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Adsorption kinetics of H on Si(111)7×7 by means of surface differential reflectivity

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The kinetics of hydrogen adsorption on Si(111)7×7 have been studied by means of real-time surface differential reflectivity. Experiments have been performed for a large exposure range and for temperature ranging from 170–370 K. Two different adsorption channels could be determined from the analysis of the spectra. The kinetics equations of the two elementary processes have been written, and their respective activation energies have been determined: a very low barrier for the H binding on the adatom dangling bonds and a barrier of about 20 meV for the H breaking of the adatom back bond. The kinetics of both processes can be understood by taking into account a large energy barrier that inhibits the adatom-back-bond breaking by H as long as the dangling bond of the adatom is not yet bound to H. [S0163-1829(97)52332-0]

The adsorption of hydrogen atoms on the Si(111)7×7 surface has recently received renewed interest, both experimentally[1–4] and theoretically.[5–9] The 7×7 surface reconstruction, well described by the dimer-adatom-stacking fault (DAS) model,[10] involving building blocks (adatoms, rest atoms, dimers...) frequently found at the reconstructed surfaces of semiconductors, can be considered, indeed, a model system for the investigation of fundamental aspects of gas chemisorption on semiconductors. The interaction of H with the Si(111)7×7 surface involves different processes which depend on the experimental conditions.[3] Low-energy electron-diffraction (LEED) studies have shown that the 7×7 pattern is progressively changing into a 7×1 pattern upon H adsorption, which has been ascribed to the removal of the adatoms (AD) or of part of them.[11,12] Two main channels for the reaction have been identified: (1) direct adsorption of H on the Si adatom dangling bonds (ADDB's); (2) breaking by H of the Si adatom back bond (ADBB).[3,4,13] In the second process, H atoms bind to the unsaturated atomic orbitals resulting from the breaking of the ADBB's.

However, several questions remain unclear so far, such as the formation of different kinds of hydrides (mono-, di-, and trihydrides), the existence or not of energy activation barriers for the reaction channels described above, and the respective rates of these reactions.[3,13–16]

We present in this communication a real-time optical study during H adsorption on Si(111)7×7. This gave us the opportunity to follow the kinetics of both reactions as a function of H-exposure rates, which are controlled by the activation energies of each process. We have developed a simple kinetic model which nicely reproduces the experimental data. Moreover, performing experiments at different temperatures permitted us to determine the energetic activation barriers for H adsorption on the Si ADDB and for H breaking of the ADBB. We showed that the direct breaking of the ADBB is not possible, but occurs only when the AD is already bound to an H atom, which yields a weakening of the back Si-Si bonds.

We used an optical technique sensitive to the surface, the real-time surface differential reflectance (SDR) spectroscopy, which has been proved recently to be very well adapted to kinetic studies of surface adsorption.[4] The SDR experiments were performed with a rapid *in situ* spectrometer in the near-visible UV range,[17] which measured the relative change of reflectivity during H adsorption: $\Delta R/R=(R^{\mathrm{Si}}-R^{\mathrm{H/Si}}/R^{\mathrm{Si}}$ where R^{Si} and $R^{\mathrm{H/Si}}$ are the reflectivities of the clean Si and of the hydrogenated Si surfaces, respectively. The incidence angle of the p-polarized light beam was fixed at 60°. The SDR signal on the whole spectra range was registered during the H adsorption, providing a real-time monitoring of the process. After outgassing the Si sample during several hours at 970 K, in an ultrahigh vacuum chamber (base pressure: 10^{-10} Torr), the reconstructed surface was obtained by heating for 5 min at 1070 K for removing the oxide layer, followed by a slow cooling down (1 K/s) to get a sharp 7×7 LEED pattern. Atomic H was produced by dissociation of molecular hydrogen by a hot tungsten filament (2070 K), located at about 10 cm in front of the sample, previously outgassed at higher temperature to prevent contamination. The adsorption of hydrogen on Si(111)7×7 was studied for temperatures of the sample ranging from 170–370 K, and about 600 spectra were recorded, at each temperature, during the hydrogenation process up to a total exposure of 1000 L [1 L(Langmuir)$=10^{-6}$ Torr s].[18]

We have demonstrated in a previous paper[4] that both elementary mechanisms of H adsorption on Si(111)7×7,

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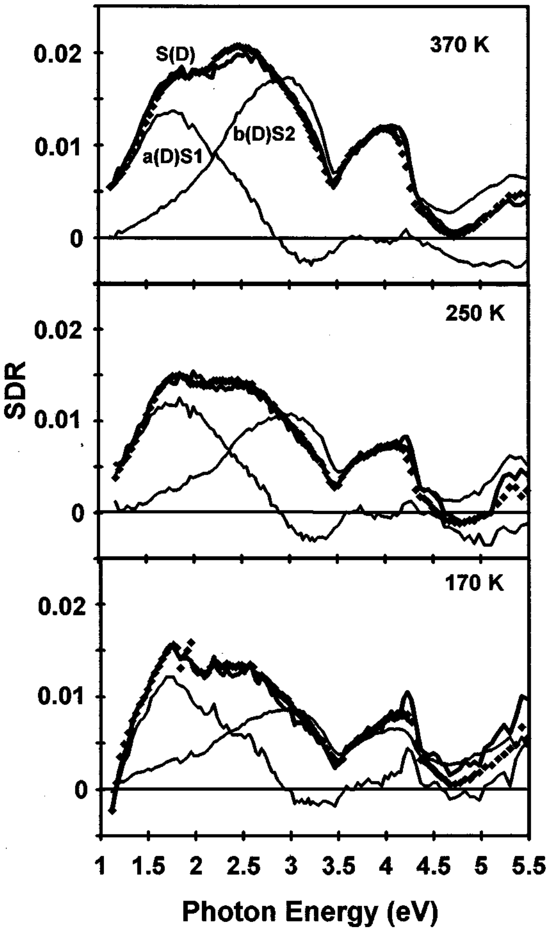

FIG. 1. SDR spectra and their decompositions at 140 L of H exposure on Si(111)7×7 for these temperatures of the substrates: 370, 250, and 170 K. Experimental SDR spectra: black diamonds; $a(D)S_1$ and $b(D)S_2$: thin lines; $S(D)=a(D)S_1+b(D)S_2$: thick lines.

namely H atom binding on adatom dangling bonds [mechanism (a)] and breaking of an adatom back bond by an H atom [mechanism (b)], are related to specific SDR spectra, S_1 and S_2, which can be considered their optical signatures. As the second mechanism (b) proceeds initially much slower than mechanism (a), S_1 is obtained from the SDR spectrum measured at a very low dose of H ($D=20$ L), for which the contribution of mechanism (b) is considered to be negligible. We have checked that taking into account a small initial contribution of mechanism (b) did not change the following results significantly. The procedure for obtaining spectra S_1 and S_2 is based on a careful comparison between experimental data and the results of microscopic semiempirical tight-binding calculations, as is explained in Ref. 4. Moreover, we have shown that each experimental SDR spectrum, obtained for a dose D of hydrogen, can be reproduced by a linear combination of S_1 and S_2: $S(D)=a(D)S_1+b(D)S_2$, where $a(D)$ and $b(D)$ are the weight factors of S_1 and S_2, respectively. All the SDR spectra obtained for increasing doses D of H, at different temperatures, have been decomposed using this procedure. It must be noticed that the S_1 and S_2 spectra slightly depend on the temperature of the sample.

Figure 1 presents a selection of three SDR spectra obtained at different temperatures for the same intermediate exposure ($D=140$ L), where mechanisms (a) and (b) have comparable weights. The experimental data are well reproduced by the linear combination $S(D)=a(D)S_1+b(D)S_2$ (thick line) of the contributions of both mechanisms $a(D)S_1$ and $b(D)S_2$ (thin lines). Spectrum S_1 is dominated by a broad peak around 1.7 eV, which originates from surface state to surface-state transitions, involving adatom states (in particular dangling-bond states) below and above the Fermi level.[4] The 2.5–3 eV peak in the S_2 spectrum is due to mixed transitions from surface to bulk states, in particular from adatom-back-bond states to bulk states in the conduction band.[4] The 4 eV peak in S_2 is caused by transition from bulk states to bulk states, perturbed by the presence of the surface and by H adsorption.[4] The observation of these peaks in the SDR spectra is done by the progressive suppression of the corresponding electronic transitions, caused by the adsorption of H atoms on the dangling bonds and by the H-induced breaking of the back bonds. Figure 1 clearly shows that mechanism (a) [H adsorption on the dangling bonds (DB's)] does not (or very little) depend on the temperature, while mechanism (b) [breaking of the back bonds (BB's)] is enhanced for larger temperatures. It is worth noting that, at our working temperatures, the diffusion of H atoms from one binding site to another one is negligible.[6,19] The kinetics of both mechanisms of H adsorption have been obtained, for a given temperature, by decomposing all the spectra recorded in real time, yielding the weight factors $a(D)$ and $b(D)$. The weight factors $a(D)$ and $b(D)$, normalized to the value of 1 which is reached at saturation, are plotted in Fig. 2 for the same temperatures as those in Fig. 1. One can first notice that the growth of coefficient $a(D)$ with D does not depend substantially on the temperature. The slope at the origin is almost the same for the three temperatures shown in Fig. 2, and saturation is reached nearly at the same dose of about 200 L. On the contrary, $b(D)$ is clearly influenced by the temperature. Saturation exposures for $b(D)$ are ≈600 L at 370 K; ≈800 L at 250 K, and ≈950 L at 170 K. In the three cases, the growth of $b(D)$ is very slow for low doses of D, and increases only after almost 50 L, where $a(D)$ has already reached a significant value, as shown in the insets of Fig. 2. This gives strong evidence that mechanism (b) is not allowed in the beginning of the adsorption process, i.e., when mechanism (a) has not yet taken place. This led us to conclude that the breaking of the back bond by an H atom is possible only if the DB of the AD is already saturated by an H atom, i.e., that there is a larger barrier which prevents the direct breaking of the back bonds, and which is strongly reduced upon H adsorption on the dangling bonds. This is in good agreement with density-functional calculations performed by Vittadini and Selloni,[6] who showed that the adsorption of H on an adatom dangling bond increases the strain in the back bonds and favors their breaking. The bonding of H to a Si ADDB can hence be considered a precursor for the breaking of the back bonds by H. From this base assumption, the kinetic equations for both processes can be written:

$$\frac{dx}{dt}=N_g P e^{-E_a/kT}(12-x);\quad (0\leqslant x\leqslant 12), \tag{1}$$

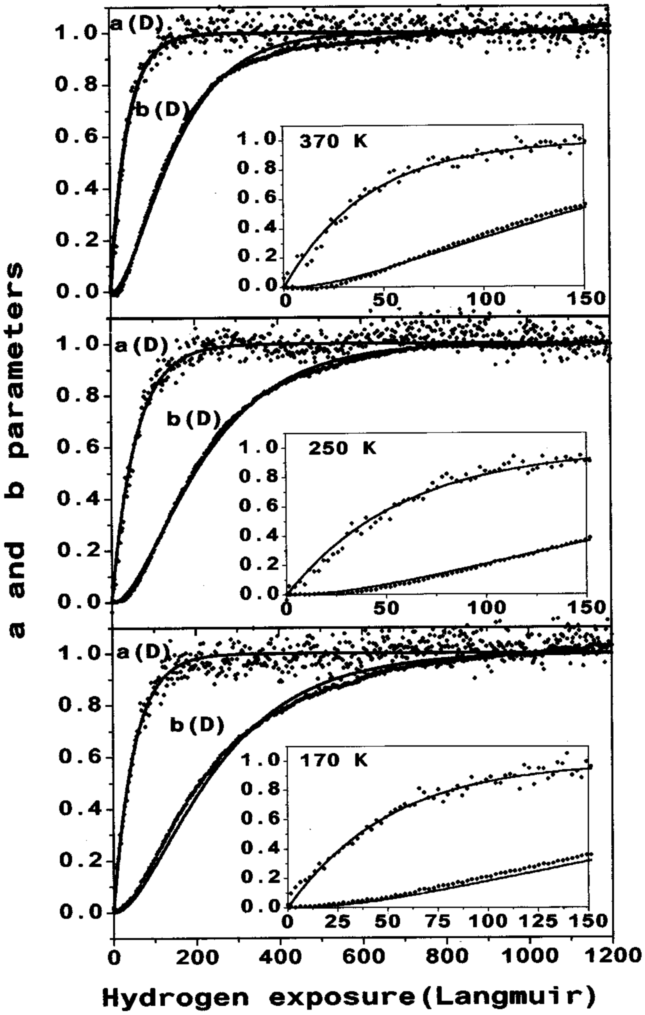

FIG. 2. Development of the weight factors $a(D)$ and $b(D)$ as a function of the H exposure D, for three temperatures of the sample: black circles, (spots). Theoretical fit from the solution of kinetics equations: continuous lines.

$$\frac{dy}{dt}=N_g P' e^{-E_b/kT}(3x-y);\quad (0\leqslant y\leqslant 3x). \tag{2}$$

The variables, $x(t)$ and $y(t)$, are the numbers of saturated ADDB's and broken ADBB's per cell as a function of the time t, respectively; N_g is the number of H atoms impinging the surface in the time unit; P and P' are the probabilities for H adsorption on ADDB's and ADBB's; finally E_a and E_b are the activation barriers for H binding to an ADDB and for breaking an ADBB, respectively. The right-hand parts of Eqs. (1) and (2) are proportional to the number of available sites per unit cell for each mechanism: $(12-x)$ is the number of free ADDB's; $(3x-y)$ is the number of BB's which can be broken, i.e., the number of back bonds of saturated adatoms. This relation considers that, when impinging on the surface, an H atom is either directly bound to an available chemisorption site, with a given probability α and β, defined by $Pe^{-E_a/kT}$ and $P'e^{-E_b/kT}$, respectively, or is reevaporated from the surface. Any diffusion of the H atom on the surface, which could finally find a binding site, is considered as negligible. If it were not the case, the development of parameter $a(D)$ would follow a linear increase until it reached its saturation value, which is not observed in Fig. 2. The solutions of these equations are

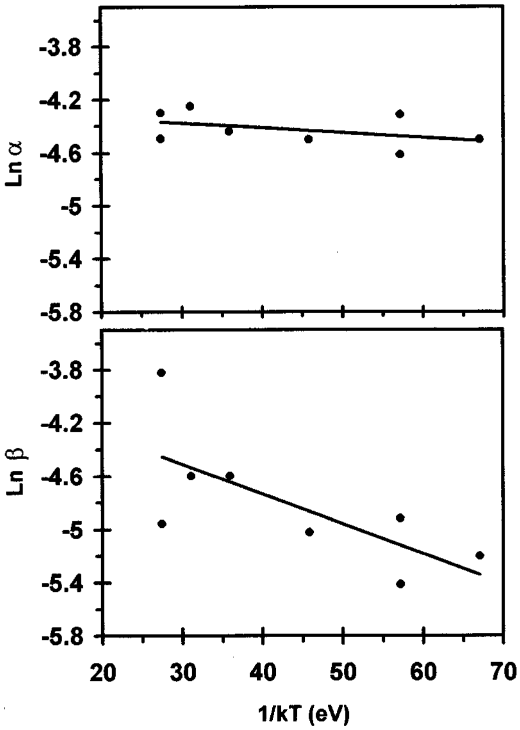

FIG. 3. Arrhenius plots of fit parameters α and β.

$$x(D)=12(1-e^{-\alpha D}),$$

$$y(D)=36\left(1-\frac{\beta}{\beta-\alpha}\,e^{-\alpha D}+\frac{\alpha}{\beta-\alpha}\,e^{-\beta D}\right),$$

where D is the dose of H designed by $D=N_g t$. The reduced quantities $\tilde{x}=x(D)/12$ and $\tilde{y}=y(D)/36$ correspond to the weight factors $a(D)$ and $b(D)$, and have been fitted to the experimental curves in Fig. 2 (continuous lines), leading to the determination of parameters α and β for every temperature. The good agreement between the experimental points [in spite of the fluctuation of the values of $a(D)$ due to light source instabilities] and the theoretical curves, strongly supports the validity of our hydrogenation model.

In order to check if parameters α and β follow an Arrhenius law, we have performed experiments at different temperatures. A semilogarithmic plot of α and β is drawn in Fig. 3. The slope of $\mathrm{Ln}\alpha$, corresponding to mechanism (a), is very small, which indicates that there is almost no activation barrier for direct absorption of H on the ADDB's. To our knowledge, it is the first time that this is experimentally shown, although this result was expected.[3] On the contrary, parameter β, i.e., mechanism (b), clearly depends on the temperature. The activation energies determined from Fig. 3 are $E_a=3\pm3$ meV and $E_b=20\pm10$ meV.[20] It must be noticed that, although larger than E_a, the value of E_b is still small.

Although several theoretical calculations concerning the binding energy of the Si(111)7×7 have been performed,[6–9] their results cannot be easily compared with our experimental values of E_a and E_b. Actually, E_a and E_b are the activation-barrier energies for the adsorption of H on the active sites and are not directly related to the binding energies which are of the order of a few eV.[7–9] On the contrary, to our knowledge, no calculation has been performed for determining the activation energies for H adsorption. Total-energy calculations for a variety of positions of a given H atom, far from the surface up to the adsorption sites, should make it possible to determine the actual path of the H atom and, as a consequence, the energy barriers the H atom has to overcome, either adsorbing on an adatom dangling bond, or breaking a back bond of a reacted or unreacted Si adatom.

Finally, Fig. 4 shows a picture of the schematic energy diagram for the reaction of a given Si adatom with an H atom. Initially, an H atom can easily adsorb on an adatom dangling bond, because of a very small or zero adsorption energy barrier, $E_a \leqslant 3$ meV. On the contrary, the bonding of H on a back bond is prevented by a large barrier E_b'. The adsorption of H on a dangling bond results in a weakening of the Si-Si back bonds, as indicated above, and therefore in a reduction of the activation barrier for the breaking of the back bond to the value $E_b \approx 20$ meV. However, this model is oversimplified and does not take into account probable forthcoming changes of this activation barrier, after one, two, and finally three back bonds have been broken. Accordingly, the E_b value determined here should instead be considered as an effective activation barrier. Moreover, our experiments could not give information on H adsorption on the rest atoms, neither could they distinguish between the different kinds of adatoms (center, corner, faulted, and unfaulted).

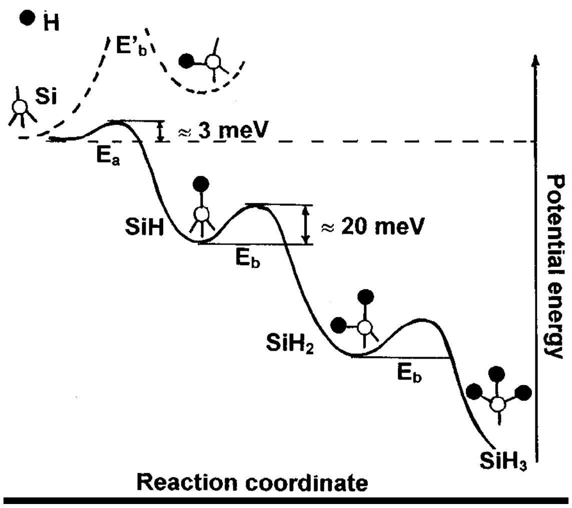

FIG. 4. Energy scheme of reaction paths between H and Si-adatom bonds.

To summarize, we have presented a real-time optical study of H adsorption on Si(111)7×7, which permitted us to distinguish two different adsorption channels and to follow their kinetics as a function of the temperature: H adsorption on the dangling bonds of the Si adatoms and H-induced breaking of adatom back bonds. We show that there is almost no activation barrier (<3 meV) for the adsorption on the dangling bonds. On the contrary, a large initial barrier prevents the breaking of the back bonds, but it reduces to $E_b = 20$ meV after the Si adatom is bound to an H atom, now making it possible for H to break the back bonds. Theoretical calculations for determining the activation barriers in the different configurations would be desirable in order to compare them to our present experimental results.

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[1] D. Rogers and T. Tiedje, Phys. Rev. B **53**, 13 227 (1996).

[2] J. J. Boland, Surf. Sci. **244**, 1 (1991).

[3] J. J. Boland, Adv. Phys. **42**, 129 (1993).

[4] C. Noguez, C. Beitia, W. Preyss, A. I. Schkrebtii, M. Roy, Y. Borensztein, and R. Del Sole, Phys. Rev. Lett. **76**, 4923 (1996).

[5] D. R. Alfonso, C. Noguez, D. A. Drabold, and S. E. Ulloa, Phys. Rev. B **66**, 1994 (1996).

[6] A. Vittadini and A. Selloni, Phys. Rev. Lett. **75**, 4756 (1995).

[7] H. Lim, K. Cho, I. Park, J. D. Joannopoulos, and E. Kaxiras, Phys. Rev. B **52**, 17 231 (1995).

[8] J. Z. Que, M. W. Radny, and P. V. Smith, J. Phys.: Condens. Matter **8**, 4205 (1996).

[9] L. Ye, A. J. Freeman, and B. Relly, Phys. Rev. B **48**, 11 207 (1993).

[10] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).

[11] C. J. Karlsson, E. Landemark, L. S. O. Johansson, U. O. Karlsson, and R. I. G. Uhrberg, Phys. Rev. B **41**, 1521 (1990).

[12] M. Roy and Y. Borensztein, Surf. Sci. **331/333**, 453 (1995).

[13] K. Mortensen, D. M. Chen, P. J. Bedrossian, J. A. Golovchenko, and F. Besenbacher, Phys. Rev. B **43**, 1816 (1991).

[14] F. Owman and P. Mörtensson, Surf. Sci. **324**, 211 (1995).

[15] U. Jansson and K. J. Uram, J. Chem. Phys. **91**, 7978 (1989).

[16] C. M. Greenlief, S. M. Gates, and P. A. Holbert, Chem. Phys. Lett. **159**, 202 (1989).

[17] Y. Borensztein, T. Lopez-Rios, and G. Vuye, Appl. Surf. Sci. **41/42**, 439 (1989).

[18] The amount of H is measured as a function of the exposure to molecular hydrogen. The actual quantity of H atoms impinging the surface cannot be determined easily, as it is a function of the H_2 pressure, of the active surface of the hot filament, of the distance between the filament and the sample, and of the temperature of the filament.

[19] G. A. Reider, U. Höfer, and T. F. Heinz, Phys. Rev. B **66**, 1994 (1991).

[20] Preliminary measurements published in Ref. 4 led us to propose a slightly underestimated value for E_b (13 meV). The present value takes into account more experimental data.