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Microscopic adsorption process of CO on Si(100)$c(4\times2)$ by means of low-temperature scanning tunneling microscopy

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The microscopic adsorption process and bonding nature of CO on Si(100) have been investigated by means of low-temperature scanning tunneling microscopy and valence-band photoelectron spectroscopy, respectively. CO molecules initially adsorb at the C-defect and then start to develop as an island. Thus, the *C* defect is an inhomogeneous nucleation center for the CO island. Upon adsorption, 5σ donation dominantly occurs from CO to the silicon down dimer atom, forming a bonding state at 10.68 eV according to the valence-band photoelectron spectra. Thus, CO preferentially interacts with the electron-deficient down dimer atom.

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The understanding of chemical reactivity of the Si(100) surface is important, not only from the scientific perspective but also from technological applications, because the Si(100) surface has been used for the substrate of the most frequently used semiconductor devices. The dimer of the Si(100) surface is asymmetric[1–8] where the up dimer atom is electron rich, while the down dimer atom is electron deficient.[1–3,7,8] Thus, from the perspective of surface chemistry, the reactivity of up and down dimer atoms should be different towards the polar molecules.

When CO, which is a typical polar and Lewis-base molecule, is dosed to the Si(100)$c(4\times2)$ surface, CO chemisorbs molecularly on Si(100) below ~200 K (Refs. 9–13) and adsorbs on the down dimer atom.[12] Despite these studies, the microscopic adsorption process and the detailed bonding nature of CO on the Si(100)$c(4\times2)$ surface are poorly understood. In the present study, we investigated the microscopic adsorption process and the detailed bonding nature of CO on the Si(100)$c(4\times2)$ surface using low-temperature scanning tunneling microscopy (STM) and valence-band photoelectron spectroscopy (PES), respectively.

The experiments were performed in ultrahigh vacuum (UHV) chambers, where the base pressure was below 1×10^{-8} Pa. Boron-doped *p*-type Si(100) wafers were used in the experiments. Clean Si(100)$c(4\times2)$ surfaces were obtained after being outgassed at ~900 K for 12 h, flashed up at 1550 K several times, and cooled slowly from ~1000 K to 70 K. During flashing, the pressure was below 1.2×10^{-8} Pa to prepare an almost defect free Si(100) surface ($<0.3\%$).[14] The CO molecules were introduced into the UHV chamber through a gas doser. The STM measurements were performed with a JSPM 4500 microscope. In the STM measurements, samples were cooled at 70 K using solid N_2. Valence PES measurements were performed at BL 16B in KEK. The incident photon energy was 50 eV, and the photoelectrons were detected at a normal emission condition. The sample was cooled at 100 K and the overall instrumental resolution of this PES system was 30 meV.

Figure 1 shows a series of occupied state STM images before and after a small exposure of CO molecules to the Si(100)$c(4\times2)$ surface. For the Si(100)$c(4\times2)$ clean surface [Fig. 1(a)], the buckled dimers with $c(4\times2)$ phase are clearly observed. Bright zigzag lines are attributed to the up dimer atoms of the silicon asymmetric dimer.[4] Note that down dimer atoms of the silicon asymmetric dimer become bright when the unoccupied states are probed.[15,16] For the Si(100)$c(4\times2)$ clean surface [Fig. 1(a)], few defects (0.2%) are observed. Type-*A*, type-*B*, and type-*C* defects were reported on the Si(100) surface.[17–19] In Fig. 1(a), "Y"-shaped depressions are due to the *A*-defect[17,20]. The depressions indicated by arrows in Fig. 1(a) are due to the *C* defect because this defect becomes bright when the unoccupied states are probed.[19] For the structure of the *C* defect, we have recently reported that the *C* defect is caused by the dissociative adsorption of H_2O on the same side of two adjacent dimers; there exist Si-OH and Si-H species and two reactive dangling bonds in these two dimers.[20] It should be noted that the defect density in this study is very low (0.2%), compared with the previous STM images on the Si(100) surface (the defect density is usually a few percent).[4,21]

At the initial stage of adsorption, CO molecules are preferentially adsorbed at the *C* defect sites [Fig. 1(b)]. Since the depression area is increased as a function of exposure, these depressions can be assigned to the effect of the adsorbed CO molecules. Therefore, CO molecules are initially adsorbed at the *C* defects and then start to develop as an island structure. Since the *C* defect has very reactive dangling bonds,[20] it is likely that CO molecules initially adsorb at the *C* defect site. Note that bright protrusions are observed in the images [Figs. 1(b)–1(d)]. However, they have not been identified yet. They may be precursor species.

According to the temperature programmed desorption (TPD) study of CO on Si(100)$c(4\times2)$, two desorption peaks were observed at 210 K and 235 K, when 0.1 ML of CO was exposed to the Si(100)$c(4\times2)$ surface at 90 K,[13] where ML stands for monolayer. The intensity ratio became 1:0.07 at saturation (0.5 ML; one CO molecule per Si dimer[10]).[13] Kubo *et al.* concluded that the former one was attributed to CO adsorbed on the silicon dimer, whereas the latter one was due to CO located in defect sites; the defect site may be a more stable adsorption site than the defect free surface. Therefore, we conclude that the initial adsorption site of CO on the Si(100)$c(4\times2)$ surface is at the *C* defect.

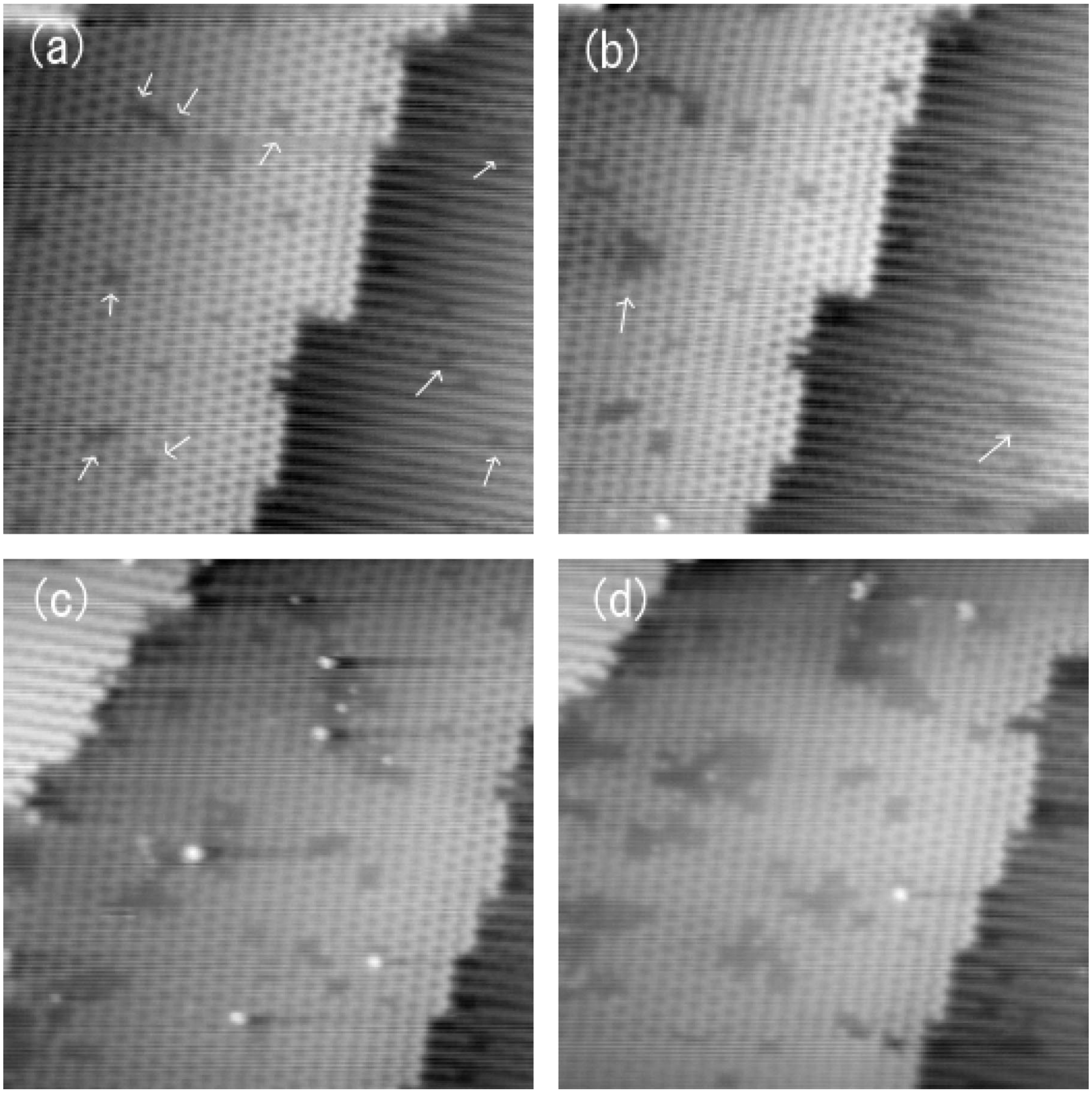

FIG. 1. A series of STM images for (a) clean Si(100)$c(4\times2)$ surface, (b)–(d) CO adsorbed surfaces after exposure of 0.02, 0.06, and 0.10 Langmuir (L), respectively. Scan area is 30×30 nm^2. All images were obtained at 70 K with the sample voltage of -1.6 V and the current of 0.09 nA. Around the *C* defects indicated by arrows in (b), island structures start to develop [compare (a) and (b)]. Slight drift occurred during the course of the experiments.

By increasing the amount of exposure [Figs. 1(c) and 1(d)], the island size increases but no isolated adsorbed CO is observed. Note that even at relatively high coverage [Fig. 1(d)], unreacted *C* defect sites are observed although the islands increases in size. Therefore, CO prefers to adsorb on the island edge than on the *C* defect site at this stage and the adsorption process may be controlled kinetically. It is assumed that when CO migrates on the surface and attaches to the edge of the island, an attractive interaction operates between adsorbed CO molecules on the Si(100) surface. Since the dipole-dipole interaction between adsorbed CO molecules is repulsive, this attractive interaction may be mediated by the Si substrate.

Figure 2 shows the coverage as a function of CO exposure at the initial stage. The coverage is estimated from the reacted area in STM images upon CO adsorption. This graph indicates that the sticking probability increases up to 0.08 L. If all the incident molecules are adsorbed and form the islands, the gradient of the plot should be unity. Therefore, at the initial stage of CO adsorption, some CO molecules may be desorbed before reaching islands or defect sites. Once the coverage becomes higher, a migrating CO molecule can reach an island within the accommodation time before desorption.

According to the previous TPD study, the CO readily adsorbs on Si(100) with a near unity adsorption probability from 0.025 ML to 0.5 ML.[11] On the other hand, the present STM study was focused on a very low coverage region (<0.05 ML). Therefore, the different adsorption behavior at the initial stage between the previous TPD study and our results may originate from the coverage region studied. It should be noted that the defect density might also play an

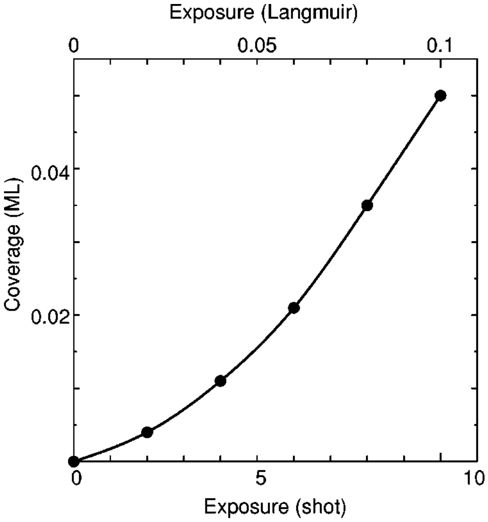

FIG. 2. The coverage as a function of CO exposure at the initial stage. The coverage was estimated from the STM images at 70 K, assuming that one CO molecule was adsorbed on one dimer.

important role in the adsorption process at the initial stage. The defect density of the Si(100) surface has usually been a few percent in most previous studies, while the defect density in this study is quite low (0.2%). If the defect density is higher, the CO molecule can easily reach a defect site within the accommodation period and then develop an island, resulting in a near unity adsorption probability even at low coverage.

Figure 3 shows a series of valence PES spectra for the Si(100)$c(4\times2)$ surface and the CO adsorbed surfaces. For the clean Si(100)$c(4\times2)$ surface, the peak due to the occupied surface state is observed at 0.8 eV below the Fermi level and several other broad peaks derive from silicon *s* and *p* bands.[22–24] Note that the density of states of the occupied surface state on Si(100)$c(4\times2)$ is mainly located at the silicon up dimer atom while that of the unoccupied surface state on Si(100)$c(4\times2)$ is localized around a down dimer atom.[1,7]

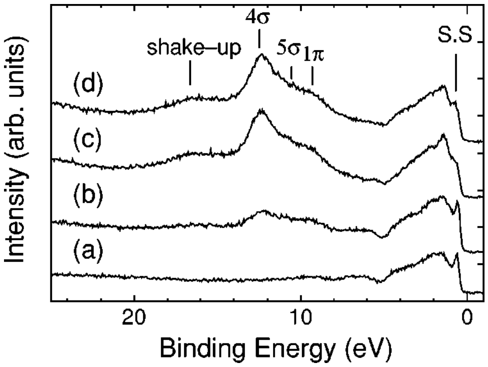

FIG. 3. The PES spectra for (a) clean Si(100)$c(4\times2)$ surface, (b)–(d) CO adsorbed surfaces after exposure of 0.08 L, 0.30 L, and 0.75 L, respectively. SS denotes the occupied surface state of Si(100)$c(4\times2)$. 0.75 L corresponds to the saturation coverage. The incident photon energy was 50 eV. The photoelectrons were detected at normal emission.

After the exposure of CO molecules [Fig. 3(b)–3(d)], new peaks are observed at 9.27, 10.68, 12.39, and 16.85 eV. The intensities of these peaks in Figs. 3(b)-3(d) monotonically increase with increasing the coverage, which is consisitent with only one adsorbed state at any coverage.[9–11]

The peaks at 9.27 and 12.39 eV can be assigned to 1π and 4σ molecular states of CO, respectively, because the binding energies of the 1π and 4σ molecular states have a similar energy level to those in the solid CO.[25] From this result, we conclude that there is little interaction of the 1π and 4σ states of CO with the Si(100) surface.

A peak at 10.68 eV is assigned to a bonding state between the 5σ molecular state of CO and an unoccupied surface state of Si(100)$c(4\times2)$ as discussed below. Kubo *et al.* report that the transition peaks at 0.9 and 1.5 eV in EELS, which were related to the unoccupied surface states, were reduced in intensity with increasing the CO coverage.[12] They conclude that CO is bonded to the Si down dimer atom. According to the previous studies, the density of states for the unoccupied surface state on Si(100)$c(4\times2)$ is mainly located at the silicon down dimer atom,[1,7] while the density of state for the 5σ of CO is mainly localized around the C atom.[26] When the bond formation occurs between CO and the Si down dimer atom, the 5σ state of CO should shift towards the higher binding energy side. Thus, we conclude that 5σ donation occurs from CO to the silicon down dimer atom. Since CO is a typical Lewis base molecule, CO is expected to interact with the electron-deficient down dimer atom. This is consistent with theoretical studies; the adsorption structure is most stable when CO adsorbs to the down dimer atom.[27–29]

A broad peak at 16.85 eV may be due to the 4σ shake-up satellite. The 4σ shake-up satellites in adsorbed CO/metal systems were observed in the binding energy region around 15 eV.[30] According to a previous study, the higher-binding energy low-intensity satellites are due to an intramolecular satellite, while the intense satellites are due to an interadsorbate-substrate excitation.[31] Here, since the peak intensity is relatively strong and the energy difference between the peak at 16.85 eV and the peak due to 4σ is small, the peak at 16.85 eV may be due to interadsorbate-substrate excitation. Since the peak at 16.85 eV is broad, the possible satellite excitation is the transition from the occupied surface state of Si(100)$c(4\times2)$ to the $2\pi^*$ unoccupied state of CO on Si(100)$c(4\times2)$ in the presence of a 4σ hole, and/or that from the occupied surface state of Si(100)$c(4\times2)$ to the antibonding state between CO 5σ and the unoccupied surface state of Si in the presence of a 4σ hole. Further theoretical studies are required to assign the satellite.

As for the occupied surface state just below E_F, the peak changes slightly upon CO adsorption; the peak shifts by 50 meV towards the higher binding energy side, the area intensity reduces to ~ 80% of that of the clean surface, and the peak width (full width at half maximum) becomes broader (from 290 meV to 400 meV) at saturation. The peak shift may be due to the change in the dimer structure upon adsorption and/or the work function change upon adsorption. The peak broadening and the change in area intensity of the peak upon adsorption may come from the electronic change in the reacted dimer. It should be noted that the ν_{CO} for adsorbed CO at 260 meV was redshifted from the gaseous CO value of 266 meV.[9] This redshift cannot be explained from the 5σ donation of CO because ν_{CO} of adsorbed CO should shift to higher vibrational energy if only the 5σ donation occurs.[32] Therefore, it is possible that the $2\pi^*$ state of adsorbed CO interacts weakly with the occupied state, resulting in the change of the occupied surface state peak as described above.

In summary, the microscopic adsorption process and the detailed bonding nature of CO on Si(100)$c(4\times2)$ were investigated by means of STM and valence-band photoelectron spectroscopy. After CO exposure, CO molecules initially adsorb at the *C* defect and then start to develop as an island. The sticking probability increases up to ~ 0.035 ML. The valence-band PES shows that 5σ donation dominantly occurs from CO to the silicon down dimer atom. Since CO is a typical Lewis base molecule, it is likely that CO preferentially interacts with the electron-deficient down dimer atom.

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