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SCIENCE DIRECT
Sensors and Actuators B 115 (2006) 123–127
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Orientation dependence of gas sensing properties of TiO_2 films

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Received 10 February 2005; received in revised form 10 August 2005; accepted 11 August 2005
Available online 30 September 2005

Abstract

Highly oriented polycrystalline TiO_2 films were grown on sapphire substrates with various orientations using rf magnetron sputtering, and the effects of the crystallographic orientation on the H_2 and CO gas sensing performance were investigated. The orientation of the TiO_2 films was strongly dependent on the substrate orientation such that (1 0 1)/(1 0 0), (1 0 1), (0 0 1), and (1 0 0) oriented TiO_2 films were formed on (1 1 $\bar{2}$ 0) (a-cut), (1 $\bar{1}$ 0 2) (r-cut), (1 0 $\bar{1}$ 0) (m-cut), and (0 0 0 1) (c-cut) Al_2O_3, respectively. A fine surface feature developed in the films grown on (1 1 $\bar{2}$ 0) and (1 0 $\bar{1}$ 0) Al_2O_3 and a rather rough surface was obtained in case of the (1 $\bar{1}$ 0 2) Al_2O_3 substrate. The deposited TiO_2 films showed a short response time and high gas response toward H_2 and CO balanced with N_2. The TiO_2 film grown on (1 1 $\bar{2}$ 0) Al_2O_3 exhibited the highest H_2 gas response possibly due to the (1 0 0) orientation and high surface area. The (0 0 1) orientation of TiO_2 showed the highest selectivity toward H_2 against CO.

Keywords: TiO_2 film; Gas sensor; Orientation dependence; Sapphire substrate

1. Introduction

Semiconducting metal oxides are widely used as gas sensing materials for the detection of inflammable and toxic gases by utilizing the resistivity changes with gas adsorption and desorption, which result in a depletion (space charge) layer change and band modulation [1,2]. Most sensors consist of sintered bodies, thick layers, and thin films of polycrystalline oxide materials, and the sensor performance (sensitivity, selectivity, and long-term stability) is strongly dependent on the microstructural features such as particle size and grain boundary characteristics [3]. Several strategies have been explored to fabricate the sensors with an improved performance, which include nano-scale crystallites [4–6], additives or surface functionalization [7–9], and solid solution [10,11].

The high surface-to-volume ratio associated with nano-structured materials makes their electrical responses extremely sensitive to the species adsorbed on the surface, which opens up a new paradigm for sensor materials. Although nano-scale gas sensors utilizing nano-tubes [12,13], nano-belts [14], and nano-ribbons [15] exhibited a superior performance, most works have focused on the high surface area for gas adsorption and little attention was paid for the effect of crystallographic orientation. Up to now, limited works have been performed to study the relationship between gas sensing characteristics and surface crystallographic orientation by employing the single crystals, whisker, and epitaxial films of SnO_2 and ZnO [3,16–18], and the fundamental understanding of surface orientation on the sensor response is still unclear.

Recently, it has been reported that a hydrogen sensor with high sensitivity can be achieved using TiO_2 with various nano-dimensional architectures [13,19,20]. TiO_2 single crystals with different surface orientations are commercially available and the epitaxial films with various orientations can be grown by several deposition techniques [21–24]. However, very little work has been done on the effect of crystal orientation upon the sensing performance of TiO_2.

In this study, four differently oriented polycrystalline TiO_2 films were fabricated by rf magnetron sputtering and their gas sensing characteristics were investigated. The orientation of the TiO_2 films was controlled by the orientation of the sapphire substrates. Indeed, the orientation of the deposited film followed an epitaxial relationship between the TiO_2 film and the Al_2O_3 substrate, which is consistent with earlier reports [21–24].

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doi:10.1016/j.snb.2005.08.024

2. Experimental

TiO_2 films were deposited by rf magnetron sputtering using a titanium oxide target (99.9% purity) on sapphire substrates (Al_2O_3) with various orientations. The substrates used were (1 1 $\bar{2}$ 0) (a-cut), (1 $\bar{1}$ 0 2) (r-cut), (1 0 $\bar{1}$ 0) (m-cut), and (0 0 0 1) Al_2O_3 (c-cut). Film deposition was carried out without substrate heating in an Ar environment with an rf power of 150 W at 1 mTorr for 60 min. For the crystallization to the rutile phase, the samples were annealed at 700 °C for 1 h in air. The phase and orientation of the films were examined using X-ray diffraction (XRD, model M18XHF-SRA, Mac Science, Japan). The surface morphology and cross-section of the films were characterized by field emission scanning electron microscope (FE-SEM, model JSM-6330F, JEOL, Japan) and atomic force microscope (AFM).

For the electrical measurements, a pair of comb-like Pt electrodes were formed by sputtering on the TiO_2 films through a mask and Pt lead wires were attached to them using a Pt paste [25]. Thereafter, all the sensors were fired at 600 °C for 1 h in order to make the electrical contact between the Pt paste and the Pt lead wires. The H_2 and CO sensing properties were determined by measuring the changes in electric resistance between 200 and 10,000 ppm H_2 (or CO) balanced with N_2 and ultra pure N_2 (99.999% pure) at 500 °C. The electrical resistance was measured using a multimeter (2000 multimeter, Keithley, USA). The magnitude of gas response (S) was defined as the ratio (R_0/R_g) of the resistance in N_2 (R_0) to that in a sample gas (R_g). The response time ($t_{90\%}$) was defined as the time required for the sensor to reach 90% of the final signal. More than five specimens were prepared under each condition. The phase, morphology, and general sensing characteristics were found to be reproducible although the magnitude of gas response slightly varied with each specimen.

3. Results and discussion

3.1. Structural characteristics

XRD patterns of the TiO_2 films deposited on the sapphire substrates with different orientations are shown in Fig. 1 and compared with that of the rutile powder. The as-deposited TiO_2 films were amorphous and became highly oriented polycrystalline rutile after annealing at 700 °C. The orientation of the TiO_2 films was strongly dependent on the substrate orientation. The (1 0 0), (0 0 1), and (1 0 1) rutile films were grown on (0 0 0 1), (1 0 $\bar{1}$ 0), and (1 $\bar{1}$ 0 2) Al_2O_3, respectively, which are consistent with the epitaxial relationship of the TiO_2 films grown on the sapphire substrates reported earlier [21–24]. The TiO_2 film deposited on (1 1 $\bar{2}$ 0) Al_2O_3 was (1 0 1) and (1 0 0) oriented instead of the heteroepitaxial (1 0 1) rutile film in previous studies [21,22].

The surface morphologies of the TiO_2 films examined by AFM are shown in Fig. 2. The as-deposited films were smooth and featureless irrespective of the substrate orientation, and the film thickness determined from the cross-section was ~90 nm. After annealing, a slightly different surface morphology developed depending on the substrate orientation. The root-mean-square (R.M.S.) values of the surface roughness were similar to each other for films deposited on (1 1 $\bar{2}$ 0) and (1 0 $\bar{1}$ 0) Al_2O_3, and a rather rough surface was obtained in case of the (1 $\bar{1}$ 0 2) Al_2O_3 substrate. In particular, a very fine surface feature developed in the films grown on (1 1 $\bar{2}$ 0) and (1 0 $\bar{1}$ 0) Al_2O_3, expecting higher surface areas.

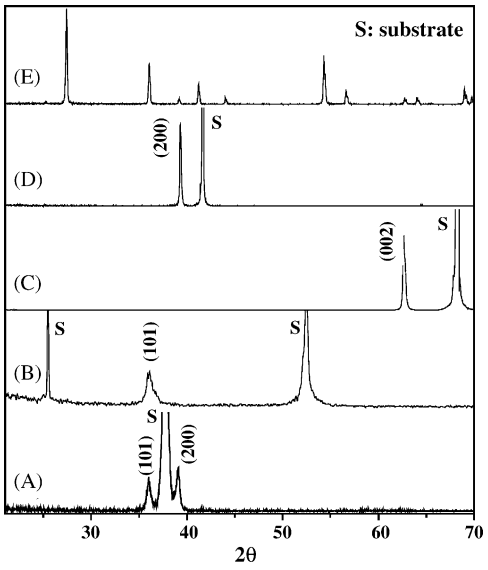

Fig. 1. XRD patterns of TiO_2 films deposited on (A) (1 1 $\bar{2}$ 0) (a-cut), (B) (1 $\bar{1}$ 0 2) (r-cut), (C) (1 0 $\bar{1}$ 0) (m-cut), and (D) (0 0 0 1) (c-cut) Al_2O_3. The pattern of the rutile powder (E) is inserted for comparison.

3.2. Gas sensing properties

Fig. 3 shows the typical response transient and the sensing properties to 1.0% H_2 balanced with N_2 of the TiO_2 films. The electrical measurements were carried out at 500 °C due to the equipment limitation (up to ~10^8 Ω) and the high resistance of the samples. Upon injecting a 1.0% H_2/N_2 sample gas, the resistance decreased rapidly by more than three orders of magnitude (Fig. 3(A)). The recovery was slightly slow but the sensing signal was quite stable and reversible even after the gases were switched several times. The gas response of the TiO_2 film to H_2 gas balanced with air was also determined, but the magnitude of gas response was three orders of magnitude lower than that to H_2/N_2 and the effects of the film orientation were hardly found. In an oxidizing atmosphere, ambient oxygen is adsorbed on the surface of a semiconducting gas sensor with a negative charge. A reducing gas such as H_2 reacts with the negatively charged surface oxygen and decreases the resistance by the injection of an electron. However, in the present experiment with a N_2 atmosphere, the chemisorption of the spilled-over hydrogen atoms and the consequent creation of an electron accumulation layer on the TiO_2 surface can be considered as a more probable reason for the enhanced electrical conductance [13].

The determined magnitude of gas response varied with the substrate orientation and the resulting TiO_2 film orientation (Fig. 3(B)). For comparison, a randomly oriented TiO_2 film was deposited on a quartz substrate. This non-oriented film exhibited the highest gas response but the surface characteristics