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# Microscopic structure of a $\text{VH}_4$ center trapped by C in Si

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## Abstract

The Si materials typically used to fabricate solar cells often contain high concentrations of carbon and hydrogen impurities. One of the more thermally stable defects in Si that contains both C and H gives rise to a Si-H vibrational line at  $2184.3 \text{ cm}^{-1}$ . We show that this center also gives rise to additional weak Si-H and C-H lines at  $2214.4$  and  $2826.9 \text{ cm}^{-1}$  (4.2 K). When D is partially substituted for H, rich isotopic splittings of these IR lines are produced. An analysis of these data reveals that the  $2184.3$ ,  $2214.4$ , and  $2826.9 \text{ cm}^{-1}$  lines are due to a  $\text{VH}_4$  defect bound to a substitutional C impurity, i.e., a  $\text{VH}_3\text{-HC}$  center.

## I. Introduction

Hydrogen is commonly introduced into Si solar cells to passivate defects in the Si bulk and improve solar-cell performance.<sup>1-5</sup> When H is introduced into multi-crystalline Si (mc-Si) with a high carbon content that is often used to fabricate solar cells, the dominant defects seen by IR spectroscopy have hydrogen in configurations in which H is trapped by C.<sup>6</sup> These C-H centers provide a reservoir of H and play a role similar to that of H<sub>2</sub> molecules in high-purity Si.

One of the more thermally stable defects found in Si that contains both C and H is a center with a vibrational line at 2183.4 cm<sup>-1</sup>. While this vibrational line has been observed previously,<sup>6,7</sup> it has not been assigned to a specific defect structure. In the present paper, vibrational spectroscopy and theory show unambiguously that the 2183.4 cm<sup>-1</sup> line is due to a VH<sub>4</sub> center trapped by a carbon impurity in Si.

Previous results for the defects that are formed by C and H in single-crystal Si provide a foundation for our studies.<sup>8-12</sup> A defect structure known as H<sub>2</sub>\* that contains one H atom at a bond-centered site (H<sub>bc</sub>) and a second H atom at an antibonding site (H<sub>ab</sub>), along the same trigonal axis, can be trapped by a substitutional C impurity to form H<sub>2</sub>\*(C) defects.<sup>8-11</sup> The vibrational properties of the two possible H<sub>2</sub>\*(C) configurations have been studied, and defect structures have been proposed (see Fig. 1). A Si-H vibrational mode at 2210 cm<sup>-1</sup> and a C-H mode at 2688 cm<sup>-1</sup> have been assigned to the SiH<sub>bc</sub>-CH<sub>ab</sub> structure.<sup>6,10,11</sup> A Si-H vibrational mode at 1922 cm<sup>-1</sup> and a C-H mode at 2752 cm<sup>-1</sup> have been assigned to the CH<sub>bc</sub>-SiH<sub>ab</sub> structure.<sup>9-11</sup>

In other experiments, electron irradiation damage was used to produce pairs of nearest-neighbor substitutional C atoms. When H interacts with these C<sub>s</sub>-C<sub>s</sub> pairs, a (CH)<sub>2</sub> defect is formed with a CH-HC structure.<sup>12</sup> The (CH)<sub>2</sub> center has a C-H mode at 2967 cm<sup>-1</sup> that is also shown in Fig. 1. It has been found

that for Si with a C concentration  $[C] > 5 \times 10^{17} \text{ cm}^{-3}$ , a substantial concentration of substitutional C pairs is formed in the absence of radiation damage and that these C pairs provide a thermally stable trap for H.<sup>6</sup>

The implantation of protons into Si produces a number of different centers in which H decorates the dangling bonds of vacancy centers that were introduced by the bombarding protons.<sup>13</sup> Similar defects are produced by the electron irradiation of Si that contains H.<sup>14,15</sup> Of particular interest here is a  $\text{VH}_4$  center in which H atoms terminate the four dangling bonds of a Si vacancy. The  $\text{VH}_4$  defect has a well-known vibrational line<sup>13</sup> at  $2223 \text{ cm}^{-1}$  (4.2 K) that can also be produced in hydrogenated Si by thermal annealing without any radiation damage.<sup>6,7,16</sup> The partial substitution of D for H produces an isotopic structure in the vibrational spectrum of  $\text{VH}_4$  that reveals its composition and symmetry.<sup>13,16</sup> Similarly, in this paper the partial substitution of D for H in Si containing a high concentration of C is shown to give a rich isotopic structure that helps us to determine the microscopic structure of the defect giving rise to the  $2183.4 \text{ cm}^{-1}$  line.

## II. Methods

### A. Experiment

Si samples containing an especially high concentration of carbon impurities were chosen for our experiments. These samples were cut from bulk, cast-Si material to have dimensions of approximately  $8 \times 6 \times 10 \text{ mm}^3$  and were multicrystalline with grain sizes from a few millimeters to one centimeter.

In order to investigate the interaction of hydrogen with C in mc-Si, samples were annealed at  $1250^\circ\text{C}$  in sealed ampoules containing  $\text{H}_2$  gas or mixtures of  $\text{H}_2$  and  $\text{D}_2$  (2/3 atm at room temperature) followed by

a rapid quench in water to room temperature.<sup>6,17</sup> Any subsequent anneals were performed in a conventional tube furnace under flowing He. These anneals were also terminated by a rapid quench.

IR spectra were measured with a Bomem DA3 Fourier transform IR spectrometer. An InSb detector (77K) was used for measurements of H-stretching modes. A Si bolometer (4.2K) was used to characterize the concentration of carbon. For IR measurements of H stretching modes, samples were cooled to near 4.2K with a Helitran, continuous-flow cryostat.

To characterize the concentration of carbon, the IR line at  $607\text{ cm}^{-1}$  assigned to substitutional C was measured at room temperature.<sup>18</sup> The mc-Si samples used in the experiments reported here had a carbon concentration of  $[C] = 8.8 \times 10^{17}\text{ cm}^{-3}$ . Reference samples for our infrared spectra were cut from Si grown by the floating zone method and had a carbon concentration of  $[C] = 0.2 \times 10^{17}\text{ cm}^{-3}$ .

## B. Theory

Several theoretical approaches were used to study these defects. The first-principles methods CRYSTAL06 (Ref. 19) and SIESTA<sup>20</sup> predicted equilibrium configurations and vibrational frequencies. Results from these calculations were then used as guidance for composite parametrized mass-and spring models that include anharmonicity in the C-H and Si-H stretch modes.

### III. Centers containing a Si-H and a C-H stretching mode

#### A. IR absorption spectra

Figure 2 shows the evolution upon annealing of the defects in a mc-Si:C sample into which H had been introduced. [The vibrational line at  $2967\text{ cm}^{-1}$  due to the  $(\text{CH})_2$  center, shown in Fig. 1, is thermally stable throughout the annealing sequence<sup>6</sup> and is not shown in this figure.] The vibrational lines due to  $\text{H}_2^*(\text{C})$  centers ( $1922$ ,  $2210$ , and  $2752\text{ cm}^{-1}$ ) begin to disappear at  $350\text{ }^\circ\text{C}$  while the  $2223\text{ cm}^{-1}$  IR line due to  $\text{VH}_4$  grows in. At  $550\text{ }^\circ\text{C}$ , the  $2223\text{ cm}^{-1}$  line due to  $\text{VH}_4$  disappears while a Si-H mode at  $2183.4\text{ cm}^{-1}$  grows in along with an additional line at  $2826.9\text{ cm}^{-1}$  in the C-H stretching range. We have found that the  $2826.9\text{ cm}^{-1}$  line shifts to  $2819.3\text{ cm}^{-1}$  in a Si sample containing the  $^{13}\text{C}$  isotope, confirming its assignment to a C-related vibrational mode.<sup>21</sup>

The  $2826.9\text{ cm}^{-1}$  line has the same annealing behavior as the Si-H mode at  $2183.4\text{ cm}^{-1}$  suggesting that both of these IR lines are due to an unknown defect structure in Si that contains both C and H. What are the possible candidates for the structure of this unknown center? The appearance of a Si-H mode and a C-H mode for this defect is similar to the vibrational properties of the known  $\text{H}_2^*(\text{C})$  centers. However, two possible  $\text{H}_2^*(\text{C})$  structures have already been assigned.<sup>9-11</sup> What alternative structures might be possible? As has been discussed above, a CH-HC structure is known in Si.<sup>12</sup> Might a SiH-HC structure also be possible? Alternatively, a HSi-SiH structure known as  $\text{H}_2^{**}$  has been reported.<sup>22</sup> Might a HSi-CH structure be possible?

#### B. Theory

These questions have been addressed in detailed calculations on  $\text{H}_2^*$ -like structures with Si-H and C-H bonds. Our theoretical treatment of the  $\text{H}_2^*$  - type defects was similar to that of Budde *et al.*<sup>23</sup> in that

we considered each Si-H or C-H bond as a Morse oscillator, with the two hydrogens coupled through a quadratic potential. We supplemented this with quantum-mechanical calculations using CRYSTAL06 (Ref. 19), whose results were used for guidance as to suitable values of the parameters in this mass-and-spring model.

The Hamiltonian may be written as

$$H = -(\hbar^2/2\mu_1)(\partial^2/\partial r_1^2) - (\hbar^2/2\mu_2)(\partial^2/\partial r_2^2) + D_1[1 - \exp(-a_1 r_1)]^2 + D_2[1 - \exp(-a_2 r_2)]^2 + f_{12}r_1r_2 \quad (1)$$

Here  $\mu_1$  and  $\mu_2$  are reduced masses;  $D_1$ ,  $D_2$ ,  $a_1$ , and  $a_2$  are Morse potential parameters for the two bonds; and  $f_{12}$  is the bond-bond coupling constant. We performed a Taylor expansion of the Morse potentials and treated the higher-order terms and the coupling term as perturbations to the harmonic oscillator potentials. This yields expressions for the ground and first excited state energies whose differences can then be fit to experimental values. We have tested this approach by comparing it to the results published by Budde *et al.*<sup>23</sup> for  $H_2^*$  centers in Si and in Ge and found agreement to within 0.2% in all cases.

The numerical solution in this approach was carried out using Sage, an open-source software package,<sup>24</sup> supplemented by Microsoft Excel. In principle, the Hamiltonian contains 7 parameters for each defect configuration. However, most of these parameters were constrained to within “reasonable” ranges based on our prior knowledge of the bonds and guidance from CRYSTAL06. To begin, we chose the reduced masses to simply equal the appropriate diatomic masses. This is consistent with standard treatments,<sup>25</sup> and we expect that any deviation from the diatomic masses would be small. Next, we assumed that the anharmonicity factor  $x_e$  (proportional to  $a/D^{1/2}$ ) has the same value for a given bond regardless of defect configuration, while the bond force constants (proportional to  $a^2D$ ) were allowed to vary to fit experiment. The coupling constant  $f_{12}$  was determined for each configuration from the results of a CRYSTAL06 calculation.

Results of these calculations, including a number of predicted values, are given in Table I. The following points should be noted. First, for the proposed structures  $\text{SiH}_{bc}\text{-CH}_{ab}$  and  $\text{CH}_{bc}\text{-SiH}_{ab}$ , the agreement between measured and calculated frequencies is excellent. This is not surprising, given the limited amount of data. It does mean that for these two cases, observation of the many other predicted frequencies would provide a good test for the proposed models. Second, two hypothetical structures have been considered,  $\text{SiH}_{bc}\text{-H}_{bc}\text{C}$  and  $\text{H}_{ab}\text{Si-CH}_{ab}$ . In these cases the predicted frequencies arise from the computed coupling constants and  $a$  and  $D$  values deduced for the observed cases, as indicated in the following example. For the Si-H bond in  $\text{SiH}_{bc}\text{-H}_{bc}\text{C}$ , the values of  $a$  and  $D$  for Si- $\text{H}_{bc}$  were taken to be equal to those deduced for  $\text{SiH}_{bc}\text{-CH}_{ab}$ . And so on. Given the total absence of experimental values, and the possibility that these proposed structures do not exist, these predicted values must be taken with a grain of salt.

One thing to be noted, however, is that because the coupling constant  $f_{12}$  for  $\text{SiH}_{bc}\text{-H}_{bc}\text{C}$  is predicted to be much larger than that for other structures, the frequency shift associated with one bond upon the deuteration of the other bond will be very large. In this case, line shifts of 10's of  $\text{cm}^{-1}$  are predicted. This could then be a signature of this defect, should such lines be observed. This is to be contrasted with the known  $\text{SiH}_{bc}\text{-CH}_{ab}$ , and  $\text{CH}_{bc}\text{-SiH}_{ab}$  structures where line shifts for the corresponding  $\text{HD}^*(\text{C})$  centers are a few  $\text{cm}^{-1}$ . And for the  $\text{H}_{ab}\text{Si-CH}_{ab}$  structure, there is hardly any shift at all in the predicted line frequencies for the corresponding centers containing H and D. These conclusions motivated additional IR absorption experiments for the 2183.4 and 2826.9  $\text{cm}^{-1}$  lines in which D is partially substituted for H.



#### IV. A $\text{VH}_4$ center trapped by substitutional carbon in Si

##### A. IR absorption spectra

Spectra for mc-Si:C samples that contain H [spectrum (i)] or mixtures of H and D [spectra (ii) and (iii)] are shown in Fig. 3. These samples had been annealed at 550 °C to produce the 2183.4 and 2826.9  $\text{cm}^{-1}$  lines and their isotopic siblings. The relative concentrations of H and D in these samples were determined independently by examining the relative intensities of the isotopically shifted lines of the  $\text{HD}^*(\text{C})$  centers that were studied prior to any post-hydrogenation annealing treatments.<sup>26</sup>

Spectra (ii) and (iii) in Figs. 3(a) and (b) for samples containing both H and D show a rich isotopic structure. The Si-H line at 2183.4  $\text{cm}^{-1}$  is split into several components, each of which has a doublet structure (Fig. 4) that is spaced by approximately 0.4  $\text{cm}^{-1}$ . The C-H line at 2826.9  $\text{cm}^{-1}$  is split into four components. Furthermore, a closer examination of spectrum (i) in Fig. 3(a) for the sample containing H alone shows a weak line at 2214.6  $\text{cm}^{-1}$  that has been ignored up to now.<sup>27</sup> All but one of the IR lines in Fig. 3 show the same behavior upon annealing, suggesting that they are isotopic siblings of a common defect structure. The one line that does not show the same behavior as the others lies at 2211  $\text{cm}^{-1}$ . The 2211  $\text{cm}^{-1}$  line has been assigned previously to the  $(\text{CD})_2$  center<sup>12</sup> which is the isotopic partner of the  $(\text{CH})_2$  defect that gives rise to the 2967  $\text{cm}^{-1}$  line shown in Fig. 1. The frequencies of the IR lines seen in Fig. 3 are listed in Table II.

The complicated vibrational structure seen for the spectra of the 2183.4, 2214.6, and 2826.9  $\text{cm}^{-1}$  lines and their isotopic siblings that is produced by the partial substitution of D for H is not consistent with a defect structure that contains just two H atoms. The annealing behavior of the 2183.4  $\text{cm}^{-1}$  line suggests another possible assignment. Fig. 5(a) shows isochronal annealing data for the 2223  $\text{cm}^{-1}$  line assigned to  $\text{VH}_4$  for a Si sample grown by the floating zone method. Fig. 5(b) shows isochronal annealing data for

the 2223 and 2183.4  $\text{cm}^{-1}$  lines for a mc-Si sample with a carbon concentration of  $[C] = 8.8 \times 10^{17} \text{ cm}^{-3}$ . These data show that the 2223  $\text{cm}^{-1}$  line disappears at a lower annealing temperature in mc-Si with a high carbon content than in FZ Si with a much lower carbon content. These annealing results suggest an interaction between  $\text{VH}_4$  and C impurities in Si.

## B. Theory

Our experiments suggest a  $\text{VH}_4$  center trapped by C (i.e., a  $\text{VH}_3\text{-HC}$  center) as a candidate for the 2183.4, 2214.6, and 2826.9  $\text{cm}^{-1}$  lines. The theoretical analysis within this model focuses on the shift of the 2214.6  $\text{cm}^{-1}$  line to 2206.1  $\text{cm}^{-1}$  and to 2197.1  $\text{cm}^{-1}$  observed by experiment as Si-H bonds are successively replaced by Si-D. This shift along with the separation of that line from the 2183.4  $\text{cm}^{-1}$  line will depend on the bond-bond coupling. First-principles calculations using SIESTA<sup>20</sup> and CRYSTAL06 (Ref. 19) have been carried out on this defect and its D isotopes. The relaxed structure for the  $\text{VH}_3\text{-HC}$  center is shown in Fig. 6 (Ref. 28).

Neither set of first-principles results is expected to agree in detail with experiment because of anharmonic corrections to the stretch modes. These calculations can, however, yield predicted couplings between the various stretch modes. Since these couplings are relatively small, their harmonic portions should dominate. So one can set up a simple 4x4 dynamical matrix with diatomic reduced masses, two stretch force constants, and two coupling force constants (C-H to Si-H and Si-H to Si-H) and find the values of the harmonic force constants that fit the first-principles calculations. It turns out that the results of interest are quite insensitive to the C-H to Si-H coupling but are very sensitive to the Si-H to Si-H coupling. (Both couplings, incidentally, are small.) Fitting the result of the SIESTA calculation yields a Si-H to Si-H coupling force constant of 22.5  $\text{cm}^{-1}/\text{\AA}^2$ , while fitting that of CRYSTAL06 yields 15  $\text{cm}^{-1}/\text{\AA}^2$ . In  $\text{eV}/\text{\AA}^2$  these are 0.00279 and 0.00186, respectively.

The next step is to fit experiment, with anharmonic corrections to the stretch modes and harmonic bond-bond coupling. This involves again a 4x4 dynamical matrix and a simplified version of the technique used in Sec. III. The best fit to experiment yields a Si-H to Si-H force constant of  $10.5 \text{ cm}^{-1}/\text{\AA}^2$ , or  $0.00130 \text{ eV}/\text{\AA}^2$ . And the fit is very good indeed, as indicated in Table II. The fair agreement of the theoretical Si-H to Si-H coupling force constant with the value deduced from experiment strongly supports the model of 4 hydrogens inside the Si vacancy (as opposed to outside the vacancy, for example).

As can be seen from the results in Table II, the positions of the Si-H stretching modes and their shifts for centers with Si-H bonds partially substituted by Si-D are reproduced by our model with near  $\text{cm}^{-1}$  accuracy.<sup>29</sup> The doublet structure of the Si-H modes is explained by the small shift in frequency that occurs when a C-H bond is substituted by C-D for a particular isotopic variant of the  $\text{VH}_3\text{-HC}$  center. Our results show the greater effect of substituting Si-D for Si-H than occurs for substituting C-D for C-H. This occurs primarily because the Si-H modes lie closer in frequency and interact more strongly than the Si-H and C-H modes. Furthermore, the relaxation of the C atom away from the vacancy that is found by theory (Fig. 6) reduces the Si-H and C-H coupling because of the greater spatial separation of the H atoms.

Small upward shifts are seen in our spectra [Fig. 3(b)] for the C-H line of the  $\text{VH}_{3-n}\text{D}_n\text{-HC}$  centers as  $n$  increases from 0 to 3 to give rise to 4 closely spaced C-H lines. This C-H line structure provides further strong support for our  $\text{VH}_3\text{-HC}$  assignment. However, these small shifts ( $\sim 0.7 \text{ cm}^{-1}$ ) are not predicted by our model calculations and must arise from anharmonic coupling effects that are not included in the theory.

In addition to the Si-H and C-H lines that have been observed in our experiments for the  $\text{VH}_3\text{-HC}$  center and its isotopic siblings, the existence of corresponding Si-D and C-D stretching modes is

anticipated. However, we have searched for these vibrational lines in our spectra without success. It is not unusual to not be able to find these additional lines. The Si-H and C-H lines that have been observed are weak, and any line broadenings for the corresponding Si-D and C-D modes would make them difficult to detect. A similar situation occurs for the  $\text{H}_2^*(\text{C})$  centers that have been assigned previously; not all of the predicted lines for the corresponding  $\text{HD}^*(\text{C})$  are seen by experiment.<sup>10</sup>

## V. Conclusion

We have studied the interaction of H with C in mc-Si. In addition to the IR lines assigned previously to  $\text{H}_2^*(\text{C})$  and  $(\text{CH})_2$  centers,<sup>9-11</sup> vibrational lines at 2183.4 and 2826.9  $\text{cm}^{-1}$  are produced when a hydrogenated sample is annealed near 550°C. Theory has investigated axial centers containing a Si-H and a C-H bond as possible candidates for the 2183.4 and 2826.9  $\text{cm}^{-1}$  lines. The partial substitution of D for H is predicted to produce characteristic shifts of the H-stretching lines for this family of defect structures.

Our spectroscopic results reveal that the 2183.4 and 2826.9  $\text{cm}^{-1}$  lines give rise to a complicated line structure when D is partially substituted for H. Furthermore, a weak line at 2214.6  $\text{cm}^{-1}$  was discovered. The vibrational line structures we have observed are too complicated to be consistent with a defect containing only two H atoms.

Theory shows that a  $\text{VH}_3\text{-HC}$  center explains the rich vibrational spectra that are seen when D is partially substituted for H. The splitting of the defect's Si-H modes are explained well by a model that accounts for the coupling of the Si-H bonds. The Si-H lines are also split into closely spaced doublets. Theory shows that these small splitting occur when a C-D bond is substituted for C-H in a particular isotopic variant of the  $\text{VH}_3\text{-HC}$  center.

The C-H line of the  $\text{VH}_3\text{-HC}$  center shifts by a few tenths of a  $\text{cm}^{-1}$  to higher frequency when Si-D bonds are substituted for Si-H. There are four components, a finding that provides further strong support for our assignment of the 2183.4, 2213.6, and 2826.9 lines to the Si-H and C-H stretching modes of a  $\text{VH}_3\text{-HC}$  center

Our experimental and theoretical results establish that one of the more thermally stable hydrogen-related centers in silicon containing a high concentration of carbon is a  $\text{VH}_4$  center trapped by a carbon impurity.

## VI. Acknowledgment

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26. We also annealed the samples whose spectra are shown in Fig. 3 at  $500\text{ }^{\circ}\text{C}$  prior to the  $550\text{ }^{\circ}\text{C}$  treatment that was used to produce the  $2183.4\text{ cm}^{-1}$  center. The  $500\text{ }^{\circ}\text{C}$  anneal produced the  $\text{VH}_4$  center (without C) and its  $\text{VH}_{4-n}\text{D}_n$  isotopic siblings. The relative intensities of the various  $\text{VH}_{4-n}\text{D}_n$  lines in our samples were also examined to determine the relative concentrations of H and D.
27. In fact, the theoretical model for the vibrational properties of the  $\text{VH}_3\text{-HC}$  center predicted the existence of the  $2214.6\text{ cm}^{-1}$  line which was subsequently found in our IR spectra.

28. P. Ugliengo *et al.*, *Z. Kristallogr.* **207**, 9 (1993); P. Ugliengo, "MOLDRAW: A program to display and manipulate molecular and crystal structures," Torino, 2006, available on the web at <http://www.moldraw.unito.it>.
29. We also note the qualitative similarity of the Si-H modes predicted for the  $\text{VH}_3\text{-HC}$  center to the vibrational properties of the isolated  $\text{VH}_3$  center that has the same symmetry and its isotopic siblings (Ref. 12). The Si-H lines of isolated  $\text{VH}_3$ , however, are not split into closely spaced doublets.



Table I. Measured and predicted frequencies for various axial configurations containing SiH and CH bonds.

<i>Configuration</i>	<i>Measured (cm<sup>-1</sup>)</i>	<i>Predicted (cm<sup>-1</sup>)</i>	<i>a(Si) (Å<sup>-1</sup>)</i>	<i>D(Si) (eV)</i>	<i>a(C) (Å<sup>-1</sup>)</i>	<i>D(C) (eV)</i>	<i>f<sub>12</sub> (eV/Å<sup>2</sup>)</i>
SiH - CH	2210, 2688	2211, 2688	1.4054	4.888	1.8773	3.9491	0.46
SiD - CH	1607, -----	1606, 2687					
SiH - CD	2214, -----	2214, 1996					
SiD - CD	1607, -----	1606, 1999					
CH - SiH	2752, 1922	2752, 1925	1.3056	4.218	1.8935	4.0175	0.165
CH - SiD	-----, 1401	2752, 1397					
CD - SiH	-----, 1923	2047, 1924					
CD - SiD	-----, 1400	2046, 1397					
SiH - HC		2113, 2670	1.4054	4.888	1.8935	4.0175	1.61
SiH --DC		2168, 1939					
SiD - HC		1543, 2661					
SiD - DC		1539, 1989					
HSi - CH		1935, 2712	1.3056	4.218	1.8773	3.9491	0.05
HSi - CD		1934, 2016					
DSi - CH		1404, 2712					
DSi - CD		1404, 2016					

Table II. Measured and predicted vibrational frequencies of Si-H and C-H stretching modes of the  $\text{VH}_3\text{-HC}$  center in Si and related centers that result from the partial substitution of D for H.

<i>Configuration</i>	<i>Measured (<math>\text{cm}^{-1}</math>)</i>	<i>Predicted (<math>\text{cm}^{-1}</math>)</i>
$\text{VH}_3\text{ - HC}$	2183.4	2184.7
	2214.6	2216.5
	2826.9	2827.1
$\text{VH}_3\text{ - DC}$	2183.9	2184.7
	2215.4	2217.2
$\text{VH}_2\text{D - HC}$	2185.0	2184.7
	2206.1	2206.2
	2827.6	2827.0
$\text{VH}_2\text{D - DC}$	2185.3	2184.7
	2206.4	2206.7
$\text{VHD}_2\text{ - HC}$	2197.1	2195.6
	2828.3	2827.0
$\text{VHD}_2\text{ - DC}$	2197.5	2195.9
$\text{VD}_3\text{ - HC}$	2828.9	2827.0

## Figure Captions

FIG. 1. (Color online) IR absorption spectrum (4.2 K) of a Si sample that had been hydrogenated by annealing in an  $H_2$  ambient at 1250 °C followed by a rapid quench to room temperature. The sample was made from cast, mc-Si with a carbon concentration of  $[C] = 8.8 \times 10^{17} \text{ cm}^{-3}$ . The inset shows the structures of  $H_2^*$  defects trapped by substitutional carbon in Si. The 2210 and 2688  $\text{cm}^{-1}$  lines have been assigned to the  $SiH_{bc}CH_{ab}$  structure shown on the left (Refs. 6, 10, 11). The 1922 and 2752  $\text{cm}^{-1}$  lines have been assigned to the  $CH_{bc}SiH_{ab}$  structure on the right (Refs. 9-11).

FIG. 2. IR spectra (4.2 K) of a mc-Si sample into which H had been introduced by an anneal at 1250 °C in an  $H_2$  ambient followed by a rapid quench to room temperature. This sample was annealed sequentially for 30 min at the temperatures shown (in degrees Celsius).

FIG. 3. IR spectra (4.2 K, 0.3  $\text{cm}^{-1}$  resolution) of mc-Si samples into which H (or H+D) had been introduced by an anneal at 1250 °C in an  $H_2$  (or  $H_2 + D_2$ ) ambient followed by a rapid quench to room temperature. These samples were subsequently annealed at 550 °C for 30 min to produce the hydrogen centers of interest. Spectrum (i) is for a sample that contained H alone. Spectrum (ii) is for a sample that contained H+D with  $H>D$ . Spectrum (iii) is for a sample that contained H+D with  $H<D$ . (a) shows the Si-H stretching region. The Si-H lines are labeled by their  $VH_{3-n}D_n\text{-HC}$  assignments. Each of the Si-H lines is split into a closely spaced doublet. The component of the doublet at lower frequency is for the center containing C-H. The component at higher frequency is for the center containing C-D. (b) shows the C-H stretching region. The C-H components are labeled by the number,  $n$ , of Si-D bonds in the  $VH_{3-n}D_n\text{-HC}$  center.

FIG. 4. An expansion of the spectra shown in Fig. 3 that reveals the splittings of the Si-H stretching modes in the frequency range 2182 to 2188  $\text{cm}^{-1}$  for samples with  $H>D$  and  $H<D$ .

FIG. 5. The isochronal (30 min) annealing dependence of the integrated intensities of the IR lines at 2223 and 2183.4  $\text{cm}^{-1}$ . These hydrogen centers were produced by a thermal treatment (1250  $^{\circ}\text{C}$ , 1 hr) in an  $\text{H}_2$  ambient. (a) is for a Si sample grown by the floating-zone method and with a carbon concentration of  $[\text{C}] = 0.2 \times 10^{17} \text{ cm}^{-3}$ . (b) is for a cast, mc-Si sample with a carbon concentration of  $[\text{C}] = 8.8 \times 10^{17} \text{ cm}^{-3}$ .

FIG. 6. (Color online) The structure (Ref. 28) of the  $\text{VH}_3\text{-CH}$  center predicted by CRYSTAL06 (Ref. 19). The C relaxes away for the vacancy by 0.29  $\text{\AA}$ , and each Si relaxes away by 0.18  $\text{\AA}$ . A H attached to Si is 1.83  $\text{\AA}$  from another H attached to Si, and it is 2.25  $\text{\AA}$  from the H attached to C.

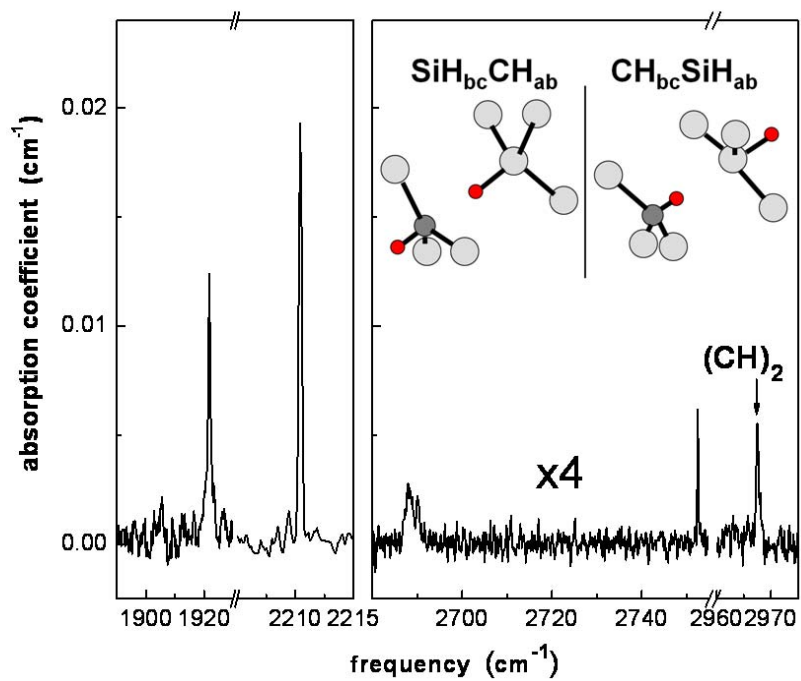


Fig. 1

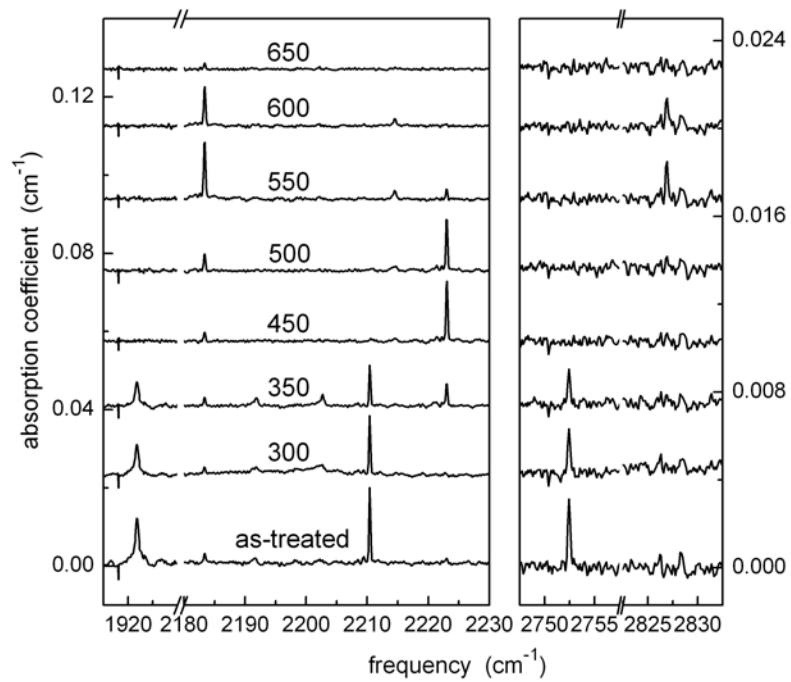


Fig. 2

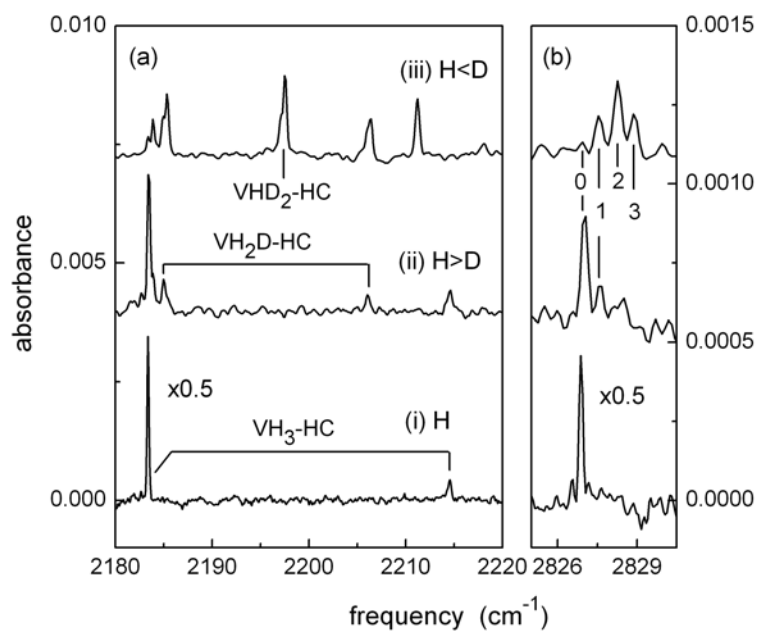


Fig. 3

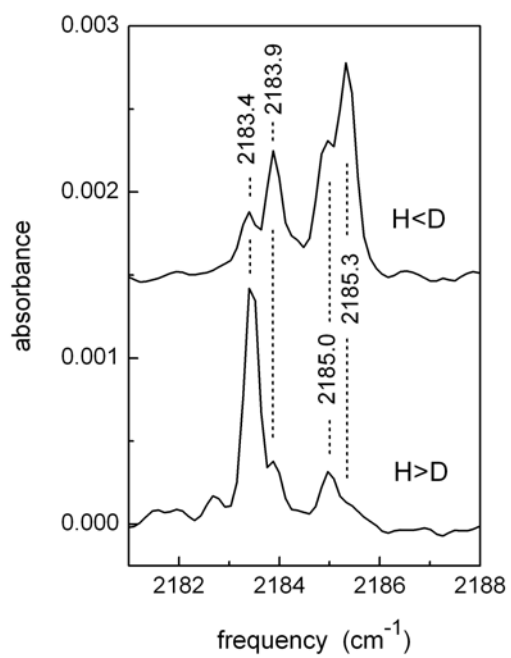


Fig. 4

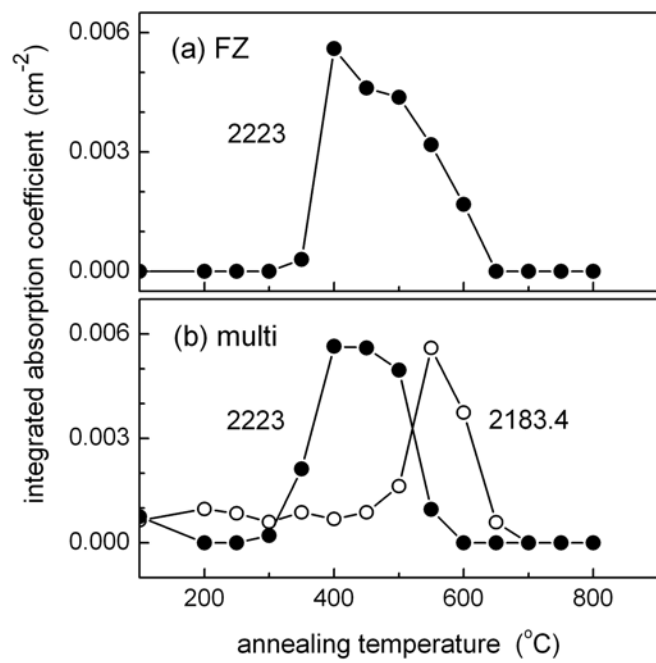


Fig. 5

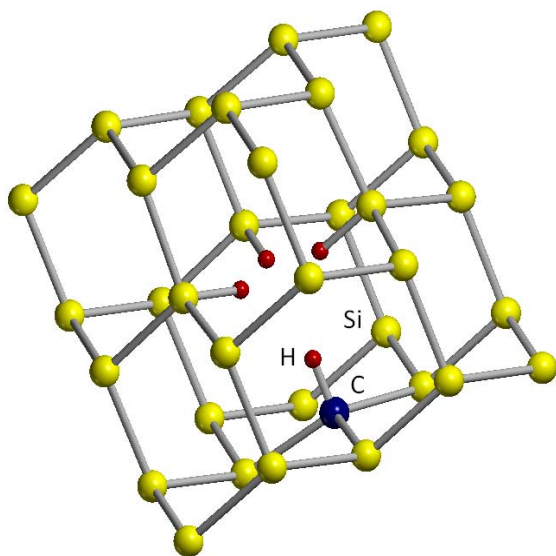


Fig. 6