ELSEVIER

Materials Science and Engineering B58 (1999) 6–12

MATERIALS SCIENCE & ENGINEERING B

Formation of hydrogen molecules in crystalline silicon

A.W.R. Leitch [a,*], J. Weber [b], V. Alex [b]

[a] *Department of Physics, University of Port Elizabeth, PO Box 1600, Port Elizabeth 6000, South Africa*
[b] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

Abstract

Molecular hydrogen was directly observed by Raman spectroscopy in silicon samples subjected to a hydrogen plasma. At lower hydrogen plasma temperatures ($\sim 150°C$) the hydrogen molecules form at tetrahedral interstitial sites within the Si lattice. For higher temperatures ($> 150°C$) the plasma treatment results in hydrogen related platelets which act as sinks to which the molecules diffuse. Once trapped within the extended voids created by the platelets, the H_2 molecules exhibit a vibrational frequency that is practically the same as the well-known value for gaseous H_2. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Raman scattering; Silicon; Hydrogen

1. Introduction

The behaviour of hydrogen in Si is a subject of considerable technological importance, because of the various ways in which hydrogen may interact with the defects and impurities in the Si, thereby modifying the electrical properties of the material [1]. A simple example that has received much attention in recent years is the passivation by hydrogen of the shallow donors and acceptors in doped Si, leading to an increase in the specific resistivity. Although not as well understood, hydrogen also forms complexes with many deep defects in the Si.

Hydrogen is also known to be responsible for the introduction of defects into the Si. Several observations of platelet-like precipitation of hydrogen in Si have been reported [2–5]. Although no detailed model of hydrogen platelet formation in Si has been completely accepted, it is most likely that the platelets form through the hydrogen passivation of Si–Si bonds broken at the type I (111) plane during the hydrogen introduction process [5,6]. Transmission electron microscopy (TEM) studies have indicated that a considerable number of H_2 molecules may be in the open space between the platelets and that the pressure of the hydrogen can be of the order of 1 GPa [5].

Hydrogen is often unintentionally introduced into the silicon during crystal or epitaxial growth as well as during subsequent processing steps such as standard wet chemical etching, plasma etching and thermal treatments. Hydrogen may also be intentionally introduced by means of implantation and plasma treatments. If the hydrogen concentration in Si that has been exposed to a hydrogen plasma is determined by secondary ion-mass spectroscopy (SIMS), a higher hydrogen concentration is found compared to the concentration of hydrogen complexes determined by electrical measurements. This difference is most pronounced close to the sample surface. The additional hydrogen is usually attributed to the formation of hydrogen dimers such as the H_2 molecule. It was first proposed by Corbett et al. [7] that molecular hydrogen would be stable in crystalline Si. Calculations by various groups have subsequently confirmed that the stable H_2 molecule would be positioned at or near the tetrahedral interstitial (T) site within the Si lattice [8–10]. Many experimental results have been explained in terms of the formation of H_2 molecules. The experimental evidence for the presence of the H_2 molecule in Si is however difficult to obtain, due to its electrical neutrality and presumed infrared inactivity. Fortunately, H_2 molecules are Raman active and can thus be studied provided the hydrogen concentration is sufficiently high.

Murakami et al. [11] measured a Raman line at 4158 cm^{-1} in Si samples treated in hydrogen plasma and

* Corresponding author. Tel.: +27-41-5042219; fax: +27-41-5042573; e-mail: phaawl@upe.ac.za.

0921-5107/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0921-5107(98)00265-7

identified the line as the vibrational excitation of the isolated H_2 molecule in Si. It is significant that their reported frequency is within a few cm^{-1} of the value of 4161 cm^{-1} for gaseous H_2 [12]. By comparison, a Raman line at 3934 cm^{-1} was reported by Vetterhöffer et al. [13] for the isolated H_2 molecule at the *T* site in hydrogenated GaAs. It is difficult to reconcile these two frequencies with the value in H_2 gas. One would firstly expect that the confinement of the H_2 molecule when placed in a crystalline solid would result in a downward shift of the Raman frequency from the gaseous value. Secondly, one would anticipate that the vibrational frequency of the H_2 molecule in the Si matrix would be even lower than the frequency for H_2 in GaAs, in agreement with very recent calculations [14].

Murakami et al. [11] have argued that the 4158 cm^{-1} Raman signal they have measured comes from the H_2 molecule situated at or close to the *T* site in Si. We have subsequently presented strong evidence for an alternative explanation, namely, that the H_2 signal originates from H_2 molecules trapped within the voids formed by the hydrogen plasma-induced platelets that are generated during the hydrogen plasma treatment [15]. Annealing studies have shown that the characteristic Raman signal from the platelets and the 4158 cm^{-1} H_2 signal are correlated, exhibiting the same annealing behaviour. This explanation is further supported by our very recent report of a Raman line at 3601 cm^{-1} in hydrogenated Si, which we attribute to isolated H_2 molecules positioned at the *T* site in Si [16]. Unlike the 4158 cm^{-1} hydrogen related Raman line which does not change frequency with temperature, the 3601 cm^{-1} line shows a very similar temperature dependence to what we have measured for the Raman signal for interstitial H_2 in GaAs [17].

In this paper we first present our Raman data of the H_2 molecules associated with the platelets in hydrogenated Si. We discuss the strong correlation of this H_2 signal with the characteristic Raman signal from the hydrogen platelets. We then present our Raman spectroscopy results for interstitial H_2 in Si and compare it with the recently reported infrared (IR) spectroscopy of hydrogenated Si [18].

2. Experimental

Float zone (FZ) as well as Czochralski (CZ) silicon wafers doped with either phosphorus (n-type) or boron (p-type) in a wide range of resistivities (0.07 to 2000 Ωcm) were studied. Hydrogen was introduced into the wafers by exposing them to a remote dc hydrogen plasma at sample temperatures ranging from room temperature to 400°C for 30 min to 8 h. The samples were mounted on a heater stage 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 reading was detected. 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 H_2:D_2 (1:1).

Raman measurements were performed at sample temperatures ranging from 4.2 K to room temperature, using the focused lines of an Ar or Kr-ion laser for excitation. The incident laser intensity was typically between 50 and 300 mW. The backscattered light, not analysed for its polarisation, 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.

3. Results

3.1. General features of the Raman spectra

Fig. 1 illustrates the hydrogen related features of a Raman spectrum that are measured after exposure of 0.07 Ωcm phosphorus-doped FZ–Si to the various plasmas at 200°C. Curve (a) shows two hydrogen related Raman peaks after exposure to a pure H_2 plasma. Firstly, the peak measured at 4157 cm^{-1} is attributed to vibrational excitations of isolated H_2 molecules and is equivalent to the 4158 cm^{-1} peak reported by Murakami et al. [11]. Its unambiguous identification with H_2 is confirmed by exposing the Si to either a pure D_2 plasma (curve (b)) or a plasma containing a H_2:D_2 mixture (curve (c)). For the case of the D_2 plasma the peak has shifted to 2991 cm^{-1}, while the H_2:D_2 mixture gives rise to the lines at 4157 cm^{-1}, 2991 cm^{-1} as well as at 3629 cm^{-1}. These three lines are therefore inter-

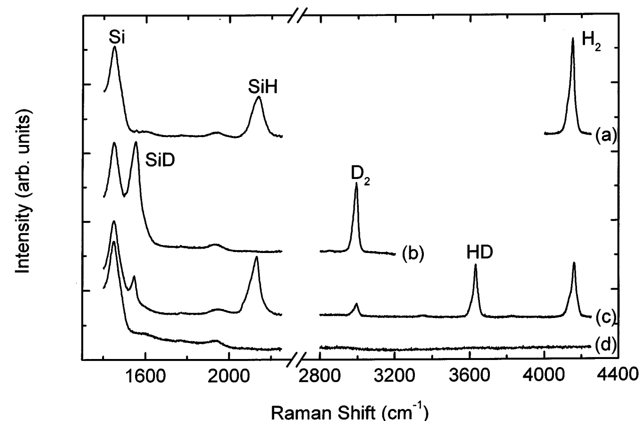

Fig. 1. Raman spectra of a Si:P sample at room temperature, after exposure at 200°C for 8 h to: (a) H_2 plasma; (b) D_2 plasma; (c) H_2:D_2 (50:50) plasma; and (d) no plasma treatment.

Table 1
Summary of the reported Raman frequencies for H_2 in various matrices

Matrix	H_2 (cm^{-1})	D_2 (cm^{-1})	HD (cm^{-1})	Reference
Si	4157 ± 2	2991 ± 2	3629 ± 2	Leitch et al. [15]
Si	4158 ± 3	2990 ± 2	–	Murakami et al. [12]
H_2 (gas)	4161.13	2993.55	3632.06	Stoicheff [12]
H_2 (liquid)	4153.78	2987.99	3623.65	Bhatnagar et al. [20]
H_2 (solid)	4151.8	2985.46	3621.85	Bhatnagar et al. [20]

preted as vibrational excitations of isolated H_2, D_2, and HD molecules in crystalline Si, respectively. 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) 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.

The second hydrogen related feature seen in curve (a) of Fig. 1 is the broad peak at 2129 cm^{-1}. By replacing the H_2 plasma with either a D_2 plasma or a H_2:D_2 mixture, the peak shifts to 1450 cm^{-1}. It is therefore identified as the well-known Raman signature associated with the stretching modes of the SiH bonds that are the building block of the platelets. The structured Raman signal indicates different Si–H bonds in the extended platelets. Polarised Raman measurements [19] have indicated that the band in fact consists of two or more lines, and that the relative strengths of the lines depend on the thermal history of the sample.

The results of Fig. 1 are summarised in Table 1, together with the values recently reported by Murakami et al. [11] for Si and the measured Raman frequencies for H_2, D_2 and HD molecules in the gas, liquid and solid phases [12,20]. We were not able to detect the $S_0(1)$ rotational line around 590 cm^{-1} reported by Fukata et al. [21], in spite of the clearly superior signal-to-noise ratios of our measured vibrational Raman frequencies.

The formation of H_2 molecules in CZ–Si was also studied by measuring the 4157 cm^{-1} Raman signal after H-plasma treatment. Typical results are presented in Fig. 2 for boron doped (p-type) as well as phosphorus doped (n-type) Si. Essentially no differences in the intensities, line-widths or Raman peak positions were found when comparing the CZ–Si with the FZ Si, for both n-type and p-type Si. Furthermore, an investigation of a wide range of resistivities failed to reveal any dependence of the H_2 Raman signal on the doping concentration. From the Raman results it would appear that the formation of the H_2 molecules is as efficient in p-type Si as in n-type Si. This interesting result will presently be contrasted with the formation of interstitial H_2 in Si.

Fig. 3 shows the effect of temperature on the 4157 cm^{-1} H_2 Raman line [22]. At room temperature the line-width (FWHM, full-width at half-maximum) is about two orders of magnitude broader than the Raman line for gaseous H_2 [12], and is also broad compared to other known hydrogen stretching modes in Si [23]. The line-shape is asymmetric, with a shoulder on the low frequency side. Reducing the temperature decreases the line-width somewhat (from 26 cm^{-1} at 295 K to 18 cm^{-1} at 7.5 K); the peak position and asymmetric line-shape however remain the same. We have been able to resolve the shoulder by a series of isochronal anneals up to 500°C [24]. The H_2 Raman signal decreases in intensity for annealing temperatures above 400°C, with the peak position at 4157 cm^{-1} moving slightly to 4152 cm^{-1}, while the peak at 4129 cm^{-1} (previously only visible as a shoulder) becomes dominant.

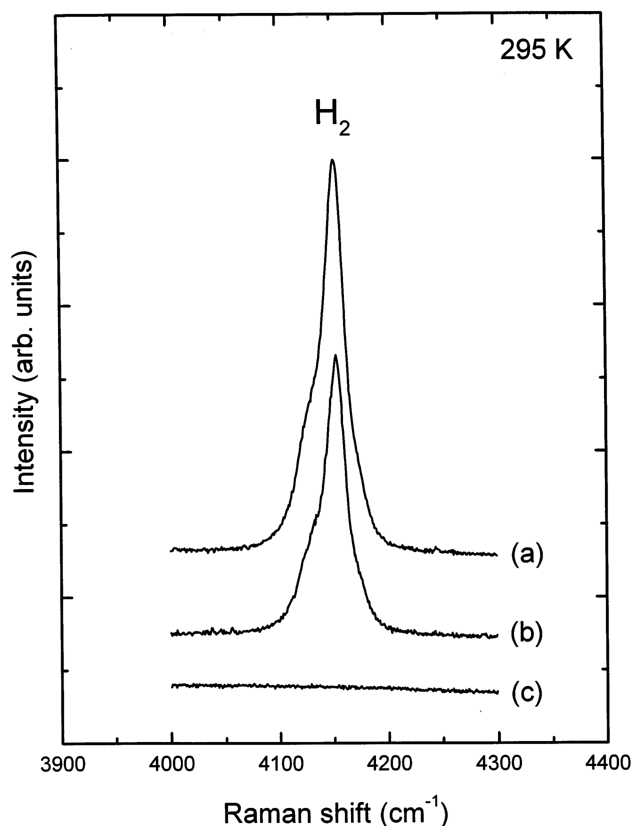

Fig. 2. Spectra of the 4157 cm^{-1} H_2 Raman signal in H-plasma treated 1 Ωcm CZ–Si: (a) B-doped Si; (b) P-doped Si; and (c) P-doped Si (no H-plasma treatment).

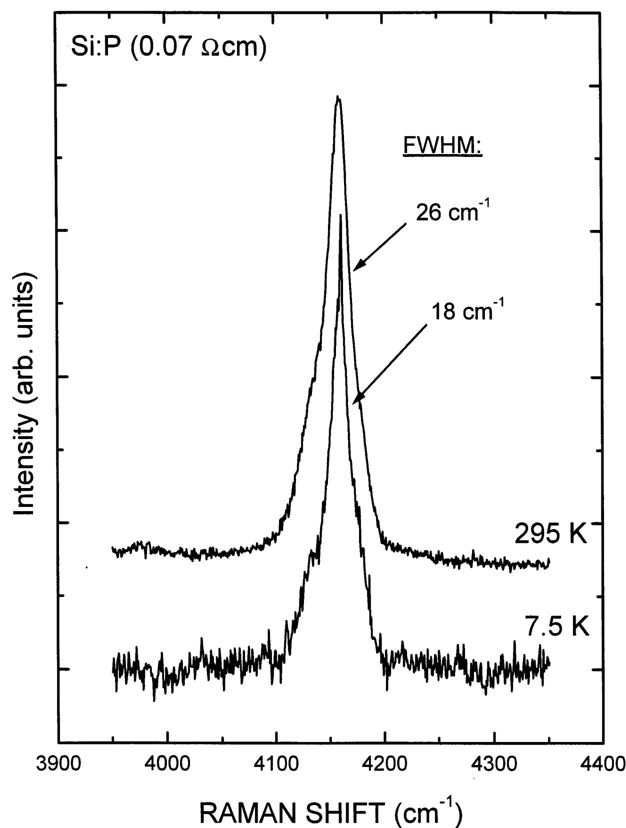

Fig. 3. Temperature dependence of the 4157 cm^{-1} H_2 Raman peak in hydrogen plasma treated Si:P.

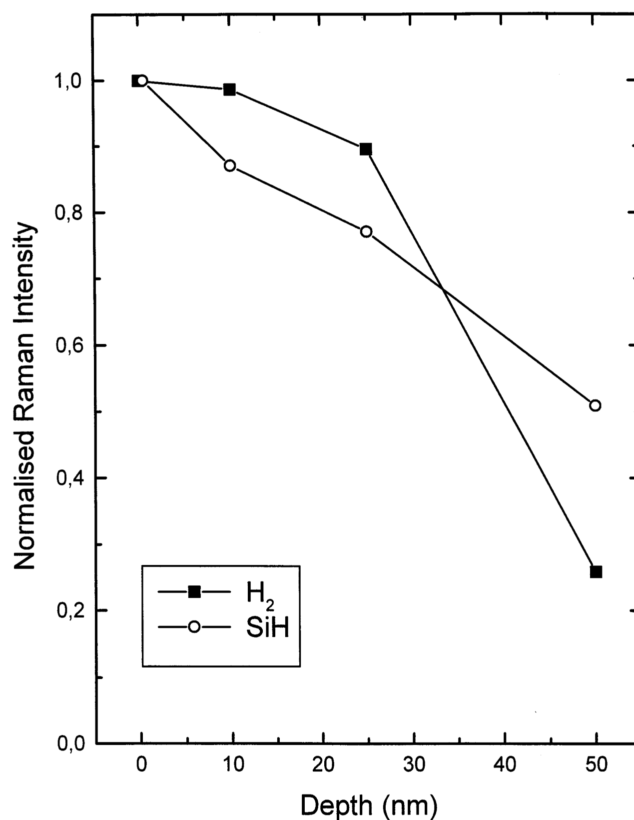

Fig. 4. Depth profiles of the integrated intensities of the 2129 cm^{-1} platelet signal and the 4157 cm^{-1} H_2 signal in Si:P.

3.2. Origin of the 4157 cm^{-1} H_2 Raman line

We have checked the depth of the defects giving rise to the 4157 cm^{-1} H_2 Raman signal by etching approximately 50 nm off a H-plasma treated sample. Fig. 4 summarises the results. We find that both the SiH and the H_2 Raman intensities are reduced, but are still measurable. This indicates that the platelets extend into the Si at least as deep as the H_2 molecules, suggesting that the presence of the 4157 cm^{-1} H_2 line in the Si is related to the existence of the platelets. An obvious candidate for the locality of the H_2 molecules within the Si lattice would be the voids formed by the extended platelets, which are generated during the hydrogen plasma treatment. It is important to note that for all the samples investigated the SiH Raman signal always accompanies the 4157 cm^{-1} H_2 Raman line.

Further evidence that the 4157 cm^{-1} H_2 line is related to the platelets in the Si comes from their annealing behaviour. After a series of isochronal anneals, both Raman signals show the same annealing characteristics with an annealing out at the same rate within the range 400–500°C. Assuming that the annealing of the SiH and H_2 signals obeys first-order kinetics and assuming a jump frequency of 10^{13} s^{-1}, we have obtained an activation energy of 2.3 eV for the process [15]. It may be noted that Beyer [25], when measuring the effusion of hydrogen from a ⟨111⟩ Si surface, calculated a free energy of desorption of 2.2 eV. As the platelets break up (resulting in a decrease in the SiH Raman signal), the high concentration of H_2 molecules will reduce, either by effusion from the surface, or by diffusing deeper into the material.

Despite the fact that the platelets and the 4157 cm^{-1} H_2 Raman signals are correlated, the optimum temper-

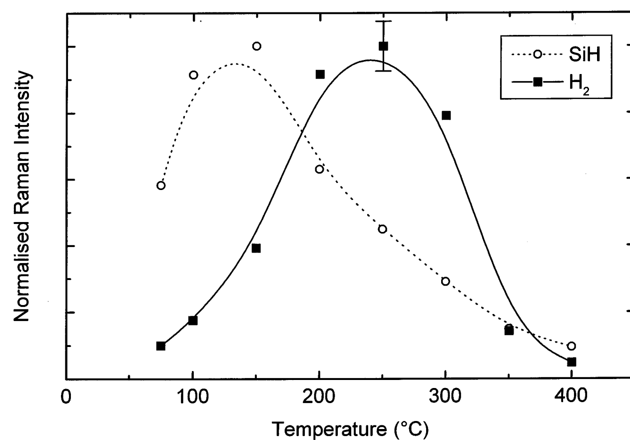

Fig. 5. Dependence of the integrated SiH and H_2 Raman signals in Si:P on the sample temperature during hydrogen plasma treatment.

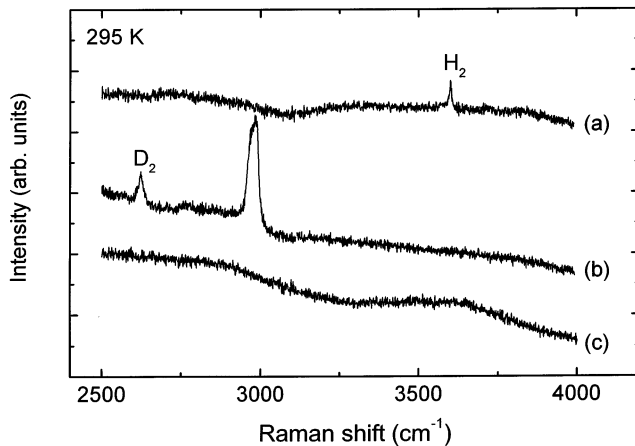

Fig. 6. Room temperature Raman spectra of Si:P (0.07 Ωcm), after exposure to the following plasmas at 150°C for 3 h. Curve (a): H_2 plasma; curve (b): D_2 plasma; and curve (c): no plasma. Excitation wavelength, 488 nm.

atures for their formation are different. Fig. 5 shows the integrated intensities of the two signals, as function of sample temperature during plasma treatment. In the case of the platelets, the signal reaches a maximum within the range 100–150°C, in agreement with the earlier Raman studies of Heyman et al. [19]. In this temperature range, the 4157 cm^{-1} line is rather weak and broad. At higher temperatures (200–300°C), however, the 4157 cm^{-1} signal becomes sharp and well defined. Once formed, both signals are stable up to a temperature of around 400°C, above which they anneal out together as already described.

We explain the results of Fig. 5 as follows: Exposure of the Si to the H-plasma results in the preferential formation of 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, so 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 [12].

3.3. Formation of H_2 molecules at tetrahedral interstitial sites in Si

In the light of Fig. 5, 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. Fig. 6 shows the room temperature Raman spectra of Si exposed to the various plasmas at 150°C for 3 h [16]. 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} 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 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 measured vibrational frequencies for the interstitial H_2 molecule are summarised in Table 2, together with the infrared local vibrational mode (LVM) data recently reported by Pritchard et al. [18] and several recent calculations of the frequency. The excellent agreement of the Raman results and the infrared LVM data at 10 K clearly indicates that we are measuring the same vibrational excitation of the isolated H_2 molecule, positioned at the tetrahedral interstitial site in Si. This assignment is also supported by the recent calculations given in Ref. [14,26–28]. The one exception to this is the calculation undertaken by Nakamura et al. [29], who calculated a frequency of 4470 cm^{-1}, a value greater than the known frequency of 4161 cm^{-1} for H_2 molecules in the gas phase.

It must be emphasised that the Raman peaks seen in Fig. 6, although much weaker in intensity are much sharper than the hydrogen-related lines of Fig. 1. Their line-widths (ca. 6 cm^{-1}) are of the same order as what has been measured for H_2 in GaAs [13]. It was not

Table 2
Summary of the reported vibrational frequencies for H_2 at the *T* site in Si, together with recent calculated frequencies

Matrix	H_2 (cm^{-1})	D_2 (cm^{-1})	HD (cm^{-1})	Reference
Si (295 K)	3601	2622	–	Leitch et al. [16]
Si (10 K)	3618	–	–	Leitch et al. [16]
Si (10 K)	3618.3	2642.5	3264.8	Pritchard et al. [18]
Si (theory)	3422	–	–	Van de Walle et al. [14]
Si (theory)	3708	2622	3217	Hourahine et al. [26]
Si (theory)	3363	–	–	Okamoto et al. [27]
Si (theory)	3723	–	–	Deak [28]
Si (theory)	4470	–	–	Nakamura et al. [29]

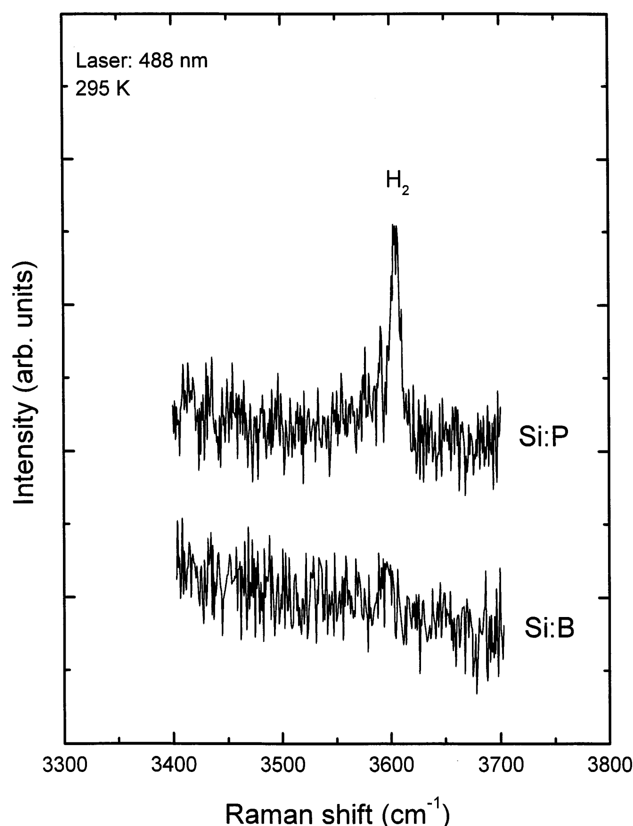

Fig. 7. Raman spectra for (a) 0.07 Ωcm Si:P and (b) 1 Ωcm Si:B, after simultaneous exposure to a H_2 plasma at 150°C.

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. [18] and the conclusions of Hourahine et al. [26].

Fig. 7 shows the Raman spectra for B-doped (1 Ωcm) Si and P-doped (0.07 Ωcm) Si, which were simultaneously exposed to a H_2 plasma. While the expected 3601 cm^{-1} interstitial H_2 signal was clearly visible in the n-type Si, the signal in the p-type Si could not be resolved above the noise. This result shows that the charge state of the atomic hydrogen has an important effect on the formation of the H_2 molecules. Thus, monitoring H_2 formation as a function of Fermi level has the potential to provide new information about the H charge states.

3.4. Temperature dependence of the interstitial H_2 Raman line

Fig. 8 shows the temperature dependence of the interstitial H_2 Raman peak in Si. As the sample temperature is lowered we see that the H_2 Raman frequency increases from 3601 cm^{-1} at 295 K to 3618 cm^{-1} at 10 K, thereby confirming the infrared LVM data [18]. We have measured a similar temperature dependence for the Raman signal of interstitial H_2 in GaAs [17]. This may be explained by the thermal expansion coefficient of the host material. Again, this result is in contrast with what was measured for the 4157 cm^{-1} H_2 line (see Fig. 3), where no temperature dependence was observed.

4. Summary

We have measured the Raman signal of the H_2 molecule in crystalline Si after exposure to a hydrogen plasma. When hydrogen is introduced into the Si at temperatures around 150°C, the H_2 molecules are positioned at the tetrahedral interstitial sites within the Si lattice. The room temperature vibrational frequency is measured to be 3601 cm^{-1}, increasing to 3618 cm^{-1} at 10 K. The effect of the Si matrix is thus to reduce the vibrational frequency by more than 500 cm $^{-1}$ from the value of 4161 cm^{-1} for gaseous H_2.

When hydrogen is introduced into the Si at temperatures in excess of 150°C, the hydrogen plasma induced platelets act as sinks for the hydrogen, and a strong Raman line at 4157 cm^{-1} is measured. This is attributed to H_2 molecules that have become trapped within the voids created by the platelets. This signal

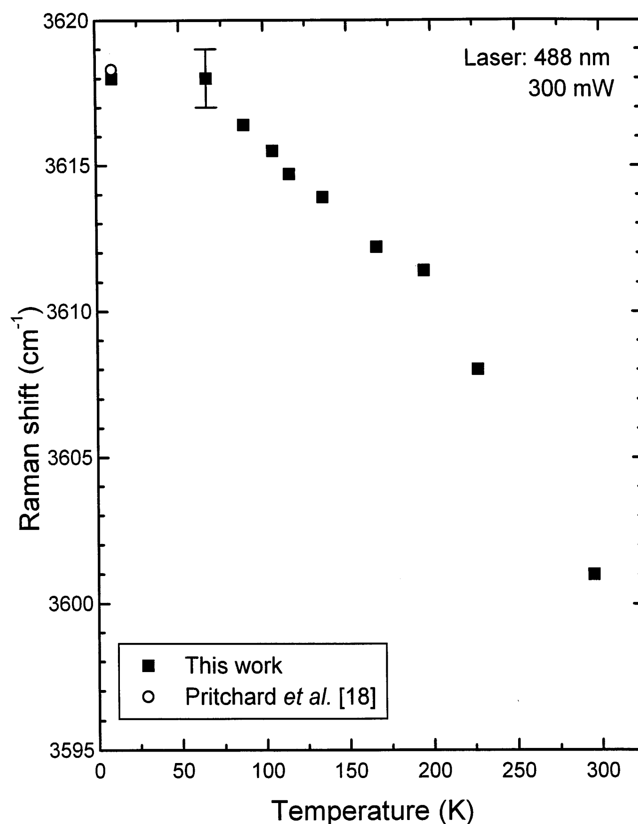

Fig. 8. Temperature dependence of the interstitial H_2 Raman line in Si:P (0.07 Ωcm). Excitation wavelength: 488 nm.

shows little temperature dependence, and is stable up to about 400°C, above which both the H_2 and the platelet signals anneal out at the same rate.

Acknowledgements

It is a pleasure to gratefully acknowledge the continued interest and support of Professor H.-J. Queisser, in whose group this work was performed. We also thank S.K. Estreicher and P. Deák for many stimulating discussions. One of us (AWRL) acknowledges the financial support of the South African Foundation for Research Development. The technical assistance of W. Heinz and W. Krause is appreciated.

References

[1] J.I. Pankove, N.M. Johnson (Eds.), Hydrogen in semiconductors, in Semiconductors and Semimetals, Vol. 34, Treatise Editors R.K. Willardson, A.C. Beer, Academic Press, Boston, 1991.
[2] W.K. Chu, R.H. Kastl, R.F. Lever, S. Mader, B.J. Masters, Phys. Rev. B 16 (1977) 3851.
[3] N.M. Johnson, F.A. Ponce, R.A. Street, R.J. Nemanich, Phys. Rev. B 35 (1987) 4166.
[4] S. Romani, J.H. Evans, Nucl. Instr. Meth. B 44 (1990) 313.
[5] S. Muto, S. Takeda, M. Hirata, Phil. Mag. A 72 (1995) 1057.
[6] P. Deák, C.R. Ortiz, L.C. Snyder, J.W. Corbett, Physica B 170 (1991) 223.
[7] J.W. Corbett, S.N. Sahu, T.S. Shi, L.C. Snyder, Phys. Lett. A 93 (1983) 303.
[8] C.G. Van de Walle, Phys. Rev. B 49 (1994) 4579.
[9] D.J. Chadi, C.H. Park, Phys. Rev. B 52 (1995) 8877.
[10] S.K. Estreicher, Mater. Sci. Eng. R 14 (1995) 319.
[11] K. Murakami, N. Fukata, S. Sasaki, K. Ishioka, M. Kitajima, S. Fujimura, J. Kikuchi, H. Haneda, Phys. Rev. Lett. 77 (1996) 3161.
[12] B.P. Stoicheff, Can. J. Phys. 35 (1957) 730.
[13] J. Vetterhöffer, J. Wagner, J. Weber, Phys. Rev. Lett. 77 (1996) 5409.
[14] C.G. Van de Walle, Phys. Rev. Lett. 80 (1998) 2177.
[15] A.W.R. Leitch, V. Alex, J. Weber, Solid State Commun. 105 (1998) 215.
[16] A.W.R. Leitch, V. Alex, J. Weber, Phys. Rev. Lett. 81 (1998) 421.
[17] A.W.R. Leitch, V. Alex, J. Weber, Phys. Rev. B (1998) (submitted for publication).
[18] R.E. Pritchard, M.J. Ashwin, J.H. Tucker, R.C. Newman, E.C. Lightowlers, M.J. Binns, S.A. McQuaid, R. Falster, Phys. Rev. B 56 (1997) 13118.
[19] J.N. Heyman, J.W. Ager, E.E. Haller, N.M. Johnson, J. Walker, C.M. Doland, Phys. Rev. B 45 (1992) 13363.
[20] S.S. Bhatnagar, E.J. Allin, H.L. Welsh, Can. J. Phys. 40 (1962) 9.
[21] N. Fukata, S. Sasaki, K. Murakami, K. Ishioka, M. Kitajima, S. Fujimura, J. Kikuchi, Jpn. J. Appl. Phys. 35 (1996) 1069.
[22] J. Weber, A.W.R. Leitch, V. Alex, in: H.R. Huff, U. Gösele, H. Tsuya (Eds.), Proceedings of the 8th international symposium on silicon materials science and technology, vols. 98–1, The Electrochemical Society, NJ, 1998, p. 973.
[23] K. Bergman, M. Stavola, S.J. Pearton, J. Lopata, Phys. Rev. B 37 (1988) 2770.
[24] A.W.R. Leitch, V. Alex and J. Weber, in: G. Davies and M.H. Nazaré (Eds.), Proceedings of the 19th international conference on defects in semiconductors, Aveiro, Portugal, 1997, Switzerland: Trans Tech Publications, 1997, p. 241.
[25] W. Beyer, Physica B 170 (1991) 105.
[26] B. Hourahine, R. Jones, S. Öberg, R.C. Newman, P.R. Briddon, E. Roduner, Phys. Rev. B 57 (1998) 12666.
[27] Y. Okamoto, M. Saito, A. Oshiyama, Phys. Rev. B 56 (1997) 10016.
[28] P. Deák (private communication).
[29] K.G. Nakamura, K. Ishioka, M. Kitajima, K. Murakami, Solid State Commun. 101 (1997) 735.