

## Theoretical and Experimental Optical Spectroscopy Study of Hydrogen Adsorption at Si(111)-(7 × 7)

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The combination of *in situ* real-time surface differential reflectivity (SDR) spectroscopy and microscopic calculations has been used for the first time to investigate gas adsorption on a Si surface. The optical signatures of some microscopic structural units of Si(111)-(7 × 7) have been identified. The development of the corresponding features in the SDR spectra upon the amount of H exposure allowed us to demonstrate the occurrence of two different mechanisms in the hydrogenation and to determine their relative kinetics. [S0031-9007(96)00523-6]

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In recent years, optical spectroscopies such as reflectance anisotropy spectroscopy (RAS) and surface differential reflectivity (SDR) have proved their ability to investigate the intrinsic electronic properties of solid surfaces [1,2] and to monitor the interaction of surfaces with gas [1,3] or the growth of thin films [4]. However, most of the experimental studies are limited to a phenomenological analysis, without a deep microscopic understanding of the optical response of the surfaces. Although the optical measurements are macroscopic in nature, they are directly linked to the microscopic structure of the surface and to its electronic structure [5,6]. A theoretical treatment of the optical response of a solid surface, based on its microscopic structure, is therefore necessary to fully understand the experimental data and to interpret them in terms of surface reconstruction, adsorption of atoms, growth of thin films, etc.

The interaction of hydrogen with the Si(111)-(7 × 7) surface, well described by the dimer-adatom-stacking fault (DAS) model [7], is a complex process of broad interest. Up to now, theoretical studies on the hydrogenation of Si(111)-(7 × 7) had been hampered by its very large unit cell and only a few attempts have been made [8,9]. On the other hand, the hydrogenation of this surface has been investigated by numerous experimental techniques, which have shown the existence of two reaction paths [10–13].

We present the first combination of theoretical and real-time experimental optical studies of Si(111)-(7 × 7) and of the H adsorption. Our experimental SDR spectra are described by means of a theoretical microscopic model, in terms of electronic transitions involving the bulk and surface states of Si(111)-(7 × 7). This permits us to understand the intrinsic optical response of Si(111)-(7 × 7), and to gain deep information on the hydrogenation process. We clearly distinguish the two main mechanisms

and we follow their kinetics: (1) adsorption of H on the dangling bonds (DBs), and (2) H breaking of the Si-Si backbonds (BBs) of the adatoms (ADs).

The SDR experiments were performed with a rapid *in situ* spectrometer [14], which delivers the change of the reflectivity upon H adsorption:  $\Delta R/R = (R^{\text{clean Si}} - R^{\text{H/Si}})/R^{\text{clean Si}}$ , where  $R^{\text{clean Si}}$  and  $R^{\text{H/Si}}$  are the reflectivities of the clean and H-covered Si surfaces. This quantity is related to the optical susceptibility of the surface and hence provides information on the changes of its electronic structure [5]. The incidence angle  $\theta$  of the *p*-polarized light beam was 60°. The SDR signal was registered during the H adsorption, providing a real-time monitoring of the process. The Si samples were heated during 5 min at 900 °C in the vacuum chamber (base pressure of 10<sup>-10</sup> torr) for removing the oxide layer, then cooled down slowly (1 K/s) to get a sharp 7 × 7 low-energy-electron-diffraction (LEED) pattern. Atomic H was produced by decomposition of H<sub>2</sub> by a tungsten filament at 1800 °C previously outgassed at higher temperature.

Figure 1 shows typical experimental SDR spectra (point curves) taken from 500 spectra registered during the H exposure, given in H<sub>2</sub> exposure (note that the vertical scales differ from one spectrum to another). The sample was maintained at -20 °C. Similar spectra were obtained at other temperatures between -140 and 300 °C. Spectrum (a) (20 L [1 L (langmuir) = 10<sup>-6</sup> torr s]) is dominated by a peak *A* at 1.8 eV, with a small negative minimum *C* at 3.2 eV. A second peak *B* is developing around 2.8 eV in spectrum (b) (90 L), together with a double structure *D* at 3.7–4.1 eV. While peak *A* saturates after about 150 L, structures *B* and *D* continue growing and become progressively dominant, as shown in spectrum (e), where peak *A* now reduces to a shoulder. The edge of another structure *E* appears above 5 eV in spectra (d) and (e). Our

LEED studies, performed at room temperature, show a progressive change from the  $7 \times 7$  pattern for the clean and lightly exposed surfaces to a " $7 \times 1$ " one for large exposures. The  $7 \times 1$  pattern corresponds to the complete etching of the Si ADs [10,15], resulting in a monohydride phase with preservation of the stacking fault (SF). Much larger amounts of H at high temperature are needed to get a  $1 \times 1$  surface [16], leading to additional optical features [17].

For the theoretical calculations, we have chosen two different models for the microstructures of the hydrogenated surfaces: (i) the  $(7 \times 7) : 19\text{H}$  phase, obtained by saturating the 19 surface DBs with H atoms; (ii) the  $(7 \times 7) : 43\text{H}$  phase, where the ADs have been removed from the surface and the resulting 43 DBs have been saturated with H atoms, which corresponds to the  $7 \times 1$  surface. The surface optical responses of both phases and of the clean  $7 \times 7$  surface have been determined within

$$\frac{\Delta R}{R} = \frac{4d\omega}{c} \cos\theta \text{Im} \left\{ \frac{[\varepsilon_b(\omega) - \sin^2\theta] \Delta\varepsilon_{\parallel}(\omega) + \varepsilon_b^2(\omega) \sin^2\theta \Delta[\varepsilon_{\perp}(\omega)]^{-1}}{[\varepsilon_b(\omega) - 1][\varepsilon_b(\omega) \cos^2\theta - \sin^2\theta]} \right\},$$

where  $\varepsilon_b(\omega)$  is the bulk dielectric function and  $d$  is the depth of the surface layer [18].  $\Delta\varepsilon_{\parallel}(\omega)$  and  $\Delta[\varepsilon_{\perp}(\omega)]^{-1}$  are given by  $\Delta\varepsilon_{\parallel}(\omega) = \varepsilon_{\parallel}^{7 \times 7}(\omega) - \varepsilon_{\parallel}^{\text{H/Si}}(\omega)$  and  $\Delta[\varepsilon_{\perp}(\omega)]^{-1} = [\varepsilon_{\perp}^{7 \times 7}(\omega)]^{-1} - [\varepsilon_{\perp}^{\text{H/Si}}(\omega)]^{-1}$ , where  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are the dielectric functions of the surface layer for light polarized parallel and perpendicular to the surface for the clean  $(7 \times 7)$  and hydrogenated (H/Si) surfaces [20].

The results of the calculations for both phases (Fig. 2) have to be compared with the experimental curves in Fig. 1. Besides an overall shift of about 0.4 eV, the same features are observed in both figures, but with different relative intensities and different widths. In particular, peak *A* is larger in theory than in the experiment. Such discrepancies between calculated and measured spectra are also common in the simpler case of bulk systems and are due to the neglect of many-body and local-field effects in the calculations [21]. The observed features are essentially due to the progressive removing of electronic states of the clean  $7 \times 7$  surface, caused by H adsorption. As it follows from the calculated band structure [18], the optical transitions giving rise to the SDR structures in Fig. 2 can be separated into three parts. (1) Up to 2 eV, the optical response (peak *A'*) originates from surface-state to surface-state transitions, involving AD states below and above  $E_F$  (in particular, AD DBs). These transitions are suppressed when DBs are saturated by H, yielding peak *A'* in spectrum (I) of Fig. 2. (2) From 2 to 3 eV, the features are due mainly to mixed transitions from surface to bulk (*s-b*) states, in particular, from AD BBs to bulk states in the conduction band. These transitions are suppressed when the ADs are removed, yielding the broad peak *B'*, centered around 2.2 eV, in spectrum (II). On the contrary, these transitions are not suppressed but only slightly shifted to larger energies by the H saturation of the DBs, giving the

a  $sp^3s^*$  semiempirical tight-binding approach [18]. For the clean surface we used a slab with 400 Si atoms in ten layers with both sides terminated by the  $7 \times 7$  DAS structure, where the coordinates of the atoms of the four upper layers were taken from Ref. [19]. For both hydrogenated surfaces, we used slabs of 366 [378] atoms, where one side of the slab was terminated by the  $(7 \times 7) : 19\text{H}$  [ $(7 \times 7) : 43\text{H}$ ] phase, and the other side was saturated with H in the ideal  $1 \times 1$  geometry. A slab with ideal H termination at both surfaces has also been considered, in order to extract by subtraction the optical properties of the  $7 \times 7$  hydrogenated surfaces. The geometries of the relaxed hydrogenated phases were taken from Ref. [9]. The optical properties were determined at three (one) special point(s) of the  $7 \times 7$  surface Brillouin zone for the clean (hydrogenated) surface [18].

The SDR for *p*-polarized light is given by

positive and negative feature  $B''-C''$  in spectrum (I). Peak *B'* is therefore expected to occur also when only a part of the BBs is broken, even without etching of the ADs. (3) Above 3 eV, transitions are from bulk to bulk (*b-b*) and *s-b* states, which lead to the structures *D'* and *E'*. It is indeed known that surface-perturbed bulk states can yield a large contribution to the surface optical response in the energy range of strong bulk absorption [22]. The dip occurring at 3.5 eV in the higher-coverage curves of Fig. 1 is due to the effect of surface perturbations on the  $E_1$  bulk structure.

Comparison between experiment and theory allows us to point out two different mechanisms in the process of hydrogenation. The first one is the adsorption of H on the DBs, which is the dominant mechanism for small H exposures, as shown by the similarity of the experimental spectrum (a) in Fig. 1 and the calculated spectrum (I) in Fig. 2. The second one, evidenced by peak *B*, is the H breaking of the BBs of the ADs, an obligatory intermediate step for AD etching [11]. It becomes dominant for larger exposures. Our measurements allow us to follow quantitatively both mechanisms in real time and to understand their kinetics. The good agreement between spectrum (a) of Fig. 1 and spectrum (I) of Fig. 2 shows that, in our experimental conditions, the H adsorption of ADs occurs alone, or almost alone, in the very initial hydrogenation. Consequently, spectrum (a) of Fig. 1 gives the optical contribution of the first mechanism alone, which will be called  $S_1$  in the following. The contribution  $S_2$  of the second mechanism alone is given by the changes in SDR from 200 to 300 L [Fig. 3(a)]. It is dominated by the *B*, *D*, and *E* structures, due to *s-b* and *b-b* transitions. Apart from the shift of 0.4 eV, it compares very well with the theoretical spectrum drawn in Fig. 3(b) giving the SDR change from the  $: 19\text{H}$  phase to the  $: 43\text{H}$  one, hence involving

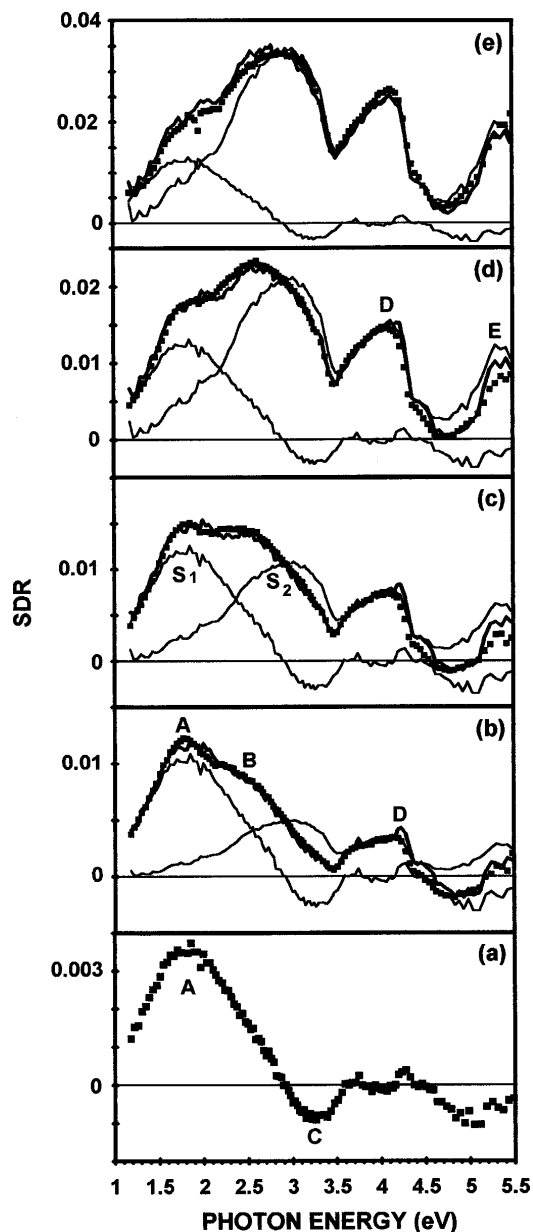


FIG. 1. SDR spectra for different exposures of atomic H on Si(111)-(7 × 7) maintained at −20 °C. (a) 20 L of H, (b) 90 L, (c) 140 L, (d) 250 L, and (e) 1200 L, experimental. Thick lines, fitting of the experimental data; thin lines, decomposition in the optical contributions  $aS_1$  and  $bS_2$ .

the second mechanism alone. This is one of the best agreements ever obtained by comparing theoretical and experimental SDR spectra [6], which is a clear confirmation of the nature of the second step of the hydrogenation process. A similar shape of the optical response has been obtained from ellipsometric measurements on Si(100)-(2 × 1) and Si(111)-(2 × 1), for which the same assignment of BB breaking may be proposed [23]. The  $S_1$  and  $S_2$  spectra are the *experimental optical signatures* of the two mechanisms. Now, each experimental spectrum  $S(D)$ , obtained for a dose  $D$  of hydrogen, can be decomposed as a linear combination of  $S_1$  and  $S_2$  :  $S(D) = a(D)S_1 + b(D)S_2$ . The coefficients  $a(D)$  and  $b(D)$  give the relative contri-

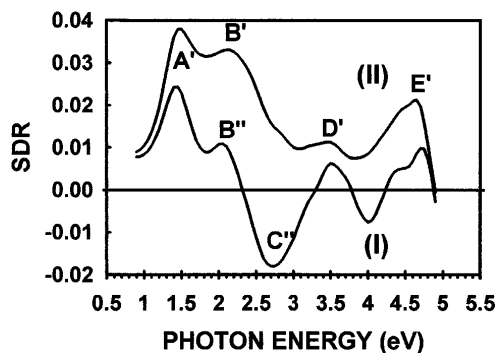


FIG. 2. Theoretical SDR: Reflectivity of the clean Si(111)-(7 × 7) surface minus that of (I) the Si(111)-(7 × 7) : 19H and (II) the Si(111)-(7 × 7) : 43H surface.

butions of the H adsorption onto the DBs and of the BB breaking by H, respectively. The data points of Fig. 1 are very well fitted by this function  $S(D)$  (thick lines). The separated contributions  $aS_1$  and  $bS_2$  are also drawn in the graphs of Fig. 1 (thin lines). The kinetics of each mechanism is given by Fig. 4, where the parameters  $a$  and  $b$  are plotted as a function of the  $H_2$  dose. This shows that H adsorption on the DBs is the fast process and saturates completely at 150 L, while BB breaking is slower and reaches the saturation (i.e., the complete etching of the ADs) at about 800 L. The very early stage of the adsorption (inset in Fig. 4) shows that the BB breaking initially occurs very weakly. This is the indication of the existence of a large barrier which prevents H from being directly bound to the

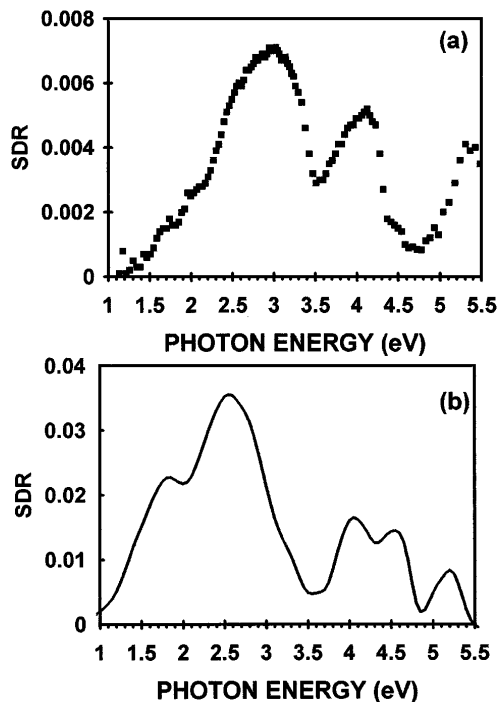


FIG. 3. (a) Experimental SDR spectrum of the second hydrogenation mechanism at −20 °C: spectrum at 300 L minus spectrum at 200 L of  $H_2$  exposure. (b) Calculated contribution of the second mechanism to the SDR spectrum.

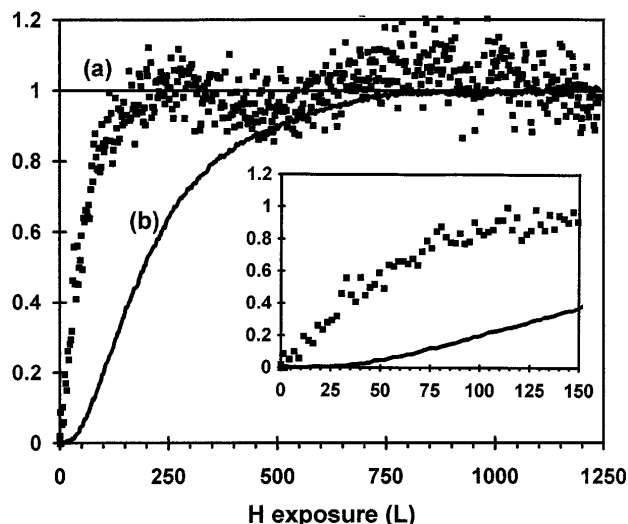


FIG. 4. Development of parameters  $a(D)$  and  $b(D)$  (normalized to 1), derived directly from the decompositions of the experimental spectra, as a function of  $H_2$  exposure.

BBs. It has been found recently that H saturation of an AD DB somehow weakens its BBs [24]; this suggests that H atoms can break only the BBs of those ADs which already have H-saturated DBs. Starting from this assumption, we have written and solved the kinetic equations for H adsorption. Because the breaking of a BB requires two H atoms, we find an initial quadratic law for  $b(D)$ , in fair agreement with the experiment [17]. Moreover, the relative dependence on the temperature of parameters  $a(D)$  and  $b(D)$  suggests that a finite activation barrier  $\Delta E$  for the breaking of BBs remains, even after the AD DB has been H saturated. Its value was estimated to be  $\Delta E = (13 \pm 3)$  meV, as will be discussed in [17], by comparison of curves  $a(D)$  and  $b(D)$  at different temperatures with the solution of the kinetic equations [25]. The second mechanism of course implies some disorder, since dihydride and trihydride ADs must be present at any stage: This, however, does not affect our measurements too much, since these species are also expected to contribute to peak B proportionally to the number of broken BBs.

To summarize, the hydrogenation of Si(111)-(7 × 7) has been studied by a combination of real-time SDR experiments with a microscopic theoretical treatment. It allowed us to obtain a deep understanding of the optical response of the clean and hydrogenated surfaces, in terms of their microscopic surface structures, and to follow the kinetics of two hydrogenation paths: (i) H adsorption on the DBs, which saturates quickly; (ii) H breaking of the BBs of the ADs, which is inhibited when no H is bound to the AD DB. An activation barrier of about 13 meV results for the second mechanism. These findings show the power of microscopic calculations combined with *in situ* fast surface optical techniques for the control and the analysis of crystal surfaces, and especially for the online monitoring of surface modification processes, which is promising for technological applications, such as semiconductor epitaxial growth or catalytic reactions.

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