

## Hydrogen microstructure in hydrogenated amorphous silicon

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We present a method to determine the local hydrogen bonding structure in hydrogenated amorphous silicon from infrared spectroscopy measurements. This approach is based on a different oscillator strength and refractive index for hydrogen atoms located in the isolated and clustered phase. It is demonstrated that the density of distributed hydrogen atoms does not exceed 3–4 at.%, independent of the deposition conditions for several deposition techniques. We suggest that changes in the infrared-absorption strength upon ion bombardment or light soaking can be attributed to a hydrogen exchange between clustered and isolated phases. [S0163-1829(96)05248-4]

### I. INTRODUCTION

It is generally believed that the structural properties of hydrogenated amorphous silicon (*a*-Si:H) are determined by the hydrogen bonding configurations. Hydrogen in the bulk of the material passivates isolated dangling bonds, and may positively influence the structure of *a*-Si:H. Hydrogen atoms gathered in a clustered phase, however, give rise to potential fluctuations in the bulk thereby deteriorating the optical and electrical properties.<sup>1</sup> It is therefore, both from a scientific and technological point of view, important to know exactly the concentration of clustered hydrogen atoms.

A method to determine the density of clustered hydrogen is nuclear magnetic resonance (NMR).<sup>2–4</sup> Two local environments for hydrogen in *a*-Si:H have been identified. The first is the isolated or distributed phase, where the SiH bonds are well separated from each other. The second phase contains the remainder, and consists of small clusters of hydrogen atoms which are either bonded to the same silicon atom or to neighbors within a few Å. This technique generally suggests that the density of hydrogen in the isolated phase cannot exceed 2–4 at.%, regardless of the preparation conditions.

In this paper, we use infrared spectroscopy to determine the density of clustered hydrogen atoms. In this approach, we assume that a hydrogen atom is isolated if the vibrating silicon-hydrogen dipole experiences screening effects of the surrounding solid state. The vibrational spectrum of hydrogenated amorphous silicon contains wagging, bending, and stretching modes. The absorption band near 640 cm<sup>-1</sup> is attributed to the wagging or rocking modes. To this absorption band monohydrides as well as dihydrides (SiH<sub>2</sub>) contribute. It appears experimentally that the integrated strength of this mode is proportional to the total hydrogen concentration.<sup>5,6</sup> Bending modes due to multihydrides appear near 850 and 890 cm<sup>-1</sup>. Two stretching modes are present near 2000 and 2100 cm<sup>-1</sup>, ascribed to SiH and SiH<sub>2</sub>, respectively.<sup>7</sup> The density of clustered hydrogen is usually correlated with the strength of the 2100-cm<sup>-1</sup> mode or by the microstructure parameter  $R^*$ , defined by the ratio of the strength of the 2100 cm<sup>-1</sup> mode and the sum of the strengths of the 2000- and 2100-cm<sup>-1</sup> modes.

### II. CALCULATIONS

Our analysis starts by establishing the matrix elements for the two stretching modes near 2000 and 2100 cm<sup>-1</sup> in *a*-Si:H and *a*-Si:C:H. The integrated absorption  $I_i$  of a mode  $i$  is defined as

$$I_i = \int_{-\infty}^{+\infty} \alpha_i(\omega) d\omega / \omega, \quad (1)$$

with  $\alpha_i(\omega)$  the absorption coefficient and  $\omega$  the frequency. The integrated absorption of mode  $i$  scales with the hydrogen concentration  $n_{H_i}$  and its proportionality constant  $\Gamma_i$ , which can be regarded as a cross-section for infrared photon absorption. Hence the absorption of the stretching modes can be written as:

$$I = I_{2000} + I_{2100} = \Gamma_{2000} \times n_{H_{2000}} + \Gamma_{2100} \times n_{H_{2100}}, \quad (2)$$

where  $n_{H_{2000}}$  is the density of hydrogen vibrating in the 2000-cm<sup>-1</sup> mode, and  $n_{H_{2100}}$  the hydrogen density in the 2100-cm<sup>-1</sup> mode.  $I_{2000}$  and  $I_{2100}$  are the integrated absorptions of the 2000 and 2100-cm<sup>-1</sup> modes, respectively. To be consistent with earlier infrared studies, we use the matrix element  $A$ , defined as  $1/\Gamma$ . Several studies have been published where the matrix elements  $A_{2000}$  and  $A_{2100}$  are determined by fitting Eq. (2) to the hydrogen content obtained from elastic recoil detection (ERD) for a series of films with varying strengths of the 2000 and 2100-cm<sup>-1</sup> mode. Shanks *et al.*<sup>5</sup> and Fang *et al.*<sup>8</sup> proposed an equal matrix element for the two modes,  $A = 14 \times 10^{19}$  cm<sup>-2</sup>; Langford *et al.*<sup>6</sup> suggested two matrix elements, i.e.,  $A_{2000} = 9.0 \times 10^{19}$  cm<sup>-2</sup> and  $A_{2100} = 22 \times 10^{19}$  cm<sup>-2</sup>. These values are close to the matrix elements proposed by Amato *et al.*<sup>9</sup> The fact that different values are found can be attributed to the possibility of different hydrogen bonding configurations in the films or to differences in the infrared data analysis methods used.<sup>10</sup> The presence of small amounts of unbounded hydrogen can also contribute to the differences in the values of  $A$  found in the literature.

It should be pointed out that these matrix elements were derived using the assumption that they do not depend on the total-hydrogen concentration. The matrix element  $A_i$  for a mode  $i$  can be written as<sup>11</sup>

$$A_i = cn_f \mu \omega_i / (2\pi^2 e_i^{*2}) \text{ cm}^{-2}, \quad (3)$$

where  $c$  is the speed of light,  $n_f$  the refractive index,  $\mu$  the reduced mass,  $\omega_i$  the frequency of mode  $i$ , and  $e_i^*$  the effective charge or oscillator strength of the dipole. This effective charge in the solid now differs from the effective charge in gaseous molecules because the vibrating dipoles are screened by the surrounding solid state. As the hydrogen concentration increases, the silicon concentration and the refractive index decrease. The amorphous network becomes less dense, and the screening decreases. Therefore, from a physical viewpoint, the matrix elements are dependent on the total hydrogen concentration. Having noted this, we are led to suggest an alternative two-phase model describing the relationship between the hydrogen bonding configurations and their matrix elements:

$$I = I_d + I_x = n_{H_d} / A_d + n_{H_x} / A_x, \quad (4)$$

with  $A_d$  and  $A_x$  the matrix elements for distributed and clustered hydrogen, respectively. In this model, a hydrogen atom is considered to be clustered if the dipole moment is not screened by the surrounding silicon network, which implies that the effective charge  $e_x^*$  for clustered SiH bonds can be taken equivalent to the effective charge of the free molecule. Brodsky, Cardona, and Cuomo<sup>12</sup> listed the absorption strength of the stretching modes of silane and various polysilane chains. From these data, we find  $e_x^* = (0.16 \pm 0.01)e$ . Within the experimental error does this charge not depend on  $n$  for the various  $\text{SiH}_n$  ( $n=1-4$ ) configurations. From Eq. (3), we calculate  $A_x = (17 \pm 1) \times 10^{19} \text{ cm}^{-2}$ . A hydrogen atom is in the distributed phase if it is tightly embedded in the silicon matrix with high refractive index.<sup>13</sup> The corresponding effective charge can be obtained indirectly from the wagging modes near  $640 \text{ cm}^{-1}$ . It appears that, in contrast to the stretching modes, the wagging mode is proportional to the total hydrogen content for a wide range of values for the total hydrogen content,<sup>5,6</sup> which implies that the matrix elements for clustered and distributed hydrogen are equal for this mode. Langford *et al.*<sup>6</sup> proposed  $A_{640} = (2.1 \pm 0.3) \times 10^{19} \text{ cm}^{-2}$  as the matrix element, corresponding to  $e_d^* = (0.47 \pm 0.03)e$  and  $e_x^* = (0.23 \pm 0.02)e$ . The effective charge  $e_d^*$  for isolated SiH bonds, corresponds to  $A_d = (6.7 \pm 1) \times 10^{19} \text{ cm}^{-2}$  as a matrix element for the stretching modes. If the total hydrogen concentration  $n_H$  is known,  $n_{H_d}$  and  $n_{H_x}$  can be calculated from Eq. (4), since  $n_H = n_{H_d} + n_{H_x}$ .

### III. RESULTS

In Fig. 1, we plot the density of isolated and clustered hydrogen versus the total hydrogen concentration as determined by ERD. The data are obtained from various sources.<sup>6,9,14,15</sup> The series include films deposited by rf glow-discharge deposition, magnetron sputtering, low-pressure chemical-vapor deposition (LPCVD) and  $a\text{-Si:C:H}$  alloys made by glow-discharge deposition.<sup>16</sup> In our approach, a hydrogen atom is distributed if it is embedded in the silicon matrix, i.e., if there are no other hydrogen atoms within a

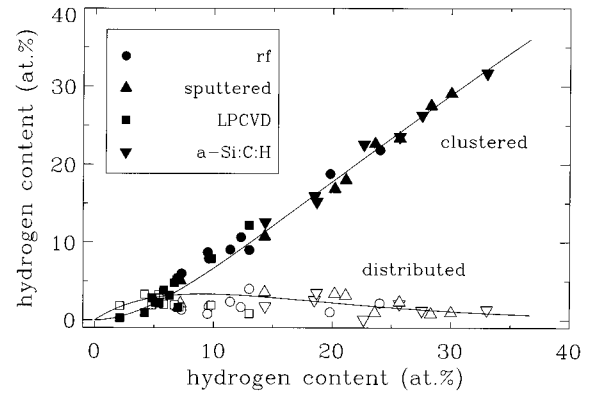


FIG. 1. Density of distributed (open symbols) and clustered hydrogen (closed symbols) versus the total hydrogen content. The error has the size of the markers, and is estimated from the error in the integrated absorption coefficient. The solid curves reflect the distribution function of Eq. (5) with  $r_c = 5.9 \text{ \AA}$ . The data are from Refs. 6, 9, 14, and 15.

critical spherical volume  $V_c$  surrounding the vibrating SiH bond. The density of hydrogen in the isolated phase is<sup>17</sup>

$$n_{H_d} = n_H \exp(-n_H V_c), \quad V_c = \frac{4\pi r_c^3}{3}. \quad (5)$$

The correlation radius  $r_c$  for the data in Fig. 1 is between 5 and 7  $\text{\AA}$ ; the best fit is obtained for  $r_c = 5.9 \text{ \AA}$ . It can be seen in Fig. 1 that the density of distributed hydrogen does not exceed 3–4 at. % for a wide variety of preparation conditions, which shows that the limited hydrogen solubility is related to the limited solubility in the matrix. Furthermore, the density of distributed hydrogen is nearly independent of the total hydrogen content between  $\approx 3$  and  $\approx 25$  at. %; these observations are in excellent agreement with NMR measurements<sup>2-4</sup> and hydrogen diffusion and small-angle x-ray-scattering experiments in hydrogen-implanted  $a\text{-Si}$ .<sup>18</sup> Another observation is that the density of clustered hydrogen does not depend on the frequency of the stretching mode. For example, the  $2000\text{-cm}^{-1}$  mode is much stronger than the  $2100\text{-cm}^{-1}$  mode for the magnetron sputtered films, while the opposite is observed for the carbon containing films, yet the data points in Fig. 1 show the same general behavior. Hence a part of the  $2000\text{-cm}^{-1}$  mode contains clustered hydrogen as well, which is also in agreement with recent NMR measurements.<sup>19</sup> The  $a\text{-Si:C:H}$  alloys reveal the same behavior as the  $a\text{-Si:H}$  films, which shows that the increase of the absorption strength of the stretching modes with carbon alloying is related to an increase of the hydrogen content. This does not support earlier suggestions that the increase of the infrared activity with increasing carbon concentration is related to a higher oscillator strength of the SiH dipole, caused by charge transfer of backbonded carbon atoms.<sup>11</sup> On the other hand, it should be noted that the carbon content in these  $a\text{-Si}_{1-x}\text{C}_x\text{:H}$  films is low ( $x < 0.2$ ), and that the matrix elements  $A_d$  and  $A_x$  may not be appropriate at higher carbon contents.<sup>20</sup>

### IV. DISCUSSION

#### A. Variability of matrix elements

The results in Sec. III suggest that the density of clustered hydrogen can no longer be associated with the  $2100\text{-cm}^{-1}$

mode alone. The microstructure parameter  $R^*$  generally underestimates the fraction clustered hydrogen since a part of the  $2000\text{-cm}^{-1}$  mode is clustered as well. Another consequence is that the matrix elements  $A_{2000}$  and  $A_{2100}$  can no longer be assumed constant, since they depend on the local hydrogen bonding configurations. As far as this point is concerned, two earlier infrared studies are noteworthy. Oguz *et al.*<sup>21</sup> found that bombardment of  $a\text{-Si:H}$  with 100- and 200-keV  $\text{He}^+$  ions selectively increases the strength of the 640- and  $2000\text{-cm}^{-1}$  modes. In view of the present results, an explanation is a change in hydrogen bonding configurations by the bombardment. A plausible mechanism is that Si-Si bonds in hydrogen-depleted regions are broken, and that some of the monohydrides precipitating in hydrogen rich clusters are transferred to the bulk, thereby passivating the dangling bonds induced by the ion bombardment. Since silicon-hydrogen dipoles in the bulk have higher infrared intensities, the absorption strength of the 640- and  $2000\text{-cm}^{-1}$  modes may increase while the total hydrogen content does not change. The same mechanism can explain the results of Zhao *et al.*,<sup>22</sup> who found that the integrated strength of the SiH stretching modes in  $a\text{-Si:H}$  increased under illumination. It was suggested that newly formed dangling bonds were passivated by free hydrogen atoms or molecules, resulting in an increase of the SiH bond density. However, to passivate the light-induced dangling bonds, a hydrogen exchange between isolated and clustered phases may take place and, it is fairly well possible that the infrared intensity increases while the bonded hydrogen content remains the same. Although such a hydrogen exchange may be accompanied by changes in the oscillator strength attributable to bombardment or light-induced defects such as dangling bonds, it still implies a dependency of the matrix elements for the stretching modes on the local environment of the vibrating dipoles.

### B. Effective charge of the IR-absorption modes

In this section we discuss the factors which determine the value of the effective charges of the wagging and stretching modes. First, we discuss the anomaly between the dynamical charges of the wagging and stretching modes. The effective charge  $e_d^*$  was assumed equivalent for the two modes, while  $e_x^* \approx 0.16e$  for the stretching modes and  $e_x^* \approx 0.23e$  for the wagging modes. Since the strength of a mode scales with the square of its effective charge [Eq. (3)], the wagging mode for clustered hydrogen is  $(0.23/0.16)^2 \approx 2$  times stronger than the stretching mode. We interpret this number in the following way. In the isolated phase, hydrogen is bonded as monohydrides only. In the clustered phase, however, hydrogen is bonded both as clustered monohydrides and dihydrides. The difference between the wagging mode and the stretching modes is that both SiH and  $\text{SiH}_2$  contribute to a single wagging mode near  $640\text{ cm}^{-1}$ , while SiH bonds have their stretching frequencies near  $2000\text{ cm}^{-1}$ , and  $\text{SiH}_2$  bonds have their frequencies near  $2100\text{ cm}^{-1}$ . Hence the wagging mode for clustered hydrogen is twofold degenerated, corresponding to a factor  $\sqrt{2}$  in its effective charge.

It remains to be explained which factors can increase the effective charge of the SiH bond in the free molecule to  $e_d^* \approx 0.47e$ . A possibility to explain this high effective charge

is to introduce local-field factors. Following the analysis of Brodsky, Cardona, and Guarnieri,<sup>12</sup> the effective charge of a SiH bond embedded in a network with dielectric constant  $\epsilon$  is

$$e^* = \frac{3\epsilon}{1+2\epsilon} e_x^*. \quad (6)$$

With  $\epsilon \approx 3.7^2$  and  $e_x^* \approx 0.16e$  we derive  $e^* \approx 0.23e$ . Hence, the calculated value for the effective charge of the isolated SiH bond using this approach is far from the experimental value, which may be expected since local-field factors do not take into account the effect of network distortions.

We point out that the infrared activity of the SiH bond in the solid state can arise from two different mechanisms. First, there is a static mechanism, associated with charge transfer of the vibrating atoms due to differences in their electronegativity.<sup>23</sup> At the same time, however, the vibrating atoms can alter the charge distribution by inducing further distortions in the amorphous network (dynamic mechanism). Winer and Cardona<sup>23</sup> argued that in general the dynamic charges dominate over the static charges in semiconductors. Of course, the latter mechanism can only contribute to the effective charge of the SiH bonds in the isolated phase. Winer and Cardona also obtained excellent agreement between theory and experiment for  $a\text{-Si}$  over the entire spectral range using a single effective dynamical charge  $e^* = 0.44e$ , determined by charge transfer due to phonon-induced bond-angle distortions.

We can understand the infrared absorption of the silicon-hydrogen dipoles in  $a\text{-Si:H}$  in the following way. The effective charge of clustered hydrogen atoms is determined by their static charge ( $0.16e$ ), while the effective charge of the SiH bonds embedded in the bulk is determined by their static and dynamic charge. It is interesting to note that if we assume no interference between the static and dynamic mechanisms, it follows that the dynamic charge of the isolated SiH bond is equal to the dynamic charge of Si-Si bonds, i.e.,  $e_d^{*2} = (0.47e)^2 = (0.16e)^2 + (0.44e)^2$ , which is an interesting result for understanding the infrared absorption process.

Finally, we present a formula to estimate the hydrogen content in  $a\text{-Si:H}$  from the integrated strength of the stretching modes. Under the assumption that the density of isolated hydrogen is constant,  $n_{\text{H}_d} \approx 1.6 \times 10^{21}\text{ cm}^{-3}$  ( $\approx 3$  at.%), the hydrogen content approximately is

$$n_{\text{H}} = n_{\text{H}_d} + n_{\text{H}_x} = n_{\text{H}_d} + A_x(I - I_d) \approx -n'_{\text{H}_d} + A_x I, \quad (7)$$

with  $n'_{\text{H}_d} = (A_x/A_d - 1) \times n_{\text{H}_d} \approx 2.4 \times 10^{21}\text{ cm}^{-3}$ .

## V. CONCLUSIONS

In summary, we have presented a method to calculate the number of distributed and clustered hydrogen atoms in amorphous silicon. This method is based on the strength of the stretching mode in the infrared-absorption spectrum. We found that the density of distributed hydrogen does not exceed 3–4 at. % for a large variety of preparation conditions.

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