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Influence of anatase-rutile phase transformation on dielectric properties of sol-gel derived TiO_2 thin films

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Abstract The phase transformation behavior and resulting dielectric properties of sol-gel derived TiO_2 thin films were investigated. Thin films showed a typical behavior of mixture systems during the phase transformation; a kinetic investigation on the isothermal curve of pre-crystallized thin films revealed that the phase transformation was a first-order reaction with an Avrami time component of 1. Dielectric constants of TiO_2 thin films increased with the increasing amount of the rutile phase while the dielectric losses showed the opposite relationship. From a fitting process using the parallel mixing rule, dielectric constants of two end members of the mixture system were calculated to be 41.4 and 145.2 for the pure anatase and rutile phase thin films, respectively.

Keywords TiO_2 · Thin film · Sol-gel method · Dielectric property · Phase transformation

1 Introduction

Ultra-thin oxide films have attracted enormous attention because of their essential roles in electronic, electrical, optical, and magnetic materials. Among the numerous thin oxide films, TiO_2 thin films have been studied intensively since they have diverse applications such as in solar cells [1, 2] and photocatalysts [3, 4]. Recently, TiO_2 thin films have been receiving new interest for their usage in high-k (dielectric constant) dielectrics in DRAMs with extremely small feature sizes (<100 nm) [5, 6]. The dielectric properties of TiO_2 thin films, especially their dielectric constants, can be designed via many means such as through the formation of solid solutions [7] and mixtures [8] including the compositions of other oxides, the doping of ions [9], and the introduction of strain to thin films [10]. The dielectric properties of TiO_2 thin films can be also designed by controlling the phase transformation between the polymorphs (anatase, brookite and rutile phases) since these polymorphs possess different dielectric properties from each other [11]. Although there have been many studies on the phase transformation of bulk TiO_2 samples, the correlation between the phase transformation behaviors and the dielectric properties of TiO_2 thin films has not yet been systematically investigated.

In the present study, dielectric TiO_2 thin films were prepared using a sol-gel method and the phase transformation behavior from anatase to rutile phase was investigated from the viewpoint of kinetics. The influence of the phase transformation on the dielectric properties of TiO_2 thin films was also studied and discussed in terms of the mixing rules of anatase-rutile mixture thin films. A good understanding of the dependence of the dielectric properties of TiO_2 thin films on the phase transformation behavior is required to control the electronic properties of devices composed of TiO_2 thin films.

2 Experimental procedure

TiO_2 thin films were prepared via a sol-gel process. After titanium-isopropoxide (TTIP, Aldrich, 97%) was dissolved in dry ethanol (Baker, 99.9%), the resultant solution was partially hydrolyzed with a mixture of distilled water, nitric acid, and ethanol. The molar ratio of the TTIP:H_2O:HNO_3 was 1:2:0.067. Following our ancillary experiments, this ratio was selected as being optimal since the sol hydrolyzed at this condition displayed the best wetting property during

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spinning as well as the best stability against gelation or precipitation. The obtained sol was spun on platinized Si substrates at 2500 rpm for 30 seconds. Then, the fabricated films were heat-treated at 350°C for 5 minutes to remove the adsorbed alcohol and water. These spinning and pyrolysis steps were repeated until the thickness of TiO_2 films was approximately 400 nm. The as-deposited films were crystallized at 800°C for 1 hour. The pre-crystallized thin films were directly put into a furnace whose temperature was sustained at 900°C and then annealed for various holding times. The precursor solution was dried in a vacuum oven at 50°C for 12 hours to obtain gel powders for the thermal analysis.

The crystal structure, microstructure, thickness, depth profile, binding energy and dielectric properties (at 1 MHz) of the thin films were investigated using X-ray diffraction (XRD; Model M18XHF, Macscience Instruments, Japan), atomic force microscopy (AFM; Model AutoProbe CP, PSIA, USA), field emission scanning electron microscopy (FE-SEM; Model JSM-6330F, JEOL, Japan), a scanning auger microprobe system (SAM; Model Model660, Perkin-Elmer, USA), a X-ray photoelectron spectroscopy (XPS; Model AXIS, KRATOS, UK) and a high precision LCR-meter (Agilent 4284A, Agilent, USA). The thermal decomposition behavior of the gel powders was also examined using SDT (Simultaneous DTA TGA; SDT 2960, TA Instrument, USA).

3 Results and discussion

3.1 Crystallization and kinetics of phase transformation

In order to investigate the rate of the anatase-rutile phase transformation, excluding the influence of the amorphous phase, TiO_2 thin films are required to be fully crystallized before the phase transformation begins. Considering that the differential thermal analysis (DTA) curve of the TiO_2 gel powder exhibited a broad exothermic peak of crystallization at approximately 450°C (not shown) and that the intensity of the anatase (101) peak of the TiO_2 thin film, when annealed at 800°C for 1 hour, did not further increase, the annealed TiO_2 film appeared to have been fully crystallized into the anatase phase. Then, the crystallized films were annealed at the transformation temperature of 900°C (which had been confirmed through the thermal analysis) for various holding times. The X-ray diffraction patterns of the TiO_2 thin films annealed at various holding times are presented in Fig. 1. In order to analyze the phase transformation, the relative ratios between the two polymorphs, i.e. anatase and rutile, were determined by comparing the intensity of the anatase (101) and rutile (110) diffraction peaks, as proposed by Spurr et al. [12]. Two of the phases showed the typical behavior of a mixture system without any secondary phases; furthermore, the amount of the rutile phase increased in accordance with increasing holding times. In the case of the thin film annealed for 4 hours, 95% of the rutile phase was obtained.

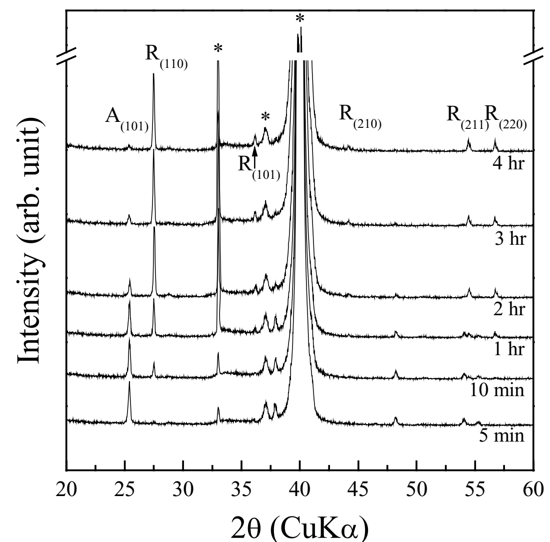

Fig. 1 XRD patterns of TiO_2 thin films annealed at 900°C for various holding times. Asterisk, A and R indicate the peaks of the substrates, the anatase phase and the rutile phase, respectively

As shown in Fig. 2, a kinetic expression for the phase transformation from anatase to rutile phase can be obtained from the isothermal curve based on the XRD results displayed in Fig. 1. By separately considering the rates of nucleation and growth, the expression for the rate of a phase transformation can be obtained. The total rate of a transformation from anatase to rutile is dependent upon both nucleation and growth rates. Assuming that both nucleation and growth rates are time-dependent, the phase transformation behavior can

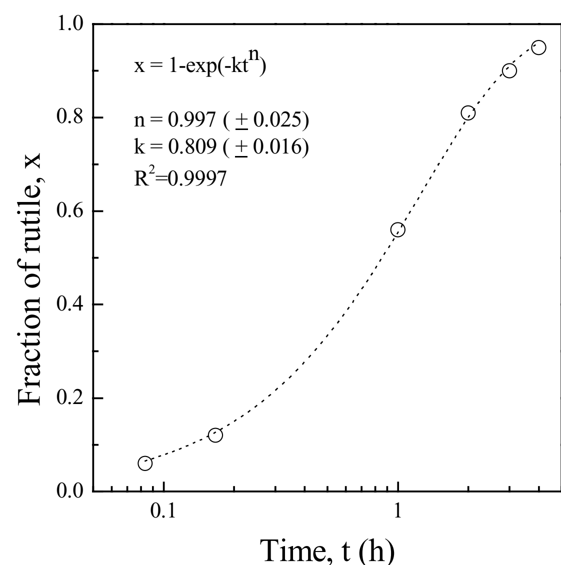

Fig. 2 Isothermal phase transformation curve (Avrami plot) of rutile phase thin films (at 900°C)

be explained kinetically through the following relationship (equation 1), as suggested by Avrami [13], between the fraction of the transformed phase and the transformation time, where k is the rate constant parameter, n is the time component, x is the fraction of transformed phase, and t is the transformation time.

$$x = 1 - \exp(-kt^n) \tag{1}$$

The fitted values of n and k were 0.997 and 0.809 h^{-1}, respectively, with a correlation factor, R^2 of 0.9997. Since the n value is very close to 1, the phase transformation from anatase to rutile in this study can be characterized as a first-order transformation with nucleation at the start followed by continuing nucleation at the grain boundaries [14]. This result is in a good accordance with the results on the anatase to rutile transformation of bulk ceramics reported by Rao et al. [15].

Figures 3(a) and (b) show the surface morphology of the TiO_2 thin films annealed at 800°C (before the phase transformation) and at 900°C for 1 hour (during the phase transformation). Both of these thin films show dense surfaces and RMS roughness increases from 44.7 Å (for thin film crystallized at 800°C for 1 hour) to 107 Å (for thin film post-annealed at 900°C for 1 hour) as the phase transformation proceeds. By comparing Figs. 3(a) and (b), it can be seen, as expected from the kinetic analysis of the phase transformation, that the larger grain sized rutile phase forms at the grain boundaries of the anatase phase. The larger grain sizes of the rutile phase can be understood through the accelerated mass transfer during the destructive anatase-to-rutile transformation. This increased grain size has also been reported as being based on the 'critical-nuclei-size-effect' by Kumar et al. [16].

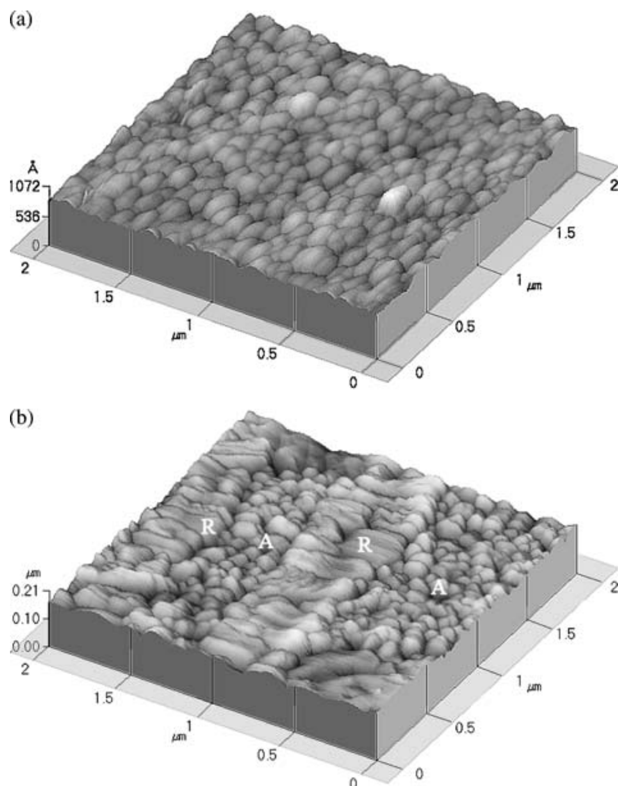

Fig. 3 AFM micrographs 2 × 2 μm of thin films (a) crystallized at 800°C for 1 hour and (b) annealed at 900°C for 1 hour

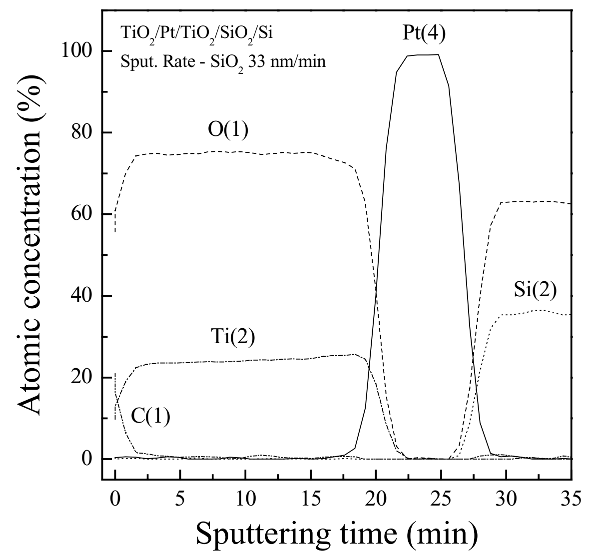

Fig. 4 Depth profile of TiO_2 thin film fired at 900°C for 4 hours

3.2 Dielectric properties

Before the measurement of dielectric properties of the TiO_2 thin films annealed at 900°C, the depth profile was analyzed to check for the possibility of degradation, i.e., internal reaction between TiO_2 and Pt bottom electrodes. As shown in Fig. 4, the TiO_2 thin films are not degraded even when they are annealed at 900°C for 4 hours. Dielectric constants of TiO_2 thin films with various ratios of the rutile phase measured at 1 MHz using MIM (metal-insulator-metal) structure are presented as hollow circles in Fig. 5. Dielectric constants, estimated using mixing rules for multiphase dielectrics, including the pure anatase and rutile phases, demonstrate an increasing manner with an increasing amount of the rutile phase. Three sets of relations are usually considered: parallel, series, and logarithmic mixing rules. Based on our experimental results, we fitted the measured dielectric constants using the three kinds of mixing rules in order to determine the dielectric constants of two end members: pure anatase and rutile phase thin films. Among them, the fitting line of the dielectric constants with the parallel mixing rule has been plotted in Fig. 5, since Fig. 3(b) indicates that each phase spans the thickness of the film where it is located. This is

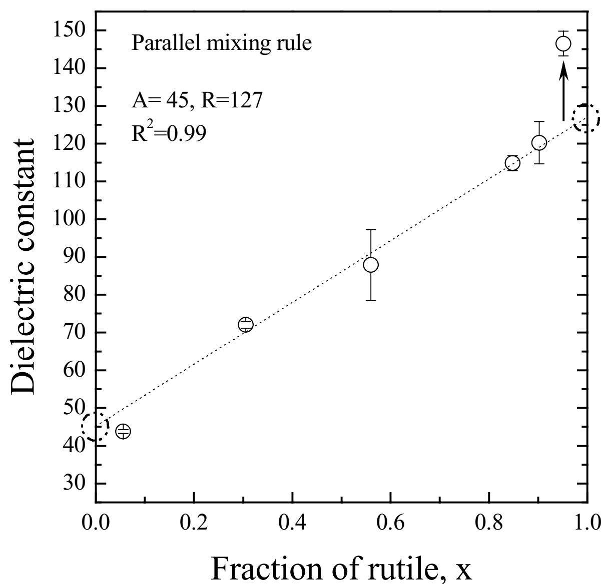

Fig. 5 Dielectric constants and fitting curve for multiphase TiO_2 thin films

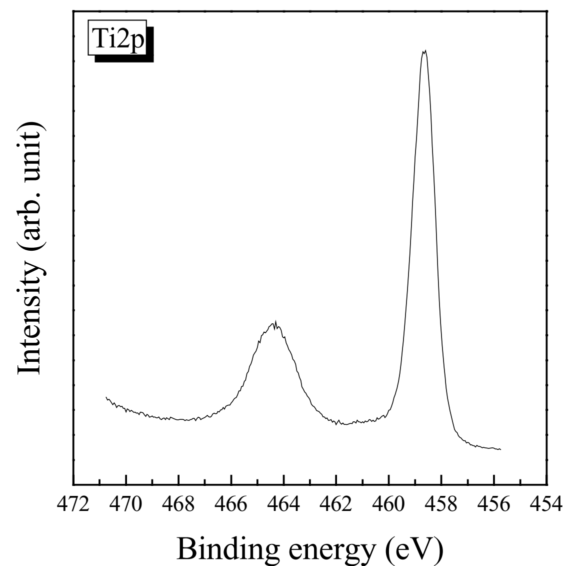

Fig. 6 XPS spectrum of TiO_2 thin film containing 95% rutile phase

exactly the physical criteria for using the parallel mixing rules, regardless of which rule seems to fit best. The relationship with the parallel rule can be expressed through the following equation, where ε_A, ε_R and V_R are the dielectric constants of the anatase phase, the rutile phase, and the volume fraction of the rutile phase, respectively.

$$\varepsilon = (1 - V_R)\varepsilon_A + V_R\varepsilon_R \tag{2}$$

The dielectric constant of the 95%-rutile thin film was excluded during the fitting process since it no longer satisfied the physical criteria for the parallel mixing rules; only a few anatase grains would be dispersed in the rutile phase. The calculated dielectric constants of pure anatase and rutile phase thin films are 45 (±3.9) and 127 (±2.8), respectively with a correlation factor, R^2 of 0.99. These results are comparable to the reported values since the dielectric constants of the anatase phase have been reported to be 48 for powders [17] and 40 for thin films [18], and since the dielectric constants of the rutile phase have been reported to be 89 along a-axis and 173 along c-axis due to its anisotropic nature [19]. However, the dielectric constant of the 95%-rutile thin film shows a considerable deviation from the fitting line. A relatively high dielectric constant of the 95%-rutile thin film can be ascribed to factors such as the preferred orientation, degradation of electrodes, and the presence of defects during the long annealing process at high temperatures. Among them, the preferred (110) orientation of the 95%-rutile thin film is most probable due to the dielectric anisotropy of the rutile. The bottom electrode does not seem to react with the thin film as can be seen in the depth profile of the 95%-rutile thin film (Fig. 4). The presence of Ti^{3+} ions may be one reason for the high dielectric constants. However, the XPS spectrum of rutile thin film (Fig. 6) shows no evidence of Ti^{3+} ions. In addition, the absence of Ti^{3+} ions is also confirmed by the frequency sweep measurement of dielectric constant from 40 Hz to 1 MHz (not shown). If defective species such as Ti^{3+} were present in the TiO_2 thin films, the films would show a high dielectric constant in the low frequency region. In our results, however, dielectric constants of the thin films increased no more than 1% at low frequencies compared with those at 1 MHz. The dielectric losses of TiO_2 thin films measured at the same conditions decreased slightly with an increasing amount of rutile phase from 0.003 and 0.001, which seemed to originate from the removal of defects such as pores and grain boundaries due to the longer annealing time.

4 Conclusions

In the present paper, we analyzed the anatase-rutile phase transformation behavior of TiO_2 thin films from the viewpoint of kinetics and measured dielectric properties as a function of the phase ratio. Thin films were crystallized with the anatase phase beginning at 800°C and then transforming to the rutile phase at 900°C with a manner of mixture systems. A kinetic analysis of the isothermal curve revealed that the phase transformation from anatase to rutile phase was a first-order reaction with a time component of 1, which can be depicted as nucleation at the start followed by continuing nucleation at the grain boundaries. Dielectric constants were affected directly by the phase transformation, i.e., the ratio between two phases. Dielectric constants increased with increasing amounts of rutile phase with a manner close to the parallel mixing rule. Dielectric constants of the two end members of this mixture system, evaluated from

a fitting process, were 45 (±3.9) and 127 (±2.8) for thin films with a pure anatase and rutile phase, respectively. This systematical investigation of the phase transformation behavior and the dielectric properties of TiO_2 thin film will be helpful in tailoring the dielectric constants of TiO_2 thin films.

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