694.6	(—)
E (Si-H wag)	812.3	(792.0)	813.3	(793.2)	634.9	(571.8)	634.9	(571.6)	812.2	(792.0)	634.8	(571.4)
Si-H wag overtone	—	(1550.2)										
E (Si-C stretch)	628.6	(—)	581.3	(—)	628.6	(—)	581.3	(—)	612.7	(—)	576.1	(—)

TABLE II: Calculated (observed) LVMs, cm^{-1}, for the $(C\text{-}H_2^*)_1$ trigonal defect ($SiH_{bc}CH_{ab}$).

Suggested LVM assignment	$SiH_{bc}{}^{12}CH_{ab}$		$SiD_{bc}{}^{12}CH_{ab}$		$SiH_{bc}{}^{12}CD_{ab}$		$SiD_{bc}{}^{12}CD_{ab}$		$SiH_{bc}{}^{13}CH_{ab}$		$SiD_{bc}{}^{13}CD_{ab}$	
A_1 (C-H stretch)	2664.5	(—)	2662.9	(—)	1946.2	(—)	1950.7	(—)	2657.4	(—)	1940.5	(—)
A_1 (Si-H stretch)	2172.3	(2210.4)	1560.5	(1606.05)	2177.8	(2214.5)	1559.9	(1607.3)	2172.2	(2210.4)	1559.9	(1607.3)
E (C-H wag)	1018.4	(—)	1018.4	(—)	750.7	(—)	750.7	(—)	1017.0	(—)	743.4	(—)
E (Si-C)	665.0	(665.3)	665.0	(665.4)	646.9	(649)	646.9	(648.8)	645.6	(645.85)	633.4	(634.6)
E (Si-H wag)	581.7	(—)	536.3	(—)	581.7	(—)	536.3	(—)	581.7	(—)	536.2	(—)

are given in Table I. Following previous theoretical results[12], it was suggested that this complex is a H_2^* defect trapped near C. There are two possible trigonal forms of the center where the anti-bonding sited H is bonded to Si or C (Fig. 1). The observed modes are due to a defect somewhat more stable than H_2^*, which disappears at $\lesssim 200$ °C[3,13], as the modes are observable after anneals up to ~ 400 °C[9,11]. We show in the present work that there is another set of LVM absorption lines, which is related to the other form of C-H_2^* center, labeled (C-H_2^*)$_1$. These assignments are based on the analyses of shifts and splitting of the LVMs resulting from ^{13}C and D isotopic substitution as well as from uniaxial stress and comparison of the results with *ab initio* modeling.

FIG. 3: The isochronal annealing temperature dependence of the integrated absorption intensity of the bands at 665.3 and 2210.4 cm^{-1} in a ^{12}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 0.5 cm^{-1}.

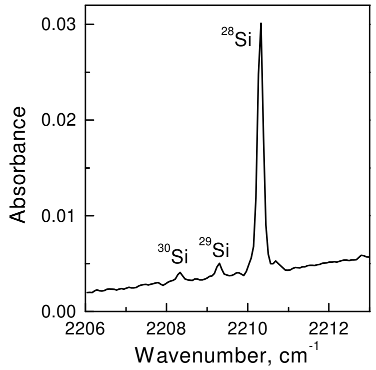


II. EXPERIMENTAL AND THEORETICAL DETAILS

Samples for this study were prepared from lightly-doped *n*-type and *p*-type float-zone-grown Si crystals with different carbon concentrations in the range (1.5-3.0)$\times 10^{17}$ cm^{-3}. A few samples were prepared from a crystal enriched with ^{13}C isotopes to about 8×10^{17} cm^{-3}. Hydrogen and/or deuterium was introduced by a heat treatment at 1250–1350°C for 30 min or 1 h in a H_2 (D_2) gas ambient at a gas pressure of about 1.0 or 1.5 atm., followed by a quench. The isochronal annealing was carried out in an argon atmosphere in temperature steps of 25°C in the range of 100-450°C, for 30 min at each temperature. The thickness of the samples was in most cases about 6 mm. The samples used for the uniaxial stress measurements had dimensions $10\times 3\times 2$ mm^3. Optical absorption spectra were measured by Fourier transform infrared (FT-IR) spectrometers at ~ 10 K. The spectral resolution varied from 0.1 to 0.5 cm^{-1}.

The properties of C-H_2^* defects in silicon, were investigated by a local density-functional technique as implemented in the AIMPRO code[14]. The defects were inserted into 64 atom supercells and a 2^3 Monkhorst–Pack k-point sampling scheme used to integrate over the band structure[15]. The basis consisted of independent s- and p-Gaussian orbitals, with four different exponents, sited at each Si atom, four at the carbon atom, and three at the H atom. In addition, a single set of s- and p-Gaussian functions was placed between every neighboring pair of

FIG. 4: High-resolution infrared absorption spectrum showing silicon isotope satellites of the 2210.4 cm^{-1} line in a Si:C crystal doped with hydrogen.



atoms. The Hartree and Perdew–Zunger[16] exchange-correlation energies were calculated using a plane-wave intermediate fit with an energy cut-off of 200 Ry. All atoms were allowed to relax by a conjugate gradient method. The second derivatives of the energy were found for the atoms of the defects and their immediate neighbors, 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 Ref 17).

III. RESULTS

Among the many sharp absorption lines observed in the frequency ranges 660-690, 790-820, 1920-1960, 2120-2230, and 2680-2950 cm^{-1} [9–11] lines at 2210.4 cm^{-1} and 665.3 cm^{-1} are of particular interest in the present work (Fig. 2). A clear linear correlation was found between the intensities of these lines in different samples and the lines were found to have an identical annealing behavior as illustrated in Fig. 3. This suggests that they originate from the same defect. The positions of the lines of this complex, labeled (C-H_2^*)$_1$, in Si crystals containing different C and H isotopes are given in Table II.

The shift of the 665.3 cm^{-1} line with ^{13}C and D (Fig. 2a) demonstrates that the defect contains one C and at least one hydrogen atom. Inspection of the shifts of the 2210.4 cm^{-1} line, as well as its splitting in the mixed H+D case (Fig. 2b), shows that there should be two weakly interacting H atoms, one of them being attached to a silicon atom. This is evidenced by the observation of silicon isotope shifts for the 2210.4 cm^{-1} line. Fig. 4 shows weak satellite lines on the low-energy side of the main line due to the presence of the naturally occurring isotopes ^{29}Si (4.7% abundant) and ^{30}Si (3.0%).

Figures 5 and 6 show the effect of uniaxial stress on the 2210.4 cm^{-1} mode. The number of lines and their relative intensities for each orientation and light polarization are consistent with a non-degenerate vibrational mode (A_1) of a trigonal center (C_{3v} point group)[18,19]. The values of the A piezospectroscopic tensor components were found to be A_{11}=2.70 ± 0.1 $cm^{-1}GPa^{-1}$ and A_{22}=4.15 ± 0.1 $cm^{-1}GPa^{-1}$.

All combinations of pairs of hydrogen atoms at bond-center and anti-bonding sites within one and two neighboring sites of substitutional carbon were structurally relaxed. Two degenerate structures with C_{3v} symmetry were found to possess the lowest energy by at least $\gtrsim$ 0.4 eV. These structures are similar to the H_2^* defect[3] and are shown in Fig. 1. The relative binding energy of the two degenerate C-H_2^* defects with respect to separated C_s and H_2 was found to be 0.79 eV (H_2 is considered to be slightly lower in energy than H_2^*[20]). The calculated LVMs are given in Tables I and II. The calculated Si-H stretch mode in $SiH_{bc}CH_{ab}$ (Fig. 1a) at 2172 cm^{-1} is close to the observed mode at 2210.4 cm^{-1}. There are undetected C-H stretch and bend modes at 2664.5 and 1018.4 cm^{-1} respectively. We assign the observed mode at 665.3 cm^{-1} to the E (C-Si) mode at the same frequency. The isotopic shifts are in good agreement with the experimental ones. Accordingly, we assign the (C-H_2^*)$_1$ defect to $SiH_{bc}CH_{ab}$.

We turn now to the previously reported modes of (C-H_2^*)$_2$ [9]. These are in good agreement with the calculated modes of $CH_{bc}SiH_{ab}$ shown in Fig. 1b. In particular, the C-H and Si-H stretch modes observed at 2752 and 1922 cm^{-1} are close to the calculated ones at 2736 and 1923 cm^{-1}. The Si-H wag mode at 792 is close to the calculated one at 812 cm^{-1}. Similarly, there is good agreement with the isotopic shifts. Accordingly, we assign the (C-H_2^*)$_2$ defect to $CH_{bc}SiH_{ab}$.

Finally, for completeness, the stress-energy B-tensor for both forms of H_2^* were calculated. The tensors are evaluated directly by first relaxing the volume of the cubic cell and then calculating $\partial E/\partial \epsilon_{ij}$ with Cartesian axes, where ϵ_{ij} is the strain[14]. For trigonal defects the tensor has principal values $\frac{1}{2}B_{11} = -B_{22} = -B_{33}$ with the principle directions $\langle 1\ 1\ 1\rangle$ (along the C_3 axis), $\langle 1\ \bar{1}\ 0\rangle$ and $\langle 1\ 1\ \bar{2}\rangle$. The values of B_{11} for $SiH_{bc}CH_{ab}$ and $CH_{bc}SiH_{ab}$ were found to be 7.69 and 11.15 eV per unit strain. The fractional volume change for the defects in a 64 atom cubic cell were found to be 0.2% and 0.3% respectively, i.e., $\Delta V/V_0 = 64 \times 0.2\%$. So the volume change caused by the defect is just $0.1 \times V_0$ where V_0 is volume of Si atom (defined as $a_0^3/8$).

The CH_2^* defects are very stable. The binding energy of a hydrogen molecule to substitutional carbon in the CH_2^* defect is ∼0.8 eV. This binding energy accounts for the stability of the defects which survive up to 400°C, in contrast to isolated H_2^* which anneals at $\lesssim$200°C [3,13]. Further hydrogen atoms can also be bound at or by carbon, leading to defects such as $C_s(H_2^*)_2$. One of the C_{2v} forms of this defect, consisting of two H_2^* units both involving a shared carbon atom as $C_s(H_{bc})_2 \cdots (SiH_{ab})_2$, is bound by 1.5 eV compared to $C_s + 2{\times}H_2$. This form of aggregation is distinct from the hydrogen platelets cre-

FIG. 5: Effect of stress, σ, on the 2210.4 cm^{-1} line in hydrogen-doped Si:C crystals. The stress direction and magnitude and the polarization vector, σ, for the incident light are given. The stick-bars show the fitted peak positions and relative intensities.

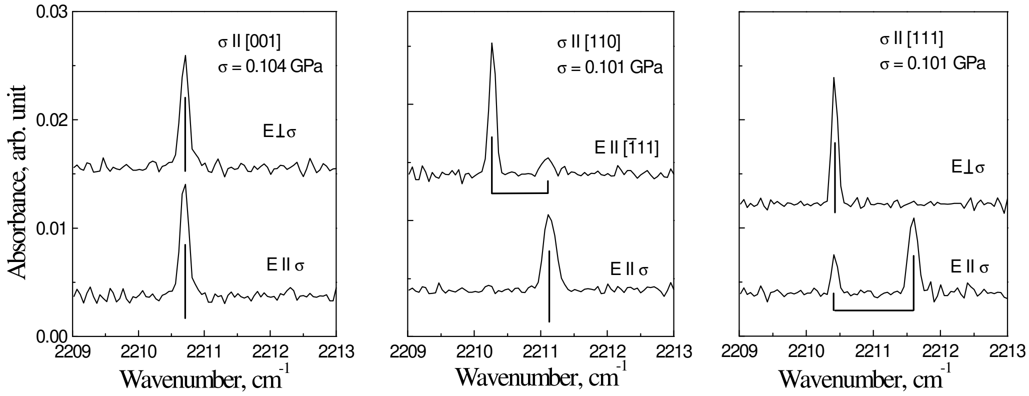
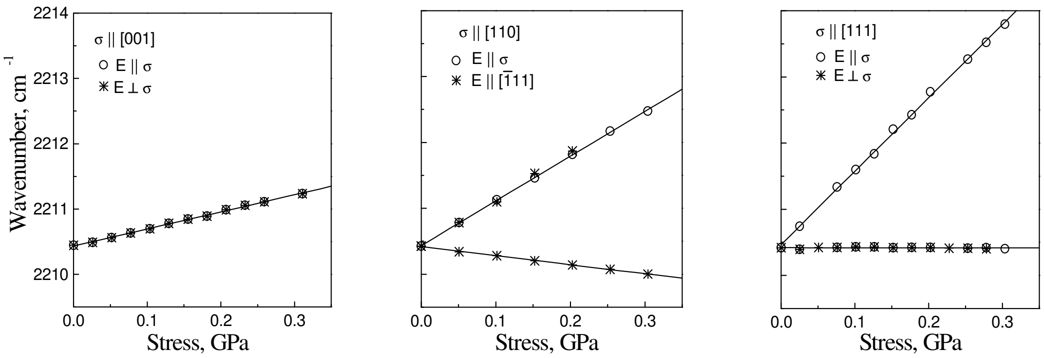


FIG. 6: The effect of uniaxial stress on the 2210.4 cm^{-1} mode. The stress direction and the polarization vector, **E**, for the incident light are indicated. The solid lines are the best-fit frequency shifts for a trigonal center with the following components of the piezospectroscopic tensor: A_{11}=2.70 cm^{-1}GPa^{-1} and A_{22}=4.15 cm^{-1}GPa^{-1}.



ated in plasma treated Si[21], one form of which having been suggested to be due to sheets of H_2^* units in (111) planes[22,23].

IV. SUMMARY

Two H-related defects have been investigated by local mode spectroscopy and *ab initio* modeling. Unlike carbon lean material where no lines (except some traces of H_2^*) are observed in the frequency ranges of 790–820, 1920–2230 and 2680–2950 cm^{-1} after heat treatments at 1200–1350 °C in H_2 gas, two strong LVM lines are observed at 1921.8 and 2210.4 cm^{-1} in carbon rich material treated with hydrogen. These lines are identified with Si-H stretch modes of two forms of C-H_2^* defects where H lies antibonded to Si and C atoms respectively. Several other modes are observed in each defect and related to particular atomic displacements. These defects are formed by breaking lattice bonds and are $\sim$ 0.8 eV more stable than a hydrogen molecule near a carbon impurity.

A pair of molecules can also be trapped by a carbon impurity leading to bond breaking and the formation of two H_2^* species. This defect possesses C_{2v} symmetry. Thus, it does not appear that the presence of carbon favors (111) platelet growth.

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