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Adsorption of small hydrocarbon molecules on Si surfaces: Ethylene on Si(001)

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The interaction between small unsaturated hydrocarbon molecules of C_2H_4 with a vicinal silicon (001) surface is studied by means of reflectance anisotropy spectroscopy and analyzed with *first principles* calculations. Our results confirm that ethylene adsorbs without breaking the silicon dimers. Comparison of theoretical optical spectra with experimental data shows that the C_2H_4 molecules lay on top of the silicon dimers from low to high coverage. This occurs even though, from a purely energetic point of view, a bridge configuration would be favorable at 1 monolayer coverage.

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I. INTRODUCTION

With the increasing demand for new organic devices compatible with current microelectronics, the knowledge of the interaction of unsaturated hydrocarbon molecules such as ethylene, acetylene, or benzene with silicon surfaces is of particular interest. It is essential to understand the mechanisms that govern the bonding of hydrocarbon molecules to the technologically relevant silicon (001) surface, especially in the field of biosensing and bioelectronics. In fact, one of the aims of this field is to be able to functionalize this surface by attaching organic molecules via cycloaddition reactions in order to develop new organic-silicon hybrid devices.[1] On the Si(001) surface, the adsorption of ethylene and acetylene is nondissociative and is based on the interaction of the C—C π bonds with the silicon dimers. In spite of the large amount of experimental and theoretical works devoted to the study of the adsorption of ethylene, the simplest molecule containing a C═C double bond, on Si(001), some aspects of this process, such as the saturation coverage or the adsorption geometry as a function of coverage, are still unclear.

In a variety of experimental works using scanning electron microscopy (STM),[2] near-edge x-ray adsorption fine structure (NEXAFS),[3,4] angle resolved photoemission spectroscopy (ARPES),[5] high resolution electron energy loss spectroscopy,[6] coaxial impact collision ion scattering spectroscopy,[7] and photoelectron diffraction imaging,[8] each ethylene molecule is thought to adsorb on top of each silicon dimer, within a 2+2 cycloaddition reaction. During this process, the carbon atoms partially dehybridize from the sp^2 configuration to the sp^3 configuration, the C—C bond length increases, and each molecule forms two σ bonds, with the silicon dimer atoms saturating the two dangling bonds. The adsorption of ethylene on Si(001) occurs without cleaving the silicon dimers. In the experimental works mentioned above, it has been shown that the Si—Si dimer bond length does not change upon adsorption of ethylene and that no dangling bond remains, leading to the conclusion that the σ bond between the silicon atoms is preserved in the adsorption process.

Many *ab initio* calculations have been performed in the past years (see, for example, Refs. 7 and 9–14, and references therein), most of them dealing with the initial adsorption geometry (low coverage) of ethylene in the on-top di-σ configuration, in which one ethylene molecule lies on top of one silicon dimer. All calculations agree on the fact that the silicon dimers do not break upon ethylene adsorption. Moreover, at low coverage, all previous calculations agree that the on-top configuration is favored. However, for what concerns the saturation coverage, the situation is not clear. As shown by Cho *et al.*[12] at 1 ML (monolayer) coverage, the bridge geometry is energetically favorable (see Fig. 1 for a schematic representation of the different geometries of adsorption). No experimental observation has evidenced so far the presence of the bridge geometry, and this contradiction between experimental observations and theoretical results could stem from the kinetics of adsorption, as pointed out in

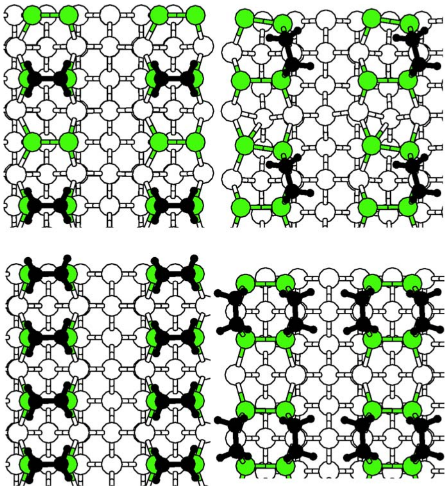

FIG. 1. (Color online) Top: Optimized geometries at 0.5 ML; bottom: Optimized geometry at 1 ML. Left: On top geometry; right: Bridge geometry. The ethylene molecules appear in black, while the Si atoms belonging to the surface's dimers are in green; the remaining Si "bulk" atoms are in white.

Ref. 13. The coverage during the adsorption process and after saturation is an important issue for determining the adsorption configuration. STM images[2] revealed that the molecule-molecule interaction is not negligible during the adsorption process. The images showed that ethylene molecules tend not to stay on top of neighboring dimers. As a consequence, it was argued that 0.5 ML (i.e., one molecule for every second dimer) could be the saturation coverage. However, ARPES experiment[5] showed that, at saturation coverage, only the adsorption of one molecule per dimer could explain the periodicity of the observed spectra in the reciprocal space. A recent core-level spectroscopy experiment[15] found a saturation coverage of 0.87 ML. This result is confirmed by surface differential reflectance spectroscopy (SDRS) measurements,[16] where a coverage of 0.90 ± 0.05 ML is found at saturation, following the same procedure as in Refs. 17 and 18. Moreover, it appears from previous experimental studies[19] and from ours[16] that the sticking coefficient decreases dramatically beyond 0.5 ML coverage. Consequently, a large amount of ethylene exposure is needed in order to reach a full monolayer coverage. This fact could explain the different interpretations concerning the coverage at saturation.

In this paper, we present a combined experimental and theoretical investigation which permits us to confirm most of the previous statements and to solve several unclear issues, in particular, the discrepancy between experiment and theory concerning the adsorption configuration at 1 ML coverage. Indeed, from a pure energetic point of view, the bridge configuration is found to be the favored one for 1 ML. The most important point of this paper is that the comparison between the experimental spectra measured by reflectance anisotropy spectroscopy[20] (RAS) and the calculated ones clearly demonstrates that at 1 ML coverage, the adsorption geometry is the on-top one. This discrepancy between what is expected and what is observed can be explained by kinetic effects which prohibit the evolution from the on-top configuration to the bridge one, when increasing the coverage above 0.5 ML. Our results about the atomic structure confirm that silicon dimers do not break during ethylene adsorption.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Experimental details

The experiments were carried out in an ultrahigh vacuum preparation chamber with a base pressure of 5×10^{-11} Torr, equipped with *in situ* low-electron energy diffraction, RAS and SDRS apparatus. The Si(001) samples were vicinal surfaces with a 4° miscut toward the $[110]$ direction, in order to have single-domain surfaces constituted of terraces of about 4 nm wide on the average, with the dimer rows aligned along the $[110]$ direction. Preparation of the surface is described in detail in Ref. 21. Ethylene was introduced by use of a precision leak valve, purity of the gas was checked with a mass spectrometer, and the exposure was monitored with a Bayard-Alpert-type ion gauge.

All the optical measurements were performed at room temperature by use of a homemade RAS apparatus similar to the one developed by Aspnes *et al.*[22] The anisotropy of the surface reflectance is given by the formula

$$\mathrm{Re}\,\frac{\Delta r}{r} = 2\,\mathrm{Re}\,\frac{r_{[\bar{1}10]} - r_{[110]}}{r_{[\bar{1}10]} + r_{[110]}}, \tag{1}$$

where $r_{[\bar{1}10]}$ and $r_{[110]}$ are the complex reflectances along the directions $[\bar{1}10]$ and $[110]$, denoted x and y, respectively. The y direction is defined along the silicon dimer rows. The experimental spectrum of the clean surface has been measured on a nominal (100) surface prepared by the procedure described in Ref. 21. Although our procedure does not achieve a single orientation domain surface, it is fast and minimizes the contamination. Surface reconstruction is, hence, favored and the surface ends up with a small amount of perpendicular domains. This results in a slight decrease of the total anisotropy. Consequently, we have rescaled our measured RAS in order to have the same total anisotropy as the one obtained by Jaloviar *et al.*[23] on a single-domain surface by using a procedure based on a controlled strain applied to the sample.

B. Computational details

Calculations have been carried out within the Car-Parrinello approach[24] in the framework of the density functional theory[25] (DFT) using gradient corrections[26] (tests have also been performed using the local-density approach). The electronic wavefunctions were expanded in plane waves with an energy cutoff of 45 Ry. The $p(2 \times 2)$ Si(001) surface was modeled with periodically repeated slabs containing eight Si layers and a vacuum region of at least 6.2 Å. A monolayer of hydrogen atoms was used to saturate the dangling bonds on the lower surface of the slabs. Ethylene molecules were added on the silicon slab, and the system was fully relaxed toward the minimum energy configuration. Structural relaxations of the atomic coordinates were performed using the method of direct inversion in the iterative subspace.[27] The optimization procedure has been repeated several times using a molecular dynamics (MD) approach with a simulated-annealing strategy. During ionic relaxations and MD simulations, the lowest Si layer and the hydrogens used for saturation were kept fixed. Other details of the method can be found in Refs. 28–30. Reflectance anisotropy calculations have been performed using 32 k points in the irreducible Brillouin zone and 50 empty bands. Tests done with 64 k points have not shown appreciable difference. In the case of the clean and 0.5 ML covered surfaces, in order to correct the usual underestimation of the electronic gaps in DFT, we have applied a scissor operator of 0.6 eV. This procedure is known to well reproduce the silicon band structure. This approximation becomes less accurate at higher coverages since the ethylene states start to contribute substantially to the RAS, and quasiparticle calculations[31] have shown that a shift of about 1.1 eV should be applied to ethylene states. For this reason, the 1 ML curve has been calculated using a scissor operator of 1.1 eV.

TABLE I. Binding energy E_b (in eV) per adsorbed molecule, for ethylene on Si(100). For comparison, also those of acetylene are shown. The experimental E_b value, at 0 coverage, for C_2H_4 is 1.65 eV (Ref. 43). All the theoretical results, except the one from Ref. 33, are related to slab geometry calculations.

	0.5 ML		1 ML	
	On-top	Bridge	On-top	Bridge
C_2H_4	2.06	1.94	1.98	2.10
C_2H_4[a]	1.94	1.82	1.91	2.01
C_2H_4[b]	2.10	1.95		
C_2H_4[c]	1.93		1.89	
C_2H_4[d]	1.57			
C_2H_4[e]	1.77		1.80	
C_2H_4[f]	1.86–2.37		1.78–2.30	
C_2H_2[g]	2.75	2.62		2.87

[a] Reference 13.
[b] Reference 9.
[c] Reference 12.
[d] Reference 32.
[e] Reference 14.
[f] Reference 33.
[g] Reference 34.

III. RESULTS AND DISCUSSION

A. Ground state geometry

In agreement with other calculations,[9,13,14,32] we find that for 0.5 ML coverage, the most stable adsorption configuration for C_2H_4 is the on-top configuration, with the molecule lying on top of one out of two silicon dimers. For the 1 ML coverage (one C_2H_4 molecule per silicon dimer) instead, the bridge configuration is the less energetic one (see Fig. 1 for sketches of the geometries). A very small tilt of the adsorbed molecules (0.03 Å) is obtained for the on-top 1 ML configuration, because of Pauling interaction between the CH_2 groups of the molecules, in agreement with experiments and previous calculations.[4,5] The adsorption energies are listed in Table I and compared with those of acetylene which have been calculated previously with the same method.[35]

Analogous to the case of acetylene, the adsorption of ethylene does not break the silicon dimers, but causes the disappearance of the buckling [found to be 0.72 Å on the clean Si(001) surface]. In fact, after the C_2H_4 adsorption, the Si—Si bond length is 2.3–2.4 Å, very close to its value for the clean surface (2.32 Å), whereas the carbon atoms of the molecule partially dehybridize to an sp^3 configuration and their π bond breaks. This can be understood through the analysis of the C—C bond length. Once C_2H_4 is adsorbed, the C—C bond length is ~1.54 Å, greater than the corresponding gas-phase value (1.31 Å) and much closer to the C—C bond length of C_2H_6 (1.52 Å), where the carbon atoms are in the sp^3 configuration. All the results concerning the geometric structure of the relaxed surface for the different coverages and different adsorption geometries, compared to the available theoretical results, are listed in Table II. As we can see, all geometrical parameters agree with the available theoretical results and with the experimental finding of a C—C bond length of 1.52 Å given by NEXAFS studies.[3] It is interesting to notice that in the 0.5 ML bridge geometry the two dimers are inequivalent. This is straightforward if one recalls that in the clean surface, two subsequent dimers of the same row have opposite buckling. As a consequence, for the 0.5 ML bridge configuration, the C_2H_4 binds to an upper silicon atom on one dimer [labeled (a) in Table II] and to a lower silicon atom on the next dimer [labeled (b) in Table II]. The two dimers become again equivalent when another molecule is added in the 1 ML bridge configuration.

B. Optical properties

As RAS is sensitive to the anisotropy of the surface it is also sensitive to the geometry of the surface and, in particu-

TABLE II. Geometric structure results of the relaxed surface for the different coverages and different adsorption geometries compared to the available theoretical results. All lengths are expressed in Å and all angles in degrees. (a) and (b) represent the two inequivalent dimers in the 0.5 ML bridge geometry (see text). The buckling angle and the Si-Si distance refer, in the 0.5 ML on-top geometry, to the dimer that is covered with the ethylene molecule.

Coverage	0.5 ML on-top	0.5 ML bridge	1 ML on-top	1 ML bridge
Si-Si dimer	2.33, 2.29,[a] 2.34,[b] 2.37[c]	(a) 2.41, (b) 2.36, 2.37[b]	2.33 2.37,[c] 2.33[d]	2.39
Buckling angle (deg)	0.0, 1.1[a]	(a) 4.01°, (b) 13.8°	0.00	0.00
Si-C	1.92, 1.94,[b] 1.95[c]	1.93, 1.95,[b]	1.93, 1.96,[c] 1.93[d]	1.94
C-C	1.54, 1.53,[a] 1.61,[b] 1.56[c]	1.55, 1.61[b]	1.54, 1.56,[c] 1.52[d]	1.55
C-H	1.09, 1.11[b]	1.09, 1.11[b]	1.09, 1.13[d]	1.09

[a] Reference 32.
[b] Reference 9.
[c] Reference 12.
[d] Reference 35.

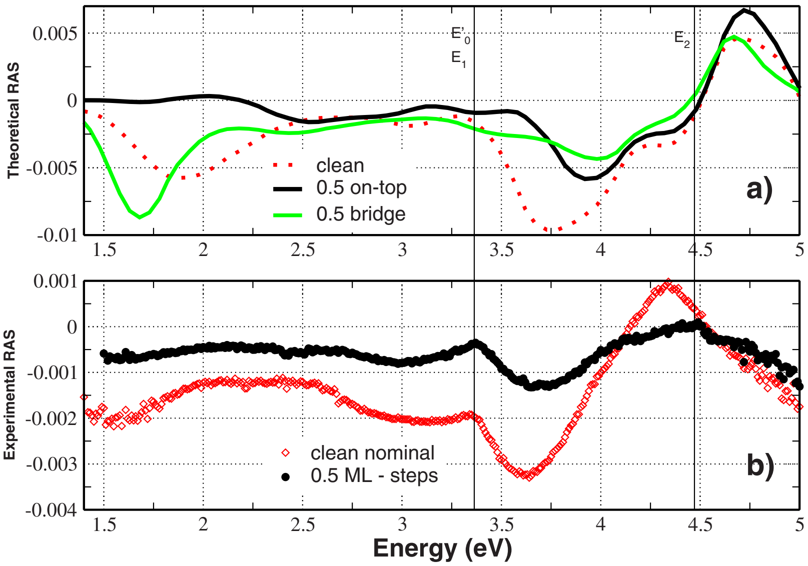

FIG. 2. (Color online) (a) Calculated RAS for the clean surface and for the two 0.5 ML geometries, namely, the bridge and the on-top one. (b) Experimental spectra for 0.5 ML coverage and for the clean nominal surface. As mentioned in the text, the step contribution of the 4° off Si(001) has been subtracted from the 0.5 ML surface spectrum to be able to compare to the ideally flat surface of the calculation. RAS is calculated according to Eq. (1).

lar, to the adsorption geometry. This is illustrated in the present section, where the geometry can be determined from the comparison of experiments and calculations. The theoretical optical properties are obtained consistently with the atomic structure minimization and the repeated slab configurations. It has been shown[36–38] within a perturbative scheme with respect to the abrupt Fresnel interface picture, and in the repeated slab framework, that the RAS signal can be calculated by

$$\mathrm{Re}\,\frac{\Delta r}{r} = \frac{4\pi\omega}{c}\,\mathrm{Im}\,\frac{\epsilon_{xx}^{hs}(\omega) - \epsilon_{yy}^{hs}(\omega)}{\epsilon_b - 1}, \qquad (2)$$

where ϵ_{ii}^{hs} is the so-called half-slab polarizability.[38] In order to clarify the adsorption geometry of the 0.5 and 1 ML covered surfaces, we have performed calculations for the RAS of the bridge and on-top geometries. We obtained the half-slab polarizability within the random phase approximation (RPA) scheme, neglecting the local fields effect.

Experimental and calculated RAS are presented in Figs. 2 and 3 at coverages of 0.5 and 1 ML, respectively. In Figs. 2(a) and 3(a), we show the calculated spectrum of the clean silicon surface: It is very similar to the experimental spectrum, ensuring the validity of the computational procedure. The clean spectrum is dominated at high energy (4.4 eV) by a positive structure associated with the E_2 critical point; transitions at E'_0 and E_1 are responsible for the structure observed around 3.4 eV. The energies of the critical points are indicated in Fig. 2(a). At 1.5 eV, a negative structure is observed in the experimental spectrum as well as in the calculated one, and is associated with transition between π and $\pi^\star$ surface states delocalized along the dimer rows. More details on the assignment of the different features can be found in Refs. 39–41.

Figure 2(a) displays the calculated spectra for the clean surface and the spectra for 0.5 ML of ethylene in the on-top and bridge configurations, whereas Fig. 2(b) displays the experimental spectrum obtained on a nominal clean silicon surface and the one for 0.5 ML of ethylene. The experimental

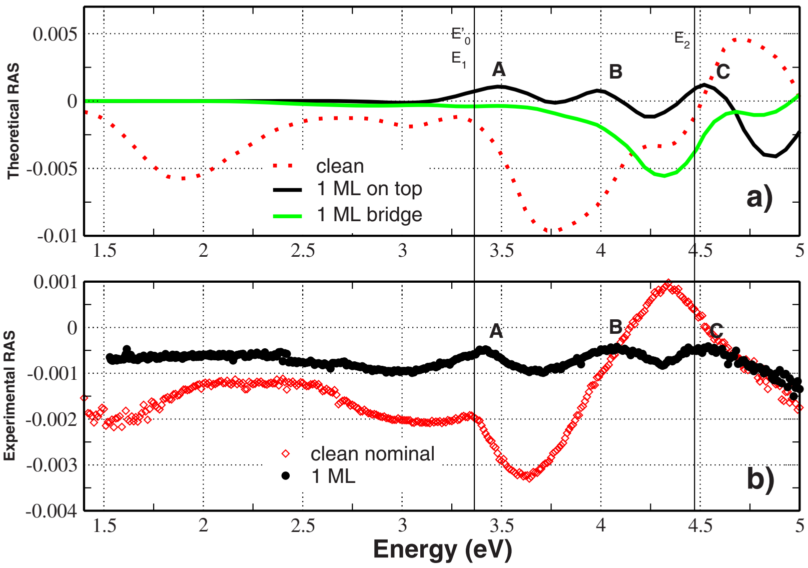

FIG. 3. (Color online) (a) Calculated RAS for the clean surface and for 1 ML coverage for the two geometries, namely, the bridge and the on-top one. (b) Experimental spectra for the ethylene saturated surface and for the clean surface. RAS is calculated according to Eq. (1).

spectrum of Si(001):C_2H_4, corresponding to a coverage of 0.5 ML of ethylene [Fig. 2(b)], has been measured on a vicinal surface. At this point, it is worthy to notice that some contribution to RAS originates from the double steps which separate the 1×2 terraces of the vicinal surface. Unfortunately, taking into account this contribution in the calculation is a huge task and has not been attempted here. However, it has been shown by Jaloviar *et al.* that this contribution can be determined by comparing the RAS of a vicinal clean silicon surface and the one measured on a single-domain nominal surface free of steps.[23] By using a similar procedure, and assuming, on one hand, that the fraction of covered steps is equal to the fraction of covered dimers and, on the other hand, assuming that the RAS signal of the decorated steps is zero, we can easily get rid of the contribution of the steps from the experimental spectra. The resulting "0.5-ML-step" spectrum is presented in Fig. 2(b): it has a smaller total anisotropy than that of the clean surface, but is still dominated by the features at the critical points. The calculated spectra for 0.5 ML of ethylene on-top and bridge configurations [Fig. 2(a)] have similar trends for energy larger than 2 eV, but present large differences for lower energies.

Figure 3(a) displays the calculated spectra for the clean (dotted line) and for the 1 ML ethylene covered surfaces in both the on-top and bridge configurations. As mentioned before, these spectra have been calculated using a scissor operator of 1.1 eV, which is more appropriate in the case of ethylene-based states.[31] As a matter of fact, looking at Fig. 1 of Ref. 31, those states have an onset for optical transitions of about 3.5 eV, which is the energy where, at full coverage, the first experimental RAS structure (labeled A in Fig. 3) occurs. This suggests that the transitions that give rise to the structures of the 1 ML spectrum all have a substantial contribution of ethylene-based states.

The experimental spectra measured on the clean nominal surface and on a vicinal silicon surface with 1 ML of ethylene are presented in Fig. 3(b). In this case, no step contribution has been removed because of the assumption that the signal of decorated steps is null.

As shown in Fig. 3(b), the total anisotropy signal of the experimental spectrum decreases with increasing coverage, and three features, labeled A, B, and C, are clearly visible. In Fig. 3(a), the calculated spectra for the two configurations display very different profiles: whereas the three features A, B, and C are present with the on-top geometry, the spectrum calculated for the bridge geometry does not fit at all with the experimental result.

C. Discussion

For 0.5 ML coverage, all previous experimental and theoretical investigations have indicated the on-top configuration as equilibrium geometry. This is also the case of our calculations (see Table I).

Concerning the theoretical optical spectra, the on-top and the bridge geometries give, for 0.5 ML coverage, very similar RAS between 2 and 5 eV, in good agreement with the experiment (see Fig. 2). The main difference between the two theoretical spectra appears below 2 eV: The surface-to-surface state transition dip around 1.7 eV of the clean surface is drastically reduced in the on-top configuration, and is instead even more intense in the bridge configuration. This effect is completely analogous to what happens in the case of the absorption of acetylene on Si(100).[34] In fact, the negative peak at 1.7 eV in the clean surface is given by the sum of a positive intradimer transition contribution and a stronger negative interdimer one.[31] The presence of ethylene in the on-top geometry, on top of one out of two dimers, removes the empty states on that dimer; therefore, it forbids the interdimer transitions. As a consequence, the negative optical structure disappears from the spectra. Vice versa, in the bridge geometry, the positive intradimer contributions are suppressed and the negative peak is enhanced. Moreover, the dip is slightly shifted to lower energies; this could be a consequence of the reduction of the buckling as it has been shown in Ref. 39. Unfortunately, the comparison of the theoretical spectra and the experimental ones cannot lead to a clear conclusion about the removal or not of the surface state transition at 1.7 eV. Actually, the experimental data, as explained above, have been performed on vicinal surfaces, where the surface state transition is strongly damped. On the contrary, it has been shown (Refs. 21 and 23) that higher energy features (i.e., $\omega > 3.5$ eV) are not damped by the presence of steps. The comparison between our experimental and theoretical spectra is then valid only in the high-energy part. Consequently, the on-top configuration as well as the bridge configuration are not in contradiction with the experimental data. Now, when the surface is saturated with ethylene at a coverage of 1 ML, the high coverage experimental RAS is well reproduced by theory only in the case of the on-top model (see Fig. 3). In particular, the three features labeled A, B, and C are well reproduced in the calculated curve for the on-top model, while they are absent in the bridge one.[42] As discussed before, all these structures can have a substantial contribution due to ethylene-based states. On the contrary, a deep minimum at 4 eV is observed for the bridge model, in contradiction with the experimental observation. Consequently, we can conclude that, for the saturated surface, the ethylene molecules are adsorbed on top of the silicon dimers, although the bridge model appears to be slightly more stable from an energy point of view (see Table I).

Cho and Kleinman[13] have calculated the different energies along reaction pathways for the adsorption of ethylene molecules; first, from a precursor state bound to the down atom of a Si dimer, overriding intermediate state, and then moving to the more stable states, bridge or on-top ones. They have shown that there is almost no energy barrier (0.02 eV) for the molecules to go to the on-top state, while a larger energy barrier of 0.12 eV has to be crossed for reaching the bridge one. The same consideration could explain the fact that for 1 ML coverage, the on-top configuration is obtained, although it is less stable than the bridge one. Indeed, let us consider ethylene molecules which are added to the 0.5-ML-covered surface, where all the already adsorbed molecules are in the on-top conformation. In order to finally obtain the thermodynamically stable bridge configuration, the previously adsorbed molecules should proceed to convert from the on-top adsorption geometry to the bridge one. Such conversion is likely to involve an energy barrier which cannot be

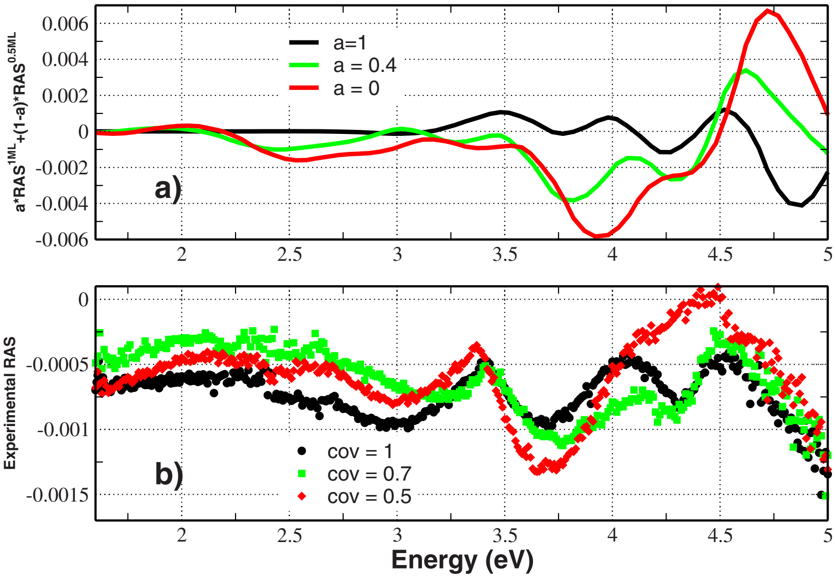

FIG. 4. (Color online) (a) calculated RAS for 0.5 ML, 1 ML, and intermediate coverage. All the spectra refer to the on-top geometry. (b) Experimental spectra for coverages ranging from 0.5 to 1 ML. RAS is calculated according to Eq. (1).

passed over at room temperature. We have, indeed, checked that in agreement with a previous thermal desorption study,[43] the heating temperature of the sample necessary desorb ethylene molecules from the surface is above 580 K (corresponding to an energy of 0.048 eV). Consequently, the only possibility for additional molecules incoming on the surface is to adsorb in the on-top geometry.

Finally, Fig. 4 shows a comparison between theory and experiment for three coverages, namely, 0.5, 0.7, and 1 ML. The theoretical curve for 0.7 ML is determined by interpolating the two curves for 0.5 and 1 ML. The spectra are calculated as a linear combination of the full and half monolayer ones according to $\mathrm{RAS}=a\mathrm{RAS}^{1\ \mathrm{ML}}+(1-a)\mathrm{RAS}^{0.5\ \mathrm{ML}}$. The parameter a, which is allowed to vary between 0 and 1, describes the mixing of the 0.5 ML spectrum ($a=0$) and the 1 ML spectrum ($a=1$). The experimental spectrum corresponds to the actual intermediate coverage. It can be seen that the agreement between theory and experiment is still excellent for 0.7 ML. This result reinforces the procedure used to simulate the experimental data and, therefore, the above conclusion.

IV. CONCLUSIONS

We have monitored the adsorption of C_2H_4 on a vicinal Si(001) surface by reflectance anisotropy spectroscopy and compared it with DFT-RPA calculations. Our data suggest that the molecules adsorb on top of the silicon dimers at 1 ML coverage, although the bridge geometry would be energetically favored. The silicon dimers are not cleaved during the adsorption process and the saturation coverage reaches almost a full monolayer. We find very good agreement between theory and experimental RAS in the whole coverage range considered, from 0 to 1 ML. These results confirm most theoretical and experimental findings and show the capability of the optical technique when experiments and theoretical calculations are combined, to probe the adsorption process.

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