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Interactions of hydrogen molecules with bond-centered interstitial oxygen and another defect center in silicon

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Infrared spectra obtained from Czochralski (CZ) silicon heated in the range $1100 \leqslant T \leqslant 1300$ °C in H_2, D_2, or mixtures of the two gases, show vibrational absorption at $1075\ \mathrm{cm}^{-1}$ due to perturbed bond-centered interstitial oxygen atoms O_i. Deconvolutions of these absorption profiles imply that the observed perturbations to the O_i atom are due to adjacent defects incorporating two H atoms. This interpretation is confirmed by detection of modes ν_1 ($\nu_{1HH}, \nu_{1HD}, \nu_{1DD}$) with $\nu_{1HH} = 3789\ \mathrm{cm}^{-1}$ and ν_2 ($\nu_{2HH}, \nu_{2HD}, \nu_{2DD}$) with $\nu_{2HH} = 3731\ \mathrm{cm}^{-1}$, that both correlate in strength with that of the $1075\ \mathrm{cm}^{-1}$ absorption. A third set of modes ν_3 ($\nu_{3HH}, \nu_{3HD}, \nu_{3DD}$), with $\nu_{3HH} = 3618\ \mathrm{cm}^{-1}$ detected in heat-treated CZ and float zone silicon and not related to the absorption at $1075\ \mathrm{cm}^{-1}$, must be due to H-H pair defects trapped at an unknown impurity or lattice defect. The frequencies of the ν_{1HD}, ν_{2HD}, and ν_{3HD} modes imply that the three defects are H_2 molecules with weakened bonds and small dipole moments resulting from interactions with either adjacent oxygen atoms (ν_1, ν_2) or a second type of trap (ν_3). Annealing treatments imply that isolated O_i-H_2 complexes can dissociate for $T \geqslant 70$ °C allowing interstitial H_2 molecules to diffuse away but they can be retrapped during a subsequent anneal at $T \leqslant 50$ °C. [S0163-1829(97)00344-5]

I. INTRODUCTION

There is considerable current interest in understanding the behavior of hydrogen impurities in silicon. There have been measurements of both the solubility[1,2] and diffusivity[1,3] of atomic hydrogen as well as observations of pairing of hydrogen with shallow dopants and centers that give rise to deep levels.[4] More recently, infrared (IR) vibrational absorption with a peak at $1075\ \mathrm{cm}^{-1}$ has been observed in Czochralski (CZ) Si that was preheated in H_2 gas at high temperatures ($T > 1000$ °C) and then given a low-temperature anneal at 50–90 °C.[5] This absorption was attributed to a hydrogen atom paired with a bond-centered interstitial oxygen impurity (O_i), i.e., a $^{16}O_i$-H pair. For samples preheated in D_2 gas, the peak of the absorption shifts to $1076.6\ \mathrm{cm}^{-1}$, demonstrating unambiguously that at least one hydrogen atom is incorporated in the defect. The isotopic shift must be due to an anharmonic[6] or a level anticrossing interaction[7] since the mode occurs at a higher frequency for the D complex than for the H complex. These absorption features were not observed in similarly treated float-zone (FZ) samples ($[O_i]$ usually less than $10^{16}\ \mathrm{cm}^{-3}$), suggesting that an O_i impurity was a constituent of the complex.[5] Nevertheless, the O_i atom was not identified directly and all that was demonstrated was that the second atom must have a low mass so that it would give rise to a localized vibrational mode (LVM). Alternative atoms to oxygen could, in principle, have been either carbon or nitrogen. Subsequent heat treatments at $T > 110$ °C, led to a loss of the absorption but it could be retrieved by a further low-temperature anneal (50 °C). There was no discussion concerning the new location of the hydrogen atoms once the proposed O_i-H complexes were lost but heating samples above 250 °C led to an irreversible loss of the $1075\ \mathrm{cm}^{-1}$ absorption.[5]

We now report high-resolution, low-noise IR absorption measurements that significantly advance the understanding of these hydrogen-related complexes. The organization of the paper is as follows: after describing experimental procedures in Sec. II, we demonstrate that the $1075\ \mathrm{cm}^{-1}$ absorption is indeed due to a perturbed bond-centered interstitial $^{16}O_i$ atom (Sec. III A) and concentrations of these centers are estimated in Sec. III B. Deconvolution procedures used to analyze this absorption for samples pretreated in hydrogen, deuterium, or mixtures of the two gases, indicate that O_i atoms form two types of complexes with H-H pair defects (Secs. III C and III D). The associated hydrogen vibrational modes are reported in Sec. III E and their analysis given in Sec. IV demonstrates that the H-H pair defects are H_2 molecules. Other results are also discussed in Sec. IV and our conclusions are summarized briefly in Sec. V.

II. EXPERIMENTAL DETAILS

High-quality as-grown CZ Si samples (with thicknesses of 3, 5, or 17 mm) lightly doped to $5 \times 10^{14}\ \mathrm{cm}^{-3}$ with either boron or phosphorus and with carbon concentrations below the detection limit of $2 \times 10^{15}\ \mathrm{cm}^{-3}$, were heated at a tem-

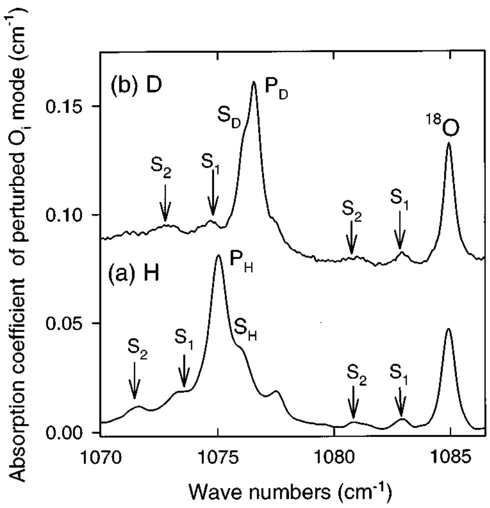

FIG. 1. Infrared absorption spectra showing satellite structure, S_1 and S_2 (due to the bonding of O_i atoms to ^{29}Si and ^{30}Si, respectively) for the LVM's of isolated $^{18}O_i$ atoms and the LVM's of $^{16}O_i$ complexed with (a) hydrogen atoms and (b) deuterium atoms. Note that the principal line of the perturbed oxygen mode is split into two components, a peak (P) and a shoulder (S). The samples were lightly boron-doped CZ Si preheated at 1300 °C in either H_2 or D_2 gas and cooled rapidly to room temperature.

perature in the range $1000 < T < 1300$ °C in H_2, D_2, or mixtures of the two gases at atmospheric pressure. The samples were either cooled rapidly by dropping them into silicone oil at room temperature (procedure designated Q_1) or they were heated in a quartz tube that was subsequently withdrawn rapidly from the furnace and plunged into water (Q_2) while the flow of hydrogen was maintained. Various other samples were treated in the same way, namely, boron-doped CZ Si ($[B]=7\times10^{16}$ cm^{-3}: $[C]<2\times10^{15}$ cm^{-3}), phosphorus-doped CZ Si ($[P]=2\times10^{16}$ cm^{-3}: $[C]<2\times10^{15}$ cm^{-3}) and high-resistivity FZ Si (1000 Ω cm: $[O_i]=3\times10^{15}$ cm^{-3}: $[C]=5\times10^{15}$ cm^{-3}). One of the hydrogenated, lightly doped CZ Si samples was subjected to a series of low-temperature annealing treatments in an oil bath ($50 < T < 260$ °C) or a furnace ($260 < T < 320$ °C) (Sec. III E). IR spectra were obtained with a Bruker IFS 113v interferometer operated at a spectral resolution of 0.1 cm^{-1} and with samples cooled to ~10 K. Scan times were extended for periods of up to 16 h in order to achieve low-noise spectra.

III. INFRARED SPECTRA

A. Vibrational absorption of complexed O_i atoms

Spectra from all our hydrogenated lightly doped (n and p-type) CZ samples show vibrational absorption from a peak (P_H) at 1075.1 cm^{-1} with a shoulder (S_H) at a higher energy of 1075.8 cm^{-1} that is resolved in some samples [Fig. 1(a)]. The unrelated LVM at 1077.5 cm^{-1} is due to isolated $^{18}O_i$ atoms present in their first excited pseudorotational state.[8] The deuterated lightly doped CZ samples show a peak (P_D) at 1076.6 cm^{-1} with an unresolved shoulder (S_D) at a lower energy close to 1076 cm^{-1} [Fig. 1(b)].

Absorption from previously unreported weak satellites (S_1 and S_2) is observed on the low-energy sides of the 1075 and 1076 cm^{-1} LVM's (Fig. 1). This pattern is the same as that found for ^{28}Si-$^{16}O_i$-^{28}Si, ^{28}Si-$^{16}O_i$-^{29}Si, and ^{28}Si-$^{16}O_i$-^{30}Si complexes observed in CZ Si. The relative strengths of the satellites are related to the natural isotopic abundances of silicon, namely, ^{28}Si (92.3%), ^{29}Si (4.7%), and ^{30}Si (3.0%).[8] The LVM at 1084.9 cm^{-1} is due to isolated $^{18}O_i$ atoms (natural abundance 0.2%, ^{16}O abundance =99.76%) and shows corresponding satellites (S_1 and S_2) separated from the main $^{18}O_i$ peak by 1.9 and 3.8 cm^{-1}, the same as the separations for the satellites of the $^{16}O_i$ LVM. The separations of the weak satellites from the LVM (P_H) at 1075.1 cm^{-1} are 1.7 and 3.6 cm^{-1} [Fig. 1(a)] and the corresponding separations from the LVM (P_D) at 1076.6 cm^{-1} are 1.9 and 3.7 cm^{-1} [Fig. 1(b)]. Within the measurement errors, these separations are consistent with those measured for both isolated $^{16}O_i$ and $^{18}O_i$ atoms. The conclusion is that the new lines [Figs. 1(a) and 1(b)] are due to a light impurity located in a bond-centered interstitial site. Since neither carbon or nitrogen is known to occupy such sites, the impurity is identified as an oxygen atom, $^{16}O_i$ perturbed by adjacent H(D) atoms, as originally suggested.[5]

B. Estimates of the complexed oxygen concentrations

We can now make a first estimate of the concentrations of O_i-H complexes that are formed by the quenching procedures. It has been shown previously that the dipole moments per unit displacement (effective charges η) of the vibrational modes for $(^{16}O_i\text{-}V)^0$ (Ref. 9), $(^{16}O_i\text{-}V)^-$ (Ref. 10), $(^{16}O_i\text{-}Si_i)$ (Ref. 11, and see also Ref. 12) and $(^{16}O_i\text{-}Li)$ (Ref. 13) pairs are essentially the same as that of isolated $^{16}O_i$ atoms (and $^{18}O_i$), even though the paired oxygen atoms have significantly lower frequencies. There are therefore reasonable grounds for proposing that the 1075 cm^{-1} LVM will also have the same effective charge. A comparison of the integrated absorption (IA) coefficients for the LVM's of isolated $^{18}O_i$ and $^{16}O_i$-H complexes at liquid-helium temperatures (Fig. 1) allows the concentration of the O_i-H complexes to be determined, since $[^{18}O_i]$ will be equal to $0.02\times[^{16}O_i]$, and $[^{16}O_i]$ is measured to be close to 10^{18} cm^{-3} using a standard calibration (at 300 K).[14] The concentrations of $[O_i\text{-H}]$ so determined were always smaller by a factor of ~2–3 than the solubility of deuterium atoms in Si (at the incorporation temperature employed), measured by secondary ion mass spectrometry (SIMS).[2] Nevertheless, Arrhenius plots (Fig. 2) of $[O_i\text{-H}]$ determined for three pairs of samples preheated at 1100, 1200, and 1300 °C and then cooled either by procedure Q_1 or Q_2 have gradients of 1.8 ± 0.2 eV (Q_1) and 1.6 ± 0.2 eV (Q_2). Within measurement errors, these two values are independent of the cooling procedure and are the same as that determined previously (1.8 eV) for the solubility of hydrogen in silicon heated in $H_2(D_2)$ gas at atmospheric pressure.[2] We shall account for the smaller absolute values of the present hydrogen concentrations by demonstrating that the $^{16}O_i$-H complex incorporates H-H pairs rather than a single hydrogen atom and that additional H-H pair defects are present at sites remote from O_i atoms.

C. Deconvolution of the 1075 cm^{-1} structure into two vibrational modes

The 1075 cm^{-1} structure is superimposed on broad background absorption (Fig. 1) that is of unknown origin and is

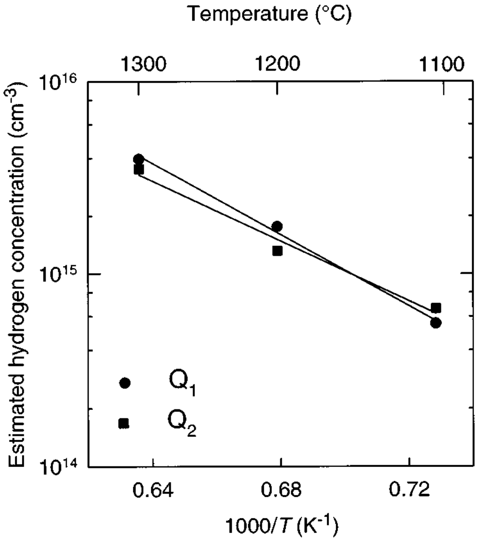

FIG. 2. Arrhenius plots of the estimated hydrogen concentrations as a function of the preanneal hydrogenation temperature for samples cooled rapidly using either procedure Q_1 or Q_2 (see text). The least squares fits (full lines) yield $[\mathrm{O}_i\text{-H}]=3\times10^{21}$ exp$(-1.8\ \mathrm{eV}/kT)$ cm^{-3} (Q_1) and $[\mathrm{O}_i\text{-H}]=3\times10^{20}$ exp$(-1.6\ \mathrm{eV}/kT)$ cm^{-3} (Q_2), with the previous assumption (Ref. 5) that the 1075 cm^{-1} absorption is due to an O_i atom complexed with only one H atom.

unrelated to the presence of either hydrogen or deuterium since it is present in as-grown samples. This broad absorption was fitted to a Gaussian profile centered at 1072.6 cm^{-1} with a full width at half maximum, $\Delta=5.8$ cm^{-1} and a peak absorption coefficient of 0.015 cm^{-1} that was subtracted from all absorption profiles prior to their further analysis. The relative strengths of the peak (P_H) to the shoulder (S_H) were fitted by two Voigt profiles (80% Lorentzian, 20% Gaussian) with equal values of $\Delta\sim0.9$ cm^{-1}, a separation of 1.1 cm^{-1} and $P_\mathrm{H}:S_\mathrm{H}\sim3:1$ [Fig. 3(a)]. For the deuterated sample [Fig. 3(b)], the profile was again fitted by two Voigt profiles (80% Lorentzian, 20% Gaussian) but with $\Delta=0.6$ cm^{-1}, a separation of 0.5 cm^{-1} and $P_\mathrm{D}:S_\mathrm{D}\sim2:1$: the reason for the different linewidths for the H and D components is not known. These deconvolutions lead to the conclusion that the oxygen vibrational mode is perturbed by two types of hydrogen (deuterium) center each incorporating one or more H atoms.

D. Perturbations of the O_i atoms by H-H pairs, H-D and D-D pairs

The IR absorption spectra of CZ Si samples annealed in mixtures of H_2 and D_2 gases with various relative partial pressures are now analyzed. The spectrum close to 1075 cm^{-1} is shown in Fig. 4(a) for a sample heated in a 50:50 mixture of H:D. A relatively weak line at 1075.1 cm^{-1} coincides with the energy of the main line detected in hydrogenated samples [Fig. 4(b)] but the strong peak observed at 1076.1 cm^{-1} is significantly lower in energy than the main peak (1076.6 cm^{-1}) detected in deuterated samples [Fig. 4(c)]. Because of this shift, it is impossible to synthesize the overall structure in Fig. 4(a) by combining the known H and D spectra in equal proportions. Neither did the simple addi-

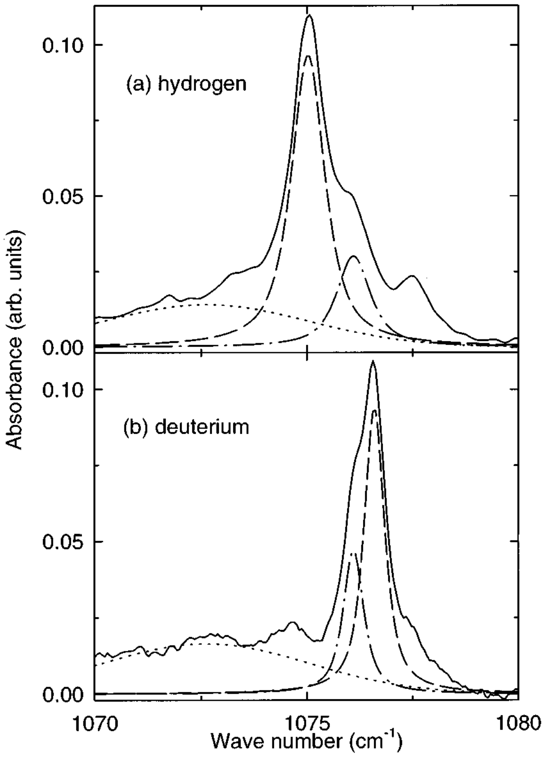

FIG. 3. Absorption profiles at 1075 and 1076 cm^{-1} for O_i atoms complexed with (a) hydrogen atoms and (b) deuterium atoms and their deconvolutions into two Voigt profiles after subtraction of a broad background absorption (dotted lines) unrelated to hydrogen (see text). The two components (broken lines) have relative intensities of 3:1 and 1:2 for the hydrogen—and deuterium—related spectra, respectively. The feature at 1077.5 cm^{-1} is due to absorption from $^{18}\mathrm{O}_i$ atoms in their first excited pseudorotational state (Ref. 8).

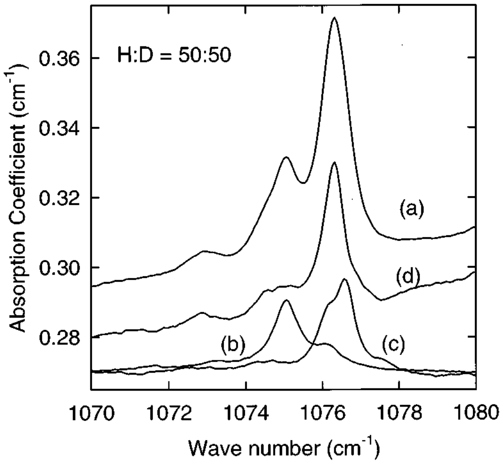

FIG. 4. Measured IR absorption spectra of samples heat treated in (a) a 50:50 H_2:D_2 mixture, (b) H_2 gas, and (c) D_2 gas. All three spectra were normalized to a common value of IA over the spectral range 1072–1077 cm^{-1} and are plotted in the ratios 100%, 25%, and 25%, respectively. The sum of spectra (b) and (c) is subtracted from spectrum (a) to reveal the contribution to the measured spectrum from O_i atoms complexed with HD pairs (d). See text for further details.

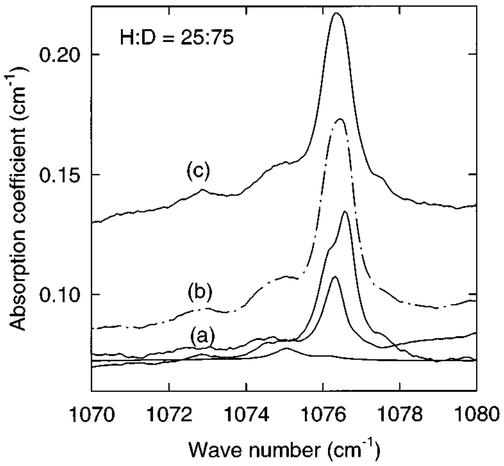

FIG. 5. Synthesis of the spectrum to be expected from a sample preheated in a 25:75 H_2:D_2 gas mixture using the measured contributions from H and D spectra (see Figs. 1 and 3) together with the derived spectrum for O_i atoms complexed with HD pairs [Fig. 4(d)]. These three contributions are added with strength ratios of 1/16, 9/16, and 6/16, respectively (a) to give the synthesized structure (b). This composite spectrum is indistinguishable from the measured spectrum (c).

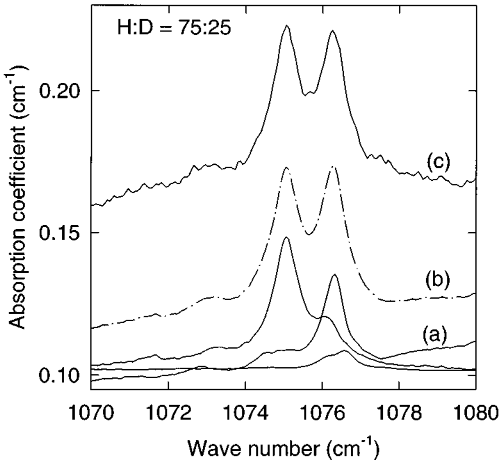

FIG. 6. Synthesis of the spectrum to be expected from a sample preheated in a 75:25 H_2:D_2 gas mixture using the measured contributions from H and D spectra (see Figs. 1 and 3) together with the derived spectrum for O_i atoms complexed with HD pairs [Fig. 4(d)]. These three contributions are added with strength ratios of 9/16, 1/16, and 6/16, respectively (a) to give the synthesized structure (b). The composite spectrum is again in agreement with the measured spectrum (c).

tion of H and D spectra in the appropriate proportions lead to acceptable profiles for the measured spectra of samples preheated in 25:75 and 75:25 H:D mixtures. It is concluded that the perturbation of the O_i vibrational mode cannot be due to the presence of a *single* H (D) atom.

The possibility that the O_i atom is perturbed by a pair of H atoms was investigated next. For the 50:50 mixed sample, there would then be H-H, H-D, and D-D components with relative strengths of 25:50:25. The H-D absorption profile [Fig. 4(d)] was deduced from the 50:50 mixed spectrum by subtracting 25% of each of the H and D spectra (using normalized values of their IA coefficients) in the spectral range 1072–1077 cm^{-1} (Fig. 4). The extracted profile [Fig. 4(d)] is essentially a single line at 1076.3 cm^{-1} with a linewidth, $\Delta = 0.7$ cm^{-1}: this procedure is not sufficiently accurate to determine whether or not there is a shoulder associated with this line (cf. Secs. III C and IV). The H-D profile was then used to synthesize spectra from samples annealed in 25:75 and 75:25 H:D mixtures (Figs. 5 and 6). The close agreement between the synthesized and the measured spectra indicates that the 1075 cm^{-1} structure is due to an O_i atom adjacent to a pair of H atoms.

The earlier analysis in Sec. III C demonstrated the existence of two components to the 1075 and 1076 cm^{-1} structures observed in hydrogenated and deuterated samples respectively. We now present direct evidence for the existence of two O_i-(H-H) complexes with slightly different structures.

E. Direct observation of LVMs due to H-H, H-D, and D-D pairs

IR spectra from the hydrogenated lightly doped CZ samples (thickness $\geqslant 5$ mm) reveal the presence of three very weak but sharp ($\Delta = 0.1$–0.2 cm^{-1}) lines $\nu_{1\mathrm{HH}}$, $\nu_{2\mathrm{HH}}$, and $\nu_{3\mathrm{HH}}$ [Table I, Fig. 7(a)] in the spectral region 3600–3800 cm^{-1} (where there is a high spectral density of absorption lines from atmospheric water). In deuterated samples, a corresponding set of three lines $\nu_{1\mathrm{DD}}$, $\nu_{2\mathrm{DD}}$, and $\nu_{3\mathrm{DD}}$, is also detected. The reason why the $\nu_{2\mathrm{DD}}$ line at ~ 2716 cm^{-1} always occurs as a close doublet with the same relative strengths [Fig. 7(a)] and a separation of 1.1 cm^{-1} is not understood but it should be noted that the $\nu_{2\mathrm{HH}}$ line does not show corresponding structure. For samples heated in a 50:50 H:D mixture, the $\nu_{1\mathrm{HH}}$, $\nu_{2\mathrm{HH}}$, $\nu_{3\mathrm{HH}}$, and $\nu_{1\mathrm{DD}}$, $\nu_{2\mathrm{DD}}$, $\nu_{3\mathrm{DD}}$ modes are detected but no additional structure close in frequency to these modes is found. However, a further three lines $\nu_{1\mathrm{HD}}$, $\nu_{2\mathrm{HD}}$, and $\nu_{3\mathrm{HD}}$ are observed with frequencies essentially midway between the ν_{HH} and ν_{DD} modes [Table I, Fig. 7(b)]. We shall show that these observations demonstrate the presence of three types of defect center (ν_1, ν_2, ν_3), each incorporating two hydrogen atoms that are bonded to each other.

Values of IA (H-H) for lines $\nu_{1\mathrm{HH}}$ and $\nu_{2\mathrm{HH}}$ plotted against values of IA (1075 cm^{-1}) (Fig. 8), for a number of hydrogenated samples, together with data from one of these samples following anneals at various temperatures (50–320 °C), demonstrate clear correlations for the two modes. It follows that the $\nu_{1\mathrm{HH}}$ and $\nu_{2\mathrm{HH}}$ modes both arise from H-H pairs located at sites adjacent to O_i atoms. Since the ratio IA $(\nu_{1\mathrm{HH}})$/IA $(\nu_{2\mathrm{HH}})$ is always the same (Fig. 8), the relative concentrations of the two types of O_i-(H-H) complexes are not dependent on the particular sample examined. This conclusion is consistent with the deconvolution of the 1075 cm^{-1} absorption (Secs. III C and III D) into two components (P and S) that always have the same relative strengths. It is not clear, however, whether ν_1 corresponds to the peak and ν_2 to the shoulder or vice versa. Our measurements show that the strength of the lowest-energy mode $\nu_{3\mathrm{HH}}$ does not correlate with the strength of the 1075 cm^{-1} absorption (Fig. 9). Even though there is a large scatter of data points, there does appear to be a weak anticorrelation with the perturbed oxygen mode. It follows that the $\nu_{3\mathrm{HH}}$ line

TABLE I. Energies (cm^{-1}) of the IR vibrational modes (ν_1, ν_2, and ν_3) of H_2, D_2, and HD pair defects observed in Si and the observed Raman transitions of H_2, D_2, and HD molecules in different environments. The frequency ratios are also given.

Defect	ν_{HH} (cm^{-1})	$\nu_{\mathrm{HH}}/\nu_{\mathrm{HD}}$	ν_{HD} (cm^{-1})	$\nu_{\mathrm{HD}}/\nu_{\mathrm{DD}}$	ν_{DD} (cm^{-1})	$\nu_{\mathrm{HH}}/\nu_{\mathrm{DD}}$	$\nu_{\mathrm{HH}}/\nu_{\mathrm{DD}}$[e] (corrected)
ν_1 (Si)	3788.9	1.147	3304.3	1.191	2775.4	1.365	1.382
ν_2 (Si)	3730.8	1.136	3285.3	1.210	2716.0	1.374	1.391
ν_3 (Si)	3618.3	1.108	3264.8	1.235	2642.5	1.369	1.387
H_2 (Si)[a]	4158				2990	1.391	1.406
H_2 (Si)[b]	4157	1.145	3629	1.213	2991	1.390	1.405
H_2 (GaAs)[c]	3934.1	1.141	3446.5	1.212	2842.6	1.384	1.400
H_2 (gas)[c]	4161.1	1.146	3632.1	1.213	2993.6	1.390	1.405
H_2O (gas)[d]	3756	1.013	3707	1.330	2788	1.347	1.364
	3657	1.341	2727	1.021	2671	1.369	1.386

[a] References 16 and 17. The Raman frequency for the HD molecule was not measured.

[b] Reference 18.

[c] Reference 19.

[d] Reference 20.

[e] Values corrected for anharmonicity (see text).

should be attributed to a mode of a H-H center located at a site remote from an O_i atom. This proposal is consistent with the detection of the $\nu_{3\mathrm{HH}}$, $\nu_{3\mathrm{HD}}$, and $\nu_{3\mathrm{DD}}$ modes in a FZ Si sample $[O_i]=2\times10^{15}\ \mathrm{cm}^{-3}$ that had been heated in a H_2:D_2 50:50 mixture. As expected, the ν_1 and ν_2 modes were not detected in this sample nor in a second hydrogenated FZ sample that also showed the $\nu_{3\mathrm{HH}}$ mode.

Preliminary annealing measurements carried out on one long-pathlength hydrogenated CZ sample revealed increases in the strength of the $\nu_{3\mathrm{HH}}$ mode and reductions in the strengths of the correlated $\nu_{1\mathrm{HH}}$, $\nu_{2\mathrm{HH}}$ and $1075\ \mathrm{cm}^{-1}$ absorption from 70 to 110 °C. At higher temperatures (110–320 °C), there was no further increase in the strength of the $\nu_{3\mathrm{HH}}$ mode even though the absorption strengths of the three correlated modes ($\nu_{1\mathrm{HH}}$, $\nu_{2\mathrm{HH}}$, and $1075\ \mathrm{cm}^{-1}$ absorption) continued to decrease to below 10% of their initial values for $T>150$ °C. These observations indicate that there is a net loss of detectable hydrogen. Reheating this annealed sample at 50 °C (see Ref. 5) led to increases in the strengths of the three correlated modes, but only to 50% of their initial values, and a reduction in the strength of the $\nu_{3\mathrm{HH}}$ mode by a factor of 2. Such annealing behavior is similar but not in complete agreement with that reported previously for the $1075\ \mathrm{cm}^{-1}$ absorption.[5]

To investigate the possibility of hole or electron trapping by the H-H pair defects, measurements were made on long-pathlength hydrogenated CZ Si samples doped with either $[\mathrm{B}]=7\times10^{16}\ \mathrm{cm}^{-3}$ or $[\mathrm{P}]=2\times10^{16}\ \mathrm{cm}^{-3}$. The $\nu_{3\mathrm{HH}}$ mode was the only high-frequency mode observed in these

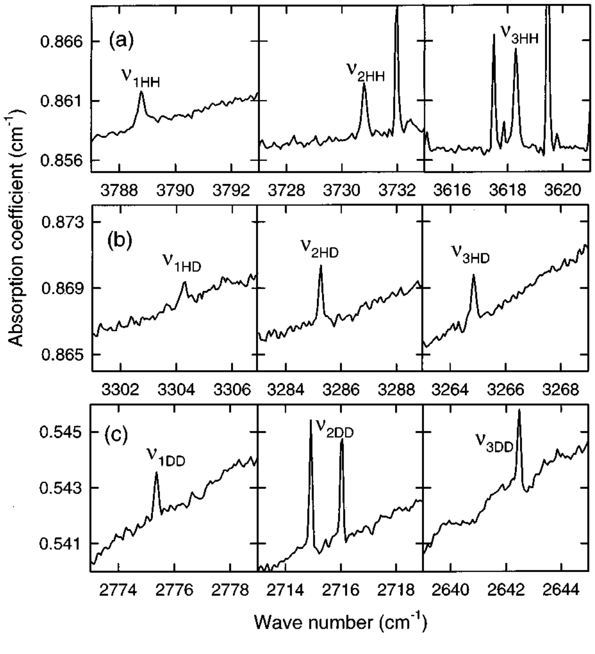

FIG. 7. High-resolution IR spectra showing the high-frequency hydrogen stretch modes from H-H pair defects (ν_1, ν_2, and ν_3). The additional lines in (a) are due to absorption from atmospheric water molecules. It should be noted that there is splitting of the line $\nu_{2\mathrm{DD}}$ into two components.

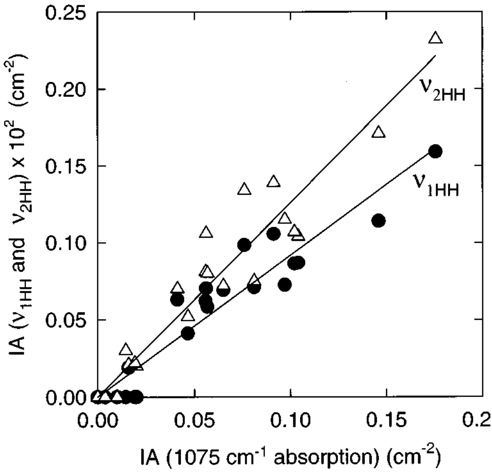

FIG. 8. Graph showing the correlation of the IA coefficients of the two high-frequency hydrogen stretch modes, $\nu_{1\mathrm{HH}}$ (full circles) and $\nu_{2\mathrm{HH}}$ (open triangles), with the integrated absorption coefficient of the $1075\ \mathrm{cm}^{-1}$ profile due to vibrations of O_i atoms complexed with hydrogen.

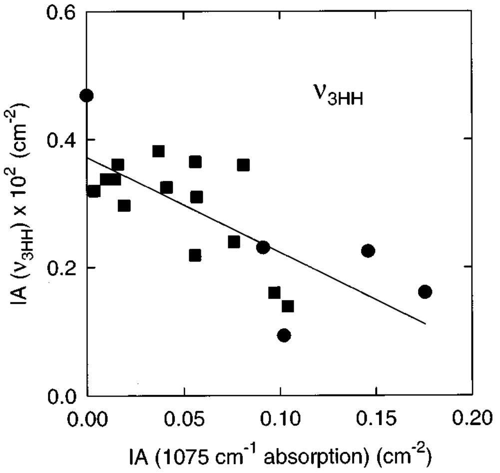

FIG. 9. Graph showing the weak anticorrelation of the integrated absorption (IA) coefficients of the high-frequency hydrogen stretch mode ν_{3HH} with the integrated absorption coefficient of the 1075 cm^{-1} profile due to vibrations of O_i atoms complexed with hydrogen. ■, data for the annealed sample; ●, data for various unannealed samples.

samples, with the implication that O_i-(H-H) centers were not present. Measurements of the 1075 cm^{-1} absorption could not be made because the samples were opaque in this spectral region due to intense electronic absorption associated with the dopants. However, measurements on similar material but with thicknesses of only 2 mm confirmed that the 1075 cm^{-1} absorption was absent. This absence, when there is detection of the ν_{3HH} mode, provides further evidence that the ν_3 defect does not incorporate an O_i atom. The lattice locations of the majority of hydrogen atoms in the n-type material are unknown since we have found no evidence for the formation of H-P pairs, in agreement with other observations.[15] On the other hand, a substantial concentration of H atoms becomes paired with boron in p-type material when the dopant concentration is increased up to 10^{17} cm^{-3}.[2,15] In summary, there was no evidence that the H-H pair defects (ν_3) acquired a static charge as a result of the doping. It is not possible to make any corresponding comments relating to the ν_1 and ν_2 modes since high doping levels inhibit the formation of O_i-(H-H) complexes.

IV. DISCUSSION

The important result of this work is the observation of high-frequency vibrational modes of H-H, D-D, and H-D pair defects (Table I). We now consider possible models for the structure of these defects.

The vibrational frequencies associated with the H-H centers (Table I) occur in the spectral region where O-H stretch modes give strong infrared absorption. An assignment of the pair defect to an H_2O molecule was, therefore, considered but we now show that this proposal is untenable. The gaseous H_2O molecule has three infrared-active vibrational modes[20] at 3756, 3652, and 1595 cm^{-1} and so, in principle, the two high-frequency antisymmetric and symmetric modes of the two H atoms could correspond to the correlated ν_{1HH} and ν_{2HH} modes (Table I). However, no absorption was detected from a third mode that should occur close to 1595 cm^{-1}. The antisymmetric and symmetric modes for a free D_2O molecule[20] at 2789 and 2666 cm^{-1} respectively, are also close to our ν_{1DD} and ν_{2DD} frequencies but again we do not detect a third mode close to 1179 cm^{-1}. The crucial point is that, for the HDO molecule,[20] the antisymmetric mode at 3707 cm^{-1} shows only a small shift from the corresponding mode of H_2O while the symmetric HDO mode at 2727 cm^{-1} is close to the corresponding mode of D_2O (Table I). These shifts are incompatible with the present measurements for ν_{1HD} and ν_{2HD} (Table I). We therefore reject the assignment of the H-H pair defect to an H_2O molecule.

The presence of ν_{HD} modes with frequencies essentially midway between those of ν_{HH} and ν_{DD} implies unambiguously, by comparison with data for H_2 molecules (Table I), that for each center (ν_1, ν_2, and ν_3), the two atoms must be bonded directly to each other as a molecule. The frequency ratios, ν_{HH}/ν_{DD}, for the three centers all have values close to 1.37 (Table I). This factor is significantly smaller than $\sqrt{2}$ but it increases to $\sim$1.39 if the ν_{HH} and ν_{DD} frequencies are increased by 150 and 75 cm^{-1}, respectively, to take account of the anharmonicity (see, for example, Refs. 21 and 22). These corrections applied to previously reported frequencies (Raman) of hydrogen molecules[16–18] lead to higher values of $\nu_{HH}/\nu_{DD}\sim 1.41$, that are close to $\sqrt{2}$ (Table I). The smaller corrected ratios for the ν_1, ν_2, and ν_3 centers imply that the trapped hydrogen molecules interact with adjacent impurities that also have associated displacements for the H-H stretch mode.

Since the strengths of the two sets of modes, ν_1 and ν_2, are correlated (Fig. 8), there is the possibility that *two* H_2 molecules are complexed with one O_i atom (4 H atoms in the complex). The interactions between pairs of adjacent molecules would lead to coupled vibrational modes so that structure comprising several adjacent lines would be expected in samples containing a mixture of H and D atoms due to the large number of H and D combinations. No such structure was observed. In addition, the probability that two H_2 molecules are captured by a *common* interstitial oxygen atom is negligible on a statistical basis.

A second possibility is that a single H_2 molecule trapped by an O_i atom may occupy one of two different local sites so that the resulting O_i-H_2 complexes have different configurations and vibrational frequencies. As well as accounting for both the ν_1 and ν_2 modes, this model would also explain the presence of two components (P and S, Sec. III C) to the 1075 cm^{-1} oxygen mode in both hydrogenated and deuterated samples. Since the ratio of the strengths, peak: shoulder (P:S), of the 1075 cm^{-1} oxygen mode is always 3:1 for samples containing 100% hydrogen and 2:1 for samples containing 100% deuterium, it would have to be concluded that an equilibrium distribution of the H_2 molecules between the two lattice locations occurs.

A third possibility is that again only one H_2 molecule is trapped at an O_i atom but that the two components (P and S) of the perturbed oxygen mode occur because the H_2 molecule can be present in either an *ortho* or a *para* state.[23] The observed ratios of the strengths, P:S, correspond to the expected concentrations of the two species, namely, 3:1 for H_2 molecules and 1:2 for D_2 molecules (see, for example, Ref.

19). The implication would be that the sharp ($\Delta = 0.1 - 0.2\ \mathrm{cm}^{-1}$) ν_1 and ν_2 modes correspond to the vibrations of *ortho*- and para- H_2 molecules, respectively. However, the frequency shift of $\sim 60\ \mathrm{cm}^{-1}$ between $\nu_{1\mathrm{HH}}$ and $\nu_{2\mathrm{HH}}$ should be compared with the much smaller value of $\sim 8\ \mathrm{cm}^{-1}$ observed for the separation of the H_2 (and D_2) vibrational modes of hydrogen molecules in GaAs.[19] It seems certain that trapped molecules would have impeded rotation at low temperatures, and so assigning them to *ortho* and *para* states may not be valid.

The arguments presented above lead us to conclude that only one H_2 molecule is trapped adjacent to an O_i atom but there are two possible atomic arrangements for the defect complex. Both configurations of the molecule must be such that they acquire a dipole moment in order to explain the IR absorption from the ν_1 and ν_2 modes. It is proposed that there is a redistribution of electron density around the two H atoms as a result of an internal electric field. The O_i atom is electronegative and calculations have indicated that, for the isolated impurity, there is a transfer of electron density of $1.2e$ primarily from its two nearest-neighbor silicon atoms.[24] In the presence of an adjacent H_2 molecule, there will be a further local redistribution of the electron density, some of which will be derived from the H_2 bond. A resulting reduction in the electron density of the H-H bond would lead to a reduction in the H_2 vibrational frequency. As the frequency of the ν_1 mode is higher than that of ν_2, it is implied that there is a smaller O_i-H_2 interaction for the former mode. By contrast, isolated molecules are expected to occupy interstitial sites with tetrahedral symmetry since this is the lowest-energy configuration, according to theory.[25] Molecules in these sites do not have a dipole moment but are Raman active and should be detectable if present in a high concentration.[16–18]

The mode labeled ν_3 is also due to a H_2 molecule that must be trapped by an impurity other than oxygen, or by a lattice defect. Since the frequency of ν_3 is significantly lower than those of ν_1 and ν_2, it is implied that the H_2 bond is weaker due to a stronger local interaction between the impurity/defect and molecule. It was also implied that during annealing (Sec. III E) there was a transfer of hydrogen molecules from O_i atoms to this second trap. It follows that, during this diffusion process, the H_2 molecules must have occupied interstitial sites remote from either O_i atoms or the second trap. At room temperature, the rate of diffusion could be sufficiently low to allow molecules to be trapped in such intermediate sites. The implied net loss of H_2 molecules would thereby be explained since molecules in these sites would have no dipole moment. Further annealing studies are required to clarify the trapping and detrapping processes.

The data shown in Figs. 8 and 9 allow us to deduce values for the effective charges η of the two correlated high-frequency H_2 modes, with the continued assumption that the effective charge of the paired O_i atom is equal to that of an isolated O_i atom ($\eta = 3.5e$).[26] It should be recalled that the absorption of a mode is proportional to η^2/μ,[27] where μ is the reduced mass of the oscillator (for a directly bonded H-H pair it is necessary to take $\mu = 0.5$ amu). We shall first consider an assignment of $\nu_{1\mathrm{HH}}$ to the H_2 mode of the O_i-H_2 complex that gives rise to the peak (P) in the absorption profile of the paired O_i mode: $\nu_{2\mathrm{HH}}$ is then assigned to the complex giving rise to the shoulder (S) of the O_i mode (Fig. 3). We then obtain values of $\eta(\nu_{1\mathrm{HH}}) = 0.07e$ and $\eta(\nu_{2\mathrm{HH}}) = 0.14e$ from the gradients of the lines given in Figs. 8 and 9. The alternative assignments of the H_2 modes ($\nu_{1\mathrm{HH}}$ and $\nu_{2\mathrm{HH}}$) to the S and P components of the O_i mode lead to $\eta(\nu_{1\mathrm{HH}}) = 0.12e$ and $\eta(\nu_{2\mathrm{HH}}) = 0.08e$. Similar analyses were made for the strengths of the modes of a deuterated sample [Fig. 7(c)]. By associating $\nu_{1\mathrm{DD}}$ and $\nu_{2\mathrm{DD}}$ (doublet) with the D_2 modes of the peak and shoulder of the O_i-D_2 absorption, respectively, we determined $\eta(\nu_{1\mathrm{DD}}) = 0.06e$ and $\eta(\nu_{2\mathrm{DD}}) = 0.17e$. The alternative assignments yielded $\eta(\nu_{1\mathrm{DD}}) = 0.09e$ and $\eta(\nu_{2\mathrm{DD}}) = 0.12e$. Greater overall consistency for the estimated values of the effective charges of the H_2 and D_2 vibrational modes is obtained when ν_1 is attributed to the O_i-H_2 (-D_2) centers that give rise to the peaks (P_H and P_D in Fig. 1) in the O_i absorption profile and ν_2 to the shoulders of the profiles (S_H and S_D). There is further support for these assignments since ν_2 has a lower frequency than ν_1, implying that the H_2 molecules incorporated in the ν_2 defects interact more strongly with the adjacent O_i atom. It follows that the ν_2 dipole moment would be expected to be greater than that of the ν_1 mode.

We can now amend the estimates of the total hydrogen content of the present as-quenched samples and compare these modified values with previous estimates of the hydrogen solubility as a function of the temperature of the preheat treatment in H_2 gas.[2] First, the values of the ordinate in Fig. 3 should be multiplied by a factor of 2 to account for the presence of two H atoms in each center giving absorption at $1075\ \mathrm{cm}^{-1}$. Second, a further contribution must be added to allow for the hydrogen present as molecules trapped by defects remote from O_i atoms (ν_3 defects). Assuming that the effective charge for the $\nu_{3\mathrm{HH}}$ mode is $\eta \sim 0.1e$, these additional concentrations are close to 1.5×10^{15} and $6 \times 10^{14}\ \mathrm{cm}^{-3}$ for preheat treatment temperatures of 1300 and 1200 °C, respectively. Absorption from the ν_3 modes is below the detection limit for samples pretreated at 1100 °C. Thus the estimated hydrogen solubilities of 1×10^{16} (1300 °C) and $4 \times 10^{15}\ \mathrm{cm}^{-3}$ (1200 °C) are in good agreement with the values determined by SIMS measurements.[2]

Since hydrogen is present primarily as H_2 molecules in as-quenched, essentially undoped samples, it is possible that enhancements in the rate of O_i diffusion[28] may be due to a catalytic reaction with H_2 molecules rather than diffusing H atoms, as assumed previously. We have now shown from measurements of the relaxation of stress-induced dichroism that enhanced oxygen diffusion occurs down to at least 225 °C and at the same rate for both hydrogenated and deuterated samples.[29] This temperature lies below the maximum value used in our preliminary annealing studies (Sec. III E) where we demonstrated that most of the hydrogen is present as molecules that can be trapped and detrapped by O_i atoms. For a catalytic process, the parameter that controls the degree of enhancement of the oxygen diffusion is the product of the diffusion coefficient of the catalytic species and its concentration. There is no doubt that the diffusion coefficient of H atoms[1,3] is orders of magnitude greater than that of H_2 molecules. Extrapolation of high-temperature solubility data[1,2] $\{[H_S] = 9.1 \times 10^{21} \exp(-1.8\ \mathrm{eV}/kT)\ \mathrm{cm}^{-3}\}$ derived from in diffusion from H_2 gas, implies a very low concentration of only $\sim 10^4$ cm^{-3} H atoms at $T \sim 225$ °C. However, this estimated concentration may be far too low because it relates to the equilibrium between a hydrogen gas phase and atomic hydrogen in solution. During our low-temperature anneals, there is no hydrogen atmosphere and dissolved H atoms would be in equilibrium with hydrogen molecules or larger clusters in the crystal. It follows that $[H_S]$ is unknown. On the other hand, we have demonstrated that the concentration of molecules is $\sim 5 \times 10^{15}$ cm^{-3} and that they diffuse at $T \geqslant 100$ °C. We conclude that there is insufficient information to distinguish the two catalytic processes.

V. CONCLUSION

There is a consensus that the first step of aggregation of hydrogen atoms in silicon is the formation of H_2 molecules.[2,4,5] The ν_1, ν_2, and ν_3 modes imply that molecular hydrogen is formed predominately in as-quenched, undoped silicon but the molecules are trapped at sites adjacent to O_i atoms in CZ silicon and at a second type of trap that is either an unknown impurity or a lattice defect. Trapping is inferred because, first, the H_2 vibrational frequencies (ν_1, ν_2, and ν_3) are significantly lower than the Raman frequencies for the free molecule (4161 cm^{-1}),[23] for hydrogen molecules assumed to be present as isolated pairs in the silicon lattice (4158 cm^{-1}),[16–18] and for hydrogen molecules in GaAs (3926 cm^{-1}).[19] Secondly, the ν_1, ν_2, and ν_3 centers must have dipole moments to account for their IR activity. Nevertheless, the effective charges measured in the present work are small ($\eta \sim 0.1e$) so that it is feasible for them to arise as a result of local internal electric fields.

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