Interfacial Reaction during Thin Film Growth of Ti on the MgO(001) Surface

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The reaction mechanism of Ti adsorbed on the MgO(001) surface has been investigated using coaxial impact collision ion scattering spectroscopy (CAICISS) and reflection high energy electron diffraction. It is found that Ti is incorporated into at least four layers of the surface through the substitutional sites of the Mg ions even at room temperature. The diffusion of Ti occurs without disorder of the MgO lattice. After 1270 K annealing, the Ti atoms, existing in the outermost layer, form a 2×2 superstructure, where no protrusion or submergence of the substituting Ti occurs from the original MgO surface. The MgO surface with the incorporated Ti ions does not suffer the charging problems during the measurement of CAICISS. This is due to the emergence of electric conduction at the surface which is confirmed in situ by a 2-pin method.

The metal−oxide interfaces have attracted attention owing to the basic physical and chemical problems they pose, in addition to the importance in various fields of technology. Applications of metal−oxide systems include solid-state gas sensors, crystal growth, and heterogeneous catalysts. In these application fields, metal−oxide interactions play important roles. For example, metal particles adsorbed onto metal oxides have been found to alter the response of the surface electric conductivity of those oxides to adsorbed gases, and this is the basic mechanism of the gas sensor operation. Furthermore, the metal−oxide interactions have been claimed to cause atomic rearrangement such as superstructure formation, ternary oxide formation, and intermixing especially on the reducible metal oxide surfaces. This surface reaction on the metal oxide surfaces strongly affects the catalytic properties. By contrast, to our best knowledge, no reaction has been reported at the metal/MgO-(001) systems, which are most frequently studied among metal−oxide systems. MgO has a rock-salt crystal structure, and the MgO(001) surface is believed to be chemically inert and stable. In theoretical approaches to the metal/MgO systems, the possibility of interfacial reaction has been excluded.

In the present letter, the adsorption of Ti on the MgO(001) surface is reported in the region of the submonolayer coverage. It was found that the Ti adsorbates on the MgO were incorporated into the bulk even at room temperature (RT) through the Mg substitutional sites without inducing significant disorder in the MgO lattice. The Ti diffusion, as a result of the substitution between the cation sites, was activated by annealing. Most of the Ti adatoms disappeared from the MgO outermost surface because of this interdiffusion mechanism after annealing at 1270 K, but a part of the Ti atoms remained on the surface even after the heat treatment, and these remaining Ti atoms formed a 2×2 superstructure.

The experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure of 3×10^{-10} Torr) equipped with coaxial impact collision ion scattering spectroscopy (CA-ICISS)[2] and reflection high energy electron diffraction (RHEED). The most striking feature of the former is the scattering angle

of $180°$ ($\pm 1.5°$). This scattering condition enables to determine the atomic positions not only at an outermost surface but for a few deeper layers. The time-of-flight (TOF) spectra were taken in the CAICISS measurements using 2 keV He$^+$ ions, where the path length of scattered particles from a sample to a microchannel plate was 60 cm. The detection of both ions and neutrals successfully avoids the ion neutralization problems,[3] so that the CAICISS peak intensity simply gives the scattering cross-section, depending on the surface atomic composition and arrangement. Sample charging during the ion irradiation was avoided by electron compensation using a tungsten filament placed behind the sample. The temperature of the substrate, fixed on the tantalum plate, was varied from RT to 1270 K by electron bombardment from the samples behind. The single crystalline MgO substrate was introduced into the UHV chamber just after the cleavage in the air. The substrate was cleaned by annealing at 1070 K for 10 min in UHV. The amount of Ti evaporated thermally was monitored using quartz crystals, and the deposition rates were controlled to be $0.5 \sim 0.8$ Å/min.

Figure 1 shows the Mg peak intensity (a) from the clean MgO(001) surface and the Ti peak intensities (b)−(e) from the Ti-deposited MgO(001) surface in the CAICISS measurements as a function of the incidence angle α along the [110] azimuth, together with the RHEED patterns ((f)−(i)). The Ti was deposited at RT with coverage of 0.8 monolayer (ML), where 1 ML corresponds to the total atomic density in the MgO(001) plane. The CAICISS intensity increases in the special geo-metrical arrangement of the constituent atoms, where the edges of shadow cones intersect the center of the target atoms (a focusing effect). This occurs in the condition of the four peaks at $18°$, $26°$, $46°$, and $74°$ in Figure 1, which are attributed to the focusing effects of He on the Mg ions in the first, second, third, fourth, and deeper layers, respectively.[4] It should be noted that the peak positions for Ti in Figure 1 (b) agree exactly with those of Mg in (a). This fact signifies that the adsorbed Ti atoms are located at the Mg ion sites for more than 4 layers of the surface, thus showing the incorporation of the adsorbed Ti via the Mg ion sites into at least the fourth internal layer of the MgO surface even at RT. Such diffusing Ti atoms are thought to be distributed randomly among the Mg substitutional sites,

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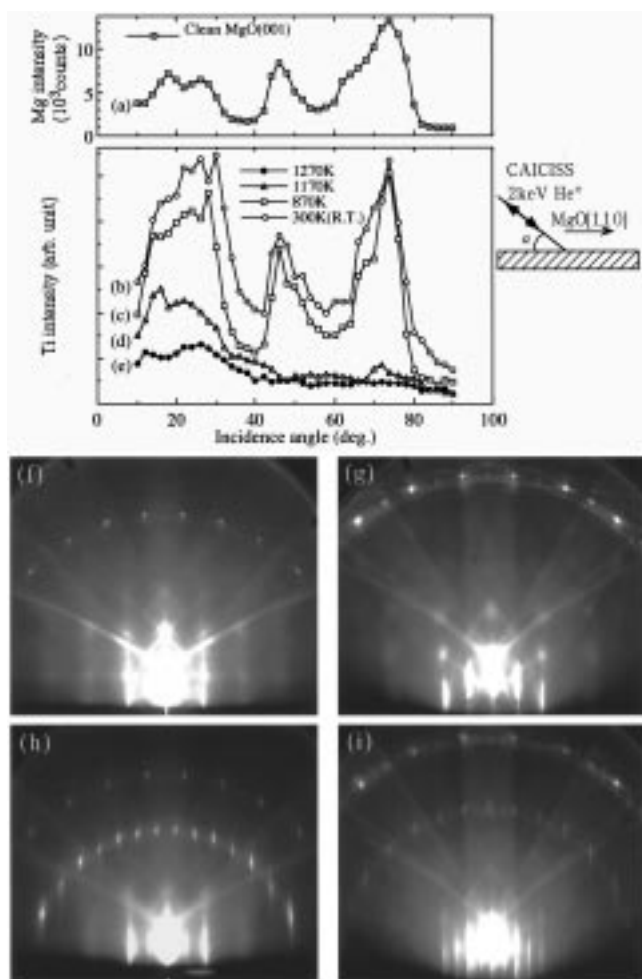
Figure 1. CAICISS α scans of Mg of the MgO clean surface (a) and Ti of the Ti (0.8 ML) deposited MgO surface (b)−(e) taken along the [110] azimuth. The spectra (b)−(e) were obtained continuously after step-by-step annealing at each temperature for 10 min, normalized by the Mg peak intensities in the normal incidence condition. The RHEED patterns indicate the 1×1 structure of a MgO clean surface for (f) and (g), and a 2×2 superstructure observed after heat treatment at 1270 K for (h) and (i). The incident electron was parallel to [100] for (f) and (h), and [110] for (g) and (i).

since the RHEED pattern changes into a slightly broadened 1×1 structure from a sharp 1×1 pattern of the clean MgO surface which is shown in Figures 1 (f) and (g). Figures 1 (b)−(e) show the effects of the sample annealing on the Ti intensity variations in the CAICISS α scan measurements. No specific change in the peak structure occurs after annealing at 870 K. By contrast, the 46° peak (the 74° peak) disappears after 1170 K (1270 K) annealing for 10 min. These two peaks are formed by the focusing effects for Ti located at the third layer and the fourth and deeper layers, respectively. The disappearance of the peaks at 46° and 74° is not due to the desorption of the Ti, because the intensity of the peak at 46° decreases prior to the peak at 74°. The series of the α scan measurements shown in Figure 1 indicate that the flux of the diffusing Ti atoms is in the direction from the surface to the bulk of the MgO substrate. Thus, the four spectra (b)−(e) in Figure 1 clearly indicate the activation of the Ti diffusion into the MgO bulk, which is the result of the heat treatment.

The peak angles observed in Figures 1 (b)−(e) agree well each other, indicating that the diffusion of Ti is not accompanied by the significant disorder of the MgO lattice. The Ti peak intensity at 90° in Figure 1 comes from the first-layer Ti atoms,
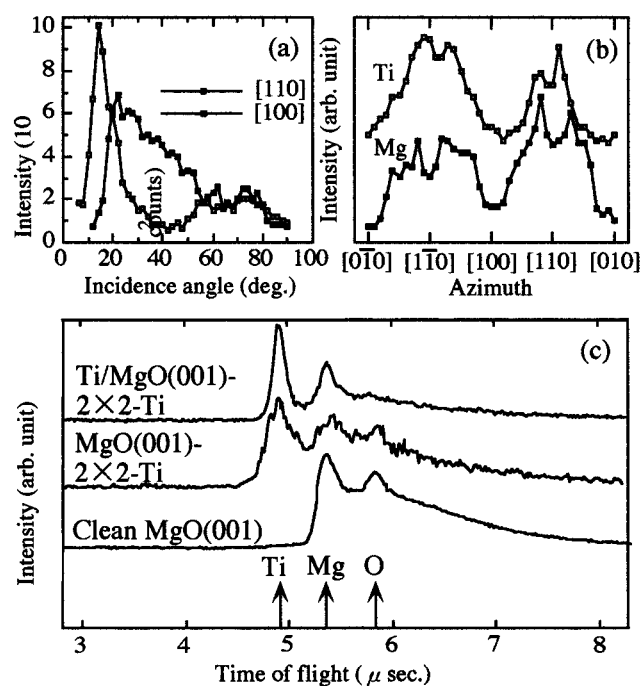
Figure 2. (a) Intensity variations of Ti in the CAICISS α scan measured at the 2×2 superstructure surface. The spectra were taken along the [100] and [110] azimuths. The sample surface was prepared by the Ti deposition (1.7 ML) on the MgO maintained at 1070 K. (b) Intensity variations of Ti and Mg in the CAICISS azimuthal angle scan measured at the same sample as (a). The incidence angle α was fixed at 20°. (c) The TOF spectra under the normal incidence condition obtained at the MgO clean surface, the MgO-2×2-Ti surface, and the surface prepared by Ti deposition (0.5 ML) on MgO-2×2-Ti surface maintained at 870 K (Ti/MgO(001)-2×2-Ti). The peak positions of Ti, Mg, and O are indicated by arrows. The absence of the oxygen peak at the spectrum of Ti/MgO(001)-2×2-Ti is due to the preferential shadowing by the Ti adatoms on the MgO-2×2-Ti surface. This indicates that the Ti adatoms are situated on the top sites of oxygen.

because the atoms located at the second and deeper layers do not contribute to the surface peak intensity because of the shadowing effects. The decrease of the Ti intensity by the step-by-step annealing in Figure 1 is mainly due to the interdiffusion of Ti, although the desorption of Ti from the surface may also be possible. The Ti atoms, remaining at the first and second surface layers even after annealing at 1270 K, form a 2×2 superstructure as shown in the RHEED patterns of Figures 1 (h) and (i).

Figures 2 (a) and (b) show the incidence and azimuthal angle dependencies, respectively, of the CAICISS intensity from a MgO-2×2-Ti surface which is prepared by the deposition of Ti with 1.7 ML on the substrate maintained at 1070 K. In Figure 2 (a), the conspicuous intensity increase at α = 14° and 22° for the [110] and [100], respectively. These peaks are due to the focusing effect on the Ti existing at the outermost layer. On the other hand, the quite similar intensity variations between Ti and Mg in Figure 2 (b) indicate that Ti is located at the substitutional sites of the Mg ions at the outermost surface. In comparison between Figure 1 (e) and Figure 2 (a), the peak at 25° which is due to Ti located at the second surface layer is missing completely in the latter. This is the result of more effective diffusion of Ti at the sample surface corresponding to Figure 2 (a) than that of Figure 1 (e). No protrusion or submergence of the Ti which is substituted for Mg occurs from the original MgO outermost surface, because the critical angles of the main peaks in Figure 2 (a) agree with that of the Mg at the clean surface for both azimuths.

Figure 2 (c) shows the normal incidence CAICISS spectra obtained at the MgO clean surface, the MgO-2×2-Ti surface, and the surface prepared by Ti deposition (0.5 ML) on the MgO-2×2-Ti surface maintained at 870K (Ti/MgO(001)-2×2-Ti). The surface of Ti/MgO(001)-2×2-Ti exhibited a 1×1 structure in the RHEED pattern (not shown). In the spectrum of Ti/MgO-(001)-2×2-Ti, the O peak almost disappears. This disappearance of the O peak is due to the shadowing effect for the O atoms by the additionally adsorbed Ti atoms on the superstructure surface. Thus, the spectra of Figure 2 (c) indicate that the Ti adsorbing on the 2×2 surface sits on the top sites of oxygen of the substrate surface.

The present study indicates that Ti is stable in the bulk of MgO rather than the surface. Colborn et al. theoretically investigated the stability of free dopants in MgO with considering the electrostatic and polarization forces.[5] They predicted that the four-valent Ti ions have lower substitution energy in the bulk of MgO compared with the surface. As mentioned already, Ti of the MgO-2×2-Ti surface is substituted for the Mg ions in the outermost layer of the MgO surface without protrusion or submergence from the MgO original surface. This result correlates to the fact that the ionic radius of Ti^{4+}(0.68 Å) is very close to Mg^{2+}(0.65 Å). The small difference in the ion size enables the substitution of Ti^{4+} for Mg^{2+} without producing the strain energy in the MgO lattice. In our former study, the ion size effect in the strain energy was shown to play a significant role in surface segregation phenomena.[6] Moreover, if the Ti which is substituted for Mg at the topmost MgO surface is not in four-valent state, the protrusion of Ti is thought to be observed. It is thus suggested that the Ti which is substituted for Mg is in four-valent state as Colborn's prediction. To maintain the local charge neutrality in MgO in which Ti is substituted for a part of Mg, some interstitial oxygen or the Mg vacancies may surround substitutional Ti.

In terms of electric properties, it should be noted that during the measurements of CAICISS, the Ti-deposited MgO surface did not suffer charging problems. However, the charging problems reappeared after the formation of the 2×2 Ti superstructure. This result suggests that the Ti-deposited MgO surface where the interfacial reaction is revealed to occur has novel electrical properties. The charging problem also disappeared when the amount of Ti deposition was only 0.8 ML. The electric conduction of the Ti-deposited MgO was measured by means of a two-point method to confirm whether this disappearance of the charging problems is due to the electrical properties at the surface. The two electrode pins separated from each other by about 7 mm were pushed to the sample surface via a load lock system, so that the measurements were done in situ. Between the two pins, 10 V was applied and electric currents were measured by picoammeter. The electric current was not detected at the MgO clean surface by this method. After Ti deposition of 1 ML, the electric currents of μ A order were detected, although the reappearance of the current values was not consistent among the several check experiments. The reappearance in the electric conduction measurement is thought to be affected by the surface steps which cause discontinuity of the Ti-reacted MgO layer.[7] The appearance of electric conduction is thought to be due to the metallic character of the Mg−Ti−O metastable phase in which a part of Mg is substituted

for Ti. For gaining more insight into the electric properties of the Mg−Ti−O metastable phase, the electric band structure is currently investigated using electron spectroscopic techniques such as ultraviolet photoelectron spectroscopy.[8]

So far, the metal−MgO interface has been investigated as a typical boundary between dissimilar materials, and the intrinsic character such as metal induced gap states (MIGS) has been discussed in the MgO/Cu interface.[9] Such a noticeable MIGS has been predicted in Ti on MgO(001) without the consideration of the interfacial reaction by the local density functional theory.[10] However, we showed clearly the occurrence of the strong chemical interaction, resulting in the Ti incorporation into the bulk of MgO. As mentioned already, the MgO substrate was prepared by cleavage in the air. Duriez et al. pointed out that the MgO surfaces cleaved in the air were damaged by water vapor which created point defects on the surfaces.[11] Although the contamination layer on the MgO surface which is produced by contacting with air is removed by annealing the substrate at 970 K in UHV, the surface defects remain after the heat treatment. Colbourn et al. reported the atomic arrangement of MgO(001) is slightly deformed at surface defects such as point defects or steps.[12] Such surface defects or the atomic distortion on the MgO surface may be the incorporation site for the Ti adsorbates.

In summary, we observe the reaction process of Ti adsorbate with the MgO substrate surface. Ti deposited on the MgO(001) surface at RT is situated at the substitutional sites of the Mg ions for more than four layers of the surface, and the incorporation of Ti is activated by heat treatment. After annealing at 1270 K, the Ti adatoms remaining on the outermost surface layer form a 2×2 superstructure. On the other hand, the Ti atoms situated below second layer of the surface diffuse into the bulk after the annealing. Ti deposition (0.5 ML) on the MgO-2×2-Ti surface maintained at 870 K changes the surface periodicity into a 1×1. On this surface, the Ti adatoms sit on the top site of oxygen of the MgO-2×2-Ti surface. The charging problems during the CAICISS measurement disappear at the metastable MgO surface where Ti is substituted for Mg for several surface layers. This is due to the emergence of a novel electrical property which is confirmed by a two-pin method.

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