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Optical investigation of benzene adsorption on vicinal single-domain Si(001)-(2×1) surfaces

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We report on an experimental investigation of benzene adsorption on single-domain Si(001)-(2×1) by means of surface sensitive optical spectroscopies which are reflectance anisotropy spectroscopy and surface differential reflectivity spectroscopy combined with scanning tunneling microscopy. These optical techniques are sensitive to the number of occupied dimers and permit us to demonstrate that benzene molecules are bound to slightly less than one dimer out of two. We investigate the modification of optical spectra on the benzene-saturated surface versus time and conclude that no thermally induced geometry conversion of benzene molecules is observed.

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I. INTRODUCTION

Surface sensitive optical spectroscopies such as reflectance anisotropy spectroscopy (RAS) and surface differential reflectivity spectroscopy (SDRS) have been extensively employed to characterize the surfaces and interfaces of semiconductors.[1–6] RAS measures the difference of the reflectance between two principal axes in the plane of surface while SDRS gives the change of the reflectivity during the deposit of the adsorbate. Clean silicon surfaces (001) have been studied in experimental[3,7,8] and theoretical investigations[9–12] within these techniques, but few studies only report on optical properties of adsorbates on Si(001).[13–18] In these works, the adsorbates (atomic hydrogen or oxygen) are used for a comprehensive investigation on the optical response of the silicon surface.[13,14] These techniques also make it possible to follow the kinetics of the hydrogenation process.[15,16] Indeed, it has been shown that surface sensitive optical spectroscopies can be a useful tool to determine the kinetics of gas adsorption.[19,20] Here, we use RAS and SDRS, combined with scanning tunneling microscopy (STM), to investigate the adsorption of benzene on the silicon (001)-2×1 vicinal surface.

Benzene adsorption has been largely studied by various surface science techniques and theoretical calculations.[21–27] In an early study, based on the combined use of Auger electron spectroscopy, thermal desorption spectroscopy (TDS), and high-resolution electron energy loss spectroscopy (HREELS), Tagushi *et al.* proved that the benzene is nondissociatively chemisorbed on the surface at room temperature with saturation coverage of 0.27 benzene molecule per surface Si atom (i.e., 0.54 benzene molecule per Si dimer).[21] A similar coverage has been also deduced from scanning tunneling microscropy (STM) at low rate of coverage, and benzene molecules are found to adsorb upon one dimer out of two[23] (i.e., 0.5 benzene molecule per Si dimer). In a different STM investigation on nominal Si(001)-(2×1) surface[25,28,29] combined with first-principles density functional methods, the authors indicate that benzene molecules first adsorb in a metastable "butterfly" geometry, where the benzene molecules are adsorbed on top of a single dimer in a 1,4-cyclohexadiene-like configuration. They prove that this butterfly geometry is a precursor to stable bridging configurations where the molecules are bound to two silicon dimers in a fourfold bound structure called a "pedestal" structure. Contrarily to the butterfly geometry, where only one dimer out of two is occupied, all the silicon dimers are now occupied in the pedestal configuration. A recent investigation[27] using polarization resolved near-edge x-ray-absorption fine-structure (NEXAFS), reveals that the geometry of adsorbed benzene on a vicinal single-domain Si(001)-(2×1) corresponds to the butterfly geometry. Even if the subject has already been extensively studied, the question of a possible thermal-activated geometry conversion to a bridging configuration is still open.

In this work, we have investigated the benzene adsorption on a vicinal single-domain Si(001)-(2×1) by using surface sensitive optical spectroscopies, RAS and SRDS, together with STM. First, we will demonstrate that surface sensitive optical spectroscopies give quantitative information on the number of occupied dimers. Then, we will use these optical properties to study the possible geometry conversion of the benzene molecules from on-top dimer configuration to bridging configuration.

II. EXPERIMENTAL DETAILS

The experiments were carried out in an ultrahigh vacuum (UHV) preparation chamber with a base pressure of 5×10^{-11} Torr, equipped with *in situ* low-electron energy diffraction, RAS and SRDS apparatus. It is connected to a chamber where STM at room temperature can be performed. The Si(001) samples were vicinal surfaces with a 4° miscut towards the $[110]$ direction. After outgasing at 650 °C during one night by direct-current heating, the samples were flashed at 1050 °C for a few seconds to remove the oxide layer. This process ensures obtaining the single-domain Si(001) with a (1×2) reconstruction, with 4 nm broad terraces separated by double steps. On the terraces, the silicon dimers are aligned along rows in the $[110]$ direction and are perpendicular to the step edges along the $[1\bar{1}0]$ direction.[30] Benzene was purified by freeze-pump-thaw cycles and was introduced in the chamber through a precision leak valve.

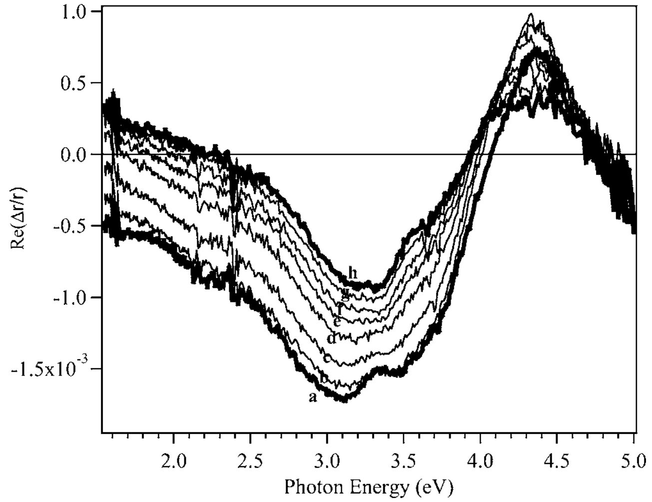

FIG. 1. RA spectra for several benzene exposures (a) 0 L; (b) 0.06 L; (c) 0.12 L; (d) 0.18 L; (e) 0.23 L; (f) 0.29 L; (g) 0.47 L; (h) 2.3 L.

The purity of the benzene was checked with a mass spectrometer and the exposure was monitored with a Bayard-Alpert-type ion gauge calibrated to benzene; pressure was maintained at 1.7×10^{-7} T during exposure. After the experiments, the samples were flashed up to 1050 °C to remove the benzene molecules. RAS measurements were performed with a homemade apparatus similar to the spectrometer developed by Aspnes,[31] which provides the anisotropy of the surface reflectance given by the formula

$$\frac{\Delta r}{r} = 2\frac{r_{[1\bar{1}0]} - r_{[110]}}{r_{[1\bar{1}0]} + r_{[110]}}, \tag{1}$$

where $r_{[1\bar{1}0]}$ and $r_{[110]}$ are the complex reflectances along the directions $[1\bar{1}0]$ and $[110]$, respectively. The SDRS was performed by use of a spectrometer, based on an optical multichannel analyzer consisting of a Si photodiode array as described in detail in Ref. 32. It delivers the relative change of reflectance of the substrate upon adsorption of molecules

$$\frac{\Delta R}{R} = \frac{R_{\mathrm{Si}} - R_{\mathrm{adsorbate}}}{R_{\mathrm{Si}}}, \tag{2}$$

where R_{Si} and $R_{\mathrm{adsorbate}}$ are the reflectances (in intensity) of the clean silicon surface, and the adsorbate-covered silicon surface, respectively. STM images were taken with a commercial room-temperature STM-AFM apparatus from Omicron.

III. RESULTS AND DISCUSSION

A. Optical properties

In Fig. 1, we present the RA spectra of the clean silicon surface [spectrum (a)], the benzene-saturated silicon surface [spectrum (h)], and intermediate benzene exposure silicon surfaces [spectra (b) to (g)]. The clean silicon signal is similar in shape and in intensity to spectra obtained previously by different authors.[3,8,7] The origin of the different features observed in the spectrum corresponding to the clean vicinal Si(001)-(2×1) surface have been tentatively interpreted by using *ab initio* calculations.[12] The positive peak around 4.4 eV, located at the E_2 critical point, corresponds to the surface modified bulk optical transitions at the X point of the Brillouin zone (BZ) modified by the surface; the small shoulder appearing at 3.35eV originates from surface-modified bulk transitions at E_1 and E_0' critical points corresponding to optical transitions at the L and Γ point in the BZ, respectively.[12,33] These structures seem to be sensitive to the stress of the surface induced by the presence of dimers and/or steps at the surface, as it has been demonstrated by Hingerl *et al.*[33] For lower energies, calculations show that the optical anisotropy observed is attributed to surface-state related transitions.[12] The interpretation of the structures in the spectra of vicinal surface is complicated by the presence of the steps. A significant step-induced component in the RA spectra has been evidenced by different authors.[7,8,12] In particular, it seems that the steps are partially responsible for the negative minimum around 3.1 eV. The influence of the steps decreases for photon energies larger than 3.4 eV, indicating that, in this range, the anisotropic signal originates only from terraces.[7] Contrarily to what is observed on a nominal surface,[8] only a small and broad feature is visible around 1.6 eV for the vicinal surface. This low-energy peak, essentially due to dimer surface states,[11,12] is progressively reduced when increasing the miscut angle[8] and consequently the density of steps.

When increasing the benzene dose, one can observe a decrease of the total anisotropy, but the general shape of the spectra is still similar to the one obtained on the clean silicon. No additional feature due to the presence of benzene molecules is expected. Liquid benzene displays optical absorption corresponding to transitions from filled to empty π orbitals between 4.7 and 5.1 eV.[34] But, when adsorbed on the silicon dimers, the benzene molecule converts to cyclohexadiene rings, as demonstrated by different authors.[21,24,27] As no absorption peaks are present in the optical region of cyclohexadiene,[35] no specific transitions coming from the adsorbed benzene are expected in the RA spectra. In the benzene-saturated silicon surface spectrum [spectrum (h)], the minimum of anisotropy located at 3.1 eV in the clean silicon spectrum has now been shifted to 3.3 eV. The small shoulder at 3.35 eV that is visible in the clean silicon spectrum has disappeared in the benzene-saturated spectrum, whereas a new weak shoulder has developed at 3.5 eV with benzene exposure. Also, the peak at 4.4 eV has decreased in the benzene-saturated spectrum and is broader than in the case of clean silicon. The general evolution of the spectra from clean silicon surface to benzene-covered silicon surface is regular, except for the maximum at 4.4 eV that presents larger anisotropy for intermediate benzene coverage than for clean silicon surface. This point will be analyzed in more detail after. To further understand the RA spectra upon benzene adsorption, we have reported, in Fig. 2(a), the evolution of the RA signal at different energies versus the benzene dose. The experimental data are extracted from the measurements presented in Fig. 1. The signal recorded at 1.68 eV is characteristic of the spectrum behavior at low energy, where only surface-related transitions are involved. The other sig-

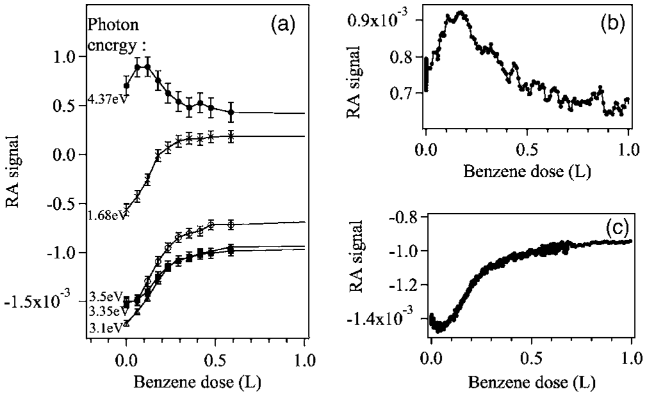

FIG. 2. (a) RA signal at different photon energies versus benzene dose; (b) RA signal at 4.3 eV and (c) RA signal at 3.35 eV.

nals correspond to the minimum of anisotropy in the clean silicon spectrum (3.1 eV), to the shoulder visible at 3.35 eV in the clean silicon spectrum, to the new shoulder appearing in the benzene-saturated spectrum (3.5 eV), and to the maximum of anisotropy at 4.37 eV. First, one can notice that the general evolution of the signals is very similar, except for the one at 4.37 eV. The saturation of the anisotropic signal is reached after an exposure of about 0.7 L. But, whereas the signal of the low energy structures increases monotonously with benzene dose, the signal at 4.37 eV first increases for low benzene doses, and then decreases to a value corresponding to the saturation coverage. The initial increase could be induced by the buckling of the dimers, which is suppressed by the presence of the molecules on the dimers. Indeed, calculations have shown that this signal, which is related to the dimer buckling, increases when the buckling of the dimer is suppressed, leading to symmetrical dimers.[11] To verify this behavior, we have recorded, in real-time measurement, the RA signal at 4.3 eV during benzene adsorption on another sample, as shown in Fig. 2(b). The anisotropy clearly increases with benzene dose up to about 0.12 L, which could correspond to a progressive suppression of the dimer buckling. It is known that the alternate buckling of dimers along a row can be perturbed by the presence of defects or impurities.[36] The expected symmetrization of the dimer, on which the benzene is adsorbed, could influence the neighbor dimers, leading to a decrease of the mean buckling at the surface. For larger exposures, the signal now decreases, which is similar to what is observed when different gases are adsorbed, for example, atomic hydrogen.[16]

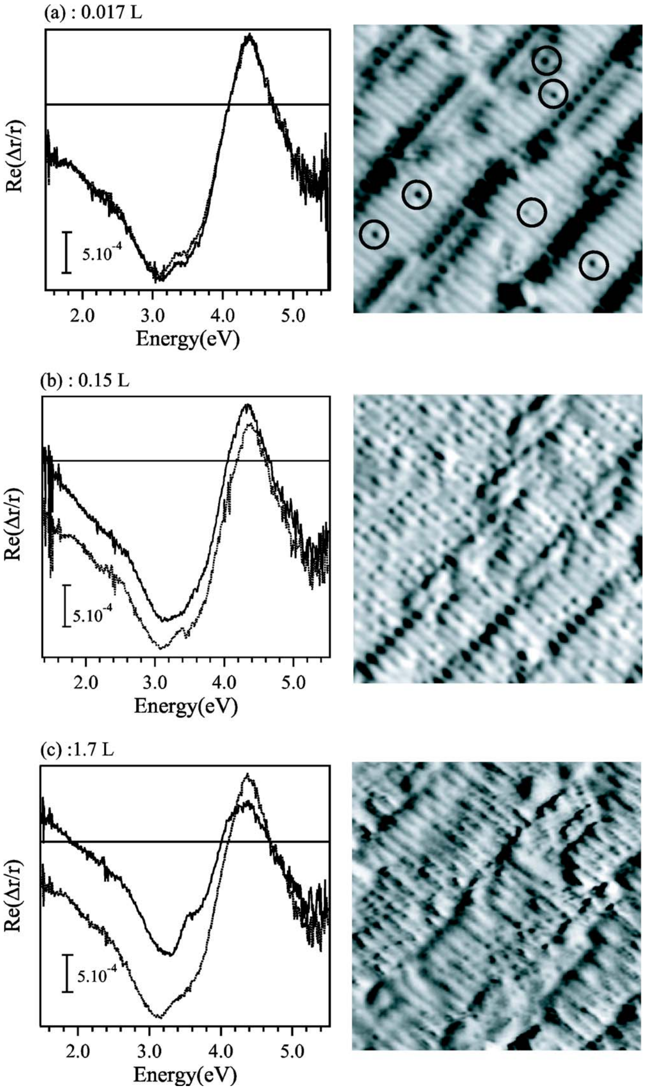

FIG. 3. (Color online) STM image 15×15 nm^2 (current mode, filled states; sample bias -2 V) and corresponding RA spectra of clean (dotted line) and benzene adsorbed surfaces (solid line) for several benzene exposures: (a) 0.017 L; (b) 0.15 L; (c) 1.7 L. Benzene molecules appear as small dots aligned on the dimer rows; in the picture (a) molecules are encircled.

To correlate the RA spectra obtained for different benzene exposures to the number of occupied dimers, we have recorded STM images after several benzene exposures. The STM images are presented in Fig. 3, together with the corresponding RA spectra before (dotted line) and after (solid line) benzene adsorption. For a very small benzene dose of about 0.017 L at room temperature, only a few molecules are present on the STM image, appearing as small dots aligned on the dimer rows. The ratio between benzene molecules adsorbed on Si dimers and the unoccupied Si dimers is estimated from a statistical analysis to be lower than 0.01. Surprisingly, a significant change in the RA spectrum for such a small coverage is observed. As the signal around the (E_1, E_0') critical points at 3.4 eV has been shown to be sensitive to surface stress,[33] we presume that the presence of a few molecules on the dimers can modify slightly the equilibrium of the surface, and can generate changes in the surface stress. This behavior is systematic for initial benzene adsorption, and has been observed also when recording the RA signal at 3.35 eV during the exposure, as it can be seen in Fig. 2(c). When the surface is exposed to about 0.15 L, the STM image, which is similar to what has been already observed,[25,23] displays a larger number of benzene molecules [Fig. 3(b)]. One can notice that the molecules are all aligned along the dimer rows, retaining the initial symmetry of the surface. The ratio of occupied dimers has been estimated from STM images at about 0.25, meaning that 25% of dimers are occupied by a benzene molecule. When the surface is saturated with benzene [Fig. 3(c)], the molecules form a homogeneous

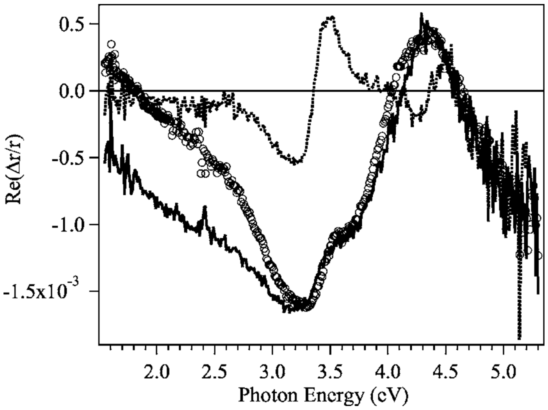

FIG. 4. RA spectra on benzene-saturated surface (open circles), partially hydrogenated surface (solid line), and monohydride silicon surface (dots).

layer. In the two last cases, the reduction of the RA signal can be explained by the modification of the surface dimers upon adsorption. As we do not expect a specific signal coming from the benzene molecules, the observed RA signal originates from the silicon substrate. Consequently, we can compare the benzene-saturated silicon surface spectrum to a partially or a completely hydrogenated silicon surface spectrum obtained by exposing the surface to atomic hydrogen at 320 °C. The partially hydrogenated surface spectrum and the benzene-saturated surface spectrum that are presented in Fig. 4 are very similar in shape and in intensity. The main discrepancy between the two spectra is the signal below 2.5 eV. In this region, theoretical calculations[12] have shown that the optical signal originates from surface states related to the dimers. The observed difference would then express the differences which occur in the surface band structure when silicon–hydrogen bonds or silicon–carbon bonds are formed. For higher photon energies, the similarity between the two spectra corroborates the fact that there are no optical transitions coming from the benzene molecules. As demonstrated by Jaloviar *et al.*,[7] there is no additional contribution coming from the steps above the energy of 3.5 eV, indicating that this signal is directly related to the terraces. Also, Shioda *et al.*[16] have demonstrated, by exposing the silicon surface to atomic hydrogen, that the structure around 3.5 eV reflects the coverage rate of hydrogen which terminates the dangling bond of the monohydride surface. Consequently, we can assume that the RA signal at 3.5 eV is proportional to the number of silicon dimers which are occupied either by hydrogen atoms or benzene molecules. The number of occupied dimers on the benzene-saturated surface has been estimated from the monohydride spectrum. Indeed, when the surface is saturated with hydrogen, all the dimers are occupied and the difference of intensity between the clean silicon spectrum and the monohydride spectrum at 3.5 eV characterizes a coverage close to unity. To determine the ratio of dimers occupied by benzene molecules, a proportionality factor is applied to the difference of intensity at 3.5 eV between the clean- and the benzene-saturated surface. Under these conditions, the ratio of occupied dimers proves to be approximately 0.47 ± 0.05, indicating that approximately 47% of dimers are occupied by benzene molecules. Although this result is only a rough estimation, because RA spectra intensity is sensitive to the surface quality, it is in good agreement with the saturation coverage obtained by thermal desorption spectroscopy experiments.[21,24] This result validates the relation between the intensity at 3.5 eV in the RA spectra and the number of occupied (or unoccupied) silicon dimers.

In order to complete the optical spectroscopy study of benzene on the Si(001)-(2×1) vicinal surface, we have performed surface differential reflectance spectroscopy (SDRS). This technique, which can be employed even on isotropic surfaces, has been shown in the case of hydrogen on Si(111)-7×7 surfaces,[19] as being able to provide quantitative information on the number of adsorbed atoms or molecules, and therefore to allow the investigation of adsorption kinetics. We have measured here the SDR spectra using *s*-polarized light parallel to the dimers with a 45° incidence. The spectrum at saturation coverage of benzene is presented in Fig. 4 and compared to the spectrum recorded on the monohydride surface. These SDR spectra have been recorded on different samples that presented the same anisotropy measured by RAS, which is a good check of the surface crystalline quality. Indeed, the RAS can be used as an efficient tool to characterize the surface quality of the vicinal Si surface.[37] First, one can notice that the shape of the SDR spectrum for benzene saturation is similar to that obtained on the monohydride phase. As we have shown previously, this indicates that the benzene molecules are bound to the dangling bonds of the dimer Si atoms, leaving unbroken.[38] This result confirms the RAS measurements where similar optical anisotropy is observed for hydrogen- and benzene-covered surfaces. Second, the SDRS intensity for the benzene-saturated surface is about half that for the monohydride surface. This result, close to the one obtained by RAS, indicates that about half of the Si dimers are bound to benzene. Contrarily to the case of the monohydride surface, where all the dimers are occupied by hydrogen atoms,[39] steric effects prevent adsorption of two benzene molecules on adjacent dimers. A coverage of 50% would then be expected if the benzene molecules were distributed regularly along a dimer row, bound to one dimer out of two. However, the actual coverage is a little bit smaller than the ideal one. STM investigation showed us that benzene molecules do not diffuse on the Si(001) surface. Consequently, benzene molecules stick at the surface locations on which they impinge. Because they impinge on the surface in a stochastic way, the ideal arrangement corresponding to one molecule out of two dimers cannot be obtained. The average number of occupied sites has been determined by using a simple Monte Carlo calculation free of diffusion. The locations on which benzene molecules impinge are randomly distributed. In this approach, benzene molecules can adsorb only on dimers which are not adjacent to a previously reacted dimer. The obtained saturated coverage is 43% for an ideal Si(001)-(2×1) surface. On a vicinal surface, with terraces holding 8 dimers on average, the calculated coverage is equal to 47%. This larger coverage originates from the adsorption favored on ends of dimers of a given row, compared to internal dimers. Monte Carlo calculation, carried out while taking an interaction

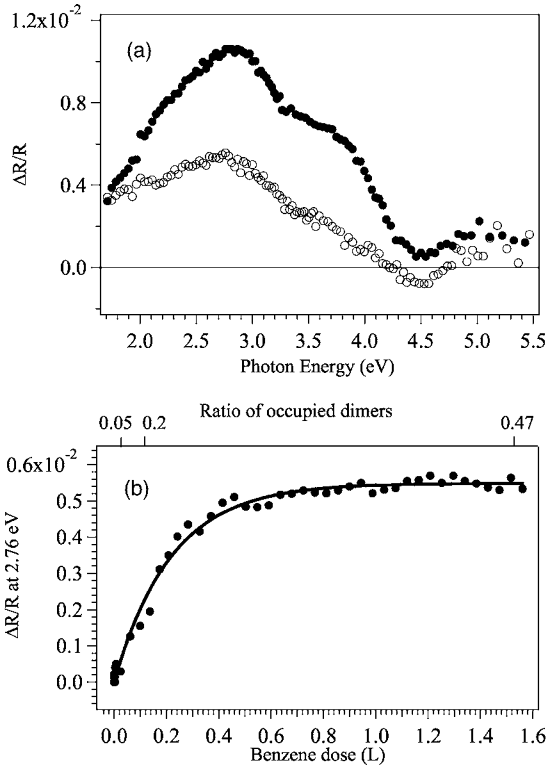

FIG. 5. (a) SDR spectra for a saturation coverage of benzene (open circles) and for the monohydride surface (dark circles); (b) Evolution of SDR signal at 2.76 eV during benzene exposure; the solid line is the calculation using Langmuir-type adsorption process.

cross section extending along three dimers, gives very similar results. Whatever the choice of the cross section, these results are in correct agreement both with SDRS and RAS measurements. We have also performed real-time SDRS measurements during adsorption, which permitted us to monitor the intensity of the signal, and therefore the amount of adsorbed benzene, as a function of time. Figure 5(b) shows the SDR signal at the energy of 2.76 eV, which corresponds to the maximum of the main feature of the benzene spectrum. The experimental data are correctly reproduced by using a Langmuir-type kinetics adsorption process,[40] $N(D) = N_0(1-e^{-\alpha D})$, where N is the number of occupied sites and D the benzene dose. In this process, the adsorption probability is proportional to the number of unoccupied sites. The kinetics curves determined by the Monte Carlo calculations are close to the Langmuir one. The inaccuracy on the experimental points prevents discrimination between the different curves. If we consider a saturation coverage of 47%, Fig. 5(b) shows that saturation is obtained for a SDR signal $\Delta R/R = 0.55 \times 10^{-3}$. Half of this signal corresponds to a coverage of about 24%, which is obtained, from Fig. 5(b), for an exposure of about 0.15 L. This result is in excellent agreement with the STM image shown in Fig. 3(b), where a 25% coverage is estimated.

B. Application to benzene adsorption configuration

As the RAS is sensitive to the number of occupied dimers, we have tried to evidence the possible conversion from an initial metastable adsorption, in a configuration where benzene molecules are bound to a single dimer, to a bridging configuration where benzene molecules are bound to two dimers.[25,28] For this purpose, the clean silicon surface was saturated with benzene and left for several hours under UHV conditions (7×10^{-11} Torr). The results are presented in Fig. 6(a). The spectrum labeled (a) was recorded immediately after the benzene adsorption, whereas the spectrum (f) was recorded 14 h later under UHV conditions. We clearly see that the spectrum at benzene saturation evolves with time; that could be a strong argument in favor of the initial metastable adsorption of benzene molecules that converts to a stable configuration where all dimers are occupied, as this final spectrum is similar to the monohydride spectrum where all the dimers are occupied (see Fig. 4). But, according to the Lopinski study,[25] the time required to convert 85% of the benzene molecules to a bridging configuration is about 150 min. Following this statement, the spectrum recorded 250 min after the benzene adsorption should resemble the monohydride spectrum where all the dimers are occupied, which is not the case here. Moreover, we have noticed that when benzene is not purified enough and when it is still slightly contaminated with water, the RA spectrum recorded for benzene saturation is similar to the spectrum (d) obtained 6 h after the clean benzene adsorption [Fig. 6(b)]. A similar contamination is also observed on the clean silicon surface [Fig. 6(b)]. When RAS on the clean silicon surface is measured after one night at a base pressure of 4×10^{-11} Torr, it has indeed the same shape as the spectrum (f) from Fig. 6(a). Under these conditions, the evolution of benzene-saturated spectrum with time does not seem to be induced by a modification of the adsorption geometry, but appears to be due to a slow contamination of the surface with the residual molecules in the chamber. We want to point out the fact that,

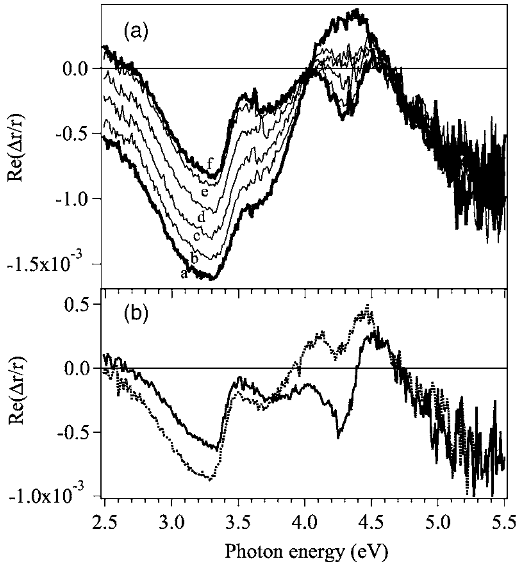

FIG. 6. (a) Evolution of RA spectra at benzene saturation with time (a) $t=0$ min; (b) $t=250$ min; (c) $t=280$ min; (d) $t=360$ min; (e) $t=540$ min; (f) $t=840$ min. (b) RA spectrum for a water-contaminated benzene adsorption (dotted line) and for an initially clean silicon surface after one night at 4×10^{-11} Torr (solid line).

even with a base pressure in the low 10^{-11} Torr range, the benzene-saturated silicon surface is still strongly reactive to residual molecules because only less than one dimer out of two is occupied. To reinforce our observation, we have checked the possible thermally induced binding state conversion, by warming up a saturated benzene silicon surface to about 120 °C for 5 min and to about 200 °C for 5 min. These temperatures are, respectively, below and above the thermal desorption temperature.[21] The annealing temperature is estimated from the applied power to heating the sample with a resistive current.

The results are presented in Fig. 7; no modification is observed in the RA spectrum after the annealing process at 120 °C, whereas the benzene has desorbed from the surface after annealing at 200 °C. In the case of a thermally activated bridging geometry conversion, one would expect an important change in the spectrum, which should be close to the one measured for a saturated hydrogen surface. This experiment confirms recent results obtained by NEXAFS, where no thermal activation was evidenced.[27] By using surface sensitive optical spectroscopies, we did not show evidence of thermally activated conversion process from on top of the dimer configuration, where the benzene is bound to a single dimer, to a bridging configuration, where the benzene is bound to two dimers. We conclude that the observed modification of the optical anisotropy with time is due to progressive contamination of the surface.

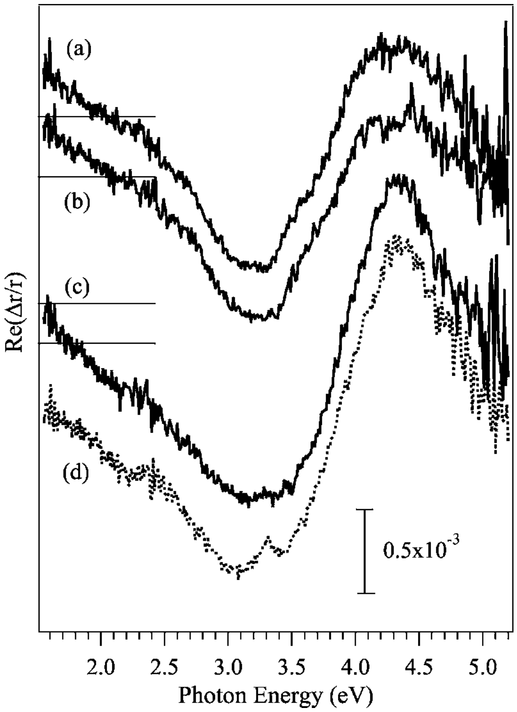

FIG. 7. (a) RA spectrum of saturated benzene layer. (b) RA spectrum after annealing 5 min at about 120 °C. (c) RA spectrum after annealing 5 min at about 200 °C. (d) RA spectrum of clean silicon. Spectra have been shifted vertically for a better comparison.

IV. CONCLUSION

In this paper, we have demonstrated that surface sensitive optical spectroscopies such as RAS and SDRS are sensitive to the dimer occupation. By using the RAS technique, we showed that the change of signal intensity at 3.5 eV is proportional to the number of occupied dimers. Also, the shape of the RA spectra with benzene is comparable to what is obtained for partially hydrogenated silicon surface, indicating that the RA signal is not specific to the signal coming from the adsorbates but is related to the surface modification upon adsorption. We have used these properties to demonstrate that at saturation coverage, benzene adsorbs on a single dimer with a coverage of about 0.47 benzene molecule per Si dimer. We did not show evidence of any thermal conversion into a bridging adsorption geometry, where the benzene would be adsorbed on two dimers. According to these results, the initial adsorption configuration on a single dimer is stable but slowly contaminated by residual molecules that adsorb on the unoccupied silicon dimers.

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