

GAS SENSING PROPERTIES OF RUTILE-TiO₂ (100) FILMS PREPARED BY PULSED LASER DEPOSITION

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ABSTRACT

GAS SENSING PROPERTIES OF RUTILE-TiO₂ (100) FILMS PREPARED BY PULSED LASER DEPOSITION. The gas sensing property of TiO₂ thin films have been demonstrated in rutile-TiO₂ (100) films grown on the α -Al₂O₃ (0001) substrates by Pulsed Laser Deposition (PLD). High quality rutile-TiO₂ (100) films were successfully grown on α -Al₂O₃ (0001) with the substrate temperature at 500°C under 15 mTorr of O₂ gas pressure. The thickness and crystallinity of TiO₂ films were evaluated by Rutherford backscattering spectrometry combined with channeling (RBS/C) and X-ray diffraction using θ -2 θ scans. To evaluate CO₂ gas sensing property of TiO₂ films, the dependence of the changing of electrical resistivity on the temperature was measured. It's found that high crystallinity rutile-TiO₂ (100) films on the α -Al₂O₃ (0001) substrate kept at 100°C exhibits good gas sensing property for CO₂ gas.

Keywords: X-ray diffraction, laser epitaxial, TiO₂ thin film, electrical resistivity, CO₂

INTRODUCTION

Titanium dioxide (TiO₂) has been considerable interest from viewpoint of basic science and applications. For example the TiO₂ is used in heterogeneous catalysis, as photo-catalyst, in solar cell for the production of hydrogen and electric energy, as corrosion-protective coating, as an optical coating in ceramic, in electric devices such as varistors, and as gas sensor. More researchers have been interest a great was addressed in the characterization of the structural and electrical properties of thin film for gas sensing⁽¹⁾. The TiO₂ is extensively used as gas sensors due to their properties, which changes their electrical resistivity under gas exposures⁽²⁻⁴⁾. TiO₂ is also interesting candidate for conductance-type gas sensor devices for the detection of NO₂⁽⁵⁾, ethanol⁽⁶⁾, and CO₂⁽⁷⁾. Usually, the resistivity of TiO₂ is high in low temperature, and that decreased at high temperature as the examples shown in references^(8,9). Fully oxidized the TiO₂ is an insulator with a resistivity on the order of 10¹³ ohm-cm. As the remove oxygen atoms from the TiO₂ lattice, the electrical resistivity decreases and begins to act like n-type semiconductor^[10]. It is generally believed that, a gas sensor should have a high selectivity and sensitivity to the target molecule. Also a short response time and stability are requested. Sensitivity and response time to gas are strongly influenced by the quality of the thin films, such as crystal structure, microstructures, chemical composition and the ohmic contact. TiO₂ films have been prepared by several deposition techniques such as conventional sputtering^[11], and RF helicon magnetron sputtering^[12]. In this present study, the rutile-TiO₂ films were prepared by pulse laser deposition (PLD) under controlled oxygen low-pressure. The crystal quality, the crystallographic orientation relationships between film and substrate with using XRD and RBS/channeling and the electrical properties including the sensitivity and response to CO₂ are reported.

METHOD

The epitaxial-TiO₂ films were deposited on the α -Al₂O₃ substrates by pulse laser deposition (KrF-Eximer laser, wavelength: 248 nm, Lambda Physik). The α -Al₂O₃ substrates were obtained commercially (mirror-polish at both sides) and the typical size is 10 × 10 × 0.3 mm³. The substrates were cleaned ultrasonically in acetone at 15 min and also in water at 5 min. The PLD chamber was pumped down to 6×10⁻⁵ Pa using a turbo molecular pump (TMP). The laser beam incident was focused to the evaporation target with incident angle of 45°. Typical laser energy and repetition rate were 150 mJ/cm² and 5 Hz. The evaporation target to substrate distance was about 50 mm. Both the target stage and the substrate holder were rotate during deposition. The single crystal rutile-TiO₂ (ϕ 30 mm) was used for the evaporation target. To oxidize and form TiO₂ film, oxygen gas (purity 99.99%) was flowed into the chamber through a mass-flow meter controlled by an absolute pressure gauge (Baratron 626, MKS)

under the pumping condition. In this study, TiO₂ films with 300–500 nm in thickness were deposited at 500°C under an oxygen pressure at 2 Pa. The crystallographic relationship between TiO₂ films was determined by X-ray diffraction measurement using a high-resolution diffractometer (X'Pert-MRD, Phillip). The X-ray source was operated at 40 kV and 30 mA for Cu-K α radiations. Rutherford backscattering/channeling (RBS/C) analysis using 3 MV single-stage of accelerator at JAERI/Takasaki was employed to characterize the epitaxial-TiO₂ films. The analyzing 2.0 MeV ⁴He⁺ ions were incident into the sample and backscattered particles were detected at 165° scattering angle with a surface barrier detector. The beam size was 1 mm in diameter and the beam current was 15 nA typically. Samples were mounted on a three-axis goniometric to pattern the planar channeling and the axial channeling in angular coordinate. The thickness and the crystallinity of TiO₂ films were evaluated from RBS/C spectra. The electrical resistivity of deposited films under the CO₂ gas atmosphere was measured by using the measuring equipment illustrated in Figure 1. The two-probe method was used with Au-contacts sputtered on the TiO₂ films. The chamber was pumped down to 6×10^{-5} Pa by a TMP, and then the CO₂ gas was flowed into the chamber through a mass-flow meter controlled by an absolute pressure gauge (Baratron 250, MKS) under the pumping condition. The deposited TiO₂ films were heated by the ceramic heater and temperatures were monitored by a thermocouple placed next to sample.

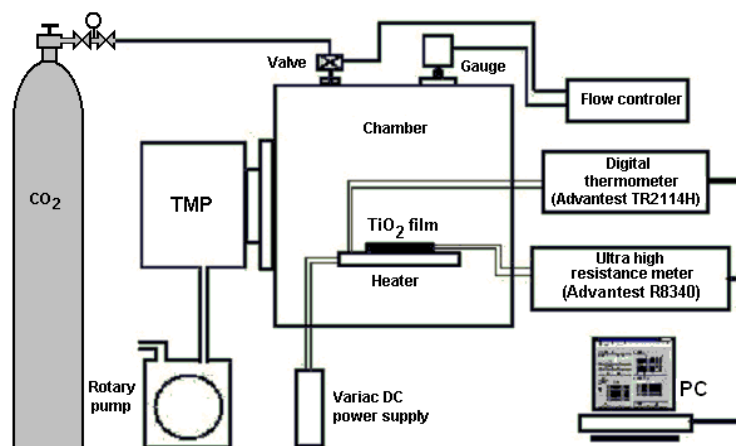


Figure 1. The instrument system measured of electrical properties including the sensitivity to CO₂.

RESULTS AND DISCUSSION

The crystal structure of deposited TiO₂ thin films was examined with X-ray diffraction technique. Figure 2 shows a typical θ -2 θ X-ray diffraction pattern from the TiO₂ film on the α -Al₂O₃ (0001) substrate. The film was deposited at 500°C with about 507 nm thickness. In this case, only the reflections from the rutile-TiO₂ (200) and (400) are observed without any reflections from the α -Al₂O₃ substrate, which indicates that the only rutile-TiO₂ (100) films are epitaxially grown on the (0001) plane of α -Al₂O₃ substrate. The peak positions at $2\theta = 39.97^\circ$ and 85.89° correspond to the reflection from rutile-TiO₂ (200) and (400), respectively. As the result, high quality rutile type TiO₂ (100) film were successfully obtained on α -Al₂O₃ (0001) with the substrates temperature kept at 500°C and an exhausted to 2 Pa of O₂ gas pressure.

RBS/channeling was employed to characterize TiO₂ films grown on α -Al₂O₃ (0001) substrates. Figure 3 shows the 2.0 MeV ⁴He⁺ RBS spectra from the rutile-TiO₂ (100) film on the α -Al₂O₃ (0001) taken under random and the TiO₂<100> aligned condition. The thickness of the film estimated by RBS spectra is 507 nm. From these RBS spectra, one can recognize clearly the separated peaks from TiO₂ film and α -Al₂O₃ substrate. The peaks at 1.43 and 0.88 MeV correspond to Ti component in the TiO₂ film and Al component in the α -Al₂O₃ substrate. Judging by the peaks intensity, the high quality TiO₂ film is grown up from the interface and the interface is not mixed with each other within the depth resolution (~ 10 nm) of this technique. The minimum yield, $\chi_{\min}$ value, the ratio between the random and the axially aligned yield at the fixed depth near the surface region, gives a measure to evaluate the

degree of disorder in crystalline solids. The $\chi_{\min}$ value in the $\langle 100 \rangle$ aligned spectrum is 0.039 at the just area behind the surface peaks of the TiO₂ film, which suggests that the crystal quality of the film is high enough as that in bulk single-crystal even if includes twins. In the peak from Ti component under the aligned spectra, one can recognize two peaks at both sides of the TiO₂ film. The peak at the high-energy side corresponds to the surface peak and the peak at the low-energy can be attributed to the imperfections at the boundary layer adjacent to the α -Al₂O₃ (0001) substrate. The planar channeling analysis around the mayor axes of the TiO₂ film and the α -Al₂O₃ gives the evidence that the TiO₂ (100) crystallographic axis is parallel to the α -Al₂O₃ (0001) axis.

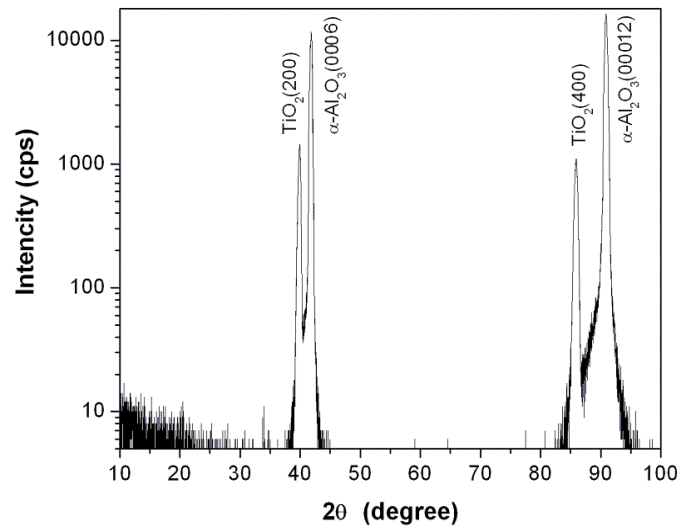


Figure 2. X-ray diffraction patterns from the epitaxial rutile-TiO₂ films on the α -Al₂O₃ (0001) substrate. The films were deposited at 500°C under the O₂ gas pressure of 15×10^{-3} Torr.

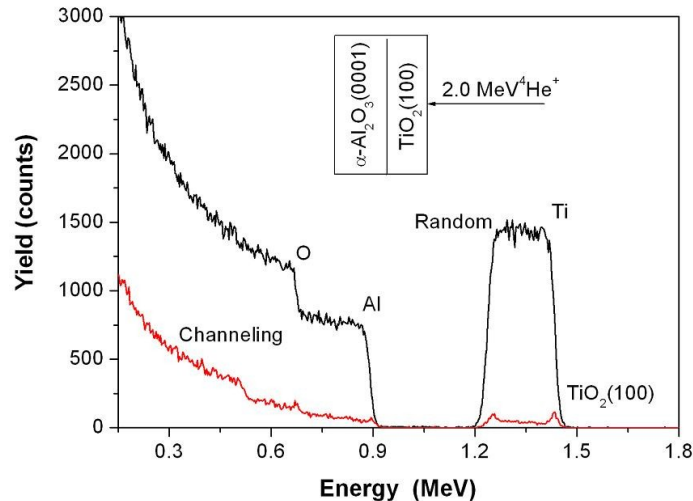


Figure 3. The 2 MeV $^4\text{He}^+$ RBS/channeling spectra from a rutile-TiO₂ film with the thickness approximately 507 nm on the α -Al₂O₃ (0001) substrate. The aligned spectrum was taken with the beam directed along the (100) axis of the rutile-TiO₂ film. The film was deposited at 500°C under the O₂ gas pressure of 15×10^{-3} Torr.

The electrical resistivity of deposited films was measured as a function of temperature (30-200 °C). In figure 4 shows the resistivity of the rutile-TiO₂ (100) film annealed at 300°C/4h in air as function of temperature. The measurement was carried out at the pressure about 6×10^{-5} Pa. The heating of film at 200°C, the resistivity decreased towards to about 1.55 Ωcm . The resistivity of TiO₂ film increases again upon subsequent cooling down

to the temperature at 30 °C. The resistivity of deposited film is exponentially dependant on the temperature which indicated the TiO₂ films have n-type semiconductor behavior. Similar behavior has been observed for the resistivity of as-deposited films. But the resistivity of the film was increased after cooling down to the temperature at 30°C. It has been assumed that the as-deposited films are not enough to oxidize in the vacuum conditions. We find the values of resistivity to be quite similar to those of the films after annealing at 300 °C in air. The TiO₂ film with doping metal showed fairly good sensing characteristics to NO₂ at 600°C⁽⁵⁾. The resistivity of TiO₂ bulk at 1200°C is in order 8.5 Ωcm⁽⁸⁾. The thin film TiO₂ was found to crystallize to a dense columnar layer of nano-crystalline rutile-TiO₂ upon annealing at 400°C, their conductivity was quite sensitive to changes in the ambient oxygen pressure between 200 and 325°C⁽¹³⁾. Nevertheless, in this work, the resistivity of rutile-TiO₂ thin film less than 10 Ωcm was obtained by the annealing 300°C/4h and if its films have been annealed at higher than 400°C, the resistivity of film increased on the order kΩcm. For practical use, high resistivity of TiO₂ films is not suitable for the gas sensing material since the resistivity measurement is needed an ultra high resistant meter.

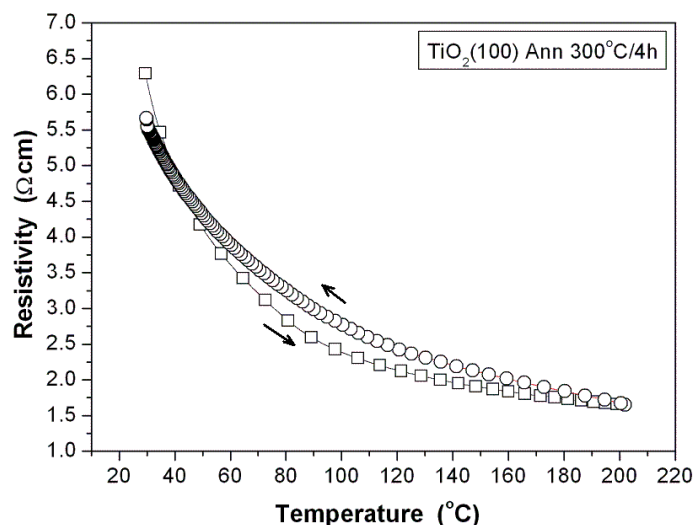


Figure 4. The resistivity of the rutile-TiO₂ (100) film annealed at 300°C/4h in air as function of temperature. The measurement was taken at the chamber condition under pressure of 6×10^{-5} Pa.

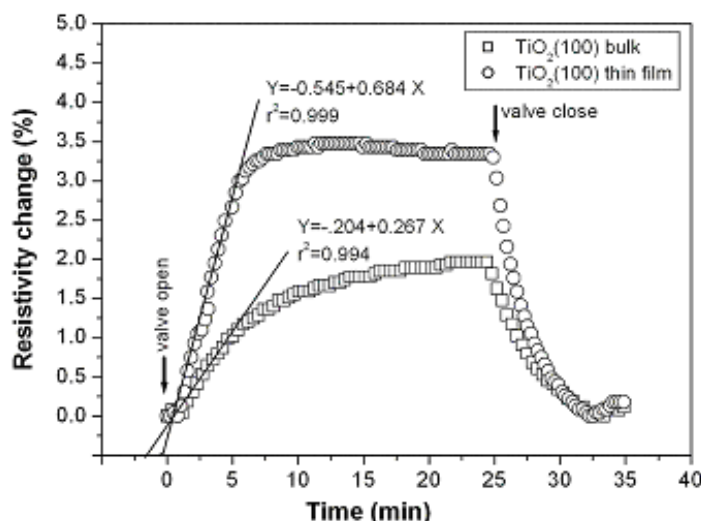


Figure 5. Curve response of rutile-TiO₂ (100) bulk and thin film to CO₂. The heating was set at 100°C and the CO₂ gas pressure at 5×10^{-3} Torr when the valve opened

In the following, we compare the gas sensing properties, i.e. time-dependent changes of the electrical resistivity of the single-crystal rutile-TiO₂(100) bulk and the as-deposited film upon exposure to 5 mTorr of CO₂ gas pressure. It is shown in Figure 5. The sample is kept at temperature of 100°C. Before the exposing CO₂ gas, the resistivity of the rutile-TiO₂(100) and the deposited film is 2.76 Ωcm and 2.27 Ωcm, respectively. When the samples were exposing CO₂, the resistivity of TiO₂(100) bulk and thin film were increased. The increasing resistivity upon CO₂ exposure is explained the participation of free charge carriers, i.e. electrons, in TiO₂ during CO₂ absorption^[10]. From both the curves in Fig 5, the maximum value of resistivity change exposing CO₂ gas was obtained at 1.75% and 3.5% for the TiO₂ bulk and thin film, respectively. In comparison between the TiO₂ bulk and the film, the resistivity change of TiO₂ bulk was lower than that of the film. This matter, the TiO₂ films have more sensitive to CO₂ than that of bulk sample. Possibility, the TiO₂ films are reasonable for CO₂ gas sensing material. Here, one can see that both the resistivity of TiO₂(100) bulk and thin film increased linearly when the times about 5 min to exposure of CO₂. The better linearity correlation coefficient ($r^2 = 0.994$ and $r^2 = 0.999$) was obtained using TiO₂(100) bulk and thin film sample in time intervals at 0 - 5 min. The tangent direction of linear regression the TiO₂(100) bulk is lower than that of the thin film, which indicates that the TiO₂(100) films have short response time in comparison with the bulk sample. In additional, the resistivity of TiO₂ bulk and thin film were decreased towards to initial values, which recognizes that TiO₂ film is suitable for gas sensor material.

CONCLUSION

The successful growth of the rutile-TiO₂ thin films by pulse laser deposition was demonstrated in detail. The high quality of rutile-TiO₂(100) film was grown on the α-Al₂O₃(0001) substrate with a thickness 507 nm. The high quality of film was characterized using XRD and RBS/Channeling. The electrical properties including the sensitivity and response time to CO₂ were demonstrated. The resistivity of TiO₂(100) films have been obtained in order a value 1 – 6.4 Ωcm at an interval of measurement to 30 – 200°C. The TiO₂(100) film with subsequent annealing to 300°C/4h significantly enhanced the sensitivity to CO₂. Also, that having the best overall characteristics of good response and recovery time (both <5 min), better linearity correlation ($r^2 = 0.999$) at the interval time 0 – 5 min, 100°C and an exhaled to 5 mTorr of CO₂ pressure. Therefore, the high quality of rutile-TiO₂(100) film prepared by pulsed laser deposition under low-controlled oxygen pressure is suitable for CO₂ gas sensor material.

REFERENCES

1. H. TANG, K. PRASAD, R. SANJINES, P. E. SCHMID, AND F. LEVY, J. Appl. Phys. 75(4), (1994) 2042-2047
2. F. BOCCUZZI, E. GUGLIELMINOTTI AND A. CHIORINO, Sensor and Actuators B7 (1992) 645-650
3. A. ROTHCHILD, F. EDELMAN, Y. KOMEM, AND F. COSANDEY, Sensor and Actuators B67 (2000) 282-289
4. P. -G. SU, WU REN-JANG, NIEH FANG-PEI, Talanta 59 (2003) 667
5. YASUSHI YAMADA, YOSHIKI SENO, YUMI MASUOKA, TADASHI NAKAMURA AND KATSUJI YAMASHITA, Sensor and Actuators B66 (2000) 164-166
6. A. RUIZ, G. DEZANNEAU, J. ARBIOL, A. CORNET, J. R. MORANTE, Thin Solid Films 436 (2003) 90-94
7. P. PARSIEB, S. KOMORNICKI, R. GAJERSKI, S. KONZINKI, M. REKAS, Solid State Ionics, 157 (2003) 357-363
8. U. DIEBOLD, Surface Science Report 48(2003) 53-229
9. A.L. LINSEBIGLER, G. LU, J.T. YATES JR., Chem. Rev. 95(1995) 735
10. JOHN R. MCCORMICK, JOHN R. KITCHIN, MARK A. BARTEAU, JINGGUANG G. CHEN, Surface Science 545 (2003) L741-L746
11. LEI MIAO, SAKAE TANEMURA, PING JIN, KENJI KANEKO, ASUKA TERA, NATALIYA NABATOVA-GABAIN, Journal of Crystal Growth 254 (2003) 100-106
12. A. VOIMERO, G. DELLA MEA, M. FERRONI, G. MARTINELLI, G. RONCARATI, V. GUIDI, E. COMINI, G. SBERVEGLIERI, Materials Science and Engineering B101(2003) 216-221
13. A. ROTHCHILD, Y. KOMEM, A. LEVAKOV, N. ASHKENASY, YORAM SHAPIRA, Applied Physics Letters, Volume 82, Number 4 (2003) 574-576