Si(100)1×1-Sb and Si(100)2×1-Sb surfaces studied with angle-resolved photoemission and surface differential reflectivity

A. Cricenti, S. Selci, A. C. Felici, L. Ferrari, G. Contini,* and G. Chiarotti†
Istituto di Struttura della Materia del Consiglio Nazionale delle Ricerche, via Enrico Fermi 38, I-00044 Frascati, Italy
(Received 30 November 1992)

Angle-resolved photoelectron spectroscopy and surface differential reflectivity have been used to study the electronic structure of Si(100):Sb-1×1 and Si(100):Sb-2×1 surfaces. For both surfaces, one occupied surface-state band has been mapped along the [010] and [011] directions. Both surfaces show a semiconducting behavior with a gap of 1.6 eV for the 1×1-Sb and 1.4 eV for the 2×1-Sb surface. A minimum-energy position at the Fermi level is derived for the empty surface-state band. The results are also compared with those obtained for the clean Si(100)2×1 surface.

INTRODUCTION

Several techniques[1–3] have been applied to the study of the atomic and electronic structures of Si(100)2×1 surfaces, and several models[4–6] have been proposed to explain the experimental data.[7] On the two-domain 2×1 surfaces, angle-resolved photoemission[8–10] (ARUPS) has shown the existence of two filled dangling-bond-type surface-state bands: one band (A) dispersing downward along the [010] azimuthal direction, which is equivalent for the two possible 2×1 domains (see Fig. 1), and one (B) slightly dispersing band around the $J'_{a,b}$ point in the surface Brillouin zone (SBZ). The shape of the dispersion and bandwidth of state A are well described by calculations of dangling-bond bands for symmetric or asymmetric dimers.[4–6] At variance, the B state cannot be accounted for in the theoretical band structure of the 2×1 reconstruction: this fact suggests that the B state is associated with imperfections on the surface, e.g., steps or point defects, or it may be a dangling-bond state from domains of asymmetric dimers on the surface, arranged into $c(4\times2)$ or $p(2\times2)$ periodicities.[11] The existence of a large number of asymmetric dimers has been very recently confirmed by high-resolution core-level spectroscopy.[12] By using scanning tunneling microscopy[13] (STM), it has been possible to investigate the atomic structure of the outer layer in real space, showing that the surface consists mainly of symmetric dimers with many defects and asymmetric dimers close to disordered areas.

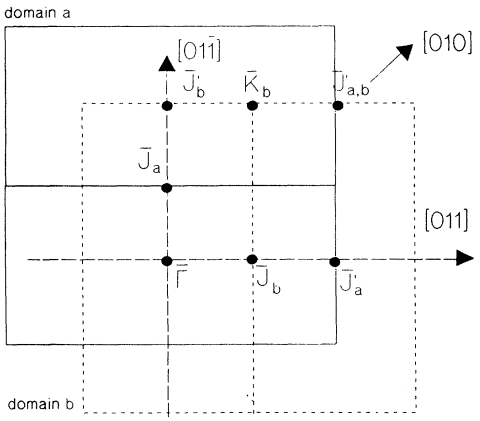

FIG. 1. Surface Brillouin zones for a two-domain 2×1 reconstruction on Si(100).

Also, the interaction of group-V adsorbates such as Sb and As with Si(100)2×1 surfaces has been the subject of much research in recent years.[14–16] Rich *et al.*[14] have shown that by evaporating Sb on Si(100)2×1 surfaces, kept at a temperature of 320–370 °C, a 1×1-Sb low-energy electron-diffraction (LEED) pattern with weak half-order spots and high background develops. Their STM images revealed an essentially disordered surface. STM experiments by Richter *et al.*[15] have shown that by evaporating a few monolayers of antimony on a Si(100)2×1 surface kept at 375 °C, and further annealing at temperatures of 550 °C, a 2×1 reconstruction is obtained. In this case, the 2×1-Sb reconstruction consists of symmetric Sb dimers with a degree of disorder higher than for the clean silicon surface,[15] but without asymmetric dimers.

In this work, we show that by evaporating antimony onto Si(100)2×1 surfaces, two different phases are present upon annealing the sample at different temperatures: a 1×1 at $T=350$ °C and a 2×1 at $T=450$ °C. The electronic properties of the two Sb-induced phases have been studied with angle-resolved photoemission and surface differential reflectivity (SDR). SDR results showed the presence of a gap in both phases (1.4 eV for the 2×1-Sb and 1.6 eV for the 1×1-Sb). ARUPS spectra along the [010] and [011] directions showed the same semiconducting behavior, with the presence of one dispersive band at energies below the Fermi level comparable to the SDR gap. The results are compared with those obtained from the clean Si(100)2×1 surface.

EXPERIMENT

Angle-resolved photoemission spectra were recorded in a Vacuum Generators VG-450 ultrahigh-vacuum (UHV) chamber at a pressure of less than 2×10^{-10} Torr. The

chamber was equipped with facilities for Auger electron spectroscopy (AES) and LEED. Unpolarized 21.2-eV radiation from a helium discharge lamp was used. The estimated total-energy resolution as determined by the analyzer voltages and the width of the He I light was 150 meV, and the angular resolution of the hemispherical analyzer was $\pm 1°$. The position of the Fermi level (E_F) was determined to an accuracy of ± 50 meV by photoemission from the metallic sample holder. Also, Auger electron-diffraction spectra have been recorded along the polar scan, and will be discussed in a forthcoming paper.[17]

The SDR experiment consists of shining light at normal incidence onto the surface of the Si(100) in UHV conditions and measuring the intensity of the reflected light with an optical multichannel array in the range between 200 and 1200 nm; a dummy silicon sample is used as reference. The details of the method and the apparatus are fully explained elsewhere.[18] With this apparatus, a single spectrum (between 1.3 and 3.0 eV) was recorded in approximately 30 s, so that the optical peak could be followed during the annealing process. The results are given in terms of $\Delta R/R$, i.e., the change in sample reflectivity during annealing: $\Delta R/R = (R_{an} - R_0)/R_0$. R_{an} is the annealed surface, while R_0 is the surface after the Sb evaporation and with the sample that has just reached 350 °C. At this temperature all but one monolayer (ML) of Sb desorbs, so that we get rid of the contribution to reflectivity of the Sb atoms exceeding 1 ML. For photon energies below the silicon gap (1.1 eV), $\Delta R/R$ gives directly the imaginary part of the surface dielectric function.[19] However, it has been shown that the same is approximately true for energies below the direct gap,[18] i.e., for Si up to 3 eV. Thus within our experimental range (1.3–3.0 eV), $\Delta R/R$ gives only transitions between surface states in the antimony-covered surfaces. The overall stability of $\Delta R/R$ was typically of the order of 10^{-3} over a few hours.

The sample was n-doped, mirror-polished Si(100) single-crystal phosphorus doped ($\rho \sim 10\ \Omega$ cm) with a size of $8 \times 15 \times 0.3$ mm^3. The surface normal was off by less than 0.1° from the [100] direction. Before insertion into the vacuum chamber, the sample was degreased and etched according to the procedure by Ishzaka, Nakagawa, and Shiraki.[20] In ultrahigh vacuum, it was thoroughly outgassed at 500 °C, and then annealed at 850 °C for 10 min. This cleaning procedure produces a sharp two-domain 2×1 diffraction pattern with low background in LEED, and a contaminant-free surface in AES spectra. The LEED and AES studies were always accomplished after the ARUPS and SDR spectra. The presented spectra for the Si(100)1×1-Sb surface were recorded from a surface obtained by evaporating 4 ML of Sb onto a clean 2×1 surface (prepared according to the procedure described above), followed by approximately 20-min annealing at 350 °C. This produced a surface with sharp 1×1 LEED pattern with low background and no traces of 2×1 spots. The 2×1-Sb surface was obtained either by annealing the 1×1-Sb surface, for 20 min at 450 °C, or by evaporating 4 ML of Sb onto a clean 2×1 surface followed by approximately 20-min annealing at 450 °C, resulting in a clear 1×1 pattern with diffuse, two-domain 2×1 spots and with high background, indicating some kind of disorder at the surface. All temperatures were measured with an infrared pyrometer. Sb was evaporated from a thoroughly outgassed Knudsen cell at a rate equivalent to 0.5 ML/min, as monitored with a quartz microbalance. 1 ML of Sb is defined as the site density for the unreconstructed surface, which is 6.8×10^{14} atoms/cm^2. Pressures during Sb deposition and sample heating did not exceed 1.0×10^{-9} Torr. ARUPS and SDR spectra have been recorded for several 1×1 and 2×1-Sb surfaces, obtained for somewhat different initial amounts of Sb, and the results show that the electronic structures of these surfaces are quite reproducible.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show ARUPS spectra recorded from the Si(100):Sb-1×1 surface for various angles of emission along the [010] and [011] directions, respectively. The spectra obtained along the [010] azimuth are dominated by a prominent peak (A'). This structure is identified in normal emission at 2.0 eV below E_F, with a small upward dispersion (0.4 eV) with maximum energy at $\Theta_e = 5°$, and then a downward dispersion (0.65 eV) for larger angles of emission. Also, the spectra obtained along the [011] direction are dominated by a single peak (A'_a) with a behavior very similar to that of Fig. 2(a), the only difference being the bandwidth (0.6 eV).

Figures 3(a) and 3(b) show ARUPS spectra recorded from the Si(100):Sb-2×1 surface for various angles of emission along the [010] and [011] directions, respective-

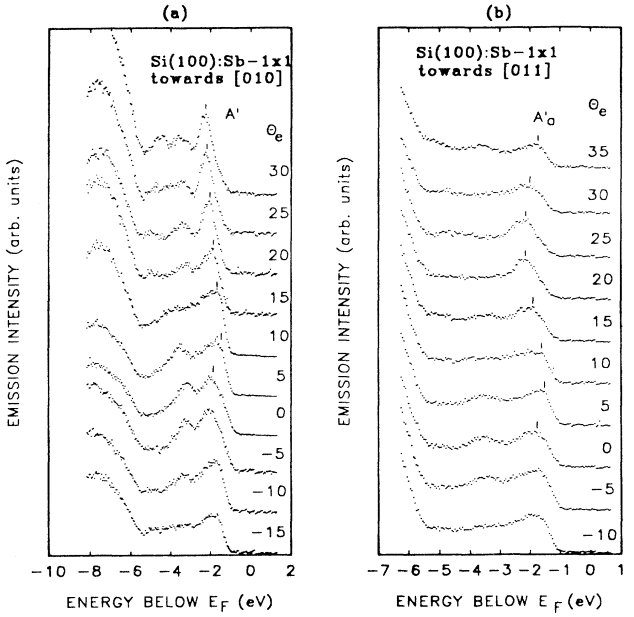

FIG. 2. Photoemission spectra recorded from Si(100):Sb-1×1 for various angles of emission along the [010] (a) and [011] (b) azimuthal directions. The angle of incidence is $\Theta_i = 45°$.

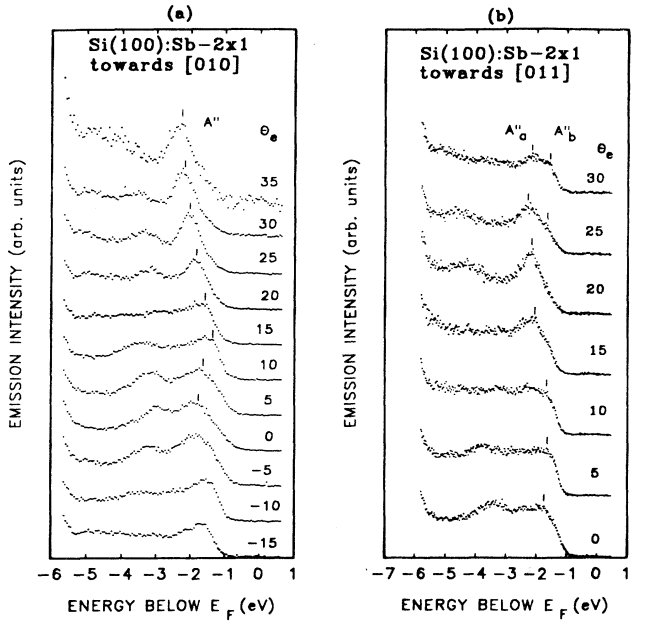

FIG. 3. Photoemission spectra recorded from Si(100):Sb-2×1 for various angles of emission along the [010] (a) and [011] (b) azimuthal directions. The angle of incidence is $\Theta_i = 45°$.

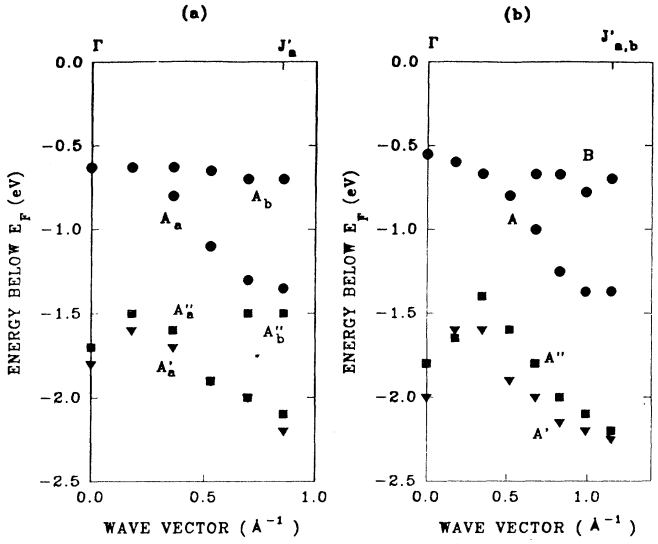

FIG. 4. The experimental energy dispersion of the filled surface states for the Si(100)2×1 surface, for the Si(100)1×1-Sb surface, and for the Si(100)2×1-Sb surface, along the [011] (a) and [010] (b) azimuthal directions.

ly. As for the 1×1-Sb surface, the spectra obtained along the [010] azimuth are dominated by a single peak (A''). Such a structure is located at 1.8 eV below E_F in normal emission, showing an upward dispersion (0.4 eV) with maximum energy at $\Theta_e = 10°$, and then a large downward dispersion (0.9 eV) for larger angles of emission. The spectra obtained along the [011] direction show a single structure (A''_a) for small emission angles, with a maximum energy of 1.5 eV below E_F at $\Theta_e = 5°$. This peak disperses downward for higher emission angles, with a bandwidth of 0.6 eV. A second structure (A''_b) becomes visible for emission angles around $\Theta_e = 25°$ and 30°.

Figure 4 shows the experimental energy dispersions of the different structures of the Si(100):Sb-1×1 and Si(100):Sb-2×1 surfaces. Also shown in the figure are the experimental dispersions of the surface states of the clean Si(100)2×1 surface. On this surface, both the energy position and dispersion for the surface states A, B, A_a, and A_b are in good agreement with previous studies.[8–10] The structures A_a and A_b are related to the two-domain reconstruction (A_a is related to domain a and A_b to domain b of Fig. 1), which are probed simultaneously.

Since all the above-described structures in the Sb-induced phases are not present in the clean surface, and present only a small part of their dispersion within the projected bulk band gap,[10] they will be regarded as Sb-induced surface states. The surface-state assignment is further supported by the periodicity of the dispersions along the probed lines in the surface Brillouin zone.

Along the [010] direction, for which we probe equivalent $k_{\parallel}$ lines, we observe, both for the 1×1-Sb and 2×1-Sb surfaces, one surface-state band that is symmetric around $J'_{a,b}$, as expected. In the [011] direction, for which we probe the line Γ-J'_a, in the case of the 1×1-Sb surface we observe one surface band, while in the case of the 2×1-Sb surface, for which the lines Γ-J'_a and Γ-J_b in the two 2×1 SBZ's are probed simultaneously, we observe two surface bands. All of the data for both 1×1-Sb and 2×1-Sb surfaces are thus consistent with a single surface state per domain.

When the angle of incidence (Θ_i) is changed to 0, the intensities of surface states A' and A'' are strongly reduced, demonstrating a marked p_z character. This p_z character and the sensitivity of surface states A' and A'' to oxygen adsorption are very similar to the behavior of surface states A and B on the clean surface.

Results from Rich *et al.*[14] show that upon Sb adsorption on the sample kept at 375 °C (1×1-Sb surface), the Si core-level spectra exhibit a single bulklike component, i.e., the surface components due to the 2×1 reconstruction are suppressed. Sb atoms should be bound to the unsaturated dangling bonds of Si atoms with the breaking of Si dimers and the bulklike fourfold arrangements of the Si surface atoms. In this configuration, every Sb atom is left with one dangling bond unsaturated (there are also the lone pair electrons, which we do not take into account). Upon annealing the sample at 450 °C, Sb atoms start to interact more with each other and to form dimers (2×1-Sb surface): the number of dangling bonds is reduced, and the surface total energy is minimized,[21] thus giving rise to a more stable surface.

The dispersion of the surface state A'' is very similar to ARUPS results on the Si(100)2×1-As surface,[16] where a symmetric dimer model [predicted by theoretical calculations and observed by STM (Ref. 22)] can account for the surface-state band dispersion. In that ARUPS study,[16] the dispersion of the filled band along the Γ-$J'_{a,b}$

line shows a maximum at $k_{\parallel}=0.33$ Å^{-1}, and then disperses downward toward the $J'_{a,b}$ point with a bandwidth of 0.8 eV. For the A'' structure, we have observed the same kind of dispersion (maximum at $k_{\parallel}=0.35$ Å^{-1}) with similar bandwidth (0.9 eV); the only difference is in the absolute energy position, which depends on the bonding between the different kind of atoms involved (As or Sb in this case). Since symmetric dimers have also been observed by STM on this 2×1-Sb surface, we expect that calculations based on symmetric dimers will fully describe our observed band structure.

A puzzling feature of the ARUPS spectra recorded for the Sb-induced 2×1 phase is the absence of the counterpart to the B state of the clean 2×1 surface. Also, for Si(100)2×1-As surfaces, a single surface-state structure (similar to the A state on the clean surface) is observed by ARUPS and is fully explained by calculations based on symmetric As-As dimers. On the same surface, STM observations[22] have revealed such symmetric dimer structure without any order of defects or asymmetric dimers. STM observations on the 2×1-Sb surface[15] clearly show the existence of symmetric dimers together with a high density of defects. However, no observation of asymmetric dimers has come out around defects, as in the case of the clean surface,[13] where asymmetric dimers are arranged around defects in $c(4\times2)$ and $p(2\times2)$ periodicities. These STM results, together with the fact that there is no evidence of a state similar to the B one in the ARUPS spectra of 2×1-Sb and 2×1-As surfaces, give a strong indication that the state B observed on the clean Si(100)2×1 surface is associated with the dangling bonds in domains with asymmetric dimers arranged in $c(4\times2)$ or $p(2\times2)$ reconstructions. Such a conclusion is also in good agreement with core-level spectroscopy results by Landmark *et al.*:[12] in fact, from very well-resolved core-level measurements, it seems very clear that the 2×1 surface at room temperature contains dynamically flipping asymmetric dimers at concentrations similar to the stable asymmetric dimers of the $c(4\times2)$ surface at low temperature.[23]

Figure 5 shows $\Delta R/R$ variation as a function of the annealing time and sample temperature. With the sample at 350 °C (1×1-Sb surface), a prominent peak (S_1) is observed to develop at 1.6 eV (see spectra 1–12). Upon annealing the sample at 450 °C (Sb-2×1 phase), peak S_1 is suppressed and a new structure (S_2) develops around 1.4 eV (see spectra 13–17). Both S_1 and S_2 peaks give the minimum-energy gap for the surface-state transition. Upon further annealing at 550 °C, the Sb atoms start to desorb, so that part of the surface returns clean: this is clearly evidenced in the SDR spectra 18–24 by a decreasing of the Sb-induced peak at 1.4 eV, and by the growth of the clean Si(100)2×1 peak around 1.7 eV. Such an observation is in agreement with STM results by Richter *et al.*[15] that show uncovered regions upon annealing at 550 °C the Sb-covered Si(100) surface.

Both the Sb-1×1 and Sb-2×1 surfaces show a semiconducting behavior. This is clearly evidenced by the fact that no emission at the Fermi level is observed in ARUPS, and by the observation of the curves in Fig. 5, which shows the presence of a gap for both surfaces, evi-

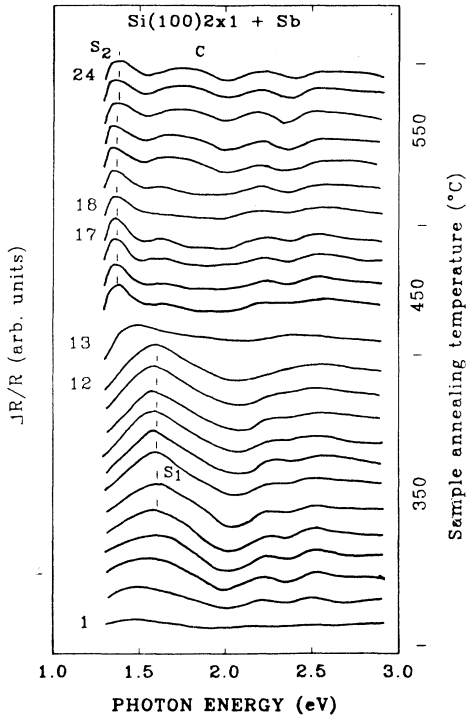

FIG. 5. Sb onto Si(100)2×1: the evolution of surface differential reflectivity spectra in the 1.3–3.0-eV photon range at different temperatures as a function of time.

denced by a well-defined peak of $\Delta R/R$, at 1.6 (S_1) and 1.4 eV (S_2).

From the ARUPS spectra of Fig. 2, and from energy considerations, two different points of the SBZ might contribute to the optical transition S_1: the points around $k_{\parallel}=0.25$ Å^{-1} along the [010] direction, and around $k_{\parallel}=0.2$ Å^{-1} along the [011] direction. In fact, in both cases the filled surface states are located at 1.6 eV below E_F. Of course, such an interpretation would need a similar energy minimum for the empty band at the above-mentioned k-parallel points. In the case of peak S_2, the occupied surface states involved in the transition must be located around $k_{\parallel}=0.35$ Å^{-1} along the [010] direction. Also, in this case an energy minimum of the empty surface-state band is expected at this k parallel. In this picture, the empty band needs to be mapped all along the symmetry lines in order to fully assign the optical transitions to precise points of the SBZ and, moreover, to check if excitonic effects are present in the SDR spectra.

SUMMARY

We have performed angle-resolved photoemission and surface differential reflectivity studies of Si(100):Sb-1×1 and Si(100):Sb-2×1 surfaces. For both surfaces, the dispersion of one occupied surface-state band has been determined along the high-symmetry lines in the surface Brillouin zone. Both surfaces show a semiconducting

behavior with a gap of 1.6 (1×1-Sb) and 1.4 eV (2×1-Sb). A minimum-energy position at the Fermi level is derived for the empty surface-state band. The comparison at the annealing temperature of reflectivity at the initial time and at time t introduces a method for studying the dynamical behavior of annealing processes, which is of importance for the study of reconstruction and relaxation of surfaces.

---

*Permanent address: Institute of Mineral Processing, via Bolognola 7, 00138 Rome, Italy.

†Also at Dipartimento di Fisica, Universitá degli Studi di Roma "Tor Vergata," Rome, Italy.

[1]R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959).

[2]F. J. Himpsel and D. E. Eastman, J. Vac. Sci. Technol. **16**, 1297 (1979).

[3]M. J. Cardillo and G. E. Becker, Phys. Rev. B **21**, 1497 (1980).

[4]J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. Lett. **35**, 729 (1975).

[5]D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[6]K. C. Pandey, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by D. J. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 55.

[7]For a recent review, see G. V. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988).

[8]P. Martensson, A. Cricenti, and G. V. Hansson, Phys. Rev. B **33**, 8855 (1986).

[9]A. Cricenti, P. Martensson, L. S. O. Johansson, and G. V. Hansson, in *Proceedings of the 18th International Conference on the Physics of Semiconductors,* edited by O. Engstrom (World Scientific, Singapore, 1987), p. 77.

[10]L. S. O. Johansson, R. I. G. Uhrberg, P. Martensson, and G. V. Hansson, Phys. Rev. B **42**, 1305 (1990).

[11]Z. Zhu, N. Shima, and M. Tsukada, Phys. Rev. B **40**, 11 868 (1989).

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

[13]R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[14]D. H. Rich, F. M. Leisble, A. Samsavar, E. S. Hirschorn, T. Miller, and T.-C. Chiang, Phys. Rev. B **39**, 12 758 (1989).

[15]M. Richter, J. C. Woicik, J. Nogami, P. Pianetta, K. E. Miyano, A. A. Baski, T. Kendelewicz, C. E. Bouldin, W. E. Spicer, C. F. Quate, and I. Lindau, Phys. Rev. Lett. **65**, 3417 (1990).

[16]R. I. G. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, J. Vac. Sci. Technol. A **4**, 1259 (1986).

[17]A. Cricenti *et al.* (unpublished).

[18]S. Selci, F. Ciccacci, G. Chiarotti, P. Chiaradia, and A. Cricenti, J. Vac. Sci. Technol. **5**, 327 (1987); S. Selci, A. Cricenti, M. Righini, C. Petrillo, F. Sacchetti, F. Alexandre, and G. Chiarotti, Appl. Surf. Sci. **56**, 637 (1992).

[19]J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. **42**, 417 (1971).

[20]A. Ishizaka, and Y. Shiraki, J. Electrochem. Soc. **133**, 666 (1986).

[21]This is in good agreement with very recent theoretical calculations on the chemisorption of Sb on Si(100) surfaces by S. Tang and A. J. Freeman, Phys. Rev. B **47**, 1460 (1993). Those authors have found that the Sb dimers are more stable than single-atom adsorption, thus resulting in the essential structure on the Si(100) surface.

[22]R. S. Becker, T. Klitser, and J. S. Wickers, J. Microsc. **152**, 157 (1988).

[23]R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).