TiO(001) single-crystal film formation by the incorporation of oxygen from MgO into the deposited Ti film

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The formation of a TiO(001) film on MgO(001) was investigated using metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (He I), impact-collision ion scattering spectroscopy, and electron diffraction techniques. It was found that epitaxial TiO films were formed by Ti deposition on the MgO surface followed by annealing at 1000 K. The TiO film formation was related to the incorporation of oxygen from MgO into the deposited Ti film. Metallic properties of the outermost surface of the TiO film were strongly suggested by the fact that electron emission due to the autodetachment mechanism occurred in MIES, where the interaction was determined by the Coulomb interaction between temporary negative He^{-*} ions and the hole created at the TiO surface. The work function increased from 2.6 to 5.0 eV when the TiO surface was exposed to O_2. The electronic structure of the MgO-(2×2)-Ti superstructure was also investigated. It is suggested that Ti is in the four-valent state at the 2×2 surface.

I. INTRODUCTION

Very recently, we reported TiO epitaxial film growth on a MgO(001) surface on the basis of a structural analysis using Li^+ impact-collision ion scattering spectroscopy (Li^+ICISS) and reflection high-energy-electron diffraction (RHEED).[1] In our earlier report, we concluded that the simultaneous supply of Ti vapor and O_2 gas on the MgO(001) surface caused the TiO(001) film formation. Single crystals of TiO are not available either in bulk form or as films grown heteroepitaxially. Thus, a surface geometric and electronic structural investigation using single-crystalline TiO has been impossible. TiO, with a rocksalt crystal structure, exhibits metallic conductivity,[2] although TiO is not as stable as Ti_2O_3 or TiO_2 and has a wide stoichiometric range. On the other hand, TiO, which has a high melting point and extreme hardness, has attracted attention as a unique system of theoretical interest as well as a valuable technological material. Several theoretical investigations of the electronic structure of TiO have been made.[3–7] Significant differences in the calculated band structure have been found between the Hartree-Fock (HF) and statistical exchange ($X\alpha$) methods. The HF results predicted the overlap of O $2p$ and Ti $3d$ bands, while the $X\alpha$ calculations exhibited a gap between these bands. These result are supported by an experiment using x-ray photoelectron spectroscopy by Ichikawa, Terasaki, and Sagawa[8] and an experiment using ultraviolet photoelectron spectroscopy (UPS) by Henrich, Zeiger and Reed[2] respectively. In these experiments, the measurements were performed on a polycrystalline $TiO_x(x\approx 1)$ surface.

In the present study, the electronic structure of single-crystal TiO(001) films formed on a MgO(001) substrate was investigated using metastable impact electron spectroscopy (MIES) and UPS (HE I). As mentioned above, TiO epitaxial film has been found to be formed by the deposition of Ti in an O_2 atmosphere of 1×10^{-8} Torr. However, in the present experiment it was found that the TiO(001) film was also formed on the MgO substrate even without supply of O_2 gas during the Ti deposition in the ultrahigh vacuum (UHV) chamber (base pressure 2×10^{-10} Torr). TiO films formed with and without an O_2 supply during Ti deposition had the same rocksalt crystal structure and the same orientation relationship with the MgO substrate, TiO(001)||MgO(001) and TiO[100]||MgO[100]. The MIES and UPS data presented in this paper were obtained from a TiO film formed by Ti deposition without a supply of O_2 gas.

From the fact that TiO single-crystal film formation on MgO was possible by Ti deposition even without a supply of O_2 gas, we considered that oxygen from the MgO substrate might be supplied for the TiO formation. However, the residual gas in the UHV chamber is also a possible source, because Ti is so chemically reactive that it is used as the material for getter pumps. In this context, the composition of the TiO film on $Mg^{18}O$, which was homoepitaxially formed on MgO(001), was investigated by Li^+ICISS to identify the oxygen source for the TiO formation. From the viewpoint of bulk thermodynamics, one could expect the oxygen source not to be the MgO substrate, because the Mg-O bond is believed to be stronger than the Ti-O bond, taking into account the heat of formation.[9] Nevertheless, the incorporation of oxygen from MgO into the deposited Ti film, resulting in TiO single-crystal film formation, was indicated in the present study.

The electronic structure of the MgO-(2×2)-Ti superstructure, which was found after heat treatment of the Ti-deposited MgO surface at 1270 K,[10,11] is also reported in this paper. To our knowledge, this is the only superstructure reported so far for metal adsorption on the MgO(001) surface.

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II. EXPERIMENT

In the present experiment, three UHV chambers were employed. These chambers were utilized for MIES and UPS measurements, Li^+ ICISS and RHEED measurements, and the homoepitaxial growth of $Mg^{18}O$ on MgO(001), respectively.

A. MIES and UPS

The apparatus for MIES and UPS has been described in detail elsewhere.[12,13] Briefly, the experiments were performed in an UHV chamber (base pressure 2×10^{-10} Torr) which was equipped with a cold-cathode He-gas-discharge source for the production of metastable He* atoms with thermal kinetic energies (for MIES) and He I photons (for UPS). A time-of-flight technique was employed in order to separate contributions to the electron spectra from He I photons and He* metastable atoms. Thus, the MIES and UPS spectra were obtained simultaneously. The incidence angle of metastable atoms and photons was 45° with respect to the sample surface. The energy spectra of electrons ejected normal to the surface were recorded using a hemispherical electron spectrometer. In addition, there exists a facility for low-energy-electron diffraction (LEED), which was used for the qualitative surface periodicity analysis. During the MIES and UPS measurements of MgO and MgO-(2×2)-Ti, a tungsten filament placed behind the sample was heated while maintaining the sample potential at the ground level to avoid charging problems. On the other hand, the measurements on the Ti-deposited MgO sample were performed without using the filament and while maintaining the sample potential at -50 V with respect to the analyzer.

The MgO(001) substrate ($10 \times 10 \times 2$ mm^3) was prepared by cleaving the MgO single crystal (K&R Creation, Japan) in air, and then immediately introduced into the UHV chamber via the sample transfer interlock system. The cleaning procedure for the MgO sample was annealing at 1070 K in UHV.[11] Ti (purity 99.98%) was evaporated using an electron-beam evaporator (Omicron EFM3). After degassing the evaporator, the pressure of the chamber was maintained below 8×10^{-10} Torr during the Ti deposition. The Ti deposition was performed at room temperature with a controlled deposition rate of 0.5 Å/min.

B. Li^+ ICISS on TiO/Mg^{18}O/MgO(001)

TiO single-crystal film formation was demonstrated in our previous study[1] when Ti was deposited on a MgO(001) surface at room temperature in an O_2 atmosphere of 1×10^{-8} Torr followed by annealing at 970 K for 10 min in UHV. In the present experiment, a TiO single-crystal film was also found to be formed even without O_2 introduction during the Ti deposition. The composition of the TiO single-crystal film formed on $Mg^{18}O$ homoepitaxially grown on the MgO(001) substrate was investigated using Li^+ICISS to identify the oxygen source for the TiO film formation. The experimental procedures were as follows.

(1) The MgO(001) substrate prepared by cleaving in air was cleaned by annealing at 1070 K for 10 min in an UHV chamber (base pressure 1×10^{-10} Torr). Then a $Mg^{18}O$ layer was grown on the MgO substrate by Mg deposition (200 Å)
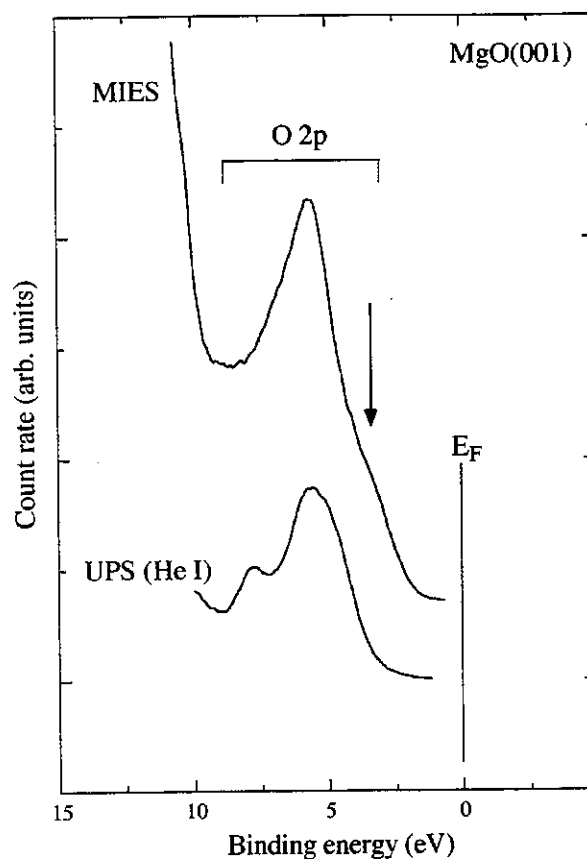

FIG. 1. MIES and UPS (He I) spectra obtained from the MgO(001) clean surface. The UPS spectrum was shifted to align the first peak below the Fermi level with that of the result by Ochs et al. (Ref. 14). The MIES spectrum was aligned at the peak position.

in $^{18}O_2$ atmosphere of 1×10^{-6} Torr. The Mg deposition was performed at room temperature with a controlled deposition rate of 5 Å/min.

(2) The $Mg^{18}O$/MgO substrate was moved into another UHV chamber (base pressure 5×10^{-10} Torr) equipped with Li^+ ICISS and RHEED to avoid contamination by the residual $^{18}O_2$ gas in the UHV chamber used in procedure 1. The $Mg^{18}O$/MgO substrate was annealed at 870 K, and the homoepitaxial growth of the $Mg^{18}O$ layer was confirmed by RHEED.

(3) Ti (10 Å) was deposited on the $Mg^{18}O$/MgO substrate followed by annealing at 1000 K for 10 min in UHV. The conditions for Ti deposition were the same as those for MIES and UPS (Sec. II A). Single-crystal TiO film formation on the $Mg^{18}O$/MgO substrate was observed by RHEED.

(4) The composition of the TiO film surface was analyzed by Li^+ ICISS. In ICISS, the Li^+ ions were generated by a thermionic-type ion source. The Li^+ ions were incident normal to the TiO film surface, and the scattered ions were detected by a hemispherical electrostatic analyzer, where the scattering angle was fixed to 160°.

III. RESULTS AND DISCUSSION

Figure 1 shows the MIES and UPS spectra of the MgO(001) surface. As mentioned in Sec. II, during the mea-

surement, a tungsten filament placed behind the sample was heated to avoid charging problems, and the spectra were obtained while maintaining the sample at the ground potential. The high-binding-energy region of both spectra was affected by the secondary electrons, so this part of the spectra was removed in Fig. 1. The Fermi level was determined by referring to the former investigation by Ochs et al.[14] concerning the MIES and UPS spectra of the MgO(001) surface, where the first peak in the UPS spectrum was observed at a binding energy of 5.6 eV with respect to the Fermi level.[14] The MIES spectrum was shifted to make the position of the main peak the same as the above-mentioned first UPS peak. The spectra in Fig. 1 exhibiting one peak for MIES and two peaks for UPS essentially agree with the results of Ochs et al., although the energy difference between the two peaks in the UPS spectrum in Fig. 1 (2.2 eV) is smaller than that found by Ochs et al. (2.7 eV). The origin of the difference between the MIES and UPS spectra was explained previously by Ochs et al.: MIES has a large detection efficiency only for O $2p_z$ which has a lower binding energy than that of $2p_{x,y}$, while UPS detects both $2p_z$ and $2p_{x,y}$. This is also the reason why the MIES spectrum exhibits a narrower peak than the UPS spectrum. Concerning the electron transition process, the He*-MgO(001) surface interaction takes place via Auger deexcitation (AD).

There is a small shoulder on the low-binding-energy side of the O$2p$ peak in the MIES spectrum, as indicated by the arrow. This shoulder was not found by Ochs et al. for MgO films. It was found to grow larger when the MgO substrate was annealed at elevated temperatures (not shown). The corresponding feature is not observed in the UPS spectrum shown in Fig. 1. This fact indicates that the feature originates from the outermost surface. The origin of this shoulder in the MIES spectrum could be the surface segregation of Ca, which is included in MgO single crystals as an impurity. It is known that the segregated Ca is located only at the MgO outermost surface.[15,16]

Figure 2 shows the MIES spectra obtained simultaneously with the Ti deposition at room temperature together with the spectrum obtained after annealing the surface exposed to Ti of 14 Å. In this series of measurements, the tungsten filament to avoid the charging effect was not used, and the sample was biased. After Ti deposition of 2 Å on MgO, the charging effect disappeared, and reliable spectra could be obtained. With increasing Ti coverage, the peak at 6.8 eV gradually disappeared, and the structure peaking around 2.5 eV appeared. These two peaks are attributed to the O $2p$ valence bands of MgO and Ti metal, respectively. Kurahashi and Yamauchi[17] have investigated the MIES spectra of polycrystalline Ti. The MIES spectrum obtained after Ti exposure of 14 Å in the present experiment is quite similar to that reported by Kurahashi and Yamauchi, and it is concluded that the outermost surface of the Ti film deposited on MgO consists of a metal Ti layer. Concerning the He*-Ti surface interaction, we performed a simulation of the MIES spectra along the lines reported by Eeken et al.[18] For the surface density of states, we adopted the s part of the density of states reported in Ref. 19. In this simulation, it was found that the spectra obtained for exposures larger than 8 Å were dominated by AD, although they contained a contribution from resonance transition and Auger neutralization
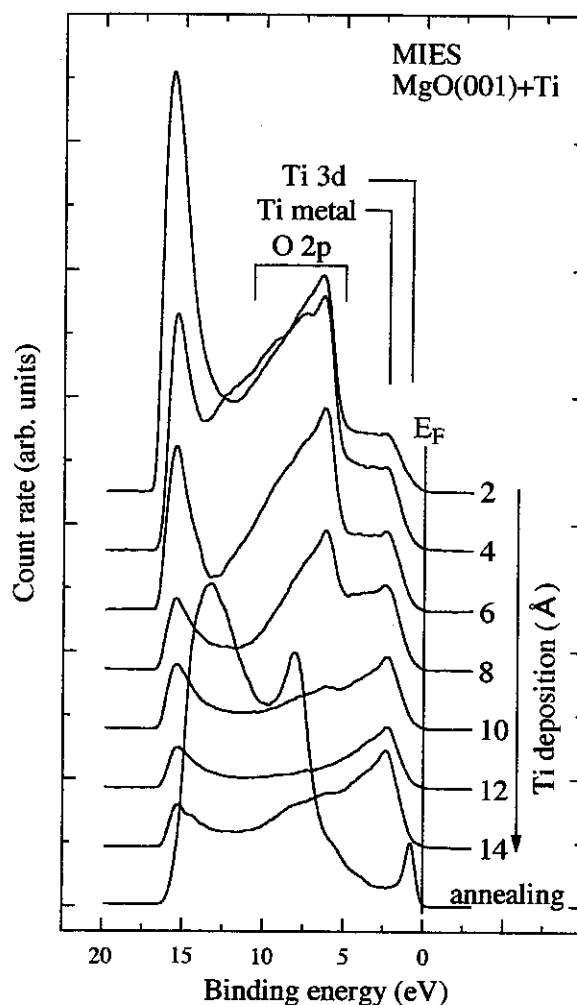

FIG. 2. MIES spectra during Ti deposition on MgO(001) at room temperature. The bottom spectrum was obtained after annealing at 1000 K for 10 min in UHV.

(RT+AN) for binding energy larger than about 4 eV. The bottom spectrum in Fig. 2 was obtained after annealing the Ti(14 Å)/MgO sample at 1000 K for 1 min in UHV. The drastic change in the spectrum is notable. The peak at 2.5 eV disappears, and two new peaks appear at 0.8 and 8.1 eV. These two peaks are attributed to the Ti $3d$ and O $2p$ bands of the Ti oxide. Thus, the changes in the MIES spectra indicate a transition at the outermost surface from a Ti metal into a Ti oxide that has surface conductivity. This Ti oxide layer was identified by ICISS, RHEED, and LEED to be a TiO single-crystal film where the orientation relationship between TiO and MgO was TiO(001)∥MgO(001) and TiO[100]∥MgO[100]. A detailed interpretation of the MIES spectra for TiO (Fig. 2 bottom and Fig. 5 top) will be given below.

Figure 3 shows the UPS spectra obtained quasisimultaneously with the MIES data during the Ti deposition, together with the spectrum acquired after annealing. As the thickness of Ti increases, the peak at 0.7 eV grows higher although the peak at 8.2 eV becomes smaller. These two peaks are attributed to Ti $3d$ and O $2p$ of MgO, respectively. After Ti deposition of 10 Å, the O $2p$ peak almost disappears. After annealing the Ti(10 Å)/MgO sample at 1000 K for 10 min in UHV (the bottom spectrum in Fig. 3), the Ti
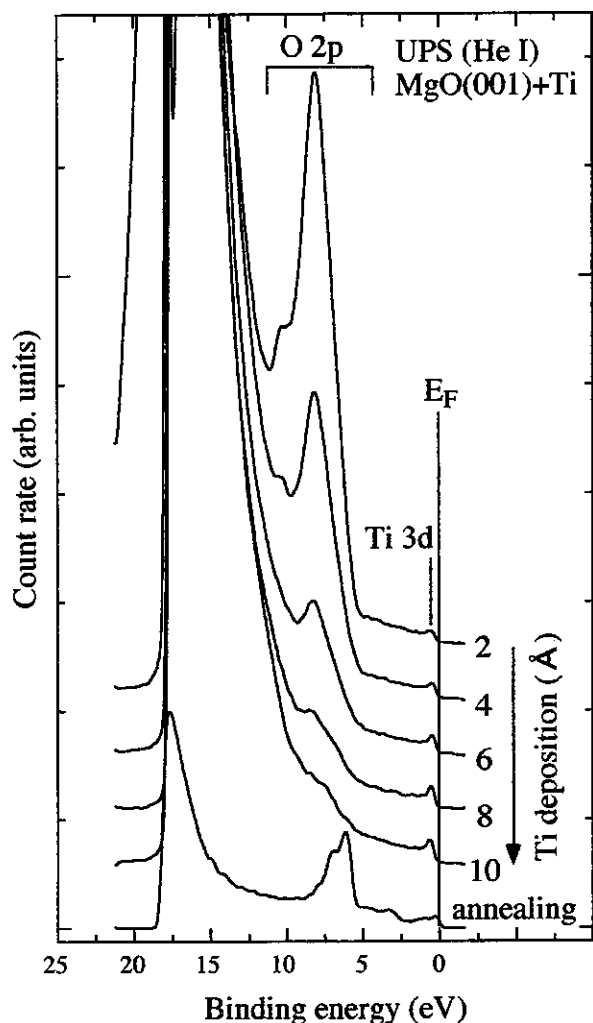
FIG. 3. UPS spectra during Ti deposition on MgO(001) at room temperature. The bottom spectrum was obtained after annealing at 1000 K for 10 min in UHV.
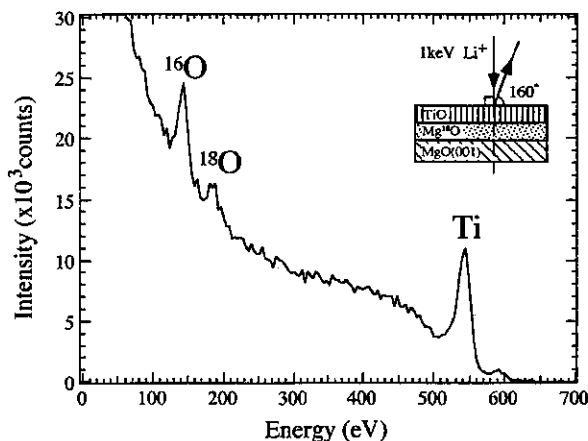

FIG. 4. The energy spectrum of Li$^+$ scattered from a TiO film formed on a Mg ^{18}O layer that was homoepitaxially grown on the MgO(001) substrate. The measurement was made using a 1 keV Li$^+$ beam at the fixed scattering angle of 160°, and the incidence angle was 90° (normal incidence).

$3d$ and O $2p$ bands are observed at the Fermi edge and at 6.5 eV in the UPS spectrum. The structure and composition of the Ti-deposited MgO surface corresponding to the bottom spectrum in Fig. 3 were also confirmed to be TiO(001). It is notable that the Ti $3d$ peak shifts slightly to the low-binding-energy side after annealing. This fact is thought to indicate that the TiO formation is complete after the heat treatment. In the UPS study on the polycrystalline TiO$_x$ surface (0.93 $\leq x \leq 1.15$) by Henrich, Zeiger, and Reed,[2] it is reported that the O $2p$ valence band is about 6 eV wide. However, it is about 3.5 eV wide in Fig. 3. This difference in the O $2p$ bandwidth may be due to contamination at the TiO surface by oxygen in the case of Ref. 2, which widens the O $2p$ bandwidth of TiO, as described later.

In a comparison between the MIES and UPS spectra TiO (the bottom spectra in Figs. 2 and 3), the O $2p$ peaks appear at different energies. However, the O $2p$ structures are expected to occur at the same energy in both MIES and UPS spectra. This is nearly fulfilled for the O $2p$ structures in the case of MgO.[14] A shift similar to that observed for TiO(001), which is also not well understood so far, was observed for TiO$_2$(110) by Brause, Skordas, and Kempter.[20]

Figure 4 shows the Li$^+$ ICISS energy spectrum in the

normal-incidence condition obtained from the TiO film formed on the Mg^{18}O layer that was homoepitaxially grown on the MgO(001) substrate. As mentioned in Sec. II, TiO was formed by Ti deposition without the introduction of O$_2$ gas into the UHV chamber. The ^{18}O peak is observed in Fig. 4, indicating that a part of the TiO film is due to the incorporation of oxygen from MgO into the deposited Ti film, although the appearance of the ^{16}O peak may indicate that the residual oxygen in the UHV chamber is also related to the TiO formation. This appearance of the ^{16}O peak might be due to the diffusion of oxygen during the annealing at 1000 K for 10 min of the Ti/Mg^{18}O/MgO(001) sample.

Isotope exchange between Mg^{18}O and Ti^{16}O, in which oxygen came from the residual gas in UHV, might be responsible for the appearance of the ^{18}O peak in Fig. 4. In our former study, it was found that a Ti film grew epitaxially on the α-Al$_2$O$_3$(0001) surface with the crystal structure of α-Ti from the initial stage of growth.[21] In that study, the film growth of Ti was performed by Ti deposition at room temperature in UHV (base pressure 3×10^{-10} Torr) followed by annealing at 1170 K for 10 min in UHV. The oxygen peak in ion scattering spectroscopy (ISS) was not observed in the Ti film formed on Al$_2$O$_3$. In comparing Ti/Al$_2$O$_3$ to Ti/MgO, it is most likely that the appearance of the oxygen peak in the ISS spectrum of the Ti/MgO sample is attributable to the MgO substrate. Moreover, it was also found that the Ti adsorbate was incorporated into the MgO substrate via Mg substitutional sites.[10,11] In this context, the appearance of the ^{18}O peak in Fig. 4 is interpreted as indicating that the TiO formation is caused by oxygen incorporation from MgO into the deposited Ti film.

Figure 5 displays MIES results as a function of O$_2$ exposure. The oxygen exposure was carried out at room temperature. The O $2p$ and Ti $3d$ features of TiO disappear immediately after the O$_2$ exposure. The work function increases remarkably from 2.6 of the TiO surface to 5.0 eV, as judged from the low-energy cutoff in the spectra. When He* approaches a metallic surface, it is well known that the image potential interaction causes a shift in the affinity level of the projectile. However, in the case of the He*-TiO surface in-
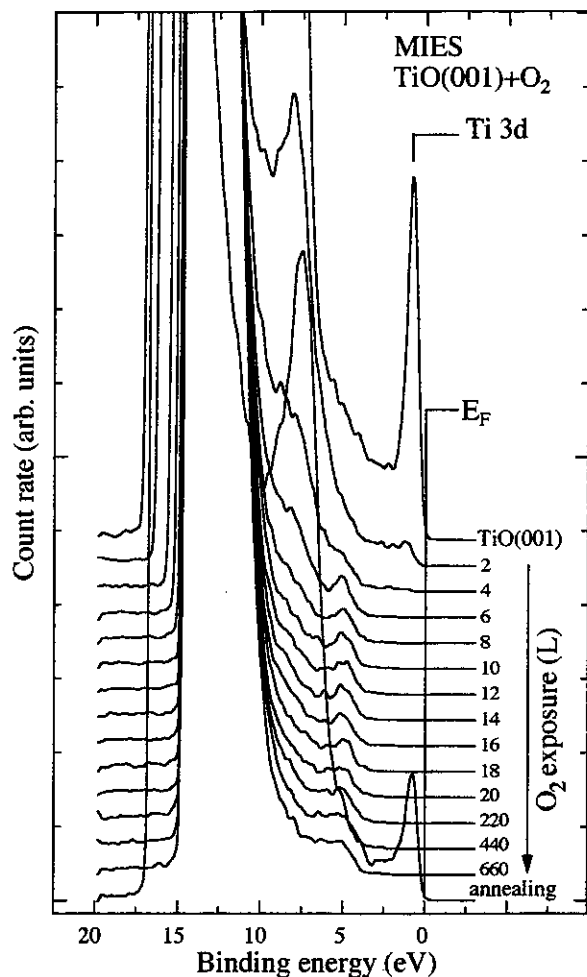
FIG. 5. MIES spectra obtained at TiO(001) formed on MgO(001) as a function of O_2 exposure. The bottom spectrum was obtained after O_2 exposure of 660 L followed by annealing at 1000 K for 10 min in UHV.

Morgner[25] that the Madelung potential caused the lifetime of the holes at the outermost surface to be longer than that in the bulk in the case of LiF and NaCl. He estimated the lifetime of the holes located at the topmost surface of NaCl: be 3.2×10^{-9} s at room temperature. Actually, a recent theoretical report,[26] in which the hole created at the surface was assumed not to hop to other lattice sites on the time scale of the interaction between the fluorine projectile and the created hole, showed good agreement with an experiment concerning negative fluorine ion formation scattered off a MgO (001) surface. In our measurement shown in Fig. 5, the Ti $3d$ peak of TiO is very sharp (full width at half maximum 0.8 eV). Moreover, the immediate disappearance of the Ti $3d$ peak is observed after O_2 exposure. These features of the Ti $3d$ peak in the MIES spectra cannot be explained except by the AU mechanism. The peaks at the Fermi edges in the MIES and UPS spectra obtained from TiO show different shapes, although both peaks are induced by Ti $3d$. This is because the physical process that leads to the Ti $3d$ structures is different; in MIES it is AU and in UPS photoemission.

After O_2 exposure of 2 langmuir (L), the Ti $3d$ peak becomes a small hump, indicating the disappearance of the surface conductivity. It is also notable that the Ti $3d$ peak position in the spectrum at 2 L shifts about 0.5 eV to the larger-binding-energy side compared with the Ti $3d$ peak position of the TiO surface. This fact suggests that the AU peak of TiO almost disappears after O_2 exposure of 2 L, and that the broad background remaining in the spectrum is caused by the AN process. On the other hand, a peak develops at 5.1 eV after O_2 exposure of more than 6 L. This peak position agrees with the recent report concerning the MIES spectra of $TiO_2(110)$ by Brause, Skordas, and Kempter.[20] They reported that this peak at 5.1 eV was due to the bridging oxygen on the TiO_2 surface, where the electron transition process was AD. In our case, O_2 exposure of the TiO surface causes a remarkable work function increase from 2.6 to 5.0 eV, indicating that the Ti $3d$ electron is transferred to the adsorbed oxygen. The disappearance of the TiO surface conductivity caused by the O_2 exposure also supports this interpretation. In our former study concerning oxygen exposure of the TiO(001) surface,[1] it was also shown that the chemisorbed oxygen was located on the top site of the titanium of TiO(001). This oxygen adsorption site on TiO suggests a bond between the adsorbed oxygen and Ti at the TiO surface. This bond formation is thought to be caused by charge transfer from titanium to adsorbed oxygen, which is confirmed by the work function change.

Figure 6 shows the UPS spectra as a function of O_2 exposure. The O $2p$ band extends to the low-binding-energy side with O_2 exposure, and the bandwidth of O $2p$ changes from 3.5 to 6.4 eV. As mentioned above, Henrich, Zeiger, and Reed reported that the O $2p$ bandwidth in TiO was around 6 eV.[2] On the other hand, the present experiment indicates that the bandwidth is only 3.5 eV. It is suggested that oxygen adsorption on a clean TiO surface is related to the difference of the bandwidth value for O $2p$ in TiO between the present result and that of Henrich et al. There are striking differences between the bottom and top spectra in Fig. 6 (O $2p$), although the corresponding MIES spectra (the bottom and top spectra in Fig. 5) show almost the same
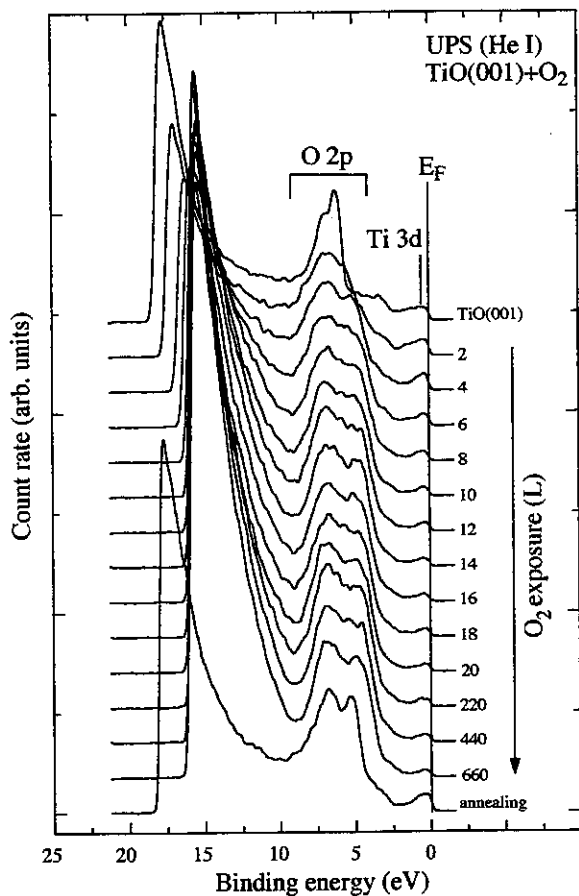
teraction, the position of the affinity level is determined by the interaction of the negative ion He^{-*} with the hole created at the O ion of the TiO surface by the resonance transition. Thus, in this case, the interaction is based on the Coulomb interaction, where electron emission should be seen via the autodetachment (AU) process. In order for the AU process to occur at the TiO surface, the He $2s$ level should go down to the Fermi level of TiO, so that the shift is estimated to be at least 2.1 eV (the affinity level[22] of He^{-*} is -0.5 eV). This large shift in the affinity level is most likely impossible if we consider only the image potential, described as $\phi(r) = e/4r$, where r is the distance between the projectile He^* and the surface. The image potential effects for a moving charge in front of an alkali halide surface, which is similar to MgO in the point that it is a predominantly ionic crystal, have been estimated to be of the order of 1–2 eV.[23] However, the large shift of 2.1 eV can be explained by the Coulomb interaction $1/r$. The possibility of electron transition by the AU process is determined by the competition between the interaction time of the He^* at the surface ($\approx 10^{-12}$ s) and the lifetime of the holes in the band, $\tau = h/W$, where W presents the bandwidth.[24] In this estimation of the lifetime of the holes ($\approx 10^{-15}$ s), the AU process seems unlikely to occur. Very recently, it was indicated by

FIG. 6. UPS spectra obtained at TiO(001) formed on MgO(001) as a function of O_2 exposure. The bottom spectrum was obtained after O_2 exposure of 660 L followed by annealing at 1000 K for 10 min in UHV.
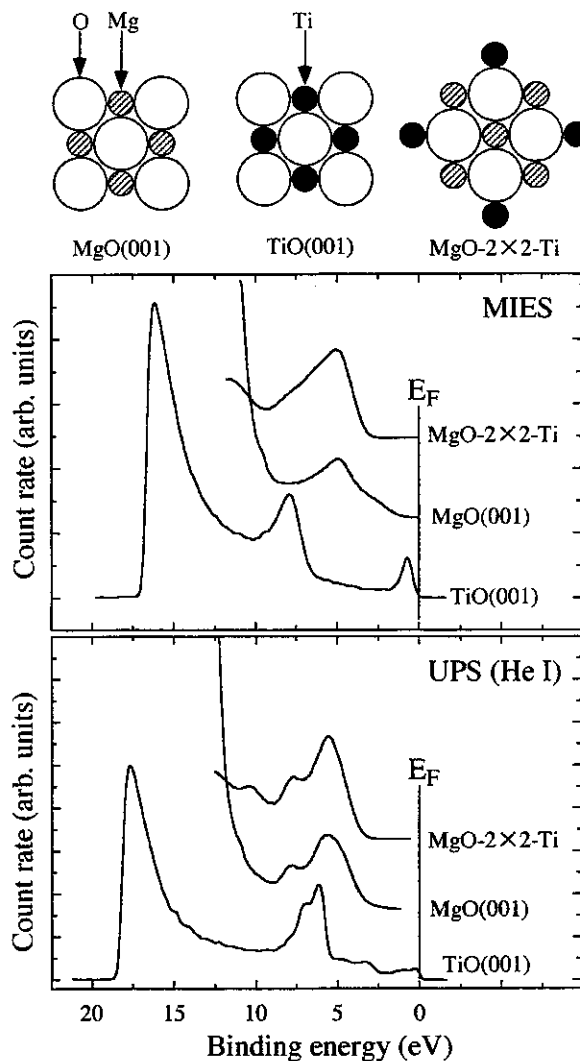

FIG. 7. MIES and UPS spectra obtained from the TiO(001), MgO(001), and MgO-(2×2)-Ti surfaces. The picture above the spectra shows the top view of the atomic arrangement of each surface.

features. This contrast between the UPS and MIES spectra suggests oxygen incorporation into the TiO film, taking into account the difference of surface sensitivity between MIES and UPS. In the UPS spectrum of the clean TiO surface, a small peak is observed at around 3.5 eV. After oxygen exposure, this small peak is included within the widened O $2p$ peak, suggesting that this small peak at 3.5 eV on the TiO clean surface may be due to slight oxygen contamination.

Figure 7 shows MIES and UPS results obtained for the MgO-(2×2)-Ti superstructure, MgO(001), and TiO(001). We have indicated that when the Ti-deposited MgO(001) surface was annealed at 1270 K in UHV, the 2×2 superstructure was formed.[10,11] A structural analysis using coaxial impact-collision ion scattering spectroscopy and RHEED proposed the 2×2 structure model indicated in Fig. 7.[11] In the proposed model, Ti is substituted for one-quarter of the Mg, ions at the outermost surface. This Ti that is substituted for Mg was located in the same plane of the MgO(001) outermost surface. It is believed that if the size of the substituting atom is different from the original one, then protrusion of the substituting atom from the original surface plane will be observed.[16] The ion radii of Mg^{2+}(0.65 Å) and Ti^{4+}(0.68 Å) are very close. Thus, our result suggests the four-valent state of Ti at the 2×2 surface.

In Fig. 7, both the MIES and UPS spectra of the 2×2 surface show essentially the same features as for MgO, but

not TiO, and there is no state at the Fermi level. This suggests that the four valence electrons of Ti ($3d^24s^2$) are probably localized at the oxygen ions at the 2×2 surface. Thus, it is also suggested that Ti at the 2×2 surface is in the four-valent state. However, if Ti is in the four-valent state in the proposed structural model, charge neutrality at the 2×2 surface is not obtained. There might be Mg ion defects or additional O ions surrounding the Ti ions in the proposed model.

In the present experiment, it was shown that TiO formation is the result of an interfacial reaction between deposited Ti film and the MgO surface, where the oxygen from MgO was incorporated into the Ti film. On the other hand, we indicated in our former study[10,11] that deposited Ti was incorporated into the MgO substrate via Mg^{2+} substitutional sites without inducing disorder of the MgO lattice. Both MgO and TiO have a rocksalt crystal structure, and their lattice constants are very close: MgO 4.21 Å and TiO 4.18 Å.[6] It may be reasonable that TiO single-crystal film formation is caused by the interdiffusion of Ti adsorbates into the MgO substrate through the Mg sites rather than the incorpo-

ration of oxygen from MgO into the deposited Ti film. In this respect, the TiO/MgO system may not belong to the category of heteroepitaxy. The Mg driven out by the substituted Ti may desorb from the surface after segregation to the TiO surface because of the high vapor pressure of Mg. From the viewpoint of bulk thermodynamics, the present result is surprising, because Mg has a larger reactivity toward O than does Ti, judging from the heat of formation.[9] The metal/MgO interface has been treated as a typical model of dissimilar material adhesion in theoretical investigations, and the possibility of an interfacial reaction has been excluded so far. Metal-induced gap states have been theoretically predicted in the Ti/MgO system without consideration of interfacial reactions.[27] However, the result presented in this paper shows an interfacial reaction between the deposited Ti film and the MgO surface. It has been theoretically reported that a slight disorder of the atomic arrangement accompanied by charge distortion occurred at the step edges on the MgO surface.[28] It is our interpretation that these surface defects may be the sites at which the incorporation of Ti adsorbates occurs.

IV. CONCLUSION

Ti deposited on the MgO(001) surface was investigated using MIES, UPS (He I), Li^+ICISS, and electron-diffraction techniques (RHEED and LEED). TiO single-crystal film formation was confirmed after Ti deposition followed by annealing at 1000 K. This TiO formation was caused by an interfacial reaction between MgO and deposited Ti film. The outermost surface of the film had metallic properties, as judged from the appearance of the autodetachment peak of He^{-*} in the MIES spectra. Oxygen exposure increased the work function of TiO from 2.6 to 5.0 eV. The electronic structure of MgO-(2×2)-Ti was also investigated. It is suggested that Ti is in the four-valent state in the 2×2 superstructure.

ACKNOWLEDGMENT

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