PHYSICAL REVIEW B **70**, 035301 (2004)

Photoemission study of metastable oxygen adsorbed on a Si(111)-(7×7) surface

Kazuyuki Sakamoto,[1,2,*] H. M. Zhang,[2] and R. I. G. Uhrberg[2]
[1]*Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*
[2]*Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden*

(Received 20 January 2004; published 7 July 2004)

We have investigated the metastable oxygen species adsorbed on a Si(111)-(7×7) surface at room temperature using real time valence-band and core-level photoemission measurements. The dosage- and time-dependent changes in the intensity of the metastable 3.8 eV peak observed in the valence-band spectra were different from those of the metastable O 1*s* components. Further, although no metastable O 1*s* components were observed in the core-level measurement after annealing the sample at 600 K, the 3.8 eV peak was still observed. These results indicate that both the stable and the metastable oxygen species produce the 3.8 eV valence-band peak, and we therefore conclude that the contradicting lifetimes reported in the literature result from a misinterpretation of the 3.8 eV peak.

DOI: 10.1103/PhysRevB.70.035301 PACS number(s): 68.43.−h, 73.20.Hb, 79.60.−i

I. INTRODUCTION

Motivated by the technological importance of nanoscale dielectric layers in semiconductor devices, an atomic level understanding of silicon oxidation has been a topic of experimental and theoretical investigations over the last two decades. From a scientific point of view, the presence of the metastable oxygen has particularly attracted a deep interest in the initial oxidation stage of the Si(111)-(7×7) surface. This metastable species, which has a finite lifetime and disappears after annealing the sample at 600 K, was observed in various spectroscopic[1–17] and microscopic studies,[17–20] and it has also been treated theoretically.[3,21–24] Despite these extensive research efforts, a complete picture of the processes determining the lifetime has not yet been obtained.

By measuring the time-dependent O 1*s* core-level spectra,[7,9,15,16] the lifetime of the metastable "ins-paul" oxygen (Fig. 1) was reported to be shorter than 20 min at room temperature, and to be longer than 1 h at temperatures below 150 K. In contrast to these results, a lifetime longer than 500 min at room temperature was reported in the valence-band photoemission studies,[5,6] by measuring the time-dependent intensity of a metastable oxygen-induced peak at a binding energy of 3.8 eV. There are two possible explanations to the origin of the inconsistent results at room temperature. First, the use of different photon energies $(h\nu)$ in the O 1*s* core-level and valence-band measurements ($h\nu$=1253.6[7,9] and 665 eV[15,16] were used in the core-level measurements and $h\nu$=40.8 eV in valence-band measurements)[5,6] can cause a difference in photon-induced dissociation and/or desorption of the metastable oxygen, i.e., dissociation and/or desorption are promoted by the use of higher photon energies. Second, compared with the intensities of the metastable O 1*s* components that give direct information about the change in the relative abundance of the metastable ins-paul oxygen, the 3.8 eV peak might contain contributions from more than one oxygen species. The lifetime obtained in the valence-band studies might therefore be overestimated. In fact, although the 3.8 eV peak observed in the valence-band spectra was assigned to the π^* orbital of a molecular "paul" species in the early valence-band studies[5–8,10,11] and theoretical investigations,[3,21] recent valence-band[12] and theoretical[22,23] studies suggest that the origin is the p_z orbital of an "ad" oxygen atom. The ad denotes an O atom bonding on top of a Si adatom of the dimer-adatom-stacking fault structure[25] of the Si(111)-(7×7) surface (Fig. 1). The knowledge of the accurate lifetime is essential in order to achieve an atomic level understanding of the initial oxidation of the Si(111)-(7×7) surface that progresses via metastable species. It is therefore important to find the reasons for the earlier inconsistent estimates of the lifetime. This calls for a reinvestigation of the origin of the 3.8 eV valence-band peak.

In this paper, we present real time valence-band and O 1*s* core-level measurements of oxygen adsorption and reaction on a Si(111)-(7×7) surface at room temperature. Real time measurements minimize the uncertainty that originates from the time lag between the completion of the O_2 exposure and the data acquisition. Measurements of both the valence band and O 1*s* core level on the same sample give information about the photon-induced reaction. The dosage and time dependence of the 3.8 eV intensity observed in the valence-

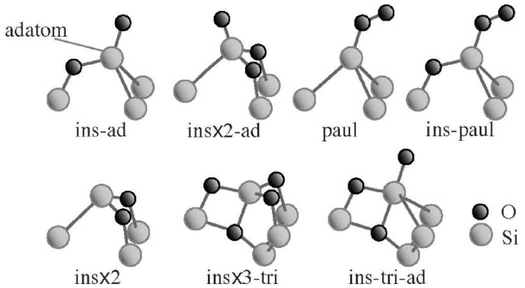

FIG. 1. Bonding configurations of the metastable and stable oxygen discussed in the text. The large gray circles are Si atoms of a Si(111)-(7×7) surface, and the small black circles are oxygen atoms. ad and ins correspond to an O atom bonding on top of a Si adatom and to an O atom inserted into a backbond, respectively. paul denotes an O_2 molecule adsorbed on top of an adatom, and tri corresponds to an O atom bonding between the first and second layer Si atoms.

band spectra were different from those of the metastable O 1*s* components obtained in the core-level measurement. Taking into account that the 3.8 eV peak was observed even after annealing the sample at 600 K, we conclude that it originates from both the metastable ins-paul oxygen and stable oxygen species. Further, by adjusting for the contribution from stable oxygen species, the lifetime of the metastable oxygen derived from the 3.8 eV peak is consistent with that from the core-level measurements. These results reconcile the former inconsistent reports on the lifetime of the metastable oxygen adsorbed on a Si(111)-(7×7) surface.

II. EXPERIMENTAL DETAILS

The valence-band and O 1*s* core-level measurements were performed at beamline I311 at the MAX-II synchrotron radiation facility in Lund, Sweden. The photoemission spectra were obtained with an angle-integrated photoelectron spectrometer with an acceptance angle of 15°. The total energy resolution was ~0.06 eV at $h\nu$=40 eV and ~0.23 eV at $h\nu$=665 eV. The vacuum chamber was also equipped with a low energy electron diffraction (LEED) system and a quadrupole mass spectrometer (QMS). The base pressure was below 7×10^{-11} Torr. We have annealed the Si(111) sample, which was cut from an Sb-doped (*n*-type) Si wafer, at 1520 K for 3 s in the vacuum chamber to obtain a clean surface. After the annealing, a sharp 7×7 LEED pattern was observed, and neither the C 1*s* nor the O 1*s* peak was detected in the core-level spectra. The quality of the O_2 gas was confirmed by QMS.

III. RESULTS AND DISCUSSION

Figure 2 shows valence-band spectra recorded while exposing the Si(111)-(7×7) surface to an ambient O_2 pressure of 5.0×10^{-9} Torr at room temperature using $h\nu$=40 eV. One Langmuir (L) corresponds to a 1 s exposure at a pressure of 1×10^{-6} Torr. A photon energy of 40 eV was chosen so that our result can be directly compared to the earlier valence-band studies.[5,6] Further, the large cross section of the 3.8 eV peak at this photon energy[7] will make it easier to follow the change in the intensity. The lowest spectrum shows the valence band of a clean Si(111)-(7×7) surface that was recorded just before the exposure. The difference in exposure between one spectrum and the next is approximately 0.14 L, and the average exposure of the highest spectrum is approximately 11 L. In the spectrum of the clean surface, the two surface states S_1 and S_2, which originate from the dangling bonds of adatoms and rest atoms, are clearly observed. The intensities of these two surface states decrease as the oxygen exposure increases, and S_1 and S_2 disappear at approximately 1.5 and 3.5 L, respectively. This means that oxygen atoms and/or molecules preferably interact with the adatoms rather than the rest atoms at the initial stage of oxidation. Regarding the oxygen-induced states, two are observed at binding energies of 3.8 and 7.0 eV.

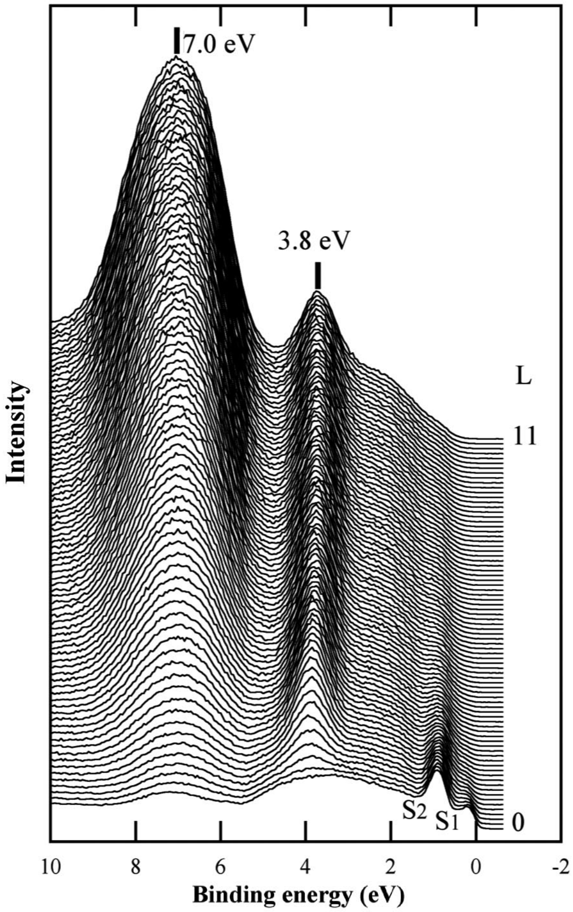

FIG. 2. Valence-band spectra recorded while exposing the Si(111)-(7×7) surface to an ambient O_2 pressure of 5.0×10^{-9} Torr at room temperature using $h\nu$=40 eV. The lowest spectrum (0 L) was recorded just before starting the exposure, and the average exposure of the highest one is approximately 11 L.

In Fig. 3, we show the time-dependent valence-band spectra of a 1.0 L O_2 exposed Si(111)-(7×7) surface. The spectra were continuously recorded starting when the exposure had just finished. The time difference between subsequent spectra is approximately 27 s, and the highest spectrum was recorded approximately 37 min after stopping the exposure. As shown in the figure, the intensity of the 3.8 eV peak decreases with time, and the intensity of the 7.0 eV peak increases together with a shift to 7.4 eV. These changes in intensity agree well with the results reported in the previous valence-band studies,[5–8,10–12] in which the 3.8 and 7.0 eV peaks were stated to originate from the metastable and stable oxygen, respectively. Further, taking into account that the presence of two oxygen-induced states was reported at around 7 eV,[7,8,10–12] the shift of the 7.0 eV peak to 7.4 eV indicates a change in relative intensity of these two states. Concerning the S_1 and S_2 states, their intensities hardly changed with time. These results indicate that the metastable ins-paul oxygen hardly desorb from the surface with time, but changes its bonding configuration without changing the number of adatom dangling bonds that are saturated by oxygen species, i.e., the ins-paul oxygen changes its bonding configuration to ins×2-ad or ins-tri-ad.

In order to obtain more information about the origin of the 3.8 eV peak, we first compare the dosage and time dependence of its intensity with those of one of the metastable O

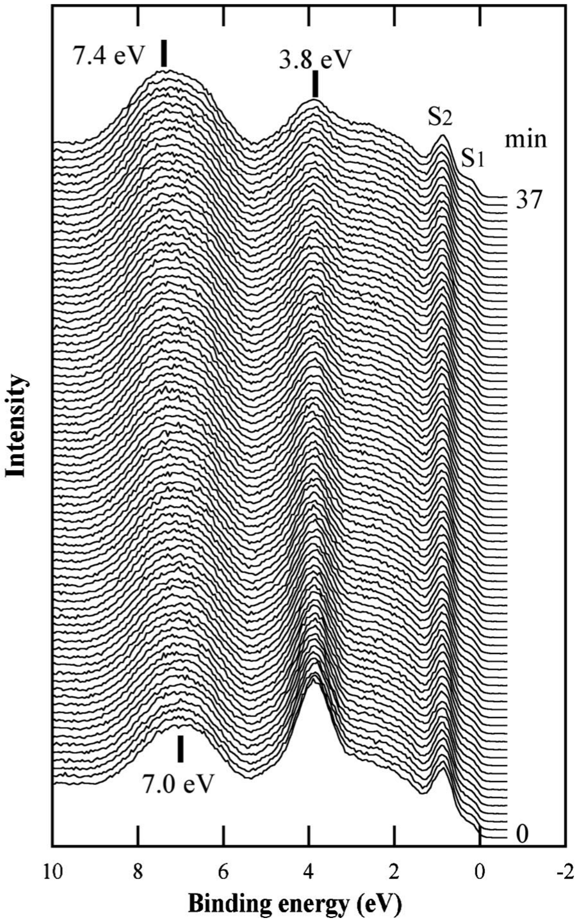

FIG. 3. Time-dependent valence-band spectra continuously recorded after exposing the Si(111)-(7×7) surface to 1.0 L of O_2 at room temperature using $h\nu=40$ eV. The lowest spectrum (0 min) was recorded just after stopping the exposure.

1*s* components. Figure 4(c) shows the O 1*s* core-level spectrum of a Si(111)-(7×7) surface that is exposed to 10 L O_2 at room temperature and recorded using $h\nu=665$ eV. The open circles are the experimental data, and the solid line overlapping the open circles is the fitting result that is obtained using the components with Voigt line shapes shown below the spectrum. A 200 meV Lorentzian full width at half maximum (FWHM) and a Gaussian width of 925 meV FWHM were used for the O 1*s* components at 300 K. The zero of the binding energy is taken at the position of the main peak. Of the six O 1*s* components, the two with relative binding energies of −4.4 and 3.1 eV originate from the paul oxygen of the ins-paul species, and the component with relative binding energy of −1.2 eV originates from the ins oxygen of the metastable ins-paul species.[15] The origins of the three observed at 0.0, 0.6, and 1.5 eV are the stable ins, tri, and ad oxygen, respectively.[16] Figure 4(a) displays the dosage-dependent intensities of the 3.8 eV peak and the metastable −4.4 eV O 1*s* component, which are obtained by continuously measuring valence-band and core-level spectra while exposing the sample to an ambient O_2 pressure of 5.0×10^{-9} Torr at room temperature. Figure 4(b) shows the time dependence of the 3.8 eV peak and the −4.4 eV component of a 1.0 L oxygen exposed surface. The intensities of the 3.8 eV peak and the −4.4 eV O 1*s* component are normalized with their maximum intensities in each figure.

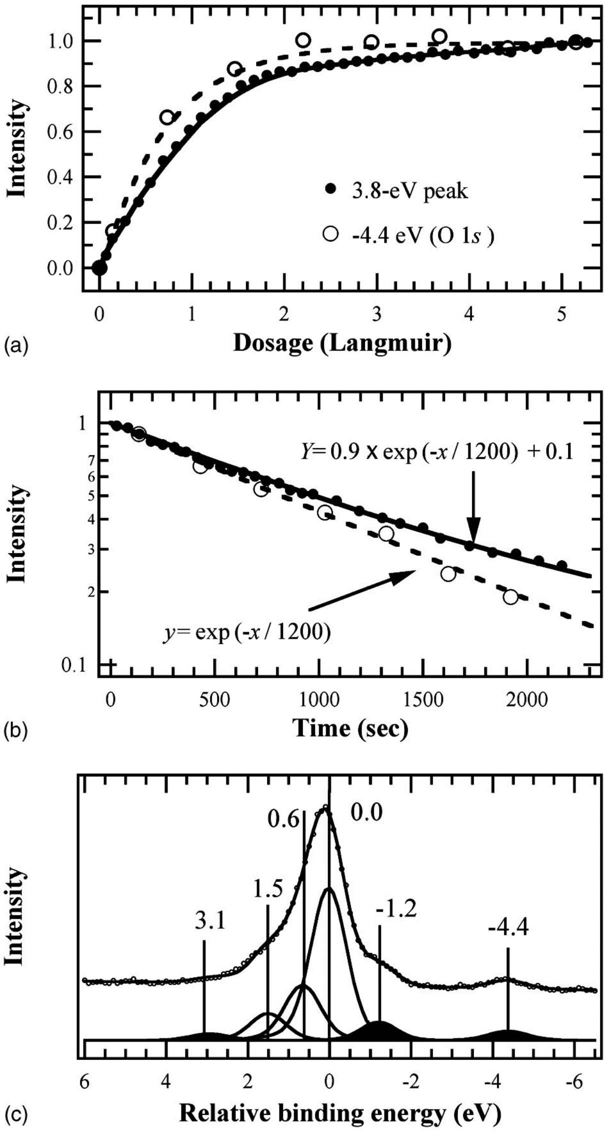

FIG. 4. (a) Dosage-dependent and (b) time-dependent intensities of the 3.8 eV peak observed in the valence-band and the −4.4 eV O 1*s* component. The intensities of the 3.8 eV peak and the metastable −4.4 eV O 1*s* component are normalized with their maximum intensities in each figure. The initial exposure in (b) is 1.0 L. (c) shows the O 1*s* core-level spectrum of a Si(111)-(7×7) surface exposed to 10 L O_2 at room temperature. The open circles in (c) are the experimental data, and the solid line overlapping those open circles is the fitting result that is obtained using the components shown below the spectrum. The zero of the binding energy is taken at the position of the main peak.

As displayed in Fig. 4(a), the intensities of both the 3.8 eV peak and the metastable O 1*s* component drastically increase at the beginning of the exposure. However, in contrast to the intensity of the metastable O 1*s* component that saturates at approximately 2 L, the intensity of the 3.8 eV peak shows no saturation within the dosage range shown in Fig. 4(a), though the increase rate becomes obviously smaller at around 1.5 L. In Fig. 4(b), the intensities of the 3.8 eV peak

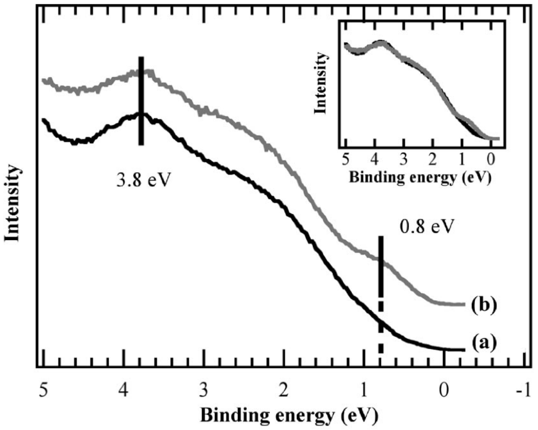

FIG. 5. (a) Valence-band spectrum recorded 2 h after a 20 L O_2 exposure on a Si(111)-(7×7) surface, and (b) a spectrum recorded after annealing a 20 L exposed surface at 600 K. Spectrum (b) is put on spectrum (a) to compare the intensity of the 3.8 eV peak in the inset.

and the metastable O 1*s* component show different time-dependent changes. The different dosage and time-dependent changes in intensity indicate that the origin of the 3.8 eV peak is not completely the same as that of the metastable O 1*s* component.

Figure 5 shows a valence-band spectrum of a Si(111)-(7×7) surface recorded 2 h after a 20 L oxygen exposure (a), and a spectrum recorded after annealing a 20 L exposed surface at 600 K (b). A peak at a binding energy of 3.8 eV is clearly observed in spectrum (a), though none of the metastable components was observed in the O 1*s* core-level spectrum recorded 2 h after the exposure.[16] Taking the time-dependent decrease of the 3.8 eV peak observed in Figs. 3 and 4 into account, this result indicates that both the stable and metastable oxygen species produce a peak at 3.8 eV in the valence-band spectra. The intensity of the 3.8 eV peak observed in spectrum (b) is almost the same as that observed in spectrum (a) as shown in the inset of Fig. 5. Further, a peak, which is not recognized in spectrum (a), is observed at a binding energy of 0.8 eV in spectrum (b). Since the binding energy of the dangling bond state of an ins$\times n$ ($n = 1, 2,$ and 3) species was reported to be between 0.5 and 0.8 eV,[3,10,20,21] the appearance of the 0.8 eV peak and the fact that the 3.8 eV intensity is the same in the two spectra suggest that oxygen species adsorbed at the on top site of an adatom hardly contribute to the stable 3.8 eV peak. Therefore, we conclude that the stable 3.8 eV peak observed in Fig. 5 originates from ins and/or tri oxygen atoms, i.e., atoms adsorbed into the backbonds of adatoms and/or between the first and second layer Si atoms.

Based on the contribution from both the stable and metastable oxygen species, we consider the metastable oxygen species that produce a peak at 3.8 eV in the valence-band spectra. The lifetime of a metastable species (τ) can be derived from fitting the decrease of the time-dependent intensity using the equation $y = \exp(-x/\tau)$. The dashed line shown in Fig. 4(b) is obtained using $y = \exp(-x/1200)$. Taking the origin of the -4.4 eV O 1*s* component into account, this means that the lifetime of the metastable ins-paul oxygen is 1200 s at room temperature. In case of a peak that is produced by both a stable and metastable oxygen species, its time-dependent decrease in intensity should follow the equation $y = a\,\exp(-x/\tau') + (1-a)$ $(0 < a < 1)$. This equation suggests that $a \times 100\%$ of the peak intensity originates from the metastable oxygen species, whose lifetime is τ', and $(1-a) \times 100\%$ results from the stable species just after the exposure. The intensity decrease of the 3.8 eV peak is well fitted using $y = 0.9 \times \exp(-x/1200) + 0.1$ as indicated by the solid line in Fig. 4(b). Taking into account that the lifetime of the metastable species, which produce a peak at 3.8 eV, is the same as that of the ins-paul oxygen, we conclude that 90% of the 3.8 eV peak originates from the metastable ins-paul oxygen and 10% results from stable ins$\times n$ and/or ins$\times n$-tri oxygen species just after the 1.0 L O_2 exposure. Moreover, the same lifetime obtained in the valence-band and core-level measurements indicates that the difference in photon energy hardly affects the lifetime of the ins-paul metastable species.

The lifetime of the metastable oxygen obtained in the present study is quite short compared with the lifetime reported in the earlier valence-band studies (more than 5 h).[5,6] This difference can be explained by the different assignment of the 3.8 eV peak, i.e., the 3.8 eV peak was stated to originate from a metastable species only, while the contribution from both the stable and metastable oxygen species is obvious in the present study. Assuming only one origin and by measuring the time-dependent intensity a long time after stopping the exposure, the apparent lifetime becomes longer as one can realize from Fig. 4. Furthermore, the presence of two origins and the short lifetime of the metastable oxygen can explain the dosage dependence of the 3.8 eV peak observed in a recent valence-band study,[11] whose result is different from the present one. The intensity of the 3.8 eV peak was reported to increase until 6 L and to then decrease drastically in the recent study,[11] while the intensity of the 3.8 eV peak did not show such a drastic decrease in the present study. Since the spectra were recorded after stopping the exposure in that valence-band study,[11] the observed drastic decrease in intensity might result from the short lifetime of the metastable oxygen. This indicates that without doing real time measurements, it is impossible to obtain precise information about the metastable oxygen.

IV. CONCLUSION

In conclusion, we have investigated the lifetime of the metastable species and the origin of the 3.8 eV valence-band peak of an oxygen adsorbed Si(111)-(7×7) surface at room temperature using real time valence-band and O 1*s* core-level measurements. The 3.8 eV valence-band peak shows different dosage- and time-dependent intensities from those of the metastable -4.4 eV O 1*s* component. Taking into account that the 3.8 eV peak was still observed in the spectrum recorded 2 h after the exposure, i.e., when no metastable O 1*s* component was observed in the O 1*s* core-level spectra, we conclude that the difference in intensity decrease results from the fact that the -4.4 eV O 1*s* component originates from one metastable oxygen species, while the 3.8 eV peak results from both the stable and metastable oxygen species. Further, the observation of the 0.8 and 3.8 eV peaks in the spectrum recorded after annealing the sample at 600 K indicates that stable oxygen species, which produce a part of the 3.8 eV peak, are the ins and/or tri oxygen species. By considering the contribution from the metastable and stable oxygen species, the lifetime derived from the 3.8 eV peak is obtained to be 1200 s, a value that is the same as the lifetime obtained in the core-level measurements. This result indicates that the cross section of the photon-induced reaction of the metastable ins-paul oxygen is quite small.

ACKNOWLEDGMENTS

Experimental support from Dr. S. A. Gorovikov, Dr. T. Balasubramanian, and the MAX-lab staff, and fruitful discussion with Dr. F. Matsui, are gratefully acknowledged. This work was financially supported by the Swedish Research Council.

---

*Electronic address: sakamoto@surface.phys.tohoku.ac.jp

[1] H. Ibach, H. D. Bruchmann, and H. Wagner, Appl. Phys. A: Solids Surf. **A29**, 113 (1982).

[2] P. Bratu, K. L. Kompa, and U. Höfer, Phys. Rev. B **49**, 14 070 (1993).

[3] Ph. Avouris, I.-W. Lyo, and F. Bozso, J. Vac. Sci. Technol. B **9**, 424 (1991).

[4] K. Sakamoto *et al.*, Surf. Sci. **306**, 93 (1994); **357/358**, 514 (1996).

[5] G. Dujardin, G. Comtet, L. Hellner, T. Hirayama, M. Rose, L. Philippe, and M. J. Besnard-Ramage, Phys. Rev. Lett. **73**, 1727 (1994).

[6] G. Comtet *et al.*, Surf. Sci. **331-333**, 370 (1995); **352-354**, 315 (1996).

[7] U. Höfer, P. Morgen, W. Wurth, and E. Umbach, Phys. Rev. Lett. **55**, 2979 (1985); U. Höfer, P. Morgen, W. Wurth, and E. Umbach, Phys. Rev. B **40**, 1130 (1989).

[8] P. Morgen, U. Höfer, W. Wurth, and E. Umbach, Phys. Rev. B **39**, 3720 (1989).

[9] B. Lamontagne, D. Roy, R. Sporken, and R. Caudano, Prog. Surf. Sci. **50**, 315 (1995).

[10] K. Sakamoto, S. Doi, Y. Ushimi, K. Ohno, H. W. Yeom, T. Ohta, S. Suto, and W. Uchida, Phys. Rev. B **60**, R8465 (1999).

[11] T. Jensen, L.-B. Tække, C. Gundlach, F. K.-Dam, P. Morgen, S. V. Hoffman, Z. Li, and K. Pedersen, Phys. Rev. B **64**, 045304 (2001).

[12] G. Comtet, L. Hellner, G. Dujardin, and K. Bobrov, Phys. Rev. B **65**, 035315 (2002).

[13] F. Matsui, H. W. Yeom, K. Amemiya, K. Tono, and T. Ohta, Phys. Rev. Lett. **85**, 630 (2000).

[14] K.-Y. Kim, T.-H. Shin, S.-J. Han, and H. Kang, Phys. Rev. Lett. **82**, 1329 (1999).

[15] K. Sakamoto, F. Matsui, M. Hirano, H. W. Yeom, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B **65**, 201309(R) (2002).

[16] K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, Phys. Rev. B **68**, 075302 (2003).

[17] G. Dujardin, A. Mayne, G. Comtet, L. Hellner, M. Jamet, E. Le Goff, and P. Millet, Phys. Rev. Lett. **76**, 3782 (1996).

[18] R. Martel, Ph. Avouris, and I.-W. Lyo, Science **272**, 385 (1996).

[19] I.-S. Hwang, R.-L. Lo, and T. T. Tsong, Phys. Rev. Lett. **78**, 4797 (1997); Surf. Sci. **399**, 173 (1998).

[20] K. Sakamoto, S. T. Jemander, G. V. Hansson, and R. I. G. Uhrberg, Phys. Rev. B **65**, 155305 (2002).

[21] B. Schubert, Ph. Avouris, and R. Hoffmann, J. Chem. Phys. **98**, 7593 (1993).

[22] S.-H. Lee and M.-H. Kang, Phys. Rev. Lett. **82**, 968 (1999); S.-H. Lee and M.-H. Kang, Phys. Rev. B **61**, 8250 (2000).

[23] S.-H. Lee and M.-H. Kang, Phys. Rev. Lett. **84**, 1724 (2000).

[24] T. Hoshino and Y. Nishioka, Phys. Rev. B **61**, 4705 (2000).

[25] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, Surf. Sci. **164**, 367 (1985).