Site Specific and State Selective Photofragmentation of Molecular Oxygen on Si(111)-(7 × 7)

G. Dujardin,[1,2] G. Comtet,[1] L. Hellner,[1,2] T. Hirayama,[2,*] M. Rose,[2] L. Philippe,[1,2] and M. J. Besnard-Ramage[1,2]
[1]*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), Bâtiment 209 D,*
Université Paris-Sud, 91405 Orsay Cedex, France
[2]*Laboratoire de Photophysique Moléculaire, Centre National de la Recherche Scientifique, Bâtiment 213,*
Université Paris-Sud, 91405 Orsay Cedex, France
(Received 18 April 1994)

Molecular oxygen chemisorbed at room temperature on Si(111)-(7 × 7) exhibits a molecular adsorption site which is unexpectedly long lived. Photofragmentation from this specific O_2 adsorption site is studied by correlating the time decay of the corresponding molecular surface state observed in photoemission with the time decay of O^+ desorbed photofragments. Photofragmentation occurs via direct nonresonant O_2/Si ($2\sigma_g^{-1}$) and resonant O_2/Si ($2p \rightarrow 3\sigma_u$) electronic transitions. State selectivity of the photofragmentation is demonstrated by translational energy measurements of the O^+ desorbed fragments.

PACS numbers: 82.65.−i, 68.45.Kg

Controlled fragmentation of adsorbed molecules is a main issue of chemical reaction studies at solid surfaces [1]. In the gas phase, fragmentation of a small molecule can be selectively initiated via absorption of monochromatic UV or VUV light which makes a transition to an excited electronic state. Such state selective fragmentations are likely to be strongly modified in adsorbed molecules on solid surfaces due to efficient nonradiative couplings with the substrate [1]. In addition, indirect photoinduced processes including heating of the substrate or secondary electron effects can also produce fragmentation of adsorbed molecules and then overcome direct state selective photofragmentation [1]. Further complications arise on silicon surfaces at room temperature which tend to spontaneously dissociate chemisorbed molecules [2–6] and often show many distinct adsorption sites. In this paper we report results on photofragmentation of molecular oxygen chemisorbed on Si(111)-(7 × 7). This is the first demonstration of site specific and state selective photofragmentation of molecules adsorbed on silicon surfaces.

Because of its well understood structure, O_2 on Si(111)-(7 × 7) is a model system for molecular photofragmentation studies on silicon surfaces. Oxidation of silicon surfaces has been the subject of extensive work over the past 20 years [7–9]. Recently the initial stages of the oxidation of Si(111)-(7 × 7) surfaces have been studied in detail both experimentally [10–14] and theoretically [15]. It was concluded that the adsorption of O_2 on a reconstructed Si(111)-(7 × 7) surface is dissociative and is preceded by a metastable precursor. This precursor was found to be molecular with an O-O axis essentially parallel to the surface and to have a lifetime estimated at about 10 min at room temperature [12]. In the present study we find that the O_2 molecular precursor is much more stable than expected. Its lifetime at room temperature extends up to 1500 min, i.e., more than 2 orders of magnitude larger than previously measured. Taking advantage of this long lifetime we perform time dependent photoemission and photoinduced fragmentation studies of O_2 on Si(111)-(7 × 7). The time correlation between the molecular surface state observed in photoemission and the fragmentation products observed by ion photodesorption enables us to specify the initial adsorption site of the fragmented O_2 molecules. Photofragmentation, as monitored by O^+ desorbed fragment detection, is shown to occur by direct nonresonant O_2/Si ($2\sigma_g^{-1}$) and resonant O_2/Si ($2p \rightarrow 3\sigma_u$) electronic transitions. In addition, translational energies of the desorbed ionic fragments exhibit a strong dependence on the electronic excitation, indicating that the fragmentation of O_2/Si is state selective.

Synchrotron radiation from Super-Aco in Orsay, dispersed by a 9 m plane grating monochromator, is used as a linearly polarized photon source of variable energy in the 10–150 eV range. Experiments are performed in an ultrahigh vacuum chamber with a base pressure of 7×10^{-11} mbar. The chamber is equipped with a total electron yield detector for photoabsorption measurements, a hemispherical electrostatic analyzer for photoemission and Auger spectroscopy, a high sensitivity quadrupole mass spectrometer for mass selected desorbed ion detection, and a spectrometer including a cylindrical mirror analyzer (CMA) followed by a mass quadrupole for simultaneous mass and kinetic energy analysis of desorbed ionic species. The Si(111) crystal is of *n* type, phosphorous doped with 1 Ω cm resistivity. The clean reconstructed Si(111)-(7 × 7) surface is prepared by 12 h direct resistive heating at 700 °C followed by a 30 s flash at 1100 °C. All the reported experiments are performed at room temperature. Oxygen exposures are given in langmuir (L) (1 L = 10^{-6} Torr s).

The photoemission spectrum of the clean Si(111)-(7 × 7) surface [Fig. 1(a)] shows the characteristic intense and well resolved S_1 and S_2 surface states 0.2 and 0.8 eV below the Fermi level corresponding to silicon

0031-9007/94/73(12)/1727(4)$06.00

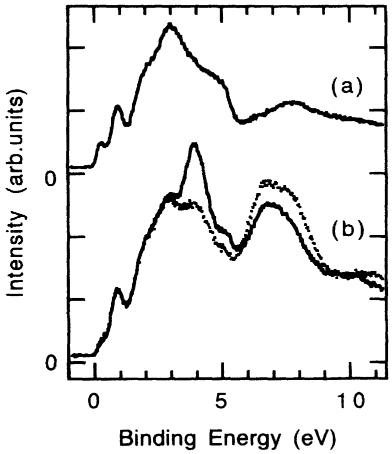

FIG. 1. Photoemission spectra recorded at $h\nu = 40.8$ eV with a p polarization for (a) a clean Si(111)-(7 × 7) surface, (b) a 0.1 L oxygen covered Si(111)-(7 × 7) surface. The full line curve is recorded immediately after exposure, the dotted line curve several hours later.

adatoms and restatoms, respectively [16]. As previously observed [9–14], after 0.1 L oxygen exposure [Fig. 1(b)] the S_1 state is quenched and two broad peaks centered at 3.8 and 7 eV build up. Higher oxygen exposures lead to the quenching of the S_2 state as well. The photoemission spectra are recorded with p polarization at $h\nu = 40.8$ eV. From comparison with density of state (DOS) calculations, the 3.8 eV peak of the photoemission spectrum has been assigned to molecular oxygen bound to a Si adatom in the paul, para, or grif geometry [15]. In these geometries, the O_2 molecule is parallel (para and grif) to the surface or slightly inclined (paul) and is singly (paul and para) or doubly (grif) bonded to a single silicon adatom. The 7 eV peak is assigned to the dissociated oxygen molecule in the ins-rest geometry (plus the π component of the preceding molecular configuration) [15]. Here the most surprising result is that the lifetime of the molecular precursor, as measured from the time decay of the 3.8 eV peak intensity, is much longer than previously reported [12]. We find that the lifetime varies from sample to sample, with a most probable value around 400 min. Lifetimes as long as 1500 min are observed. Oxygen exposure is varied from 0.05 to 10 L without any noticeable change in the lifetime. The discrepancy with previously measured lifetimes of about 10 min [12] may have several reasons. First, the molecular precursor lifetime was found to be markedly reduced by x-ray irradiation [12]. In our case the dose of irradiation is much reduced and is found to be of no influence on the lifetime. Second, the measured lifetime is not the intrinsic lifetime since it varies from sample to sample. This may reflect the influence of defects and impurities of the Si(111)-(7 × 7) surface which are believed to shorten the molecular lifetime [12]. Third, we think that molecular lifetime measured from the time decay of the well resolved 3.8 eV ultraviolet photoemission spectroscopy peak is more reliable than from the deconvolution of the O 1s x-ray photoemission spectroscopy peak [12]. It follows that the intrinsic lifetime of the O_2 molecular precursor is most probably very long (>1500 min) and perhaps infinite for ideal Si(111)-(7 × 7) surfaces.

Photofragmentation of molecular oxygen on Si(111)-(7 × 7) is studied by recording the intensity of desorbed O^+ ions as a function of the photon energy. O^+ ion desorption is not *a priori* an unambiguous probe of O_2 fragmentation since it could also be produced from adsorbed atomic oxygen in the ins-rest geometry. However, by monitoring the time decay of the O^+ ion intensity, we find exactly the same lifetime as that of the molecular peak at 3.8 eV in the photoemission spectrum (PES) whereas the PES atomic peak at 7 eV increases with time (Fig. 2). Furthermore the O^+ intensity variation with the O_2 exposure follows exactly that of the PES molecular peak. They both reach a saturation at about 0.2 L, whereas the atomic peak in the PES goes on increasing at higher coverages (Fig. 3). Similar results are obtained at any photon energy producing O^+ ion desorption. We conclude that the observed O^+ ions are specifically issued from the photofragmentation of molecular O_2 on Si(111)-(7 × 7) in the paul, para, or grif geometry [15].

The photofragmentation intensity recorded as a function of the photon energy is shown in Fig. 4. In the valence region, the threshold energy for O^+ ion formation is

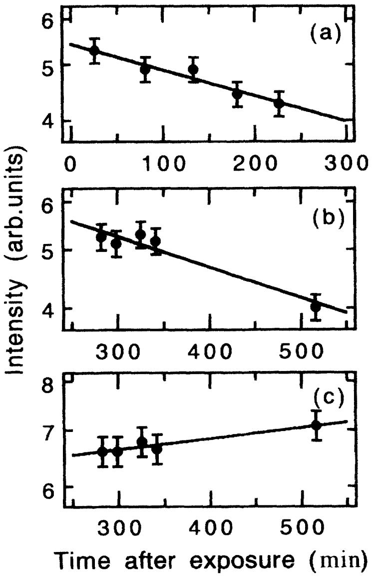

FIG. 2. 1 L oxygen covered Si(111)-(7 × 7) surface. Semilogarithmic plots versus time of the intensities of (a) the O^+ photofragment at $h\nu = 108$ eV (the O^+ signal decays with a lifetime of ≈970 min, (b) the "molecular" peak at 3.8 eV in the PES (the signal decays with a lifetime of ≈860 min), (c) the "atomic" peak at 7 eV in the PES (the signal increases with time).

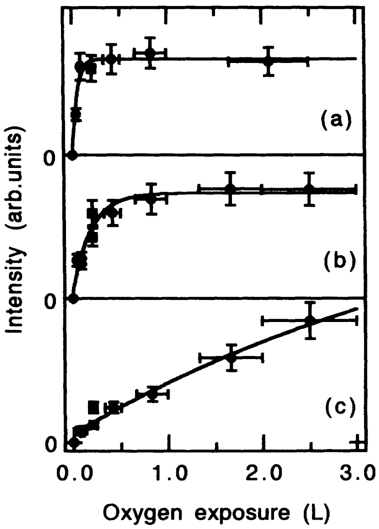

FIG. 3. Oxygen exposure dependence of the intensities of (a) the O^+ photofragment signal at $h\nu = 108$ eV, (b) the "molecular" peak at 3.8 eV in the PES, (c) the "atomic" peak at 7 eV in the PES.

found at 33 eV. This most probably corresponds to the excitation of a $2\sigma_g$ electron of O_2 on Si(111)-(7 × 7) whose binding energy relative to the Fermi level was calculated at about 31 eV [7]. Excitation energies of other O_2 electronic bands such as shake-up and shake-off bands, known in the gas phase [17] to be 7 and 4 eV less bound than the $2\sigma_g$ level, are expected to be much lower than 33 eV. We note that electronic excitation of O_2/Si Si(111)-(7 × 7) from its $2\sigma_u$ band located about 19 eV below the Fermi level [7] does not produce any noticeable fragmentation in the present experiment. This is likely due to insufficient energy for producing O^+ fragment ions since breaking the O-O bond (5.2 eV), ionizing the O atom (13.6 eV) and imparting the observed 2 eV kinetic energy to the ion require photons of at least 21 eV.

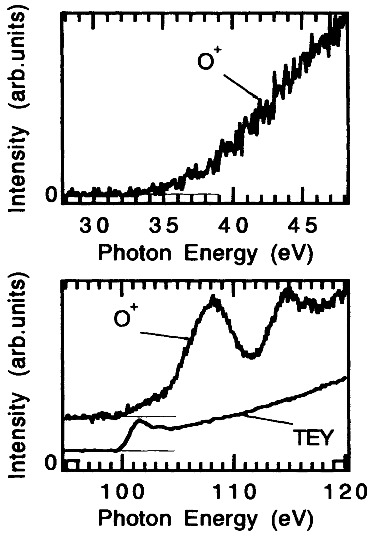

FIG. 4. O^+ yield and total electron yield (TEY) recorded as a function of the photon energy for a 0.4 L O_2 exposed Si(111)-(7 × 7) surface.

Photofragmentation of molecular oxygen on Si(111)-(7 × 7) is also produced in the Si(2p) excitation region. A threshold energy at 100 eV and two broad resonances centered at 108 and 115 eV appear in the O^+ ion yield curve (Fig. 4). These two resonances are not observed in the total electron yield (photoabsorption) spectrum (Fig. 4) nor in the partial Auger electron yields (not shown here). It follows that they can be ascribed to direct photofragmentation of chemisorbed O_2 molecules rather than to indirect processes initiated by secondary electrons. The resonance at 108 eV is assigned to absorption of a photon from the Si(2p) level approximately 100 eV below the Fermi level [11,18] to the $3\sigma_u$ unoccupied level of molecular oxygen calculated at 8 eV above the Fermi level for O_2 chemisorbed on Si(111)-(7 × 7) in the paul, para, or grif geometry with an internuclear O-O distance of 1.28 Å [15]. This assignment is in good agreement with that derived from the oxygen K edge near edge x-ray absorption fine structure spectrum [10]. The second resonance at 115 eV is more difficult to identify. It may be a satellite of the previous resonance associated with a multiple electronic excitation. Alternative explanations would be to consider electronic transitions from the Si(2p) level to higher lying unoccupied O_2 levels or to the $3\sigma_u$ level of O_2 in the trival geometry. Further calculations are necessary to clarify this assignment.

In order to get a more detailed insight into the photofragmentation of O_2 chemisorbed on Si(111)-(7 × 7) we perform translational energy analysis of photodesorbed O^+ fragment ions. In addition to O^+ ions, fluorine F^+ ions are photodesorbed. No F^+ ion desorption signal is observed immediately after flashing and exposing the silicon sample to oxygen but it increases slowly with time after oxygen exposure. It is considered to result from fluorine impurities trapped into the bulk silicon wafer during its fabrication which migrate to the surface during the UHV experiment. However, we cannot completely exclude that the F^+ signal results from a very small amount of adsorbed fluorine issued from the UHV chamber. F^+ desorption is expected indeed to have orders of magnitude larger cross section than O^+ desorption, due to the large ionicity of any bonds to F and because they are all localized single bonds. No O_2^+ ion desorption is observed. But because of the F^+ desorbed impurities, it is essential to measure simultaneously mass and kinetic energy of the desorbed species. We note that this is the first experiment where mass and kinetic energies of photodesorbed ions can be simultaneously analyzed. Measured kinetic energy distribution (KED) of mass selected O^+ fragment ions is shown in Fig. 5

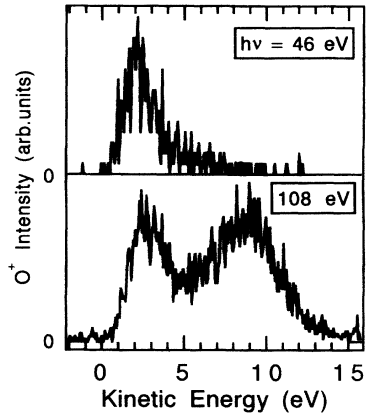

FIG. 5. Kinetic energy distributions of O^+ photofragments at $h\nu = 46$ eV and $h\nu = 108$ eV for a 1 L O_2 exposed Si(111)-(7 × 7) surface.

for two photon energies of 46 and 108 eV corresponding to O_2/Si ($2\sigma_g^{-1}$) and O_2/Si ($2p \rightarrow 3\sigma_u$) electronic excitations, respectively. Kinetic energies are relative to the vacuum level of the sample and are calibrated as described in Ref. [19]. Results in Fig. 5 indicate that the kinetic energy distribution (KED) of photofragments markedly depends on the electronic excitation. After 46 eV photon absorption and subsequent formation of one electron hole in the Si-O_2 ($2\sigma_g$) inner valence orbital, the KED consists in a peak centered around 2.5 eV. The $2\sigma_g$ inner valence hole is expected to relax by rapid Auger processes into two valence hole states before any fragmentation can occur. The 2.5 eV peak of the KED is then believed to result from the removing of two valence electrons from the π and 3σ orbitals of O_2 chemisorbed on Si(111)-(7 × 7), the π orbitals having a Si-O bonding character [15]. After O_2/Si ($2p \rightarrow 3\sigma_u$) core excitation at 108 eV the KED is dominated by a high kinetic energy distribution (HKED) which has a maximum around 9 eV and extends up to around 13 eV. Such very high kinetic energies are usually observed in the fragmentation of highly ionized molecular species. This indicates that the HKED fragmentation process most probably results from the removing of more than two valence electrons from the π and 3σ orbitals as produced by Auger relaxation following the O_2/Si ($2p \rightarrow 3\sigma_u$) core excitation. The strong dependence of the KED of O^+ photofragments on the electronic excitation demonstrates the state selectivity of the photofragmentation. It suggests that the fragmentation processes are direct and do not involve significant radiative or nonradiative relaxation processes.

In conclusion, we have shown that molecular O_2 chemisorbed at room temperature on Si(111)-(7 × 7) in the paul, para, or grif geometry has a very long lifetime (>1500 min). Photofragmentation from this specific adsorption site has been demonstrated to occur via nonresonant O_2/Si ($2\sigma_g^{-1}$) and resonant O_2/Si ($2p \rightarrow 3\sigma_u$) electronic excitations. Each of these electronic excitations gives rose to a particular fragmentation process as shown by the kinetic energy distributions of the O^+ desorbed fragments. These results demonstrate that site specific and state selective photofragmentation of chemisorbed molecules can be achieved on silicon surfaces.

---

*Permanent address: Department of Physics, Gakushuin University, 1-5-1 Mejiro, Toshimaku, Tokyo 171, Japan.

[1] Ph. Avouris and R.E. Walkup, Annu. Rev. Phys. Chem. **40**, 173 (1989).
[2] R.A. Rosenberg, P.J. Love, V. Rehn, I. Owen, and G. Thornton, J. Vac. Sci. Technol. A **4**, 1451 (1986).
[3] C.U.S. Larsson, A.S. Flodström, R. Nyholm, L. Incoccia, and F. Senf, J. Vac. Sci. Technol. A **5**, 3321 (1987).
[4] J.A. Yarmoff, A. Taleb-Ibrahimi, F.R. McFeely, and Ph. Avouris, Phys. Rev. Lett. **60**, 960 (1988).
[5] J.A. Yarmoff and S.A. Joyce, Phys. Rev. B **40**, 3143 (1989).
[6] R. McGrath, I.T. McGovern, D.R. Warburton, D. Purdie, C.A. Muryn, N.S. Prakash, P.L. Wincott, G. Thornton, D.S-L. Law, and D. Norman, Phys. Rev. B **45**, 9327 (1992).
[7] M. Chen, I.P. Batra, and C.R. Brundle, J. Vac. Sci. Technol. **16**, 1216 (1979).
[8] H. Ibach, H.D. Bruchmann, and H. Wagner, Appl. Phys. A **29**, 113 (1982).
[9] U. Höfer, P. Morgen, W. Wurth, and E. Umbach, Phys. Rev. Lett. **55**, 2979 (1985).
[10] U. Höfer, A. Puschmann, D. Coulman, and E. Umbach, Surf. Sci. **211**, 948 (1989).
[11] P. Morgen, U. Höfer, W. Wurth, and E. Umbach, Phys. Rev. B **39**, 3720 (1989).
[12] U. Höfer, P. Morgen, and W. Wurth, Phys. Rev. B **40**, 1130 (1989).
[13] Ph. Avouris, In-Whan Lyo, and F. Boszo, J. Vac. Sci. Technol. B **9**, 424 (1991).
[14] F. Boszo and Ph. Avouris, Phys. Rev. B **44**, 9129 (1991).
[15] B. Schubert, Ph. Avouris, and R. Hoffmann, J. Chem. Phys. **98**, 7593 (1993); **98**, 7606 (1993).
[16] R.J. Hamers, R.M. Tromp, and J.E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986); J.E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).
[17] S.D. Price and J.H.D. Eland, J. Phys. B **24**, 4379 (1991).
[18] G. Hollinger and F.J. Himpsel, Phys. Rev. B **28**, 3651 (1983).
[19] G. Dujardin, L. Hellner, L. Philippe, M.J. Besnard-Ramage, and P. Cirkel, Phys. Rev. B **48**, 14529 (1993).