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External stress-induced chemical reactivity of O_2 on Si(001)

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In the dissociation reaction of O_2 on the Si(001)-$c(4\times2)$ surface, a trapping-mediated reaction is accelerated by external tensile stress. This alteration of the reactivity is more than an order of magnitude greater than estimations based on the alteration of the electronic structure caused by strain of the surface lattice. It was found that on the Si(001)-$c(4\times2)$ surface, the stress destabilized the antiferromagnetic ordering of topmost Si atoms forming buckled dimer and induced the collective phason-flip motion of the dimer. The alteration of the reactivity caused by such a collective instability of the arrangement of surface atoms is discussed.

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I. INTRODUCTION

The coupling of mechanical stress and a chemical reaction, which is called stress reaction or mechanochemical reaction, gets into a wide range of chemical reaction.[1,2] Stress reactions at solid surfaces, in particular, open new possibilities for the control of a wide range of reaction processes from catalysis to self-organization in nanotechnology.[3,4] Stress effects in the surface reactions have often been attributed to alteration of the electronic structure of the surface due to lattice strain, which makes it possible to predict the stress reaction using potential-energy surfaces. However, most involved lattice strains are too great (several percent) to be achieved experimentally without causing plastic deformation or fracture.[5–7] Here we show that, in the dissociation reaction of O_2 on Si(001), external stress which causes the lattice strain within elastic limit (several tenths of a percent at the most) alters the reactivity by several tens of a percent. This result is more than an order of magnitude greater than estimations based on the alteration of the electronic structure caused by the lattice strain. We found, in this system, that the collective phason flip motion of the topmost atoms on Si(001) was induced by the stress. Here we discuss that this motion facilitated a change in orientation of the adsorbed O_2 molecule to a direction in which a dissociation reaction advanced, from a direction in which molecular adsorption was stable. Our results strongly suggest that collective instability in the arrangement of the surface atoms induced by macroscopic stress alters chemical reactivity through a stereoelectronic effect.

II. EXPERIMENTAL PROCEDURES

We performed the experiment in an ultrahigh-vacuum apparatus at base pressure less than 7×10^{-9} Pa, equipped with a supersonic molecular beam line, low-energy electron-diffraction (LEED)/Auger electron spectroscopy optics and a quadrupole mass spectrometer. An O_2 beam with a narrow distribution of kinetic energy was used in this experiment using a supersonic molecular-beam technique.[8] The O_2 beam at the sample position was 2.5 mm in diameter. The samples used were Si(001) wafers (B-doped *p*-type, 1–10 Ω cm, $8\times28\times0.5$ mm^3) miscut by <0.5° to the (001) plane along the [110] direction. The sample surfaces were cleaned *in situ* by direct resistive heating to 1430 K. The samples were then cooled to 160 K using a Liquid N_2 reservoir. Uniaxial tensile stress within elastic limit was applied to the Si(001) surface along the [110] direction by three-point-bending method;[9] both of edges of the sample were loosely clamped through Ta spring wires and the center of the back of the sample was pushed by a wedge-shaped Ta anvil. At the center of the sample surface the tensile stress is maximum, σ_{max}, and is expressed as $\sigma_{\text{max}}=(6\text{Yt}/\text{L})\delta$, where Y is the bending modulus of elasticity, t and L are the thickness and the length of the sample, respectively, and δ is the deflection at the center of the sample. The value of Y for $\langle110\rangle$ direction of Si(001) is 168.9 GPa.[10] The anvil moves to bend the sample on a high-precision micrometer. A 0.15-mm deflection of the anvil corresponds to tensile stress of 100 MPa at the center of the sample surface. The stress experiments were done at the surface temperatures well below room temperature, RT, in order to minimize the elastic deformation of the sample and/or the morphological change in the sample surface.[11,12] The initial dissociation probability was determined by the King and Wells method.[13] The surface structure was observed at the center of the sample by LEED. The electron energy of incidence, E_{electron}, was 110 and 146 eV. As no significant difference was observed between the two results, only the result at 110 eV is shown in this paper. The LEED intensity distribution was measured by a computer-controlled data acquisition system equipped with an intensified charge-coupled device video camera. As the surface structure of Si(001) is very sensitive to surface contamination and to electron radiation, the LEED measurements were accomplished under 1×10^{-8} Pa within 3 min. After each measurement, the sample was annealed at 900 K for 16 min to eliminate residual stress and was again cleaned by flash heating at 1430 K.

III. RESULT AND DISCUSSION

In the dissociation reaction of O_2 on Si(001), trapping precursor-mediated dissociation is one of the main channels:[14,15] the impinging O_2 molecule is trapped in a weakly bound precursor well and subsequently it either dissociates or desorbs from the surface. Thus, the dissociation probability, S_0, is determined by the trapping probability, α, in the precursor well and the subsequent kinetic competition

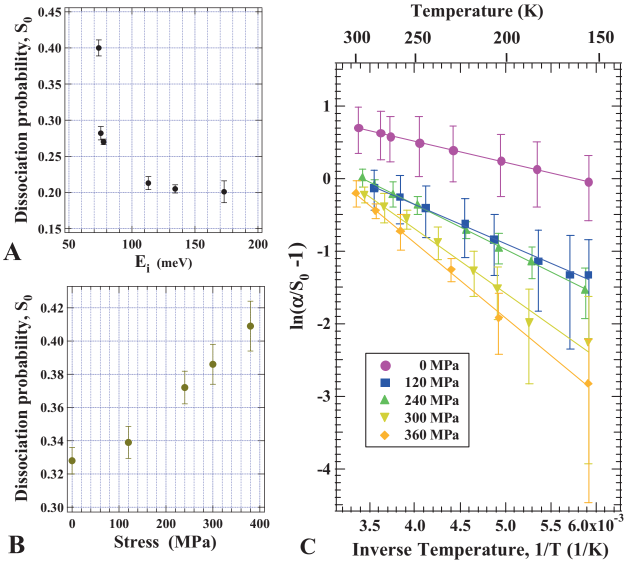

FIG. 1. (Color) Dissociation probability of O_2 on Si(001). (A) Dissociation probability at $T=202$ K for different kinetic energies of the impinging O_2, E_i. Most of the data plotted here previously appeared in the Fig. 1 of Ref. 9. (B) Dissociation probability in the low kinetic-energy region ($E_i=75.3$ meV) as a function of stress applied to the Si(001) surface, $T=169$ K. C, Dissociation probability in the low E_i region ($E_i=75.3$ meV) as a function of T, at variable stresses, which is displayed by linearizing the data of S_0 versus T. From Eq. (1) in the text, the linearized formula is given as $\ln(\alpha/S_0-1)=\ln(\nu_d/\nu_c)-(\Delta E/k_BT)$. Most of the data plotted here previously appeared in Fig. 2 of Ref. 9.

between dissociation and desorption, which is expressed by the following equation:[16] $S_0=\alpha K_c/(K_c+K_d)$, where K_c and K_d are the rate constants for dissociative chemisorption and desorption, respectively. Taking the simple Arrhenius rate forms $K_c=\nu_c\exp(-E_c/k_BT)$ and $K_d=\nu_d\exp(-E_d/k_BT)$ into consideration, S_0 is expressed

$$S_0=\alpha/[1+(\nu_d/\nu_c)\exp(-\Delta E/k_BT)], \tag{1}$$

where k_B is Boltzmann's constant, ν_d and ν_c are the preexponentials for the desorption and the dissociation, respectively, T is the surface temperature, and ΔE is the difference in activation barrier heights between desorption, E_d, and dissociation, E_c, ($\Delta E=E_d-E_c$). A molecule is trapped in the precursor well if it dissipates sufficient energy in the gas-surface collision to have a negative total energy (kinetic plus potential) after the collision: the lower the kinetic energy of the impinging O_2, E_i, the higher the probability of α. Due to the dependence of α on E_i, S_0 decreases with increasing E_i, as shown in Fig. 1(A). Thus the dissociation reaction by a trapping-mediated mechanism is dominant for the low E_i region ($E_i<100$ meV). The dissociation reaction via a trapping precursor was facilitated by external stress, as shown in Fig. 1(B). The stress dependence of the kinetic parameters in this reaction can be estimated by fitting Eq. (1) to the temperature-dependence data of S_0 for various stresses [Fig. 1(C)]. The resultant fitting parameters of α and ΔE depending on stress are shown in Figs. 2. ΔE increases with increasing stress, which then leads to an increase in the dissociation probability with stress. In contrast, α decreases slightly as stress increases. A molecule is trapped at the surface (a precursor well) if it dissipates sufficient energy in the molecule-surface collision. The decrease in α with stress suggests that the degree of energy dissipation decreases and/or the precursor well becomes shallow as stress increases. Assuming that the O_2 molecule desorbs from the precursor well, the activation barrier for desorption, E_d, corresponds to the depth of the precursor well. $\Delta E(=E_d-E_c)$ increases with increasing stress while E_d decreases slightly with stress, indicating that E_c decreases with increasing stress.

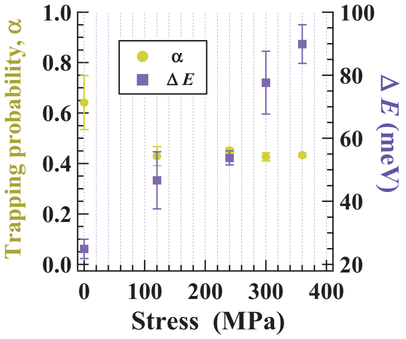

FIG. 2. (Color) External stress dependence of kinetic parameters for trapping mediated dissociation: trapping probability, α, and difference in activation barrier heights between desorption and dissociation, ΔE, as a function of the stress. These quantities are obtained from the results of linearization fits in Fig. 1(C).

According to the frontier orbital theory, the dissociation reaction of O_2 on the Si(001) surface can be described by the interaction between the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO) of O_2 molecule and the surface states of Si(001). A free O_2 molecule has a spin-triplet ground state ($^3\Sigma_g^-$) with a half-filled antibonding state ($2p\pi_g^*$) where HOMO and LUMO exist, and the dissociation reaction is accompanied with conversion from spin-triplet state to the spin-singlet state. On a clean Si(001) surface, the pairing of neighboring surface atoms forms a dimer with multiple bonds of π and σ conjugations to reduce the number of the dangling bond, and the dimer is buckled to stabilize the surface energy: one atom of the dimer moves up, adopting an s^2p^3-like configuration, while the other moves down, adopting an sp^2-like configuration.[17] This rehybridization induces a charge transfer from the lower dimer atom to the upper atom, resulting in a surface band gap between filled (π) and empty (π^*) electronic states.[18,19] The Fermi level is located within the surface band gap and these surface states lie in the fundamental gap. It seems to be straightforward that the effect of external stress on the surface reaction is due to the alteration in such surface states by the elastic strain of the surface lattice. The limit of the elastic strain of the Si(001) surface must be several tenths of a percent at the most: in our experiments the approximate limit was 0.35%. The alteration in the surface states caused by such a strain is estimated to be approximately 17 meV, which is too small to alter the surface reactivity effectively.[20] Thus there must be other factors involved in amplifying the reactivity.

We detected the intensity distribution of the LEED of the Si(001) surface under the external stress. Figure 3(A) shows

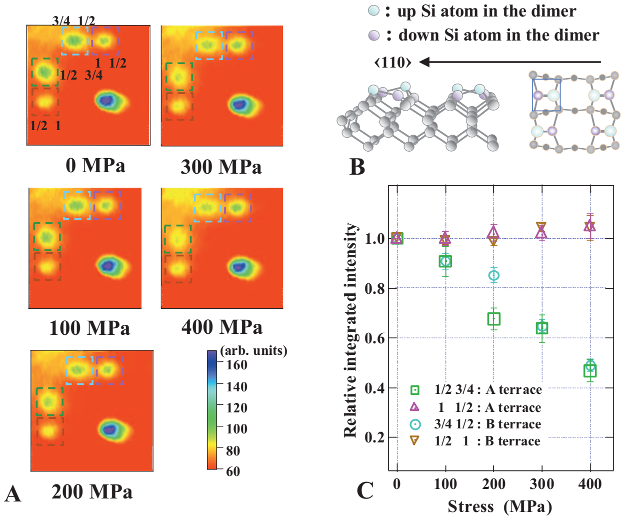

FIG. 3. (Color) External stress dependence of the LEED intensity of the Si(001)-$c(4\times2)$ superstructure. $T=169$ K. (A) LEED intensity distribution versus stress. The electron energy of incidence, E_{electron} was 110 eV. Integral regions of the quarter-order reflections were depicted as dashed lines. All of the data shown here previously appeared in Fig. 1 of Ref. 30. (B) Schematic representation of the real-space structure for the Si(001)-$c(4\times2)$ superstructure surface. Left: side view of the structure showing the dimer layer and the four sublayers. Right: top view of the structure. The dimer layer and the first and second sublayers are shown. The size of the unit lattice of bulk is depicted as a blue line. (C) The relative integrated intensities of fractional-order reflections versus stress. Some of the data plotted here previously appeared in Fig. 2 of Ref. 30.

the dependence of the LEED intensity distribution on the external stress. The surface temperature was 169 K. Under stress-free conditions (0 MPa), the LEED pattern shows a $c(4\times2)$ superstructure, which is characterized by quarter-order reflections such as 1/2 3/4 and 3/4 1/2. In the $c(4\times2)$ reconstructed surface, the buckled dimer is arranged in an antiferromagnetic order,[21–23] as shown in Fig. 3(B), which is the ground state of the clean Si(001) surface.[24–26] On terraces separated by an odd number of monatomic-height steps, the direction of the dimer bond is orthogonal, which results in the $c(4\times2)$ and its 90°-rotated symmetry equivalent $c(2\times4)$ LEED patterns. We refer to the terrace where the direction of the dimer bond parallel to the [110] direction as A terrace and the terrace where the direction of the dimer bond perpendicular to it as B terrace. Then the quarter-order reflections of 1/2 3/4 and 3/4 1/2 originate from the $c(4\times2)$ superstructure of the A terrace and the B terrace, respectively. With increasing in stress, while the half-order reflections as well as the integer-order reflections were independent of the stress, the integrated intensities of both quarter-order reflections decreased, as shown in Fig. 3(C), which was reversible with respect to the stress. In the result shown in Fig. 3, E_{electron} was 110 eV. In the case that E_{electron} was 146 eV, the result was almost the same as that shown in Fig. 3. We also confirmed from the previous data in Refs. 27 and 28 that the dependence of the intensities of the half-order reflections on E_{electron} for the $c(4\times2)$ surface is almost the same as that for the (2×1) surface. This implies that the change in the intensities of both quarter-order and half-order reflections with stress is chiefly due to the structural change in the surface and is hardly affected by the dynamical effect of the electron scattering. Then the kinematical approach can be applicable to the approximate analysis of these diffraction intensities although dynamical approach is most commonly used in the analysis of LEED intensity. According to the kinematical theory of electron diffraction, the integrated intensities of the quarter-order reflections are proportional to the area of the ordered phase of the $c(4\times2)$ superstructure and the integrated intensities of the half-order reflections are proportional to the number of the dimers in the surface.[29,30] Thus the result of the decrease in the integrated intensities of the quarter-order reflections with stress means that the area of the ordered phase of the $c(4\times2)$ superstructure decreases with stress, resulting in a (2×1) structure. In the (2×1) structure, the surface also consists of buckled dimers and the buckled dimer spontaneously fluctuates by flipping between the two possible asymmetric configurations. The flipping motion of the dimer can be interpreted in the terms of a phason, which is a phase defect in the dimer alignment.[31,32] The buckled dimer appears symmetric due to the time average of the phason-flip motion of the buckled dimer, resulting in the (2×1) structure.

From the results of the first-principles calculations of the surface stress of Si(00),[19,33] the (2×1) surface is less tensile along the dimer bond direction and is more compressive in the direction perpendicular to the dimer bond than the $c(4\times2)$ surface. Thus the (2×1) surface is more favorable for the elastic energy than the $c(4\times2)$ surface in that case that the external tensile stress is applied to the surface along the direction which is either parallel to or perpendicular to the dimer bond. The $c(4\times2)$ surface exhibits a multiscale hierarchical structure with respect to the surface stress.[34] The external tensile stress destabilizes such an intrinsic stress field at the surface and consequently the collective phason-flip motion as well as the elastic strain occurs to relax the external stress.[30] Thus, with increase in the external tensile stress, the area of the ordered phase of the $c(4\times2)$ structure decreases and conversely the area of the disordered phase of the (2×1) structure increases on both A and B terraces. The half-order reflections of 1 1/2 and 1/2 1 originate from the (2×1) structure of the A terrace and the B terrace, respectively. Because both half-order reflections were independent of the stress, the number of the dimers on both terraces remained unchanged under the stress condition. This means that the area of each terrace did not depend on the stress. This result is in contrast with the dependence of the terrace population on the stress at an elevated temperature. At a surface temperature well above RT, the external stress produces unequal population of the A and B terraces.[11] The change in the population of the two terraces requires the motion monatomic steps caused by thermal activation. In our stress experiment, however, the surface temperature was too low (<RT) for the steps to move.

From the result of the first-principles calculation with the spin-polarized gradient approximation,[35] the most reactive part on a Si(001) surface is the dimer site, and the activation barrier for O_2 dissociation at the dimer site is strongly de-

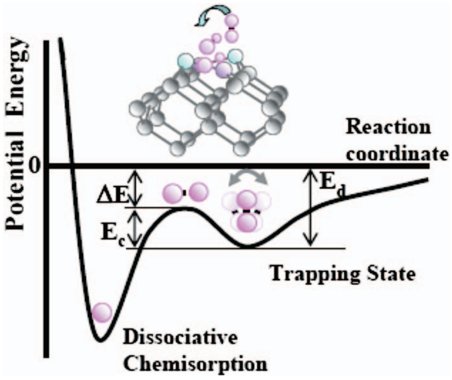

FIG. 4. (Color) Schematic representation of the potential-energy curve for trapping mediated dissociation of a O_2 molecule on the Si(001)-$c(4\times 2)$ superstructure surface.

pendent on the orientation of the O_2 molecule. A spin-triplet O_2 molecule approaching the dimer site with its axis parallel to the surface, that is, with an orientation angle of $\theta=\pi/2$, can dissociate without overcoming any energy barrier, while the O_2 molecule constrained to having its axis normal to the surface, $\theta=0$, must overcome the high activation barrier of about 2.64 eV.[36,37] In previous experiments,[38] only the presence of physisorbed O_2 with $\theta=0$ has been shown and, to the best of our knowledge, there has been no direct evidence of the presence of physisorbed or chemisorbed O_2 with $\theta=\pi/2$. Thus an O_2 molecule with $\theta=0$ is physisorbed stably in a precursor well. It is easily deduced that the physisorbed O_2 molecule can dissociate via a lower activation barrier if it rotates to $\theta=\pi/2$. Then a trapping O_2 molecule with $\theta=\pi/2$ is the critical configuration, called the transition state and the activation energy for the dissociation, E_c, corresponds to the energy necessary for the physisorbed O_2 with $\theta=0$ to rotate to $\theta=\pi/2$. A schematic of such a dissociation reaction is shown in Fig. 4. The results of first-principles calculation[35,37] showed that as the dissociation reaction proceeded, the physisorbed O_2 with $\theta=0$ rotated its axis to $\theta=\pi/2$ and the configuration of the dimer became symmetriclike with synchronism with the O_2 rotation. Such a change in configuration of the dimer can be interpreted using frontier orbital theory. According to frontier orbital theory, the interaction preferentially occurs at the position where the overlapping of the HO and LU orbitals between the O_2 molecule and the surface is largest when the O_2 molecule physisorbs to a trapping precursor. The position of the largest HO density at the surface is the upper atom of the buckled dimer.[18] Thus the LU orbital of the O_2 molecule with $\theta=0$ interacts predominantly there. The orbital interaction accompanies the charge transfer from the HO to LU orbital, which weaken the bonds of the upper atom. Consequently the bond angle of the upper atom, as well as the bond length of the dimer, becomes larger, which means that the configuration of the dimer becomes symmetriclike. Shkrebtii *et al.*[39] showed by the calculation of the finite-temperature *ab initio* molecular dynamics that the dimers were in a nearly symmetric configuration before flipping and that the attempt frequency of flipping could be estimated to be about 10^{14} Hz. The activation barrier for flipping has been reported to be less than 150 meV.[40–42] The inverse of the attempt frequency is equal to the interval of time for which the configuration of the dimer changes from asymmetric to symmetric configuration and vice versa. This interval of time, ~100 fs, is comparable with the time required for dissociation of the physisorbed O_2 at the dimer site.[43] As was shown previously, the external tensile stress induced the collective phason-flip motion, which frequently made the chance for the dimer to take the symmetric configuration. Owing to the symmetriclike configuration of the dimer, the HO density is delocalized and spreads over the dimer axis. Then the O_2 molecule tends to rotate its axis to $\theta=\pi/2$ because such a configuration makes the LU orbital $2p\pi_g^*$ interact more efficiently with the HO orbital of the dimer. Thus we deduce that the phason-flip motion induced by the stress promotes this dissociation reaction following from the rotation of the molecular axis of the physisorbed O_2. This means that the steric factor for the trapping precursor-mediated dissociation reaction increases due to the phason flip, which lowers the apparent E_c. The surface reaction involves the deformation of the surface lattice. And we want to make a point that the reaction is promoted by the stress which assists the deformation of the surface lattice along the reaction path.

IV. CONCLUSIONS

Previous studies have attributed the stress reaction at single-crystal surfaces largely to elastic strain of the surface. However, in the case in which the surface exhibits a multiscale hierarchical structure with respect to elastic strain, the surface relaxes the external stress in a hierarchical way, causing an alteration of the surface reactivity that cannot be estimated by the existing methods. We have emphasized that the collective instability of dimers resulting from the relaxation of external stress can cause the conformation of the reactants to fluctuate, leading to an enhancement of the sensitivity of the surface reaction: new mechanisms for chemistry at surfaces. It is still difficult to simulate such a reaction dynamics by model calculations. However, we hope that near future, collaborative works of both ultrafast experiments and theoretical calculations will elucidate such a reaction dynamics in detail.

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[34] The asymmetric dimer tends to shrink along the dimer bond direction, e.g., the $[110]$ or $[1\bar{1}0]$ direction, due to the σ bond, and the down atom of the dimer pushes the second-layer atoms under it outwardly in the direction of the dimer row; meanwhile, the up atom of the dimer pulls them inward. Thus, an asymmetric dimer produces a local stress field on the subnanometer scale. Neighboring dimers minimize their strain energy by antiferromagnetic ordering, which results in the modulation of stress in the direction parallel to and perpendicular to the dimer row on a terrace over several nanometers. On terraces separated by an odd number of monatomic height steps, the dimer bond direction (and hence the direction of the modulation) is orthogonal. Consequently the direction of the stress modulation is also orthogonal on their terraces. The mean terrace size is several hundreds nanometers. The surface is consists of such terraces and steps. Thus, the Si(001) surface exhibits a multiscale hierarchical structure with respect to the surface stress.

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