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Atomic Structure of TiO Epitaxial Layers Deposited on the MgO(100) Surface

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ABSTRACT

Impact-collision ion scattering spectroscopy was applied to study the geometrical structure of epitaxially grown TiO layers on the MgO(100) surface. Hetero-epitaxial TiO layer was formed by thermal evaporation of titanium onto the MgO(100) surface followed by the exposure to oxygen at 400°C. The well-ordered TiO structure was confirmed by the impact-collision ion scattering spectroscopy and reflection high energy electron diffraction patterns. It is revealed that the Ti and O atoms are located on the on-top site of the MgO(100) surface and the TiO overlayers are composed of little three dimensional islands.

Key words* : *Atomic structure, TiO epitaxial layer on MgO, Impact-collision ion scattering spectroscopy, Time-of-flight, Reflection high energy electron diffraction

1. Introduction

The surface properties of solids such as atomic structure at the surface or interface, atomic defect structure, segregation of impurities, electronic structure of the surface and surface phonon play important roles in the characteristics of catalysts, sensors, sinterability, friction and corrosion.1) The interfacial characteristics also play an important role in the epitaxial film growth.2,3) Low-Energy(LE) Ion Scattering Spectroscopy(ISS) has been established as an effective tool for the structural analysis of solid surfaces.4,5) The excellent surface sensitivity of LEISS comes from the efficient ion neutralization process at a surface. Inert-gas ions such as He^+, Ne^+ and Ar^+ are often used as an ion beam because they are readily neutralized via Auger neutralization process and show no target-element dependence of the neutralization probability.6) On the other hand, LEISS using alkali metal ions (Li^+, Na^+ and K^+) contains signals of inelastically scattered ions since the alkali metal ions survive neutralization. This makes the positioning of the atoms in deep layers possible.7)

Similar characteristic is expected in an LEISS system when the Time-Of-Flight(TOF) analyzer is adapted, because both the scattered ions and the neutralized atoms are detected. This ocx xffers another advantage of using non-reactive (noble-gas) primary ions.8) In Impact-Collision Ion Scattering Spectroscopy(ICISS) with scattering angle of near 180°, which is a special mode of LEISS, the geometrical structures of several layers deep can be analysed and simulations of the scattering trajectories are simplified because the trajectory taken by the scattered ions is almost identical with that of incident ions and the blocking effect by adjacent atoms can be avoided. Therefore the combination of TOF and ICISS will provide us the information about the atomic structure of films on a substrate.

Titanium oxides were studied widely because of their importance as catalyst supports and photocatalysts. They show various interesting electrical properties according to the state of oxidation which is expressed by the general formula of Ti_nO_{2n-1} ($n=1\sim\infty$).9) For example TiO_2, which is an insulator, converts to n-type semiconductor as the amount of oxygen vacancies increases by reduction. Among the categories of Ti-O system, TiO shows typical characteristics of covalent bonding such as high melting point and high hardness even though the atomic bonding is mainly ionic with rock salt crystal structure.1) These conflicting characteristics have attracted interests on the electronic structure. However there are few experimental studies because of the lack of TiO single crystal, while many theoretical studies have been performed.10-13)

We report here the growth of TiO epitaxial layer on the MgO(100) surface and the structure analysis of TiO layers. It was shown that titanium monoxide could be epitaxially grown by evaporation and oxidation process. Magnesium oxide was chosen as a substrate because both magnesium oxide and titanium monoxide have a rock salt structure and the lattice mismatch between them is very small(0.9%). The atomic structure of TiO layers was investigated by using TOF-ICISS and Reflection High Energy Electron Diffraction(RHEED).

2. Experimental

The TOF-ICISS experiment was performed at room temperature in an Ultrahigh Vacuum(UHV) chamber equipped

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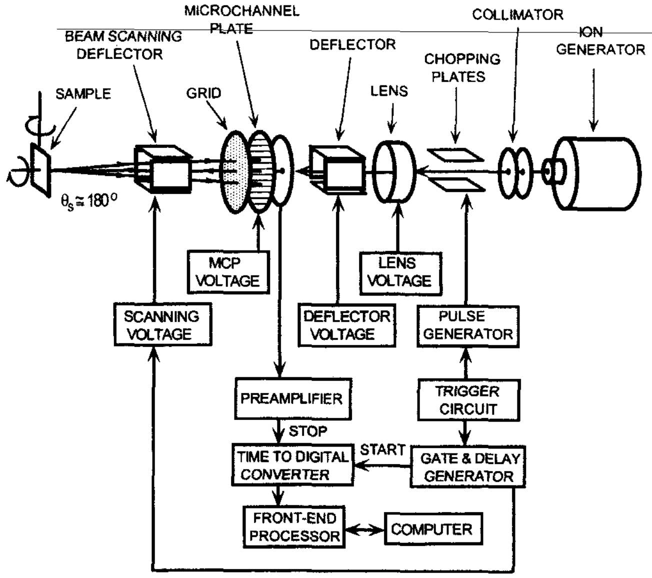
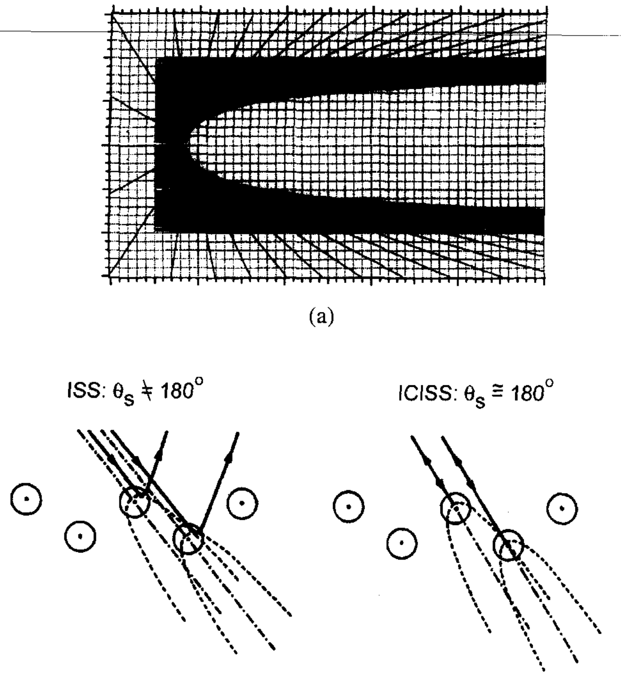


Fig. 1. Schematic diagram of time-of-flight impact-collision ion scattering spectroscopy system.



(a)

(b)

Fig. 2. (a) Schematic diagram of a shadow cone and (b) a comparison between ISS and ICISS.

with the RHEED optics. The part of TOF-ICISS measurement is composed of the ion generator, the transfer line for pulsed ion beam and the detecting system of scattered particles. The schematic diagram of the system is shown in Fig. 1.

The 2 keV He^+ ions were generated in a discharge type ion source and were mass-analyzed by a Wien filter. The primary energy of the ions can be changed from 0.5 to 3 keV. Energy analysis of the back scattered ions or neutral atoms was made by measuring the flight time from the sample to the detector. The ion beam was chopped by the electrostatic deflection plates, which produced a pulsed beam with a full width at half maximum of 40 ns. The scattered particles were detected by a Micro Channel Plate(MCP) which was placed at a distant of 69 cm from the sample. All spectra were measured for 20 s at the sample current of 20 nA.

The MgO single crystal with the dimension of $20 \times 10 \times 1$ mm was fixed to a tantalum holder and introduced into the UHV chamber via the load-lock system. Sample cleaning was carried out by heating the Ta holder up to 800°C for 20 h by electron bombardment. Titanium(99.9% purity) was thermally evaporated onto the MgO(100) surface by resistive heating until no Mg(substrate) peak was observed by ICISS in situ at the incident angle of 90° from the surface. Titanium was oxidized by 10 L(1 L=1×10^{-6} Torr·s) exposure of oxygen at 400°C. The amount of oxygen exposure does not necessarily mean the minimum amount to oxidize the evaporated Ti metals.

3. Results and Discussion

When the ion beam is projected onto an atom, a region called shadow cone is generated where projectile ions cannot penetrate due to the Coulomb repulsion as shown in the Fig. 2(a). The target atoms which reside at the surface of the shadow cone show extremely large scattering intensity owing to the large density of incident ions at the surface. This phenomenon is called the focusing effect.

Since the de Broglie wave length of the incident ion is much smaller than the lattice parameter of the target in the low energy range, the effect of diffraction is negligible and the scattering process is sufficiently described by classical mechanics. Therefore the atomic position of the surface layers can be determined from the intensity variation of scattered ions with the incident angle. If the scattering angle is set at near 180° as shown in Fig. 2(b), the blocking effect that happens by the screening of neighboring atoms can be avoided and considering only the focusing effect makes the calculation possible.

Fig. 3 shows the TOF spectra of TiO deposited MgO(100) surface measured by 2 keV He^+ ion. The incident angle along the [001] azimuth varied from 10° to 90° at the interval of 2° and selected spectra which exhibit large scattering intensities due to the focusing effect were shown. The He^+ ion peaks scattered from Ti can be found. The background is formed by the multiple scattered ions from several surface layers. The oxygen atoms cannot be identified because the scattering cross section of the oxygen is small and the peak is located on the background.

Mg and Ti peak intensity variations in the ICISS spectra as a function of incident angle along the [011] azimuths of the clean and TiO deposited MgO(100) surface, respectively, are shown in Fig. 4. It should be noted that focusing peaks are observed even at a large incident angle where the He^+ ions penetrate into deep layers. This can be attributed to

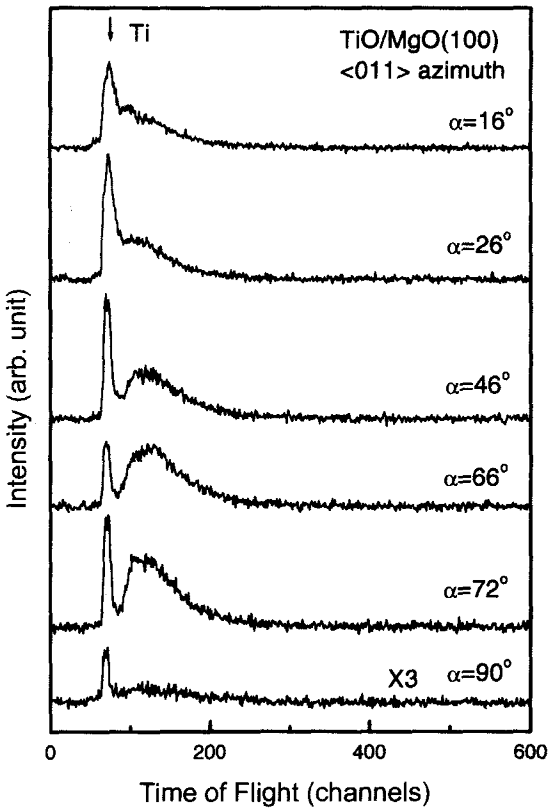


Fig. 3. Time-of-flight spectra of 2 keV He^+ ions scattered from the TiO deposited MgO(100) surface taken at selected incident angles with a fixed scattering angle of 180°. The measurement was done along the [011] azimuth.

the characteristics of TOF-ICISS method as is mentioned in Introduction. In Fig. 4, five focusing effects onto Ti atoms of the TiO deposited surface occur at the incident angles of 16°, 26°, 46°, 64° and 72°. The focusing peaks can be explained by calculating universal shadow cones for the Ti and O atoms and the possible focusing effects are schematically shown in Fig. 5. The calculation was performed using the Thomas-Fermi-Moliere(TFM) potential with the screening length proposed by Firsov.[14] In this figure, the small and large circles represent oxygen and titanium atoms, respectively. The calculated angles agree well with the experimental results shown in Fig. 4.

In Fig. 3, the peak from Mg of the substrate cannot be found at α=90° where only topmost atoms are visible by the incident ion beam and the axial channeling occurs. As the incident angle decreases from 90° to low angle, the ions which suffer multiple scattering with MgO begin to appear as a background. Furthermore the focusing angles of Ti and Mg atoms coincide each other within an experimental error as can be seen in Fig. 4. In consequence, it is concluded that the Ti and O atoms are located on the on-top site of the substrate.

It is difficult, however, to confirm from calculation on which atomic site of the substrate Ti and O atoms lie because the radius of the shadow cone does not differ

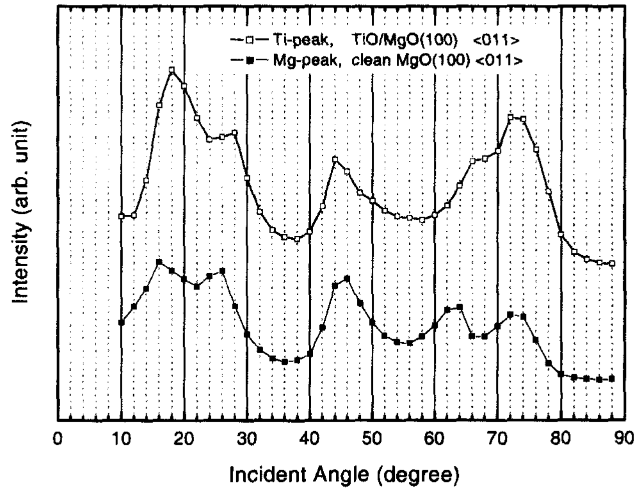


Fig. 4. Polar angle scan of Mg and Ti peak intensities at the clean and TiO deposited MgO(100) surface, respectively. Measurement was done along the [011] azimuth.

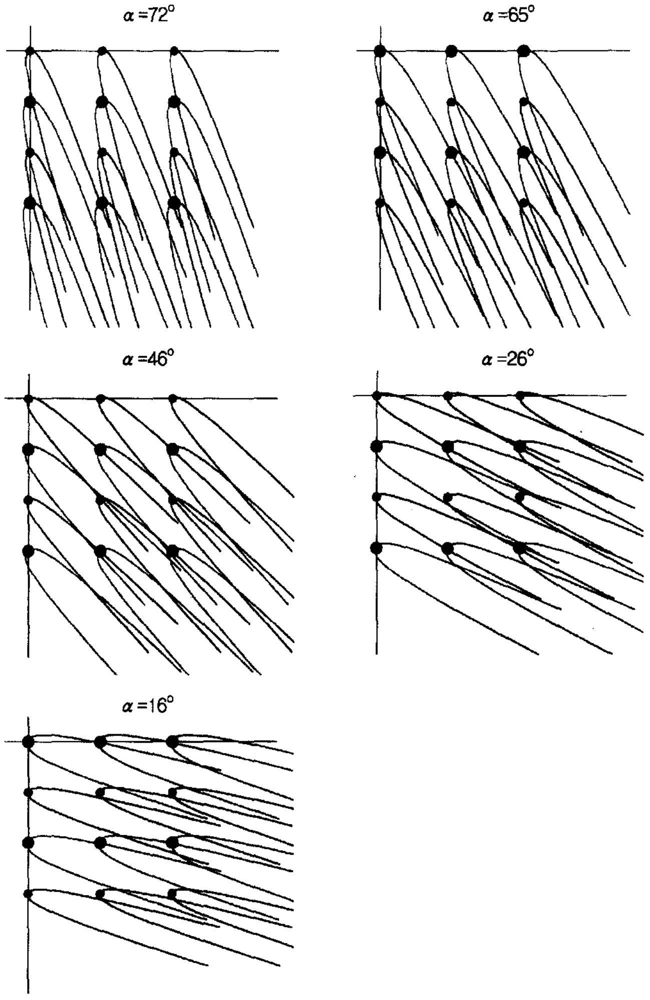
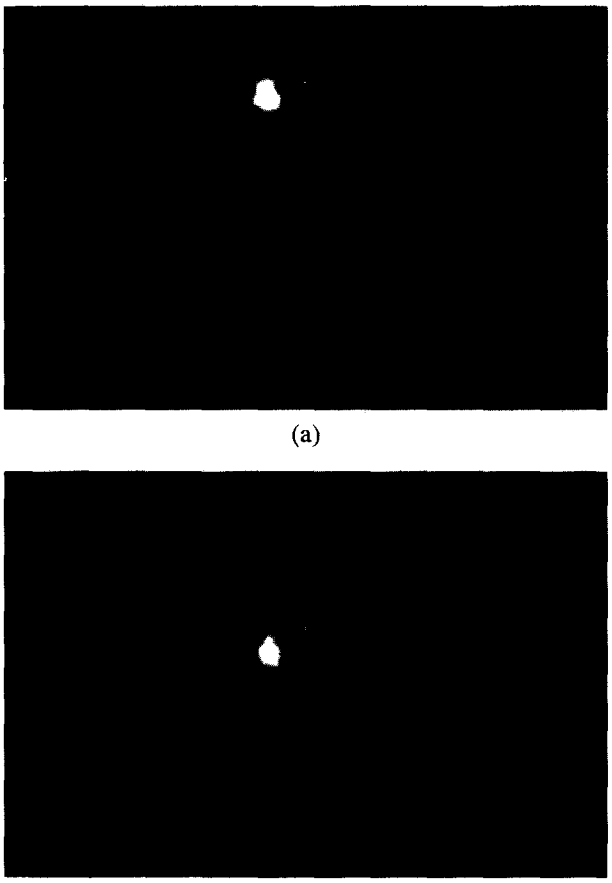


Fig. 5. Schematic views of the shadow cones for 2 keV He^+ ions impinging on the TiO deposited MgO(100) surface along the [011] azimuth. Small and large circles represent oxygen and magnesium atoms, respectively.

greatly in Ti and O. There is recent report that the layer stability in heteroepitaxy is determined by a layer-by-layer energy minimization associated with interfacial electrostatics.[15] Deposition of cation on the on-top site of anion and vice versa enables electrostatic stability. For example, in case of the deposition of $BaTiO_3$ on MgO(100) surface, if the BaO(100) surface is deposited at first it is not possible to deposit a film with good quality because bonding between the same charge of ions is inevitable. On the contrary, bonding between TiO_2 and BaO surface is composed of the opposite charged ions. Therefore it is expected that the Ti and O atoms locate on the O and Mg sites of the substrate, respectively.

The lattice constant along the surface normal and the distance between the TiO layer and the MgO substrate are not determined because of the low depth resolution of ICISS. The calculation of shadow cone also shows no difference of focusing angles in 1~2% variation of lattice constant along the surface normal direction. Considering the small amount of lattice mismatch and very thin overlayers, however, it is likely that the coherent strain due to lattice mismatch is reduced via relaxation along the surface normal rather than forming misfit dislocations.[16]


(a)

(b)

Fig. 6. Reflection high energy electron diffraction patterns of the (a) clean and (b) TiO deposited MgO(100) surface obtained using a 2.5 keV beam incident along the [011] azimuth.

It is expected that the TiO film has stoichiometric composition with little vacancies because no additional focusing peaks are found in Fig. 4 at low incident angle along the [011] azimuth. It is known that the oxygen exposure of metals at room temperature can lead to the formation of oxide phase.[17,18] The inter-diffusion of Ti and O atoms occurs during the oxidation of Ti and this results in the formation of titanium oxide phase. Even though the sample is exposed to excess oxygen, it is thought that the deposited TiO layer is composed of equal number of Ti and O atoms because the adsorption of oxygen atoms on oxide surface is difficult.

Fig. 6 is the RHEED pattern of the clean and TiO deposited MgO(100) surface. We can see that the composition of the deposited layer is TiO rather than TiO_2 because the 1×1 pattern is maintained after deposition. If the composition is TiO_2, the 2×2 pattern should be observed due to the existence of Ti vacancies. Furthermore reciprocal rods implying smooth surface morphology are also shown the diffracted pattern. It is expected that there exist little three dimensional islands on the TiO layers.

4. Conclusion

Time-of-flight impact-collision ion scattering spectroscopy was applied to study the geometrical structure of the epitaxially grown TiO layers on MgO(100). Hetero-epitaxial TiO layers can be deposited by thermal evaporation of titanium onto the MgO(100) surface and subsequent exposure of oxygen at 400°C. Well ordered TiO structure was confirmed from the ICISS spectra and RHEED diffraction pattern. It was revealed that TiO was deposited on the on-top site of the MgO substrate and had smooth surface morphology without three dimensional islands.

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