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Electron Spin Resonance Observation of the Si(111)-(7 × 7) Surface and Its Oxidation Process

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Electron spin resonance (ESR) observation of dangling-bond states on the Si(111)-(7 × 7) surface is demonstrated for the first time. The ESR spectra clearly show that a reaction of molecular oxygen with the Si(111)-(7 × 7) surface is associated with the appearance of a new dangling-bond center at unreacted Si adatoms. Most of the oxidized surface sites do not show ESR signals, but in a minor part of the surface another new type of surface defect is detected. The well known P_b center at the SiO₂/Si interface is found to evolve at an oxide thickness as thin as 0.3 nm.

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Electron spin resonance (ESR) is widely used to study defect structures and chemical reactions that involve unpaired electrons. Although ESR has great potential as a surface probe, its application in surface studies has been limited to indefinable surfaces of powder or porous samples [1,2]. To make it possible to study well-defined single-crystal surfaces, an ultrahigh-vacuum scanning tunneling microscope (UHV-STM) was combined with radio-frequency (rf) ESR [3]. This successfully achieved a single-spin detection on the Si(111)-(7 × 7) surfaces. However, the spectroscopic information on the rf signal was rather limited as compared to the usual ESR spectroscopy, due to a lack of g -anisotropy data, a sensitivity problem, and unknown factors for the spin-dependent tunneling [3]. Alternatively, a conventional ESR technique had been applied to cleaved Si surfaces; however, the detection of surface signals was not successful [4,5].

In this Letter, we report ESR measurements on the Si(111)-(7 × 7) surface when it is chemisorbed by oxygen molecules. The combination of a state-of-the-art ESR system and a carefully designed UHV sample cell enables us to detect and identify new ESR signals on the clean single-crystal surface. Since the Si(111)-(7 × 7) surface [6–10] shows 19 surface dangling bonds (DBs) per unit cell, it is an ideal sample for demonstrating the capability of the UHV-ESR technique. The spectroscopic information establishes that those DBs can be revealed by a new ESR center. In addition, ESR spectra clearly show that the oxygen chemisorption upon the Si(111)-(7 × 7) surface [11–16] greatly changed the DB states and induced another new paramagnetic defect. The present results are useful in analyzing oxidation of Si layers which is an important reaction in Si technology. Also defects in SiO₂/Si structures are of technological interest because such defects are related to reliabilities of metal-oxide-semiconductor devices [17–19]. Our method is expectedly applicable to surface studies on a variety of clean surfaces and their reaction processes.

Our experimental setup consists of an X-band ESR spectrometer and a UHV chamber to which a sample cell (a silica glass tube of 1 cm in diameter) is attached. The UHV

chamber (base pressure = 9×10^{-9} Pa) is arranged so that the sample cell is located within the microwave cavity of the ESR system. A sample of Si single crystal ($8 \times 0.3 \times 0.030$ cm³) is supported on the tip of a vacuum transfer rod. In the UHV chamber, we are able to prepare the sample surface by standard surface treatment and analysis techniques. Subsequently, we perform ESR measurements on the processed surface by inserting the sample into the UHV sample cell. The transfer rod is rotatable so that the ESR spectrum of the surface can be measured as a function of an angle, θ , between the surface normal and magnetic field \mathbf{B} . When $\theta = 0$ and 90° , the magnetic field parallels [111] and $\bar{1}10$ axes, respectively. Si(111) wafers used in our study had a resistivity higher than 1000 Ω cm and were polished on both sides in order to increase the signal-to-noise ratio in the ESR measurements. A Si(111)-(7 × 7) surface was prepared in the chamber by direct-current heating of the wafer above 1400 K. For oxidation experiments, molecular oxygen was introduced in the chamber through a calibrated variable-leak valve. After the surface cleaning and oxidation, we confirmed the surface structure by reflection high energy electron diffraction (RHEED). All measurements and surface oxidations were carried out at room temperature.

Our Si sample originally involved the so-called P_b center [17] that is formed at the native oxide-Si(111) interface. The oxide removal by the direct-current heating completely annihilated the interfacial P_b signal [20]. As a result, the ESR spectrum of the Si(111)-(7 × 7) surface [Fig. 1(a)] shows a weak but detectable resonance at a g factor of $g = 2.006$. A RHEED measurement [inset of Fig. 1(a)] ensures well-ordered (7 × 7) reconstruction on our surface. The double integral intensity of the ESR signal at $g = 2.006$ corresponds to a spin density on the order of 10^{12} cm⁻², which is much lower than the predicted density of DBs on an ideal Si(111)-(7 × 7) surface, 3.04×10^{14} cm⁻². Thus, ESR is largely insensitive to the DBs on the Si(111)-(7 × 7) surface at room temperature. A similar phenomenon has been observed for powder systems that contain a high density of surface paramagnetic ions [1]. In such systems the high degree

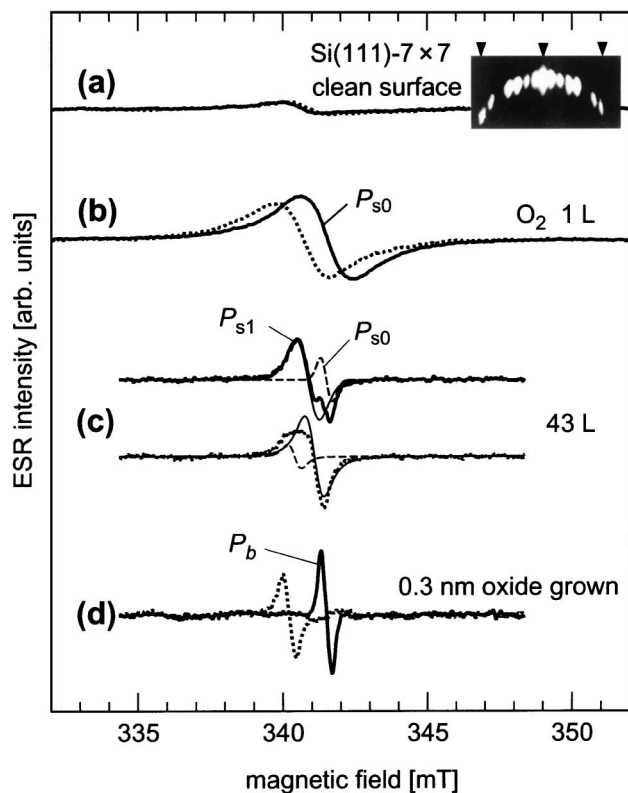


FIG. 1. ESR spectra of the Si(111)-(7 × 7) surface. (a) Clean surface. (b) After exposure of the clean surface to O₂ for 1 L, (c) 43 L, and (d) to 1-atm O₂ for 1 h. The spectra shown by solid and dashed lines were measured for $\theta = 0$ and 90° , respectively. Each spectrum was accumulated for 2 to 6 h with a microwave power of 1 to 200 mW and field modulation frequency and amplitude of 100 kHz and 0.4 to 0.8 mT, respectively. Deconvoluted P_{s0} and P_{s1} signals in (c) were obtained by simulations of a combination of two Voigt peaks. A RHEED image in (a) was taken for $[\bar{1}10]$ -incidence configuration. Arrows above the image indicate elementary reflections.

of coupling between neighboring unpaired electrons broadens the ESR line, making the signal unobservable [1]. The $g = 2.006$ resonance observed here is probably due to a sort of defected surface sites or contaminants rather than normal DB states of the Si(111)-(7 × 7) surface [21], because the DB states can be revealed by another resonance, as is seen in the following oxidation experiments.

Chemisorption of oxygen on Si(111)-(7 × 7) eliminates the DB states of the topmost Si atoms, the so-called Si adatoms [6], as reported in previous STM studies [11–14]. We have found that a new ESR signal appears in conjunction with such a reduction in the surface DBs. The pairs of spectra measured for $\theta = 0$ and 90° are also shown in Fig. 1 for different oxygen exposures. As is shown in the figure, the spectra (b) taken at the 1-L exposure (1 L $\approx 10^{-4}$ Pa sec) reveal a new resonance whose g factor is clearly anisotropic. We name this new paramagnetic center P_{s0} . The angular dependence of its g factor, the so-called g map (Fig. 2), shows that this center has an axial symmetry about the [111] axis with principal g fac-

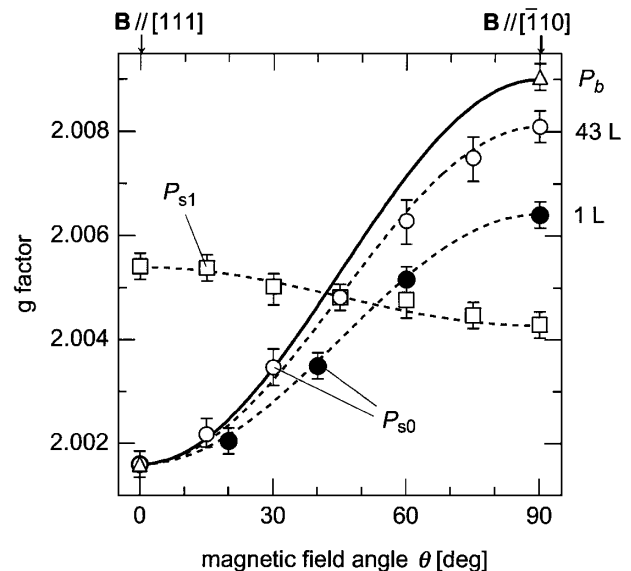


FIG. 2. The g maps for the observed ESR centers. The solid line represents the known g map for the P_b center [17], and dashed lines are fitted to the experimental data.

tors of $g_{\parallel} = g(\theta = 0^\circ) = 2.0015$, which is close to the factor for the free electron (2.0023), and $g_{\perp} = g(\theta = 90^\circ) = 2.0064$. These spectroscopic features indicate that the P_{s0} center originates from the [111]-oriented DB states of Si(111)-(7 × 7).

As the O₂ exposure was increased, ESR spectra were increasingly dominated by another new resonance. Figure 1(c) obtained at a 43-L exposure shows this new resonance (solid thin lines) superposed on the decayed P_{s0} signal (broken thin lines). The origin of this signal is not clear at present, and we tentatively call it P_{s1} . The g map of this center (Fig. 2) does not agree with that for any known center in the SiO₂/Si structure [17–19]. Further, it does not agree with that for any of a variety of oxygen complexes and radicals in Si [22] and SiO₂ [23]. We point out that the P_{s1} centers are a type of surface defect, because they exist only transiently during oxidation of the adatom and underlying “rest-atom” layers and thus disappear completely once oxidation proceeds to the next surface layers, as is clear from the spectra (d) in Fig. 1.

The spectra (d) in Fig. 1 were measured after an oxide layer of approximately 0.3 nm in thickness was formed on the surface by exposure of 1-atm O₂. The thickness was estimated from an Auger electron measurement [24] of the sample. The (7 × 7) RHEED pattern was no longer detected from the surface. We attributed the observed ESR signal to the P_b center at the oxide-Si(111) interface, since the spectrum is identical to that reported for this center [17]. On the basis of the estimated oxide thickness of 0.3 nm, we estimate that the P_b center in our sample is formed in the third atomic layer from the surface. This layer lies approximately 0.43 nm below the adatom layer [7]. The Si atoms in the third layer have [111]-oriented bonding toward the second layer [7] and therefore can adopt [111]-oriented DBs.

Figure 3 shows the ESR results as a function of the O_2 dose up to 1000 L. The oxidation primarily involves the adatom and rest-atom layers, because the RHEED image at 1000-L exposure retained a faint (7×7) pattern, in consistency with the previous result [15]. Also shown in the figure are STM images of the surface measured at 0.4, 1, and 2 L. The STM observation was carried out in a separate vacuum chamber under the identical condition as that of the ESR experiments. First, we point out that the density of the P_{s0} centers monotonically decreases with the oxygen chemisorption [Fig. 3(c)], showing the same behavior as unreacted adatom DBs [see Fig. 3(a)]. Reduction of the P_{s0} density is completed by approximately 10-L exposure of O_2 . The observed change is consistent with previous observations by STM [11] and photoemission [15] that unreacted Si adatoms disappeared at 10 to 20 L. Therefore, it is reasonable to consider that the P_{s0} centers correspond to the $[111]$ -oriented DB states of unreacted Si adatoms. For the clean (7×7) surface, the P_{s0} centers are not detectable due to the extensive signal broad-

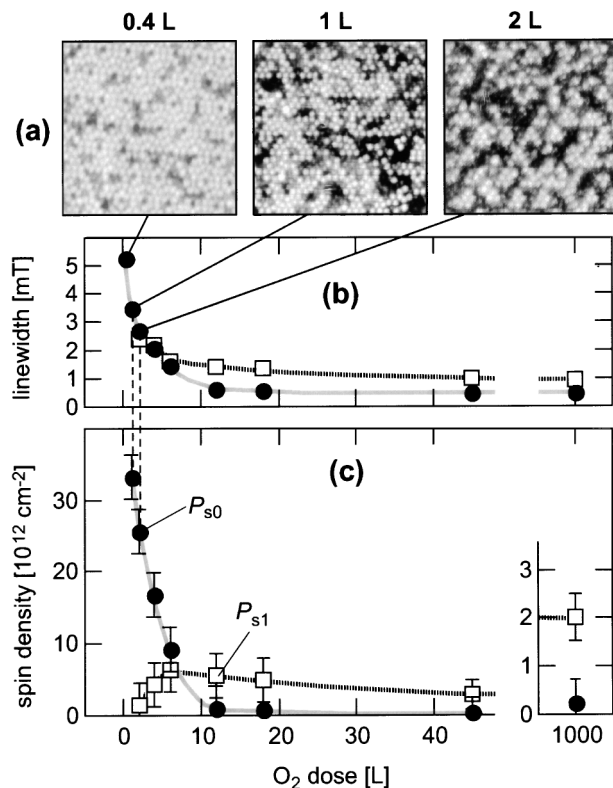


FIG. 3. Oxidation-induced changes of the $\text{Si}(111)-(7 \times 7)$ surface as a function of O_2 dose. (a) Reduction in the density of unreacted adatom DBs (bright spots) observed by STM. The area shown here is approximately 20 nm by 20 nm and was measured with a constant current of 0.1 nA and a sample voltage of 1 to 2 V. The sharpness of the RHEED pattern was used as a common measure in order to guarantee that the STM and ESR samples are similar in integrity in the original (7×7) reconstruction. (b) Change in linewidths of the P_{s0} and P_{s1} centers. These widths correspond to full-widths-at-half-maximum of absorption peaks of the ESR signals at $\theta = 0^\circ$. (c) Change in the spin densities.

ening. However, the signal linewidth narrows by oxygen chemisorption [Fig. 3(b)], resulting in the appearance of the P_{s0} signal. The P_{s0} signal becomes detectable at 0.4-L exposure [Fig. 3(b)], although a large signal broadening and overlap of the $g = 2.006$ signal make it difficult to estimate the P_{s0} density. As the spin density and linewidth are reduced, the g_\perp factor of P_{s0} increases and saturates to 2.008 (Fig. 2). The variable g_\perp factor and signal broadening for the P_{s0} center reflect on the fact that the electronic structures and environments are appreciably different between the P_{s0} (surface Si DBs) and P_b (interface Si DBs).

The areal density of the P_{s0} centers is approximately $3 \times 10^{13} \text{ cm}^{-2}$ at the O_2 exposure of 1 L [Fig. 3(c)]. However, the STM image for the same exposure [see Fig. 3(a)] gives an adatom DB density of $9 \times 10^{13} \text{ cm}^{-2}$. We tentatively attribute this difference to the fact that ESR selectively detects paramagnetic (i.e., neutral) Si adatoms. It has been reported [8,9,12] that on the $\text{Si}(111)-(7 \times 7)$ surface, electron transfer takes place from the adatom DBs (twelve atoms per unit cell) to rest-atom and corner-hole DBs (six and one per unit cell, respectively). This process leaves five paramagnetic Si adatoms per unit cell, and all other DBs are stabilized in charged states. If we take this effect into account, a reasonable agreement between ESR and STM data is obtained: 5/12 of the unreacted Si adatoms observed by STM is $4 \times 10^{13} \text{ cm}^{-2}$, which is close to the spin density measured by ESR. The same relation is also found for the case of a 2-L exposure. In the 2-L image of Fig. 3(a), the unreacted adatom DB density is $6 \times 10^{13} \text{ cm}^{-2}$, and 5/12 times that is about $3 \times 10^{13} \text{ cm}^{-2}$ which is also comparable with ESR data.

We found that the broadened P_{s0} signal remains unsaturated even at a microwave power exceeding 200 mW and that its line shape is well fit by a Lorentzian distribution function. These facts indicate that the lifetime broadening of the signal is caused by a very short spin-lattice relaxation time (T_1) of unpaired electrons. The origin of such a short T_1 may be attributed to metallic electronic states of the $\text{Si}(111)-(7 \times 7)$ surface that originate from a high density of adatom DBs [7–9]. Specifically, if the unpaired electrons of the adatom DBs are delocalized at the surface [9,10], T_1 values as short as those for the conduction electrons in metals and doped semiconductors can be obtained [25,26]. For instance, the 5-mT linewidth observed at 0.4-L exposure corresponds to 10^{-8} sec of T_1 . The T_1 value will be much shorter on the clean surface, due to more delocalization of the DB's electrons. In the STM images shown in Fig. 3(a), most of the unreacted Si adatoms neighbor upon each other. Such grouping of the unreacted adatoms can assist the delocalization of their unpaired electrons. The dipolar broadening of the P_{s0} signal may be compensated by the exchange or motional narrowing effects of the delocalized electrons.

Since the DB states of oxidized adatoms are removed far from the Fermi level [12,15], the delocalization of the P_{s0} centers cannot extend to the oxidized adatoms. In addition, the oxidized adatoms are a barrier to the electron

conduction across them. Accordingly, the more oxygen chemisorption on the Si(111)-(7 × 7) surface is considered to result in the less delocalization of the unpaired electrons. Reduction of the signal broadening effect seen in Fig. 3(b) is supposedly a consequence that the localization of the unpaired electrons proceeds with the submonolayer chemisorption of O₂. If the electrons are localized, their T₁ will no longer be so short as to cause the lifetime broadening of the P_{s0} signal. The localization phenomenon is also suggested from the increase in g_⊥ of the P_{s0} center (Fig. 2), because the g_⊥ value of the DB-like centers becomes larger with the more localization [27]. In addition, we speculate that the local structure of the P_{s0} centers is distorted with the oxidation-induced strain, which also leads to the increase in g_⊥ as observed in the P_b system [28].

The formation of the P_{s1} centers is induced by the O₂ exposure with 2 to 4 L, as is shown in Fig. 3(c). They are alive even after the whole surface area has been oxidized by the oxygen exposure much larger than 10 L. These facts suggest that the P_{s1} center is related to oxygen-chemisorbed sites. In contrast with the P_{s0} center (= unreacted Si adatoms), the P_{s1} center may involve oxygen atoms in its structure. However, the areal density of the P_{s1} center is less than 1% of that of the oxidized sites (≈10¹⁴ cm⁻²). It means that a small number of spin centers are introduced by the oxidation process of the top surface, although it mainly annihilates spin centers on the Si(111)-(7 × 7) surface.

The result that the reaction of molecular oxygen with the surface eliminates an electron spin from the oxidized site would be valuable for examining the oxidation processes on Si surfaces. One possible process of the O₂ chemisorption is that O₂ attaches to a surface Si DB, forming the peroxy radical (≡Si-O-O) [16]. In the other models [12,13,16], dissociated oxygens are assumed to generate the nonbridging oxygen (≡Si-O) or Si-O-Si backbonds of the Si DB. All of those atomic structures, however, have an unpaired electron [23], unless they are charged. Therefore, the formation of those sites should be associated with the electron transfer between surface sites in order to annihilate the unpaired electron.

In summary, we have performed the ESR measurements on the chemisorption process of molecular oxygen on the Si(111)-(7 × 7) surface. It was shown that there exist two kinds of new paramagnetic center on the surface: a DB center on unreacted Si adatoms (P_{s0}) and another new type of surface spin center (P_{s1}). Most of the oxidized sites were found to have no unpaired electrons. Our experiments have demonstrated that electron-spin states on single-crystal surfaces can be resolved by the UHV-ESR technique. The present technique will open up a new approach in surface science analysis.

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