H_2* Defect in Crystalline Silicon

J. D. Holbech and B. Bech Nielsen
Institute of Physics and Astronomy, University of Aarhus, DK-8000, Århus C, Denmark

R. Jones and P. Sitch
Department of Physics, University of Exeter, EX44QL, Exeter, United Kingdom

S. Öberg
Department of Mathematics, University of Luleå, S-95187, Luleå, Sweden

(Received 22 April 1993)

Detailed infrared studies have been carried out on proton- and deuteron-implanted Si. A dominant trigonal defect involving a pair of inequivalent hydrogen atoms has been identified, with local modes at 2061.5, 1838.3, 1599.1, and 817.2 cm^{-1}. The structure, the local modes, and the isotopic shifts of the H_2* defect have been calculated using *ab initio* pseudopotential cluster theory. The structure is consistent with channeling and uniaxial stress experiments. The calculated frequencies and isotopic shifts are in close agreement with those observed.

PACS numbers: 61.72.Ss, 61.72.Vv, 63.20.Pw, 78.50.Ge

Hydrogen is an important impurity in silicon and its properties have been studied extensively [1]. In this Letter a long-standing problem is addressed. According to theoretical calculations [2–4] the formation of hydrogen molecules H_2 at the interstitial tetrahedral (T) site is expected but no direct observation of this has been reported so far. An alternative pair structure is the H_2* defect shown in Fig. 1 which has C_{3v} symmetry with one hydrogen close to the bond-center (BC) site and the other at an antibonding (AB) site. This structure arose from theoretical calculations [3–5] and its stability is expected to be comparable to that of H_2 [5–7].

A number of hydrogen-related local vibrational modes have been observed in crystalline silicon implanted with protons [8–10], in particular a set of modes with frequencies 817, 1599, 1838, and 2062 cm^{-1} at 77 K. The two modes at 1838 and 2062 cm^{-1} have the same annealing properties [8,9] and they both originate from trigonal defects [9]. Channeling studies [10] have indicated that these two modes are associated with hydrogen near a T site and a BC site, respectively. Mukashev, Tokmoldin, and Tamendarov [11] ascribed the four modes to the same defect and suggested a model with one hydrogen atom attached to a silicon dangling bond inside a divacancy and another at a near-T site adjacent to the furthest silicon atom bordering the divacancy. This model is consistent with the channeling results but inconsistent with the observed trigonal symmetry. The H_2* defect has trigonal symmetry and is also consistent with the channeling sites. Therefore H_2* is a simple and plausible alternative to the other model. To distinguish it is necessary to correlate experiments with reliable large-scale calculations of the local modes for given defect structures. In particular, it is important to compare the shifts in frequency due to replacement of one hydrogen atom by a deuterium atom. These isotopic shifts give a direct measure of the effective H-H interaction and are therefore very sensitive to the structure.

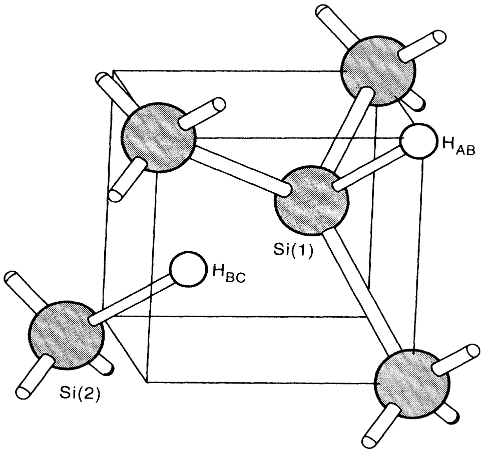

FIG. 1. The structure of the H_2* defect.

Samples were cut from single crystalline, 3–5 kΩ cm, n-type, float-zone silicon. The implantation of protons and/or deuterons was carried out at room temperature with a beam flux of about 2×10^{13} $\mathrm{cm}^{-2}\mathrm{s}^{-1}$ and with energies ranging from 800 to 2300 keV for protons and from 1000 to 3000 keV for deuterons. The resulting depth profiles were nearly uniform from 11 to 60 μm below the surface with a local concentration of 5.0×10^{19} cm^{-3} (0.1 at.%) for each isotope. The absorption measurement were carried out at 77 K and a resolution of 0.78 cm^{-1} with a Nicolet System 800 Fourier-transform spectrometer with a home-built stress rig.

After proton implantation a series of lines was observed in the ranges for Si-H bend and stretch modes, as found previously [9,11]. In particular, sharp lines were observed at 817.2, 1599.1, 1838.3, and 2061.5 cm^{-1} which shifted down to 587.7, 1160.0, 1339.6, and 1499.7 cm^{-1} when deuterons were implanted (see Fig. 2). These lines

0031-9007/93/71(6)/875(4)$06.00

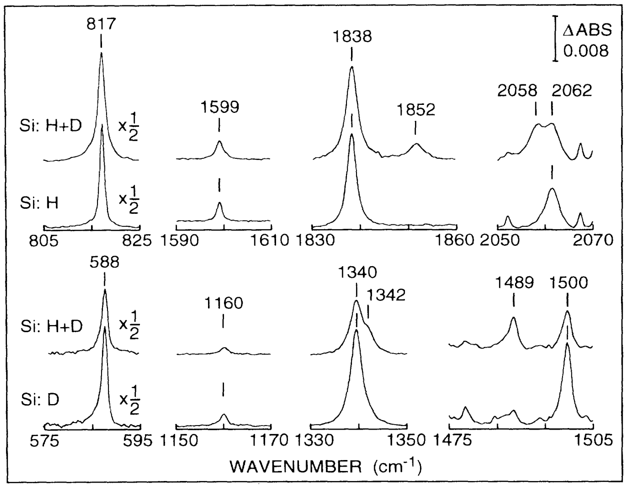

FIG. 2. Sections of the absorbance spectra observed after implantation with protons and/or deuterons.

annealed out together at ~200 °C and the relative intensities of the lines were unchanged when the hydrogen concentration varied from 0.01 at.% to 0.32 at.%. Thus the four modes originate from the same defect. The lines at 1838.3 and 2061.5 cm^{-1} are ascribed to Si-H stretch modes and the line at 817.2 cm^{-1} to a Si-H bend mode. The weak mode at 1599.1 cm^{-1} is assigned to an overtone of the 817.2 cm^{-1} mode as the ratio of their frequencies is so close to 2 [12]. Moreover the intensity ratio between an overtone and its fundamental is expected to scale with $m_{\rm eff}^{-1/2}$ where $m_{\rm eff}$ is the effective mass of the hydrogen isotope. The intensity ratio between the 1599.1 and the 817.2 cm^{-1} Si-H lines is 0.10, while the corresponding ratio for the Si-D lines at 1160.0 and 587.7 cm^{-1} is 0.07, in agreement with the $m_{\rm eff}^{-1/2}$ scaling. If both lines were associated with fundamental modes of the same defect their intensity ratio should be rather insensitive to the hydrogen isotope. These findings support our assignment of the 1599.1 cm^{-1} line.

Details of the spectrum obtained from a sample implanted with protons and deuterons are also shown in Fig. 2. Four new stretch modes have appeared at 1342.0, 1488.5, 1851.5, and 2058.1 cm^{-1}, which also annealed out together at ~200 °C. This indicates that the defect contains two inequivalent hydrogen atoms. No new bend modes were revealed around 817.2 cm^{-1} or 587.7 cm^{-1}.

Uniaxial stress studies showed that the lines at 1599.1, 1838.3, and 2061.5 cm^{-1} represent nondegenerate modes of trigonal defects, in agreement with our previous findings [9]. As can be seen from Fig. 3, the peak at 817.2 cm^{-1} splits into two when the stress is along the [001] axis. This is consistent with a trigonal defect only if the 817.2 cm^{-1} mode is a two-dimensional mode [13]. The solid lines in Fig. 3 represent the best fit to the data in that case. The fit was obtained with the A_1, A_2, B, and C parameters of Ref. [13] equal to 1.35, 0.80, 0.45, and 2.51 cm^{-1}/GPa, respectively. The agreement between the fit and experiment is good and the intensities for different polarizations of the light are also consistent with this assignment [13]. Three lines are expected for [111] stress and four for [110] stress while only two and three peaks are observed. However, the linewidth does not allow separation of all the components and the solid lines in Fig. 3 represent the peak positions we expect to resolve.

In conclusion, the modes at 817.2, 1599.1, 1838.3, and 2061.5 cm^{-1} are associated with a trigonal defect involving a pair of inequivalent hydrogen atoms. These properties are consistent with those expected for H_2^*. Therefore we have analyzed the structure and dynamical properties of the H_2^* complex using *ab initio* local density functional (LDF) cluster theory, applying a 73 atom cluster with three shells of host atoms surrounding a central one and with 36 hydrogen atoms saturating the dangling bonds at the surface of the cluster. Further details of the method are described in Ref. [14].

At the start of the calculations the hydrogen atoms, H_{BC} and H_{AB}, were placed at the central BC and AB sites. Upon relaxing all the cluster atoms, the H_{BC} was only slightly displaced from its initial site and bonded to Si(2) with a bond length of 1.50 Å (see Fig. 1). The H_{AB} moved to a near-T site pulling Si(1) with it. The resulting Si-H_{AB} bond length was 1.56 Å and the Si(1) relaxed into an almost planar configuration with its three silicon neighbors. The different bond lengths imply that the two Si-H stretch modes have very different frequencies, the

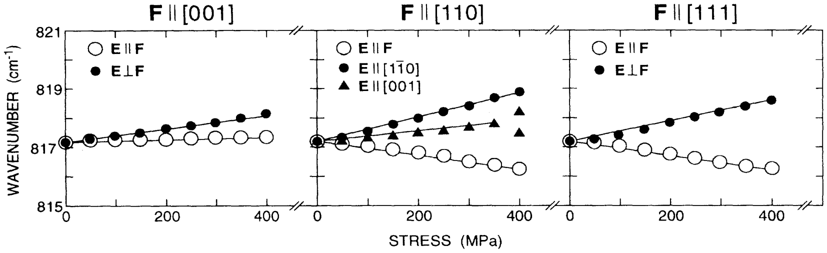

FIG. 3. The effect of uniaxial stress on the 817.2 cm^{-1} mode. **F** is the force and **E** is the electric-field vector of the incident light. The solid lines are discussed in the text.

Si(1)-H_{AB} being the lower. The structure is similar to that found in Refs. [3,5,15] but differs slightly from that reported by Deák *et al.* [16].

The local-mode frequencies were evaluated from the dynamical matrix of the cluster. Contributions from the two hydrogen atoms, the two silicon atoms bonded to hydrogen, and the surrounding six silicon atoms were evaluated directly. Other Si-Si contributions to the dynamical matrix of the cluster were calculated from a Musgrave-Pople potential found previously [17].

Table I shows the calculated frequencies consisting of two Si-H stretch modes around 2165 and 1844 cm^{-1} and two bend modes (two-dimensional) around 1002 and 612 cm^{-1}. The 2165 and 612 cm^{-1} modes are predominantly associated with vibrations of H_{BC} and the others with vibrations of H_{AB}. In the table the calculated and the observed modes are compared. The maximum difference between the two sets of stretch frequencies of $H_{BC}H_{AB}$ is 103 cm^{-1} while the bend mode at 817 cm^{-1} is overestimated by 185 cm^{-1}. The agreement is better for $D_{BC}D_{AB}$, indicating that the deviations may be partly due to anharmonicity. The additional stretch modes observed in the mixed-implantation study are assigned to $H_{BC}D_{AB}$ or $D_{BC}H_{AB}$ as shown in the table. The Si-H stretch modes were shifted by -3 cm^{-1} for H_{BC} and by $+13$ cm^{-1} for H_{AB} when the other hydrogen was replaced by deuterium. This is in close agreement with the calculated shifts of -5 cm^{-1} and $+12$ cm^{-1}. For the Si-D stretch modes the observed shifts were -11 cm^{-1} for D_{BC} and $+2$ cm^{-1} for D_{AB}, again in agreement with the calculated shifts of -10 and $+3$ cm^{-1}. Moreover the insensitivity of the bend modes at 817.2 cm^{-1} (H_{AB}) and 587.7 cm^{-1} (D_{AB}) to isotope replacement at the near-BC site is in accordance with the calculations. The remarkable agreement between observed and calculated isotope shifts shows that the force constant between the two hydrogen atoms, -0.73 eV/Å^2, is accurately given. As this depends critically on the H-H separation, the H-H distance must be very close to that calculated here, i.e., 3.4 Å.

TABLE I. Frequencies (cm^{-1}) and effective charges $\eta(e)$ of local modes of H_2^*. The type of mode and the site associated with the largest vibrational amplitude is also indicated.

Configuration	Mode	Calculation	Experiment	η
H_{BC}-H_{AB}	Stretch (BC)	2164.5	2061.5	0.29
	Stretch (AB)	1843.7	1838.3	0.41
	Bend (AB)	1002	817.2	0.41
	Bend (BC)	612	···	0.11
H_{BC}-D_{AB}	Stretch (BC)	2159.3	2058.1	
	Stretch (AB)	1324.3	1342.0	
	Bend (AB)	712	587.8	
	Bend (BC)	612	···	
D_{BC}-H_{AB}	Stretch (AB)	1855.9	1851.5	
	Stretch (BC)	1538.4	1488.5	
	Bend (AB)	1002	817.2	
	Bend (BC)	586	···	
D_{BC}-D_{AB}	Stretch (BC)	1548.1	1499.7	
	Stretch (AB)	1321.4	1339.6	
	Bend (AB)	712	587.7	
	Bend (BC)	586	···	

The H_{BC} bend mode was calculated to be at 612 cm^{-1} but was not observed. Either this mode absorbs weakly or it falls below the Raman peak at 523 cm^{-1} and broadens significantly. The intensity of the absorption line is proportional to the square of the effective charge η of the model [18]. The calculated η values are shown in Table I and so the intensity ratios of the modes, H_{BC} stretch, H_{AB} stretch, H_{AB} bend, and H_{BC} bend should be 1.0:2.0:2.0:0.1, in agreement with the observed ratios at 1.1:2.0:1.9:(0.0). Presumably the H_{BC} bend mode has very little infrared activity.

There are several objections to the model of Mukashev, Tokmoldin, and Tamendarov [9]. First, it does not have trigonal symmetry. Second, the distance between the two hydrogen atoms would be at least 5.9 Å which would be much too large to explain the observed isotope shifts. Third, it is difficult to accept that a hydrogen atom should prefer a near-*T* site adjacent to a silicon atom neighboring a divacancy, instead of saturating a nearby silicon dangling bond. It is virtually impossible to construct realistic trigonal models involving two Si-H bonds and a vacancy or a Si interstitial in which one of the hydrogen atoms occupies a near-*T* site and remains close to the other at a near-BC site. The absorption lines discussed above also appeared after electron irradiation of silicon samples doped with hydrogen from the gas phase [19,20]. This does not imply that the defect involves vacancies or interstitials but may give some insight into the formation of H_2^*.

It has been shown that the dominant Si-H modes at 817.2, 1599.1, 1838.3, and 2061.5 cm^{-1} in proton-implanted silicon originate from a trigonal defect involving a hydrogen pair. The observed isotopic shifts are in excellent agreement with those calculated for the H_2^* defect using *ab initio* LDF cluster theory. Moreover, the structure calculated for H_2^* is consistent with the trigonal symmetry and with the previous lattice location experiments [11]. Thus strong evidence for the existence of H_2^* has been obtained from a combination of experiment and theory.

This project has been supported by the Danish Natural Science Research Council, jr. nr. 11-7961. One of us (S.Ö.) thanks SuperDatorCentrum Norr in Sweden for computer time on the IBM 3090-600 J/VF in Skellefteå and for financial support from NFR and TFR (Sweden).

[1] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1992).

[2] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam,

and S. T. Pantelides, Phys. Rev. B **39**, 10791 (1989).

[3] K. J. Chang and D. J. Chadi, Phys. Rev. B **40**, 11644 (1989).

[4] P. Briddon, R. Jones, and G. M. S. Lister, J. Phys. C **21**, L1027 (1988).

[5] K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **62**, 937 (1989).

[6] R. Jones, Physica (Amsterdam) **170B**, 181 (1991).

[7] P. Deák and L. C. Snyder, Radiat. Eff. Defects Solids, **111-112**, 77 (1989).

[8] H. J. Stein, J. Electron. Mater. **4**, 159 (1975).

[9] B. Bech Nielsen and H. G. Grimmeiss, Phys. Rev. B **40**, 12403 (1989).

[10] B. Bech Nielsen, Phys. Rev. B **37**, 6353 (1988).

[11] B. Mukashev, S. Tokmoldin, and M. Tamendarov, in *Proceedings of the International Conference on the Science and Technology of Defect Control in Semiconductors, Yokohama, Japan, 1989*, edited by K. Sumino (North-Holland, Amsterdam, 1990), p. 429.

[12] The anharmonic contribution to the Si-H frequency is proportional to the inverse of the effective mass of the hydrogen atom [21]. Thus it is possible to estimate the pure harmonic frequency for a given mode from the observed Si-H and Si-D frequencies. The effective mass is estimated by $m_{\mathrm{eff}}^{-1} = m_{\mathrm{H}}^{-1} + (\chi M_{\mathrm{Si}})^{-1}$, where χ is assumed equal to 2.8 (see Ref. [21]). With this the pure harmonic frequencies for the 817.2 and 1599.1 cm^{-1} lines are estimated to be 848 and 1707 cm^{-1}, respectively. This gives a frequency ratio of 2.01, in close agreement with the factor 2 required by our assignment.

[13] A. E. Hughes and W. A. Runciman, Proc. Phys. Soc. London **90**, 827 (1967).

[14] R. Jones, Philos. Trans. R. Soc. London A **341**, 351 (1992).

[15] E. Kim, K. H. Lee, H. J. Lee, and Y. Hee Lee, J. Phys. Condens. Matter **4**, 6443 (1992).

[16] P. Deák, M. Heinrich, L. C. Snyder, and J. W. Corbett, Mater. Sci. Eng. B **4**, 57 (1989).

[17] R. Jones, J. Phys. C **20**, L271 (1987).

[18] R. C. Newman, *Infra-red Studies of Crystal Defects* (Taylor and Francis, London, 1973).

[19] T. S. Shi, G. R. Bai, M. W. Qi, and J. K. Zhou, Mater. Sci. Forum, **10-12**, 597 (1986).

[20] M. J. Binns, S. A. McQuaid, and R. C. Newman, Appl. Phys. Lett. (to be published).

[21] R. C. Newman, Physica (Amsterdam) **170B**, 409 (1991).