Zirconium Titanate Thin Film Prepared by Surface Sol-Gel Process and Effects of Thickness on Dielectric Property

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Single phase of multicomponent oxide $ZrTiO_4$ film could be prepared through surface sol-gel route simply by coating the mixture of 100 mM zirconium butoxide and titanium butoxide on Pt/Ti/SiO_2/Si(100) substrate, following pyrolysis at 450 °C, and annealing it at 770 °C. The dielectric constant of the film was reduced as the film thickness decreased due to of the interfacial effects caused by layer/electrode and a few voids inside the multilayer. However, the dielectric property was independent of applied dc bias sweeps voltage (-2 to +2 V). The dielectric constant of bulk film, 31.9, estimated using series-connected capacitor model was independent of film thickness and frequency in the measurement range, but theoretical interfacial thickness, t_i, was dependent on the frequency. It reached a saturated t_i value, 6.9 Å, at high frequency by extraction of some capacitance component formed at low frequency range. The dielectric constant of bulk $ZrTiO_4$ pellet-shaped material was 33.7 and very stable with frequency promising as good applicable devices.

Keywords : $ZrTiO_4$ film, Surface sol-gel process, Thickness-dependent dielectric constant, Series-connected capacitor model.

Introduction

Zirconium titanate based materials are widely applicable for dielectric resonators in telecommunication system.[1-3] electronic fibers.[4] and refractory oxides.[5] Moreover, the preparation of $ZrTiO_4$ thin film has been of interest because of the high resistivity and high dielectric constant which provides a high charge storage capacity.[6] So, several methods- for example, RF magnetron sputter deposition,[7] chemical vapor deposition, polymeric precursor route,[6] and pulsed laser deposition- have been tried out to fabricate the thin films. Sol-gel deposition method is interesting for application of film capacitors processing, large area coating ability, precise composition controlling, and low cost.

In this work, surface sol-gel process was applied for the synthesis of polycrystalline $ZrTiO_4$ single phase film by coating the mixture of reactant precursors on Pt/Ti/SiO_2/Si(100) substrate and sintering it at proper temperature conditions. The Pt on substrate works as an electrode when the dielectric property is measured. Compared to the conventional bulk sol-gel route, the surface sol-gel process is more improved and attractive because only surface metal alkoxide group adhered on substrate is hydrolyzed partially in dried air and the group is useful for next linkage with another alkoxide group coming to the surface subsequently. In addition, it does not require any complicated procedure of controlled atmosphere during preparation. The substrate is dipped into the solution and uniformly withdrawn into atmospheric moisture. The liquid film adheres to the substrate surface and solidifies rapidly through the evaporation of the solvent. Multicomponent oxide product can be simply prepared by chemical reaction on the surface of substrate through decompositions of reactants at optimum temperature if adhesion rate of each precursor on substrate is not quite different.

The purpose of this work is also to investigate thickness dependency of dielectric properties. $ZrTiO_4$ films ranging in thickness of 160 to 350 nm were studied using series-connected capacitor model in which there is an interfacial "dead layer effect" that reduces the effective dielectric constant in this film.[8]

Experimental Section

To compare the dielectric properties of $ZrTiO_4$ films with bulk material, bulk powder of $ZrTiO_4$ was fabricated by heating TiO_2 (m.p. = 1825 °C, 99.9+%, Aldrich) and $ZrOCl_2 \cdot 8H_2O$ (98%, Aldrich) instead of ZrO_2 (m.p. = 2715 °C) at 1400 °C for 15 hrs. According to Differential Thermal Analysis of $ZrOCl_2 \cdot 8H_2O$, Cl_2 was dissociated from $ZrOCl_2$ at 323.7 °C while each $4H_2O$ was separated at 98.3 °C and 153.6 °C.[9] The powder sample was pressed into cylindrical pellet (1.3 cm in diameter) under a pressure of 400 kg/cm^2. Gold was coated on both sides of the annealed pellet as the electrodes.

As starting materials of films titanium butoxide (98%) and zirconium butoxide (98%) were obtained from Aldrich. Pt substrate was purchased from Inostek Corp. as a Pt film (1500 Å) grown on the Ti adhesion layer (100 Å)/SiO_2 adhesion layer (3000 Å)/Si wafer (100). The substrate was primed with hydroxide layer of 5 wt% 2-mercaptoethanol (98%, Aldrich)/anhydrous ethanol solution as the anchoring solution. 100 mM zirconium butoxide/100 mM titanium butoxide solutions (in 3 : 1 anhydrous ethanol/toluene) equal to the mole ratio 1/1 were mixed in an dried atmosphere box. The mixture was dropped on the hydroxyl terminated substrate, spinned for 3 min. (3000 rpm/min), followed by pyrolysis at 450 °C for 20 minutes after 2-4 coating cycles,

then annealed at 770 °C for 15 minutes to obtain crystalline phase. The process was repeated until the 10-15 multilayer films were grown for the property measurements. The reaction temperatures and annealing time were controlled according to DTA results of reactants.

The phase of each product was confirmed by X-ray diffractometer (Philips X'Pert) equipped with monochromatized Cu Kα radiation and thin film attachments. Thickness of film was measured by α-step (Utencor Instr., 250) and ellipsometer (Rudolph Res., flanders NJ07836) with He laser (632.8 nm) source. The optical constants of Pt (Ns = 2.186, Ks = 3.446) were estimated by assuming the thickness of substrate being zero. Then gold was deposited on the film using the mask designed to have several electrode holes with 300 μm in diameter size.

The measurement of capacitance was performed between 3 kHz to 1 MHz using HP4192A LF Analyzer and HP 4284A LCR meter at room temperature. The capacitance was also measured under applied forward and reverse dc bias sweeps (-2 to 2 V) with a measuring step of 20 mV/sec and ac oscillator level 10 mV at 1 MHz. Dielectric constants were estimated from the capacitance data using the equation

$$k = Ct/(k_0 A), \quad (1)$$

where k_0 is permittivity of free space, 8.854×10^{-12} F/m, C is capacitance, t is thickness of the pellet or film, and A is the area of gold plate.

Results and Discussion

DTA curves of titanium butoxide and zirconium butoxide in Figure 1 show the endothermic peaks around 380-460 °C caused by decompositions of precursors. Although surface sol-gel process is suitable for preparing ceramic films with large coating area, cracks are likely produced. In order to avoid these cracks and possible electric short circuit during measurement, it was required to form multiplayer film by repeating the coating.

Figure 2 shows the SEM images of multilayer $ZrTiO_4$ film

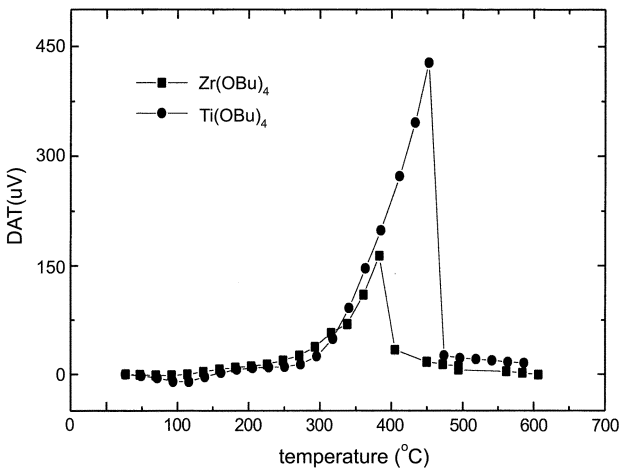
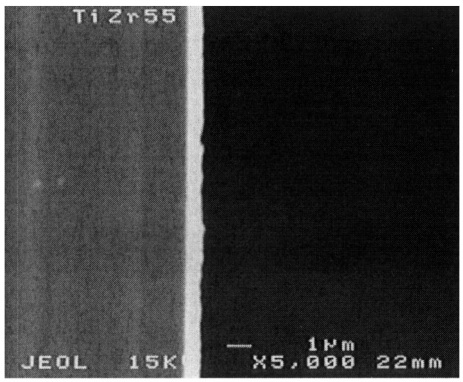
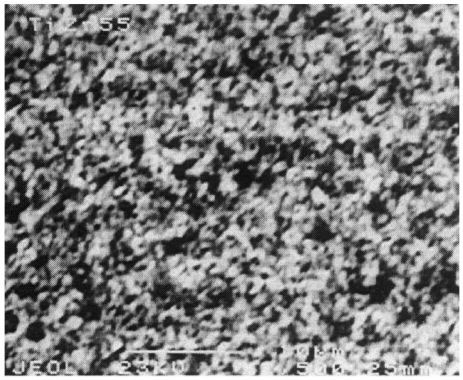


Figure 1. DTA spectrum of zirconium butoxide and titanium butoxide.



(a)



(b)

Figure 2. SEM images of $ZrTiO_4$ film (a) at cross section (white region) and (b) on surface after annealing at 770 °C. Voids are observed mainly on surface (black region).

fabricated with several coating cycles. The cross sectional part displays uniform thickness, respectively, throughout the film. The grains are well crystallized and widely distributed in the surface micrograph. A few voids found on the surface come from the process of pyrolysis and contraction during firing which produce denser specimen than green film,[10] as grown, but less dense one than $ZrTiO_4$ bulk and so the reduction in dielectric property compared with the property of bulk can be expected.

The x-ray patterns of $ZrTiO_4$ bulk and film are shown in Figure 3. Both of them display same patterns confirming $ZrTiO_4$ polycrystalline phase.

The thickness dependent dielectric properties are represented in Figure 4. It does not exhibit any significant variation of dielectric constant in measurement frequency range, especially, in bulk sample. As expected, dielectric constant of film is lower than that of bulk material. We can find that thinner the film thickness, lower the dielectric constant and the property is more dependent on frequency. When the film is thinner, the contribution of surface at layer/electrode to the total dielectric property is larger and so is the space charge stored at layer/electrode. The capacitance formed at layer/electrode can be subtracted as measuring frequency increases thus dielectric reduction induced by the extraction with frequency increment is easily observed in thinner film. K. Natori *et al.* have proposed that "the local dielectric constant

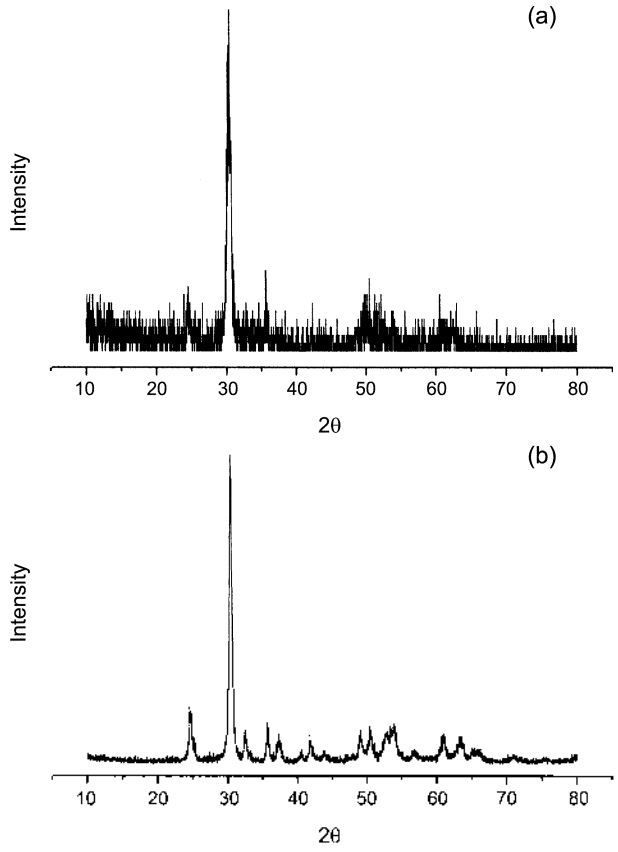


Figure 3. XRD patterns of $ZrTiO_4$ (a) thin film and (b) bulk.

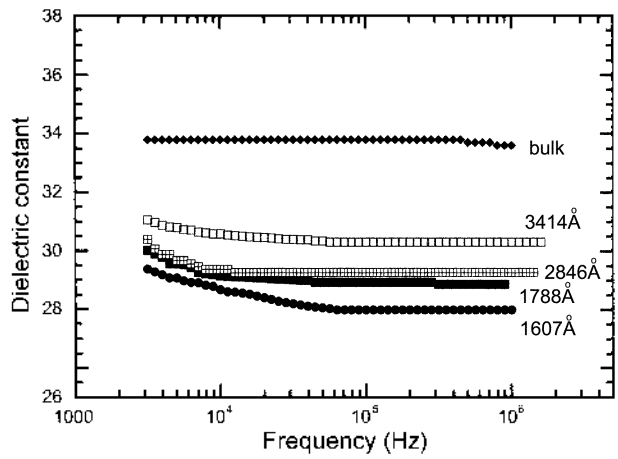


Figure 4. Thickness dependence of dielectric constant with frequency.

at the edge site has a reduced value due to the absence of an enforcing field effected by the adjacent layer, which fact yields a smaller effective constant in a thinner sample structure"[11] by simulation of Lorentzs local field theory. A few voids existing in multilayer are also one of factors which influence the dielectric properties.

On the other hand, the contribution of surface in bulk specimen is very low and the density is higher than that of film. It shows higher and stable dielectric constant, 33.7, compared with that of film in wide range of frequency.

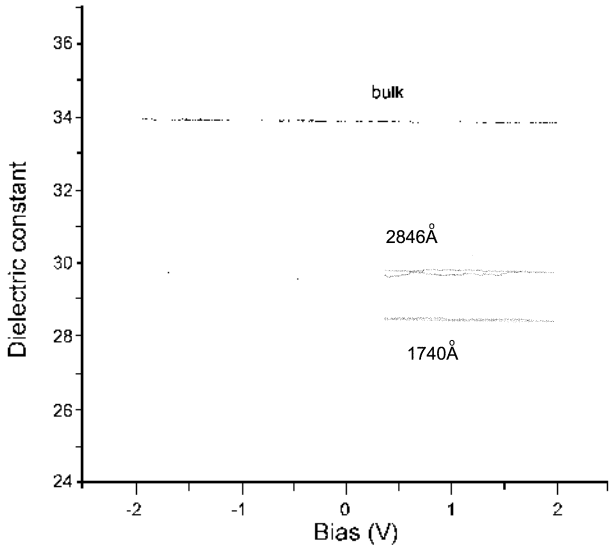


Figure 5. Dielectric constant *vs.* applied dc bias.

Figure 5 indicates that the dielectric properties of $ZrTiO_4$ system are independent of the applied forward and reverse dc bias sweeps (-2 to +2 V) and these results are different from the cases of piezoelectrics, PZT, and (Ba, Sr)TiO_3.[12,13] Therefore, the reduction of dielectric constant in thin film of $ZrTiO_4$ system mainly comes from the "interfacial effects" caused by top and bottom layers/electrodes and the existence of a few voids in film.

The measured capacitance, C, can be expressed as bulk film capacitance C_b, and interfacial capacitance, C_i, connected in series

$$1/C = 1/C_b + 1/C_i \tag{2}$$

so using equation (1)

$$\begin{aligned} Ak_0/C &= Ak_0/C_b + Ak_0/C_i \\ &= (t-t_i)/k_b - t_i/k_i \\ &= t/k_b - t_i(1/k_i - 1/k_b), \end{aligned} \tag{3}$$

where k_b is substantial bulk film dielectric constant, k_i is the interfacial layer dielectric constant, t is total film thickness, and t_i is theoretical interfacial layer thickness which includes two layers/electrodes and some voids in film. From the equation (3), the plot Ak_0/C *vs.* t displayed in Figure 6 gives the information about k_b from the slope and t_i from the intercept if we assume that k_i is 1.006 corresponding to the dielectric constant of air, approximately, although the k_i value has some deviation by other factors such as oxygen diffusion, chemical reaction, changes in defect, or trace of contamination on $ZrTiO_4$ surface.[8,13] The slopes at four frequencies in the figure show all parallel straight lines indicating that the estimated value k_b = 31.88 is constant for any thickness of film and at any frequencies in the measurement range. As frequency increases, however, the t_i values calculated from the intercepts increases from 4.8 Å at 5 kHz to 6.9 Å at 500 kHz and 1 MHz. Since 6.9 Å is the saturated t_i value in measurement range, the interfacial layer thickness depends on the frequency nonlinearly. The large t_i value at

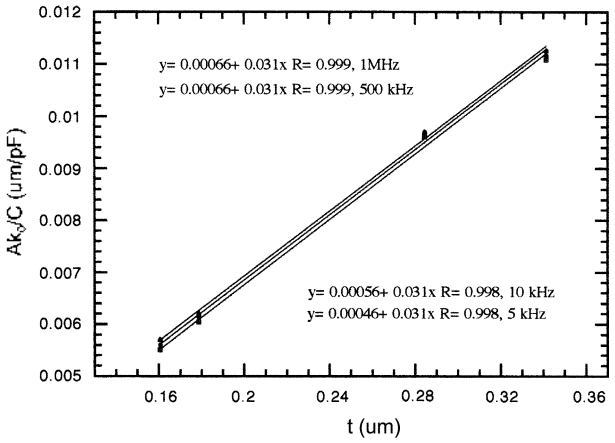


Figure 6. Inverse of the zero-bias capacitance density as a function of $ZrTiO_4$ film thickness at frequencies of 5, 10, 500 kHz, and 1 MHz.

high frequency has same effect as small C_i at high frequency in accordance with equation (1) and (3). In other words, some capacitance component occurred by interfacial effects - polarization formed at low frequency range - is excluded at high frequency, which result in a saturated thickness of interfacial layer, t_i.

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