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GAS SENSING PROPERTIES OF RUTILE-TiO_2 (100) FILMS PREPARED BY PULSED LASER DEPOSITION

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ABSTRACT

GAS SENSING PROPERTIES OF RUTILE-TiO_2 (100) FILMS PREPARED BY PULSED LASER DEPOSITION. *The gas sensing property of TiO_2 thin films have been demonstrated in rutile-TiO_2 (100) films grown on the α-Al_2O_3 (0001) substrates by Pulsed Laser Deposition (PLD). High quality rutile-TiO_2 (100) films were successfully grown on α-Al_2O_3 (0001) with the substrate temperature at 500°C under 15 mTorr of O_2 gas pressure. The thickness and crystallinity of TiO_2 films were evaluated by Rutherford backscattering spectrometry combined with channeling (RBS/C) and X-ray diffraction using θ-2θ scans. To evaluate CO_2 gas sensing property of TiO_2 films, the dependence of the changing of electrical resistivity on the temperature was measured. It's found that high crystallinity rutile-TiO_2 (100) films on the α-Al_2O_3 (0001) substrate kept at 100°C exhibits good gas sensing property for CO_2 gas.*
Keywords: *X-ray diffraction, laser epitaxial, TiO_2 thin film, electrical resistivity, CO_2*

INTRODUCTION

Titanium dioxide (TiO_2) has been considerable interest from viewpoint of basic science and applications. For example the TiO_2 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 TiO_2 is extensively used as gas sensors due to their properties, which changes their electrical resistivity under gas exposures[(2-4)]. TiO_2 is also interesting candidate for conductance-type gas sensor devices for the detection of NO_2 [(5)], ethanol[(6)], and CO_2 [(7)]. Usually, the resistivity of TiO_2 is high in low temperature, and that decreased at high temperature as the examples shown in references[(8,9)]. Fully oxidized the TiO_2 is an insulator with a resistivity on the order of 10^{13} ohm-cm. As the remove oxygen atoms from the TiO_2 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. TiO_2 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-TiO_2 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 CO_2 are reported.

METHOD

The epitaxial-TiO_2 films were deposited on the α-Al_2O_3 substrates by pulse laser deposition (KrF-Eximer laser, wavelength: 248 nm, Lambda Physik). The α-Al_2O_3 substrates were obtained commercially (mirror-polish at both sides) and the typical size is $10 \times 10 \times 0.3$ mm^3. 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/cm^2 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-TiO_2 (ϕ30 mm) was used for the evaporation target. To oxidize and form TiO_2 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, TiO_2 films with 300~500 nm in thickness were deposited at 500°C under an oxygen pressure at 2 Pa. The crystallographic relationship between TiO_2 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-Kα radiations. Rutherford backscattering/channeling (RBS/C) analysis using 3 MV single-stage of accelerator at JAERI/Takasaki was employed to characterize the epitaxial-TiO_2 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 TiO_2 films were evaluated from RBS/C spectra. The electrical resistivity of deposited films under the CO_2 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 TiO_2 films. The chamber was pumped down to 6×10^{-5} Pa by a TMP, and then the CO_2 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 TiO_2 films were heated by the ceramic heater and temperatures were monitored by a thermocouple placed next to sample.

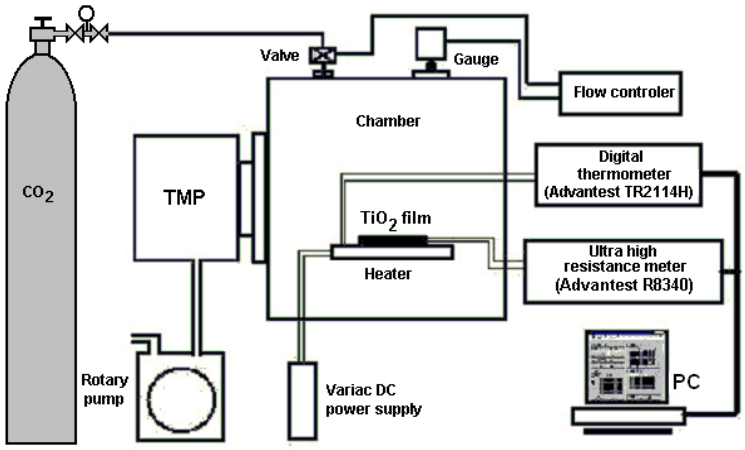

Figure 1. The instrument system measured of electrical properties including the sensitivity to CO_2.

RESULTS AND DISCUSSION

The crystal structure of deposited TiO_2 thin films was examined with X-ray diffraction technique. Figure 2 shows a typical θ-2θ X-ray diffraction pattern from the TiO_2 film on the α-Al_2O_3 (0001) substrate. The film was deposited at 500°C with about 507 nm thickness. In this case, only the reflections from the rutile-TiO_2 (200) and (400) are observed without any reflections from the α-Al_2O_3 substrate, which indicates that the only rutile-TiO_2 (100) films are epitaxially grown on the (0001) plane of α-Al_2O_3 substrate. The peak positions at 2θ = 39.97° and 85.89° correspond to the reflection from rutile-TiO_2 (200) and (400), respectively. As the result, high quality rutile type TiO_2 (100) film were successfully obtained on α-Al_2O_3 (0001) with the substrates temperature kept at 500°C and an exhaled to 2 Pa of O_2 gas pressure.

RBS/channeling was employed to characterize TiO_2 films grown on α-Al_2O_3 (0001) substrates. Figure 3 shows the 2.0 MeV$^4He^+$ RBS spectra from the rutile-TiO_2 (100) film on the α-Al_2O_3 (0001) taken under random and the TiO_2<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 TiO_2 film and α-Al_2O_3 substrate. The peaks at 1.43 and 0.88 MeV correspond to Ti component in the TiO_2 film and Al component in the α-Al_2O_3 substrate. Judging by the peaks intensity, the high quality TiO_2 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, χ_{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 χ_{min} value in the <100> aligned spectrum is 0.039 at the just area behind the surface peaks of the TiO_2 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 TiO_2 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-Al_2O_3 (0001) substrate. The planar channeling analysis around the mayor axes of the TiO_2 film and the α-Al_2O_3 gives the evidence that the TiO_2 (100) crystallographic axis is parallel to the α-Al_2O_3 (0001) axis.

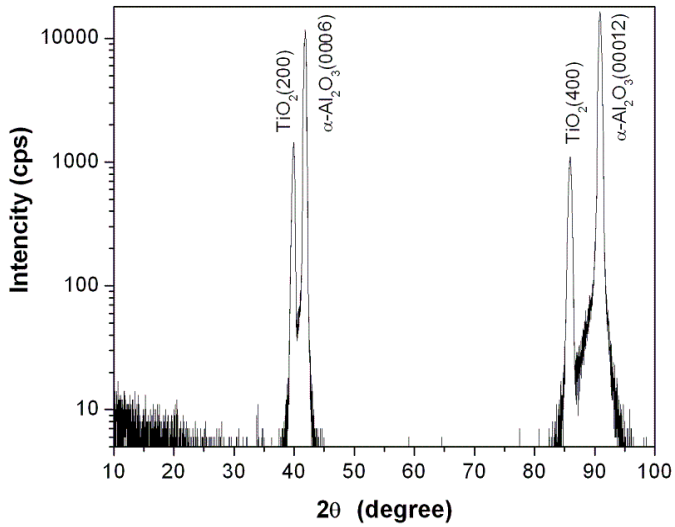

Figure 2. X-ray diffraction patterns from the epitaxial rutile-TiO_2 films on the α-Al_2O_3 (0001) substrate. The films were deposited at 500°C under the O_2 gas pressure of 15×10^{-3} Torr.

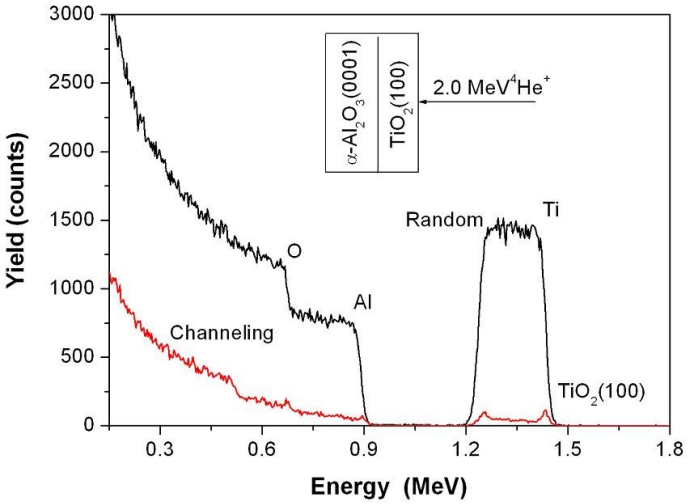

Figure 3. The 2 MeV $^4He^+$ RBS/channeling spectra from a rutile-TiO_2 film with the thickness approximately 507 nm on the α-Al_2O_3 (0001) substrate. The aligned spectrum was taken with the beam directed along the (100) axis of the rutile-TiO_2 film. The film was deposited at 500°C under the O_2 gas 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-TiO_2 (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 TiO_2 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 TiO_2 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 TiO_2 film with doping metal showed fairly good sensing characteristics to NO_2 at 600°C[5]. The resistivity of TiO_2 bulk at 1200°C is in order 8.5 Ωcm [8]. The thin film TiO_2 was found to crystallize to a dense columnar layer of nano-crystalline rutile-TiO_2 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-TiO_2 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 TiO_2 films is not suitable for the gas sensing material since the resistivity measurement is needed an ultra high resistant meter.

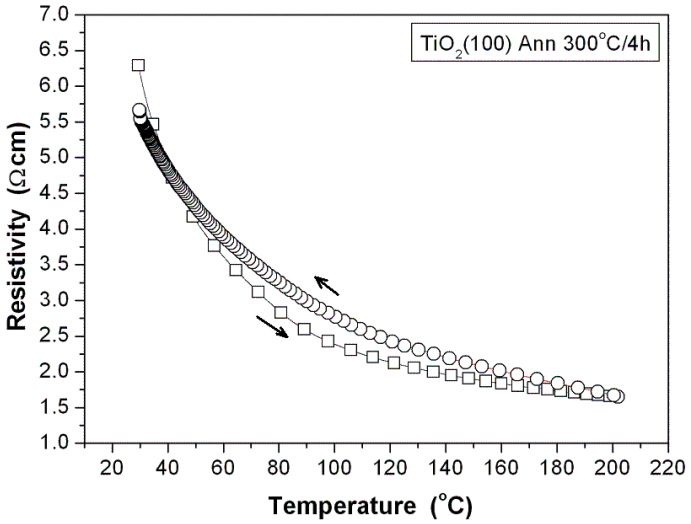

Figure 4. The resistivity of the rutile-TiO_2 (100) film annealed at 300°C/4h in air as function of temperature. The measurement was taken at the chamber condition under pressure of 6×10^{-5} Pa.

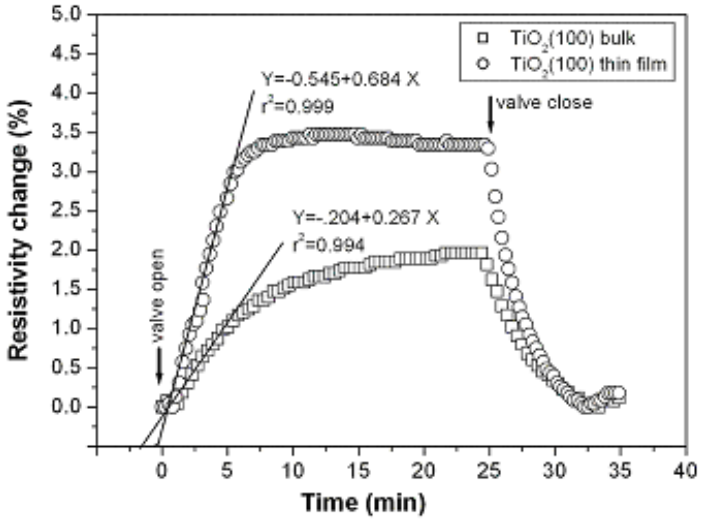

Figure 5. Curve response of rutile-TiO_2 (100) bulk and thin film to CO_2. The heating was set at 100°C and the CO_2 gas pressure at 5×10^{-3} Torr when the valve opened

In the following, we compare the gas sensing properties, i.e. time-dependent changes of the electrical resistivity of the single-crystal rutile-TiO_2 (100) bulk and the as-deposited film upon exposure to 5 mTorr of CO_2 gas pressure. It is shown in Figure 5. The sample is kept at temperature of 100°C. Before the exposing CO_2 gas, the resistivity of the rutile-TiO_2 (100) and the deposited film is 2.76 Ωcm and 2.27 Ωcm, respectively. When the samples were exposing CO_2, the resistivity of TiO_2 (100) bulk and thin film were increased. The increasing resistivity upon CO_2 exposure is explained the participation of free charge carriers, i.e. electrons, in TiO_2 during CO_2 absorption[10]. From both the curves in Fig 5, the maximum value of resistivity change exposing CO_2 gas was obtained at 1.75% and 3.5% for the TiO_2 bulk and thin film, respectively. In comparison between the TiO_2 bulk and the film, the resistivity change of TiO_2 bulk was lower than that of the film. This matter, the TiO_2 films have more sensitive to CO_2 than that of bulk sample. Possibility, the TiO_2 films are reasonable for CO_2 gas sensing material. Here, one can see that both the resistivity of TiO_2 (100) bulk and thin film increased linearly when the times about 5 min to exposure of CO_2. The better linearity correlation coefficient (r^2= 0.994 and r^2= 0.999) was obtained using TiO_2 (100) bulk and thin film sample in time intervals at 0 - 5 min. The tangent direction of linear regression the TiO_2 (100) bulk is lower than that of the thin film, which indicates that the TiO_2 (100) films have short response time in compression with the bulk sample. In additional, the resistivity of TiO_2 bulk and thin film were decreased towards to initial values, which recognizes that TiO_2 film is suitable for gas sensor material.

CONCLUSION

The successful growth of the rutile-TiO_2 thin films by pulse laser deposition was demonstrated in detail. The high quality of rutile-TiO_2 (100) film was grown on the α-Al_2O_3 (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 CO_2 were demonstrated. The resistivity of TiO_2 (100) films have been obtained in order a value 1 – 6.4 Ωcm at an interval of measurement to 30 – 200°C. The TiO_2 (100) film with subsequent annealing to 300°C/4h significantly enhanced the sensitivity to CO_2. Also, that having the best overall characteristics of good response and recovery time (both <5 min), better linearly correlation (r^2= 0.999) at the interval time 0 − 5 min, 100°C and an exhaled to 5 mTorr of CO_2 pressure. Therefore, the high quality of rutile-TiO_2 (100) film prepared by pulsed laser deposition under low-controlled oxygen pressure is suitable for CO_2 gas sensor material.

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