Hydrogen molecules trapped by multivacancies in silicon

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We report an observation of a Raman line of H_2 in silicon after Si^+-ion implantation followed by a hydrogen atom treatment. The vibrational frequency of the H_2 is 3822 cm^{-1} between the two different vibrational frequencies, 4158 and 3601 cm^{-1}, of H_2 observed so far in silicon. The assignment is confirmed by the observation of isotope shifts to 2770 cm^{-1} for D_2 and to 3353 cm^{-1} for HD. The ion-fluence dependence of the Raman intensity of the H_2 at 3822 cm^{-1} correlates with the total intensity of peaks in the Si-H stretching region that are attributed to H-terminated dangling bonds in multivacancies and/or interstitial-H complexes. We propose that the hydrogen molecule corresponding to the 3822 cm^{-1} vibrational line is trapped in or adjacent to H-terminated multivacancies. [S0163-1829(99)12739-5]

Hydrogen molecules in crystalline semiconductors have attracted much experimental and theoretical attention since their observation by means of Raman spectroscopy in 1996.[1,2] Murakami and co-workers have revealed the existence of H_2 in the float zone (FZ) *n*- and *p*-type crystalline silicon treated with atomic hydrogen.[1,3] The $S_0(1)$ rotational and Q_1 vibrational Raman lines of H_2 in crystalline silicon appear at 587 and 4158 cm^{-1}, respectively [we label this hydrogen molecule as H_2(I)]. The observed Raman shifts are very close to those of gaseous hydrogen, whereas their widths are much broader. The small peak shift suggests little interaction with the surrounding host lattice. It has been discussed that these Raman lines are attributable to hydrogen molecules trapped in platelets, or planar defects aligned along the {111} plane at tens of nanometers scale.[4]

Pritchard *et al.* have reported three infrared- (IR-) absorption lines due to H-H pair defects in Czochralski (CZ) silicon after exposure to hydrogen gas at temperatures between 1100 and 1300 °C.[5] From the isotope shifts the absorption lines have been attributed to hydrogen molecules. Two of the absorption lines, at 3788.9 and 3730.8 cm^{-1}, correlate in their intensities with the vibrational line of interstitial oxygen atoms (O_i) and have been assigned as H_2 adjacent to O_i atoms. The other absorption line, at 3618.3 cm^{-1} at 10 K, is not correlated with the absorption due to O_i and is observed also in FZ silicon. The downshift in the vibrational frequencies with respect to gaseous hydrogen implies the H-H bond is weakened because of the interaction with the surroundings. Very recently a Raman line has also been observed at 3601 cm^{-1} at room temperature [we label it as H_2(II)] in a FZ *n*-type silicon exposed to a hydrogen plasma at 150 °C.[6] The Raman line shifts to 3618 cm^{-1} when measured at 10 K, showing a good agreement with the IR result. The width of the H_2(II) Raman line is approximately 6 cm^{-1}, significantly smaller than that of H_2(I) but still greater than that of gaseous hydrogen.

Several theoretical calculations showed that H_2 is stable at the tetrahedral (Td) site of the silicon lattice.[7–9] They predicted a charge redistribution between H_2 and the surrounding Si lattice, which results in the screening of the intramolecular proton-electron attraction and the weakening of the H_2 bond. On the bases of the computational results the Raman line of H_2(II) has been attributed to hydrogen molecules at Td sites of silicon.[6]

The difference in the vibrational frequencies of the two Raman lines, H_2(I) and H_2(II), is accounted for in terms of different interactions with the surroundings in different trapping environments; platelets and Td sites are the two extremes in terms of the size. It is then reasonable to expect a third vibrational frequency for H_2, if any, that exists stably in a trap with a medium size. Such medium-sized traps will be created by ion implantation into crystalline silicon,[10,11] and the Si dangling bonds will be terminated with H atoms by hydrogenation. In the present study we succeeded in observing H_2 trapped in multivacancies in silicon using Raman-scattering spectroscopy. Multivacancies were introduced into silicon in a controlled manner by means of Si^+-ion implantation. The vibrational frequency of the H_2 trapped by multivacancies was found to be between those of H_2(I) and H_2(II).

FZ *p*-type Si(100) wafers were used as crystalline silicon samples. In order to create point-defect complexes, i.e., multivacancies and interstitial complexes, we implanted 200-keV Si^+ ions in the crystalline silicon at fluences ranging from 1×10^{13} to $5\times10^{15}\,Si/cm^2$ at room temperature. It is well known that vacancies formed as a primary product under ion implantation migrate quickly at room temperature and end up with multivacancies and impurity-vacancy complexes.[10,11] Much less is known concerning the final state of interstitials; most likely they form interstitial complexes, or otherwise diffuse to the surface. The macroscopic degree of disorder of the ion-implanted silicon was estimated in terms of phonon correlation length by applying the spatial correlation model,[12] to the Raman line shape of the optical phonon. Phonon correlation length, which corresponds to the dimension of phonon delocalization, was obtained to be 500,

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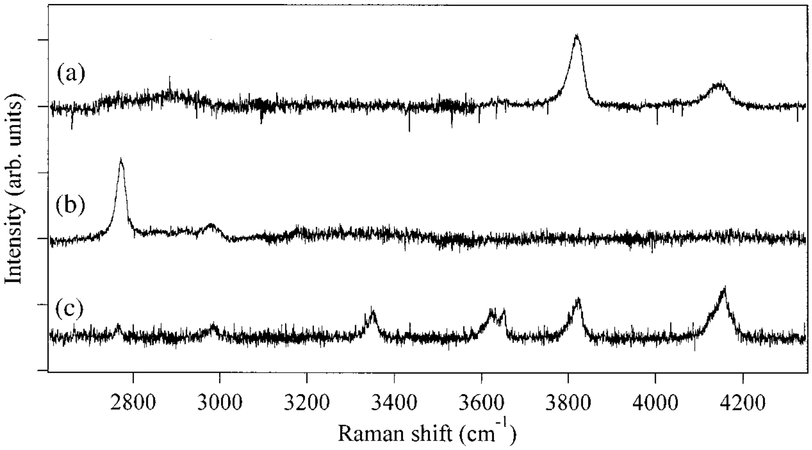

FIG. 1. Raman spectra of silicon after implantation with 200-keV Si^+ ions at a fluence of $2\times10^{14}/cm^2$ followed by a treatment with (a) H atoms, (b) D atoms, and (c) H+D atoms at 250 °C for 3 h. The smaller relative intensity of $H_2(III)$ to $H_2(I)$ in (c) compared with (a) is attributed to a higher flux of ion implantation that may lead to annealing of defects.

34.9, 17.4, 16.5, and 15.8 nm for silicon after the implantation of 1×10^{13}, 1×10^{14}, 5×10^{14}, 1×10^{15}, and $2\times10^{15}\,Si^+/cm^2$, respectively.[13] The Raman spectrum of the silicon after implantation with a dose of $5\times10^{15}\,Si^+/cm^2$ showed the formation of a continuous amorphous layer.

The implanted samples were treated with atomic hydrogen at 250 °C for 3 h in a remote downstream of hydrogen plasma. The samples were placed at a distance 60-cm apart from the plasma to suppress damage from the activated species in the plasma. Details of the hydrogen-atom treatment are described elsewhere.[14] Atom treatments were also performed replacing hydrogen gas with deuterium gas or with 0.5:0.5 hydrogen-deuterium mixture to check the isotope shift. All the Raman-scattering measurements were performed at room temperature using a 514.5-nm light as an excitation source. The wave-number resolution for the local vibrational mode was 3 cm^{-1}. The optical penetration depth for the 514.5-nm light is approximately 500 nm for crystal silicon and covers the average projectile range of the 200-keV Si ions, 250 nm from the surface.

Figure 1 shows the typical Raman spectra of hydrogen molecules in silicon implanted with $2\times10^{14}\,Si^+/cm^2$ followed by the hydrogen-atom treatment. Two Raman lines were observed at 4158 and 3822 cm^{-1}. The 4158-cm^{-1} line is the Q_1 vibrational line of $H_2(I)$ that had been observed in unimplanted silicon after hydrogenation.[1–3] We believe the 3822-cm^{-1} line is observed for the first time in the present study, and appears only for the silicon samples implanted with fluences between 1×10^{13} and $5\times10^{14}\,Si^+/cm^2$. No Raman signals due to hydrogenation are observed at around 3600 cm^{-1} for any implanted samples studied in the present study.

To investigate the origin of the 3822-cm^{-1} peak we performed a deuterium (D) atom treatment, as well as a treatment using a hydrogen-deuterium mixture (H+D atom treatment), at 250 °C for 3 h. The Raman spectra of silicon after implantation with $2\times10^{14}\,Si^+/cm^2$ followed by an isotopic hydrogen atom treatment are compared in Fig. 1. The 3822-cm^{-1} line shows an isotope shift down to 2770 cm^{-1} for a D atom treatment. The ratio between the vibrational frequencies is 1.38, in good agreement with that between gaseous H_2 and D_2, 1.39. After the H+D atom treatment a peak was observed at 3353 cm^{-1} in addition to those at 3822 and 2770 cm^{-1}, which is apparently attributed to the HD molecule. The isotope shifts confirm that the 3822-cm^{-1} line arises from H_2 in silicon [we label this hydrogen molecule as $H_2(III)$], and not from any XH_2 complexes (e.g., H_2O).

Figure 2 summarizes the integrated Raman intensities of the two vibrational lines of H_2 as a function of the implantation fluence. The intensities are normalized by that of the optical phonon of silicon. The intensity of $H_2(I)$ decreases monotonically with increasing implantation fluence, whereas that of $H_2(III)$ has a maximum at $2\times10^{14}\,Si^+/cm^2$. The ion-fluence dependence indicates that $H_2(III)$ is not related to defects created during hydrogenation (e.g., platelets), but to those created by ion implantation. The downshift in the vibrational frequency, ca. 340 cm^{-1} from that of gaseous hydrogen, suggests that the interaction of $H_2(III)$ with a silicon lattice is stronger than $H_2(I)$ (almost no downshift) but weaker than $H_2(II)$ (downshift by ca. 560 cm^{-1}). Thus we consider $H_2(III)$ to be located in a defect created by ion implantation, whose size is greater than the tetrahedral site but smaller than the platelet site.

Candidates for such traps are multivacancies and interstitial complexes. An electron paramagnetic resonance study on intrinsic silicon implanted with 160-keV O^+ ions, for example, confirmed the formation of divacancy and four-vacancy.[10] The four-vacancy was observed at fluences between 2×10^{12} and $2\times10^{14}\,O^+/cm^2$, with a maximum at around $2\times10^{13}\,O^+/cm^2$, while divacancy and localized

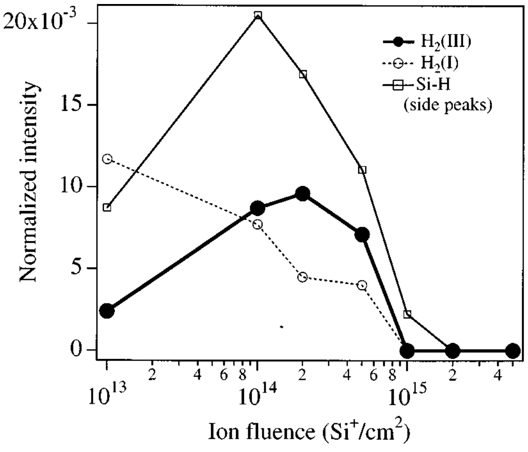

FIG. 2. Raman intensities of the H_2 vibrational lines and the sum of the Si-H side peaks in silicon after implantation with 200-keV Si^+ ions at different fluences followed by a H atom treatment at 250 °C for 3 h.

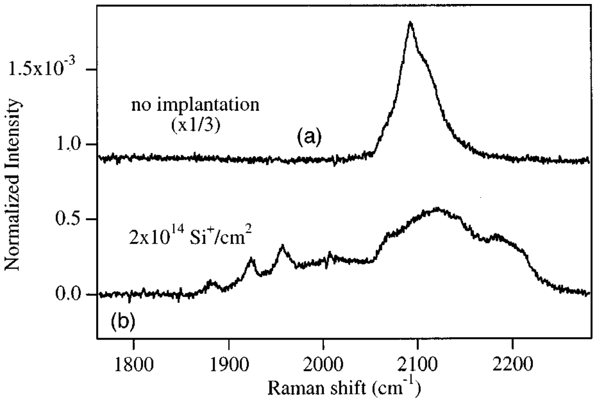

FIG. 3. Raman spectra of (a) crystalline silicon after a H atom treatment at 250 °C for 3 h, and (b) silicon after implantation with 200-keV Si^+ ions at a fluence of $2\times10^{14}/cm^2$ followed by a H atom treatment at 250 °C for 3 h.

amorphous regions are formed effectively at lower and higher fluences, respectively. This study suggests that multivacancies larger than the divacancy are effectively created in the ion fluence range in which H_2(III) was observed in the present study. The Raman spectra of Si-H stretching in unimplanted silicon and silicon implanted with $2\times10^{14}\,Si^+/cm^2$ are compared in Fig. 3, both after the hydrogen atom treatment at 250 °C. The Si-H Raman band for implanted silicon exhibits several side peaks, three at the low-frequency side (1883, 1926, and 1957 cm^{-1}) and at least two at the high-frequency side (2187 and 2213 cm^{-1}). These side peaks are similar to those attributed to hydrogen-terminated dangling bonds observed in hydrogen-implanted Si.[15] Some of the side peaks are also possibly originated from complexes of Si interstitials and hydrogen.[16] The integrated total intensity of the above-mentioned side peaks is plotted in Fig. 2. The ion-fluence dependence of the Si-H side peaks exhibits an evident correlation with that of H_2(III), indicating that multivacancies and interstitial complexes play an important role in the formation of H_2(III).

Calculations have shown that H_2 is stable in multivacancies with and without H termination. The vibrational frequency of H_2 in H-terminated divacancy (V_2H_6) was approximately 3800 cm^{-1}, assuming H_2 is located at the Td site adjacent to the Si-H bonds in the divacancy.[17] The vibrational frequency was calculated to be approximately 4000 cm^{-1} for H_2 in six and ten vacancies (V_6H_{12} and $V_{10}H_{16}$) with H termination,[17,18] and 3780 cm^{-1} without H termination.[18] These calculations agree roughly with the experimentally observed frequency of H_2(III), 3822 cm^{-1}, and supports its assignment as a hydrogen molecule trapped by H-terminated multivacancies in silicon. It is noted that the width of the H_2(III) line is about 30 cm^{-1}, being comparable to that of H_2(I) and much broader than that of H_2(II). The large width is accounted for by inhomogeneous broadening; hydrogen molecules are plausibly trapped in multivacancies with several different sizes (divacancy, four vacancy, five vacancy, etc.), or located at several metastable sites in or adjacent to the same multivacancy.

In conclusion, we have presented the existence of a H_2 molecule trapped by multivacancies in ion-implanted silicon. The ion-fluence dependence and the isotope shifts confirmed the assignment. The vibrational frequency of the H_2 was 3822 cm^{-1}, between the two Raman lines observed in crystalline silicon, 4158 and 3601 cm^{-1}. This result encourages us to further investigate hydrogen molecules existing in a defective environment in silicon that have not yet been investigated.

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