Ortho and Para Interstitial H_2 in Silicon

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A Raman scattering study of H_2 trapped at the interstitial T site in Si is presented. Both ortho and para nuclear-spin states of H_2 and D_2 have been observed. It is shown that the Raman signals of H_2 and D_2 in the $J = 0$ state, where J is the rotational quantum number, disappear preferentially from the spectra during laser excitation or prolonged storage at room temperature in the dark. This surprising behavior is tentatively explained by different diffusion rates of H_2 in the $J = 0$ and $J = 1$ states.

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Identification of a molecular form of hydrogen in semiconductors has been a major challenge ever since it was proposed in the beginning of the 1980s by Corbett *et al.* [1] and Mainwood and Stoneham [2]. Experimentally, H_2 in semiconductors has been observed only recently, first by means of Raman scattering in GaAs [3] and soon after by means of Fourier-transform infrared (FTIR) absorption [4,5] and Raman scattering in Si [6]. Today, several different H_2 species are known in semiconductors [7,8]. In this Letter, we study only the interstitial form of H_2, where the molecules are trapped at a tetrahedral interstitial site.

The microscopic behavior of H_2 in Si has been a very controversial issue. Most of the theoretical calculations have found that H_2 is a nearly free rotator [9–11]. Experimentally, this should result in two stretching local vibrational modes (LVM's) originating from ortho and para nuclear-spin states split by rovibrational coupling [6]. Such a splitting of 8 cm^{-1} has been observed for H_2 in GaAs [3]. H_2 in Si, however, was found to possess only one LVM [4–6]. This led to the conclusion that H_2 in Si has a barrier for rotation.

The contradiction between theory and experiment has been solved by Chen *et al.,* who found a new IR absorption line at 3191.1 cm^{-1} for the interstitial HD molecule in Si [12]. This line was interpreted as a $J = 1$ to $J = 1$ transition, whereas the line at 3265.0 cm^{-1}, previously assigned to HD [4,5], was reassigned to a $J = 0$ to $J = 1$ transition. This immediately led to the conclusion that H_2 in Si exhibits rotational motion. To explain the absence of an ortho-para splitting, Chen *et al.* argued that the $J = 0$ to $J = 0$ transition is an A_1-to-A_1 transition, which is forbidden in IR absorption and, thus, no ortho-para splitting could be detected. The model of Chen *et al.* could also elegantly explain the puzzling results of uniaxial stress studies of interstitial H_2 [13,14] as well as the relative intensities of the H_2, HD, and D_2 signals [15], which could not be understood by random pairing of H and D in the sample.

However, the absence of an ortho-para splitting in Raman spectra remains puzzling, because it is impossible to imagine that the selection rules for IR absorption and Raman scattering are identical, so that only the ortho component of H_2 could be detected by both techniques.

In this Letter, we present a Raman scattering study of silicon treated in a hydrogen plasma, which proves that the ortho-para splitting of the LVM of H_2 does exist and is equal to 9 cm^{-1}. Temperature dependencies of the Raman intensities show that the Raman signals of para-H_2 and ortho-D_2 ($J = 0$) disappear from the spectra during laser excitation at temperatures above 125 K or after 2 days of room temperature (RT) storage in the dark. This explains why the first Raman measurements performed at RT failed to detect the ortho-para splitting. We tentatively explain this surprising behavior by the slower diffusion rate of the molecule in the $J = 1$ state, which cannot relax to the ground $J = 0$ state in the Si matrix due to the lack of a magnetic field gradient that could induce a nuclear-spin flip.

Silicon samples used in this study were n-type, arsenic-doped, Czochralski (100) wafers with a resistivity of 0.09 Ω cm. Hydrogen was introduced into the samples by means of a remote dc plasma system. The sample temperature during the plasma treatment was 230 °C. The details of the experimental setup are given in Ref. [6].

Raman measurements were performed with the 532 nm line of a Nd:YVO_4 laser for excitation. The laser power was varied from 250 to 500 mW and the spot size on the sample surface was 50 μm. The spectral resolution was 2 cm^{-1}. Typical integration time was 3 h. The measurements were carried out in a flow cryostat, which was capable of cooling the samples down to 8 K. The local sample temperature within the excitation spot was, however, much higher. It was estimated from the Stokes to anti-Stokes ratio of the Raman phonon line (524 cm^{-1} at 8 K [16]).

Figure 1 shows the spectra of the silicon samples treated at 230 °C with hydrogen or deuterium plasma. Both hydrogen isotopes result in two lines in the spectra. In the case of hydrogen, the lines are very well resolved and located at 3618 and 3627 cm^{-1}, whereas for the deuterium-treated sample, a weaker line at 2642 cm^{-1} is seen only as a shoulder on a stronger peak positioned at 2645 cm^{-1}. The 3618- and 2642-cm^{-1} lines have been

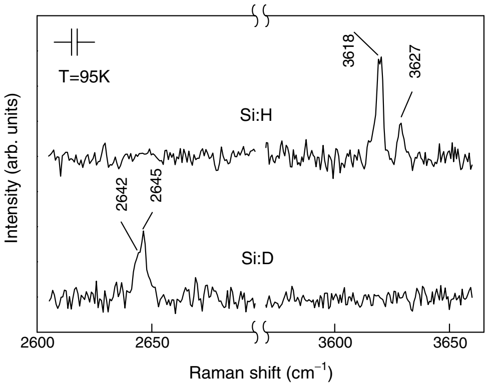

FIG. 1. Raman spectra measured after exposure to hydrogen (top) or deuterium (bottom) plasma at 230 °C for 4 h. Spectra are offset vertically for clarity.

previously observed by means of Raman and/or FTIR spectroscopy and assigned to the LVMs of H_2 and D_2 trapped at the T site of the silicon lattice [4–6]. As mentioned above, Chen *et al.* found that the $J = 0$ to $J = 0$ transitions are forbidden in IR absorption and, based on this, assigned the 3618- and 2642-cm^{-1} lines to ortho-H_2 and para-D_2, respectively.

For Raman scattering, however, both ortho and para transitions are equally allowed due to the selection rules $\Delta v = 0, \pm 1$ and $\Delta J = 0, \pm 2$. Therefore, we assign the 3827- and 2645-cm^{-1} lines to para-H_2 and ortho-D_2, respectively. The intensity ratios of the Raman signals for each pair of the lines (3:1 for H_2 and 1:2 for D_2) strongly support this assignment [6].

We strengthen the above assignments by calculating the ortho-para splitting from the anharmonic part of the potential, which could be determined from the LVM frequencies of H_2 and D_2. Here we assume that the potential energy of the molecule may be described by the Morse function

$$V(r) = D_0[\exp(-2\alpha r) - 2\exp(-\alpha r)], \qquad (1)$$

where D_0 is the dissociation energy and r is the interatomic distance. Keeping only terms up to fourth order, Eq. (1) may be rewritten as

$$\begin{aligned} V(r) &= D_0\left[(\alpha r)^2 - (\alpha r)^3 + \frac{7}{12}(\alpha r)^4\right] \\ &\equiv \frac{\mu\omega_e^2}{2}r^2 - ar^3 + br^4, \end{aligned} \qquad (2)$$

where μ is the reduced mass and

$$D_0\alpha^2 \equiv \frac{\mu\omega_e^2}{2}, \qquad D_0\alpha^3 \equiv a, \qquad \frac{7}{12}D_0\alpha^4 \equiv b.$$

Considering the terms of third and fourth order as perturbations, we get the rotational-vibrational part of the molecular energy, which is generally written as [17]

$$\begin{aligned} E(v, J) = \hbar\omega_e(v + \tfrac{1}{2}) - x_e\hbar\omega_e(v + \tfrac{1}{2})^2 + B_vJ(J + 1) \\ - D_eJ^2(J + 1)^2, \end{aligned} \qquad (3)$$

where

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right), \qquad B_e = \frac{\hbar^2}{2I}, \qquad D_e = \frac{4B_e^3}{\hbar^2\omega_e^2}, \qquad (4)$$

$$\alpha_e = \frac{6B_e^2}{\hbar\omega_e}\left(\frac{a\hbar}{\mu\omega_e^2}\sqrt{\frac{2}{\mu B_e}} - 1\right), \qquad (5)$$

$$x_e = \frac{3}{2\hbar\omega_e}\left(\frac{\hbar}{\mu\omega_e}\right)^2\left(\frac{5a^2}{2\mu\omega_e^2} - b\right). \qquad (6)$$

Here $I = \mu r_0^2$ is the moment of inertia of the molecule and r_0 is the internuclear distance. Using only the LVM frequencies of H_2 and D_2 and $r_0 = 0.788$ Å reported by Chen *et al.* [12] as fitting parameters, we obtain the dissociation energy D_0 and the ortho-para splittings $\Delta_{H_2(D_2)} = 2\alpha_e$ of H_2 (D_2) in Si. These values are gathered in Table I together with the calculated and experimental data known for free H_2 and H_2 in GaAs. Note that, due to the lack of the experimental data for H_2 in GaAs, we took r_0 equal to that of the free H_2.

From Table I one can see that the experimental values of the ortho-para splittings are somewhat higher than those calculated from Eq. (3), which is apparently explained by the crudeness of the approximation used. However, the calculated values follow the trend expected: The ortho-para splitting grows with the anharmonicity of the potential energy.

An important question concerns why the ortho-para splitting of H_2 has not been detected previously? Being shifted by 9 cm^{-1} from the ortho-H_2 line, the para-H_2 line should be easily detected even at RT, when its FWHM is only 5 cm^{-1}. An answer to this question is provided by Fig. 2, which shows Raman spectra of a Si sample just after the hydrogen plasma treatment [Fig. 2(a)] and after RT storage for 1, 2, and 18 days [Figs. 2(b)–2(d)]. As one can see, the Raman signal of H_2 decreases with storage time. Interestingly, the decay of the H_2 signal in the $J = 1$

TABLE I. Experimental and calculated dissociation energies (D_0) and ortho-para splittings ($\Delta_{H_2(D_2)}$) of the free H_2, H_2 in GaAs, and H_2 in Si. Note that zero-point energy is included in the dissociation energy. All frequencies are in cm^{-1}.

			D_0 (eV)		$\Delta_{H_2(D_2)}$	
Matrix	ω_e	$x\,\omega_e$	Calc.	Expt.	Calc.	Expt.
Free H_2	4411	125	4.8	4.75	4.4 (1.5)	5.9 (2.1)
GaAs	4230	148	3.7		5.9 (2.1)	8 (–)
Si	4015	194	2.6		7.7 (2.7)	9 (3)

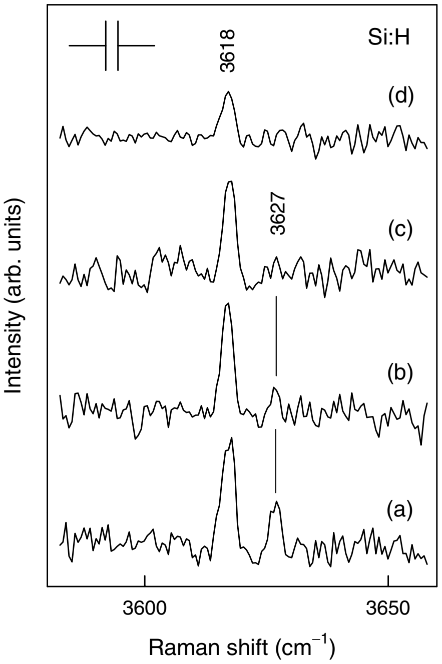

FIG. 2. Raman spectra measured at 95 K after exposure to hydrogen plasma at 230 °C for 4 h: Just after the plasma treatment (a) and after storing the sample at RT for 1 (b), 2 (c), and 18 days (d).

state is slower by approximately a factor of 20 compared to the $J = 0$ state.

The excitation laser light also affects the disappearance of the H_2 signal in the $J = 1$ and $J = 0$ states differently. Figure 3 shows the temperature dependencies of the Raman intensities. The 3627- and 2645-cm^{-1} lines originating from the $J = 0$ states of H_2 and D_2 could be detected only at temperatures below 125 K. These lines decrease in intensity with the temperature and cannot be observed above 160 K. The H_2 and D_2 signals in the $J = 1$ state are much more stable and remain nearly unchanged up to 160 K. At RT measurements, however, ortho-H_2 and para-D_2 are not stable either and could be detected only within the first 10 min of the Raman measurements [18]. Thus, the preferential disappearance of H_2 in the $J = 0$ state from the Raman spectra both during a prolonged RT storage and during the excitation explains why para-H_2 has escaped observation so far.

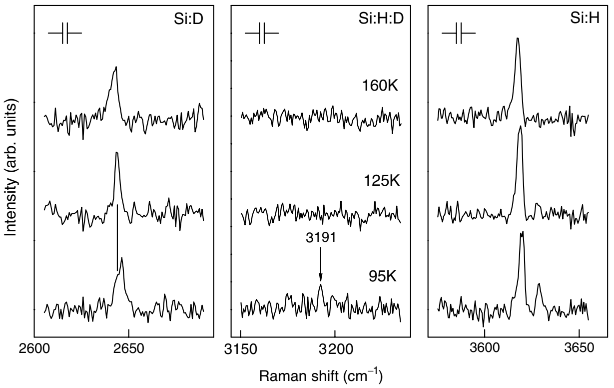

FIG. 3. Raman spectra measured after exposure to hydrogen and/or deuterium plasma at 230 °C for 4 h. The arrow shows the position of the HD line reported by Chen *et al.* Spectra are offset vertically for clarity.

In order to explain this unexpected behavior of the molecule in different rotational states, we consider the following possibilities: (i) different dissociation rates of para- and ortho-H_2; (ii) para-to-ortho transition; (iii) preferential adsorption of para-H_2 at the surface; and (iv) different diffusion rates of para- and ortho-H_2.

The dissociation energy of H_2 is $\sim$5 eV in gas phase and $\sim$3–4 eV in solids (see Table I). This energy is entirely determined by the chemical binding. The difference of the ortho- and para-H_2 ground states is of the order of meV. A preferential dissociation of the para-H_2 species at RT is difficult to envision due to the large energy required and the small energy difference between the two species.

The transition of ortho- to para-H_2 is well known. In particular, the participation of paramagnetic atoms is documented in many papers. However, to our knowledge, a selective transfer to the excited ortho state has not been reported.

A preferential adsorption of ortho-H_2 at low temperature has been long considered as a method for the ortho-para separation [19,20]. This phenomena is explained in terms of hindered rotations of the admolecule. The interaction with the surface does not mix the nuclear-spin states but splits the rotational $J = 1$ state of ortho-H_2. This splitting results in unequal equilibrium concentrations of the ortho and para H_2-admolecules [21]. The preferential adsorption of ortho-H_2 is, however, a temperature dependent process and both ortho- and para-H_2 have equal surface concentrations at RT. We therefore rule out preferential adsorption as a mechanism for the more rapid disappearance of the molecule in the $J = 0$ rotational state.

The probing depth of our Raman experiment is $\sim$1 μm. The total decrease of the H_2 signal with storage time is due to the diffusion of H_2 into the depth of the sample. Because of the equal surface concentration of ortho- and para-H_2 at RT, the relative decrease of para-H_2 to ortho-H_2 is possible only if ortho and para species have different diffusivities.

From the probing depth of the Raman scattering and the spectra presented in Fig. 2, we may estimate the diffusion coefficients of para- and ortho-H_2 at RT, which are equal to 3×10^{-13} and 1.5×10^{-14} cm^2/sec, respectively.

While we cannot provide a full theoretical description of the diffusion process, a qualitative explanation of the different H_2 diffusivities in the $J = 0$ and $J = 1$ states might be as follows. The ortho-para splitting of H_2

implies that the molecule is a free rotator. This situation, however, is specific only for the T site. In the hexagonal interstitial site H of the Si matrix, through which the diffusion takes place, the $J = 1$ state should split into the two states with $m_j = 0$ and $m_j = \pm 1$, where m_j is the projection of the angular momentum. This splitting results in a higher mean energy of ortho-H_2 at the H site, thus increasing its diffusion barrier compared to para-H_2. Note that a difference in the diffusion barrier height of 70 meV between ortho- and para-H_2 could explain our data.

Different diffusivities of ortho- and para-H_2 also provide a direct explanation for why we could never unambiguously observe a Raman line for HD (see Fig. 3). HD is a heteronuclear molecule, and because of this, at low temperature, only the $J = 0$ state is populated. For equal concentrations of H and D in a sample, the ratio of the concentrations of para-H_2, HD, and ortho-D_2 should be 0.25:0.5:0.25. Here we assume that total amounts of all isotope species of the molecule in H- and (H + D)-treated samples are equal. The intensities of the Raman lines are proportional to μ^{-1} times the concentration of the scattering species, where μ is the reduced mass of the molecule [22]. Thus, the expected intensity of the HD line should be only $3/8$ of the para-H_2 line intensity in a *hydrogen*-treated sample, which is apparently below our detection limit.

At higher temperatures, however, when the species of HD with $J = 0$ diffuses quickly into the bulk of the sample, HD molecules with $J = 1$ convert into the $J = 0$ state and leave the surface layer as well.

Here we should mention the Raman scattering studies of Si treated with hydrogen and deuterium plasma performed by Kitajima *et al.* [23]. They reported a Raman line at 3177 cm^{-1} that they assigned to the interstitial HD molecule. However, Kitajima *et al.* conducted their measurements only at RT with H_2:D_2 (1:9) plasma and, therefore, at this stage it is rather difficult to compare this value with the 3191-cm^{-1} line observed by Chen *et al.* at 23 K [12].

Our explanation suggests that the lower diffusivity of ortho-H_2 should occur not only in Si but in any nonparamagnetic matrix. In order to check this idea, we performed Raman measurements on GaAs treated with a hydrogen plasma and have found that, indeed, H_2 trapped at the interstitial T site of GaAs behaves precisely the same way as in Si, i.e., para-H_2 can be detected only at temperatures below 150 K [18].

In summary, we have presented Raman scattering spectra measured on the H_2 and D_2 molecules trapped at the T site of Si. Each isotope gives rise to two Raman lines. Based on the intensity ratios of each pair of the lines as well as on the value of splitting, we conclude that they are due to the ortho and para species of the molecule. The preferential disappearance of para-H_2 and ortho-D_2 ($J = 0$) during laser excitation or during prolonged RT storage was observed. This behavior is tentatively explained by different diffusion rates for ortho- and para-H_2.

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