Effective Conversion of CO_2 to Carbonate in Surface Oxidation Processes at Si(100)

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It is found that effective carbonate formation occurs at a clean Si(100) surface between CO_2 and surface oxidants: N_2O and O_2. The reactions of CO_2 with N_2O or O_2 are studied by temperature-programmed desorption and X-ray photoelectron spectroscopy. CO_2 physisorbed on Si(100) desorbs exclusively at ∼75 K. However, when CO_2 is coadsorbed with N_2O or O_2, CO_2 is converted very effectively into surface carbonate species below 140 K. The carbonate species are dissociated to produce desorbed species of CO or CO_2 in the temperature range 200−600 K. By using $C^{18}O_2$, it is confirmed that the carbonate is composed of the adsorbate CO_2 and one oxygen atom from the surface oxidant. In the case of N_2O/CO_2 coadsorption, the carbonate formation is mainly induced by thermal dissociation of N_2O adsorbates. In the case of O_2/CO_2 coadsorption, the carbonate formation is not only induced by dissociative chemisorption of O_2, but also proceeded with chemisorbed dioxygen that likely adsorbs in a peroxy bridging configuration.

1. Introduction

The initial stages of silicon surface oxidation have been a subject of numerous studies.[1] In particular, the adsorption of O_2 on Si(111) and Si(100) has been extensively investigated both experimentally and theoretically. It has been well established that O_2 is dissociatively adsorbed on Si(111) and Si(100) above 300 K.[2−6] Metastable molecular precursors are considered to exist at lower temperatures (20−150 K).[3,7−9] The various structures of the precursor species including a peroxy bridging configuration have been proposed. N_2O is also used as a typical oxidant, which is a source of atomic oxygen as it dissociates at the surfaces: $N_2O(a) \rightarrow O(a) + N_2(g)$. Silicon surface oxidation with N_2O at 300 K has been investigated by Silfhout et al.[10,11] with Auger electron spectroscopy, optical reflectometry, and low-energy electron diffraction. One of the striking differences of the surface oxidation with N_2O compared with O_2 is that N_2O is no longer dissociated thermally when one monolayer oxygen coverage is formed; the oxidation is saturated at $\theta_0 = 1$ ML $(= 6.8 \times 10^{14}$ cm$^{-2})$.

We have studied the thermal dissociation process of N_2O adsorbed on a clean Si(100) surface at less than 60 K.[12] By means of temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS), it was concluded that physisorbed N_2O molecules either decompose or desorb at around 80 K, leaving oxygen adatoms and a small amount of chemisorbed N_2O molecules on the surface. Furthermore, the thermal desorption of the physisorbed N_2O is likely induced by thermal dissociation of neighboring N_2O molecules. This finding suggests that oxygen transients with excess energy released in the oxidation reaction by N_2O can induce other chemical reactions.

As for chemical reactions on metal surfaces involving O_2 or N_2O, the importance of oxygen transients generated in dissociative oxidation processes has been well established by Roberts and co-workers.[13] They have studied systematically a role of transient oxygen intermediates in oxidation reactions of ammonia, carbon monoxide, and hydrocarbons on metal surfaces. Both atomic $O^{\delta-}$ and dioxygen $O_2^{\delta-}$ transients have been shown to participate in these reactions; e.g., at Zn(0001) the dioxygen transient plays a significant role, while at Mg(0001) the atomic oxygen transient is the main participant. In contrast, few studies have concentrated on the reactivity of oxygen transients at silicon surfaces.

Recently, we reported the preliminary results on the chemical reactivity of the transient species in the course of the silicon oxidation by N_2O: surface carbonate formation between N_2O and CO_2 coadsorbed at a clean Si(100) surface.[14] In this paper, we provide a detailed study on the carbonate formation in the coadsorbed systems of N_2O and CO_2 as well as O_2 and CO_2. Here, CO_2 molecules work as a probe for the reactivity of oxygen adsorbates and transients on the silicon surface. Although various spectroscopic works performed in the past have provided information on the adsorption states of oxygen adsorbates, this approach sheds light on it from another side.

Surface chemistry involving CO_2 has not gathered much attention prior to the 1980s. This might be due to its chemical stability. However, within these two decades, several metal surfaces were found to be active to CO_2 and extensive studies have been performed recently on the interaction between CO_2 and metal single crystals.[15] In addition, it has been established that alkali metal adatoms on metal surfaces activate CO_2 leading to its dissociation and surface carbonate formation,[15] while oxygen adatoms on Ag[16] and Ni[17] metal surfaces form carbonate with CO_2. At metal oxide surfaces,[15,18] such as MgO and TiO_2, surface oxygen atoms at low-coordinated sites preferentially form surface carbonate intermediates with CO_2. The carbonate formation on these surfaces often results in extensive oxygen redistribution between CO_2 and the surface oxygen atoms.

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A clean Si(100) surface is inert to CO$_2$. CO$_2$ weakly adsorbs on Si(100) and exclusively desorbs at ∼75 K. However, we demonstrate in this paper that physisorbed CO$_2$ adsorbates on Si(100) are converted effectively to carbonate species when N$_2$O or O$_2$ is coadsorbed. The carbonate species is dissociated above 200 K to produce CO$_2$ and CO desorbed from the surface. Although the product carbonate species follow a similar reaction scheme in both two cases, i.e., N$_2$O/CO$_2$ and O$_2$/CO$_2$ coadsorption systems, the mechanism of carbonate formation seems to be different, depending on the distinct oxidation scheme of the two cases.

2. Experimental Methods

Details of the UHV system used in this study have been described elsewhere.[19] Briefly, it is equipped with a retractable LEED, a differentially pumped quadrupole mass spectrometer, an X-ray source, a photoelectron analyzer, an ion gun, a high-precision sample manipulator, a closed-cycle He refrigerator, and a gas doser. The main chamber is evacuated to a base pressure better than 1×10^{-10} Torr by cascaded turbo-molecular pumps. A Si(100) sample (Sb-doped, 0.005−0.01Ω, 9 × 20 mm^2) was mounted on a copper block and could be cooled to 45 K with the closed-cycle He refrigerator and heated above 1150 K by resistive heating. The surface was initially cleaned by repeating procedures of Ar$^+$ sputtering and annealing followed by flashing to 1150 K, which gave sharp (2 × 1) and dim c(4 × 2) LEED patterns revealing two domains below 100 K. The sample was cleaned by flashing to 1150 K after each measurement to remove oxygen adatoms on the surface.

TPD and XPS were performed in a similar manner as has been reported elsewhere.[12] $^{14}N^{15}NO$ and $C^{18}O_2$ were used for the TPD measurements to avoid large signals at $m/e = 28$ and $m/e = 44$ from the background gas. The Si crystal was kept at 45−50 K during sample gas exposures. The heating rates in the TPD measurements were programmed as 0.4 K/s and 4.0 K/s in the temperature range 50−200 and 200−900 K, respectively. XPS spectra were obtained with a Mg-Kα characteristic X-ray source and a hemispherical electron energy analyzer (40 eV pass energy).

3. Results and Discussion

A. CO$_2$/N$_2$O on Si(100). Preliminary results for the carbonate formation between CO$_2$ and N$_2$O coadsorbed on Si-(100) have been reported elsewhere.[14] Figure 1 shows TPD results in the temperature range 50−150 K at (a) $m/e = 29$ ($^{14}N^{15}N$) and (b) $m/e = 45$ ($^{14}N^{15}NO$). As shown in dotted curves in Figure 1a,b, neat N$_2$O physisorbed on Si(100) is dissociated into a desorbing N$_2$ molecule and an oxygen adatom at around 75 K. A small fraction (<10%) of N$_2$O desorbs in the same temperature range. Solid curves in Figure 1a,b are TPD results of N$_2$ and N$_2$O from Si(100) covered with the coadsorbates of CO$_2$ and N$_2$O, respectively. Although the TPD profile of N$_2$ is not affected significantly by the CO$_2$ coadsorption, the profile of N$_2$O shows clear deviations from that obtained with neat N$_2$O.

More remarkable deviations from the neat adsorption systems are observed in CO$_2$ TPD results. Figure 2 shows the TPD results of $C^{18}O_2$ ($m/e = 48$) coadsorbed with N$_2$O as a function of N$_2$O exposure. The sample was first exposed to CO$_2$ and then to N$_2$O for preparation of the coadsorption system of CO$_2$ and N$_2$O. We designate this sequence of gas exposure as N$_2$O-on-CO$_2$, and CO$_2$-on-N$_2$O if the sequence of gas exposure is reversed. In contrast to N$_2$O, CO$_2$ adsorbates do not show any reactivity on both a clean and an oxidized Si(100) surfaces.
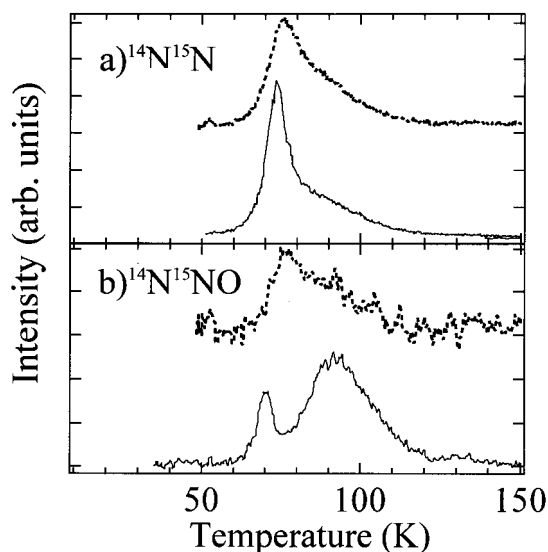

Figure 1. TPD results measured at (a) $m/e = 29$ ($^{14}N^{15}N$) and (b) $m/e = 45$ ($^{14}N^{15}NO$). Dotted curves are signals from neat N$_2$O (1.0 L) adsorbed on Si(100), and solid curves are from CO$_2$ (0.4 L) and N$_2$O (1.0 L) coadsorbed on Si(100).
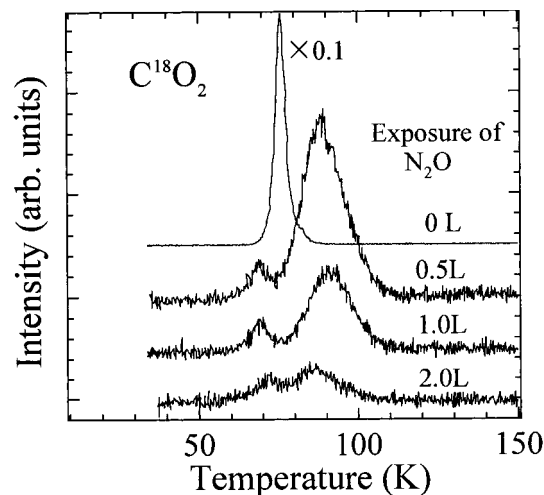

Figure 2. Series of the TPD results measured at $m/e = 48$ ($C^{18}O_2$) from CO$_2$ and N$_2$O coadsorbed on Si(100) as a function of N$_2$O exposure as indicated in the figure. The exposure of CO$_2$ was 0.4 L. The sample at 45 K was exposed to the gases. The heating rate was 0.4 K/s.

CO$_2$ weakly adsorbs on the clean Si(100) surface and shows a single desorption peak at around 75 K (Figure 2, top trace). However, with increasing N$_2$O exposure, the total intensity of the CO$_2$ peak in this temperature range is strongly depleted. The quenching of the CO$_2$ signal is due to the formation of surface carbonate, which is stable to 200 K, as will be shown below.

The direct evidence for the surface carbonate formation was given by measurements of C(1s)-XPS and TPD in the higher temperature range. Figure 3a−c shows C(1s)-XP spectra taken from the Si(100) surface exposed to CO$_2$ and N$_2$O as a function of annealing temperature. The C(1s) peak from the surface without annealing appears at 292 eV which is identical to the C(1s) peak of neat CO$_2$ physisorbed on Si(100). After annealing to 140 K, the C(1s) peak shifts to 291 eV and the spectral line becomes slightly broadened. This peak disappears completely by annealing to 600 K. The binding energy of 291 eV is in good agreement with the one assigned to surface carbonate formed on aluminum surfaces.[20]
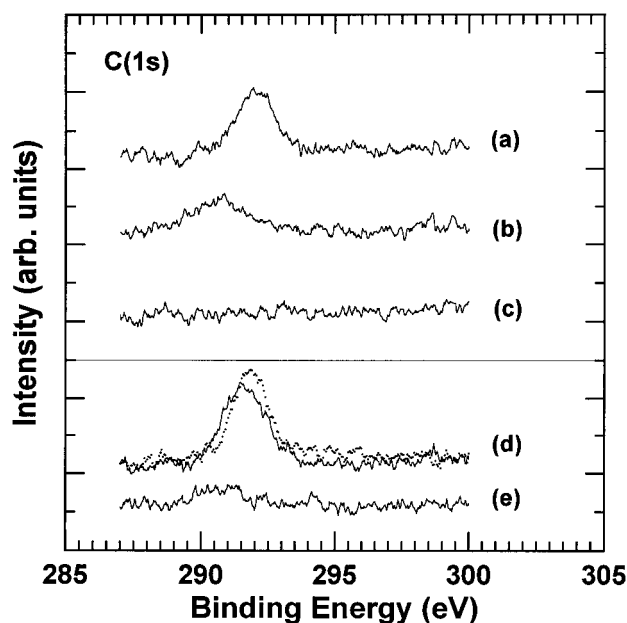
Figure 3. (a)−(c): XP spectra of C(1s) taken from Si(100) exposed to CO_2 (0.4 L) and N_2O (1.0 L) as a function of annealing temperature. After the surface at 45 K was exposed to gases, it was annealed and cooled to 45 K again and then the spectra were obtained. The annealing temperatures are (a) 0 K (without annealing), (b) 140 K, and (c) 600 K. (d) and (e): XP spectra of C(1s) taken from Si(100) exposed to CO_2 (0.72 L) at 50 K. Before the CO_2 exposure, the sample was exposed to 2.0 L N_2O at 50 K and annealed to 90 K. The spectra were obtained immediately (d) after CO_2 exposure, and (e) after subsequent annealing to 140 K and cooling to 50 K. The dotted curve is the C(1s)-XP spectrum of physisorbed CO_2 (0.72 L) on Si(100) at 50 K.
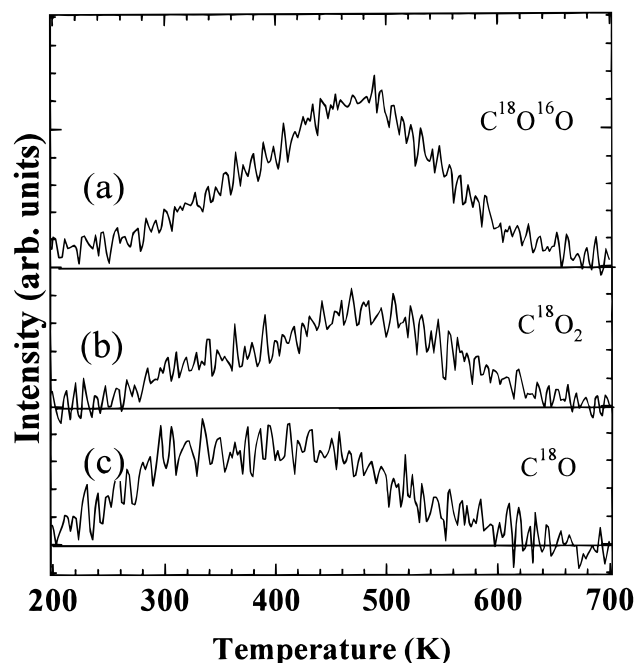

Figure 4. TPD results measured at (a) $m/e = 46$ ($C^{18}O^{16}O$), (b) $m/e = 48$ ($C^{18}O_2$), and (c) $m/e = 30$ ($C^{18}O$) taken from Si(100) exposed to CO_2 (0.4 L) and N_2O (1.0 L). The heating rate was 4.0 K/s.

Figure 4 shows TPD results in the temperature range 200−700 K obtained by monitoring $C^{18}O^{16}O$ ($m/e = 46$), $C^{18}O_2$ ($m/e = 48$), and $C^{18}O$ ($m/e = 30$) from Si(100) covered with $C^{18}O_2$ and $N_2^{16}O$. The absence of detectable N(1s) signals in the XPS measurement after flashing to 150 K (not shown) excludes contribution from $^{14}N^{16}O$ to the signals at $m/e = 30$. The
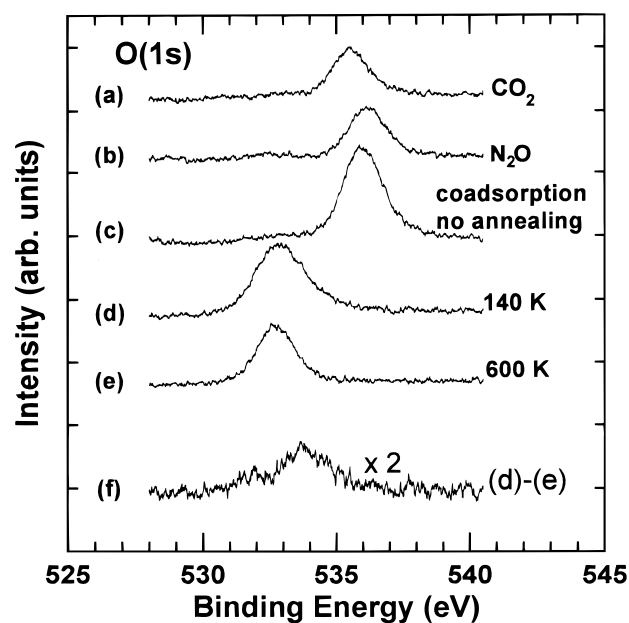

Figure 5. XP spectra of O(1s) taken from Si(100) exposed to (a) CO_2 (0.4 L), (b) N_2O (1.0 L), and (c) CO_2 (0.4 L) and N_2O (1.0 L). The sample at 45 K was exposed to the gases. The traces in (d) and (e) are O(1s) spectra obtained after annealing the Si(100) surface coadsorbed with CO_2 (0.4 L) and N_2O (1.0 L) to 140 and 600 K, respectively. The trace in (f) is the result obtained by subtracting the spectrum in (e) from the spectrum in (d).

desorption profile peaking at ∼470 K of $C^{18}O_2$ is very similar to that of $C^{18}O^{16}O$. The integrated intensity ratio, $C^{18}O_2$: $C^{18}O^{16}O$, is approximately 1:2. The TPD result of $C^{18}O$ shows a broad peak around 350 K. The observed desorption of CO_2 and CO is consistent with the disappearance of C(1s)-XPS signals at 291 eV in the range 140−600 K (Figure 3). Thus, these desorbed species are produced by decomposition of carbonate species. The significant oxygen isotope mixing in CO_2 indicates that the carbonate formation occurs between CO_2 and an oxygen atom released from N_2O. Reversing the sequence of gas exposures did not give any significant differences in the obtained results.

The carbonate formation also manifests itself in O(1s)-XP spectra as shown in Figure 5. Neat CO_2 and neat N_2O adsorbed on Si(100) give O(1s) spectra peaked at 535.5 and 536 eV, respectively (Figure 5a,b). The spectrum of the coadsorbed system without annealing (Figure 5c) can be regarded as a simple summation of the O(1s) spectra of neat CO_2 and neat N_2O; this indicates that sticking probability and the adsorption state of each adsorbate are not affected by its coadsorbate. Annealing of the coadsorbed surface to 140 K leads to a shift of the O(1s) peak to 533 eV (Figure 5d), apparently corresponding to the formation of silicon oxide. Note that the intensity at the higher binding energy side of the O(1s) peak is decreased by further annealing to 600 K (Figure 5e). This change is more clearly shown in the difference spectrum of Figure 5f. The integrated intensity of the O(1s) signal observed at the annealing temperature of 600 K decreases to 70% of that observed at 140 K. Considering the desorption of CO_2 and CO in the range 200−600 K shown in Figure 4, we believe that the intensity loss at ∼534 eV is due to the decomposition of carbonate formed below 140 K.

We also examined the carbonate formation and the oxygen-exchange reactions on a fully oxidized Si(100) surface. The oxidized surface was prepared by repeating the procedure of saturation with N_2O at 45 K and annealing the Si(100) surface
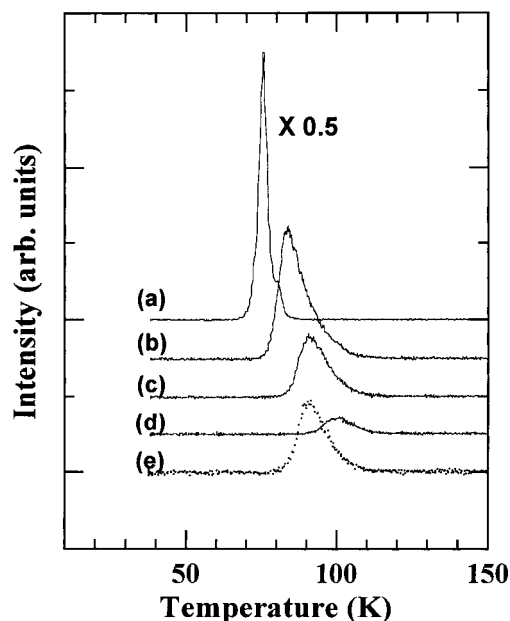
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Figure 6. TPD results measured at $m/e = 48$ ($C^{18}O_2$) from CO_2 (0.4 L) and O_2 coadsorbed on the Si(100) surface. The O_2 exposures were (a) 0 L, (b) 0.25 L, (c) 0.5 L, (d) 1.0 L, and (e) 1.0 L. The surface at 45 K is exposed first to CO_2 and then to O_2, except for the trace (e), in which the order was reversed.

Figure 7. XP spectra of C(1s) taken from Si(100) exposed at 40 K to (a) CO_2 (0.4 L) only, and (b) CO_2 (0.4 L) and O_2 (1.0 L). The spectra (c) and (d) were obtained after annealing of the Si(100) surface coadsorbed with CO_2 and O_2 to (c) 140 K, (d) 600 K, respectively, and cooling to 40 K. The surface was first exposed to CO_2 and then to O_2.

to 500 K a few times. CO_2 and N_2O coadsorbed on the oxidized Si surface are desorbed completely at 110 K. No depletion of the CO_2 desorption peak due to coadsorption of N_2O was observed. Besides, the desorption signals of CO and CO_2 in the temperature range 200−700 K were not detectable. It has been known that N_2O adsorbates do not decompose on the fully oxidized Si(100) surface.[12] Therefore, the thermal dissociation of N_2O adsorbates must play a key role in the formation of the surface carbonate species in the coadsorbed system.

B. O₂/CO₂ on Si(100). Carbonate formation also occurs between O_2 and CO_2 at Si(100). Figure 6 shows TPD results at $m/e = 48$ ($C^{18}O_2$) in the temperature range 50−150 K as a function of O_2 exposure. The sequence of the sample gas exposure was first CO_2 and second O_2, except for Figure 6e. The TPD peak of CO_2 is strongly quenched and slightly shifted to the higher temperature with increasing O_2 exposure.

Figure 7 shows C(1s)-XP spectra of neat CO_2 and O_2/CO_2 on Si(100) with various annealing temperatures. Exposure of O_2 onto the CO_2-precovered Si(100) surface induces a shift of the C(1s) peak from 292 to 291 eV, indicating that carbonate formation occurs as in the case of N_2O/CO_2. The C(1s) peak intensity decreases with increasing annealing temperature and disappear completely when the surface is annealed to 600 K. It is worth noting that the C(1s) peak shift occurs even at 40 K, without annealing of the coadsorbed surface. This is quite distinct from the case of N_2O/CO_2, where the carbonate formation was not realized unless the surface is annealed to induce thermal decomposition of N_2O.

Figure 8 shows TPD results of $C^{18}O^{16}O$ ($m/e = 46$), $C^{18}O_2$ ($m/e = 48$), and $C^{18}O$ ($m/e = 30$) from Si(100) covered with $^{16}O_2$-on-$C^{18}O_2$ in the temperature range 200−700 K. As in the case of N_2O/CO_2, CO_2 and CO are desorbed and the significant oxygen isotope mixing takes place. The TPD results representing the decomposition of carbonate are quite like those observed in the case of N_2O/CO_2. Although the formation mechanism of carbonate seems to be different, the features of desorption, dissociation, and the isotope mixing of carbonate are almost the same in these two cases.
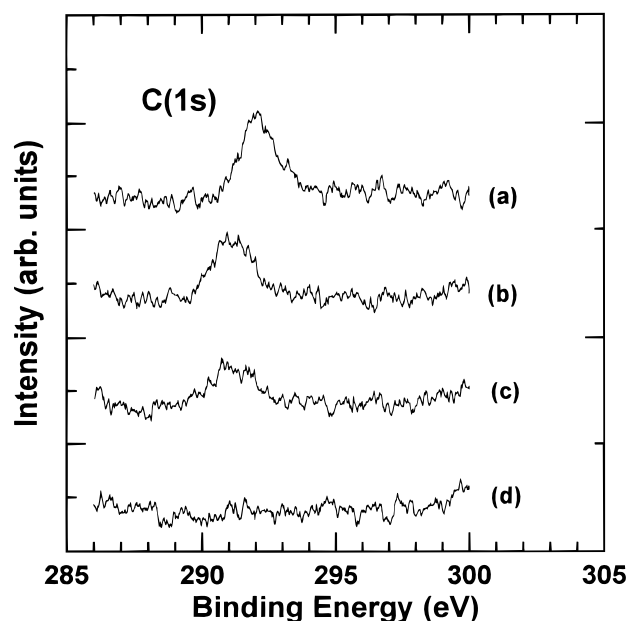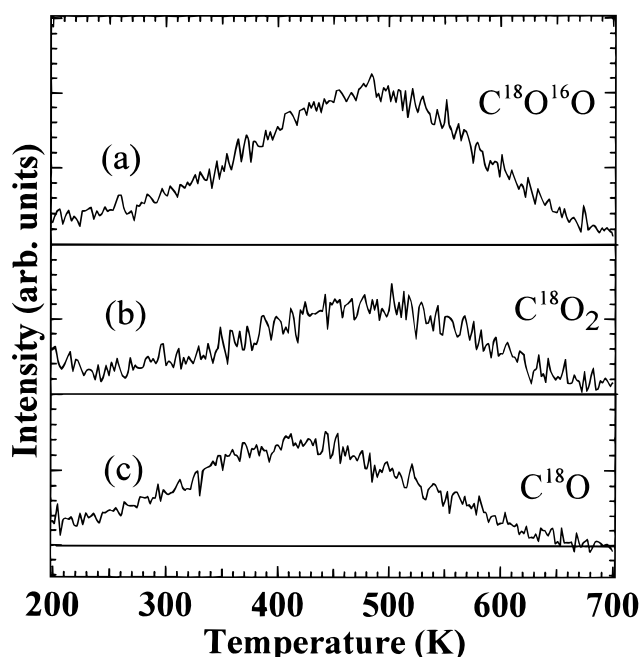

Figure 8. TPD results measured at (a) $m/e = 46$ ($C^{18}O^{16}O$), (b) $m/e = 48$ ($C^{18}O_2$), and (c) $m/e = 30$ ($C^{18}O$) taken from Si(100) exposed to CO_2 (0.4 L) and O_2 (1.0 L). The surface was first exposed to CO_2 and then to O_2. The heating rate was 4.0 K/s.

Figure 9 shows a comparison of O(1s)-XP spectra of O_2/CO_2 coadsorbates with those of neat adsorbates. The bottom traces in Figure 9 show O(1s)-XP spectra taken from Si(100) adsorbed with O_2-on-CO_2 (solid curve) and CO_2-on-O_2 (dotted curve). These spectra show the peak at 533 eV due to silicon oxide and an additional shoulder at 535 eV due to CO_2. Since the integrated intensity of the spectral line is the same in the two spectra, the sticking coefficients of these gases are irrelevant to the exposure sequence. Note that the shoulder at 535 eV is more pronounced for CO_2-on-O_2 than O_2-on-CO_2, indicating
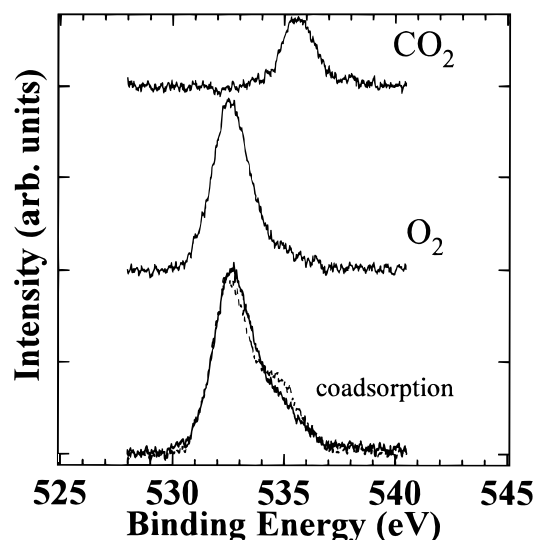
Figure 9. XP spectra of O(1s) taken from Si(100) exposed at 50 K to CO_2 (0.4 L) (top trace), O_2 (1.0 L) (middle), and both CO_2 (0.4 L) and O_2 (1.0 L) (bottom). In the bottom traces, the order of gas exposure was first CO_2 and second O_2 for the solid curve, and reversed for the broken curve.

that the conversion of CO_2 to carbonate in the former is less effective than the latter. This behavior is more clearly seen in the TPD results of CO_2 in Figure 6e. The CO_2-TPD in the case of CO_2-on-O_2 shows less quenching of CO_2 signals than in the case of O_2-on-CO_2. As is expected, the TPD signal intensity of CO_2 and CO in the temperature range 200−700 K in the case of CO_2-on-O_2 (not shown) decreased to ∼60% compared with that of O_2-on-CO_2, while the desorption profile was not affected by the exposure sequence. Therefore, the carbonate formation is more effective in O_2-on-CO_2 than CO_2-on-O_2.

C. Reaction Mechanisms. *(i) N_2O/CO_2.* The experimental results show that once an oxygen atom produced by dissociation of N_2O forms stable covalent Si−O bonds, it does not show any reactivity to CO_2 to form the surface carbonate. This is quite different from the oxygen-precovered Ag(110), Ni(100), and the metal oxide surfaces such as MgO and TiO_2, where oxygen-exchange reactions readily take place via surface carbonates. Therefore, the carbonate formation should be accomplished before produced oxygen atoms lose the reactivity by forming the stable covalent bonds with silicon atoms.

On ammonia activation process at Mg(0001) surfaces by nitrous oxide,[21] it has been established that surface transient oxygen generated by N_2O dissociation, which has not been thermally accommodated, is a significant participant of the reaction. Since the silicon oxide formation is largely exothermic, N_2O dissociation generates a hot oxygen atom with a large translational energy or a vibrationally excited Si−O bond. Thus, similar to the case of Mg surfaces, a reaction between CO_2 and the transient hot oxygen species may take place before its excess energy is completely dissipated to form stable silicon oxide. This mechanism is energetically favored if a large energy barrier exists along the reaction coordinate for the carbonate formation.

Another important factor for the carbonate formation is electron density at the oxygen atom to be reacted with CO_2. It is known that CO_2 reacts effectively with a molecule or an ion with lone pair electrons because of electron deficiency at a carbon atom of CO_2. Thus, negatively charged oxygen atoms are electronically favored for the carbonate formation.

In the study of the adsorption states and thermal reactions of N_2O on Si(100),[12] we showed that physisorbed N_2O is converted to more strongly bound chemisorbed states when the surface is

partially oxidized by the dissociation of other N_2O molecules. The O(1s) peak of the chemisorbed species is shifted to the lower binding energy by 0.9 eV, indicating that some electron transfer takes place from the substrate to the adsorbate in the chemisorbed states. Thus, the chemisorbed states of N_2O existing on the partially oxidized surface suggests that the dissociation of physisorbed N_2O takes place via a negatively charged transient intermediate, N_2O^-, induced by electron transfer from the substrate. In the gas phase, it is well-known that N_2O^- is dissociated to O^- and N_2.[22] Involvement of N_2O^- species in N_2O photodissociation has been also proposed in the study of photochemistry of N_2O on Si(100).[23,24] Note that the TPD results of N_2O in Figure 1 and CO_2 in Figure 2 become very similar to each other when those molecules are coadsorbed. This may imply that weakly bound complexes of N_2O and CO_2 are formed in the coadsorbed system. Thus, one possible reaction pathway is that carbonate is formed from the complexes between CO_2 and N_2O in a concerted fashion with the cleavage of the N_2−O bond via the intermediate N_2O^-.

Even after physisorbed N_2O is dissociated, carbonate formation takes place on the partially oxidized surface. To demonstrate this activity of the surface, we performed the following measurements. The N_2O precovered Si(100) surface was annealed to 90 K, quenched to 50 K, and then exposed to CO_2. Figure 3d shows the C(1s)-XP spectrum obtained from this surface. Most of N_2O molecules decompose below 90 K and Si−O bonds are formed. The XP spectrum shows a slight peak shift to the lower binding energy as compared to that of CO_2 physisorbed on clean Si(100). This shift indicates that part of the CO_2 molecules are converted to carbonate on this surface and the carbonate C(1s) peak at 291 eV overlaps on the physisorbed CO_2 peak (292 eV). After further annealing of this surface to 140 K, only the carbonate C(1s) peak is left (Figure 3e). On the other hand, when the N_2O-precovered surface is annealed to 400 K instead of 90 K, CO_2 exposure on this surface at 45 K brings about just the same C(1s) spectrum as CO_2 physisorbed on clean Si(100).

There are two ways to account for the carbonate formation on the partially oxidized surface. (1) Since some of N_2O molecules are converted to chemisorbed N_2O^- species when N_2O molecules decompose and desorb at 90 K, the chemisorbed N_2O^- species may proceed to form carbonate via complex formation with CO_2. (2) Some of metastable oxygen atoms remain in distorted Si−O−Si bridges, unfavorable bond distances, or even unsaturated bonds as suggested by Morgen et al.[7] may be responsible for the carbonate formation. The metastable oxygen adatoms could fall into stable bridging configurations by relaxation of bond distortions during the annealing process. Thus, the partially oxidized surface becomes inactive for carbonate formation after annealing to >400 K.

(ii) O_2/CO_2. The initial stage of the reaction of oxygen with Si(100) at low temperature (T ∼ 20 K) has been investigated by Silvestre et al.[8] with high-resolution electron energy loss spectroscopy (HREELS) and work function measurements. Other than monatomic bridging oxygen species, they observed physisorbed molecular oxygen below 35 K, and deduced from the work function measurements that dioxygen species adsorb at peroxy bridging configurations to 90 K. The absence of corresponding HREELS peaks led them to exclude the existence of monatomic or diatomic nonbridging oxygen and peroxy radical dioxygen.

As shown in the TPD (Figure 6) and O(1s)-XPS (Figure 9) measurements, the reaction yield in the case of O_2-on-CO_2 is higher than that of CO_2-on-O_2. Since it is likely that O_2 adsorbs

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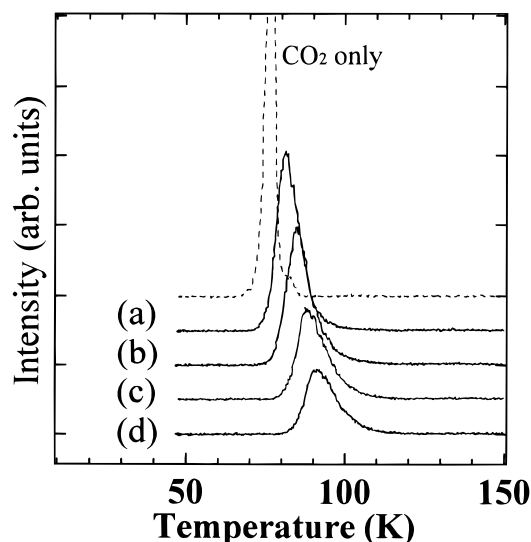*J. Phys. Chem. B, Vol. 102, No. 41, 1998* **8047**

Figure 10. TPD results measured at $m/e = 48$ ($C^{18}O_2$) from the Si-(100) surface exposed to CO_2 (0.4 L) at 50 K. Before CO_2 exposure, the surface was exposed to 1.0 L of O_2 and subsequently annealed to (a) 500 K, (b) 200 K, (c) 100 K, and (d) 50 K (no annealing). The top trace (broken curve) is a CO_2 TPD trace obtained with CO_2 (0.4 L) exposure onto a clean Si(100) surface.

Figure 11. XP spectra of O(1s) taken from Si(100) exposed to O_2 (1.0 L) and annealed to various temperatures. The annealing temperatures were (a) 50 K (no annealing), (b) 100 K, (c) 200 K, and (d) 500 K. The measurements were done with cooling to 50 K after respective annealing.

dissociatively on the CO_2-precovered surface at 40 K, this exposure−sequence dependence implies that the carbonate formation is induced by the dissociation of the oxidant as in the case of N_2O/CO_2 coadsorption. However, this is not the only way for carbonate formation in the coadsorbed system. Oxygen adsorbates thermally accommodated are also effective in carbonate formation, since carbonate species are also formed in the case of CO_2-on-O_2 at 40 K. We tried to identify the oxygen adsorbates accommodated with the surface by examining their thermal stability.

The oxygen adsorbates, which are active to the carbonate formation, lose their reactivity with subsequent annealing. Figure 10 shows TPD traces of CO_2 exposed at 50 K onto the O_2-precovered Si(100) surface; the surface is exposed to O_2 at 50 K and subsequently annealed to various temperatures prior to CO_2 exposure. CO_2 signal intensity in the temperature range 50−150 K increases with the annealing temperature of the O_2-precovered surface; the carbonate formation yield decreases with an increase of the annealing temperature. Desorption signals of CO_2 and CO in the higher temperature range (200−600 K) decrease with increase of the annealing temperature, which is consistent with the TPD results in the lower temperature range. Figure 11 shows the O(1s)-XP spectra taken from the Si(100) surface that was exposed to O_2 at 50 K and subsequently annealed to various temperatures. The spectra show slight peak shifts to a higher binding energy and narrowing with an increase of the annealing temperature. These spectral changes may correspond to the thermal conversion of oxygen adsorbates active in carbonate formation to inactive species. The peak shift to the higher binding energy indicates the loss of excess negative charge on the adsorbate. Thus, the oxygen adsorbates reactive to CO_2 to form carbonate are in electron-rich states, and subsequent annealing converts them into less negatively charged states.

According to the characterization of the initial oxidation process by Silvestre et al.,[8] one possible candidate for the reactive oxygen species is the peroxy bridging oxygen. Its negatively charged character would be important in promoting the carbonate formation because of electron deficiency at a carbon atom of CO_2. The loss of its reactivity with annealing
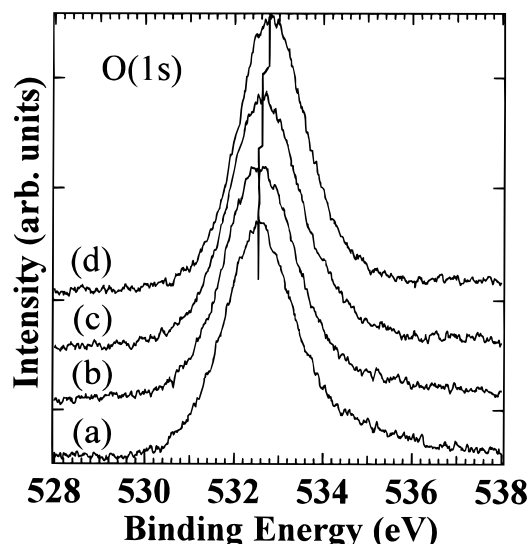
would be due to the irreversible conversion of the peroxy bridging oxygen to monatomic bridging oxygen (Si−O−Si). The O(1s)-XPS shift of oxygen-precovered surface by subsequent annealing (Figure 11) may correspond to this thermal conversion of peroxy bridging oxygen.

4. Summary

Effective carbonate formation associated with the surface oxidation processes at Si(100) surfaces has been confirmed by TPD and XPS measurements. At both N_2O/CO_2 and O_2/CO_2 coadsorbed Si(100) surfaces, significant conversion of physisorbed CO_2 into surface carbonate was observed. The produced carbonate decomposes in the range 200−600 K, and CO_2 and CO are desorbed as its fragment in this temperature range. These TPD profiles are almost identical in the N_2O/CO_2 and O_2/CO_2 coadsorption systems, suggesting that the adsorption state of the carbonate species is almost the same in the two cases. Obviously, detailed spectroscopic studies such as HREELS are needed for further understanding the structure of the carbonate species on Si(100).

The dissociation of oxidants is a key process in carbonate formation for the two coadsorption systems. Although the details of the reaction pathway are still unresolved, negatively charged species play an important role in the processes of carbonate formation. The production of negatively charged species in the case of N_2O/CO_2 is associated with the dissociation of N_2O adsorbates at 75 K. On the other hand, there exist the negatively charged oxygen adsorbates such as peroxy bridging dioxygen even at 40 K in the case of O_2/CO_2.

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