

# Hydrogen isotopic substitution experiments in nanostructured porous silicon

W.D. Palacios<sup>a</sup>, R.R. Koropecski<sup>b,\*</sup>, R.D. Arce<sup>b</sup>, A. Busso<sup>a</sup>

<sup>a</sup> *Facultad de Ciencias Exactas y Naturales y Agrimensura - (UNNE), Avenida Libertad 5500, 3400 Corrientes, Argentina*

<sup>b</sup> *INTEC (CONICET-UNL), Güemes 3450, 3000 Santa Fe, Argentina*

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## Abstract

Nanostructured porous silicon is usually prepared by electrochemical anodization of monocrystalline silicon using a fluorine-rich electrolyte. As a result of this process, the silicon atoms conserve their original crystalline location, and many of the dangling bonds appearing on the surface of the nanostructure are saturated by hydrogen coming from the electrolyte. This work presents an IR study of the effects produced by partial substitution of water in the electrolytic solution by deuterium oxide. The isotopic effects on the IR spectra are analyzed for the as-prepared samples and for the samples subjected to partial thermal effusion of hydrogen and deuterium. We demonstrate that, although deuterium is chemically indistinguishable from hydrogen, it presents a singular behaviour when used in porous silicon preparation. We found that deuterium preferentially forms Si–D groups. A possible explanation of the phenomenon is presented, based on the different diffusivities of hydrogen and deuterium.

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## 1. Introduction

Porous silicon (PS) is a nanocrystalline spongy-type material conformed by a porous network. It presents interesting semi-conducting as well as chemical and optical properties [1–3]. These characteristics can be tailored making the material adequate for a large variety of applications in several fields [1]. PS is generally prepared by anodic electrochemical etching of monocrystalline silicon in an electrolytic solution containing HF. A hydrogen rich layer covers the surface of the PS nanostructure after the anodization. This layer results from the saturation of superficial dangling bonds by protons present in the solution.

The role of hydrogen within the silicon structure has been extensively studied in hydrogenated amorphous and microcrystalline silicon. In these materials IR spectroscopy has been a valuable tool to understand the way in which hydrogen is incorporated to the network [4–7]. In some cases the results have also been used to study the subjacent structure [7,8].

Deuterium has been widely used in replacement of hydrogen to clarify the vibrational properties of the Si–H group. Earlier works [4,9] revealed two main absorption regions in the a-Si:H IR spectrum. One of these regions is a band corresponding to Si–H stretching modes, with contributions peaking at 2000 and 2080 cm<sup>-1</sup>. The effect of the surface is very important on this band. In fact, in a-Si:H samples having a large void density the 2000 cm<sup>-1</sup> peak is almost negligible [10], and the stretching band shifts to larger wavenumbers. The other region, corresponding to the wagging vibrational modes of Si–H bonds presents a band around 650 cm<sup>-1</sup>. In some cases weaker absorption bands at 850 cm<sup>-1</sup> and 890 cm<sup>-1</sup> have also been observed, which were assigned [4,9] to bending vibrations of Si–H bonds in SiH<sub>2</sub> or SiH<sub>3</sub>.

The presence of hydrogen on the surface of the fresh PS nanostructure allows to model the material as a composite involving crystalline silicon, air, and amorphous hydrogenated silicon (a-Si:H) phases. This approach can be tested using the same experimental procedure for PS as for a-Si:H in order to study the hydrogen bonding. Deuterium has also been used as an aid to study hydrogen bonding in PS. Different approaches have been employed to incorporate the deuterium atoms to the

\* Corresponding author.

E-mail address: [rkoro@intec.ceride.gov.ar](mailto:rkoro@intec.ceride.gov.ar) (R.R. Koropecski).

porous silicon structure. Matsumoto and collaborators reported the electrolytic anodization of silicon by using deuterated reagents containing no hydrogen [11,12] to study the luminescence and IR spectra of both free-standing PS samples, and PS layers integrated to the Si substrate. Allongue et al. [13] used SIMS spectroscopy on samples anodized in D<sub>2</sub>O and HF based solutions to study the evolution of the pore network during the preparation. Other authors [14] exposed the samples to atomic deuterium or deuterated reagent in order to study hydrogen interactions in PS using FTIR. Chen et al. [15] studied the stability of PS with FTIR and luminescence spectroscopy on conventionally prepared samples exposed to a deuterium plasma. This work presents results of FTIR combined with incomplete hydrogen effusion experiments. Some samples were prepared using D<sub>2</sub>O in order to achieve partial isotopic substitution of hydrogen bonded in the inner walls of the PS structure. All the results confirm the a-Si:H like nature of the PS nanostructured surface. We show that, unlike the case of partially deuterated a-Si:H, deuterium bonds in preferential sites in PS. This result seems to be incompatible with the usual hypothesis of chemical indistinguishability between deuterium and hydrogen. This hypothesis led us to believe that Si–D and Si–H would be equally distributed in deuterated and hydrogenated samples respectively. However the present results show that this is not the case. We propose a possible explanation for this fact, based on the different diffusivity of H and D.

## 2. Experimental procedure

Samples were prepared by electrochemical anodization of *p*-type monocrystalline silicon substrates, having (100) orientation and a resistivity of 7–17 Ω cm. The anodization was performed in a Teflon reactor with a platinum cathode and using the sample itself as anode. The area exposed to anodization was a 0.5 cm<sup>2</sup> circle. A solution of HF (50%), ethanol and H<sub>2</sub>O in proportions 1:1:1 was used as the electrolyte for standard “hydrogenated” PS samples preparation. The reaction took place during 20 min, at a constant current density of 20 mA/cm<sup>2</sup>. The resulting samples were washed with ethanol and dried in a nitrogen flow. In order to avoid photo-oxidation [16,17] the samples were stored in the dark previous to IR characterization. The same procedure was followed with the deuterated samples replacing H<sub>2</sub>O by D<sub>2</sub>O in the electrolyte to achieve partial substitution of H by D.

IR measurements were performed in the 400–4000 cm<sup>-1</sup> range, using a Spectrum RX-FTIR Perkin-Elmer single beam spectrometer. A piece of non-etched substrate was used as reference.

Hydrogen effusion was measured as described elsewhere [18] in a vacuum chamber pumped with a turbomolecular pump. Ultimate pressure was in the order of 10<sup>-5</sup> Pa. Part of the chamber consists of a quartz tube that can be introduced in a tubular oven. In our complete effusion experiments the temperature was raised up to ~700 °C at a constant rate of 7 °C/min [18]. For the present work the samples were heated up at the same rate, but the temperature ramp was interrupted at 375 °C, and after that the samples were rapidly cooled down. This

procedure results in a partial H (or D) effusion. A Veeco SPI-10 Monopole residual gas analyzer was used to track atomic hydrogen, deuterium, and molecules resulting from their combination (H, D, H<sub>2</sub>, D<sub>2</sub>, and DH).

## 3. Results and discussion

In Fig. 1 we present the IR spectra of the hydrogenated and deuterated samples in the ranges 1400–1700 cm<sup>-1</sup> and 1900–2300 cm<sup>-1</sup>. They resemble the features of the a-Si:H and a-Si:DH IR spectra [9]. Two peaks and a shoulder are clearly distinguishable in the high energy region of the spectra (Fig. 1b). These structures can be observed for the hydrogenated as well as for the partially deuterated samples. It is well known that this region of the spectrum corresponds to stretching vibrational modes of the Si–H<sub>*n*</sub> bonds. Depending on the network structure surrounding the bond, the peaks may be shifted in energy. The lower energy peak in this range is usually assigned to the mono-hydride vibrations, followed by the di- and tri-hydride structures [4]. Fig. 1a shows a peak in the spectrum of the deuterated sample centred at 1528 cm<sup>-1</sup> which has no equivalent feature in the spectrum of the hydrogenated sample.

It is well known that the substitution of H by D gives rise to an isotopic shift of the IR peaks associated with hydrogen bonded as mono-hydrides and di-hydrides. As the substitution is partial in our samples, each peak associated with the Si–H modes will be now split in two. One peak corresponding to Si–H (which remains centred at about the same wavenumber as usually observed in Si:H compounds), and the other corresponding to Si–D (which is downshifted as a consequence of the larger mass of D as compared to H). Furthermore, in the deuterated sample each double oscillator (di-hydride mode) gives rise to three peaks: one of them corresponds to Si–H<sub>2</sub>,

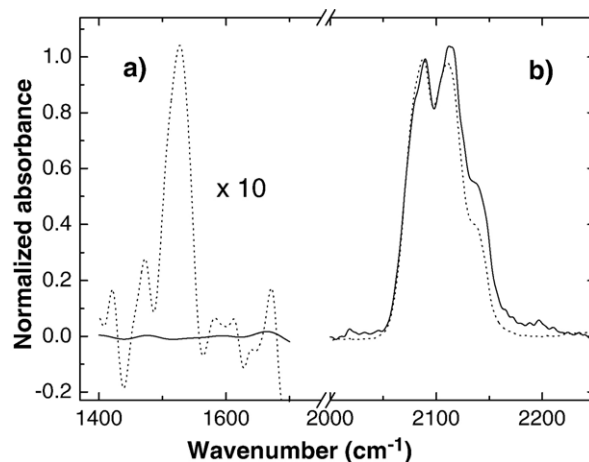


Fig. 1. IR stretching bands of Si–D and Si–H bonds in porous silicon samples. The wavenumber axis was split in two regions. In a) the modes corresponding to the stretching of Si–D bonds are plotted (dotted line) together with the spectrum for the non deuterated sample (full line). In b) the region corresponding to the Si–H stretching modes is plotted for both samples and represented using the same type of lines as in a). In order to compare the behaviour of the different stretching bands, both spectra in b) were normalized to the absorbance band peaking at 2088 cm<sup>-1</sup>, which corresponds to mono-hydride oscillators. The absorbance of both spectra in b) was magnified by a factor of 10.

which remains at the usual wavenumber, and the other two correspond to Si–HD and Si–D<sub>2</sub>, which are shifted to lower wavenumbers.

The ratio between wavenumbers for the peak of Fig. 1a and the centre of the band in Fig. 1b is 1.38. According to the elastic oscillator model this factor should be, for stretching modes, equal to the square root of the ratio between the Si–H and Si–D reduced masses, if only nearest neighbours are considered. This ratio is 1.39, in good agreement with the experimental value. This result is also in agreement with previous reports [12].

A comparison between IR spectra for non deuterated (hereafter referred as “hydrogenated”) and deuterated samples in the range 400–1400 cm<sup>-1</sup> is presented in Fig. 2. This region of the spectrum contains bending modes associated to Si–H (Si–D) bonds. Some characteristics are common to both spectra: the broad band centred at 650 cm<sup>-1</sup>, normally attributed to Si–H wagging modes in a-Si:H, and the rather sharp structure centred around 910 cm<sup>-1</sup>, assigned to SiH<sub>2</sub> scissors modes in a-Si:H. The spectrum corresponding to the deuterated sample shows in this region the existence of at least two extra bands coming from the isotopic substitution, one of them located at 798 cm<sup>-1</sup> and the other at 514 cm<sup>-1</sup>.

The scissors mode of Si–H in SiH<sub>2</sub> group may be interpreted as coming from a classical oscillator composed by the two H atoms connected by a spring. If one of the H atoms is replaced by a D, then the spring should not modify its characteristics, however the oscillation frequency should decrease to 0.87 of the original value. This number corresponds, in good agreement, with the observed value of 798/910=0.88. Likewise, following the same reasoning the replacement of both H atoms by deuterium should shift the central frequency by a factor of 0.707, so that an absorption band located at 643 cm<sup>-1</sup>, corresponding to the scissors mode of the SiD<sub>2</sub> group can be expected. This peak is not visible in our spectra because it is masked by the Si–H

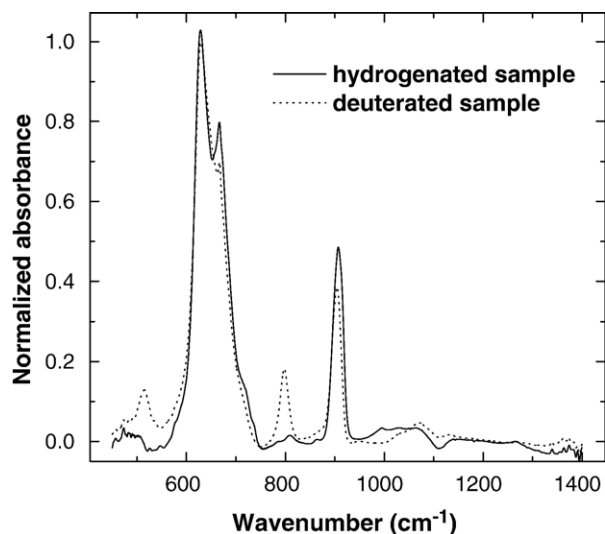


Fig. 2. Spectra of the hydrogenated (full line) and deuterated (dotted line) samples, in the low energy region. Both spectra were normalized to the height of the band peaking at 630 cm<sup>-1</sup>. The isotopic effect becomes apparent through the presence of an extra peak at 798 cm<sup>-1</sup> that corresponds to the scissors mode of Si–D bonds in Si–DH sites.

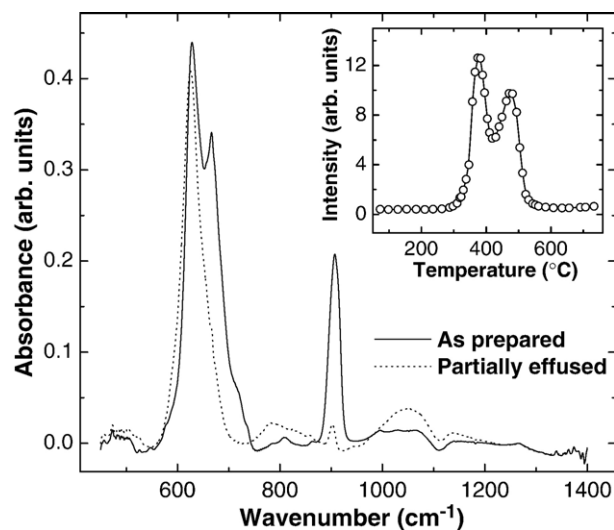


Fig. 3. Comparison between the IR spectra of an as-prepared hydrogenated sample and that of the same sample after a partial hydrogen effusion process (see the text). The complete effusion spectrum of a similar sample is plotted in the inset. The low temperature peak of the effusion spectrum (375 °C) corresponds to hydrogen effusion from di-hydride sites, whereas the high temperature one is related to mono-hydride sites. Since the partial effusion process was let to proceed up to 375 °C, the di-hydride sites were almost totally emptied.

wagging band. It is worth to note that a band at 650 cm<sup>-1</sup> appears in fully deuterated amorphous silicon samples [4,9] as well as in fully deuterated PS [11].

The weak band observed at 514 cm<sup>-1</sup> in the spectrum of the deuterated sample can be attributed to the isotopic shift of wagging modes, which peak between 600 and 700 cm<sup>-1</sup> for the hydrogenated sample. The wavenumber ratio, which should be also 1.39 for such isotopic change, is actually  $\sim 650/514=1.26$ . The reason for this discrepancy can be attributed [4,9] to the interaction of the Si–D wagging mode with nearby transverse optical vibrations of the Si–Si matrix, which are at 480 cm<sup>-1</sup>. This assignment has been made previously to similar features in a-Si:D IR spectra [4,9].

Some structures may be observed in the 660 cm<sup>-1</sup> band, whose origin was clarified by a partial hydrogen effusion experiment. Fig. 3 depicts the results of that experiment. The plot in the inset (Fig. 3) shows the complete hydrogen effusion spectrum in which two distinct peaks are noticeable [18]. The low temperature (LT) peak corresponds to H effused from di-hydrides, whereas the high temperature (HT) peak corresponds to H effused from mono-hydrides [19]. In the partial effusion experiment the sample was heated up at the same heating rate used in a complete effusion experiment, but the temperature ramp was stopped at 375 °C and the sample was rapidly cooled down. In this way hydrogen bonded as di-hydrides was preferentially effused. Fig. 3 shows a comparison between the spectrum of a hydrogenated sample before and after effusion. As it can be seen, although thermal rearrangement of the hydrogen bonding might occur during the effusion experiment, the peaks that reduce their height after effusion correspond to modes associated to H bonded as di-hydrides (according to the assignments made for a-Si:H). This result supports the assignment made for the 908 cm<sup>-1</sup> peak, because after partial hydrogen

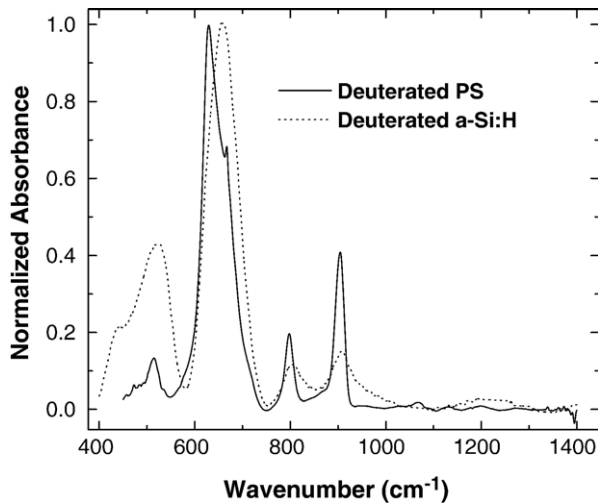


Fig. 4. Comparison between the spectra of a deuterated porous silicon sample with that of a deuterated a-Si:H one. The a-Si:DH spectrum has been taken from Ref. [9].

effusion this band almost disappears. Based on identical reasons, the peak at  $666\text{ cm}^{-1}$  can be associated to the wagging mode of Si–H bonds in di-hydrides, and the peak at  $628\text{ cm}^{-1}$  should be associated to the wagging mode of Si–H bonds in mono-hydrides. These assignments will be considered later on, as basis for a simple model constructed to study the behaviour of the spectra.

Fig. 4 compares the IR spectrum of our PS deuterated sample with the spectrum of a-Si:H deposited by sputtering using hydrogen and deuterium in the gas mixture [9] (hereafter named a-SiD:H sample). Peaks in both spectra are centred at the same wavenumbers. On the other hand, peak assignments for IR spectra obtained after partial substitution of H by D indicates that: a) The band at  $798\text{ cm}^{-1}$  corresponds to scissors modes from Si–DH bonds. b) The band at  $514\text{ cm}^{-1}$  corresponds to wagging modes from Si–D and Si–D<sub>2</sub> bonds.

It is worth noting that in the plot of Fig. 4 the ratio between the areas corresponding to the scissors modes of SiH<sub>2</sub> and SiHD bonds for the PS deuterated sample is different from the ratio of areas corresponding to the wagging modes. This is a rather unexpected behaviour because hydrogen and deuterium are chemically identical so that, in principle, the probability of substitution of H by D should be independent of the bond type. Based on the fact that deuterium and hydrogen are chemically indistinguishable, this effect on PS samples can only be explained through processes controlled by the mass of participating atoms, e.g., the diffusion constant involved in the mass transport during sample preparation.

To corroborate the validity of the previous analysis on the area ratios, we made a computer simulation based on a simple model which takes into account the chemical equivalence of hydrogen and deuterium. Let us consider a hydrogenated PS sample, with  $M$  mono-hydride and  $N$  di-hydride sites. The simulated IR spectrum of a deuterated sample is obtained from this ideal hydrogenated sample using the following hypotheses:

- A number of hydrogen atoms of the hydrogenated sample is replaced by deuterium. The probability of a given hydrogen

atom to be replaced by a deuterium is  $p$ , independently of the site.

- The oscillator strengths of the modes associated to Si–D bonds are equal to those of the equivalent Si–H ones.
- The wagging mode of the hydrogenated sample consists of the superposition of two contributions; one corresponding to mono-hydrides and the other — located at a larger wavenumber — corresponding to di-hydrides. The oscillator strengths of the two kinds of oscillators are assumed to be the same.

The parameters of the model are obtained by fitting experimental spectra. The low wavenumber region ( $400$  to  $1400\text{ cm}^{-1}$ ) of the spectrum of the hydrogenated sample (full line in Fig. 2) can be fitted by the superposition of three peak functions. The best fit is obtained by using two Lorentzian functions  $W_{\text{H}}^{\text{F}}(\omega)$  and  $W_{\text{H}_2}^{\text{F}}(\omega)$  for the wagging modes and a Gaussian function  $\text{Sc}_{\text{H}_2}^{\text{F}}(\omega)$  for the scissors mode.

The absorbance  $A(\omega)$  can be written as:

$$A(\omega) \sim K_w \cdot (M W_{\text{H}}(\omega) + 2N W_{\text{H}_2}(\omega)) + K_{\text{sc}} N \text{Sc}_{\text{H}_2}(\omega) \quad (1)$$

Where  $W_{\text{H}}(\omega)$ ,  $W_{\text{H}_2}(\omega)$ , and  $\text{Sc}_{\text{H}_2}(\omega)$ , are the corresponding fitting functions ( $W_{\text{H}}^{\text{F}}(\omega)$ ,  $W_{\text{H}_2}^{\text{F}}(\omega)$ , and  $\text{Sc}_{\text{H}_2}^{\text{F}}(\omega)$ ) normalized to unit area.  $K_w$  and  $K_{\text{sc}}$  are the oscillator strengths of the wagging and scissors modes, respectively. The oscillator strength for the mode  $i$  is defined as

$$K_i = \frac{1}{N_i^{\text{osc}}} \int_0^{\infty} \frac{\alpha}{\omega} d\omega \approx \frac{C}{N_i^{\text{osc}}} \int_0^{\infty} \alpha d\omega$$

where  $N_i^{\text{osc}}$  is the density of oscillators for the  $i$  mode,  $\alpha$  is the absorption coefficient, and  $C$  is a constant.

The values of  $N$ ,  $M$  and the oscillator strengths can be obtained from the spectrum fit as follows:

Provided the  $W_{\text{H}}$ ,  $W_{\text{H}_2}$  and  $\text{Sc}_{\text{H}_2}$  functions are normalized, the areas under the wagging bands of the experimental spectrum are:

$$\begin{aligned} A_{\text{H}}^{\text{Wagg.}} &= M K_w, \\ A_{\text{H}_2}^{\text{Wagg.}} &= 2N K_w, \end{aligned}$$

whereas the area under the scissors mode is:

$$A^{\text{Sc}} = N K_{\text{sc}}.$$

The  $N$  value can be arbitrarily taken as one, so that  $K_w = \frac{A_{\text{H}_2}^{\text{Wagg.}}}{2}$ ,  $K_{\text{sc}} = A^{\text{Sc}}$ , and  $M = \frac{2A_{\text{H}}^{\text{Wagg.}}}{A_{\text{H}_2}^{\text{Wagg.}}}$ .

Taking into account the above mentioned hypotheses, the density of sites for the deuterated sample are:

$$\begin{aligned} [\text{D}_2] &= p^2 \text{ for Si - D}_2, \\ [\text{H}_2] &= (1 - p)^2 \text{ for Si - H}_2, \\ [\text{DH}] &= 2 p (1 - p) \text{ for Si - DH}, \\ [\text{H}] &= M(1 - p) \text{ for Si - H, and} \\ [\text{D}] &= M_p \text{ for Si - D.} \end{aligned}$$

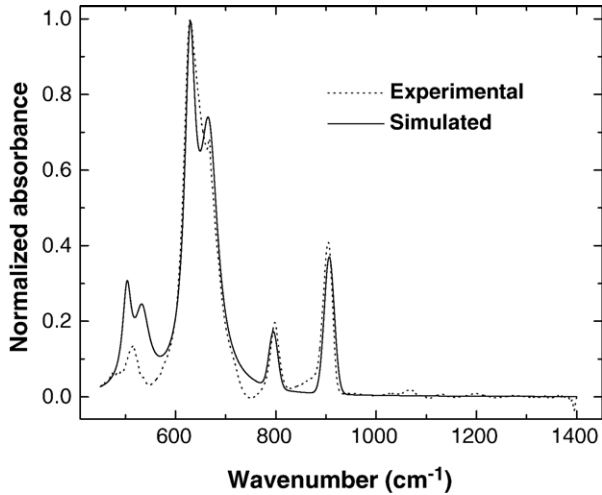


Fig. 5. Comparison between the experimental spectrum of a deuterated porous silicon sample, and the result of the simulation obtained with Eq. (2). The main hypothesis of the simulation is that deuterium occupies all the sites with the same probability.

Considering the isotopic shifts, the central frequencies of the different bands of the spectrum for our PS deuterated sample are  $\omega_{\text{Sc}}^{\text{DH}} = 798 \text{ cm}^{-1}$ ,  $\omega_{\text{Sc}}^{\text{D}_2} = \frac{\omega_{\text{H}_2}}{1.41} = 643 \text{ cm}^{-1}$ ,  $\omega_{\text{W}}^{\text{D}} = \frac{\omega_{\text{H}}^{\text{H}}}{1.26} = 499 \text{ cm}^{-1}$  and  $\omega_{\text{W}}^{\text{D}_2} = \frac{\omega_{\text{H}_2}^{\text{H}}}{1.26} = 529 \text{ cm}^{-1}$ . We take two new normalized Lorentzians,  $W_{\text{D}}(\omega)$  and  $W_{\text{D}_2}(\omega)$ , centred at  $\omega_{\text{W}}^{\text{D}}$  and  $\omega_{\text{W}}^{\text{D}_2}$ , for the D and D2 wagging modes; and two new normalized Gaussians,  $\text{Sc}_{\text{D}_2}$  and  $\text{Sc}_{\text{DH}}$ , for the scissors modes involving deuterium. Therefore, the absorbance spectrum of the deuterated sample can be written as:

$$A_{\text{D}}(\omega) \sim K_{\text{W}} \cdot ([\text{H}] W_{\text{H}}(\omega) + 2[\text{H}_2] W_{\text{H}_2}(\omega) + [\text{DH}] W_{\text{H}_2}(\omega) + [\text{DH}] W_{\text{D}_2}(\omega) + [\text{D}] W_{\text{D}}(\omega) + 2[\text{D}_2] W_{\text{D}_2}(\omega) + K_{\text{Sc}}([\text{H}_2] \text{Sc}_{\text{H}_2}(\omega) + [\text{DH}] \text{Sc}_{\text{DH}}(\omega) + [\text{D}_2] \text{Sc}_{\text{D}_2}(\omega)) \quad (2)$$

where  $[\text{H}]$ ,  $[\text{H}_2]$ ,  $[\text{DH}]$ ,  $[\text{D}]$ , and  $[\text{D}_2]$  are the  $p$ -dependent concentrations.

The experimental spectrum of the deuterated PS sample is plotted in Fig. 5, together with the outcome of the simulation using  $p=0.19$ . As can be clearly observed in Fig. 5, the proposed model reproduces reasonably well the spectrum of the deuterated sample except in the region of the wagging modes involving deuterium.

A similar analysis can be made for the spectrum of the a-Si:DH sample taken from Ref. [9]. Since we have no spectrum of an a-Si:H sample prepared using the same deposition system and conditions as that of the a-Si:DH one, the corresponding a-Si:H must be inferred. In order to derive that spectrum we assume that the wagging and scissors peaks corresponding to the Si–H bonds in a-Si:H are centred at the same wavenumber, and they have the same width as those of the a-Si:DH sample. In this case there is no structure in the Si–H wagging band, so that it can be well fitted using a single Gaussian. Fig. 6 shows the fitting for the a-Si:DH spectrum as well as the inferred spectrum for the a-Si:H sample.

Unlike the PS case, when the model is applied to a-Si:DH, it predicts the same area ratio between the wagging and scissors modes of hydrogenated and deuterated bonds, in agreement with the experimental result shown in Fig. 6. Considering this fact, the behaviour shown in Fig. 5 for the PS spectrum can be explained assuming that deuterium substitutes hydrogen preferentially in multiple hydride sites. Otherwise, the ratio between those wagging modes related to hydrogen, and those related to deuterium should be the same as that observed for scissors modes, as in the case of the a-Si:DH sample.

This interpretation is also supported by the behaviour of the stretching band in the spectrum of the deuterated sample when compared with that of the hydrogenated one. This can be observed in fact in Fig. 1b, where the spectra of the deuterated and hydrogenated samples were normalized to the intensity of the peak located at  $2088 \text{ cm}^{-1}$ , corresponding to the stretching mode of the Si–H bonds in mono-hydrides. The peak at  $2110 \text{ cm}^{-1}$  and the shoulder at around  $2150 \text{ cm}^{-1}$ , which are related to stretching vibration of Si–H bonds in di- and tri-hydrides respectively, are lower in the normalized spectrum for the deuterated sample than the corresponding features in the spectrum for the hydrogenated sample. Since the two samples should be chemically indistinguishable, it can be concluded that deuterium atoms substitute H atoms at multiple bonds to silicon in a larger proportion than at single bonds, which is a rather unexpected result.

Since the chemical indistinguishability hypothesis is very well supported, the reason for the observed effect should be searched in a dependence of the  $p$  value on the site where deuterium is bonded. Considering the difference between the mobilities of hydrogen and deuterium atoms present in the electrolyte, the pore size distribution of PS may produce differences in  $p$ .

It is well known that very small pores can be present in PS, and that more than one size scale may coexist [16,18]. The diffusion coefficient of hydrogen is considerably larger than that of deuterium [20]. Therefore, it is expected that during

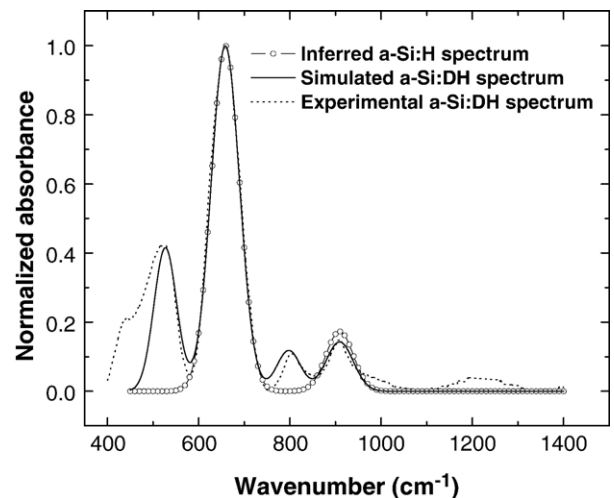


Fig. 6. Comparison between the spectrum of the a-Si:DH sample with the simulated one. The circles show the inferred spectrum for the a-Si:H sample.

preparation, hydrogen could reach the inner surfaces of smaller pores easier than deuterium. If due to size reasons the probability of multiple bonding were larger in pores having a larger size than in smaller ones, the probability of having Si–H bonds in small pores will be larger than that of having Si–D bonds. This situation is equivalent to have lower isotopic substitution probability for sites having mainly mono-hydride bonds.

#### 4. Conclusions

Experiments of partial hydrogen effusion and isotopic substitution of H by D were performed on porous silicon samples. A detailed analysis of the resulting IR spectra together with a numerical simulation turned evident that, despite the chemical indistinguishability between H and D, deuterium incorporates to the sample preferentially in multiple hydride sites. This behaviour can be attributed to the difference between diffusion constants of deuterium and hydrogen in the pore network, combined with size effects which preclude the formation of multiple hydrides in small pores during preparation.

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