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Adsorption equilibria and kinetics of H_2 at nearly ideal (2×1)Si(100) inner surfaces

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ABSTRACT

Silicon nanocavities can be terminated with hydrogen by wet chemical etching. Their infrared spectra can to a large extent be interpreted in terms of silicon monohydrides on H(7×7)Si(111), H(1×1)Si(111) and H(2×1)Si(100), and of silicon dihydrides on H(1×1)Si(100). The time evolution under isothermal conditions (600 °C) of the (1 0 0) faces admits a description in terms of transformation from H(1×1)Si(100) into (2×1)Si(100) with simultaneous H_2 adsorption onto (2×1)Si(100) neat dimers. In so doing the inner H_2 pressure decreases by about one order of magnitude from the initial value of 3×10^3 Torr. The unique properties of nanocavities allow their use as nanoreactors; this has led to the determination of the sticking coefficient for H_2 adsorption in conditions of pressure, temperature and adventitious contamination otherwise not achievable.

1. Introduction

Nanocavities (NCs) in silicon can be formed by implantation of helium at high fluence ($1-4\times10^{16}$ cm^{-2}) followed by a heat treatment at high temperature ($\gtrsim$700 °C). This procedure first promotes the simultaneous coalescence of vacancies and helium in nanobubbles, then reverts them to NCs after helium out-diffusion, and eventually reshapes them to tetrakaidecahedron voids with mean diameter of tens of nanometers, however increasing with the implanted fluence and strength of the annealing [1]. Tetrakaidecahedra are defined by eight (1 1 1) faces truncated by two (1 0 0) planes and four rounded vertices, that can be regarded as defective (1 1 0) planes, as required by Wulff's construction [2–4]. After complete helium effusion [5], the residual atmosphere in the cavities is formed by silicon at its vapour pressure, so that they can be viewed as the best realization of *vacuum* achievable in the laboratory. The inner surface of cavities may be contaminated only by the segregation of impurities (in practice, interstitial oxygen only) contained within a diffusion length, and the remaining surface can be preserved clean for an indefinite time. They would therefore be ideal nanoreactors for studying the reactivity of silicon surfaces were it not for the difficulties of inserting the wanted species therein and of probing their state.

Limiting the attention to hydrogen, the NCs can also be terminated with hydrogen using standard methods for sub-surface treatments, like ion implantation or plasma immersion [6,7]. The IR spectra of the samples so prepared give however evidence for large disorder, thus showing that the quality of the inner surfaces is greatly depressed by these treatments [8].

Actually, a method for the room temperature (RT) injection of a species (hydrogen) into silicon is known— etching of silicon in HF aqueous solution (HF$_{aq}$). This process is responsible for the passivation of acceptors and donors and results in the formation of complexes (like bond-centred hydrogen H$_{bc}$, antibonding hydrogen, H$_{ab}$, or H_2^*—the H$_{bc}$–H$_{ab}$ pair) that are infrared (IR) active with absorption lines falling in the spectral region 1800–2000 cm^{-1} [9].

However, we have recently discovered that in the presence of an NC layer the above phenomenology is not the prevailing one [10]: no absorption lines were indeed observed in the said spectral region whereas an absorption band in the region 2070–2100 cm^{-1} (characteristic of surface Si–H bonds) appeared after thermal treatments at temperature higher than 500 °C [11]. Since heat treatments at this temperature are sufficient to destroy completely silicon hydrides at outer surfaces [12,13], these signals must be assigned to hydrogen terminations of inner surfaces.

In Refs. [10,11] we limited our analysis to the IR spectra of silicon–hydride species, trying to assign them to characteristic configurations of the (1 1 1) and (1 0 0) faces only; in so doing we however ignored the (possibly large) reconstruction of the inner surfaces resulting after prolonged treatments in H_2 at high temperature and pressure (Fig. 1). In this work, taking into account the actual cavity structure produced by this process, we propose a new, more confident, decomposition of the IR spectra (Figs. 2 and 3). These spectra allow a detailed description of the formation–destruction kinetics of hydrogen terminations of (1 0 0) faces as a function pressure (Fig. 4). The theoretical description of these kinetics shows that in the temperature and pressure conditions considered in this work the sticking

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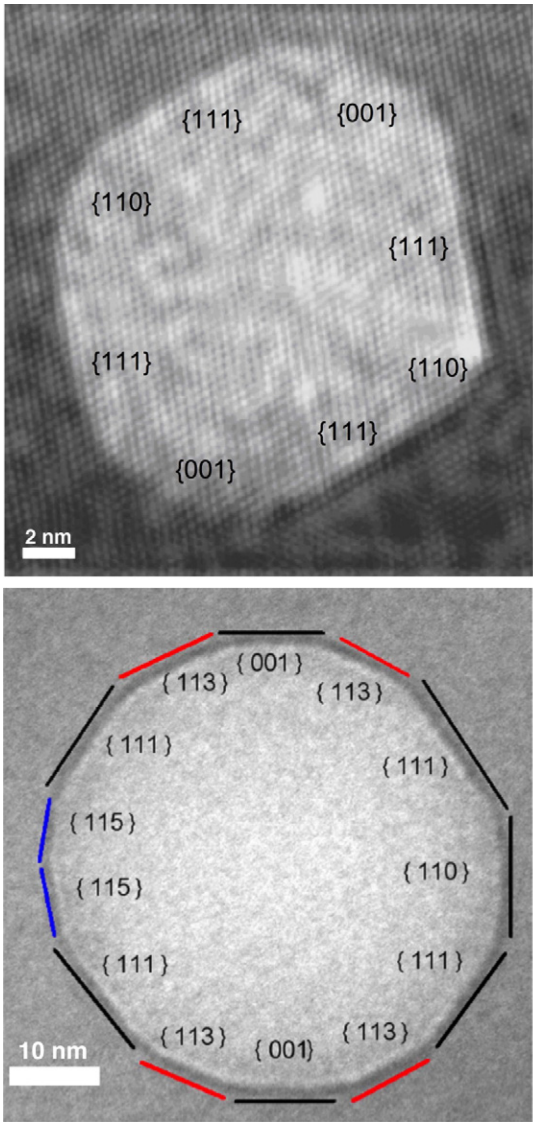

Fig. 1. Shape and size evolution of nanocavities: (top) tetrakaidecahedron-shaped cavity produced by helium implantation and recovery of the radiation damage at 950 °C for 2 h; and (bottom) nearly spherical cavity resulting after repeated sequences of etching in HF_{aq} and annealing for a thermal budget of 32 h at 850 °C in argon. Together with a dramatic increase of size (by a factor of 2.5), the heat treatment in H_2 produces the formation of faces (marked in colour) with different orientation: of them, the (1 1 3) faces have only occasionally been observed (but never after prolonged annealing), whereas to the best of our knowledge the (1 1 5) faces have never been reported yet.

coefficient of H_2 on neat 2×1 dimers on the (1 0 0) surface is of the order of 10^{-14}. Decorating the NC walls with hydrogen via etching in HF_{aq} provides thus a new tool for studying a problem, the adsorption–desorption mechanisms of H_2 at silicon surfaces, still open in spite of the numerous studies [14,15].

2. Experimental

Preparation method and analytical details have preliminarily been presented [10,11]; in the following we shall therefore mention only the information which we consider essential for understanding the analysis of this work.

The samples were single crystalline, Czochralski grown, (1 0 0) oriented, p type, boron doped, silicon slices with resistivity in the interval 11.5–15.5 Ω cm. Before undergoing the implantation, the samples were shaped into prisms, to allow the IR analysis. To avoid contamination during implantation, the prism surfaces were protected with an SiO_2 film of thickness 10 nm. The samples were then implanted with He^+ at an energy of 30 keV and a fluence of 2×10^{16} cm^{-2} and the radiation damage was recovered at 850 °C for 2 h. The shape of a typical cavity resulting after this process is shown by the high resolution electron micrograph displayed on the top of Fig. 1.

After a sequence of oxidation-HF_{aq} etching cycles to remove the unavoidable organic contamination during the implantation followed by an additional prolonged thermal treatment at the same temperature [16], the samples were dipped in diluted HF_{aq} for 10 min and eventually heated at 700 °C for 1 h.

After that, the samples were analyzed *ex situ* via IR spectroscopy, at room temperature and with a resolution of 2 cm^{-1}, using an MCT (mercury-cadmium telluride) detector operating in a N_2-purged atmosphere. Each spectrum was formed by 1024 co-added scans and was ratioed against the reference spectrum to obtain the absorbance spectrum. The reference spectrum was collected before the formation of the sacrificial oxide, when the external surface was terminated with hydroxyl groups.

To be sensitive to molecules in the monolayer regime, the IR beam must interact a large number of times before its detection; denoting this number with ω, the geometry was chosen to have $\omega\simeq110$. An important fact is however noted: whereas the outer surfaces interact with the evanescent beam, thus working in multiple internal reflection (MIR) configurations, inner centres interact with the travelling beam, thus working in multiple internal transmission (MIT) configuration [7]. The atomic absorption coefficient in transmission mode ϵ^{tra} does not coincide with that in attenuated-reflection mode ϵ^{ref}; according to Ref. [17] for silicon their ratio r is given by

$$\begin{aligned} r &= \epsilon^{\mathrm{tra}}/\epsilon^{\mathrm{ref}} \\ &= 30\pm10. \end{aligned} \tag{1}$$

Due to the absorption of bulk silicon, in both cases the useful IR window goes from 1500 to 4500 cm^{-1}.

The IR spectrum after the treatment at 700 °C for 1 h is shown on the left hand side of Fig. 2. The various silicon hydrides species (mainly monohydrides) at the inner surface have lines with full width at half maximum of 2.5–5.0 cm^{-1} [11]. The signals related to the (1 1 1) faces with 1×1 or 7×7 reconstruction are in the region 2065–2084 cm^{-1}, whereas those related to the (1 0 0) faces are in the region 2085–2100 cm^{-1}. Consider now the line at 2099.5 cm^{-1}, assigned to silicon dihydrides on highly ordered unreconstructed (1 0 0) surfaces. This assignment rests on the fact that the same line is characteristic of highly ordered (1 0 0) silicon surfaces treated at high temperature (850–1100 °C) in H_2 at sub-atmospheric pressure (see top of Fig. 3) [12,13].

After the thermal treatment at 700 °C the sample underwent a sequence of heating at 600 °C for a total duration of 8 h. The total absorbance $A(t)$ increased with the duration t of the treatment at 600 °C (at least for $t\leq t_f:=6$ h); the slight decrease of A on going from 6 to 8 h is attributed to a modest out-diffusion of hydrogen occurring with a time constant of the order of 2×10^4 s at 600 °C [2]. Limiting the attention to the (1 0 0) surface (for which the energies of the H_2 adsorption on different reconstructions are known [18]), the IR spectrum (shown on the right of Fig. 2) underwent substantial changes, with the strengthening of the absorbance A_M of the lines at 2086.5 and 2097.6 cm^{-1} due to monohydride dimers on $H(2\times1)Si(100)$, and the almost complete disappearance of the absorbance A_D of the line at 2099.5 cm^{-1} assigned to dihydrides on $H(1\times1)Si(100)$.

We explicitly mention that we have been unable to assign all lines in Fig. 2 to known species; this fact, however, may be understood observing that the etching–annealing sequence rounds off the original tetrakaidecahedron shape of cavity with the appearance of faces with unusual (1 1 3) or even exotic (1 1 5) orientations, as shown in the bottom of Fig. 1.