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# TiO epitaxial film growth on MgO(001) and its surface structural analysis

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## Abstract

The metallic TiO single crystal film formed epitaxially on MgO is reported. It was found that the simultaneous supply of Ti vapor and $O_2$ gas on the MgO(001) surface resulted in the TiO(001) film formation. The surface structure of the TiO(001) film was investigated using $Li^+$ impact-collision ion scattering spectroscopy and reflection high energy electron diffraction. The surface of TiO formed on MgO was very close to an ideal truncation of the TiO bulk structure, while the O vacancies, whose concentration was estimated to be 28%, exist on the outermost surface. When the TiO film was exposed to the $O_2$ atmosphere of $1 \times 10^{-8}$ Torr partial pressure with maintaining the substrate temperature at 1070 K, the TiO-2 × 2-O superstructure was found to be formed. In the 2 × 2-O structure, the adsorbed O atoms were located on the top sites of Ti of the outermost TiO surface, where the distance between O and Ti was equal to that in the bulk, which was 2.09 Å. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The oxides of Ti have been extensively studied, because they are technologically important as catalyst supports and in photocatalytic applications. The Ti oxides also have an attraction in theoretical investigations as a relatively simple model of the transition-metal oxide. The oxides of Ti, which are well known to exhibit different electronic properties depending on the oxidation states, are expressed by the general formula $Ti_nO_{2n-1}$ ($n=1$–$\infty$) [1]. For example, $TiO_2$ ($n=\infty$), which is the most widely studied in the Ti–O system, is an insulator. $TiO_2$ can be reduced to an n-type semiconductor, and when the Ti–O stoichiometry reaches 2:3 ($n=2$), a stable and homogeneous phase having the corundum structure appears. This $Ti_2O_3$ is a semiconductor whose bandgap is 0.1 eV at room temperature [2]. Single crystalline $Ti_2O_3$ are available, and a number of investigations were performed on the $Ti_2O_3$ surface, especially in terms of its electronic structure [3]. $Ti_2O_3$ can be further reduced to the rock-salt oxide TiO ($n=1$), which exhibits metallic conductivity. TiO is not stable as $Ti_2O_3$, and a wide stoichiometry range exists, extending over $0.71 \le n \le 1.4$ [2]. The single crystal of TiO is not available, so there is no experimental report concerning the TiO surface structure. TiO has typical properties of covalent crystals such as high melting point and extreme hardness, whereas the bonds usually have ionic character in the rock-salt structure of TiO. These two aspects of TiO have attracted attention as a

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special theoretical interest system, as well as a valuable technological material. Actually, many theoretical groups have studied the electronic structure of TiO [4–8], although the experimental determination has not been performed because of the unavailability of the TiO single crystal.

In the present study, it was found that the TiO epitaxial film was grown on the MgO(001) surface by Ti deposition in $O_2$ atmosphere. The surface structure of the TiO film, in addition to the oxygen adsorption structure of TiO formed on MgO, was investigated using Li$^+$ impact-collision ion scattering spectroscopy (Li$^+$ ICISS) [9] and reflection high energy electron diffraction (RHEED).

## 2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure $7 \times 10^{-10}$ Torr) equipped with a sample transfer interlock system, RHEED optics, and a Li$^+$ ion source. A beam of Li$^+$ was generated by a thermionic-type ion source. The Li$^+$ ions were incident upon a surface by changing glancing angles, $\alpha$, and scattered ions were detected by a hemispherical electrostatic energy analyzer, where the scattering angle was fixed to 160°. In the present study, the measurements were made using a Li$^+$ beam of 1 keV. A MgO(001) substrate ($10\ \text{mm} \times 10\ \text{mm} \times 1\ \text{mm}$) was prepared by cleaving MgO single crystals (Nakazumi Crystal Laboratory, Japan) in air, and was introduced into the UHV chamber immediately. The MgO sample surface was cleaned by annealing at 1070 K in UHV. This sample treatment produced the $1 \times 1$ clean surface [10]. Ti (purity 99.98%) was deposited using an electron-beam evaporator (omicron EFM3). The amounts of the deposits were monitored using quartz crystals with controlled rates of 0.5 Å/min.

## 3. Results and discussion

### 3.1. The TiO single crystal film formation on MgO(001)

Fig. 1 shows the RHEED patterns obtained at the MgO clean surface (a and b) and the Ti deposited-MgO surface (c and d), in addition to the Li$^+$ ICISS energy spectrum in the normal incidence condition obtained at the Ti deposited-MgO surface (e). The RHEED patterns (c) and (d) and the Li$^+$ energy spectrum (e) were taken at the same surface. A Ti layer with thickness 10 Å was deposited on the MgO substrate at room temperature (RT) in $O_2$ atmosphere of $1 \times 10^{-8}$ Torr followed by annealing at 970 K for 10 min in UHV. In the RHEED observation, the lattice constant of the overlayer film formed by the Ti deposition is estimated to be 4.18 Å, which corresponds to that of TiO [7]. In the thickness

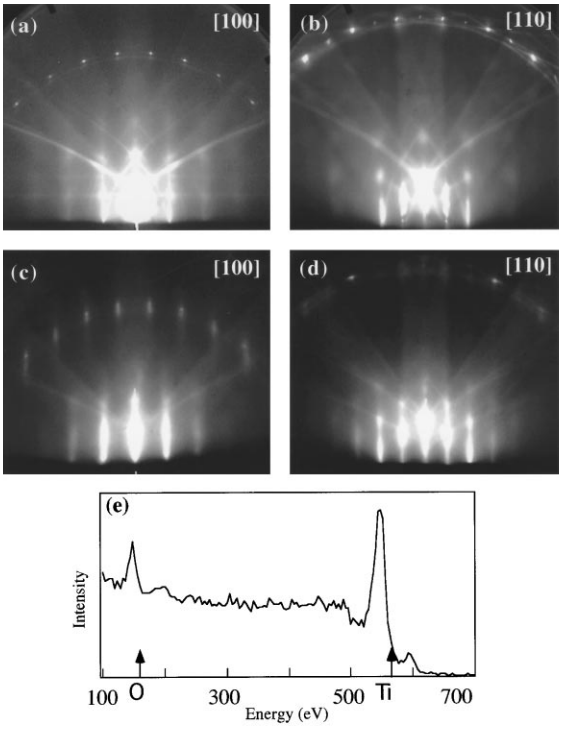

Fig. 1. The RHEED patterns obtained for the MgO(001) clean surface (a and b) and for the TiO(001) film formed on MgO (c and d), and the energy spectrum of Li$^+$ scattered from the TiO film under normal incidence conditions. The TiO film was prepared by Ti deposition of 10 Å in $O_2$ atmosphere of $1 \times 10^{-8}$ Torr partial pressure followed by annealing at 970 K for 10 min in UHV. The incident electron in RHEED was parallel to [100] for (a) and (c), and [110] for (b) and (d). The measurement of (e) was made with use of a 1 keV Li$^+$ beam at the fixed scattering angle of 160°. The front edges of the elastic binary collisions are indicated by the arrows on the energy axis in (e).

range of Ti from 10 Å to 50 Å, the RHEED patterns consistently exhibited the reciprocal rods as shown in Fig. 1c and d, and no transmission spot, indicating islanding of the overlayer film, was found. Before sample annealing at 970 K for 10 min in UHV, however, the RHEED patterns showed transmission ones (not shown), while spots were located on the line of the above-mentioned rods. Therefore, the lattice constant of the overlayer film was the same before and after annealing. The extinction rule observed in the transmission RHEED patterns corresponds to a crystal structure of rock-salt type. In the $Li^+$ energy spectra obtained at the Ti deposited-MgO surface, only the peaks of Ti and O are observed as shown in Fig. 1e. The small peak appearing at around 590 eV is due to $^6Li$, while the main Ti peak is due to $^7Li$. The sharp surface peaks of Ti and O straightforwardly indicate that the outermost layer consists of both Ti and O. From this series of measurements, it is concluded that the TiO film is epitaxially formed on the MgO substrate. The epitaxial orientation relationship is TiO(001)// MgO(001) and TiO[100]//MgO[100].

The TiO film was also formed by the Ti deposition in $O_2$ atmosphere of $1 \times 10^{-8}$ Torr on the MgO substrate maintained at 770 K. The quality of the TiO film was slightly improved by the heat treatment at 970 K for 10 min in UHV.

The TiO/MgO sample annealing at 1270 K for 10 min in UHV changed the surface periodicity from $1 \times 1$ into $2 \times 2$. In the $Li^+$ energy spectra obtained at the $2 \times 2$ surface, the Ti peak intensity drastically decreased, and the Mg peak coming from the underlying MgO substrate was detected. In our previous work, it was found that the Ti adatoms were incorporated into the MgO(001) substrate via the Mg substitutional sites in the initial stage of the Ti deposition in UHV, and a MgO-$2 \times 2$-Ti superstructure was formed [10,11]. It is our interpretation that the appearance of the $2 \times 2$ periodicity after the annealing of the TiO/MgO sample is also due to the interfacial reaction.

### 3.2. Surface structure of TiO(001) formed on MgO(001)

Fig. 2 shows the Ti peak intensities of ICISS with energies of 548 eV (corresponding to the Ti peak position in Fig. 1e) as a function of α along the [100] and [110] azimuths. The sample was the same as that of Fig. 1c–e. The ICISS peak intensity is strongly enhanced by the focusing effect of the $Li^+$ beam. This occurs in the scattering conditions of the peaks a–f indicated in Fig. 2. The atomic pairs for the focusing conditions are indicated above the spectra, which is estimated using shadow cones calculated by assuming Thomas–Fermi–Moliere potential [12]. The calculated focusing angles for the peaks a–f are indicated by arrows. The intensity drop for both [100] and [110] at around 20° is due to the shadowing effect of the Ti atom by the adjacent O or Ti atom. The Ti intensity obtained along the [100] azimuth shows the small hump below 16°. By contrast, the Ti intensity along the [110] azimuth sharply decreases below 20°. This difference is attributable to the oxygen vacancies at the TiO outermost surface and its concentration is estimated to be 28% from the intensity ratio of the hump to the focusing peak at 21°. However, the reason for the broaden-

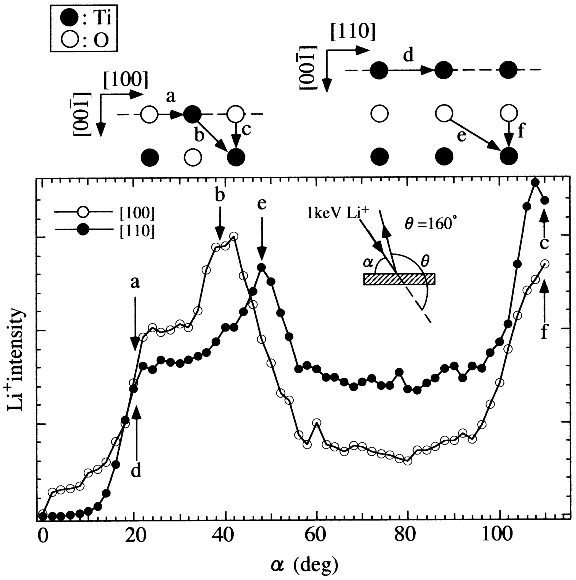

Fig. 2. The polar angle scans of $Li^+$ ICISS along the [100] and [110] azimuths on the TiO(001) film formed on MgO(001). The preparation conditions for the TiO film were the same as those of Fig. 1. The Ti surface peak intensity with energy 548 eV is plotted against α, with fixed scattering angle of 160°. The atomic arrangements indicated above the spectra show the focusing conditions for the peaks a–f observed in the spectra.

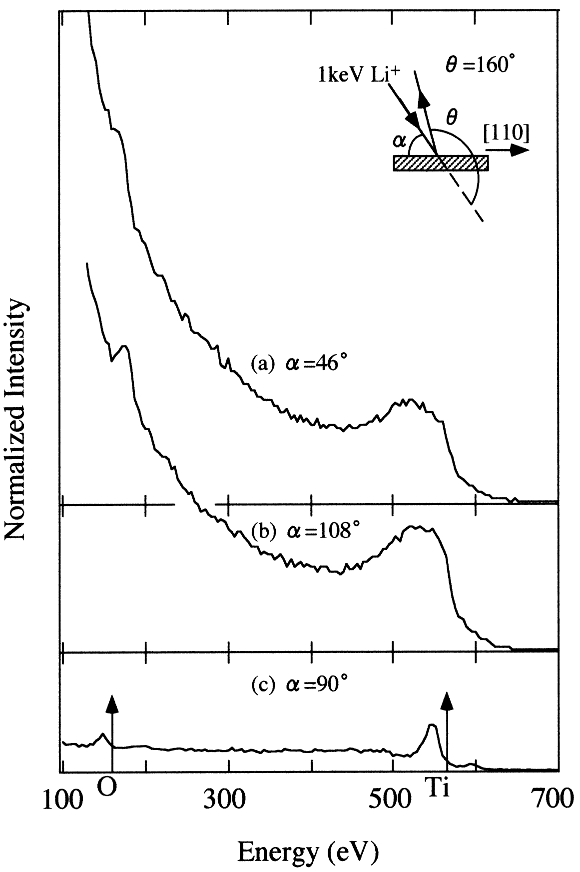

Fig. 3. Energy spectra of $Li^+$ ions scattered from the TiO(001) film formed on MgO(001). The measurements were made along the [110] azimuth at a fixed scattering angle of 160°. The polar angles were (a) 46°, (b) 108°, and (c) 90°. The preparation conditions for the TiO film were the same as those of Fig. 1.

ing of the shoulder appearing below 16° in the [100] azimuth is not clear.

Using a combination of RHEED in Fig. 1 and $Li^+$ ICISS in Fig. 2, it is concluded that the TiO single crystal formed on the MgO(001) surface has a rock-salt crystal structure. In Fig. 2, all the peaks caused by focusing effects are explained by the TiO bulk structure. This indicates no notable surface relaxation of TiO(001) formed on MgO(001).

Fig. 3 shows the energy spectra of $Li^+$ scattered from the TiO(001) thin film. The sample preparation was the same as that of Fig. 1c–e. The measurements were made along the [110] azimuth at three glancing angles, 46°, 108°, and 90°, with a fixed scattering angle of 160°. The spectra exhibit the surface peaks of Ti and O, appearing around the elastic collision energy indicated by the arrows on the energy axis, as well as the extended backgrounds. The surface peaks are due to the $Li^+$ ions experiencing quasi-single scattering by the surface atoms while the backgrounds originate from multiple scattering. It is notable that the surface peak width of Ti and O strongly depends on $\alpha$. When $\alpha$ is 90°, the surface peaks of Ti and O of TiO are contributed only from Ti and O atoms respectively located at the outermost surface because of the shadowing effect. On the other hand, in the $Li^+$ incidence condition of $\alpha=46°$ and 108°, the ions coming from the second layer, which lose kinetic energy more than those from the topmost layer, also contribute to the peak intensity. Thus, the broadening of the Ti and O peaks in Fig. 3a and b originates from the stopping power in the inelastic scattering process [13]. The sharp contrast in the Ti surface peak width between Fig. 3a (or Fig. 3b) and Fig. 3c indicates the good crystallinity of the TiO film formed on MgO.

### 3.3. Oxygen adsorption on TiO(001) formed on MgO(001)

Fig. 4 shows the $Li^+$ energy spectra of the TiO film in the normal incidence condition obtained after $O_2$ exposure at RT, where the exposure is given in Langmuirs ($1\ L \equiv 10^{-6}$ Torr s). As little as 1 L exposure decreases the Ti intensity by a factor of 2.6. The $O_2$ exposure for TiO changed the RHEED spectra into a broad 1 × 1 structure. The decrease of the Ti peak intensity in Fig. 4 and the debasement of the quality in the TiO 1 × 1 RHEED patterns indicate the disordered adsorption of oxygen on the TiO surface. On the other hand, the ordered adsorption structure of oxygen was found when the TiO surface was exposed to $O_2$ atmosphere whilst maintaining the substrate temperature at 1070 K. When the $O_2$ exposure of $1\times10^{-8}$ Torr for 10 min (6 L) was performed keeping the substrate temperature at 1070 K, the TiO-2 × 2-O superstructure was observed in RHEED (not shown). The appearance of the 2 × 2 periodicity after the $O_2$ exposure is due to oxygen

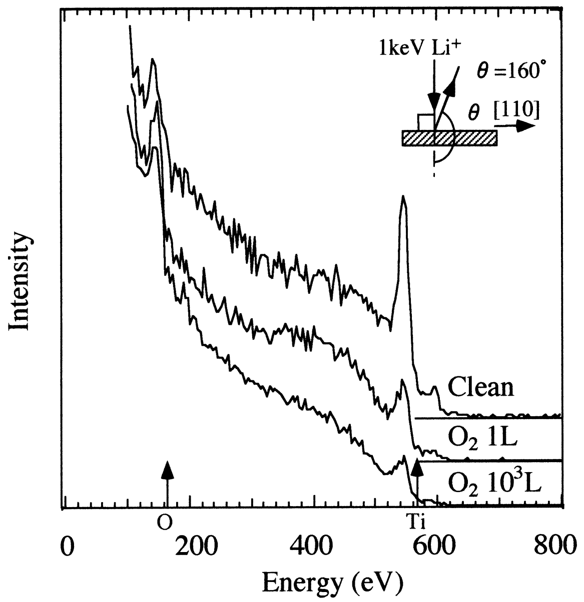

Fig. 4. Normal incidence energy spectra of $Li^+$ ions scattered from the TiO(001) film formed on MgO(001) after various $O_2$ exposures at RT (given in Langmuirs, where $1\ L \equiv 10^{-6}$ Torr s). The preparation conditions for the TiO film were the same as those of Fig. 1. The spectra are normalized by the O surface peak heights.

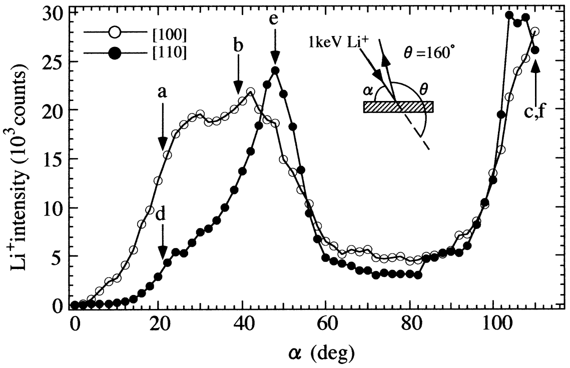

Fig. 5. The polar angle scans of $Li^+$ ICISS along the [100] and [110] azimuths of the TiO-2 × 2-O surface. The sample surface was prepared by annealing the TiO film at 1070 K for 10 min in $1 \times 10^{-8}$ Torr $O_2$ atmosphere. The Ti surface peak intensity with energy of 548 eV is plotted against α, with fixed scattering angle of 160°. The arrows a–f indicate the peak positions calculated using the TiO bulk structure.

adsorption, but not due to the interfacial reaction between TiO and MgO. The polar angle scans of ICISS at the TiO-2 × 2-O surface were performed as shown in Fig. 5. The focusing peaks in Fig. 5 corresponding to those in Fig. 2 are labeled a–e. In the comparison between Figs 2 and 5, it is notable that the peak d almost disappears in Fig. 5, while peaks a–c, e, and f are clearly observed. This feature in the intensity variation indicates that the adsorbed O atoms are located on the top sites of the Ti atoms of the outermost TiO surface. The disappearance of peak d after oxygen adsorption is due to the shadowing effect of the adsorbed O atoms. The focusing peaks observed in Fig. 5 almost agree with the calculated positions using the TiO bulk structure indicated by arrows. Therefore, the distance between the adsorbed O atom and the outermost Ti atom is thought to be equal to the bulk value, which is 2.09 Å.

The superstructure formation on the TiO surface by $O_2$ exposure indicates the dissociation of $O_2$ molecules on the TiO surface. This suggests the metallic character of the TiO outermost surface. Very recently, we confirmed that the TiO(001) outermost surface was metallic using metastable impact electron spectroscopy [14].

All of the above mentioned data were obtained at the TiO film produced by simultaneous supply of Ti and $O_2$. From the viewpoint of the crystallinity of the TiO film, the optimum partial pressure of $O_2$ was $1 \times 10^{-8}$ Torr or lower. When Ti was deposited in the oxygen partial pressure of $1 \times 10^{-7}$ Torr, the RHEED patterns exhibited a very broad 1 × 1 structure. Furthermore, the TiO sample prepared in the oxygen partial pressure of $1 \times 10^{-7}$ Torr showed the 2 × 2 superstructure after heat treatment at 1070 K in UHV. This superstructure is thought to also be due to the oxygen adsorption on the TiO surface, where the O adatoms are supplied from the inside of the TiO film. The TiO film which is produced in the oxygen partial pressure of $1 \times 10^{-7}$ Torr is expected to contain excess oxygen that segregates to the surface.

The $TiO_2$ film growth on MgO(001) by Ar ion beam sputtering has been investigated by Aoki et al. [15]. They reported that the $TiO_2$ film having anatase or rutile structure was formed on the MgO substrate by the simultaneous supply of Ti and $O_2$, while the $TiO_2$ film formation was not observed by X-ray diffraction (XRD) when Ti and $O_2$ were supplied alternately. The partial pressure of $O_2$ in their conditions was on the order of $10^{-5}$ Torr. They interpreted the feature of XRD showing only the periodicity of the MgO substrate at the film formed by the alternative supply of Ti and $O_2$ as due to the amorphous formation of the deposited film. However, we propose that their results indicate the formation of TiO. The structure of TiO is rock-salt, and the lattice mismatch between TiO and MgO is only 0.71%, so that it is difficult to distinguish between TiO and MgO by the diffraction technique. If our interpretation is correct, the results of Aoki et al. may indicate that the structure of the deposited Ti oxide is able to be controlled between $TiO_2$ (anatase and rutile) and TiO by changing the partial pressure of $O_2$ gas.

As mentioned in the Introduction, the electronic structure of TiO has attracted attention, and many theoretical efforts have been devoted to its study. Significant differences in the calculated band structure have been found between Hartree–Fock and statistical exchange ($X\alpha$) [8]. The experimental determination of the electronic structure of TiO, which was found to be available as the epitaxial film on MgO in the present study, is expected.

## 4. Conclusions

The TiO epitaxial film was found to be available by the simultaneous supply of Ti vapor and $O_2$ gas on MgO for the first time using $Li^+$ ICISS and RHEED. The surface structure of the TiO film was investigated, no notable surface relaxation being found on the TiO(001), while the O vacancies exist on the outermost surface whose concentration was estimated to be 28%. A TiO-2 × 2-O superstructure was found to be formed when the TiO film was exposed to $O_2$ atmosphere of $1 \times 10^{-8}$ Torr partial pressure whilst maintaining the substrate temperature at 1070 K. In the 2 × 2-O structure, O adsorbed on the top sites of Ti of the outermost TiO surface, where the distance between O and Ti was 2.09 Å.

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