Raman Spectroscopy of Hydrogen Molecules in Crystalline Silicon

A. W. R. Leitch,* V. Alex, and J. Weber
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-70506 Stuttgart, Germany

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We report on a Raman spectroscopy study of float-zone crystalline silicon after exposure to a hydrogen plasma. New lines measured at 3601 and 2622 cm^{-1} are attributed to vibrational excitations of H_2 and D_2 molecules, respectively, positioned at the tetrahedral interstitial site within the Si lattice. These results correct a recent identification of molecular hydrogen in Si and confirm recent calculations that the vibrational frequency of the H_2 molecule in Si will be reduced by several hundred wave numbers from the known value for the H_2 molecule in the gas state. [S0031-9007(98)06576-4]

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The importance of hydrogen as an impurity in silicon has prompted many experimental and theoretical studies on the subject [1]. A relevant problem that needs to be addressed in this regard has to do with the position of the hydrogen molecule in the silicon. Theoretical calculations have indicated that two stable forms of hydrogen dimers in Si are possible: the H_2^* defect, in which one hydrogen atom is in the bond-centered position while the other is in the antibonding position, and the H_2 molecule, positioned at or near the tetrahedral interstitial (T) site within the Si lattice [2–6]. There is not much difference in the relative stabilities of these two species, but most calculations show the H_2 molecule to be slightly more stable (by about 0.1 eV) than the H_2^* defect. While infrared modes measured in p^+-implanted Si by Holbech *et al.* [7] gave the first evidence for the presence of the H_2^* defect in Si, direct experimental evidence for the existence of the H_2 molecule in crystalline Si has proved to be difficult to obtain, due to its presumed infrared inactivity.

Very recently, Murakami *et al.* [8] measured a broad Raman line at 4158 cm^{-1} in hydrogenated Si. In several subsequent papers [9–12], they have argued that this Raman frequency is associated with the vibrational excitation of the isolated H_2 molecule, situated at or near the T site in Si. On the other hand, we have recently presented strong evidence that the 4158 cm^{-1} signal results from H_2 molecules, not situated at T sites as claimed by Murakami *et al.*, but trapped within the voids formed by the hydrogen plasma-induced platelets that are generated during the hydrogen plasma treatment [13]. The platelets, which are tens of nanometers in length and aligned along $\{111\}$ crystallographic planes, are characterized by a dilation of the lattice by about 20–30% and a saturation of the Si dangling bonds by hydrogen [14]. Transmission electron microscopy studies have also indicated that the platelets contain a high density of hydrogen at pressures of the order of 1 GPa [14]. Our explanation is furthermore supported by several recent calculations [15–17], which have predicted that the vibrational frequency of the H_2 molecule at the T site will be reduced by several hundred wave numbers from the known value of 4161 cm^{-1} for H_2 in the gas state [18]. This expected down-shift of the Raman frequency is due to the weakening of the molecular bond as a result of the close proximity of the Si host matrix. Such an effect has recently been measured for isolated H_2 molecules in GaAs [19].

It is therefore important that experimental verification of the H_2 molecule situated at the T site in crystalline Si be presented. In this Letter, we present the first results for the Raman frequencies of H_2 and D_2 molecules positioned at the T site in Si. Our measurements correlate well with the low temperature infrared spectroscopy local vibrational modes (LVM) very recently reported by Pritchard *et al.* [20] for hydrogenated Si.

Float zone (FZ) silicon wafers, doped n-type with phosphorus and having 0.07 Ω cm resistivity, were used in this study. Hydrogen was introduced into the Si samples by means of a remote dc plasma system at typically 200–300 °C for 3 to 8 h. The samples were mounted on a heater stage which was located downstream from the plasma. The temperature was monitored with a thermocouple mounted next to the sample. No effect of the plasma on the thermocouple temperature was measured. The hydrogen pressure was held constant at 1.5 mbar. For some samples the hydrogen atmosphere was replaced by either deuterium or a mixture consisting of 50:50 H_2:D_2.

Most of the Raman measurements were performed at room temperature, using the focused 488 nm line of an Ar-ion laser for excitation. The laser intensity was typically 300 mW. Some measurements were also performed at low temperatures, with the sample mounted in a cold finger cryostat. The focused incident laser beam made an angle of 40° with the sample normal. The backscattered light, not analyzed for its polarization, was dispersed using a 0.3 m single grating spectrometer and detected with a cooled Si CCD detector array. Appropriate holographic notch filters were used to reduce the scattered laser light. The full spectral range up to 4500 cm^{-1} was investigated.

We first discuss the typical Raman spectra obtained from crystalline Si after exposure to H_2, D_2, or H_2:D_2

plasmas at 200 °C. Curve (*a*) of Fig. 1 shows two hydrogen-related Raman peaks after exposure to a pure H_2 plasma. The peak at 4157 cm^{-1} is attributed to vibrational excitations of isolated H_2 molecules [21] and is equivalent to the 4158 cm^{-1} peak reported by Murakami *et al.* [8]. The broad peak at 2129 cm^{-1} is the characteristic signal for the SiH-related platelets [22]. Using a pure D_2 plasma [curve (*b*)] resulted in the expected isotopic shifts of these two peaks to 2991 cm^{-1} for D_2 molecules and 1450 cm^{-1} for the SiD platelets, respectively. By exposing the Si to the H_2:D_2 plasma [curve (*c*)], all of these peaks were detected in addition to a new peak at 3629 cm^{-1}, which is attributed to vibrational excitations of HD molecules. The ratio of the frequencies of the H_2 signal to the D_2 signal is 1.39, close to the $\sqrt{2}$ value expected from the isotope shift. Finally, curve (*d*) of Fig. 1 shows that none of these Raman lines were present in the material before hydrogen-plasma treatment. Note that the 1400 cm^{-1} peak appearing in each spectrum is an overtone of the principle Si phonon. These spectra therefore give convincing evidence for the presence of H_2 molecules in crystalline Si.

It is worth noting that the H_2 Raman peak in Fig. 1 is broad, having a linewidth of 25 meV. This is about 2 orders of magnitude broader than the Raman peak for H_2 in the gas phase [18]. We have previously shown [13] that the signal actually comprises two peaks: By annealing above 400 °C the broad peak decreases in intensity and a peak at 4129 cm^{-1} [just visible as a shoulder in Fig. 1(a)] becomes dominant.

Figure 2 shows the integrated intensities of the SiH and H_2 Raman signals, as a function of sample temperature during the plasma treatment. There is clearly an optimum temperature regime for the formation of the SiH and H_2 signals, and these temperatures are quite different in both cases. In the case of the SiH platelets, there is a maximum within the range 100–150 °C, in agreement with Heyman *et al.* [22]. In this temperature range, the H_2 Raman signal is rather weak and broad. At higher temperatures (200–300 °C), however, the H_2 signal becomes sharp and well defined, as can be seen in Fig. 1. Once formed, both signals are stable up to a temperature of around 400 °C, above which they anneal out together with an annealing energy of 2.3 eV [13].

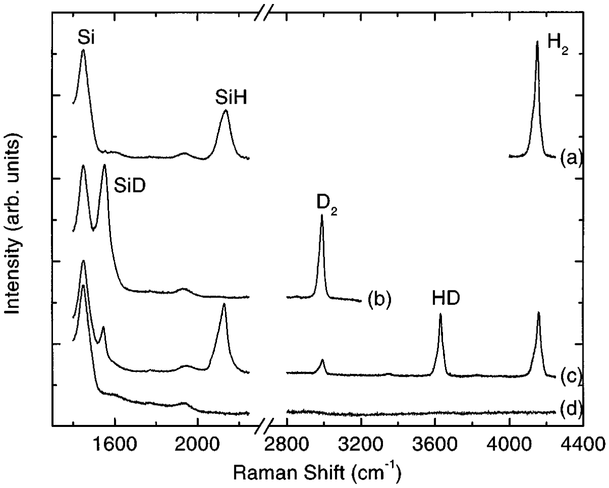

FIG. 1. Room temperature Raman spectra of FZ-Si:P (0.07 Ω cm), after exposure for 8 h at 250 °C to a H_2 plasma [curve (*a*)]; a D_2 plasma [curve (*b*)]; a H_2:D_2 (50:50) plasma [curve (*c*)]; and no plasma [curve (*d*)]. Excitation wavelength: 488 nm.

We explain the above results as follows: Exposure of the Si to the H_2 plasma results in the preferential formation of SiH platelets within the range 100–150 °C. Once formed, these defects become effective traps for any further hydrogen being introduced into the material during the plasma treatment. As more H_2 molecules are trapped within the voids formed by the platelets, the H_2 Raman signal at 4157 cm^{-1} becomes more intense. This explains why the measured H_2 Raman frequency of 4157 cm^{-1} is so close to the reported value of 4161 cm^{-1} for H_2 in the gas phase.

We now consider the formation of H_2 molecules at *T* sites within the lattice. In the light of the above, it is clear that a sufficiently low temperature during plasma treatment is required to minimize the trapping of the H_2 by the platelets. On the other hand, one requires a temperature sufficiently high for the atomic hydrogen to be able to diffuse through the Si and form the molecules. We have found that a plasma temperature of 150 °C is suitable for the formation of H_2 molecules. Figure 3 shows the room temperature Raman spectra of Si exposed to the various plasmas at 150 °C for 3 h. A small but clear signal appears at 3601 cm^{-1} after treatment in a H_2 plasma [curve (*a*)]. Not shown in the spectrum is a larger peak at 4157 cm^{-1} corresponding to the H_2 signal associated with the platelets. Exposure to a D_2 plasma results in a peak at 2622 cm^{-1} [curve (*b*)]. The larger peak at 2991 cm^{-1}

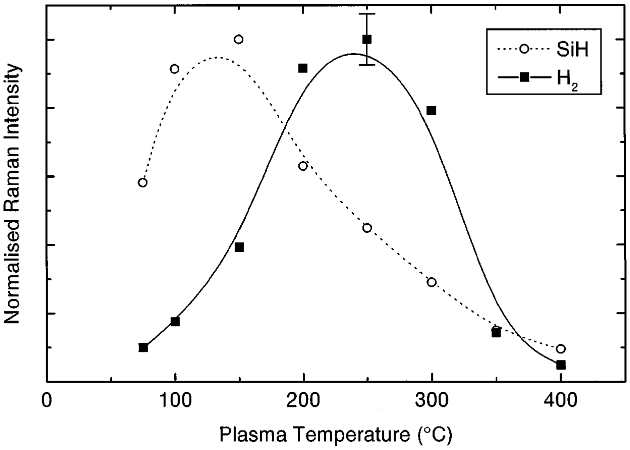

FIG. 2. Dependence of sample temperature during hydrogen plasma treatment on the integrated SiH and H_2 Raman signals in Si:P (0.07 Ω cm). Excitation wavelength: 488 nm.

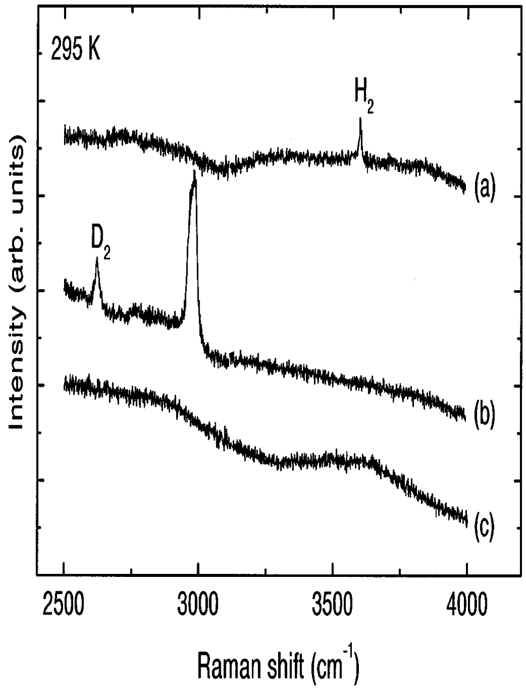

FIG. 3. Room temperature Raman spectra of Si:P (0.07 Ω cm), after exposure to the following plasmas at 150 °C for 3 h. Curve (*a*): H_2 plasma; curve (*b*): D_2 plasma; and curve (*c*): no plasma. Excitation wavelength: 488 nm.

corresponds to the platelet-related D_2 signal seen in Fig. 1 [curve (*b*)]. The ratio of the H_2 to D_2 frequencies is 1.37, thus providing clear evidence that these peaks arise from H_2 and D_2 molecules, respectively. Again, curve (*c*) shows that these peaks were not measured in a sample that had not been exposed to the plasma. It was not possible to identify the expected HD frequency in a sample that had been exposed to a H_2:D_2 plasma, because of the weakness of the signals. The results of Fig. 3 are summarized in Table I, together with the infrared LVM data recently reported by Pritchard *et al.* [20] for the H_2 molecule in Si, and the Raman data reported by Vetterhöffer *et al.* [19] for H_2 in GaAs. With decreasing temperature we have found that the H_2 Raman frequency increases, reaching a value of 3618 cm^{-1} at 10 K, thereby confirming the infrared LVM data [20].

TABLE I. Comparison of the measured Raman frequencies for H_2 at the T site in Si and GaAs, with the data for H_2 in the gas phase.

Matrix	H_2 (cm^{-1})	D_2 (cm^{-1})	HD (cm^{-1})	Ref.
Si (295 K)	3601	2622	···	This work
Si (10 K)	3618	···	···	This work
Si (10 K)	3618.3	2642.5	3264.8	[20]
GaAs (77 K)	3934.1	2842.6	3446.5	[19]
H_2 (gas)	4161.1	2993.6	3632.1	[18]

It must be emphasized that the Raman peaks seen in Fig. 3, although much weaker in intensity, are much sharper than the hydrogen-related lines of Fig. 1. Their linewidths (approximately 6 cm^{-1}) are of the same order as what has been measured for H_2 in GaAs [19]. It was not possible, however, to resolve the splitting due to the *para*- and *ortho*-H_2 rotational states of the vibrational Raman lines, in agreement with the infrared LVM results of Pritchard *et al.* [20] and the calculations of Hourahine *et al.* [16].

In summary, we have presented experimental evidence for the presence of H_2 molecules in crystalline Si. The measured Raman frequencies at room temperature are reduced by more than 500 cm^{-1} from the frequencies for H_2 molecules in the gas phase. Good correlation with theoretical calculations indicates that the H_2 molecules are positioned at the tetrahedral interstitial sites within the Si lattice. Finally, the Raman frequencies correlate well with the recently reported infrared LVM data for the H_2 molecule in Si.

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*Permanent address: Department of Physics, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa.

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