Probing the Si-Si Dimer Breaking of Si(100)2×1 Surfaces upon Molecule Adsorption by Optical Spectroscopy

Y. Borensztein,* O. Pluchery,† and N. Witkowski‡

Institut des Nanosciences de Paris (UMR CNRS No. 7588), Universities Paris VI and Paris VII, 4 place Jussieu,
F-75252 Paris cedex 05, France

(Received 21 December 2004; revised manuscript received 20 May 2005; published 7 September 2005)

The adsorption of atoms and molecules of several gases of the Si(100)2×1 silicon reconstructed surface is investigated by surface differential reflectance spectroscopy. This UV-visible optical spectroscopy makes possible the discrimination between two adsorption modes, depending on whether or not the adsorption leads to breaking the Si-Si dimers. The observation of two different optical features is assigned to the bonding on dangling bonds or to the breaking of dimers, and gives access to the adsorption mode of hydrogen, water, oxygen, and pyridine. Moreover, the technique being quantitative, we can determine the total amount of dimers involved in the adsorption and monitor the adsorption kinetics.

DOI: 10.1103/PhysRevLett.95.117402 PACS numbers: 78.68.+m, 68.43.−h, 73.20.−r

In the past few years, an increasing amount of work has been dedicated to the grafting of organic molecules on the Si(100) surface [1]. Such hybrid systems open the way for integrating the electronic, optical, or biological properties of organic layers in silicon-based devices. In this so-called "bottom-up" approach, the well-ordered Si(100)2×1 surface can be used as a template in order to organize and grow ordered organic layers [2]. To this end, it is critical to understand and to control the atomic-level phenomena at the interface between Si and the molecular layer. The Si(100) surface, prepared in ultrahigh vacuum, displays a 2×1 reconstruction, due to the formation of rows of parallel Si-Si dimers [3]. Each Si atom of a dimer exhibits one dangling bond, which is particularly reactive towards adsorption of atoms or molecules. Understanding the nature of the interface between molecules and silicon requires one to determine the structural changes of the Si dimers (and their possible breaking) and of the number of dimers involved in the bonding with the adsorbed molecules [4–6]. However, the structural investigation of the interface, by the usual laboratory surface techniques using electrons [low-energy-electron diffraction (LEED), high-resolution-electron-energy-loss spectroscopy] or by scanning-tunnel microscopy (STM), is actually a difficult task, because direct access to the interface is prevented by the presence of the adlayer. On the contrary, techniques based on photons can be used to study the interface through the adsorbed thin film. Infrared spectroscopy can probe Si-molecule bonds and internal molecule vibrations [7], but does not inform on the Si-Si bond itself. Synchrotron-based techniques like x-ray photoelectron diffraction (XPD) [5], x-ray photoelectron spectroscopies [6], inelastic x-ray scattering [8], and x-ray absorption spectroscopy [9] have recently given valuable information on the interface between organic molecules and Si(100). However, these techniques require synchrotron and cannot be used in a routine manner. Although the previous techniques (except XPD [5]) give access to the configuration of the adsorbed molecules, they cannot directly determine the possible changes of the Si-Si bonds at the interface, such as dimer breaking of the dimers. On the other hand, several surface-sensitive linear optical techniques have been developed in the past two decades and have proved to be efficient for studying surfaces, buried interfaces, growth of thin films, or adsorptions [10]. They are easy-to-use and versatile laboratory techniques. Reflectance anisotropy spectroscopy (RAS), measuring the optical anisotropy of the surface of a crystal [e.g., Si(100)2×1], has been applied successfully for semiconductor [10] and metal surfaces [11]. Surface differential reflectance spectroscopy (SDRS) measures changes of the reflectance of a crystal, induced by adsorption (removal of surface states, additional interface states, etc.) [10]. Moreover, real-time SDRS, during gas exposure, reveals the adsorption kinetics [12].

We demonstrate that SDR spectroscopy may unravel the bonding mode of different molecules on Si(100)2×1 and provides a clear way to discriminate between the breaking of the surface Si dimers and their preservation upon gas adsorption. This is shown by comparing two model cases: the monohydride Si(100)2×1:H surface (mono-H) where the Si dimers are intact and the dihydride Si(100)1×1:H surface (di-H) where they are broken. The corresponding SDR spectra are used as the "optical fingerprints" of the adsorption processes. These results are compared to the case of other adsorbed molecules (water, oxygen, pyridine). SDRS giving quantitative information, we can estimate the number of surface dimers involved in the bonding and determine kinetics.

The Si(100)2×1 surfaces were prepared in ultrahigh vacuum (5×10^{-11} mbar) by flashing the samples at 1050 °C. Heating is achieved by direct current flow through the samples. The samples, 4° misoriented along the [011] direction, are constituted of 2×1-reconstructed terraces separated by double steps, with all the dimers parallel to the steps in the $[1\bar{1}0]$ direction [13]. Surface quality was verified, not only by LEED and STM, but also by RAS, which is very sensitive to the quality of the reconstruction and to possible contamination. Purity of gases was checked by use of a mass spectrometer. H_2 molecules, introduced at a pressure of 10^{-6} mbar, were dissociated by a hot tungsten filament located at 5 cms in front of the sample. SDRS was performed by use of a homemade apparatus [14], with an incidence of 45° and with s-polarization perpendicular to the dimers.

In the first part, we consider adsorption of hydrogen atoms (H_{at}) on Si(100)2×1. Adsorption at high temperatures (HT) around 600 K yields a mono-H surface, where the 2×1 organization of the surface is maintained, and where every dangling bond (DB) is bound to a single H_{at} [15]. On the contrary, adsorption at room temperature (RT) breaks all the dimers, and leads at saturation to a slightly disordered hydrogenated surface, with large parts of the surface made of ordered di-hydrogenated Si atoms (as an ideal unreconstructed Si surface saturated by H) [15]. In this di-H phase, Si atoms are bound to two underneath Si atoms and two H_{at} at the surface. These two surfaces obtained at H saturation (mono-H at 600 K and di-H at RT) can be considered as archetype surfaces. Figure 1 gives the corresponding SDR spectra (a) and (b), defined by $\frac{\Delta R}{R} = \frac{R_{\mathrm{Si}} - R_{\mathrm{Si:H}}}{R_{\mathrm{Si}}}$, where R_{Si} and $R_{\mathrm{Si:H}}$ are the reflectances of the clean and the hydrogenated surfaces, respectively. At this point, it is important to make explicit the information gained from SDRS. The optical reflectance R_{Si} of the Si(100)2×1 surface is the sum of a bulk component and of a surface one, which originates both from the presence of surface states and from the 2×1 symmetry of the surface [16]. As known from density functional theory (DFT) [17], the surface component involves numerous electronic transitions: (i) transitions from or to specific surface states, which can be surface-to-surface, surface-to-bulk, or bulk-to-surface transitions; these transitions are evidently very sensitive to any change of the surface electronic structure, for example, induced by adsorption. (ii) Transitions between bulk electronic states in the vicinity of the surface, which can be different from the same transitions within the bulk, because of the different symmetry at the surface or of strain induced by the surface, and therefore can also contribute to the "surface optical response"; these surface-modified bulk transitions (mainly transitions at the so-called critical points, as indicated below) are sensitive to more important structural changes at the surface. When H_{at} is adsorbed at the surface, the appearance of optical features in the SDR spectrum is therefore related to the removal or to modifications of these different transitions.

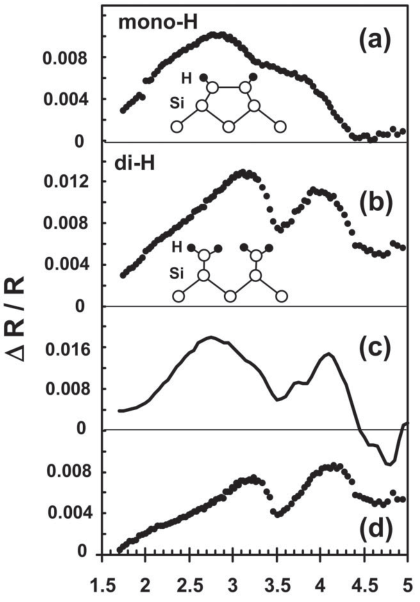

FIG. 1. (a) SDR spectrum after complete H adsorption on Si(100)2×1 at 600 K; (b) SDR spectrum after complete H adsorption at 300 K; (c) DFT calculation corresponding to (b), from Ref. [17]; (d) contribution of the dimer breaking to the SDR signal.

When H is adsorbed at HT, the spectrum drawn in Fig. 1(a) displays only one main peak centered at 2.9 eV, with a small shoulder at higher energy. At this temperature, the surface is an almost perfect mono-H phase, where each DB of the Si dimers is bound to 1 H atom, and the Si-Si bond within each dimer remains intact [see inset of Fig. 1(a)]. Consequently, the spectrum of Fig. 1(a) displays only (or mainly) the contribution of the transitions involving the DB electronic states, and can be viewed as the optical fingerprint of the adsorption on the dangling bonds. It cannot be excluded that the weak shoulder around 4 eV could be due to a small amount of hydrogen atoms incorporated in silicon that would break some of the Si dimers. It is worthwhile to note that this spectrum does not display any sharp feature at the critical point (CP) energies of silicon, $E_0 - E_1'$ at 3.45 eV and E_2 at 4.35 eV, which is the indication that no surface-modified bulk transition is involved in this spectrum [18]. On the contrary, when H is adsorbed at RT, giving the di-H surface, all dimers are broken and the 2×1 reconstruction is removed. The spectrum, drawn in Fig. 1(b), displays two main peaks around 3.1 and 4 eV. As the comparison is now made between the initial clean reconstructed surface and the fully hydrogenated surface with no reconstruction, whose reflectance $R_{\mathrm{Si}-1\times1:\mathrm{H}}$ is close to the one of bulk silicon [19], this spectrum provides the intrinsic surface optical response of the bare Si(100)2×1 surface. This experiment is, indeed, in good agreement with DFT calculations [13,17], drawn in Fig. 1(c) [20]. The differences with experiment can be due to the approximations used in the theoretical model and to the fact that the effect of steps is not included. In order to isolate the only contribution to SDR of the breaking of the dimers, we have studied in more detail the RT H adsorption, which appears to occur in a two-stage process: adsorption on the dangling bonds [giving a spectrum similar to spectrum 1(a)], followed by the breaking of the dimers [21]. The change from the first to the second stage provides this contribution, and is drawn in Fig. 1(d). This difference spectrum is therefore the optical fingerprint of the dimer breaking, and originates both from suppression of surface transitions involving specific electronic states of the Si-Si dimers, and from suppression of surface-modified bulk transitions due to the removal of the 2 × 1 reconstruction. This spectrum can be viewed as a broad positive feature, extending from about 3 to 4.5 eV, superimposed with a sharp negative one located close to the energy 3.45 eV of the $E_0 - E_1'$ CP, which gives the observed minimum. This minimum is therefore most likely related to bulk transitions, which are modified in the vicinity of the 2 × 1-recontructed surface. It has been shown, indeed, that such features can originate from strain extending into bulk caused by surface stress related to reconstruction, dimerization, and presence of steps [18].

This approach provides a phenomenological tool which permits us to discriminate between the adsorption on the Si dangling bonds [Fig. 1(a)] and the breaking of the Si dimers [Fig. 1(d)]. Spectrum 1(b) gives the sum of both effects resulting from the complete removal of the reconstruction and the passivation of dangling bonds.

The second part of this Letter is the validation of the previous results and their use for investigating other adsorptions. The first purpose is achieved by checking that similar optical spectra are obtained with other adsorbed molecules, which means that SDRS depends little on the kind of adsorbate, but rather on the bonding of the adsorbate with the substrate. The case of H_2O adsorbed at RT on Si(100)2 × 1 is presented in Fig. 2(a). The spectrum is very similar to the one obtained for the mono-H surface [Fig. 1(a)], but different from the di-H one [Fig. 1(b)]. This shows clearly that water is bound to the DBs of the dimers and that the dimers are not broken. This is in agreement with the dissociation picture, where water molecules are dissociated into an H_{at} and an hydroxyl OH, bound to both DBs of a dimer [22]. Moreover, the almost equal intensity between spectra for H and H_2O confirms that all Si dimers accommodate water molecules (it is shown in the next paragraph that SDRS gives quantitative information). The second comparison is with the case of oxygen. Spectra (b) and (c) of Fig. 2 have been measured after RT adsorption of 160 Langmuirs (L) and 2 L of molecular oxygen, respectively. Spectrum 2(c) is very similar to spectrum 1(d), with a smaller intensity. It means that, at small amounts, O molecules break the dimers, removing the corresponding internal states and reducing the surface-induced strain but that, on the contrary, the surface states related to the dangling bonds are preserved. The exact mechanism of oxidation of Si(100) at RT is still under intense debate, several mechanisms being proposed [23]. Our observation is actually in excellent agreement with a very recently proposed picture for the adsorption of a small amount of oxygen (schematized in Fig. 2), where O_2 is dissociated, with one oxygen atom incorporated within the Si-Si dimer bond leaving the DB unsaturated and the other one incorporated in a backbond [24]. The feature around 2.2 eV is probably due to noise, originating from intense lines of the deuterium lamp, although it cannot be excluded that it could be an oxygen-related optical transition [24]. For a larger amount, the spectrum 2(b) is similar to spectrum 1(b), which we explain as a further oxidation, which now removes the surface states of the Si dangling bonds. The smaller intensity with respect to the case of H [1(c)] is likely due to incomplete oxidation of the surface at 160 L, therefore to the preservation of Si dimers that have not reacted.

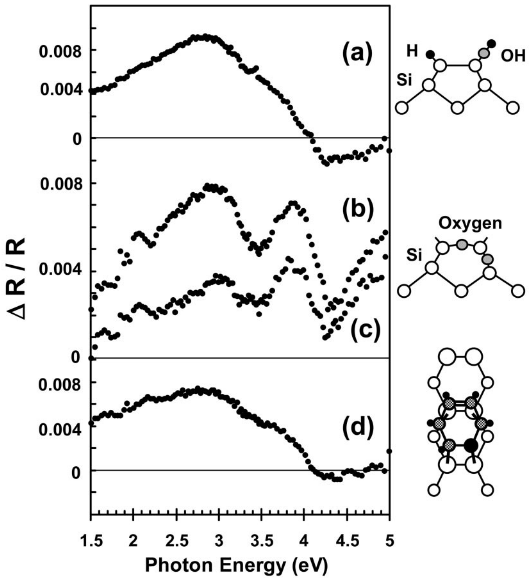

FIG. 2. SDR spectrum after adsorption of different molecules on Si(100)2 × 1 at 300 K. (a) saturation of water; (b) 160 L oxygen; (c) 2 L oxygen (× 1.5); (d) saturation of pyridine. The schemes on the right give the most probable configurations for the molecule geometries on the surface.

Finally, we have also used SDRS to study the adsorption of pyridine, which has been so far very little investigated [25–27]. Figure 2(d) gives the spectrum obtained after saturation at RT. It has a similar shape as the one obtained for mono-H [Fig. 1(a)] and for water [Fig. 2(a)]. We can conclude that pyridine molecules do not break the Si dimers, but adsorb on Si dimers via the available dangling bonds. Moreover, quantitative information on the amount of adsorbed species can also be obtained from SDRS [12], which gives an insight into the adsorption kinetics. In order to illustrate this property, Fig. 3 shows the SDR intensity integrated over the whole energy range, during H_{at} exposure at 600 K. The increase is linear almost up to saturation, where the Si(100)2 × 1:H is obtained, and does not follow a Langmuir kinetics, whose best fitted curve is also drawn. Such a behavior has been previously experimen-

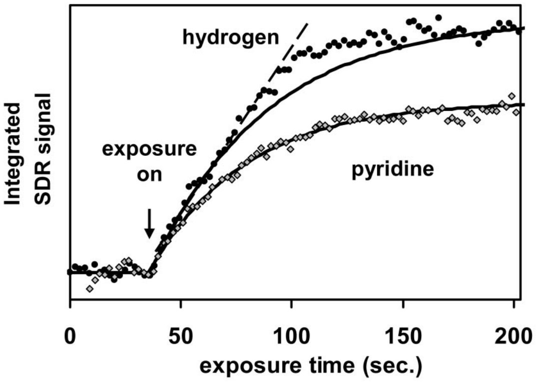

FIG. 3. Variation of the integrated SDR signal as a function of time during H_{at} exposure at $T = 600$ K and pyrdine exposure at room temperature. Continuous lines are best fittings within the Langmuir model.

tally obtained and is explained by the formation of "hot precursors" on the surface, leading to a linear increase of chemisorbed H [28]. This shows that SDRS gives a measure of the H coverage or, more precisely, of the number of dangling bonds that have reacted with H. This quantitative property of SDRS can be exploited for determining coverage and kinetics for other adsorptions, in particular, for pyridine. The intensity of the SDR signal at saturation of pyridine [Fig. 2(d)] is about 75% the one of the signal for the mono-H phase [Fig. 1(a)]. We can therefore conclude that about $3/4$ of the dimers are affected by the adsorption. Very recent *ab initio* calculations have concluded that each pyridine molecule is adsorbed on a bridge site and is bonded to two successive dimers on a row [26], as indicated in the corresponding scheme in Fig. 2. In the ideal case where the molecules would be perfectly ordered along the dimer rows, all dimers would be involved in a bonding with a pyridine molecule. Our observation that only 75% of the dimers are affected by the adsorption is not contradictory and can be explained by the proposed bridging sites for the adsorption: the locations where molecules impinge the surface are distributed in a stochastic way, and consequently some of the dimers remain unbound (e.g., a single dimer between two reacted pairs of dimers). Monte Carlo calculations have shown us that, on the vicinal surface, the average number of dimers bound to pyridine should be about 84%, which would lead to a SDR intensity reduced to the same amount, not far from our observation. In contrast to hydrogen, the experimental points for pyridine, drawn in Fig. 3, are perfectly reproduced by a Langmuir mechanism, which is expected for the previous adsorption picture.

In conclusion, by the use of SDRS during adsorption, we could determine whether the Si dimers of Si(100) are broken or not upon molecule absorption, and we could get a good estimation of the number of dimers involved in the bonding. Different kinetics for H and pyridine adsorptions could be distinguished by real-time SDRS. This opens the way for monitoring kinetics of adsorption, for determining successive stages in complex adsorption processes, and for investigating evolution of buried interfaces between silicon and thicker organic layers.

---

[*] Electronic address: yves.borensztein@insp.jussieu.fr
[†] Electronic address: olivier.pluchery@insp.jussieu.fr
[‡] Electronic address: nadine.witkowski@insp.jussieu.fr

[1] J. T. Yates, Science **279**, 335 (1998); M. Schulz, Nature (London) **399**, 729 (1999); G. P. Lopinski, D. D. M. Mayer, and R. A. Wolkow, Nature (London) **406**, 48 (2000); R. A. Wolkow, Annu. Rev. Phys. Chem. **50**, 413 (1999); J. M. Buriak, Chem. Commun. **12**, 1051 (1999).
[2] S. F. Bent, Surf. Sci. **500**, 879 (2002).
[3] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).
[4] A. J. Fisher, P. E. Blochl, and G. A. D. Briggs, Surf. Sci. **374**, 298 (1997).
[5] P. Baumgärtel *et al.*, New J. Phys. **1**, 1 (1999).
[6] Masashi Nagao *et al.*, Surf. Sci. **513**, 413 (2002).
[7] R. J. Hamers *et al.*, Acc. Chem. Res. **33**, 617 (2000).
[8] A. Föhlisch *et al.*, Phys. Rev. B **69**, 153408 (2004).
[9] N. Witkowski *et al.*, Phys. Rev. B **68**, 115408 (2003).
[10] P. Chiaradia and G. Chiarotti, in *Photonic Probes of Surfaces*, edited by P. Halevi (Elsevier Science, New York, 1995), Chap. 3; Y. Borensztein, Surf. Rev. Lett. **7**, 399 (2000).
[11] Y. Borensztein *et al.*, Phys. Rev. Lett. **71**, 2334 (1993).
[12] C. Noguez *et al.*, Phys. Rev. Lett. **76**, 4923 (1996); C. Beitia, W. Preyss, R. Del Sole, and Y. Borensztein, Phys. Rev. B **56**, R4371 (1997).
[13] Y. Borensztein and N. Witkowski, J. Phys. Condens. Matter **16**, S4301 (2004); Y. Borensztein, N. Witkowski, and S. Royer, Phys. Status Solidi (c) **0**, 2966 (2003).
[14] Y. Borensztein, T. Lopez Rios, and G. Vuye, Appl. Surf. Sci. **41–42**, 439 (1989).
[15] J. J. Boland, Surf. Sci. **261**, 17 (1992).
[16] R. Del Sole, in *Photonic Probes of Surfaces*, edited by P. Halevi (Elsevier Science, New York, 1995), Chap. 2; W. G. Schmidt *et al.*, Phys. Rev. B **67**, 085307 (2003).
[17] M. Palummo *et al.*, Phys. Rev. B **60**, 2522 (1999).
[18] K. Hingerl *et al.*, Appl. Surf. Sci. **175–176**, 769 (2001).
[19] C. Hogan, R. Del Sole, and G. Onida, Phys. Rev. B **68**, 035405 (2003).
[20] The intensity of the theoretical curve has been divided by $\sqrt{2}$ for comparison with the experiment performed at 45°.
[21] Y. Borensztein and N. Witkowski (unpublished).
[22] M. K. Weldon *et al.*, Phys. Rev. Lett. **79**, 2851 (1997).
[23] Yuhai Tu and J. Tersoff, Phys. Rev. Lett. **89**, 086102 (2002); Y. J. Chabal *et al.*, Phys. Rev. B **66**, 161315 (2002); B. D. Yu *et al.*, Phys. Rev. B **70**, 033307 (2004).
[24] A. Incze, R. Del Sole, and G. Onida, Phys. Rev. B **71**, 035350 (2005).
[25] Q. Li and K. T. Leung, Surf. Sci. **541**, 113 (2003).
[26] H.-J. Kim and J. H. Cho, J. Chem. Phys. **120**, 8222 (2004).
[27] Feng Tao *et al.*, J. Phys. Chem. B **107**, 6384 (2003).
[28] W. Widdra *et al.*, Phys. Rev. Lett. **74**, 2074 (1995).