Calorimetry of hydrogen desorption from *a*-Si nanoparticles

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The process of hydrogen desorption from amorphous silicon (*a*-Si) nanoparticles grown by plasma-enhanced chemical vapor deposition (PECVD) has been analyzed by differential scanning calorimetry (DSC), mass spectrometry, and infrared spectroscopy, with the aim of quantifying the energy exchanged. Two exothermic peaks centered at 330 and 410 °C have been detected with energies per H atom of about 50 meV. This value has been compared with the results of theoretical calculations and is found to agree with the dissociation energy of Si-H groups of about 3.25 eV per H atom, provided that the formation energy per dangling bond in *a*-Si is about 1.15 eV. It is shown that this result is valid for *a*-Si:H films, too.

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I. INTRODUCTION

The process of hydrogen desorption takes place essentially through two sequential steps leading to bond rearrangement [Fig. 1(a)]. There is wide agreement that the breaking of Si-H is favored in those cases where neighboring Si-H groups allow the simultaneous formation of a H_2 molecule.[1–3] In this way, the activation energy is greatly reduced and, consequently, desorption takes place at a lower temperature. Once the energy barrier is surpassed, two dangling bonds are left behind and the covalent network of *a*-Si reconstructs, leading to dangling bond recombination. Thus, experimental studies of H desorption offer the opportunity of quantifying the energies involved in the process and, consequently, the energy of several point defects in *a*-Si such as Si-H groups and Si dangling bonds which can be compared with the corresponding theoretical values.

From the experimental side, most studies measure the H concentrations after or during heat treatments. In this way, the kinetics of several dehydrogenation processes have been evaluated.[4–7] In particular, the process best characterized occurs at low temperature (below 400 °C) and is especially valuable because its activation energy can be compared with confidence to the result of theoretical calculations. According to Allan *et al.*,[8,9] the energy needed to release a H_2 molecule that leaves behind two dangling bonds at the initial Si-H sites is 2.0 or 2.05 eV when hydrogen is released from two neighboring Si-H units or one Si-H_2 group, respectively [see Fig. 1(b)]. These values are close to the experimental activation energy of 1.9 eV.[1]

Complementary information could be obtained from the measurement of the heat exchanged during the evolution of hydrogen. In particular, the heat released due to dangling bond recombination could be deduced. This information is relevant because, in contrast with the energies of H states in silicon, the energy of dangling bonds in *a*-Si has not been calculated under realistic conditions. Kelires and Tersoff[10] have performed numerical simulations of *a*-Si formed by quenching the liquid and obtain a formation energy for threefold-coordinated atoms of 0.6 eV. This value is much lower than the energy of 1.35 eV calculated for an isolated dangling bond in crystalline silicon (*c*-Si) by van der Walle.[2,3] In fact, both authors admit that their values constitute a lower and upper bound to the dangling bond energy in *a*-Si. In spite of its interest, a small number of inconclusive works are devoted to calorimetric experiments.[11–14] Battezzati *et al.*[11,12] deal with *a*-SiCGe:H alloys and not with pure *a*-Si:H. The thermograms by Lee *et al.*[14] are unreliable because they give inconsistent values for the crystallization energy, whereas from the data published by Budagan *et al.*[13] only an approximate value of the enthalpy can be estimated.

In this paper, we report on calorimetric experiments done

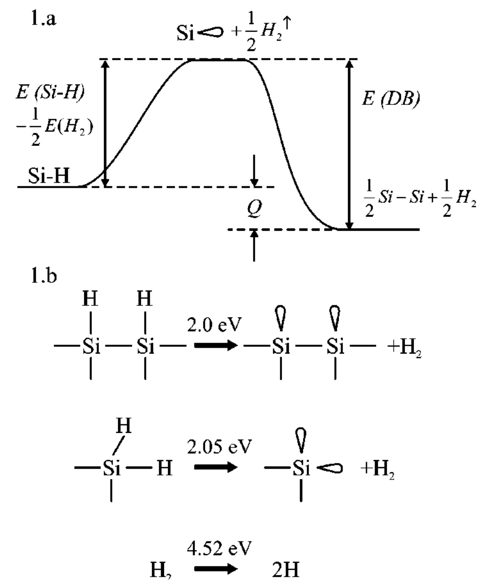

FIG. 1. (a) Schematic representation of the mechanism of hydrogen desorption. Its kinetics are controlled by the formation of one hydrogen molecule leaving behind two dangling bonds (DB's). In a second step, dangling bonds recombine. *Q* is the heat released per H molecule. (b) Theoretical activation energies of two Si-H configurations [according to Allan *et al.* (Refs. 8 and 9)].

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TABLE I. Summary of the energy exchanged during dehydrogenation in several silicon nanopowders and thin films.

Material	n_H/n_{Si}	$(n_H/n_{Si})_{LT}$ [a]	Q_{LT} (J/g)	Q_{HT} (J/g)	Q_{LT} [meV/(H atom)]	Q_{HT} [meV/(H atom)]	Q(mean) [meV/(H atom)]
particles	– – –	1.06	143	– –	47	– –	47
particles	0.63	0.36	44	30	42	38	41
particles	0.44	0.24	64	11	93	20	60
film[b]	– – –	0.07-0.16	8-38	– –	<40	– –	<40

[a]Hydrogen desorpted during the LT process.

[b]Estimation made from the results published by Budagan *et al.* (Ref. 13).

with the aim of quantifying the energy exchanged during hydrogen desorption. Although experiments are done on *a*-Si nanoparticles, it will be shown that the results are also valid for thin films.

II. EXPERIMENTAL DETAILS

Amorphous Si nanoparticles with diameters below 100 nm have been obtained by plasma-enhanced chemical vapor deposition (PECVD) from a mixture of silane and argon. The diameter of particles and their hydrogen content can be controlled by glow discharge parameters like rf power, duration of the ON-OFF cycle, and degree of gas dilution (for a more detailed explanation see Ref. 15). Unless high-energy conditions are established in the plasma, particles are amorphous and highly hydrogenated. The H concentration has been measured by elementary analysis (EA). EA measurements were done by Thermoquest model EA 1110 CHNS-O, which determines C, H, N, and S contents on a sample from their gas oxides obtained after complete burning. In order to avoid any contribution from extraneous sources, every experiment was corrected by subtracting the blank signal obtained by burning an empty crucible. In this way, a precision better than 0.5% was reached. The hydrogen content measured in samples obtained in different conditions is detailed in Table I.

The states of H bonded to Si have been identified by means of infrared (IR) spectroscopy (Mattson Galaxy). In order to avoid any structural modification due to sample preparation, the powder was spread on the ground surface of a KBr pellet. In Fig. 2, typical IR spectra are shown where the band related to Si-H stretching vibrational modes is observed. This band has been deconvoluted into two characteristic peaks corresponding to SiH ($2000\ \mathrm{cm}^{-1}$) and SiH_2 groups ($2090\ \mathrm{cm}^{-1}$).[16] Their relative intensity indicates that a significant fraction of H is bonded as SiH_2.

Hydrogen evolution experiments during heating ramps at constant rate were monitored *in situ* by means of mass spectrometry and differential scanning calorimetry (DSC). In the first case, the powder was held in vacuum inside a tube of fused silica and the hydrogen evolved was detected with a quadrupolar spectrometer (Dataquad-100). Although the signal is always proportional to the evolution rate, it has not been calibrated to give an absolute value. Calorimetric experiments were done with a heat flux cell DSC (Mettler DSC30) which allows quantitative determination of the heat exchanged. Its maximum operating temperature is 600 °C. Additionally, the hydrogen content remaining after the heating sequences was measured by means of elementary analysis.

Special care has been taken with calorimetric experiments. The DSC signal has been calibrated down to the very small power exchanged during dehydrogenation. With a precision better than 5%, the DSC response has been found to be linear over more than two orders of magnitude. On the other hand, according to Refs. 11 and 14, the absolute quantification of the heat exchanged becomes problematic during dehydrogenation. This is so because the high thermal conductivity of H_2 [187 W/(K m) at 300 K Ref. (21)] compared to that of Ar [17.7 W/(K m)] can result in a substantial perturbation of the sensitivity of the apparatus. In fact, Battezzati *et al.*[11] obtain different results depending on the kind of DSC. Their analysis suggests that the perturbation due to hydrogen is important with a power compensation DSC whereas it has a minor effect in the kind of DSC we have used (heat flux cell). Anyway, in order to have a greater confidence on our DSC results, we have done complementary measurements with the third powder of Table I. The heat released has been measured in He, which has a heat conductivity [150 W/(K m)] very close to that of H_2 and, conse-

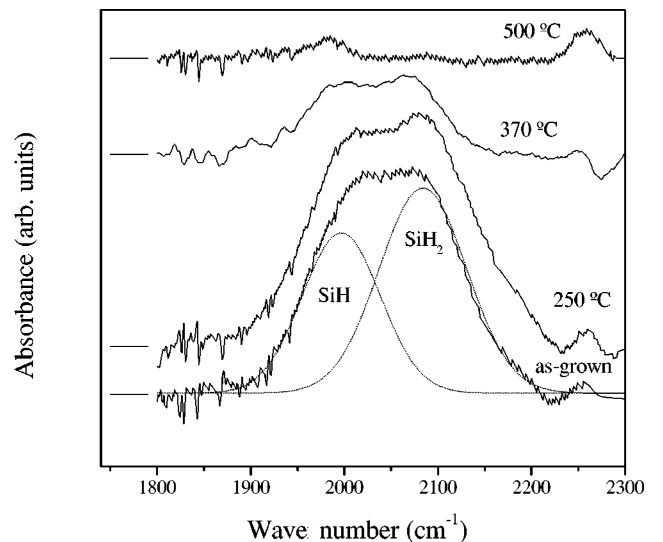

FIG. 2. Infrared absorption spectra in the region of the Si-H stretching modes. Both SiH and SiH_2 groups disappear at the same rate.

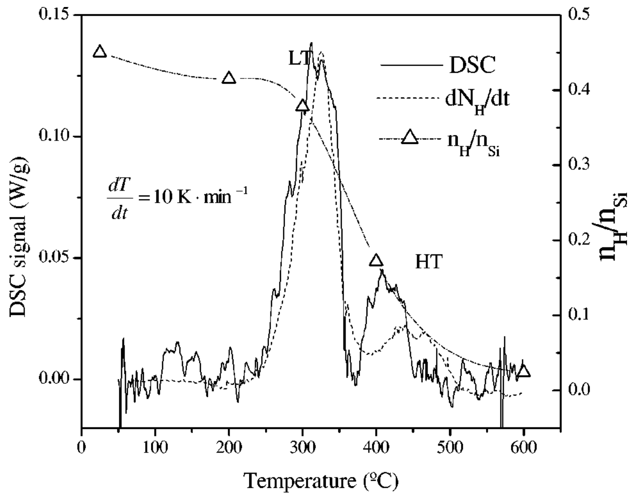

FIG. 3. Heat released during a heating ramp in inert atmosphere, rate of H desorption under the same conditions, and the remaining hydrogen content. The line connecting the experimental points provides a guide to the eye. All of these results have been obtained with the same powder.

quently, any perturbation due to hydrogen is minimized. The result is essentially the same as that obtained with Ar.

III. RESULTS

A typical thermogram is shown in Fig. 3. For clarity, the continuous base line signal corresponding to relaxation phenomena[13,17] has been subtracted. Two exothermic peaks are resolved, centered at 330 and 410 °C, which correspond to the hydrogen desorption processes. This assignation can be clearly established when the DSC curve is compared with the rate of hydrogen desorption measured by means of mass spectrometry (dashed curve in Fig. 3). The low-temperature (LT) peak coincides in both experiments, whereas the high-temperature (HT) one appears at a lower temperature in the DSC curve. Concerning peak intensities, their relative value is similar in both curves for every powder we have analyzed.. This means that the heat evolved per H atom is of the same order of magnitude in both processes.

In order to evaluate the dynamics of H desorption, we have fitted the LT peak to a first-order rate equation:

$$\frac{d(N/N_0)}{dt} = A\left(1-\frac{N}{N_0}\right)\exp\left[\frac{-\Delta H}{kT}\right], \tag{1}$$

where N/N_0 is the fraction of remaining hydrogen, k is Boltzmann's constant, T is the absolute temperature, and ΔH is the activation enthalpy of the process. The preexponential factor A is related to the activation entropy, ΔS, according to[1]

$$A = \frac{kT}{h}\exp\left[\frac{\Delta S}{k}\right], \tag{2}$$

where h is Planck's constant. The LT peak measured in both experiments (DSC and mass spectrometry) can be fitted with the same parameters, i.e., $\Delta H = 1.04 \pm 0.02$ eV and $\Delta S = -1.5 \pm 0.3\ 10^{-3}$ eV/K. As we will see in next section, these values serve to identify unambiguously this LT process.

The remaining H contents after heating up to intermediate temperatures have been measured by means of elementary analysis. The result is plotted in Fig. 3. From these data the hydrogen released during every desorption process (HT and LT) can be obtained. The states of the remaining H have been analyzed by IR. Typical IR spectra measured after the LT and HT peaks are shown in Fig. 2. We see that the peaks corresponding to SiH and SiH_2 units decrease simultaneously after the LT desorption process whereas, in agreement with elementary analysis, after the HT process no significative amount of H remains.

A summary of the quantitative results obtained from a number of samples grown at different conditions is detailed in Table I. Initial hydrogen contents in nanoparticles ranged from $n_H/n_{Si} = 1.06$ to 0.44 and the heat released per unit mass from 140 to 70 J/g. Thus the heat released per hydrogen atom is about 50 meV/(H atom). Although the heat evolved during the HT peak is measured with lower accuracy, its value per H atom shows no significant deviation with respect to the LT peak. A similar value can be estimated for *a*-Si films from the experiments reported by Budagan *et al.*[13]

IV. ANALYSIS AND DISCUSSION

The two-peak structure observed in H-desorption experiments has been reported by other authors in *a*-Si films with high concentrations of hydrogen.[18] The LT peak has been attributed to hydrogen located at the surfaces of internal voids or at the surface or near-surface regions in more compact films.[18,19] The significance of its kinetic parameters was clarified by Khait *et al.*[1] According to their theory, hydrogen atoms bonded to neighboring Si atoms can evolve with activation enthalpies (ΔH) that can change depending on the contribution to the process of carriers trapped in deep levels. This change in ΔH results in great displacements of the peak temperature from 650 K down to 490 K. Anyway, one can identify this particular evolution process because a linear relationship exists between the activation enthalpy ΔH and activation entropy, ΔS, which constitutes its signature:

$$\Delta H = 665\ \text{K}\ \Delta S + 1.90\ \text{eV}. \tag{3}$$

Additionally, Khait *et al.*[1] stated that when carriers do not contribute, then $\Delta S = 0$ and the activation enthalpy is just the energy needed to break the two Si-H bonds with the simultaneous formation of a H_2 molecule. In this case, Eq. (3) gives an activation enthalpy of about 1.9 eV, which is similar to the value computed by Allan *et al.*[8,9] The values of $\Delta H = 1.04 \pm 0.02$ eV and $\Delta S = -1.5 \pm 0.3\ 10^{-3}$ eV/K we have obtained by fitting the LT peak agree with Eq. (3). Thus, the LT desorption processes in our nanoparticles and that in *a*-Si films are the same. Concerning the HT peak, it is attributed to a process controlled by diffusion,[18] due to the fact that after LT desorption, the material becomes more compact.

This interpretation is reinforced by our experiments because during the LT process heat is exchanged (DSC curve in Fig. 3) at a temperature lower than that of hydrogen release (mass spectrometry curve in Fig. 3). This means that, in a first step, an energy exchange occurs related to bond breaking and reconstruction. The value of the exchanged energy (similar to that of the LT peak) is consistent with formation of trapped molecular hydrogen. In a second step hydrogen diffuses to the external surfaces. However, a quantitative analysis[20] reveals that the diffusion coefficient is higher than expected.

Let us now analyze the energy exchanged during dehydrogenation. The overall process is exothermic with $Q=50\pm20$ meV/(H atom). Although the error bar might seem excessive, it has no practical importance because the energies involved in breaking and forming bonds are much greater. For instance, 2.26 eV/(H atom) are released when two H atoms form a H_2 molecule.[21] So we can consider that the overall energy balance of hydrogen desorption is approximately zero. The information contained in Q can be analyzed in view of the microscopic processes that take place during dehydrogenation (see Fig. 1). As explained above, Si-H bond breaking occurs simultaneously with formation of a H_2 molecule. General agreement exists about this first step. Once hydrogen has left its site, two dangling bonds remain which constitute a point defect of high energy. The question is whether subsequent structural relaxation is efficient enough to achieve complete recombination of dangling bonds or, on the contrary, a substantial fraction of them survive. Independent experiments show that recombination is almost complete. From the spin density measured by Biegelsen *et al.*,[7] after dehydrogenation of *a*-Si films, a very conservative upper bound of 10^{-2} can be deduced for the fraction of remaining dangling bonds. So less than 1% of the dangling bonds survive. This result is independent of the initial local environment.[7] On the other hand, we have reported in a recent work[22] that oxidation occurs at low temperature in our nanoparticles ($T<300\,°C$). Oxygen is mainly incorporated at dangling bond sites. If particles are left, after dehydrogenation, in air at room temperature, a rapid mass gain lower than 1% is measured. For an initial composition of $SiH_{0.6}$ this value means that more than 96% of the dangling bonds recombine. In summary, the bond breaking and reconstruction scheme of Fig. 1 can be used to equate the energy balance of dehydrogenation. We can write (see Fig. 1)

$$E(\text{Si-H})-E(\text{DB})\approx\frac{1}{2}E(H_2)-Q=2.21\frac{\text{eV}}{\text{H atom}}, \qquad (4)$$

where $E(\text{DB})$ is the formation energy of one dangling bond and $E(\text{Si-H})$ is the dissociation energy of a Si-H group (i.e., the energy needed to break one Si-H bond, leaving behind one dangling bond and the H atom in vacuum). Equation (4) allows one to calculate $E(\text{DB})$ if $E(\text{Si-H})$ is known and vice versa. The fact is that, both from experiments and from theory, the energy of Si-H is known with reasonable accuracy. In *c*-Si, first-principles calculations[2,3] give $E(\text{Si-H})=3.60$ eV/(H atom) for a completely hydrogenated Si(111) surface, 3.55 for an isolated dangling bond, and 3.15 for a hydrogenated vacancy. The same authors argue that in *a*-Si one should expect an intermediate value due to hydrogen clustering.[23] This hypothesis is confirmed by semiempirical calculations done in *a*-Si,[8,9] which yield 3.28 eV/(H atom) with slight differences depending on the particular Si-H groups involved [see Fig. 1(b)]. Finally, the experiments reported by Khait *et al.*[1] lead to an energy of 3.21 eV/(H atom). So we think that the value $E(\text{Si-H})=3.25$ eV/(H atom) is close to reality. From this value, the formation energy of one dangling bond can be calculated by means of Eq. (4). This yields $E(\text{DB})=1.15$ eV.

In the literature, very few experiments are reported which could eventually serve to quantify the dangling-bond formation energy. From photoemission experiments,[24] van der Walle and Street[23] assign an experimental value to $E(\text{DB})$ as low as 0.5 eV. From the concentration of point defects in *a*-Si,[25] Pantelides[26] and Bar-Yam *et al.*[27] extract "tentative" values of 0.8–0.7 eV. On the other hand, from theoretical calculations only upper and lower bounds can be established with confidence: $0.6<E(\text{DB})<1.35$.[10,23] Intermediate values are obtained by other authors. A rough estimation of 1.3 eV in *a*-Si is given by Allan *et al.*[8] whereas a "more accurate" value of 0.9 eV can be obtained from the formation energy of a vacancy in *c*-Si.[28]

Let us finish this section noting that our 1.15 eV energy is (fortuitously) the same value that would be obtained when considering the energy of formation of monatomic Si gas [4.66 eV/(Si atom)].[21]

V. CONCLUSIONS

The heat exchanged during hydrogen desorption in *a*-Si has been measured and, in view of the energies involved in bond breaking and reconstruction, the overall energy of the process can be considered approximately zero. This value corresponds essentially to the difference between the dissociation energy of one Si-H group with the formation of one H_2 molecule $[E(\text{Si-H})-\frac{1}{2}E(H_2)]$ and the formation energy of one dangling bond $[E(\text{DB})]$. Although our experiments do not provide any measurement of these individual energies, $E(\text{DB})$ can be deduced when $E(\text{Si-H})$ is known from independent sources. We consider that from literature the value of $E(\text{Si-H})$ is known with an accuracy of ±0.1 eV. This accuracy is, then, translated to $E(\text{DB})$, which would be equal to 1.15 ± 0.10 eV.

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