

Isolated interstitial hydrogen molecules in hydrogenated crystalline silicon

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Infrared spectra of hydrogenated lightly doped Czochralski silicon show absorption due to (a) modes of O_i - H_2 centers (binding energy 0.26 eV), and (b) a mode labeled ν_{3HH} at 3618 cm^{-1} due to H_2 molecules. Annealing produces reversible changes in the equilibrium concentrations of O_i - H_2 and ν_{3HH} that reveal a linear anticorrelation. An analysis using a two-center statistical model indicates that the number density of available sites for ν_{3HH} centers is 10^{22} – 10^{23} cm^{-3} and we propose that the ν_{3HH} centers are *isolated* molecules occupying interstitial lattice sites. The H_2 alignment must be $\langle 111 \rangle$ or $\langle 110 \rangle$ to account for the infrared activity. [S0163-1829(98)51924-8]

There continues to be considerable interest in the behavior of hydrogen impurities in silicon. Previous work has concentrated on the passivation of both shallow and deep defects or impurity centers by the formation of complexes with hydrogen atoms.¹ Observations of enhanced rates of oxygen diffusion in Czochralski (CZ) silicon ($T \leq 500\text{ }^\circ\text{C}$) (Refs. 2 and 3) have also been interpreted in terms of catalytic interactions with H atoms.^{4–6} The presence of hydrogen molecules occupying interstitial sites has, however, been predicted by theory.^{7–9} It was then found that boron-doped samples contained “hidden hydrogen” after heat treatments in H_2 gas at $1300\text{ }^\circ\text{C}$, followed by a quench to room temperature.¹⁰ It was argued that at least some of this hydrogen was present as molecules that were not detected by IR absorption but were subsequently converted to H_2^* defects by 2 MeV electron irradiation.¹⁰

Direct evidence for the presence of hydrogen molecules in plasma-treated silicon was obtained from recent Raman-scattering measurements.¹¹ The observed vibrational frequency was 4158 cm^{-1} , close to that of gaseous H_2 (and similarly for D_2),¹² and it was presumed that the molecules giving rise to this line were located at isolated interstitial lattice sites.^{11,13} Calculations using the *ab initio* Hartree-Fock method¹⁴ predicted a vibrational frequency of $\sim 4500\text{ cm}^{-1}$ in support of this interpretation. However, other groups have performed *ab initio* calculations using density-functional theory and predicted much reduced frequencies in the range 3000 – 3600 cm^{-1} .^{15–17} It was then argued that, alternatively, the molecules giving rise to the Raman signal are located in voids created by the plasma treatment of the samples.^{16,18} This latter interpretation could explain the correlated Raman signals from hydrogen-passivated Si dangling bonds.¹⁸ Soon after, IR absorption lines from interstitial H_2 molecules trapped at sites adjacent to bond-centered interstitial oxygen atoms, O_i , were identified¹⁹ in lightly doped CZ Si that had been preheat treated in hydrogen gas at $1300\text{ }^\circ\text{C}$. Vibrational absorption showing a peak at 1075.1 cm^{-1} with a shoulder at 1075.8 cm^{-1} was assigned to modes of two O_i - H_2 complexes with slightly different configurations.¹⁹ The hydrogen molecules in these centers are weakly IR active and give rise to modes at $\nu_{1HH} = 3789$ and $\nu_{2HH} = 3731\text{ cm}^{-1}$, respec-

tively, with dipole moments per unit displacement, η , close to $0.1e$.¹⁹ An additional line (labeled ν_{3HH}) also due to H_2 molecules was detected at 3618 cm^{-1} ($\Delta = 0.2\text{ cm}^{-1}$) by infrared-absorption measurements. This mode had an integrated absorption coefficient (C_{IA}) similar to those of ν_{1HH} and ν_{2HH} and was also detected in hydrogenated floatzone Si. This implies that the H_2 molecules in the ν_{3HH} center are not associated with O_i atoms and it was originally suggested that the molecules might be trapped by an unknown defect or impurity center.¹⁹ At this time, isolated interstitial H_2 molecules were thought to be infrared inactive but recent theoretical analysis¹⁶ has shown that molecules with a $\langle 110 \rangle$ or $\langle 111 \rangle$ alignment have a dipole moment per unit displacement of $\sim 0.1e$.

We now present low-temperature annealing data (35 – $130\text{ }^\circ\text{C}$) of hydrogenated Czochralski silicon that provide information about the lattice location of hydrogen molecules in the ν_{3HH} center. It has been shown previously that such treatments produce reductions in the strength of the 1075 cm^{-1} absorption^{19,20} and increases in the strength of the ν_{3HH} mode.¹⁹ However, a definite anticorrelation was not established because changes in the absorption strengths occurred while the samples were stored at room temperature prior to measurement. New data have now been obtained and analyzed with the assumption that all H_2 molecules dissociated from O_i - H_2 complexes are converted to ν_{3HH} centers. This analysis leads to a determination of the difference in binding energy of the O_i - H_2 complex and the ν_{3HH} center. More importantly, the number density of ν_{3HH} sites accessible to H_2 molecules is found to be close to $5 \times 10^{22}\text{ cm}^{-3}$. This leads to the proposal that ν_{3HH} centers are isolated hydrogen molecules located at tetrahedral lattice sites.

An as-grown CZ Si sample (thickness = 17 mm) with an oxygen concentration of 10^{18} cm^{-3} , a carbon concentration below 10^{15} cm^{-3} and doped with phosphorus ($5 \times 10^{14}\text{ cm}^{-3}$) was heated in a quartz tube at $1300\text{ }^\circ\text{C}$ for 60 min in flowing H_2 gas. The sample was cooled rapidly by plunging the tube into water while the hydrogen flow was maintained. The sample was then subjected to sequential anneals in the temperature range 35 – $130\text{ }^\circ\text{C}$ in an oil bath for periods of 30–60 min. Following each anneal, the sample

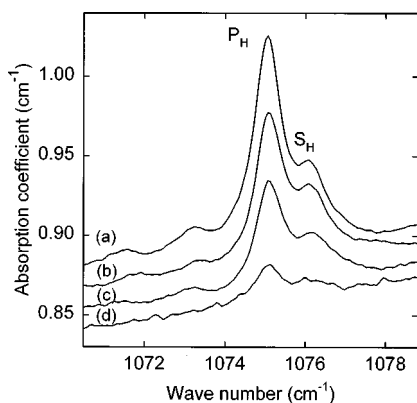


FIG. 1. Infrared-absorption spectra showing the vibrational absorption from O_i-H_2 centers from (a) the as-quenched hydrogenated CZ and (b), (c), and (d) following anneals at 60, 70, and 130 °C, respectively. The spectra are shifted vertically for clarity of presentation. The absorption comprises a peak P_H at 1075.1 cm^{-1} and a shoulder S_H at 1075.8 cm^{-1} that have relative absorption strengths close to 3:1 following the anneals at all temperatures. This result demonstrates that the binding energy of the two types of O_i-H_2 centers must be essentially the same.

was immediately degreased and cooled to 10 K. The sample was scanned for at least 16 h using a Bruker IFS 113v interferometer operated at a resolution of 0.1 cm^{-1} . Weak modes from passivated Si dangling bonds¹⁸ that occur in the spectral range 1800–2300 cm^{-1} are sometimes detected in hydrogenated samples, presumably as a result of the introduction of point defects into the crystal during the quenching process. However, these lines were not detected in the present sample, neither immediately after quenching nor at any stage of the annealing treatment.

Figure 1(a) shows vibrational absorption from the as-quenched, hydrogenated sample after storage at 23 °C for ~ 1 week. The absorption from the O_i-H_2 centers at $\sim 1075 \text{ cm}^{-1}$ has a total integrated absorption coefficient, $C_{IA} = 0.149 \text{ cm}^{-2}$. The two weak satellites at 1073.4 and 1071.5 cm^{-1} occur because O_i atoms occupy bond-centered

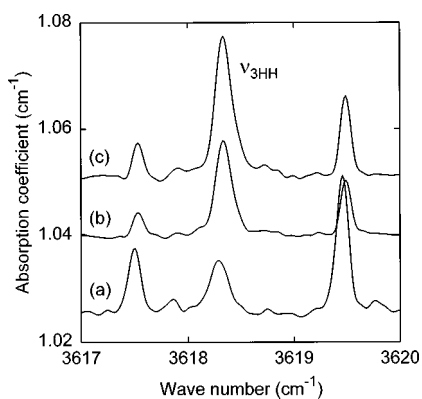


FIG. 2. Infrared-absorption spectra showing the ν_{3HH} line in (a) the as-quenched hydrogenated Cz Si, and (b), (c) following anneals at 50 and 130 °C, respectively. The spectra are shifted vertically for clarity of presentation. The lines on either side of ν_{3HH} are from residual water vapor in the interferometer. It should be noted that small shifts ($\sim 0.01 \text{ cm}^{-1}$) in the line frequencies have occurred for these spectra.

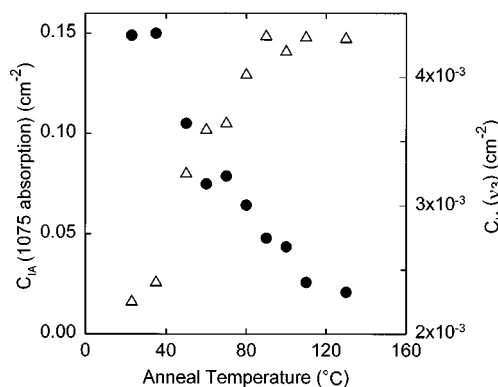


FIG. 3. The total integrated absorption coefficient of the 1075- cm^{-1} absorption feature (full circles, left-hand scale) and the C_{IA} of the ν_{3HH} mode (open triangles, right-hand scale) as a function of anneal temperature.

sites ($\text{Si}^{16}\text{O}_i\text{-Si}$ bonding) and the satellites originate from $^{28}\text{Si}^{16}\text{O}_i\text{-}^{29}\text{Si}$ and $^{28}\text{Si}^{16}\text{O}_i\text{-}^{30}\text{Si}$ complexes.¹⁹ The associated high-frequency hydrogen modes of the O_i-H_2 centers have C_{IA} of $1.1 \times 10^{-3} \text{ cm}^{-2}$ (ν_{1HH}) and $1.7 \times 10^{-3} \text{ cm}^{-2}$ (ν_{2HH}) while the ν_{3HH} center has $C_{IA} = 2.3 \times 10^{-3} \text{ cm}^{-2}$ (Fig. 2). To minimize the error in the evaluation of $[O_i-H_2]$ (see below), we have used the C_{IA} of the 1075 cm^{-1} absorption profile rather than the appropriate sum of the much smaller C_{IA} of ν_{1HH} and ν_{2HH} .

As the temperature of the anneal is increased sequentially, the strength of the 1075 cm^{-1} absorption decreases monotonically (Fig. 1) but the relative strengths of the peak and shoulder components show no detectable change. As the 1075 cm^{-1} absorption decreases, there are corresponding increases in the strength of the ν_{3HH} line (Figs. 2 and 3). There is, in fact, a linear anticorrelation (Fig. 4) implying that a fixed fraction of the molecules released by dissociation of O_i-H_2 centers diffuse to form ν_{3HH} centers. These are *reversible* cycles that occur in the temperature range 23–130 °C, but the period of the anneal must be sufficiently long to achieve equilibrium (30 min for $T > 50$ °C). By extrapolating the line shown in Fig. 4 to a value of $[\nu_{3HH}] = 0$, and taking the calibration for the 1075 cm^{-1} absorption feature to be the same as that for isolated O_i atoms (as discussed in Ref. 19),

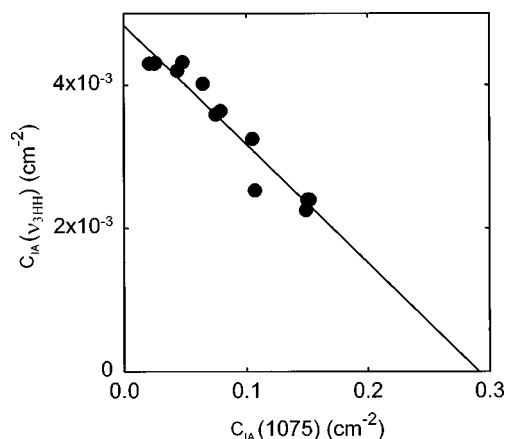


FIG. 4. The integrated absorption coefficient C_{IA} of the ν_{3HH} mode plotted against the C_{IA} of the 1075- cm^{-1} absorption feature, showing their *linear* anticorrelation.

we determine the maximum concentration of $[O_i-H_2]_{\max}=4 \times 10^{15} \text{ cm}^{-3}$. The equivalent atomic hydrogen concentration of $8 \times 10^{15} \text{ cm}^{-3}$ is consistent with the previously measured hydrogen solubility of $\sim 10^{16} \text{ cm}^{-3}$ at a preheat treatment temperature of $1300 \text{ }^\circ\text{C}$.^{10,21} We therefore infer that the maximum concentration of H_2 molecules located at ν_{3HH} sites is $[\nu_{3HH}]_{\max}=[O_i-H_2]_{\max}=4 \times 10^{15} \text{ cm}^{-3}$. Combining this concentration with the extrapolated maximum value of $C_{1A}(\nu_{3HH})=4.8 \times 10^{-3} \text{ cm}^{-2}$ leads to a minimum value of $\eta_{3HH} \sim 0.08e$, comparable to the values estimated for the H_2 modes of the O_i-H_2 centers (ν_{1HH} and ν_{2HH}).

We now make an initial determination of the density of states available to the H_2 molecule in the ν_{3HH} center. We assume a two-center statistical model based on the reversibility in absorption strengths of the anticorrelated O_i-H_2 and ν_{3HH} modes upon annealing. This reversibility implies diffusion of molecules between the two sites, $H_2(O_i) \leftrightarrow H_2(\nu_{3HH})$. If a third trap were present, it would have to have essentially the same density of states and binding energy for H_2 as those of the ν_{3HH} site to maintain the linear anticorrelation and reversibility. Molecules present in this third site would also have to be infrared inactive. These possibilities are discussed in more detail later. We write the ratio of the concentration of O_i-H_2 centers to ν_{3HH} centers at a temperature T as

$$[O_i-H_2]_T/[\nu_{3HH}]_T = (g_1/g_2) \exp(+\Delta E/kT),$$

where ΔE is the difference in energy of a H_2 molecule bound to an O_i atom (to give the O_i-H_2 complex) and a H_2 molecule present as the ν_{3HH} center. Initially, g_1 and g_2 are taken to be the number densities of sites accessible to the molecule in the two types of complexes. For an O_i-H_2 complex, there are six equivalent interstitial sites around a $\langle 111 \rangle$ Si- O_i -Si axis, and we take g_1 equal to $6 \times [O_i] = 6 \times 10^{18} \text{ cm}^{-3}$. An Arrhenius plot of $[O_i-H_2]_T/[\nu_{3HH}]_T$ allows us to determine ΔE from the gradient and a value of g_1/g_2 from the intercept (Fig. 5). We obtain $\Delta E = 0.26 \pm 0.02 \text{ eV}$ and $g_2 = 1.3 (+1.0, -0.7) \times 10^{23} \text{ cm}^{-3}$. The latter value is close to the concentration of interstitial silicon lattice sites ($5 \times 10^{22} \text{ cm}^{-3}$) and so it is proposed, on the basis of this two-center model, that ν_{3HH} sites should be identified with these lattice locations. It is important to note that the concentrations of both inadvertently introduced impurities or lattice defects would be orders of magnitude smaller than 10^{23} cm^{-3} .

We next consider the parameters g_1 and g_2 in more detail. First, the binding energy of a H_2 molecule to an O_i atom determined above must be a weighted average since the molecules adopt two different configurations leading to the peak and shoulder components of the 1075 cm^{-1} absorption.¹⁹ As the two binding energies must be close (to within 10% of ΔE), we increase the first estimate of g_1 by a factor of 2. It follows that g_2 should also be increased by a factor of 2 so that it lies in the range $(1.3-2.6) \times 10^{23} \text{ cm}^{-3}$. This latter value corresponds to the product of the number density of interstitial lattice sites and the number of accessible orientations of the H_2 molecule in each site. If, for example, only

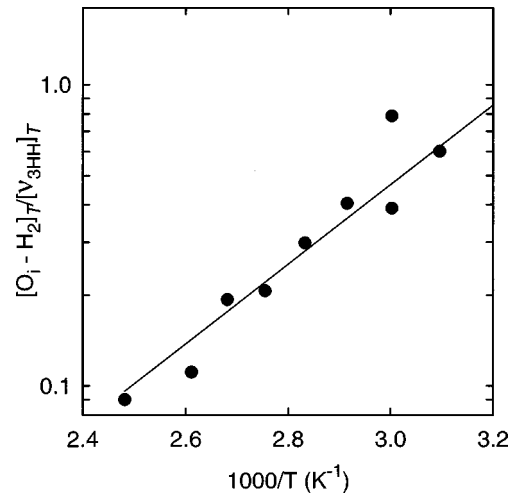


FIG. 5. The ratios of the concentrations of $[O_i-H_2]_T$ to $[\nu_{3HH}]_T$ centers at various anneal temperatures as a function of $1000/T$. The concentrations are normalized with respect to their maximum values (see text).

$\langle 111 \rangle$ alignments occur, this latter number should be set equal to 4 (there are four equivalent $\langle 111 \rangle$ orientations). If all alignments are accessible, namely 4 $\langle 111 \rangle$ directions, 6 $\langle 110 \rangle$ directions, and 3 $\langle 100 \rangle$ directions, this number should be set equal to a maximum value of 13. Accordingly, we infer revised maximum and minimum values for the number density of ν_{3HH} sites of 6×10^{22} and $1 \times 10^{22} \text{ cm}^{-3}$ but it is clear that consideration of the various alignments of the molecule makes only small changes to the final value of g_2 . Therefore, the proposal that the ν_{3HH} line is a mode of isolated infrared-active molecules is unchanged.

We now consider the possible alignments of an isolated molecule that can account for its infrared activity. Molecules aligned along $\langle 100 \rangle$ directions have a zero dipole moment because of their D_{2d} symmetry but alignments along $\langle 110 \rangle$ and $\langle 111 \rangle$ can have nonzero dipole moments because of their lower C_{2v} and C_{3v} symmetries, respectively. Recent *ab initio* theory¹⁶ has indicated that the effective charges for the two alignments are both close to the value of $\eta \sim 0.1e$ obtained experimentally for the ν_{3HH} mode (see above). The two alignments are, however, expected to have different H_2 vibrational frequencies but only one mode is detected for sample temperatures up to 77 K. An assignment to the $\langle 110 \rangle$ direction is favored since the mixed ν_{3HD} mode appears as a single line ($\Delta = 0.2 \text{ cm}^{-1}$), as expected, whereas theory¹⁶ predicts a small splitting (0.2 cm^{-1}) for $\langle 111 \rangle$ orientations (HD is not equivalent to DH). The narrow line width of the ν_{3HH} mode implies that the molecules are not interacting with each other and are not in regions of inhomogeneous strain.

There is no doubt that the IR-active ν_{3HH} mode (3618 cm^{-1}) described here and the modes detected by Raman-scattering measurements (4158 cm^{-1}) (Refs. 11, 13, and 18) both relate to vibrations of hydrogen molecules. An analysis using a two-center statistical model leads to an estimate of the number of available sites for the molecule to form ν_{3HH} centers in the range 10^{22} – 10^{23} cm^{-3} . It is therefore proposed that this center should be identified with isolated interstitial lattice sites. The ν_{3HH} center corresponds to

a particular orientation of the molecule, either $\langle 110 \rangle$ or $\langle 111 \rangle$, and may be compared with the frequencies predicted by density-functional theory, 3100 cm^{-1} (Ref. 15), 3700 cm^{-1} (Ref. 16), and 3400 cm^{-1} (Ref. 17). These calculated frequencies are all significantly smaller than the calculated frequencies for either the free molecule [4000 cm^{-1} (Ref. 15), 4300 cm^{-1} (Ref. 16), and 4100 cm^{-1} (Ref. 17)] or an H_2 molecule in a small passivated void in Si 4300 cm^{-1} (Ref. 16). The lower vibrational frequency of the molecule at an interstitial Si site compared with that of the free molecule is due to interactions between the molecule and the surrounding cage of Si atoms that must occur in order that the molecule acquires a dipole moment. The present experimental study therefore supports the interpretation of Leitch *et al.*¹⁸ that the broad Raman signal at 4158 cm^{-1} ($\Delta = 34 \text{ cm}^{-1}$) relates to hydrogen molecules trapped in voids.

Finally, we recall our previous finding that “hidden hydrogen” was present in as-quenched hydrogenated boron-doped Si.¹⁰ We have now detected the $\nu_{3\text{HH}}$ mode in such boron-doped samples with path lengths of 17 mm. It is clear that this mode could not have been detected in the 1-mm-thick samples used in the earlier study¹⁰ because of the small dipole moment of $\nu_{3\text{HH}}$. The estimated total hydrogen concentration in this thick sample corresponds to the hydrogen solubility at the quench temperature used, implying that so-called “hidden hydrogen” is in the form of isolated interstitial molecules.

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