PHYSICAL REVIEW B, VOLUME 63, 125324

Resonant photoexcitation of Si(001) measured with two-photon photoemission spectroscopy

Ken-ichi Shudo* and Toshiaki Munakata
The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan

(Received 6 September 2000; published 13 March 2001)

Photoexcitation processes of Si(001) are measured by means of two-photon photoemission (2PPE) spectroscopy. The 2PPE spectra obtained at different photon energies exhibit a sharp peak that is enhanced at 3.95 eV photon energy. The peak width is approximately 0.3 eV and the width of the resonance enhancement is less than 0.35 eV. The photon energy dependence has revealed that the peak arises from an occupied state at 0.46 eV below E_F, and is enhanced at resonance with an unoccupied state at 3.49 eV above E_F. The occupied and unoccupied states are assigned to the bulk bands on the basis of the light polarization dependence.

DOI: 10.1103/PhysRevB.63.125324 PACS number(s): 79.60.−i, 71.20.Mq, 73.20.At

I. INTRODUCTION

The electronic structure of silicon has been extensively investigated[1] for its scientific and practical importance. In particular, information on an excitation process from an occupied valence state to a normally unoccupied state is of great importance, because the excitation of a normally unoccupied state near the Fermi level (E_F) governs various atomic processes such as adsorption/desorption and surface reconstructions.[2,3] The electronic structure is frequently discussed on the basis of ultraviolet photoemission spectroscopy (UPS) for occupied states, and inverse photoemission spectroscopy (IPES) for normally unoccupied states.[4,5] Scanning tunneling spectroscopy is also effective for probing occupied and unoccupied states in the vicinity of E_F.[6,7] A limitation of these conventional methods is that they are not direct probes of the valence excitation process. When we are interested in photon-induced processes with VIS/ultraviolet (UV) photons, we require information on transition probabilities and their resonance widths. Such information is, however, scarce in the literature.

Two-photon photoemission (2PPE) spectroscopy[8–11] is a method for probing surface electronic structures; it can probe both occupied and unoccupied states simultaneously. Information on the resonance widths is also available from the 2PPE photon energy dependence.[8,12] Another advantage of 2PPE spectroscopy is its high time resolution. By utilizing ultrafast lasers, extensive research has been devoted to investigating the hot electron dynamics of semiconductors.[13–19] On the other hand, the capability of 2PPE as a high-resolution spectroscopic method has not been fully applied to semiconductors. The general trend of 2PPE spectrum for semiconductors with UV photons is a smooth curve without clear peaks due to occupied/unoccupied states. This situation is in clear contrast with 2PPE results on metal image states[8,20] and adsorbed molecules,[12,21–23] where sharp peaks are observed in both electron energy distribution curves and in their photon energy dependence.

The purpose of this study is to search for resonant excitation of a silicon surface. By finely tuning the excitation photon energy, we have identified a resonant excitation between bulk bands. This study demonstrates the capability of 2PPE spectroscopy to probe the valence excitations of semiconductors.

2PPE processes measured with different photon energies are briefly summarized.[8] A one-color two-photon absorption from a fixed initial state at E_0 below E_F generates a photoelectron with energy E_K as

$$E_K = 2h\nu - E_0, \tag{1}$$

where $h\nu$ is the photon energy. When a fixed intermediate state at E_1 above E_F is populated by the first photon, the second photon can stimulate photoemission from the intermediate state. The photoelectron energy E_K is then

$$E_K = h\nu - E_1. \tag{2}$$

By plotting E_K against $h\nu$, photoelectrons from process (1) lie on a line with slope two, and those from Eq. (2), on a line with slope one. At the crossing photon energy of the two lines, the intermediate state at E_1 is resonantly excited. The intensity of the photoelectron reaches maximum under the resonant condition. Thus, we can determine E_0, E_1, and the resonance width from the 2PPE spectra measured with different photon energies. This analysis has been successfully applied to two-dimensional systems such as image states and adsorption-induced states, where the electron momentum normal to the surface can be neglected. On the other hand, the analysis is not always accurate for three-dimensional systems, because the momentum of the probed electron is dependent on the photon energy. We will demonstrate the usefulness of the analysis even for a three-dimensional system, silicon.

II. EXPERIMENTAL

The sample was a 4×10 mm^2 strip cut from a commercial wafer of *p*-type Si(001) single crystal (Shinetsu Kagaku CZ-P, 0.625 mm thickness) whose resistivity was 6 Ω cm. It was mounted in a turbopumped UHV chamber of 10^{-8} Pa base pressure. A clean surface was obtained by a standard procedure, i.e., repeated Ar-ion sputtering and annealing cycles. The sample was heated with direct current up to 1420 K. To achieve reproducibility of the step density on the surface, the sample was slowly cooled at the rate of 150°/min in the temperature range between 1220 and 920 K.

The light source consisted of a mode-locked Ti:sapphire laser (Coherent Mira900F), a regenerative amplifier (Coherent RegA9000) operated at a repetition rate of 250 kHz, and an optical parametric amplifier (Coherent OPA9400). The Ti:sapphire laser and the regenerative amplifier were pumped by an Ar-ion laser. Output from the parametric amplifier was frequency doubled into a photon energy range between 3.75 and 4.50 eV. Pulse duration was about 150 fs. The power of the UV light was approximately 10 nJ per pulse. The UV light was focused on the sample surface with a quartz lens of 30 cm focal length. To avoid a thermal effect, the lens was set so that the photoelectron yield was one-third of that under the tightly focused condition. The sample was kept at room temperature during the measurements. Thermal heating of the sample by light irradiation was negligible. The incident light was introduced onto the surface along the (010) direction, at an angle of 45°from the surface normal. During the measurements, the sample was biased by -1.00 V from the chamber ground. Photoelectrons emitted normal to the sample surface were detected with a hemispherical energy analyzer (VG Fisons 100AX) of 50 meV resolution. The count rate was on the order of 10^4 counts/s, which was sufficiently low to avoid the space-charge effect.

III. RESULTS

The 2PPE spectra measured with *p*-polarized light of several photon energies are shown in Fig. 1. The horizontal axis is the final energy (E_K) of photoelectrons with respect to the Fermi level (E_F). E_F is determined from the 2PPE of a molybdenum part of the sample holder. The spectra were obtained with the laser power, that was constant within 10% fluctuation. The spectra exhibit two structures, peak *A* and broad hump *B*, and a scattered electron component near 4.8 eV (the work function cutoff). Peak *A* shifts to higher energy as the photon energy increases. Hump *B* exhibits a similar but weaker tendency. As a visual aid, some traces around hump B are also plotted with a magnification factor of three. The work function of clean Si(001) is determined from the low-energy cutoff to be 4.76 eV, which is in agreement with values reported in the literature.[24]

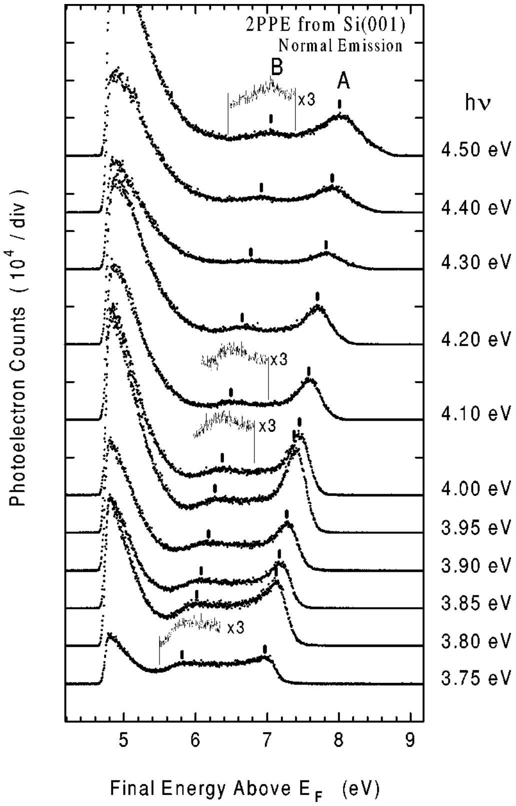

FIG. 1. 2PPE spectra of Si(001) measured with *p*-polarized light in the energy region between 3.75 and 4.50 eV. The photon energies are shown on the right-hand side of the spectra. Two series of structures are denoted as *A* and *B*. Peak *A* is enhanced at 3.95 eV photon energy. Some traces around structure *B* are enlarged by a factor of three.

In order to find out the origin of peak *A* in Fig. 1, the spectra are replotted in Fig. 2 on a scale of the intermediate energy, $E_K - h\nu$. For $h\nu \geqslant 4.30$ eV, magnified curves are also shown. As shown in the bottom spectrum, at 3.75 eV photon energy, peak *A* is weak, superimposed on a stepwise background. It becomes clearer as the photon energy increases. The peak position shifts closer to a vertical line at 3.49 eV. At 3.95 eV photon energy, the intensity of peak *A* reaches maximum. The width of the peak is approximately 0.3 eV. At photon energies higher than 3.95 eV, the peak positions align vertically, indicating the photoemission from a fixed intermediate state at 3.49 eV above E_F. The intensity gradually becomes weak as the photon energy increases up to 4.20 eV. This variation of the intensity is due to the resonant enhancement. At photon energies of 4.10 and 3.85 eV, the peak heights are less than half of the height at 3.95 eV. Thus, the resonance width is estimated to be less than 0.35 eV. At photon energies above 4.30 eV, the high-energy side of peak *A* gains intensity, making its width broader. This broadening is due to the contribution from states other than the fixed intermediate state causing peak *A*.

The final energy of peak *A* is plotted against the photon energy in Fig. 3. Two lines with slopes of one and two fit the experimental points very well. The line of slope two indicates that the photoelectrons originate from the two-photon absorption from an occupied state at 0.46 eV below E_F. The other line with slope one indicates the one-photon absorption from the intermediate state at 3.49 eV above E_F. At the cross point of the fitted lines, the photon is resonant with the transition from the occupied initial state to the intermediate state. This is consistent with the observed enhancement of the intensity at $h\nu = 3.95$ eV (Fig. 2).

The polarization dependence of the 2PPE spectra is shown in Fig. 4. Photon energies are chosen as (a) 3.95 eV, at the resonance, and (b) 4.50 eV, above the resonance. The spectra with *p* and *s* polarizations are denoted as Y_p and Y_s, respectively. The dotted points represent the intensity ratio, Y_s/Y_p. The ratio forms a clear peak at the 2PPE peak *A* for the resonance condition (a). The enhanced ratio indicates that the transition is enhanced with *s*-polarized light. For the above resonance condition (b), the ratio forms a broad structure around peak *A*. The enhancement of the ratio at the high-energy side of peak *A* also suggests the additional contribution of the intermediate state higher than 3.49 eV.

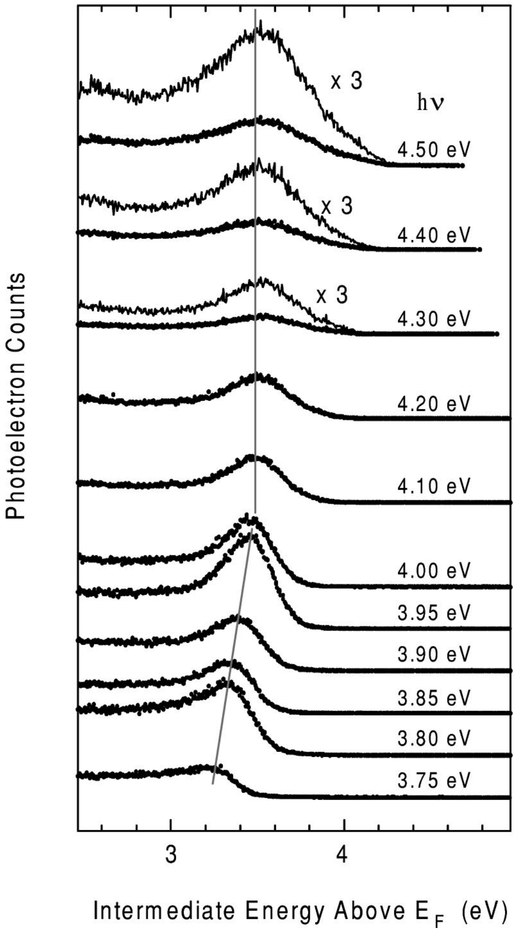

FIG. 2. 2PPE spectra in Fig. 1 are rearranged on the intermediate energy, $E_K - h\nu$. Spectra enlarged by a factor of three are also shown. For photon energies higher than 3.95 eV, peak *A* aligns vertically, indicating the photoemission from a fixed intermediate state at 3.49 eV.

IV. DISCUSSION

The 2PPE results reveal that the occupied state is at 0.46 eV below E_F and that the normally unoccupied one is at 3.49 eV above E_F. When the photon energy is 3.95 eV, the transition from the occupied state is resonant with the unoccupied state. These energy levels should be compared with UPS (Refs. 25,24) and IPES (Refs. 5,26) results. In Fig. 5, UPS and IPES results are represented by open and closed circles, respectively, together with the calculated dispersion curves of the bulk bands.[27] Also shown in Fig. 5 is the dispersion curve of a free electron taken from IPES analysis.[28] In the IPES process, an electron coming from the vacuum feels the inner potential (U_0) of the crystal before the IPES process occurs. The value of the inner potential is chosen[26] to be -9.0 eV from the valence band maximum (E_{VBM}), which is reported[29] to be 0.35 eV below E_F. Assuming that the final state of the 2PPE process is the same as the free electron curve of IPES, the momenta of the photoelectrons in the present experiment fall in the shaded region of Fig. 5. Solid bars marked by ‘‘init’’ and ‘‘int’m,’’ respectively, represent the occupied and unoccupied states of the 2PPE results. The transitions are indicated by arrows (1) to (3) corresponding to the increase in the photon energy.

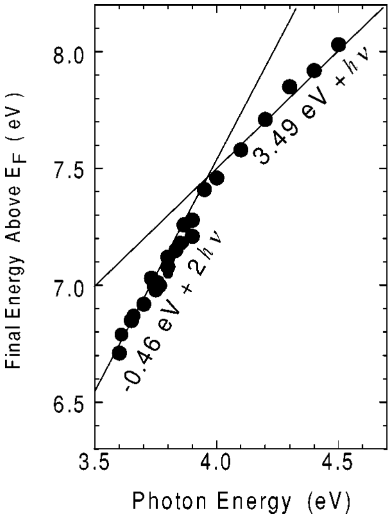

FIG. 3. The final energies of peak *A* are plotted against the photon energy. The experimental points represented by filled circles fit on a line of slope one for $h\nu \geqslant 3.95$ eV, and on a line of slope two, for lower photon energies. The line fits indicate that the initial occupied state is 0.46 eV below E_F, and the intermediate state is 3.49 eV above E_F.

As shown in Fig. 5, the observed occupied state is close to the branches from the $\Gamma_{25'}$ point and the S_1 surface state.[1,30] The polarization dependence indicates that the S_1 state is not related to the occupied state, as discussed later. The unoccupied state is between the two subbranches from the Γ_{15} point. It is noted that Fig. 5 shows only one-third of the first Brillouin zone (bottom scale). Small differences between the presently observed energy levels and the other ones may be due to the exaggerated horizontal axis. Thus, the occupied and unoccupied states observed in 2PPE can be assigned to bulk bands. One of the advantages of 2PPE spectroscopy is its sharp spectral structures as narrow as 0.3 eV. This allows a more detailed comparison of small differences in energy levels.

The unoccupied state in 2PPE is electrically neutral, while that measured by IPES is negatively charged. Thus, the binding energies of the states can be slightly different. Such a charge effect, however, may not be very significant for bulk bands. The small differences among the energy levels shown in Fig. 5 may be caused by the inaccuracy of the U_0 or E_{VBM}. A slight decrease of U_0 results in a decrease in the photoelectron momentum of the present experiment. For example, U_0 was also reported to be -10.8 eV from a UPS experiment.[24] Taking this U_0 value, the observed occupied state comes close to the upper subbranch connecting the $\Gamma_{25'}$ and X_4 points, and the unoccupied state, to the lower subbranch connecting the Γ_{15} and X_1 points, respectively. An increase in E_{VBM} causes similar shifts. We believe that the present results are in agreement with the bulk band structures except for a slight change of U_0 and/or E_{VBM}.

At photon energies higher than 4.20 eV, the high-energy side of peak *A* gains intensity (Fig. 2). This is a contribution

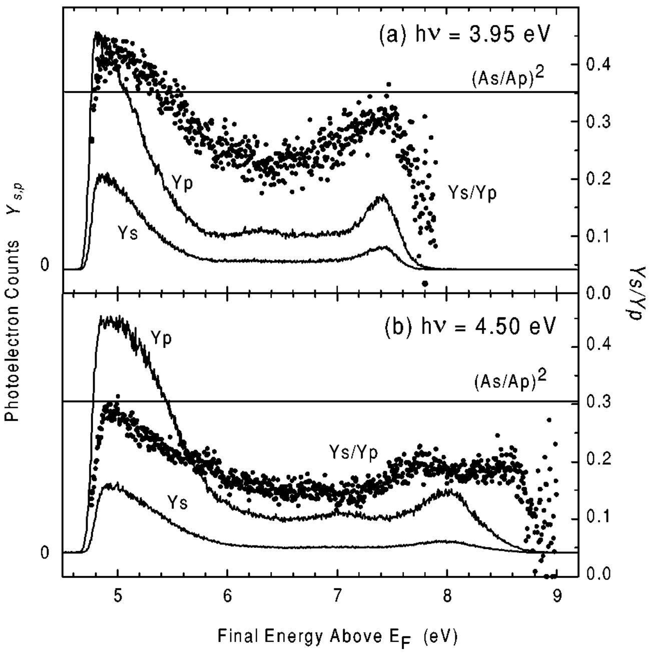

FIG. 4. Polarization dependence of the spectrum measured (a) with the resonant photon energy, 3.95 eV, and (b) with the above-resonant photon energy, 4.50 eV. The dots (Y_s/Y_p) are the ratio of 2PPE spectra measured with *s*- (Y_s) and *p*-polarized (Y_p) light. The horizontal lines represent the Y_s/Y_p ratios estimated for bulk two-photon transitions. The ratio in (a) at peak *A* is close to the estimated value, indicating that peak *A* arises from bulk bands. The ratio in (b) forms a broad feature around peak *A*, suggesting a contribution from a high-lying intermediate state in the bulk.

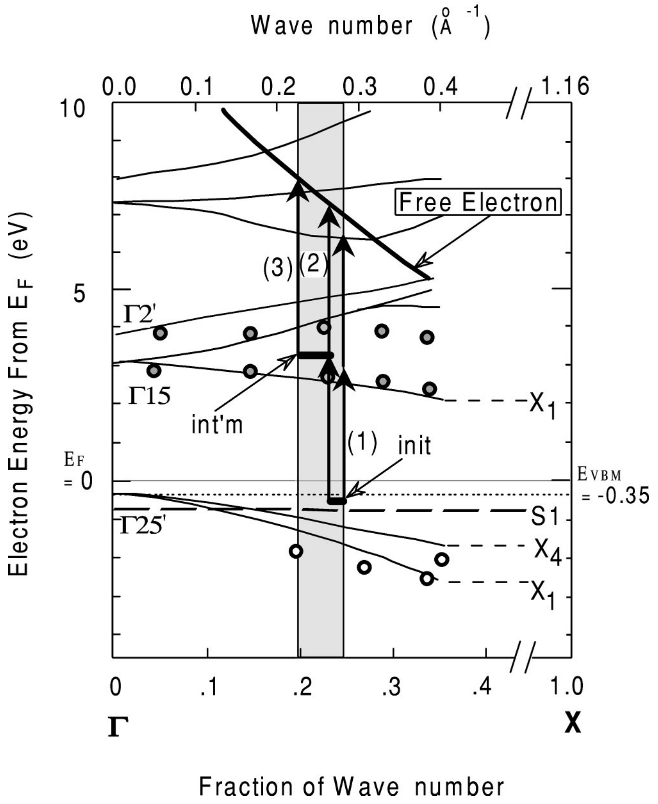

FIG. 5. 2PPE results (solid bars marked by ''init'' and ''int'm'' for the occupied and unoccupied states, respectively), compared with the band-structure calculation (thin curves) (Ref. 27), UPS (open circles) (Ref. 25), and IPES (filled circles) (Ref. 26). The horizontal axis is a fraction of the wave number with respect to the *X* point. The wave number of the present experiment falls in the shaded region. The arrows (1) to (3) schematically show the transition. The curve labeled ''Free Electron'' is the IPES initial state (Ref. 28), and the horizontal dashed line is an occupied surface state (Ref. 30), *S*1.

from a high-lying unoccupied state, which acts as an intermediate state in this photon energy region. The high-lying intermediate state is assigned to the upper subbranch from the Γ_{15} or $\Gamma_{2'}$ points. On the basis of the dispersion diagram in Fig. 5, it is expected that the resonance with the state will occur at the photon energy of approximately 4.9 eV.

As noted in the Introduction, the momentum of the probed electron is dependent on the photon energy in the three-dimensional system. Thus, the analysis in Fig. 3 is appropriate only when the dispersions of the initial and intermediate states are negligible. In reality, the energy shifts of relevant branches in the observed momentum region (shaded area in Fig. 5) are smaller than 0.1 eV. This makes the analysis useful.

As shown in Fig. 4, the polarization-dependent intensity ratio (Y_s/Y_p) is $\sim$0.3 at peak *A* under the resonant condition. This ratio is to be compared with the strength of the electric fields in the bulk or on the surface. The electric field at the surface is estimated from Fresnel's equations[3] and the optical constants of silicon.[31] With *p*-polarized light, the field normal to the surface is enhanced at the surface. By taking the 2PPE intensity to be proportional to the fourth power of the electric field, the Y_s/Y_p ratio estimated for a transition at the surface is much smaller than 0.3. The maximum value of 0.3 occurs only when the optical transition moments are parallel to the surface. Such an extreme condition is difficult to explain. The absorption coefficients for the resonant photon energy can similarly be estimated to be $A_s=0.32$ and $A_p=0.53$ for *s* and *p* polarizations, respectively. When optical transitions occur in the bulk, the intensity ratio Y_s/Y_p is estimated from $(A_s/A_p)^2$ to be 0.35. Because the observed Y_s/Y_p ratio of 0.3 at peak *A* is very close to the estimated value, we attribute peak *A* to originate from the two-photon absorption in the bulk. This is consistent with the above assignment of the occupied and unoccupied states. For the condition above resonance (b), the Y_s/Y_p ratio is enhanced at the high-energy side of peak *A*. This supports the assignment of the high-lying intermediate state to the upper subbranch from the Γ_{15} or $\Gamma_{2'}$ points.

As shown in Fig. 5, the initial occupied state is close to the occupied surface state, S_1. We cannot, however, assign the initial state to S_1, because photoemission from the surface state should be enhanced under *p* polarization, in contrast to Fig. 4. We speculate that 2PPE from the surface state cannot be enhanced by resonance with bulk unoccupied states whose wave functions are spatially separated from that of S_1.

Finally, we note the width of the 2PPE features. The line width of peak A is $\sim$0.3 eV at the resonant photon energy, 3.95 eV. The photon energy dependence in Fig. 2 indicates that the resonance width is $\sim$0.3 eV. These widths are in clear contrast with the UPS and IPES results. The linewidth of the UPS feature[25] is $\sim$0.8 eV for the state corresponding to the 2PPE initial state, and that of IPES (Ref. 26) is $\sim$0.9 eV for the state corresponding to the intermediate state. The sharp width of the 2PPE features suggests that the UPS and IPES features do not exhibit the natural bandwidths. Similar sharp features have been discussed for the 2PPE of molecular adsorbates on a metal surface,[12,21] though the details remain uncertain. Nevertheless, the sharp 2PPE feature is helpful in refining the energy levels.

In summary, 2PPE spectroscopy of Si(001) has revealed resonant excitation of the excited (normally unoccupied) state at 3.49 eV above E_F. The resonance width is less than 0.35 eV. Because of the narrow resonance width, sharp 2PPE features appear only when the wavelength and the polarization are appropriately selected. In contrary to peak A, hump B exhibits only weak photon energy dependence. The presently used wavelength may be far from the resonance between the states relevant to structure B. Under far-resonant conditions, determination of energy levels is difficult. The difference between A and B features is a general characteristic of 2PPE process. 2PPE spectroscopy is very effective in determining pairs of occupied and unoccupied states when pump/probe wavelengths, polarization, and emission angle are properly selected. Fine wavelength tuning is essentially important to find out a resonant photoexcitation. The narrow resonance width also suggests the importance of wavelength tuning in the photochemical process.[32] Effective excitation under the resonance condition will promote the efficiency and selectivity of surface reactions.

ACKNOWLEDGMENT

This study was partially supported by the Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

---

*Corresponding author's present address: Faculty of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501 Japan. Phone: +81 45 339-4202 (automatic switchover to fax). Email address: ken1@ynu.ac.jp

[1] G. V. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988); Crit. Rev. Solid State Mater. Sci. **17**, 133 (1991).

[2] X.-L. Zhou, X.-Y. Zhu, and J. M. White, Surf. Sci. Rep. **13**, 73 (1991).

[3] *Laser Spectroscopy and Photochemistry on Metal Surfaces*, edited by H.-L. Dai and W. Ho (World Scientific, Singapore, 1995).

[4] F. J. Himpsel and Th. Fauster, J. Vac. Sci. Technol. A **2**, 815 (1984); F. J. Himpsel, Phys. Scr., T **31**, 171 (1990).

[5] F. J. Himpsel, Surf. Sci. Rep. **12**, 1 (1990).

[6] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).

[7] Ph. Avouris, J. Phys. Chem. **94**, 2246 (1990).

[8] W. Steinmann, Appl. Phys. A: Solids Surf. **49**, 365 (1989); Phys. Status Solidi B **192**, 339 (1995).

[9] R. Haight, Surf. Sci. Rep. **21**, 275 (1995).

[10] H. Petek and S. Ogawa, Prog. Surf. Sci. **56**, 239 (1997).

[11] M. Wolf, Surf. Sci. **377-379**, 343 (1997).

[12] T. Munakata, Surf. Sci. **454-456**, 118 (2000); I. Kinoshita, A. Misu, and T. Munakata, J. Chem. Phys. **102**, 2970 (1995).

[13] J. Bokor, R. Haight, R. H. Storz, J. Stark, R. R. Freeman, and P. H. Bucksbaum, Phys. Rev. B **32**, 3669 (1985); R. Haight, J. Bokor, J. Stark, R. H. Storz, R. R. Freeman, and P. H. Backsbaum, Phys. Rev. Lett. **54**, 1302 (1985).

[14] M. W. Rowe, H. Liu, G. P. Williams, Jr., and R. T. Williams, Phys. Rev. B **47**, 2048 (1993).

[15] S. Jeong and J. Bokor, Phys. Rev. B **59**, 4943 (1999).

[16] U. Höfer, Appl. Phys. B: Lasers Opt. **68**, 383 (1999).

[17] J. R. Goldman and J. A. Prybyla, Phys. Rev. Lett. **72**, 1364 (1994); Semicond. Sci. Technol. **9**, 694 (1994).

[18] M. Baeumler and R. Haight, Phys. Rev. Lett. **67**, 1153 (1991).

[19] S. J. Diol, C. C. Miller, C. A. Schmuttenmaer, J. Cao, Y. Gao, D. A. Mantell, and R. J. D. Miller, J. Phys. D **30**, 1427 (1997); S. Xu, C. C. Miller, J. Cao, D. A. Mantell, M. G. Mason, A. A. Muenter, B. A. Parkinson, R. J. D. Miller, and Y. Gao, J. Vac. Sci. Technol. A **15**, 1510 (1997).

[20] U. Höfer, I. L. Shumay, C. Reuss, U. Thomann, W. Wallauer, and T. Fauster, Science **277**, 1480 (1997).

[21] T. Munakata and K. Shudo, Surf. Sci. **433-435**, 184 (1999); T. Munakata, T. Sakashita, M. Tsukakoshi, and J. Nakamura, Chem. Phys. Lett. **271**, 377 (1997).

[22] D. Velic, A. Hotzel, M. Wolf, and G. Ertl, J. Chem. Phys. **109**, 9155 (1998); K. Ishioka, C. Gahl, and M. Wolf, Surf. Sci. **454-456**, 73 (2000).

[23] K. J. Gaffney, C. M. Wong, S. H. Liu, A. D. Miller, J. D. McNeill, and C. B. Harris, Chem. Phys. **251**, 99 (2000).

[24] A. Goldmann, P. Koke, W. Monch, G. Wolfgarten, and J. Pollmann, Surf. Sci. **169**, 438 (1986).

[25] A. L. Wachs, T. Miller, T. C. Hsieh, A. P. Shapiro, and T. -C. Chiang, Phys. Rev. B **32**, 2326 (1985).

[26] J. E. Ortega and F. J. Himpsel, Phys. Rev. B **47**, 2130 (1993).

[27] J. R. Chelikowsky, T. J. Wagener, J. H. Weaver, and A. Jin, Phys. Rev. B **40**, 9644 (1989); J. R. Chelikowsky and M. L. Cohen, *ibid.* **10**, 5095 (1974).

[28] D. Straub, L. Ley, and F. J. Himpsel, Phys. Rev. B **33**, 2607 (1986).

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

[30] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, Phys. Rev. B **24**, 4684 (1981).

[31] D. F. Edwards, *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic Press Inc., London, 1985).

[32] J. Kanasaki, T. Ishida, K. Ishikawa, and K. Tanimura, Phys. Rev. Lett. **80**, 4080 (1998).