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Ethylene on Si(001)-2×1 and Si(111)-7×7: X-ray photoemission spectroscopy with synchrotron radiation

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The adsorption of ethylene on Si(001)-2×1 and Si(111)-7×7 has been studied at 300 K using core-level (Si 2p, C 1s) and valence-band x-ray photoemission with synchrotron radiation. Dangling bonds play a very different role in the chemisorption process on these two surfaces. While for Si(001)-2×1 the quenching of the surface states ''monitors'' the molecule uptake, this is not the case for Si(111)-7×7: the adsorption process continues well after all surface states have disappeared, and carbon coverages greater than that deduced from the rest-atom/adatom bridge model are obtained. An alternative model is proposed, in which molecules are bonded directly to the rest plane. The thermal stability of both surfaces covered by ethylene is also studied. We relate the formation of carbon-rich layers at 820–860 K to the strong changes in the electronic structure of the silicon surface. [S0163-1829(98)02840-9]

I. INTRODUCTION

In recent years, there has been a great deal of interest in the adsorption and surface reaction mechanisms of olefins—molecules having at least one C═C bond—on clean silicon surfaces. The recent discovery[1] that a cyclic diolefin (1,5-cyclo-octadiene) adsorbs orderly at room temperature on a Si(001)-2×1 surface, through the addition of only one of its two unsaturated bonds to a Si_2 dimer, will certainly contribute to stimulate the research effort in that field: indeed, as the other C═C bond remains free for further types of surface attachment chemistry, the door is now open to fascinating developments in the field of microelectronic technologies.[2] In other respects, small π-hydrocarbons molecules, such as ethylene, cracked over Si surfaces in the temperature window 770–870 K, are used as carbon sources[3]—alternative to solid sources[4]—in the processes leading to the growth of pseudomorphic silicon-carbon alloys. Consequently, a detailed understanding of the mechanisms leading to olefin chemisorption, as well as an examination of their thermal stability on silicon surfaces, is useful for achieving the controlled growth of both organic thin films and $Si_{1-x}C_x$ ($x<1$) layers on silicon substrates.

Ethylene (C_2H_4) is the smallest olefin molecule. Despite its simplicity and the considerable amount of work devoted to the study of its interaction with Si surfaces, many aspects of the adsorption process remain misunderstood. On the ''technological'' face Si(001), which has been by far the most studied, there is strong experimental evidence[5–9] that, in a wide range of temperatures between 77 and ~600 K, C_2H_4 chemisorbs nondissociatively on the Si(001)-2×1 surface, *through the interaction of its* π *bond with the* π *bond of the surface* Si_2 *dimers*: the cleavage of the π bonds permits the formation of two new Si-C σ bonds—hence the adsorption geometry is called di-σ—and judging from the C-C stretching mode (1100 cm^{-1}) observed in high-resolution electron-energy-loss spectroscopy (HREELS), the C atoms are rehybridized to a state near sp^3.[5,8,9] Given that recent theoretical calculations[10] indicate that the σ bond of the Si_2 dimer remains intact—this issue has been in fact hotly debated (see Ref. 10)—the chemisorption process boils down to the cycloaddition of an ethylene molecule with a silicon dimer [a schematic picture of the final bonding geometry is given in Fig. 1(a)]. Only very recently, Liu and Hamers[11] proved by infrared spectroscopy that, at low coverage, the addition of ethylene on Si(001) *retains the stereochemistry* of the molecule. Eliminating the concerted suprafacial reaction mechanism, which is symmetry forbidden according to the Woodward-Hoffmann rules,[12] and the antarafacial +suprafacial mechanism, which inverts the stereochemistry, the latter authors proposed various nonconcerted addition reactions involving low-symmetry intermediates. Although it is generally admitted that the process is mediated by a molecular precursor, the kinetical aspects are not fully understood. Whereas the kinetical uptake measurements of Cheng *et al.*[6] and Clemen *et al.*[7] (carried out at 105 K) concluded that the measured saturation coverage of 0.8±0.07 monolay-

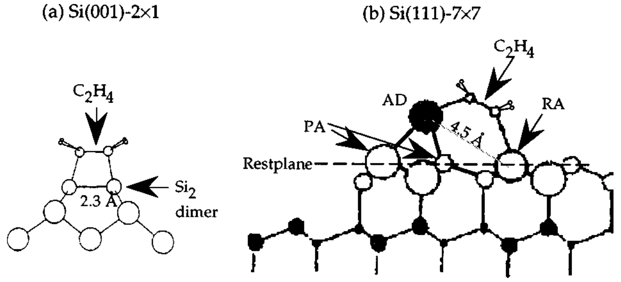

FIG. 1. (a) Schematic model (side view) of C_2H_4 adsorbed on Si(001)-2×1 (the uncleaved Si_2 dimer model). Calculations (Ref. 10) indicate a C_{2v} symmetry, although the angular dependence of HREELS loss features [in particular the symmetric Si-C loss peak (Refs. 5 and 8)] points to a lower symmetry. (b) Schematic model (side view) of C_2H_4 adsorbed on Si(111)-7×7 (the rest-atom/adatom bridging model), according to Ref. 18: RA, AD, and PA are the acronyms of rest-atom, adatom, and pedestal-atom, respectively (note that three PA bear one AD). Other adsorption sites (e.g., the ''removal'' of the AD) have to be envisaged to account for the adsorption kinetics (see text).

ers (ML) corresponds, in effect, to one molecule *per* silicon dimer if one assumes that 20% of the surface is defective *and* nonreactive, on the other hand, scanning tunneling microscopy (STM) (Ref. 13) (carried out at 300 K) pointed to a maximum coverage of only ~0.5 molecules *per* silicon dimer. In the latter experiment, it was observed that for exposures smaller than six Langmuirs (L) (1 L correspond to an exposure of 10^{-6} Torr s), *the chemisorption on neighboring silicon dimers is avoided*, the molecules forming, locally, a 2×2 or $c(2\times4)$ structure; even at exposures larger than 100 L, the fraction of molecules on neighboring dimers is still relatively small. To resolve this discrepancy, Hamers and Wang proposed that the defective sites are indeed very reactive,[14] and that after their reaction with ethylene, adsorption proceeds on normal sites, with the ratio of one molecule *per* two ''regular'' silicon dimer. In any case, there are hints, as stated by Liu and Hamers,[11] that ''the bonding of ethylene changes at high coverage.''

The thermal stability of an ethylene/Si(001) system has also been studied by HREELS combined with Auger electron spectroscopy (AES) (Ref. 5) and thermally programmed desorption (TPD) combined with AES.[7] The conclusions drawn from these experiments are at variance. In the HREELS/AES experiment (Ref. 5), the surface was exposed to 170 L (Ref. 15) at 300 K, and then heated to higher temperatures for one minute each. After the heating step at 650 K, AES evidenced the desorption of about 40% of the initial ethylene coverage, while the energy-loss peak attributed to CC stretching disappeared from the HREELS spectra, indicating that the CC bond is cleaved. [The molecule remaining on the surface would be decomposed to CH_x $(x=1,2)$ species and SiH species.] On the contrary, the TPD/AES experiment (Ref. 7) indicated that chemisorbed ethylene desorbs intact from Si(001) in the temperature range 550–590 K, with approximately 2% of the molecules undergoing dissociation. It has been recently shown[9] that the presence of coadsorbed hydrogen on the surface modifies substantially the branching ratio between molecular desorption and surface decomposition. Atomic hydrogen could indeed be coadsorbed unwillingly as a result of ethylene decomposition by gauge hot filaments or ion pumps, etc. As in the HREEL spectrum of Ref. 5, the SiH stretching mode is not visible after surface cleaning, nor after gas adsorption at 300 K; the origin of the discrepancy has to be sought elsewhere.

In comparison with the C_2H_4/Si(001) system, much less attention has been devoted to the study of C_2H_4 adsorption on Si(111)-7×7 although the complex reconstruction of that surface—the so-called dimer-adatom-stacking fault (DAS) reconstruction[16]—''provides a rich array of chemically inequivalent atoms ... resulting in a rich variety of spatially inhomogeneous chemical reactions.''[14] After a series of studies devoted to the reactivity of hydrocarbons on the cleaved Si(111) surface (see, for instance, Ref. 17), Piancastelli and co-workers tackled with the study of ethylene adsorption on Si(111)-7×7 at 300 K, using both STM (Ref. 18) and synchrotron radiation photoemission.[19] Photoemission spectroscopy ($h\nu=37$ eV) showed that valence-band surface states (the rest-atom band and the occupied part of the adatom band) are quenched simultaneously upon adsorption. Moreover, an upward shift of the shallower molecular orbitals is explained by an electron donation from the substrate to the molecule, a process also observed for Si(111)-2×1.[17] Adatoms are certainly involved in the adsorption process, because their brightness changes in STM topographies during an exposure to the gas [in contrast to the (001) face, the ''imprint'' of the molecule is not seen]. These experimental facts, joined to previous HREELS data,[20] showing that the molecule is adsorbed nondissociatively with a strong stretching of the CC bond (C hybridization changes from sp^2 to sp^3), led Piancastelli and co-workers to propose a model in which the molecule bridges a rest atom (RA) and an adatom (AD), separated by ~4.5 Å [the RA/AD bridging model is reported in Fig. 1(b)]—a distance considerably larger than the interatomic separation of the Si_2 dimers on Si(001), i.e., ~2.3 Å. To our knowledge, no thorough study of the thermal stability of the C_2H_4/Si(111) system has been carried out yet.

Although HREELS has made an important contribution to the present issue, synchrotron radiation x-ray photoemission (XPS) sheds light on various aspects of the surface reaction which are not attainable by a vibrational spectroscopy. Highly surface-sensitive Si $2p$ and C $1s$ photoemission permits a (semi)quantitative determination of the amount of adsorbates (molecules, fragment of molecules, C atoms) and of reactive surface sites (surface states).[21] Such a straightforward approach is practically impossible with HREELS, because the intensity of a loss feature is strongly affected by incident electron energy, scattering geometry, and molecule orientation.

The goal of this study is to determine the electronic structure—by synchrotron radiation XPS—of the molecule adsorbed at room temperature and to examine its thermal stability, both on Si(001)-2×1 and Si(111)-7×7. As the sites envisaged for di-σ bonding on (001) and (111) reconstructed faces strongly differ, we have examined comparatively the adsorption kinetics and the role played by silicon dangling bonds. Moreover, the ethylene coverage at saturation on the ''simpler'' Si(001)-2×1 surface was used as a template to determine the carbon uptake vs exposure on the Si(111)-7×7 face, which is documented incompletely.[22] As expected, the occupancy of surface levels is modified, on both surfaces, by the adsorption process, and the relationship between their ‘‘quenching’’ and carbon coverage is examined in detail and discussed with respect to the models of the literature. For instance, we have found—this is one of the major findings of this study—that the role played by the silicon dangling bonds strongly differs on each surface: whereas the adsorption process stops on Si(001)-2×1 when all surface states are consumed, the complete quenching of the rest-atom state of the Si(111)-7×7 surface need not mean the end of the adsorption process, in contradiction with the image of chemisorption we have formed so far for this surface [for the analogous case of acetylene adsorption on Si(111)-7×7, see Ref. 23]. Concerning the thermal stability of ethylene on Si(001), our results are essentially consistent with the HREELS/AES data of Ref. 5 (see above). For its part, the heating of a Si(111)-7×7 surface covered by ethylene up to a temperature of 860 K leads to the appearance of ‘‘1×1’’ reconstruction with a peculiar distribution of surface states in the gap, very likely related to the formation of a C-rich region close to the surface.

TABLE I. Durations, C_2H_4 pressures (uncorrected ion gauge reading), and corresponding exposures ($1\ L=10^{-6}$ Torr s) to which the Si(001) and Si(111) surfaces are submitted at 300 K.

C_2H_4/Si(001)-2×1 Time (s), pressure (Torr)	Total dose (L)
50, 7.5×10^{-9}	0.325
100, 7.5×10^{-9}	0.75
250, 3×10^{-8}	7.5
250, 3×10^{-8} +250, 3×10^{-7}	82.5
250, 3×10^{-8} +250, 3×10^{-7} +600, 3.75×10^{-6}	~2330
C_2H_4/Si(111)-7×7 Time (s), pressure (Torr)	**Total dose (L)**
120, 1.5×10^{-6}	180
480, 1.5×10^{-6}	720
960, 1.5×10^{-6}	1440
2160, 1.5×10^{-6}	3240
2700, 3×10^{-6}	8100

II. EXPERIMENT

A. Clean surface preparation and exposure to acetylene

The Si samples are prepared in the ultrahigh-vacuum (UHV) analyzing chamber whose base pressure is $\sim10^{-10}$ Torr. The chamber is evacuated by an ion-pump (400 l/s) (always valved off during measurements and sample preparations), a turbomolecular pump (500 l/s), and a cryopump (1000 l/s). The samples (phosphorus-doped silicon wafers, of resistivity 0.002–0.005 Ω cm) are heated by the Joule effect; temperature measurements are then made by infrared pyrometry. The silicon wafers are cleaned of their silica protective layer by heating at ~1520 K, in order to minimize SiC contamination.[24] The surface cleanliness is checked by the intensity of the Si $2p$ core-level surface state, by a survey of the C $1s$ region, and by the sharpness of the low-energy electron-diffraction (LEED) patterns.

Then the silicon surface is exposed to ethylene in the analysis chamber itself, under pressures in the range $0.75\times10^{-8}-3.75\times10^{-6}$ Torr. While the gas is introduced through a leak-valve, the cryopump is isolated, and the chamber is evacuated by the turbomolecular pump. Ethylene pressures are measured with an ionization gauge whose reading is not corrected. Exposures to the gas are given in Langmuirs (L) (pressures are indicated in Table I).

B. X-ray photoemission

Photoelectron energy distribution curves are measured for valence bands, Si $2p$, and C $1s$ core levels with monochromatic synchrotron radiation and a partially angle-integrating electrostatic electron energy analyzer (RIBER MAC2). The linear polarization of the synchrotron radiation **E** is at 40° with respect to the axis of the cylindrical electron analyzer, defining an horizontal scattering plane. The sample surface is put in the common focus of the light beam and of the analyzer entrance lens and can be oriented about the vertical axis through the photoemission spot. The sample surface normal is always parallel to the analyzer axis and the light polarization vector is contained in the (110) plane of the Si(001) surface and in the (112) plane of the Si(111) surface. The light source is the linear undulator DOMINO of beam line SU7 of the SuperACO storage ring. The undulator radiation is monochromatized by a 10-meter toroidal grating monochromator covering the 130–800 eV photon range. Photons of energy 145 eV are used to excite the Si $2p$ core level of binding energy (BE) around 99 eV, in conditions of maximum surface sensitivity: for photoelectrons of kinetic energy around ~45 eV an escape depth of about 3.3 Å is estimated.[25] The C $1s$ spectra (BE around 284 eV) are recorded at $h\nu=330$ eV, so that the kinetic energy of the C $1s$ photoelectrons and thus their escape depth equal those of the Si $2p$ photoelectrons. Valence bands are also measured at $h\nu=145$ eV.

In order to improve the resolution of the various components that contribute to the Si $2p$ spectra, the procedure given in Ref. 21 is followed. The background is first subtracted. Then the low j component of the Si $2p_{1/2,3/2}$ doublet is removed, mathematically (assuming identical shapes for the two components), with a branching ratio $2p_{1/2}:2p_{3/2}$ of 0.5 (the statistical ratio) and a spin-orbit splitting of 0.6 eV. In order to fit the Si $2p_{3/2}$ spectra, each chemical state is represented by a Gaussian convoluted by a Lorentzian of 0.1 eV full width at half maximum (FWHM). On the other hand, the C $1s$ spectra are simply reconstructed by sums of pure Gaussian components. In the least-squares fitting routine, we fix the Gaussian FWHM for each chemical state and in most cases BE positions are free parameters.

The zero binding energy (the Fermi level E_F) is taken at the leading edge of the Si(111)-7×7 adatom surface states (this surface is metallic[26]).

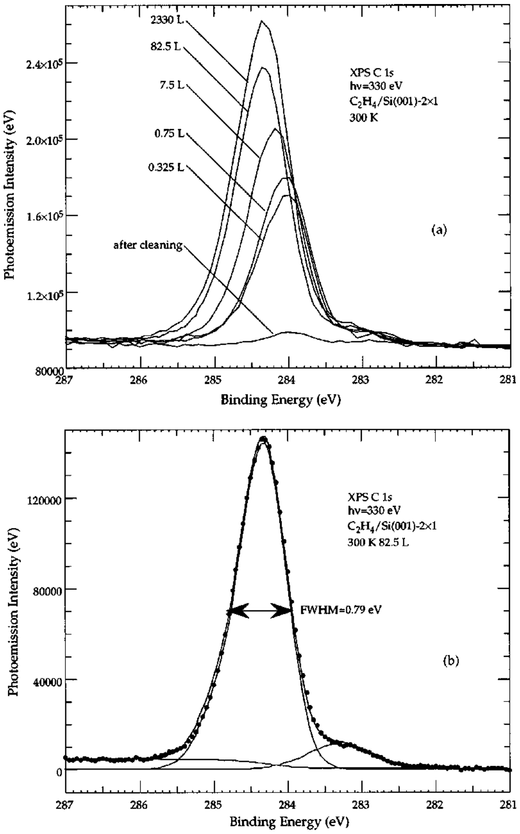

FIG. 2. (a) C 1*s* core-level photoemission spectra of the Si(001) surface after successive exposures to acetylene at 300 K. Note the BE energy shift (~+0.3 eV) of the C 1*s* peak centroid at saturation. (b) Typical C 1*s* spectrum (dots) and fit (solid line) by a Gaussian at 283.25 eV (FWMH=1 eV) and an asymmetric line simulated by a doublet (two Gaussians with a branching ratio of 0.21 and an energy splitting of +0.58 eV, the main component being at 284.3 eV).

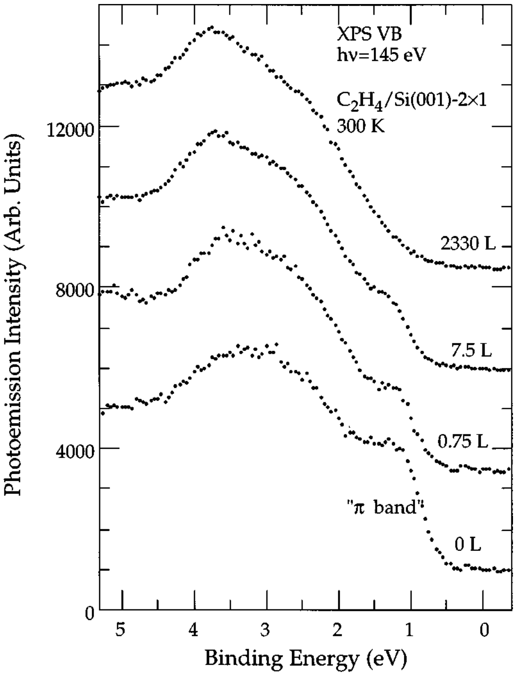

FIG. 3. Valence-band spectra of a Si(001)-2×1 surface exposed to increasing doses of ethylene at 300 K.

III. RESULTS AND DISCUSSION

A. Ethylene on Si(001)-2×1

1. Adsorption at room temperature

During ethylene adsorption, in the 0–2330 L range, the LEED patterns remain characteristic of a 2×1 reconstruction. The evolutions of the C 1*s*, valence band, and Si 2*p* spectra with increasing exposures to ethylene (see Table I) at room temperature are reported in Figs. 2, 3, and 4, respectively. The measurement of C 1*s* intensity and that of the core-level surface-state weight, clearly visible in the Si 2*p* spectra, allows a kinetic study of ethylene adsorption and of surface silicon dimer reaction. Obviously this is possible only if both core levels are obtained with an identical experimental configuration, a condition fulfilled by our measurements, and if the adsorption process affects only the top silicon layer, which is demonstrated unequivocally in the present XPS work. We give in Fig. 5(a) the variation of C 1*s* intensity, normalized to its maximum intensity—reached at 2330 L—vs exposure and in Fig. 5(b) we report the intensity of the core-level surface states vs C 1*s* intensity, i.e., carbon coverage.

The C 1*s* line, whose overall shape does not change appreciably with increasing coverage [Fig. 2(a)], is composed of two lines [Fig. 2(b)]: a small peak at 283.3 eV (FWHM~1 eV), whose intensity is always 8–9 % of the whole spectral weight, and a main line (FWHM~0.80 eV), centered around 284 eV (note that the peak centroid shifts slightly from 284 to 284.3 eV with increasing coverage). These two components are attributed to two different chemical states of the adsorbed molecule. Indeed, the low BE structure is found where products of the thermal decomposition (Sec. III A 2) show up—in the 283.9–283.4 eV range. However, a silicon carbide contamination due to a nonefficient thermal cleaning of the surface is excluded, as silicon carbide and carbidelike products have BE's in the energy range 282.7–282.4 eV (Ref. 23 and Sec. III A 2). For its part, the main line at high BE comes certainly from the molecule adsorbed *intact* on a Si dimer. Its shape asymmetry might be explained by an insufficiently resolved vibrational fine structure. In the gas phase the C 1*s* spectrum shows a distinct peak at ~400 meV from the main line due to excitation of a C–H stretching vibration.[27] Naturally, deuterium-labeled gas needs to be used to obtain a clear-cut answer, since there would be a difference in the energies (by a factor of $\sqrt{2}$ assuming a linear harmonic oscillator) of the vibrational losses for H and D due to their different masses.

Although the attachment, on the surface, of molecular fragments [e.g., CH_2 (Ref. 28)], or of such species such as ethylidene ($CH\text{-}CH_3$), has to be envisaged, the C 1*s* photoelectron spectra point to the fact that nondissociative chemisorption is the major pathway, whatever the exposure to the gas, in agreement with HREEL spectroscopy (Ref. 5).

The valence-band surface states (Fig. 3) are strongly affected by the adsorption process. As expected for a di-σ chemisorption and in accord with the scanning tunneling spectroscopy data,[13] the intensity of the occupied silicon dimer π-band states diminishes with increasing exposures. This implies that the weak π bond formed by the silicon dangling bonds is removed and that stronger silicon-carbon

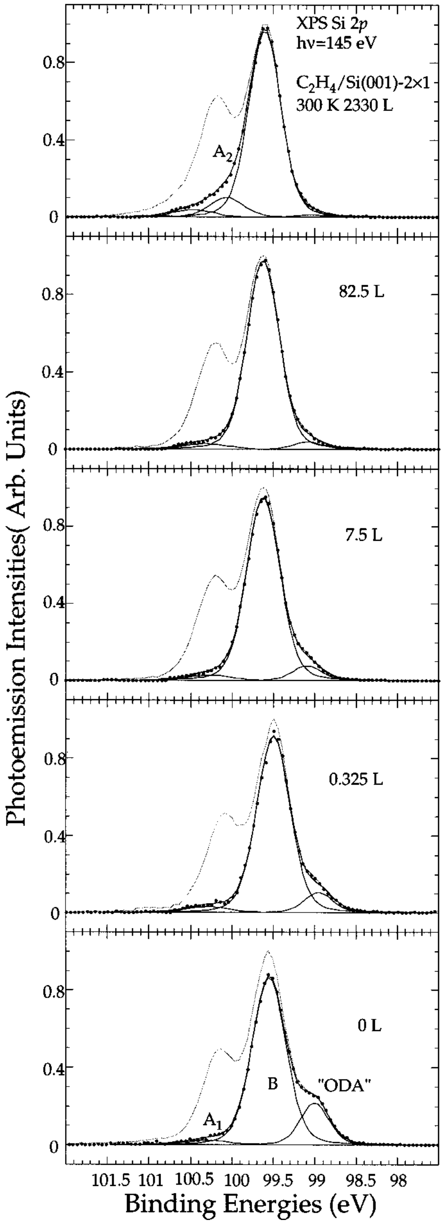

FIG. 4. Si $2p$ core-level photoemission spectra (gray solid line) and Si $2p_{3/2}$ component, after $2p_{1/2}$ stripping (dots), obtained from a Si(001)-2×1 surface exposed to increasing doses of ethylene at 300 K. Fits of the Si $2p_{3/2}$ spectra are also given (dark solid line). The Gaussian FWHM is 0.35, 0.41, 0.5, and 0.55 eV, for components ''ODA,'' B, A_1, A_2 (the Lorentzian FWHM is 0.1 eV for all components).

bonds are formed. We note no shift in the energy position of the surviving surface states greater than 0.1 eV.

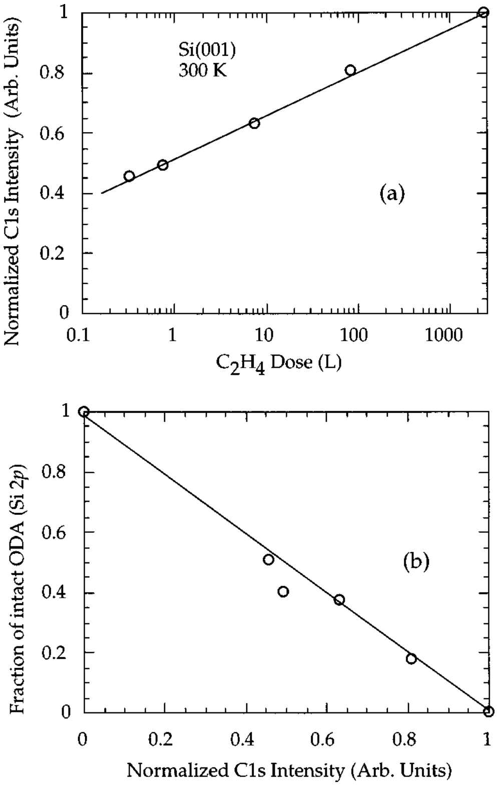

FIG. 5. (a) C $1s$ photoemission intensity vs ethylene dose (L) to which the Si(001) surface is exposed. (b) Fraction of intact ODA (the clean surface ODA weight is 17% of the overall Si $2p$ intensity) as a function of C $1s$ intensity.

The gradual quenching of the valence surface states is directly reflected by changes affecting the Si $2p$ core-level surface states, whose intensity measurement is much more handy than that of valence-band surface states. The clean surface Si $2p_{3/2}$ spectrum (Fig. 4) can be fitted by three components. The pronounced surface core level at ~ -0.55 eV above the bulk line B is assigned, in the framework of the *asymmetric dimer model*, to half a monolayer (ML) of negatively charged outer dimer atoms (ODA) (Ref. 21): its weight is 17% of the total spectral intensity. Calculations[29] and high-energy resolution spectra[30] suggest that the surface core level corresponding to the positively charged inner dimer atoms is expected to be contained in the bulk line B. A slightly larger FWHM of line B with respect to the ODA line may account for this. The third line (line A_1) situated at ~0.9 eV below the bulk line (about 2.5% of the total spectral intensity) needs to be introduced to take into account the slight asymmetry towards higher BE. Its origin is unclear. With increasing exposure to ethylene, the bulk line BE does not vary (there is no appreciable E_F shift); the ODA line intensity decreases, but its BE does not change either. This means that the electronic structure of the ODA's (charge and core-hole screening) ''spared'' by ethylene adsorption does not change much with increasing coverages, in agreement with valence-band spectroscopy. A very important observation is the lack of any *visible structure related to the formation of a silicon-carbon bond*, at least up to an exposure of 82.5 L, for which ~80% of the initial Si dimers are reacted [Fig. 5(b)]. Only after an exposure to 2330 L has the ODA peak definitely disappeared and a new line, denoted A_2, shifted by +0.5 eV from B, weighing about 8% of the total spectral intensity, is introduced to account for the increased Si $2p$ asymmetry towards higher BE.

We can now discuss the kinetical aspects of ethylene adsorption at 300 K. We have observed that C $1s$ intensity does not increase for exposures typically greater than 2330 L, in other words the surface appears to be saturated. Equating C $1s$ intensity with carbon coverage θ, let us normalize this maximum coverage to 1 [Fig. 5(a)]. It is then clear that ethylene adsorption follows a fast regime for $\theta \leqslant 0.5$, reached after exposures to 0.75–1 L: when 1.3×10^{14}–1.7

$\times 10^{14}$ molecules/cm^2 have impinged on the surface (we take a gauge correction factor of 2.3), about half the silicon dimers are reacted [Fig. 5(b)]. As the surface density of silicon dimers is 3.4×10^{14} per cm^2, the sticking coefficient should be constant and nearly equal to unity in the fast initial regime for which $\theta \leqslant 0.5$. For $\theta > 0.5$, a much slower regime follows as thousands of Langmuirs are required to reach saturation. In opposition to the guess of Hamers and Wang,[14] there is no initial regime where ''defective'' sites react preferentially: Fig. 5(b) shows clearly that in both regimes (fast and slow) θ is equal to the fraction of reacted silicon dimers. Although the adsorption rate diminishes strongly for $\theta > 0.5$ [Fig. 5(a)], ethylene reaction with the dimer sites always governs the process. Finally, our kinetical data obtained at 300 K resemble those obtained by Clemen *et al.*[7] at a lower temperature of 105 K. Only the concept of defective dimers, and their surface density, has to be explained. The discrepancy emphasized by Mayne *et al.*[13] between a saturation coverage of one molecule per dimer (as measured from kinetic uptake[6,7]) and a saturation coverage of one molecule per *two* Si dimers [as deduced from the STM observation of local 2×2 or $c(4\times 2)$ ordering] is only apparent. There is most certainly a critical coverage $\theta_c = 0.5$ after which the adsorption rate decreases strongly, but nothing forbids the completion of 1 ML of adsorbed ethylene if the surface is exposed to large doses. In the present work (see Table I), we have increased the pressure to 3.75×10^{-6} Torr to obtain thousands of L within reasonable times (600 s). Pressure may be an important parameter, whose effect needs a proper study.

The reason why ethylene adsorption on neighboring silicon dimers is avoided for $\theta < \theta_c$ remains obscure. In the scanning-tunneling-spectroscopy curves of Ref. 13, measured on the Si_2 dimer left intact after exposure to the gas, the π state moves apparently by 0.4 eV further away from E_F: the decrease in reactivity is attributed to such a downward motion.[31] In contrast, the present study does not indicate a measurable change in the electronic occupancy of the surviving dimers.

The very puzzling observation is the absence of any resolvable Si $2p$ core-level shift associated to the formation of two Si-C bonds per Si_2 dimer. It is true that, given the present resolution, a component weighing ~34% of the overall intensity (i.e., the spectral contribution of one top surface ML), and shifted from B by less than +150 meV, could not be evidenced. In any case, the shift of the Si-C component is smaller than that estimated from the empirical rules familiar to the spectroscopists. Core-level shifts are indeed due to initial-state and final-state effects. Because of the large dielectric constant of Si (and nearly complete screening of the core hole), it is often stated that final-state effects are minimized.[21] Initial-state shifts are interpreted in terms of charge transfer, from or to the Si valence orbital. This charge transfer is empirically correlated with Pauling's electronegativity difference $\Delta\chi$ between the ligand and silicon. With respect to silicon, carbon is more electronegative than silicon and $\Delta\chi$ amounts to 0.7.[32] Arsenic, whose electronegativity difference with silicon is smaller ($\Delta\chi = 0.2$), gives core-level shifts of about 0.2 eV (Ref. 25)–0.25 eV (Ref. 33) per ligand. Consequently, if this picture were always valid, we would expect a core-level shift to higher BE larger than 0.2 eV for surface silicon atoms, each of them being tied up with one carbon atom and three silicon atoms. This is not observed in the present case, in contrast with a recent synchrotron radiation Si $2p$ core-level study of the dissociative adsorption of neopentane on Si(111):[34] the growth of components shifted by +0.5 and +1 eV from the bulk line was attributed to monocarbide and dicarbide species, respectively. We need certainly a more refined examination of charge transfer between substrate and molecule and of core-hole screening, in a manner similar to what has been done for the Si $2p$ surface core-level states of the clean surface (Ref. 29).

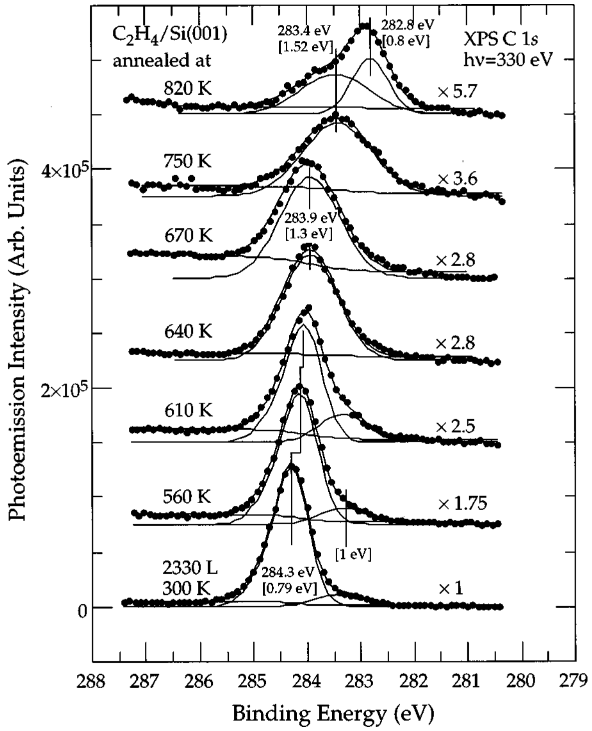

FIG. 6. C 1*s* photoelectron spectra of a Si(001) surface previously exposed to 2330 L of ethylene at 300 K and submitted to isochronal annealings (of 1 mn each). The FWHM of each fitting component is given between brackets. The various spectra are multiplied by coefficients such that their areas, after background subtraction, are equal.

2. Thermal stability of the $C_2H_4/Si(001)$-2×1 system

We have followed, by C 1*s* and Si $2p$ core-level photoemission (the spectra are given in Figs. 6 and 7, respectively), the thermal stability of ethylene on Si(001)-2×1 by performing successive isochronal (1 mn) annealings of a surface previously saturated by ethylene (2330 L) at room temperature. The XPS core-level spectra are recorded at room temperature after each annealing step at 560, 610, 640, 670, 750, and 820 K. All along the annealing procedure, no reconstruction other than the 2×1 one is observed by LEED.

C 1*s* spectra show that for annealing temperatures lower than or equal to 610 K, the shape of the main peak is not affected. We only observe a gradual shift of the main line to lower BE (by 0.3 eV), which is opposite to the one we observed during increasing exposures at room temperatures. After the 610 K annealing step the overall C 1*s* intensity is

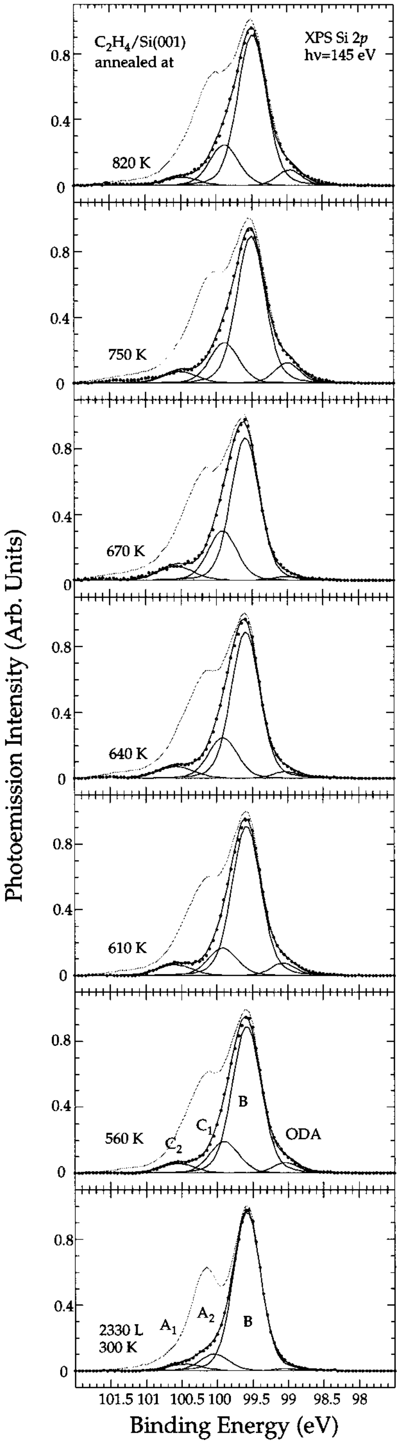

FIG. 7. Si $2p$ photoelectron spectra (gray solid line) and Si $2p_{3/2}$ component, after $2p_{1/2}$ stripping (dots), obtained from a Si(001)-2×1 surface previously exposed to 2330 L of ethylene at 300 K and submitted to isochronal annealings (of 1 mn each). Fits of the Si $2p_{3/2}$ spectra are also given (dark solid line). For $C1$ and $C2$ the Gaussian FWHM is 0.4 and 0.5 eV, respectively.

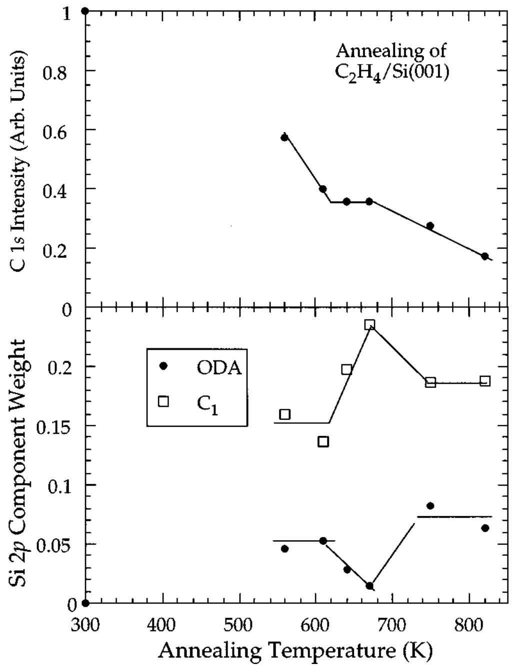

FIG. 8. Upper panel: C 1s photoemission intensity of the ethylene-saturated Si(001) surface vs annealing temperature. Lower panel: Si 2p components (ODA, C_1) vs annealing temperature.

only 40% of the initial one (Fig. 8). These data indicate a sizeable but not complete desorption at 610 K in agreement with the HREELS/AES work.[5] Moreover, as the C 1s spectra do not change appreciably, one could infer that the electronic structure of the molecule is not affected by the thermal treatment. Also consistent with Ref. 5 (where C-C cleavage is demonstrated at 650 K) is the observation of a modification in the C 1s spectra, only after annealings in the temperature range 640–670 K: the C 1s peak, while still centered at 283.9 eV, broadens and its FWHM is now 1.3 eV, a value too large to correspond to a single chemical configuration.

Annealings to higher temperatures (750–820 K) lead to the gradual formation of a carbon-carbon compound (the very broad structure at 283.4 eV) and to that of a carbon-silicon compound, clearly manifested by the appearance of a narrow component (FWHM~0.8 eV) at 282.8 eV. The present thermal treatment, which leads to C incorporation, is analogous to that used by Rücker and co-workers[4] to produce pseudomorphic layers of an $Si_{1-x}C_x$ alloy (with x up to 0.20) on Si(001): according to these authors, the solution consists in depositing about one monolayer of pure carbon (from a graphite source), *without* coevaporation of silicon,[35] and in heating the substrate at a temperature of ~870 K. In a successive paper,[36] where this thermal process was examined by conventional XPS, they report a C 1s BE of 282.8 eV after the annealing of 1 ML of carbon at 870 K: on the basis of a C 1s BE theoretical calculation, such an energy position would be characteristic of a silicon-carbon alloy (10–20 % of carbon in silicon). Consequently, the decrease in C 1s intensity (Fig. 8) from 750 K is interpreted in terms of C-atom clustering on the surface on the one hand, and, given the small C 1s photoelectron escape depth (~3.3 Å), of C penetration into the silicon subsurface layers on the other hand. The formation of a surface alloy is not completed at 820 K as not all the carbon atoms have four silicon neighbors. [On the other hand, the heating of the C_2H_4/Si(111) system to 820–860 K, as shown further on in Sec. III B 2, led to the formation of an alloy, with almost no carbon jumble remaining at the surface.]

Both C 1*s* photoelectron spectra and HREEL spectra seem to indicate that below ~650 K, the remaining molecules have not undergone decomposition. One expects then that after moderate heating, the surface states associated to the Si dimers will reappear. In the Si 2*p* spectrum (Fig. 7), the first annealing step at 560 K leads indeed to the regrowth of a structure at the ODA binding energy. It weighs ~5% of the total spectral intensity: about 30% of the amount of initial dimers are reformed after the loss of about 40% of the initial C coverage (Fig. 8). Consequently, molecular desorption, with little decomposition, is the dominating process at this annealing temperature. This observation is in good agreement with STM images[13] showing an ethylene-dosed surface after heating, where *intact dimers are restored* and *nondissociated* molecules still bond to the surface. Nevertheless, the introduction of a component, denoted C_1, situated at +0.3 eV from the bulk peak *B*, becomes necessary in the fitting procedure (the effect on the Si 2*p* spectrum is readily seen after the 560 K annealing, as the dip between $p_{3/2}$ and $p_{1/2}$ is filled in).

Surprisingly, after the 610 K annealing, the Si 2*p* spectrum has not changed much with respect to that of the previous annealing step, although 60% of the initial carbon coverage is now lost. However, no new Si_2 dimers reform. This is the hint that molecular fragments tie up now with surface silicon atoms, or that the silicon surface turns out to be defective.

From 640 K [a temperature at which C-C bond breaking and SiH formation is ascertained by HREELS (Ref. 5)], the intensity of the ODA line, after the initial increase due to the 560 and 640 K annealing steps, diminishes again. It nearly vanishes after the 670 K annealing step, while peak C_1 becomes now very intense (Figs. 7 and 8). The decomposition products of the molecule passivate now nearly all Si dangling bonds of the silicon surface. Although peak C_1 is situated in a range of energy where SiH_x components are expected—silicon monohydride and dihydride [observed after exposure of Si(001)-2×1 to atomic hydrogen] are found at +0.25 and +0.48 eV from the bulk line[37,38]—its attribution to species other than silicon hydrides (or to surface defects) is also possible (see below).

At 750 K and above, the reformation of Si dimers (Fig. 7) is thus associated to carbon rearrangement on the surface, to C in-diffusion and *very likely* to H desorption. According to Ref. 7, D_2 desorbs from C_2D_4/Si(001) at ~760 K [on the other hand, in Ref. 5 the SiH mode is intense in the HREEL spectra, still after the annealing of C_2H_4/Si(001) at 800 K]. H_2 is found to desorb from H/Si(001) at two temperatures 680 K (dihydride) and 795 K (monohydride).[39] We note that the weight of component C_1—the Si 2*p* line situated approximately where monohydrides are expected—behaves, as a function of temperature, in ''antiphase'' with respect to the ODA variation curve (Fig. 8). The variation of C_1 weight would reflect only *in part* the process of molecular dehydrogenation, silicon hydride formation (peaked at 670 K), and final H_2 desorption. If hydrogen has desorbed at 820 K, C_1, which is not nought, must also be due to surface species other than H bonded to silicon, or to a surface defect. The relatively low intensity of the ODA state after the 820 K annealing step (~7% instead of ~17% for the clean surface) might indeed be explained by the fact that a *c*(4×4) reconstruction, probably disordered and hence unobservable by LEED, begins to form [such a reconstruction appears after heating a H (Ref. 40) or C_2H_4 (Ref. 41) -exposed surface in the temperature window 870–970 K]. According to Ref. 40, the three structures that could account for this reconstruction, namely the missing dimer model, the parallel ad-dimer model, and the mixed ad-dimer model, have a dangling-bond density which is, respectively, 75%, 50%, and 75% of the 2×1 buckled dimer model density.

The present XPS experiment agrees by and large with the HREELS/AES study of Ref. 5, and contrasts with the TPD/AES (Ref. 7) and TPD works (Ref. 8), which point to a complete ethylene desorption upon heating. This contrast needs, however, to be somewhat attenuated. The fact that a maximum in the desorption rate is observed at 590 K in TPD experiments agrees well indeed with our observation of a strong decrease in the C 1*s* core-level intensity after the 610 K annealing step. The essential discrepancy is found when our XPS data are compared with the AES data of Ref. 7, which were obtained with the same temperature program as in the TPD experiment. It was found that carbon was under the Auger detectability limit for temperatures above 600 K. In reality, the experiments which are confronted here are not strictly equivalent. Linear temperature rampings, with typical heating rates of 1 K/s, are used in TPD experiments, while thermal processings in the present XPS study and in the HREELS/AES work (Ref. 5) consist of a 1 mn stay at a given temperature, followed by cooling. Such a thermal history of the surface—in particular, a prolonged annealing at a temperature below that of the desorption rate maximum—may affect the branching ratio between molecular desorption and decomposition.

B. Ethylene on Si(111)-7×7

1. Adsorption at room temperature

With increasing exposures to ethylene (see Table I) at room temperature, the LEED patterns change from 7×7 to 7×1. As in the case of acetylene adsorption,[23] this can be interpreted in terms of a rearrangement of the adatoms on each triangular subunit of the DAS cell, and of a conservation of the dimer walls, corner holes, and stacking fault, in order to maintain the 7× periodicity. C 1*s* XPS spectra [and C 1*s* intensity variation with exposure, normalized to C 1*s* intensity reached at saturation for Si(001)-2×1] are given Fig. 9. Valence-band and core-level Si 2*p* spectra are presented in Figs. 10 and 11, respectively. Finally the fraction of unreacted rest atoms (Si 2*p* core-level surface state) vs C 1*s* intensity is reported in Fig. 12.

With increasing exposures, the overall shape of the C 1*s* spectrum does not change much, nor does the energy position of its centroid. As for the C_2H_4/Si(001) system, in the reconstruction procedure of the C 1*s* XPS spectra [Fig. 9(a)], we use a component at low BE (283.3 eV), which weighs typically 12–14 % of the total intensity, and an asymmetric main line centered at 284.2 eV. Its FWHM (about 0.96 eV) is somewhat larger than that of the corresponding component observed in the case of the C_2H_4/Si(001) system. Because of the similarity between C 1*s* spectra of ethylene on Si(111) and Si(001), we can draw the same conclusions: if the low BE C 1*s* component results from the attachment of molecu-

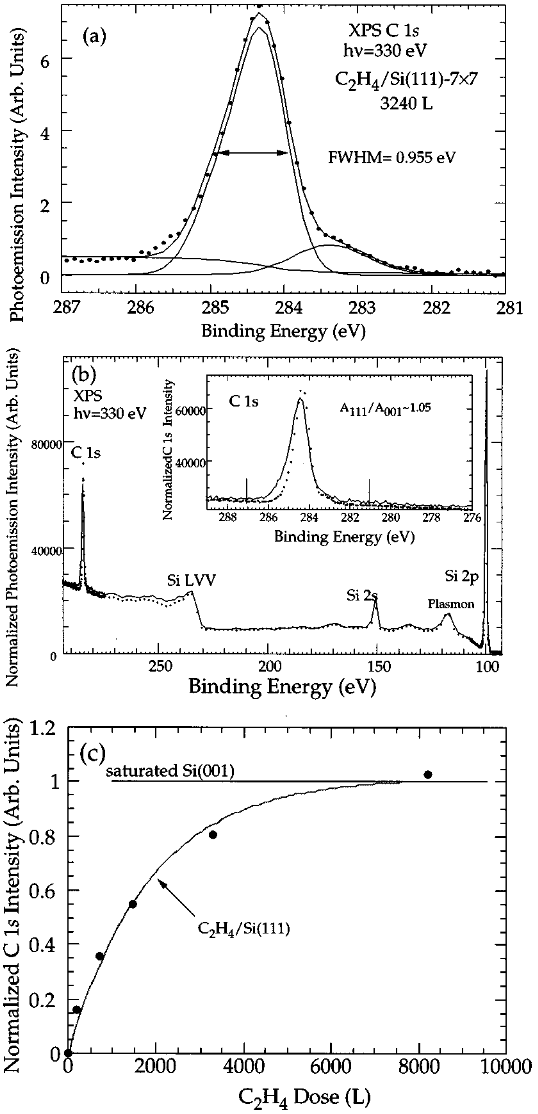

FIG. 9. (a) C 1s photoelectron spectrum (dots) of the Si(111)-7×7 surface exposed to 3240 L of ethylene at 300 K, and corresponding fit (solid line) by a Gaussian at 283.25 eV (FWMH=1 eV) and an asymmetric line simulated by a doublet (two Gaussians with a branching ratio of 0.35 and an energy splitting of +0.61 eV, the main component being at 284.2 eV). (b) Photoemission wide scans of the Si(001) surface (dots) and Si(111) surface (solid line) exposed, at 300 K, to 2330 and 8100 L of ethylene, respectively. In the inset, the C 1s region is shown in more detail [A_{hkl} is the C 1s peak area of the (hkl)-oriented surface]. (c) C 1s photoemission intensity vs ethylene dose (L) to which the Si(111) surface is exposed at 300 K.

lar fragments, dissociative adsorption is also a minor pathway on Si(111)-7×7. The C 1s intensity after the maximum exposure we made (8100 L) is compared [Fig. 9(b)] to that obtained for the Si(001) surface after saturation: normalized C 1s areas are nearly equal. Consequently, if one assumes that a monolayer of carbon saturates the Si(001) surface, then about 0.9 ML of carbon are fixed on Si(111) after an exposure of 8100 L.[42] As we shall discuss in more detail later on, this surprising observation invalidates the rest-atom/adatom (RA/AD) bridging model that would lead to a carbon saturation coverage of only ~0.25 ML.

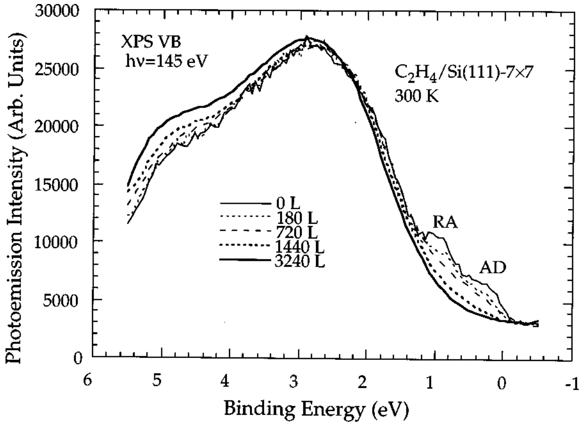

FIG. 10. Valence-band spectra of the Si(111)-7×7 surface exposed to increasing doses of ethylene at room temperature (RA=rest atoms, AD=adatoms).

The two surface states of the valence band (Fig. 10), attributed, respectively, to rest atoms (RA), at ~0.8 eV, and adatoms (AD), at E_F,[25] disappear gradually in a concerted manner. For an exposure of 1440 L these are all nearly quenched. In excellent agreement with Ref. 19, these data show that the electron occupancy of both types of tricoordinated Si atoms is affected by chemisorption. Parallel to changes in the valence band, the intensity of the Si 2p line (Fig. 11), attributed to the rest atoms[43,44]—well separated from the bulk silicon line B by a BE shift −0.75 eV, which makes its intensity easily measurable by curve fitting although it represents only 6.2% of the clean surface Si 2p spectral intensity[45]—gradually decreases when more ethylene is added. On the other hand, the bulk line *plus* surface components A_1—containing in part the adatoms—and A_2 remain practically unaffected (shape and energy position) by the bonding with ethylene. (Only after the 8100 L exposure does the peak asymmetry towards high BE increase slightly, which is reproduced by a structure at +0.85 eV from the bulk line B.) This is in line with the data obtained on the C_2H_4/Si(001) system: shifts related to silicon bond formation are very small and remain unobservable with the present energy resolution, although charge transfer from the substrate to the molecule has been clearly evidenced in Ref. 19.

The fact that the electronic structure of RA's and AD's changes with an increasing exposure to the gas does not necessarily mean that these peculiar surface silicon atoms provide the only sites to which the molecule can bond. For exposures greater than or equal to 1440 L, all surface states are quenched (Fig. 11). Consequently, saturation should be attained in the case of ''RA/AD bridge'' sites [Fig. 1(b)]. In fact, the adsorption phenomenon proceeds for higher exposures [Figs. 9(c) and 12]. *Consequently, sites other than the RA/AD bridge need to be involved in the adsorption process.* Moreover, with a carbon coverage of ~0.9 ML at 8100 L, the carbon coverage is already ~0.5 ML when all RA's are quenched (Fig. 12). This is twice as much as what is expected from the RA/AD bridging model.

We are forced to admit that the RA/AD bridging model is not satisfactory. In fact, (i) the density of available adsorption sites is *at least* four times larger than the density of RA/AD bridges; (ii) LEED points to a severe rearrangement of the AD positions. The removal of the AD's from their

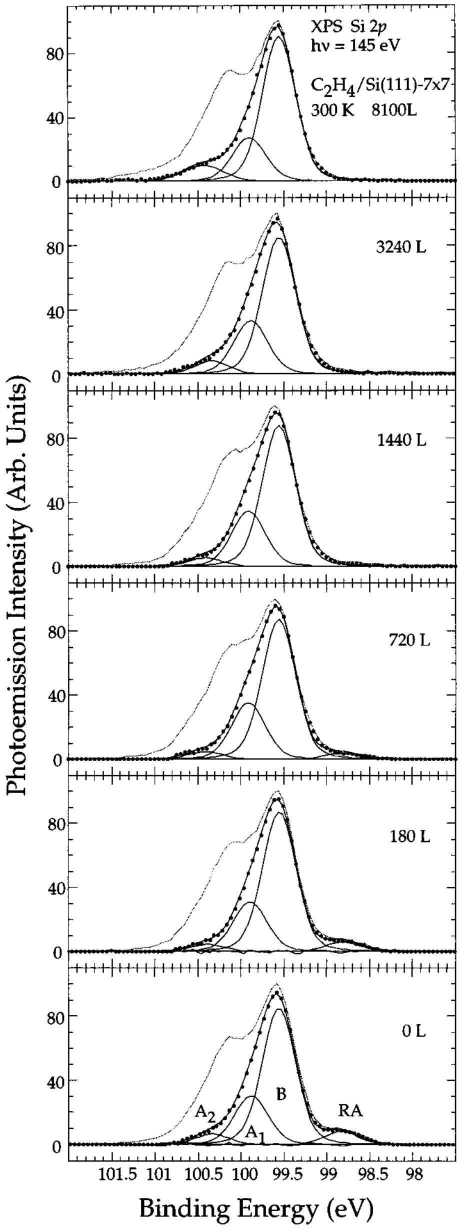

FIG. 11. Si $2p$ core-level photoemission spectra (gray solid line) and Si $2p_{3/2}$ component, after $2p_{1/2}$ stripping (dots), obtained from a Si(111)-7×7 surface exposed to increasing doses of ethylene at 300 K. Fits of the Si $2p_{3/2}$ spectra are also given (dark solid line). The Gaussian FWHM is 0.35, 0.40, 0.5, and 0.55 eV, for components "RA," B, A_1, A_2 (the Lorentzian FWHM is 0.1 eV for all components).

initial position in the T_4 sites can be a solution to the problem. Si dangling-bond pairs (each pair is potentially a site for a di-σ adsorption) are then produced, having a shorter Si-Si distance (3.8 Å instead of 4.5 Å) and a higher surface density than those of the RA/AD bridge: for each removed AD, three "pedestal" atoms (PA), with one dangling bond each, are formed [see Fig. 1(b)]. In all, 42 dangling bonds (DB's) are available [$6\,(\mathrm{RA})+3\times12\,(\mathrm{PA})=42$ DB's] in the DAS cell: if each of them bonds to a carbon atom, then a coverage of 42/49 ML (0.85 ML) should be attained, a value close to the estimated C coverage at 8100 L.

One can speculate that the molecule would bond to one RA and one PA of a near-neighbor AD (the PA would be

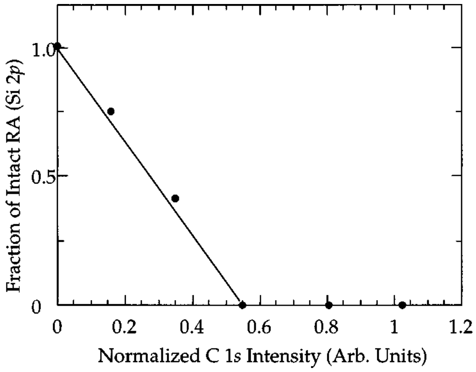

FIG. 12. Fraction of intact RA vs C $1s$ intensity, as deduced from the Si $2p$ spectra.

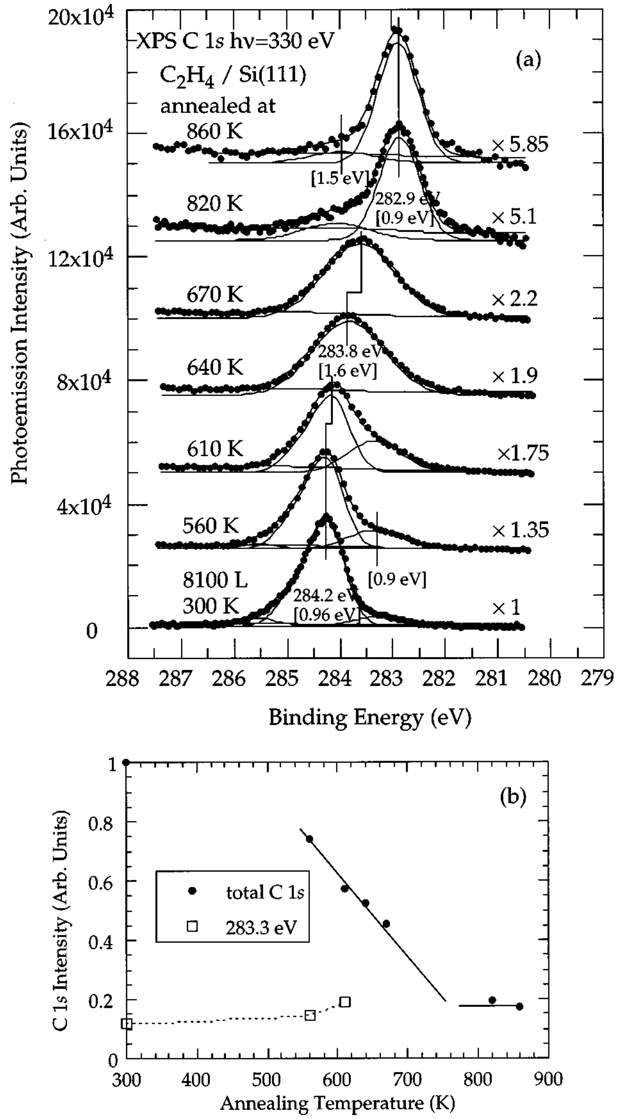

FIG. 13. (a) C $1s$ photoelectron spectra of a Si(111) surface previously exposed to 8100 L of ethylene at 300 K and submitted to isochronal annealings (of 1 mn each). The FWHM of each fitting component is given between brackets. The various spectra are multiplied by coefficients such that their areas, after background subtraction, are equal. (b) C $1s$ photoemission intensity (total and 283.3 eV component) vs annealing temperature.

fivefold coordinated). The AD would be destabilized. It could ''walk'' away on the surface and finally bond to a step, but we do not lean towards this solution: although it is true that AD's can move easily back and forth between a T_4 site and a nearby H_3 site,[46] surface diffusion is unlikely at room temperature [the critical temperature for AD's disordering is 1130 K on clean Si(111)]. Moreover, in the STM topographic images,[18] reacted AD's looking dark at a bias of +1.5 V reappear at a bias of +2 V, at positions close to T_4 sites (high bias voltages may also induce molecular desorption and the AD, previously in the metastable position, may turn back to its original place). So we propose that the molecule is di-σ bonded directly on the rest plane; the adatoms are displaced to metastable sites, not too far from their initial position (for example, as subsurface interstitialcies[47]). By removing the AD, two new DB's (a pair of atoms of the rest plane, separated by 3.8 Å) would then be available, making an adsorption site for a second molecule. If such a mechanism is at work, two molecules are chemisorbed when one RA is consumed. We note that this is the rate at which C is fixed at the surface (Fig. 12), in the first regime of adsorption where RA's are still visible. When all RA's are quenched, a coverage of about 0.5 ML of carbon should result. Then the adsorption process could continue with the ''removal'' of the remaining AD's or the involvement of other adsorption sites, such as the dimer sites, whose strained bonds could be broken. Unfortunately, STM images of this surface exposed to very high doses [larger than 600 L (Ref. 18)] have not been published.

2. Thermal stability of the C_2H_4/Si(111)-7×7 system

We have followed by C 1*s* and Si 2*p* core-level photoemission [Figs. 13(a) and 14, respectively] and valence-band photoemission (Fig. 15) the thermal stability of ethylene on Si(111)-2×1 by performing successive isochronal (1 mn) annealings of a surface previously exposed to 8100 L of ethylene at room temperature. The XPS spectra are recorded at room temperature after each annealing step at 560, 610, 640, 670, 820, and 860 K. The variation of the C coverage is given in Fig. 13(b).

The LEED patterns show that the 7×1 reconstruction is stable up to an annealing temperature of 670 K. After the 820 K annealing step, a 1×1 pattern is observed. This means that the DAS structure is definitely destroyed at this temperature.

From the ambient to a temperature of 610 K, the C 1*s* photoemission spectra are still fitted with the same asymmetric main line at about 284.2 eV and the low BE structure at 283.3 eV. About 40% of the initial amount of carbon is lost after the 610 K annealing step [Fig. 13(b)], but, in contrast to the Si(001) surface, no surface states reappear in the Si 2*p* core level spectrum (Fig. 14), nor in the valence-band spectrum (not shown). Instead, a structure at ~+0.3 eV from *B* increases slightly. This may be attributed in part to the formation of silicon hydrides.[20] As a matter of fact, the intensity of the C 1*s* structure at 283.3 eV (which is attributed to decomposed ethylene) increases with increasing temperature [Fig. 13(b)]: at 640 K, a broad peak (centered at 283.8 eV) results from the merging of the latter two components. This is indicative of a molecular decomposition on the surface, analogous to what is observed at the same temperature on the Si(001) surface.

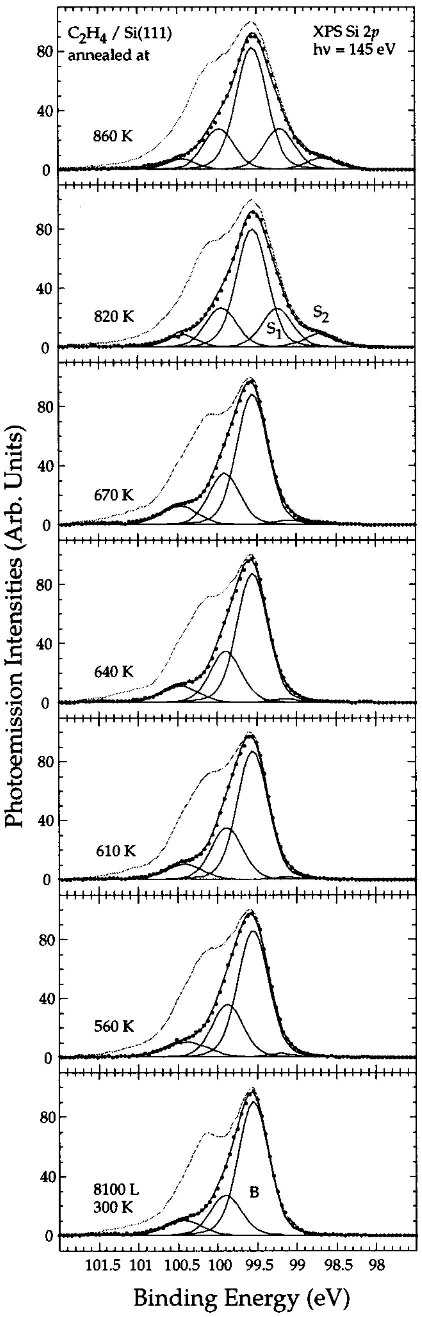

FIG. 14. Si 2*p* photoelectron spectra (gray solid line) and Si $2p_{3/2}$ component, after $2p_{1/2}$ stripping (dots), obtained from a Si(111)-7×7 surface previously exposed to 8100 L of ethylene at 300 K and submitted to isochronal annealings (of 1 mn each). Fits of the Si $2p_{3/2}$ spectra are also given (dark solid line). For S_1 and S_2 the Gaussian FWHM is 0.4 eV and their spectral weight, after the 860 K annealing step, is 18% and 5% of the total intensity, respectively.

Only after the 820 K annealing does the C 1*s* spectra give a clear signature of a compound for which C bonds to four Si neighbors, as a peak grows at 282.9 eV. A feature common to the C_2H_4/Si(001) system annealed at 820 K, or to that of the C_2D_2/Si(111) system annealed at 850 K,[23] is the growth of a narrow peak (FWHM=0.9±0.1 eV) at a BE of 282.8 ±0.1 eV, which, according to Ref. 36, is characteristic of a

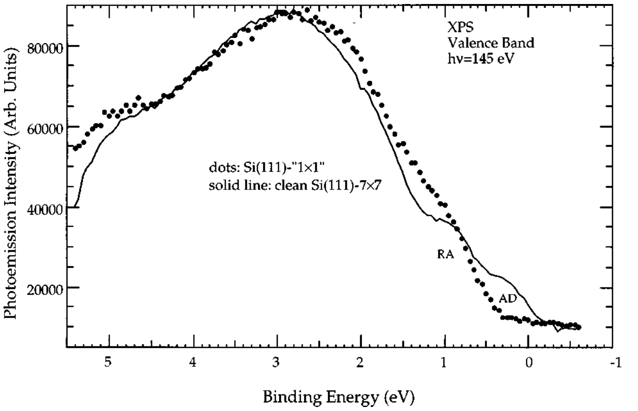

FIG. 15. Valence-band spectrum of Si(111)-''1×1'' (formed after the annealing step at 860 K) compared to that of clean Si(111)-7×7.

$Si_{1-x}C_x$ ($x<1$) alloy. [In contrast to the C_2D_2/Si(111) system, surface carbon residues at 284.0–283.8 eV are nearly all eliminated in the present case after the 860 K annealing.] Then the C 1*s* intensity strongly decreases from $T \geqslant 820$ K [Fig. 13(b)], simply because C atoms reach subsurface sites and because the C 1*s* photoelectron escape depth is small. (The process of C diffusion into the substrate may be already incipient at 670 K, given the breadth of the C 1*s* peak.) Both Si 2*p* (Fig. 14) and valence-band spectra (Fig. 15) show the appearance of silicon surface states after the 820 K annealing, a temperature at which the H atoms resulting from the decomposition of the molecule have desorbed.[48]

The valence-band spectrum of the ''1×1'' surface (Fig. 15) shows no occupied levels close to E_F (in contrast to the clean 7×7 case, where the AD band is partly filled). On the other hand, an intense structure is seen at about ~0.8 eV, at the energy position of the clean 7×7 RA's, but with a comparatively larger intensity. These dangling bonds present a remarkable chemical reactivity: ethylene chemisorbs readily on the ''1×1'' surface at room temperature.[49] We correlate the observation of an intense rest-atom-like state in the valence band to the growth of two core-level surface states in the Si 2*p* spectra (Fig. 14), peak S_2 at ~ -0.80 eV from B (close to the energy position of the clean 7×7 RA's), and peak S_1 found at ~ -0.35 eV from B, which weigh ~5% and 18% of the overall spectral intensity, respectively. The present Si 2*p* core-level and valence-band spectra are reminiscent of those obtained for the laser-annealed Si(111)-''1×1'' surface,[50] which can be viewed as a no-stacking-fault, disordered 2×2 adatom structure.[51] However, in the present case, the ''1×1'' reconstruction is certainly related to the formation of a surface silicon-carbon alloy with a high carbon concentration. The examination of Figs. 13(a) and 13(b) makes reasonable the assumption that, from the 640 K annealing step, molecular desorption does not occur any longer. Surface carbon would then amount to about 0.5 ML, before the annealing steps leading to carbon atom penetration into the substrate. The intensity of the C 1*s* peak ($I_{C\,1s}$) after the 860 K annealing step is reduced to about one-third of the value reached after the 640 K annealing step. To estimate an average C concentration, we consider, for simplicity, the case that the total amount of carbon (0.5 ML) which has penetrated into the silicon lattice is distributed homogeneously over a layer of thickness D near the surface. Then $I_{C\,1s}$ obeys

$$I_{C\,1s} \propto \lambda/D[1-\exp(-D/\lambda)],$$

where λ is the effective C 1*s* photoelectron escape depth (~3.3 Å). One easily finds that spreading half a monolayer of carbon over $D \sim 10$ Å reduces the C 1*s* intensity by a factor of $\frac{1}{3}$ and leads to an average carbon concentration of ~8%, a value notably larger than the bulk solubility of C in Si (3.5×10^{17} atoms/cm^3 at the melting point, see Ref. 52 and references therein). Rücker *et al.* (Ref. 4) have calculated that pseudomorphic $Si_{n-1}C$ ($n \geqslant 5$) alloys can form, with C atoms arranged in positions of third nearest neighbors. The presence of a large concentration of carbon atoms in the surface layers destroys the 7×7 reconstruction: the similarities with the electronic structure of the laser-annealed surface point to a bulklike stacking sequence for the surface double plane.

IV. SUMMARY AND CONCLUSION

In summary, the room-temperature exposure of ethylene to Si(001)-2×1 and Si(111)-7×7 has been reexamined using XPS spectroscopies. Similarities in the final molecular bonding (di-σ bonding is common to both) but strong differences in the kinetics and microscopic mechanisms (surface topographies are very dissimilar) are evidenced for these two crystal orientations. For both surfaces, the resolution of the C 1*s* XPS spectra is sufficient to distinguish a nondissociated molecular state (nondissociative chemisorption is by far the major route) from a dissociated one, which had eluded previous vibrational spectroscopic studies. The asymmetric shape of the main peak (nondissociated state) may be due to a vibrational fine structure, although this needs to be confirmed using deuterated ethylene. Another feature common to both surfaces is the absence of a detectable Si 2*p* core-level shift due to silicon-carbon bond formation upon room-temperature adsorption, although empirical rules relating BE shifts to Pauling's electronegativity differences predict an appreciable one.

The comparison of these two systems is useful for at least one practical reason [i.e., the Si(001) surface can serve as a template to estimate the carbon coverage on Si(111)] and interesting because of the contrasted role played by the dangling bonds resulting from each type of reconstruction. While the adsorption rate at 300 K is ''slow'' on Si(111)-7×7, the initial adsorption rate is extremely ''fast'' on Si(001)-2×1, with a sticking coefficient close to 1, as long as the carbon coverage is less than $\theta_c=0.5$ (then adsorption proceeds at a slower pace, but all the adsorption sites, the Si_2 dimers, finally react). The major difference between these two orientations concerns the behavior of the surface states ''visible'' in the valence band and Si 2*p* spectra with increasing molecular coverage: whereas on Si(001)-2×1 the quenching of the surface state ''monitors'' the adsorption kinetics (through the process of cycloaddition of C═C to Si═Si), on Si(111)-7×7, molecular adsorption proceeds even after the complete elimination of the surface states. This latter observation enters in conflict with the model of the rest-atom/adatom bridge, which has been envisaged so far as the sole adsorption site for ethylene and acetylene on Si(111)-7×7. Moreover, carbon coverages of about one monolayer are estimated for Si(111)-7×7 exposed to high doses (~8000 L). This is four times greater than the maximum coverage expected from the rest-atom/adatom bridge model. Other adsorption sites must necessarily exist or be created as a consequence of chemisorption. A ''reconstruction'' of the 7×7 structure must be envisaged: indeed the LEED patterns become 7×1, a feature shared by the adsorption process of other π hydrocarbons.[53] A speculative but simple solution to this intriguing problem is proposed: the adatom could be ''removed'' from its normal T_4 site and could go as an interstitialcy under the plane containing the rest atoms and the pedestal atoms. Its downward motion would then liberate new dangling-bond pairs for di-σ chemisorption.

The thermal stability of Si(001)-2×1 and Si(111)-7×7 surfaces both exposed to ethylene, up to a carbon coverage of about one ML, has also been examined. Submitted to similar annealing steps in the temperature range 300–860 K, both surfaces give similar results, i.e., at about 600 K about 60% (40%) of the molecules have desorbed from Si(001)-2×1 [Si(111)-7×7], in strong contrast with the acetylene/Si(111)-7×7 system[23] where desorption is very limited in this range of temperature. While ''pristine'' Si_2 dimers can show up on Si(001) after thermal desorption of the molecules, no surface states (rest atoms and adatoms) reappear in the Si(111) case. Final heatings in the 820–860 K range (above the H desorption temperature) lead to the formation of a carbon-rich surface layer [an average carbon concentration of ~8% is estimated for Si(111)]. On Si(001), this is associated to a depressed surface density of dimer-related surface states, and although the $c(4\times4)$ reconstruction is not evidenced by LEED, missing dimers or ad-dimers are expected to form. On Si(111), the LEED shows that the 7× periodicity is destroyed. The ''1×1'' surface reconstruction corresponds spectroscopically to the appearance of intense *rest-atom-like* surface states, both in valence and core-level photoemission spectra. The absence of electron state density close to E_F points to a surface reconstruction devoid of adatoms, or alternatively, to the presence of adatoms with empty dangling bonds, by analogy to the case of the laser-annealed Si(111) surface.

To conclude, this study of ethylene adsorbed at room temperature on Si(001)-2×1 and Si(111)-7×7 poses a number of intriguing problems, (i) at the spectroscopic level (e.g., the Si $2p$ core-level shifts due to di-σ bonding), that could benefit largely from new advances in high resolution synchrotron radiation photoemission and in *ab initio* core-level calculations, and (ii) at the mechanistic level [e.g., the origin of the critical coverage $\theta_c = 0.5$ on Si(001), the possible adatom displacement on Si(111)-7×7 upon adsorption], that could find an answer from further STM studies associated to theoretical calculations. We also believe that the electronic structure, the (local) reconstruction, and the chemical reactivity of the carbon-rich silicon layers, formed on both faces by annealing at ~870 K after exposure to the gas, are of interest and need a more thorough study.

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[1] J. S. Hovis and R. J. Hamers, J. Phys. Chem. **101**, 9581 (1997).

[2] J. T. Yates, Jr., Science **79**, 335 (1998).

[3] L. Simon, L. Kubler, J. Groenen, and J. L. Balladore, Phys. Rev. B **56**, 9947 (1997).

[4] H. Rücker, M. Methfessel, E. Bugiel, and H. J. Osten, Phys. Rev. Lett. **72**, 3578 (1994).

[5] J. Yoshinobu, H. Tsuda, M. Onchi, and M. Nishijima, J. Chem. Phys. **87**, 7332 (1987).

[6] C. C. Cheng, R. M. Wallace, P. A. Taylor, W. J. Choyke, and J. T. Yates, Jr., J. Appl. Phys. **67**, 3693 (1990).

[7] L. Clemen, R. M. Wallace, P. A. Taylor, M. J. Dresser, W. H. Weinberg, W. J. Choyke, and J. T. Yates, Jr., Surf. Sci. **268**, 205 (1992).

[8] W. Widdra, C. Huang, and W. H. Weinberg, Surf. Sci. **329**, 295 (1995).

[9] W. Widdra, C. Huang, S. I. Yi, and W. H. Weinberg, J. Chem. Phys. **105**, 5605 (1996).

[10] A. J. Fisher, P. E. Blöchl, and G. A. D. Briggs, Surf. Sci. **374**, 298 (1997).

[11] H. Liu and R. J. Hamers, J. Am. Chem. Soc. **119**, 7593 (1997).

[12] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* (Academic, New York, 1970).

[13] A. J. Mayne, A. R. Avery, J. Knall, T. S. Jones, G. A. D. Briggs, and W. H. Weinberg, Surf. Sci. **284**, 247 (1993).

[14] R. J. Hamers and Y. Wang, Chem. Rev. **96**, 1261 (1996).

[15] In Ref. 5, pressures are corrected by an ion-gauge sensitivity factor of 2.3.

[16] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).

[17] M. N. Piancastelli, R. Zanoni, D. W. Niles, and G. Margaritondo, Solid State Commun. **72**, 635 (1989).

[18] M. N. Piancastelli, N. Motta, A. Sgarlata, A. Balzarotti, and M. De Crescenzi, Phys. Rev. B **48**, 17 892 (1993).

[19] M. Carbone, R. Zanoni, M. N. Piancastelli, G. Comtet, G. Dujardin, L. Hellner, and A. Mayne, J. Electron Spectrosc. Relat. Phenom. **76**, 271 (1995).

[20] J. Yoshinobu, H. Tsuda, M. Onchi, and M. Nishijima, Solid State Commun. **60**, 177 (1986).

[21] F. J. Himpsel, B. S. Meyerson, F. R. McFeely, J. F. Morar, A. Taleb-Ibrahimi, and J. A. Yarmoff, in *Proceedings of the Enrico Fermi School on ''Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation,''* edited by M. Campagna and R. Rosei (North-Holland, Amsterdam, 1990), p. 203.

[22] P. Klimesch, G. Meyer, and M. Henzler, Surf. Sci. **137**, 79 (1984).

[23] F. Rochet, G. Dufour, P. Prieto, F. Sirotti, and F. C. Stedile, Phys. Rev. B **57**, 6738 (1998).

[24] B. S. Schwartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).

[25] F. Rochet, C. Poncey, G. Dufour, H. Roulet, W. N. Rodrigues, M. Sauvage, J. C. Bouliard, F. Sirotti, and G. Panaccione, Surf. Sci. **326**, 229 (1995).

[26] G. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988).

[27] B. Kempgens, H. Köppel, A. Kivimäki, M. Neeb, L. S. Cederbaum, and A. M. Bradshaw, Phys. Rev. Lett. **79**, 3617 (1997).

[28] Carbon-carbon bond scission ($C_2H_4 \rightarrow 2\,CH_2$) and formation of a (1×1) phase where CH_2 fragments bond two close neighbor

surface silicon atoms have been envisaged by Craig and Smith [B. I. Craig and P. V. Smith, Surf. Sci. **276**, 174 (1992); **285**, 295 (1993)]. Their total-energy calculation (MINDO calculation in a slab geometry) shows that the C_2H_4 (2×1) phase (di-σ adsorption on uncleaved Si dimers) is still 0.328 eV above the energetically preferred $CH_2(1\times1)$. If the energy barrier between those two phases is large, the attachment of CH_2 fragments should be a minor pathway at room temperature.

[29] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).

[30] E. Landemark, C. J. Karlsson, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. Lett. **69**, 1588 (1992).

[31] The reasoning of Mayne *et al.* (Ref. 13) connecting a reduced surface reactivity to a downward motion of the silicon dimer π bond energy enters (not explicitly) in the framework of frontier orbital theory (Ref. 12) where the frontier orbitals of the silicon dimers are π bonding and π^* antibonding orbitals, analogous to those of alkenes.

[32] L. Pauling, *The Nature of the Chemical Bond*, 2nd ed. (Cornell University Press, Ithaca, NY, 1945).

[33] M. A. Olmstead, R. I. G. Uhrberg, R. D. Bringhans, and R. Z. Bachrach, Phys. Rev. B **35**, 7526 (1986).

[34] J. K. Simons, S. P. Frigo, J. W. Taylor, and R. A. Rosenberg, Surf. Sci. **346**, 21 (1996).

[35] Sequential exposures to carbon and silicon may not be necessary to obtain C-rich pseudomorphic layers on silicon. Simon *et al.* (Ref. 3) report the growth of such layers during silicon deposition in the presence of ethylene. The exposure of silicon to monomethylsilane [D. Bouchier (private communication)] leads to similar observations.

[36] H. J. Osten, M. Methfelssel, G. Lippert, and H. Rücker, Phys. Rev. B **52**, 12 179 (1995).

[37] K. Yamamoto and M. Hasegawa, J. Vac. Sci. Technol. B **12**, 2493 (1994).

[38] C. H. Bjorkman, J. L. Alay, H. Nishimura, M. Fukuda, T. Yamazaki, and M. Hirose, Appl. Phys. Lett. **67**, 2049 (1995).

[39] G. Hess, M. Russel, B. Gong, P. Parkinson, and J. G. Ekerdt, J. Vac. Sci. Technol. A **15**, 1129 (1997).

[40] R. I. G. Uhrberg, J. E. Northrup, D. K. Biegelsen, R. D. Bringhans, and L.-E. Swartz, Phys. Rev. B **46**, 10 251 (1992).

[41] T. Takaoka, T. Takageki, Y. Igari, and I. Kusunoki, Surf. Sci. **347**, 105 (1996).

[42] We take into account the surface density of (001) and (111), which are 6.8×10^{14} and 7.8×10^{14} Si/cm^2, respectively.

[43] C. J. Karlsson, E. Landemark, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. B **50**, 5767 (1994).

[44] G. Le Lay, M. Göthelid, T. M. Grehk, M. Björkquist, U. O. Karlsson, and V. Yu. Aristov, Phys. Rev. B **50**, 14 277 (1994).

[45] The rest atoms amount to $\frac{1}{7}$ of a (111) monolayer, while the outer dimer atoms are $\frac{1}{2}$ of a (001) monolayer.

[46] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. B **49**, 10 757 (1994).

[47] A metastable site for a displaced AD could be an interstitialcy site: from its T_4 site, the AD moves down, below the plane of its three PA's, towards the underlying Si atom of the second layer, in order to form a $\langle111\rangle$ split interstitial or a bond-centered interstitial. Self-interstitials in diamondlike lattices have been proposed first by Watkins *et al.* [G. D. Watkins, R. P. Messmer, C. Weigel, D. Peak, and J. W. Corbett, Phys. Rev. Lett. **27**, 1573 (1971)].

[48] Ch. Kleint and K. D. Brzoska, Surf. Sci. **231**, 177 (1990).

[49] F. Jolly, F. Bournel, G. Dufour, and F. Rochet (unpublished).

[50] F. J. Himpsel, D. E. Eastmann, P. Heimann, B. Reihl, C. W. White, and D. M. Zehner, Phys. Rev. B **24**, 1120 (1981).

[51] See R. S. Becker, J. A. Golovchenko, G. S. Higashi, and B. S. Schwartzentruber, Phys. Rev. Lett. **57**, 1020 (1986). In the 2×2 structure, the number of adatoms equals that of rest atoms (two per cell): in the framework of a charge-transfer mechanism, adatom dangling bonds are empty and rest-atom dangling bonds are fully occupied.

[52] S. C. Jain, H. J. Osten, B. Dietrich, and H. Rücker, Semicond. Sci. Technol. **10**, 1289 (1995).

[53] C. D. McPherson, D. Q. Hu, M. Doan, and K. T. Leung, Surf. Sci. **310**, 231 (1994).