

# A Raman scattering study of H<sub>2</sub> trapped near O in Si

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## Abstract

Single-crystal silicon wafers exposed to a hydrogen plasma are studied by Raman scattering. Three Raman signals at 3727(1), 3733(1), and 3740(1) cm<sup>-1</sup> ( $T \rightarrow 0$  K) are assigned to ro-vibrational modes of H<sub>2</sub> bound to interstitial oxygen (O–H<sub>2</sub>). By monitoring the trapping kinetics of interstitial H<sub>2</sub> at oxygen it is found that *ortho*- and *para*-H<sub>2</sub> have similar diffusivities. At 77 K, an *ortho*-to-*para* conversion of H<sub>2</sub> within the O–H<sub>2</sub> complex is observed. This conversion occurs with similar kinetics as has been previously observed for isolated interstitial H<sub>2</sub> in Si, and is suggested to be caused by interaction of H<sub>2</sub> with the nuclear magnetic moment of <sup>29</sup>Si.

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## 1. Introduction

Molecular hydrogen can be trapped at different sites of the silicon host lattice. In this study, only isolated interstitial H<sub>2</sub> and O–H<sub>2</sub> in Si are considered. Molecular hydrogen consists of two protons with nuclear spin 1/2, resulting in a total nuclear spin  $I$  of the molecule of either 0 (*para*-H<sub>2</sub> or *p*-H<sub>2</sub>) or 1 (*ortho*-H<sub>2</sub> or *o*-H<sub>2</sub>). The Pauli principle requires the total wave function of the system to be antisymmetric with respect to the permutations of the nuclei, thus allowing only even (odd) values for the rotational quantum number  $J$  for *p*-H<sub>2</sub> (*o*-H<sub>2</sub>) [1]. In the following, if not stated otherwise, the term *o*-H<sub>2</sub> always refers to the  $J = 1$  rotational quantum number, whereas *p*-H<sub>2</sub> stays for  $J = 0$ .

In Raman scattering, *o*-H<sub>2</sub> and *p*-H<sub>2</sub> trapped at the interstitial  $T$  site of the Si lattice [2–4] reveal local vibrational modes at 3618 and 3627 cm<sup>-1</sup> (95 K), respectively, with an intensity ratio of approximately 3:1 at low temperatures [5,6]. With rising temperature, the *ortho*-to-*para* ratio rises due to thermal excitation of *p*-H<sub>2</sub> from the  $J = 0$  to the  $J = 2$  state [6].

Due to the Pauli principle, the conversion from the *ortho* state with  $J = 1$  to the ground state with  $J = 0$  is not allowed for isolated H<sub>2</sub>. However, the presence of a nearby magnetic moment renders this transition allowed [7] and it has recently been observed for isolated interstitial H<sub>2</sub> in Si, occurring with a conversion rate of approximately 0.015 h<sup>-1</sup> at 77 K [8]. This process was suggested to be caused by interaction of H<sub>2</sub> with the nuclear magnetic moment of <sup>29</sup>Si [8].

Additionally, in oxygen-rich Cz Si at elevated temperatures an O–H<sub>2</sub> complex is formed when interstitial H<sub>2</sub> migrates and becomes trapped near an oxygen impurity [2,3,9–12]. IR absorption and the formation kinetics of O–H<sub>2</sub> have been studied by Markevich et al. [9,10] and Pritchard et al. [2,3]. In IR absorption, O–H<sub>2</sub> gives rise to high-frequency vibrations of H<sub>2</sub> at 3731.0, 3737.1, and 3788.9 cm<sup>-1</sup> (4.2 K) [2,11]. Chen et al. have shown that the mode at 3737.1 cm<sup>-1</sup> is due to *p*-H<sub>2</sub> (O–*p*-H<sub>2</sub>), whereas the other two originate from *o*-H<sub>2</sub> (O–*o*-H<sub>2</sub>) [11].

## 2. Experimental

The Cz (FZ) Si samples used in this study were *n*-type, As (P) doped (100) wafers with a resistivity of 0.09 Ω cm (2.6–4.4 Ω cm) and an oxygen concentration of roughly  $7 \times 10^{17}$  cm<sup>-3</sup> ( $3 \times 10^{15}$  cm<sup>-3</sup>). The samples were

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hydrogenated in a remote RF (13.56 MHz, 40 W) plasma for 1 h at a temperature of about 220 °C.

Raman measurements were performed in a pseudo-backscattering geometry using the frequency doubled 532 nm line of a Nd:YVO<sub>4</sub> laser for excitation. Spectral resolution was 3 cm<sup>-1</sup>. Details of the Raman setup and the experimental procedure can be found in Refs. [6,8].

### 3. Results and discussion

#### 3.1. H<sub>2</sub> bound to oxygen

Fig. 1 shows the annealing behavior of a Cz Si sample after hydrogenation. Right after the plasma treatment, two Raman signals at 3617 and 3626 cm<sup>-1</sup> (100 K) appear in the spectra (Fig. 1(a)), originating from *o*-H<sub>2</sub> and *p*-H<sub>2</sub> trapped at the interstitial *T* site of the Si lattice, respectively [2–6]. Upon annealing of the sample at 300 K, these two bands become weaker while three new lines at 3723, 3729, and 3736 cm<sup>-1</sup> (100 K) grow in with the same time constant (Fig. 1(b)–(d)).

Interstitial H<sub>2</sub> diffusing through the Si lattice is trapped by interstitial O available in Cz Si in great amounts. At 300 K, from Ref. [10] one can estimate the trapping time constant  $\tau$  expected for our Cz Si samples with an oxygen content of  $7 \times 10^{17}$  cm<sup>-3</sup> to be  $\tau \approx 21 \pm 2$  h. Fig. 2 shows the change in intensity of the H<sub>2</sub> lines with annealing time for Cz and FZ Si as observed in our experiments. The signals from interstitial H<sub>2</sub> in Cz Si and the three lines at 3723, 3729, and 3736 cm<sup>-1</sup> (100 K) anticorrelate with a time constant of  $\tau \approx 24 \pm 4$  h. Within error bars the both values for  $\tau$  match, suggesting that the three lines originate from H<sub>2</sub> bound to interstitial O (O–H<sub>2</sub>). The results obtained for FZ Si shown in Fig. 2 support this assign-

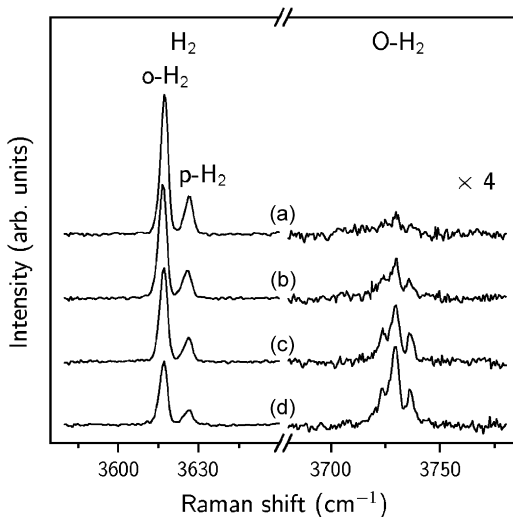


Fig. 1. Raman spectra of (100)-Si after exposure to a hydrogen plasma measured at  $\sim 100$  K: right after the plasma treatment (a), and after annealing the sample at 300 K for 7.5 (b), 19 (c), and 77 h (d). The intensity in the spectral range 3680–3785 cm<sup>-1</sup> was scaled up by a factor of 4. Spectra are baseline corrected and offset vertically for clarity.

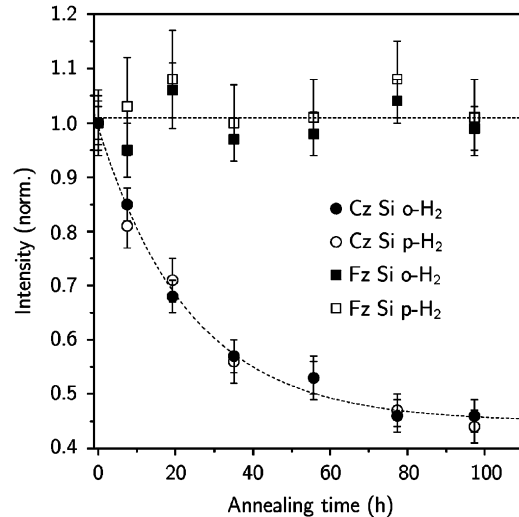


Fig. 2. Normalized intensity of isolated interstitial *ortho*- and *para*-H<sub>2</sub> in Cz and FZ Si as a function of annealing time at 300 K. For Cz Si, the intensity development can be described by  $I(t) \approx 0.54 e^{-t/24} + 0.45$ .

ment. In this case interstitial H<sub>2</sub> remains stable over the whole annealing time and no additional lines were observed in the course of the annealing process (spectra not shown).

In tetrahedral symmetry, the  $J = 1$  *ortho*-state is three-fold degenerate and belongs to a  $T_2$  representation. The presence of oxygen at a neighboring bond centered site leads to a reduction in symmetry, which results in a splitting of the  $T_2$  states into one singly ( $m_J = 0$ ) and one doubly ( $m_J = \pm 1$ ) degenerate levels. Hourahine and Jones calculated the energy difference between these two levels ( $v = 0, J = 1$ ) to be 60 cm<sup>-1</sup>, the doubly degenerate state being higher in energy [13].

For the O–H<sub>2</sub> complex, a line seen in IR absorption at 3737.1 cm<sup>-1</sup> (4.2 K) has previously been assigned to O–*p*-H<sub>2</sub>, and two transitions at 3731.0 and 3788.9 cm<sup>-1</sup> (4.2 K) have been assigned to O–*o*-H<sub>2</sub>, where the initial state for both transitions is the singly degenerate level belonging to  $J = 1$  (see inset in Fig. 3) [11].

The positions of the O–H<sub>2</sub> related lines seen in our spectra when extrapolated to 0 K (see Ref. [6]) are approximately 3727(1), 3733(1), and 3740(1) cm<sup>-1</sup>. We suggest that the 3733 (3740) cm<sup>-1</sup> line seen in our spectra corresponds to the 3731.0 (3737.1) cm<sup>-1</sup> line seen in the IR spectra at 4.2 K, since these transitions are both Raman and IR active [13]. The signal seen in the IR spectra at 3788.9 cm<sup>-1</sup> is not Raman active and can thus not be seen in our spectra [13].

Fig. 3 shows the temperature dependence of the ratio of the intensities of the lines at 3727 and 3733 cm<sup>-1</sup> (0 K) on a logarithmic plot. The linear fit yields an activation energy of  $61 \pm 13$  cm<sup>-1</sup>, which is in good agreement with the predicted splitting of 60 cm<sup>-1</sup> between the two levels belonging to the  $J = 1$  rotational quantum number. Thus we assign this signal to the transition between the twofold degenerate levels of the  $J = 1$  states of O–H<sub>2</sub> with

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