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Preparation and Characterization of Ti_2O_3 Films Deposited on Sapphire Substrate by Activated Reactive Evaporation Method

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SYNOPSIS

(001)-oriented Ti_2O_3 films were epitaxially grown on a (001)-face of sapphire single-crystalline substrate by an activated reactive evaporation method. The formation ranges of stoichiometric and nonstoichiometric Ti_2O_3 films were determined as a function of the substrate temperature (Ts), the oxygen pressure (Po_2) and the deposition rate. Stoichiometric Ti_2O_3 films were grown at Ts$\geqq$ 673K under $Po_2 \geqq 1.0\times10^{-4}$Torr, which showed the metal-insulator transition with a sharp change in electrical resistivity from 3.5×10^{-2} to $2.6\times10^{-3}\Omega$cm at 361K. Nonstoichiometric films prepared under less oxidized conditions did not exhibit the transition. The nonstoichiometry of the Ti_2O_3 films was discussed in terms of excess Ti ions.

1. INTRODUCTION

The crystal structure of titanium sesquioxide (Ti_2O_3) can be described as a corundum-type structure. The metal-insulator transition in Ti_2O_3 is a very unique and well-known phenomenon. The intrinsic electrical properties of this oxide causes the transition.[1-3] The bulky single-crystal of Ti_2O_3 grown by a Czochralski method exhibits the transition at 435K with a sharp decrease in electrical resistivity from 9×10^{-3} to$3\times10^{-4}\Omega$cm on increasing temperature.[4] Although Ti_2O_3 thin films are expected to be useful in a practical view point such as an application to the thermistor in the electric devices, there are few investigations of preparation and physical properties of Ti_2O_3 thin films. In general, the electrical properties of thin films are sensitive to morphological, crystallographic and chemical properties such as shape, grain size, orientation and stoichiometry of films. These properties depend upon preparation method as well as preparation conditions.

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The activated reactive vapor deposition method, in which metals evaporate to react with activated gases, is a powerful technique to prepare well-crystallized ceramic films with good properties. Through this method, YBC superconducting films with high Jc[5,6], ferroelectric $BaTiO_3$ films[7], and transparent Al-doped ZnO films with good conductivity[8] were reported.

The aim of this paper is first to clarify optimum preparation conditions for epitaxial growth of Ti_2O_3 on a (001)-face of sapphire. For this purpose, the effects of the substrate temperature, oxygen pressure and deposition rate on the morphology, crystallographic properties and stoichiometry of the films were discussed. Secondly the electrical properties of the obtained films were studied with a particular attention to the metal-insulator transition.

2. EXPERIMENTAL

Fig.1 shows a schematic diagram of an activated reaction evaporation system (JEOL JST-EB1000) used. Ti metal with a purity of 99.9% (Furuuchi Chemical Co. Ltd.) was evaporated by heating with an electron-beam gun (JEOL JEBG-102UB), and deposited on a (001)-face of α-Al_2O_3. The source-substrate distance was about 77cm. The substrate was heated by a resistance heater and the substrate temperature (Ts) was measured with an alumel-chromel thermocouple. During the deposition, the substrate was kept at a constant temperature of 473, 673, or 873K. The film thickness and the deposition rate (Rd) was controlled by a thickness controller with a quartz-crystal oscillator. Oxygen gas was introduced into the chamber as a reactive gas, the pressure (Po_2) of which was measured by an ionization vacuum gauge. During the deposition oxygen plasma was generated in the chamber by a rf power supply (150W) in order to increase the reactivity of introduced oxygen gas and evaporated titanium atoms. After deposition the sample films were cooled down to room temperature in a vacuum, and were not post annealed. The thickness of the obtained films were measured using a surface texture measuring instrument (SURFCOM 1500A). The deposition conditions are summarized in Table 1.

The crystallinity and phases of the deposited films were examined by X-ray diffraction (XRD) method using a conventional θ-2θ scanning mode. The distribution of the crystallographic orientation was also examined by X-ray rocking curves taken in the following

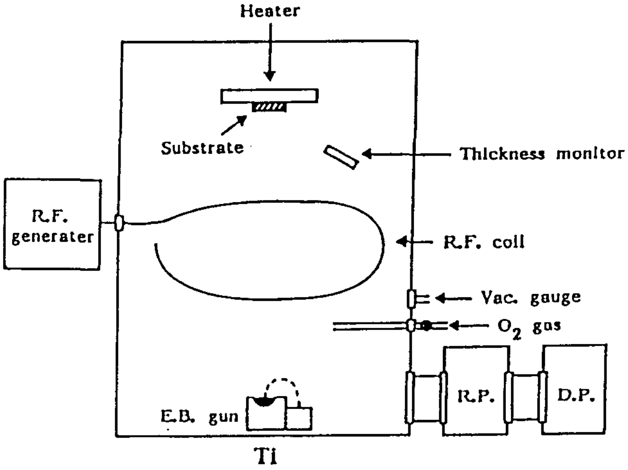

Fig.1 Schematic diagram of an activated reactive evaporation system.

way : the 2θ axis was fixed at about 39.54 deg, the angle of (006)-diffraction of Ti_2O_3, and then only the θ axis was scanned. The surface morphology of the films was observed by SEM (JEOL JCXA-733). The electrical resistivity was measured by a dc two-probe method with gold electrodes. The measurement was performed in the temperature range between 300 and 600K in a vacuum (10^{-3}Torr). For this measurement the films with a thickness of 2000Å were used.

Table 1 Deposition conditions

Substrate	sapphire (001)-face
Substrate temperature	473~873K
Evaporating source	Ti metal (99.9%)
Reactive gas	O_2 : (0.5~3.0)×10^{-4}Torr
r.f. power	150W
Deposition rate	1.0~5.0Å/s

3. RESULT AND DISCUSSION

3.1 Formation of Ti_2O_3 film

Fig.2 shows a typical XRD pattern of a Ti_2O_3 film deposited on a (001)-face of sapphire (α-Al_2O_3) at Ts=873K, Po_2=1.0×10^{-4}Torr and Rd=1.0Å/s. Only two diffraction peaks (2θ=39.5 and 85.1 deg) were observed besides the peaks of the substrate. The d-spacings corresponding to these peaks are 2.277 and 1.138Å, which are consistent with those of the (006) and (00$\underline{12}$) planes of Ti_2O_3 crystal, respectively. Both Ti_2O_3 and α-Al_2O_3 have the similar corundum structure. The metal-insulator transition was clearly observed in this film as mentioned in the following section. It is thus reasonable to consider that the (001)-oriented Ti_2O_3 film was epitaxially grown on the (001)-face of sapphire.

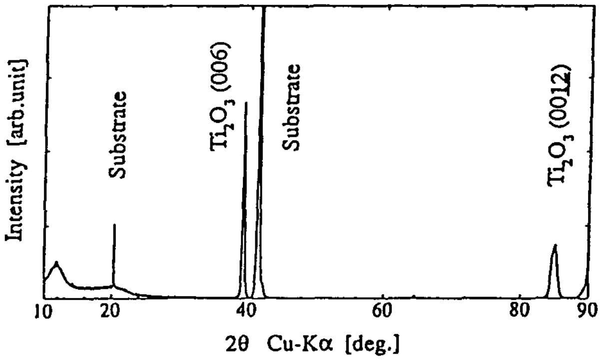

Fig.2 Typical X-ray diffraction pattern of a Ti_2O_3 film deposited on a (001)-face of sapphire at Ts=873K, Po_2=1.0×10^{-4}Torr and Rd=1.0Å/s.

Typical rocking curves of (006) diffraction peaks are shown in Fig.3 for the films prepared at different substrate temperatures of 673 and 873K. The peak widths of the films prepared at Ts=673 and 873K were 1.04 and 0.75 deg, respectively. These results reveal that the films have good orientation. And with increasing the substrate temperature, the crystallinity and the orientation of the films became better. It suggests that a part of the crystallization energy of the film is supplied by the thermal energy of the substrate to make the adatoms migrated on the substrate surface.

The SEM image in Fig.4 shows that the film was homogeneous and had a flat surface. The film is also found to consist of small grains with diameters of <1000Å. Small particles observed on the surface were the clusters of Au atoms deposited to prevent from charging up of the film.

A formation map of Ti_2O_3 films are illustrated in Fig.5 as a function of Ts, Po_2 and Rd. Stoichiometric Ti_2O_3 was grown at Ts≧673K and Po_2≧1.0×10^{-4}Torr. With decreasing Ts and Po_2 and increasing Rd, the peak position of the (006) diffraction was shifted toward smaller angles than that of the stoichiometric film (2θ=39.5 deg), and the color of the films changed to dark blue from faint blue. It means that the oxidation degree of Ti_2O_3 films depends on Ts, Po_2 and Rd. Note that the nonstoichiometric Ti_2O_3, the less oxidized phase, was formed at relatively low Po_2 and high Rd. The substrate temperature would also influence the numbers of both the chemisorbed O_2 molecules and condensed Ti atoms on the surface. Ti/O ratio of this system would increase with a decrease in Ts. The lattice parameters of nonstoichiometric Ti_2O_3 films increased with increasing Ti/O ratio. Therefore, the nonstoichiometry of Ti_2O_3 films probably results from the excess Ti ions not from the oxygen vacancies. Details of structural properties of nonstoichiometric Ti_2O_3 films will be reported elsewhere.

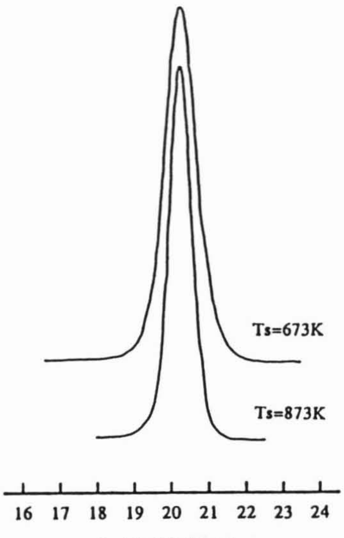

Fig.3 Rocking curves of (006) diffraction of Ti_2O_3 films prepared at Ts=673 and 873K.

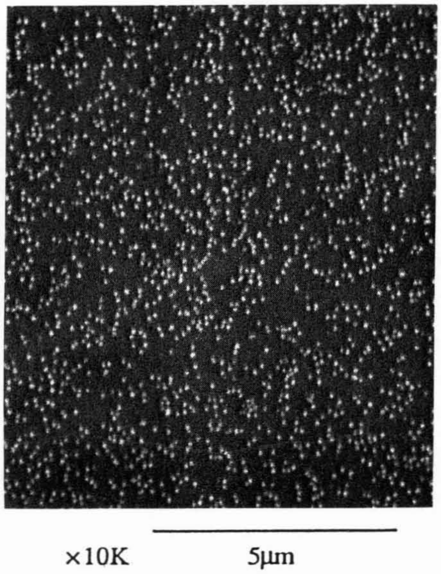

Fig.4 SEM image of a (001)-oriented Ti_2O_3 film prepared at Ts=873K, Po_2=1.5×10^{-4}Torr and Rd=1.0Å/s.

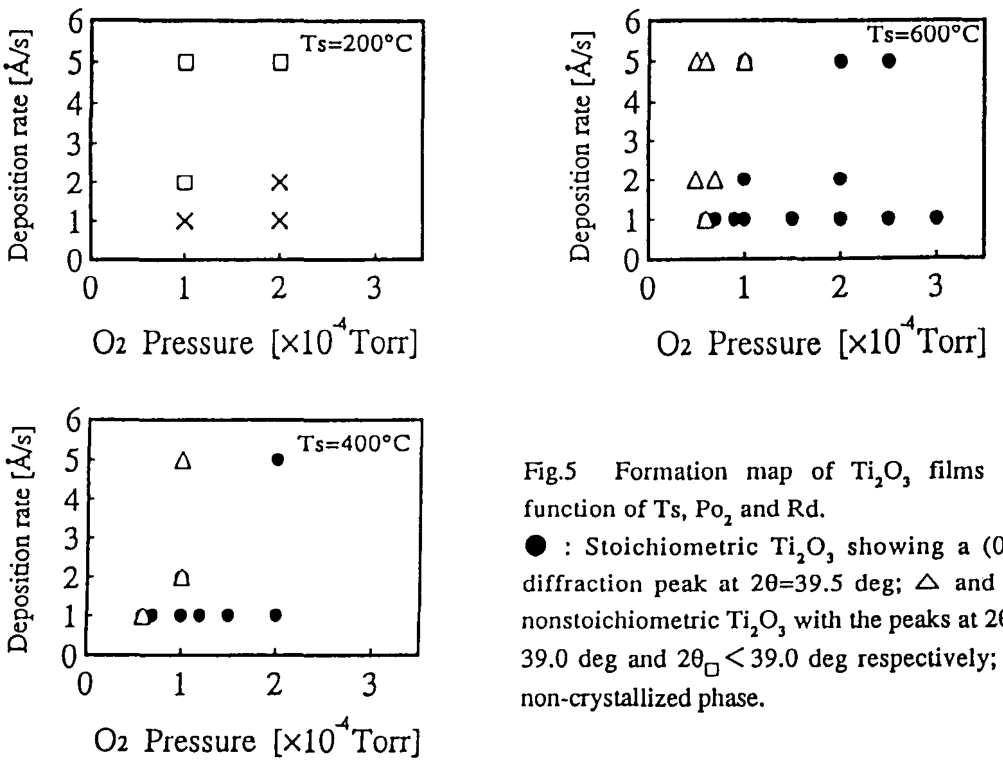

Fig.5 Formation map of Ti_2O_3 films as a function of Ts, Po_2 and Rd.
● : Stoichiometric Ti_2O_3 showing a (006)-diffraction peak at $2\theta=39.5$ deg; △ and □ : nonstoichiometric Ti_2O_3 with the peaks at $2\theta_{\triangle} \geqq 39.0$ deg and $2\theta_{\square} < 39.0$ deg respectively; × : non-crystallized phase.

3.2 Electrical properties

Fig.6 shows the electrical resistivity of Ti_2O_3 films as a function of Po_2 at 673 and 873K. All films were prepared at Rd=1.0Å/s and the resistivity was measured at room temperature. It was clearly indicated that the resistivity was decreased with decreasing Po_2 and Ts. Stoichiometric Ti_2O_3 is a n-type semiconductor. Nonstoichiometric films prepared at low Po_2 and low Ts contained a number of structural defects caused by the excess titanium ions. The excess cations would supply the electrons into the conduction band. Thus the resistivity of nonstoichiometric Ti_2O_3 films was smaller than that of stoichiometric ones.

Fig.7 shows the temperature dependence of the resistivity of stoichiometric Ti_2O_3 films prepared

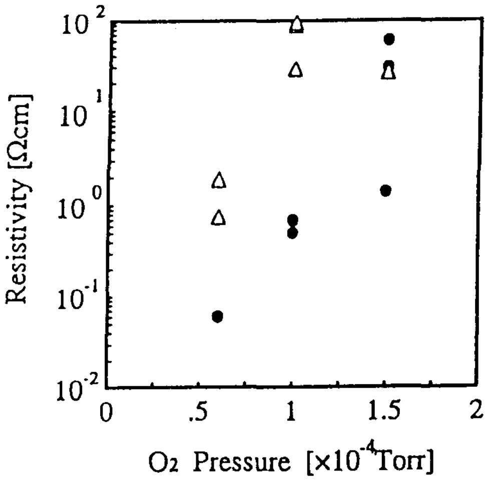

Fig.6 Electrical resistivity of Ti_2O_3 films prepared at Rd=1.0Å/s as a function of Po_2 at Ts=673K (●) and 873K (△).

at Ts=673K, $Po_2=0.6\times10^{-4}$Torr and Rd=1.0Å/s. A change in resistivity due to the metal-insulator transition was clearly detected. The transition commenced at 361K and the resistivity was dropped from 3.5×10^{-2} to $2.6\times10^{-3}\Omega$cm on increasing temperature. But the transition temperature was about 80K lower than that of the bulk crystal. The difference in the temperature and the magnitude of the transition may be due to the morphological and chemical properties such as grain size, orientation, stoichiometry and lattice strain. It is noteworthy that the films prepared under less oxidized conditions did not show the transition.

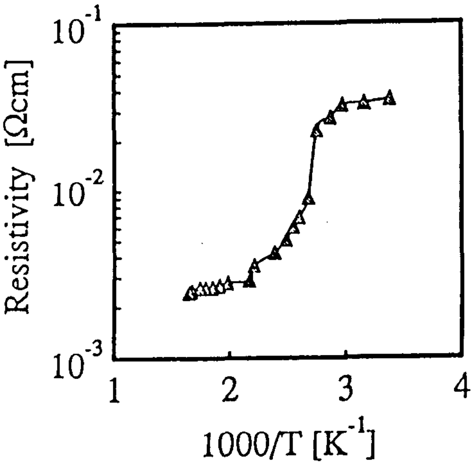

Fig.7 Variation of electrical resistivity with temperature in a stoichiometric Ti_2O_3 film prepared at Ts=673K, $Po_2=0.6\times10^{-4}$Torr and Rd=1.0Å/s.

4. CONCLUSIONS

Stoichiometric and nonstoichiometric Ti_2O_3 films have been prepared on a (001)-face of sapphire single crystalline substrate by an activated reactive evaporation method. The stoichiometric and (001)-oriented Ti_2O_3 films were epitaxially grown at Ts≧673K and $Po_2 \geqq 1.0\times10^{-4}$Torr. The films with the smooth and homogeneous surface consisted of small grains with diameters of <1000Å. The stoichiometric films exhibited the metal-insulator transition at about 360K. The resistivity was sharply dropped by about one order of magnitude. But the nonstoichiometric films formed under the less oxidized conditions did not show the transition. The lattice spacing of Ti_2O_3 films increased with increasing nonstoichiometry. This tendency was interpreted by the excess Ti ions in the lattice of Ti_2O_3 films.

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REFERENCES

1) S.C.Abrahams, Phys.Rev., **130**, 2230 (1963).
2) J.Yahia and H.P.R.Frederikse, Phys.Rev., **123**, 1257 (1961).
3) F.J.Morin, Phys.Rev.Letters, **3**, 34 (1959).
4) J.M.Honig and T.B.Reed, Phys.Rev., **174**, 1020 (1968).
5) T.Terashima, K.Iijima, K.Yamamoto, Y.Bando and H.Mazaki, Jpn.J.Appl.Phys., **27**, 91 (1988).
6) T.Terashima, K.Iijima, K.Yamamoto, J.Takada, K.Hirata, H.Mazaki and Y.Bando, J.Cryst.Growth, **95**, 617 (1989).
7) K.Iijima, T.Terashima, K.Yamamoto, K.Hirata and Y.Bando, Appl.Phys.Lett., **56**, 527 (1989).
8) S.Nakata, T.Kawamura, J.Takada, T.Nanba, T.Fujii, A.Osaka and Y.Miura, Extend Abstracts (The 52nd Autumn Meeting, 1991), The Japan Society of Applied Physics, Vol.2, 481.