RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 19 15 MAY 1994-I

Kinetics of oxygen dissociation on Si(111)7 × 7 investigated with optical second-harmonic generation

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(Received 25 February 1994)

Optical second-harmonic generation is used as a sensitive, nondestructive probe for the thermally activated dissociation of molecular oxygen on Si(111)7 × 7. Isothermal measurements show that the dissociation kinetics strongly depend on the total oxygen coverage. At room temperature the $1/e$ lifetime of chemisorbed O_2 is $\sim$ 15 min for saturation coverage but $\sim$ 50 min for low oxygen coverage. The temperature dependence of the dissociation rates between 80 and 500 K indicates that more than one dissociation channel and/or molecular oxygen species exist on the surface.

The interaction of oxygen with silicon surfaces has been investigated intensively in order to reveal the oxidation mechanisms of silicon and the formation of Si/SiO_2 interfaces on a microscopic level.[1] Several years ago, a metastable precursor was observed in the dissociative adsorption of O_2 on Si(111)7 × 7.[2] Based on the combined results of several high-resolution electron spectroscopies[2–4] it was suggested that in the initial stage of oxygen interaction with silicon surfaces a chemisorbed $O_2{}^-$-like species is formed via charge transfer from Si dangling bonds to the oxygen $2\pi^*$ level.[4] The subsequent dissociation of this intermediate state leads to the formation of Si-O-Si bridges[2,3,5] and thus to the oxidation of the surface. This model explain many different aspects of oxygen interaction with silicon surfaces, such as the coverage and temperature dependence of sticking of O_2 on Si(111)7 × 7,[4,6] the influence of different surface structures and treatments on the oxidation kinetics,[4,6–8] and the photochemical[8] and alkali promotion of oxidation.[9] Evidence for the formation of molecular oxygen as a short-lived intermediate to adsorption on Si(100) surfaces has been provided by scattering experiments.[1,10]

Recently, new information on the initial stages of oxygen adsorption on Si(111)7 × 7 was gained with the scanning tunneling microscope (STM).[11–13] Two oxygen species (or better, two kinds of oxygen-containing sites) were observed that appeared brighter and/or darker than the unreacted Si adatoms. Relating the STM data to the electron spectroscopic information proved to be difficult. Since some of the "bright" sites turned "dark" as a function of time it was discussed whether this conversion is due to oxygen dissociation.[11–14] But apparently the "bright" sites are too stable to be directly identified with the molecular oxygen precursor. Whereas a lifetime at room temperature of 10–20 min had been deduced from x-ray photoelectron spectroscopy[4] (XPS) and work function ($\Delta\Phi$) measurements[15] the changes seen in the STM experiments occurred on a time scale of 1 h and more.[12,13] However, the STM data correspond to much lower oxygen coverages than present in previous experiments, and the total oxygen coverage may very well influence the stability of the molecular species.

The data presented in this paper provide the missing link in the kinetics of oxygen dissociation between the (high coverage) photoemission and the (low coverage) STM experiments. As a monitor for the thermally activated dissociation we use optical second-harmonic generation (SHG).[16] This technique was already employed by several groups to study adsorption and desorption phenomena.[16–18] Recently a particularly high adsorbate sensitivity was achieved on silicon surfaces.[19] But so far SHG has not been employed to investigate dissociation or other more complicated adsorbate reactions. We will demonstrate below that in the case of O_2/Si(111)7 × 7 the second-harmonic (SH) signal is not only dependent on the total oxygen coverage but also on the adsorbate configuration. This allowed us to use SHG as a real-time monitor of dissociation. Compared to the previous XPS and $\Delta\Phi$ experiments the sensitivity achieved in the present work is considerably higher and enables measurements at fairly low coverages. At the same time the SHG technique is completely nondestructive.

The results show that oxygen dissociation on Si(111)7 × 7 is strongly coverage dependent. In agreement with the results of Refs. 4 and 15 the lifetime τ of the molecular state at room temperature is $\tau \sim 15$ min for saturation coverage. For low oxygen coverages ($\Theta = 0.1$ monolayers) we find a much longer lifetime of $\tau \sim 50$ min which is compatible with the conversion rate of "bright" sites into "dark" ones observed in the STM experiments. We also show that the kinetics of the dissociation process change over the temperature range $T = 80$–500 K.

The experiments were performed in an ultrahigh-vacuum chamber at a base pressure of 5×10^{-11} mbar. The sample was cut from a phosphorus-doped 10-Ω cm Si(111) wafer. It was mounted on a liquid-nitrogen-cooled cryostat and could be heated resistively. The temperature was measured by a NiCr/NiAl thermocouple glued on the back of the crystal with a ceramic cement. Clean, well-ordered 7 × 7 surfaces were prepared by outgasing the sample at 900 K and removing the oxide layer at 1300 K. Sample cleanliness and order were checked regularly with Auger electron spectroscopy and low-energy electron diffraction.

For the SHG measurements laser pulses at 1064 nm with 10-ns pulse duration from a Q-switched Nd:YAG (yttrium aluminum garnet) laser operating at 10 Hz were incident on the sample under 45°. The fluence of the pump radiation was $\leq$ 150 mJ/cm^2. It was verified that with this fluence the probe laser had no measurable influence on the oxygen dissociation. The generated SH radiation was detected with a standard setup using gated electronics. Sample orientation and polarization of the incident pump radiation and the detected SH signal were chosen such that only the anisotropic component of the nonlinear susceptibility tensor $\chi_s^{(2)}$ contributed to the measured SH intensity $I(2\omega) \propto |\chi^{(2)}_{s,\xi\xi\xi}|^2 I^2(\omega)$. For oxygen exposure a known amount of gas was directly effused onto the surface with the help of a capillary-array doser. Oxygen coverages were obtained from an XPS calibration.[4] One monolayer is defined as the density of surface atoms of unreconstructed Si(111): 1 ML= 0.8×10^{15} O atoms/cm^2.

The sensitivity of SHG to the adsorbate configuration of O_2/Si(111)7 × 7 is demonstrated in Fig. 1. The main panel shows the nonlinear susceptibility $\chi_s^{(2)}$ of Si(111)7 × 7 for various oxygen exposures between 0 and 8×10^{15} O_2 molecules/cm^2 measured at a substrate temperature of 80 K. The nonlinear response of Si(111)7 × 7 decreases as a function of oxygen exposure, in agreement with previous observation.[18] However, $\chi_s^{(2)}$ is further reduced by annealing the layer at 500 K for a few minutes. This reduction is caused by the changed composition of the oxygen layer due to dissociation of the molecular species.

The composition of a layer (Θ = 0.3 ML) before and after annealing can be deduced from XPS O 1s core-level spectra shown in the inset of Fig. 1. These data were measured in a different UHV chamber but under similar conditions. The O 1s peak with a binding energy of 530.5 eV corresponds to molecular oxygen and disappears due to annealing whereas the intensity of the peak at 531.6 eV, which is characteristic of dissociated oxygen, increases.[4] The initial fraction of oxygen coverage present in molecular form, as derived from the XPS data, is $\sim \frac{1}{3}$ or $\sim \frac{2}{3}$ depending on the model assumptions of the O_2^- configuration.[4,14]

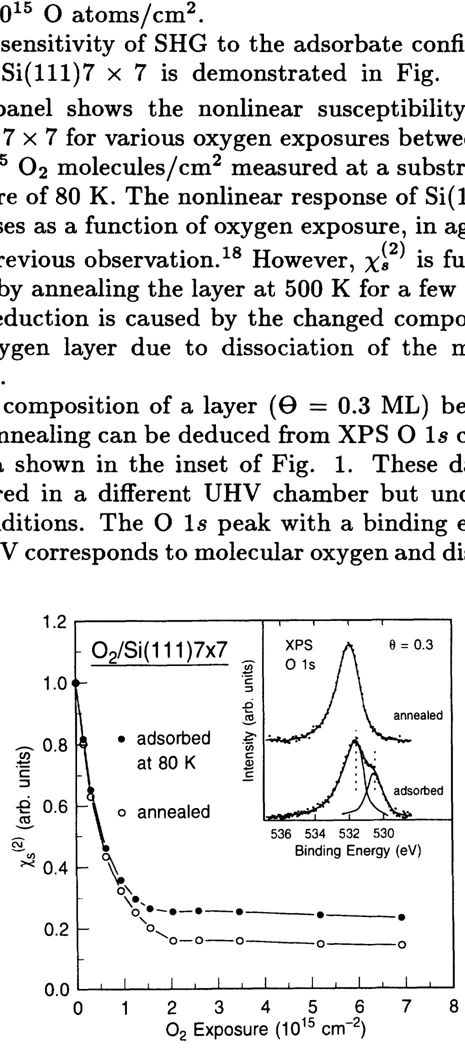

FIG. 1. Sensitivity of SHG to the oxygen adsorbate configuration on Si(111)7 × 7. Full dots denote the measured nonlinear susceptibility $\chi_s^{(2)}$ immediately after exposing the sample to molecular oxygen at 80-K substrate temperature. Open symbols indicate $\chi_s^{(2)}$ of the same layers after annealing the sample for 5 min at 500 K in order to dissociate molecular oxygen. Inset: XPS O 1s core-level spectra showing the conversion of molecular oxygen (shoulder at 530.5 eV) into stable dissociated oxygen (main peak at 531.6 eV) for an O_2 exposure of 0.9×10^{15} cm^{-2} under similar conditions.

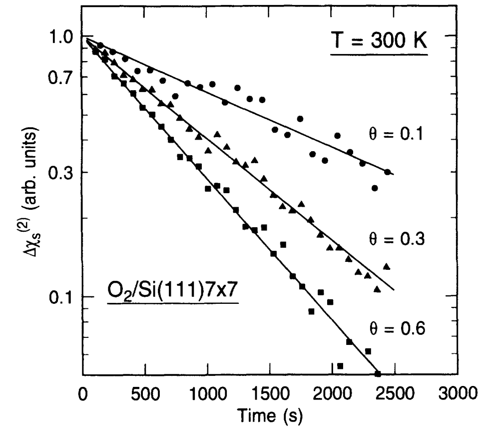

FIG. 2. Coverage dependence of the decay of the nonlinear susceptibility $\chi_s^{(2)}$ during isothermal oxygen dissociation at 300 K. The total oxygen coverages Θ of 0.1, 0.3, and 0.6 ML (1 ML= 0.8×10^{15} atoms/cm^2) correspond to O_2 exposures of 0.3, 0.9, and 3.0×10^{15} cm^{-2}, respectively.

With the correlation between the decrease of $\chi_s^{(2)}$ and the dissociation of O_2 established, SHG may now be used as a real-time monitor for the dissociation process. Results of isothermal measurements that show the coverage dependence of oxygen dissociation at 300 K are plotted in Fig. 2. Results obtained for different sample temperatures but corresponding to the same coverage of Θ = 0.3 ML are displayed in Fig. 3. For these measurements molecular O_2 was absorbed at a substrate temperature of 80 K, then the sample temperature was stepped to the desired value and the SH signal was recorded as a function of time. The quantity $\Delta\chi_s^{(2)}$ plotted in the figures is the measured change of the nonlinear susceptibility resulting from oxygen dissociation, $\Delta\chi_s^{(2)}(t) = \chi_s^{(2)}(t) - \chi_s^{(2)}(t \to \infty)$.

For quantitative analysis an exponential decay law was

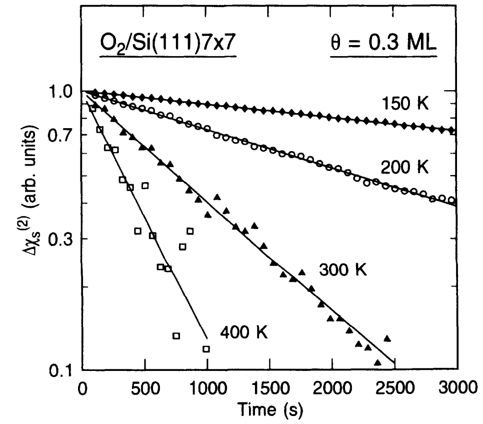

FIG. 3. Isothermal oxygen dissociation at 0.3-ML coverage for various substrate temperatures.

fitted to the data points $\Delta\chi_s^{(2)}(t) = \Delta\chi_s^{(2)}(0)\exp(-kt)$. The obtained decay rates k may be identified with the rates of oxygen dissociation if $\chi_s^{(2)} = \chi_s^{(2)}(\Theta_{\rm at}, \Theta_{\rm mol})$ is a linear function of $\Theta_{\rm at} - \Theta_{\rm mol}$. Linear proportionality $\chi_s^{(2)} \propto \Theta$ is frequently observed in adsorption studies with SHG.[16,17,19] From a Taylor expansion of $\chi_s^{(2)}(\Theta)$ one expects deviations from linear behavior to be significant mainly for large values of Θ. Since at $T = 300$ K the decay rates for high coverages ($\Theta = 0.6$ and 0.3 ML) derived from the present data agree with equivalent XPS results,[4] we believe that $\Delta\chi_s^{(2)}$ reflects the dissociation rate of molecular oxygen within a possible error of $\leq 20\%$ for *all* coverages.[20]

At low coverages our accuracy in determining small dissociation rates is limited by the adsorption of residual gases during the experiments. Adsorption also leads to a decrease of the SH response and cannot easily be distinguished from the decrease due to O_2 dissociation. For $\Theta = 0.1$ ML the maximum change of $\chi_s^{(2)}$ due to dissociation is only 8%. For a clean surface at 80 K, for which residual gas adsorption is strongest, we observed the same decrease of $\chi_s^{(2)}$ in 1.2×10^4 s. This is why we restricted our analysis of the low coverage data to temperatures $T > 200$ K where the measured rates are $k > 10^{-4}$ s^{-1}. A lower limit for the dissociation rates may then be obtained by simply subtracting the decrease of $\chi_s^{(2)}$ measured for the clean surface at 80 K. The upper limit is given by totally neglecting residual gas adsorption. This procedure results in an error of 25–40 % for the rates. For $\Theta \geq 0.3$ ML the influence of residual gas adsorption is insignificant.

In Fig. 4 we have plotted the evaluated dissociation rates for different coverages as a function of the inverse substrate temperatures. Our results clearly show that oxygen dissociation on Si(111)7 × 7 is strongly coverage dependent. The main differences of the rates by far exceed all possible errors discussed above. On a surface with low oxygen coverage ($\Theta = 0.1$ ML) the dissociation rate is approximately by a factor of 3 smaller than on a surface with high oxygen coverage $\Theta > 0.3$ ML. For $T = 300$ K the rates are $k^{\Theta=0.1} = 0.35 \times 10^{-3}$ s$^{-1} \pm 35\%$, $k^{\Theta=0.3} = 0.9 \times 10^{-3}$ s$^{-1} \pm$ 10%, $k^{\Theta=0.6} = 1.2 \times 10^{-3}$ s$^{-1} \pm 15\%$.

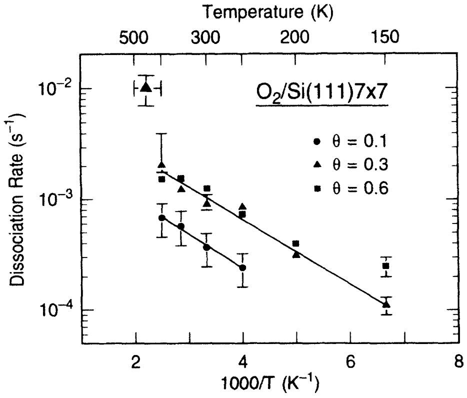

FIG. 4. Temperature dependence of the dissociation rates of molecular oxygen for three differen coverages Θ. The solid lines indicate fits to Arrhenius laws for $\Theta = 0.1$ and 0.3 ML.

For $\Theta = 0.1$ ML the dissociation rate corresponds to a lifetime for molecular oxygen of approximately 50 min. This has important consequences for the interpretation of the STM results.[11–13] Based on the stability of the bright sites it can no longer be excluded that they are due to molecular oxygen. In contrast, the fact that the conversion into dark sites takes place on a similar time scale as the O_2 dissociation at low coverage and that the conversion was observed to be accelerated as a function of oxygen dosage[11] are strong arguments that these sites are indeed directly related to the molecular precursor. Another argument has been given by Avouris and Lyo[13] who suggested that the tip-induced conversion of bright to dark sites they observed could be due to dissociative electron attachment during tunneling. With XPS the decay of the molecular precursor was found to be partially caused by the high number of created secondary electrons.[4] Most likely the underlying mechanisms are similar in both experiments.

The identification of the bright sites with molecular oxygen is also supported by the near-edge x-ray absorption fine structure (NEXAFS) of O_2/Si(111)7×7.[4] These measurements have shown that the O_2 $2\pi^*$-derived levels of the adsorbed molecular oxygen precursor are only partially filled and that the $1s \to 2\pi^*$ NEXAFS transition is rather close to the O 1s binding energy. Unfilled O_2 $2\pi^*$-derived levels should thus give rise to a high density of empty states near the Fermi level and appear bright in STM topographs recorded with +2-V bias between sample and tip.[11,12] We note, however, that the extended Hückel calculations of O_2/Si(111)7×7 performed recently by Schubert, Avouris, and Hoffmann[14] fail to predict the existence of empty O_2 $2\pi^*$-like levels.

Finally, as already pointed out by Avouris and coworkers,[11] the formation of an O_2^- intermediate quite naturally explains the site selectivity of oxygen adsorption observed in the STM experiments. The bonding of O_2 on Si(111) involves considerable charge transfer from the Si dangling bonds to the oxygen $2\pi^*$ level.[4] In analogy to a gas-phase "harpooning" reaction an O_2 molecule approaching the surface is therefore expected to stick predominantly at those sites which give high electron density above the surface. These are the corner adatoms of the faulted half of the 7 × 7 unit cell, exactly where most of the bright sites appear in the STM topographs.[11,12]

We now discuss the temperature dependence of the dissociation rates of the high coverage data ($\Theta = 0.3$ and 0.6 ML). Between 150 and 350 K the dissociation rates are well described by the Arrhenius law $k = \nu_0 \exp(-E_a/k_B T)$ with $\nu_0^{\Theta=0.6} \simeq 0.5 \times 10^{-2}$ s^{-1}, $E_a^{\Theta=0.6} = 41 \pm 10$ meV and $\nu_0^{\Theta=0.3} \simeq 10^{-2}$ s^{-1}, $E_a^{\Theta=0.3} = 58 \pm 10$ meV. The small activation energies E_a and the extremely low prefactor ν_0 are in agreement with the results of Silvestre and Shayegan[15] who deduced $E_a = 45 \pm 10$ meV and $\nu_0 = 0.5 \times 10^{-2}$ s^{-1} from isothermal $\Delta\Phi$ measurements and for a coverage that was probably close to our highest coverage $\Theta = 0.6$ ML.[21] However, if these parameters are used to calculate dissociation rates for temperatures $T \gg 300$ K they no longer fit the experimental results. Both the present SHG and the previous XPS experiments show that after annealing the surface at

$T \sim 450$ K for a couple of minutes all detectable molecular oxygen is dissociated. The corresponding dissociation rate (big triangle in Fig. 4) leads to an apparent activation energy of $E_a \sim 0.2$ eV for $T > 300$ K.[4] Also for $T < 150$ K (not shown) the measured dissociation rates are significantly higher than predicted by the Arrhenius parameters given above.

Both the deviations from Arrhenius behavior and the extremely low (apparent) prefactor indicate that the reaction paths for O_2 dissociation on Si(111) must be rather complicated. A possible but somewhat speculative explanation is suggested by the above-mentioned calculations. Schubert, Avouris, and Hoffmann showed that several different O_2^- configurations on Si(111)7 × 7 have similar total energies and may thus coexist on the surface.[14] The population of these configurations and consequently the dissociation pathways would then change as a function of temperature. In addition, the dissociation reaction could be site dependent and involve diffusion between sites. The fact that the O_2 dissociation on Si(111)7 × 7 is observable over an unusually wide temperature range is consistent with the presence of different species as well as with a strong influence of the adsorption site on the dissociation process.

In summary we have shown that SHG is able to detect dissociation of molecular O_2 chemisorbed on Si(111)7×7. Isothermal measurements reveal a strong coverage dependence of the dissociation kinetics. The lifetime of approximately 1 h determined for molecular oxygen at room temperature and low coverage is compatible with the stability of the so-called bright sites in recent STM topographs of O_2/Si(111)7 × 7. The temperature dependence of the dissociation rate departs form a simple Arrhenius law, probably due to interconversion of different O_2 configurations on the surface or a strong site dependence of the dissociation reaction.

This project was financially supported by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 338.

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[20] The relationship $\Delta\chi_s^{(2)} \propto \Theta_{\mathrm{at}} - \Theta_{\mathrm{mol}}$ can be applied only if no phase change of the complex quantity $\chi_s^{(2)}$ is associated with oxygen dissociation. We have verified experimentally that for $\chi_{s,\xi\xi\xi}^{(2)}$ this phase change is less than 5°; P. Bratu, Doctoral dissertation, Ludwig Maximillians Universität, München, Germany, 1994.

[21] An activation energy E_a of only 25 ± 10 meV was obtained in Ref. 15 from $\Delta\Phi$ measurements using a temperature ramp.