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Processing of PbTiO₃ thin films. I. *In situ* investigation of formation kinetics

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A novel *in situ* stress measurement technique to study the formation kinetics of multicomponent oxide thin films was developed and was applied to PbTiO₃. Single phase PbTiO₃ thin films were formed from the reaction between films in the deposited PbO/TiO₂ multilayer. The film stoichiometry was accurately controlled by depositing individual layers with the required thickness. The development of film stresses associated with the formation of the product layer at the PbO/TiO₂ interface of the multilayers was used to monitor the growth rate of the PbTiO₃ layer. It was found that growth of the PbTiO₃ phase obeyed the parabolic law, and the effective activation energy was estimated to be 108 kJ/mole. It is believed that the mechanism of this reaction was dominated by grain boundary diffusion of the participating cations. © 1996 American Vacuum Society.

I. INTRODUCTION

Thin films of multicomponent oxides such as PbTiO₃ have been extensively studied because of their remarkable ferroelectric, pyroelectric, and piezoelectric properties. The applications of these thin films include optoelectronic devices, sensors, transducers, and nonvolatile memory devices.¹ A variety of vapor deposition techniques have been applied to the fabrication of these thin films. Physical vapor deposition techniques such as sputtering and evaporation often encounter problems in controlling film stoichiometry. One way to overcome this problem is the use of the multilayer approach,² in which the composition of the films is accurately controlled by depositing the required thickness for individual layers (e.g., A+B→AB). For PbTiO₃ system, either metallic,



or oxide multilayers,



can be used to obtain the compound.

In order to optimize the process of thin film fabrication, it is of great importance to understand the formation kinetics. When a thin film, A, is deposited on a substrate, the total film stress of film A can be a function of temperature, time, substrate, and film thickness.³ If a second film, B, is deposited on top of A, the total film stress of this bilayer can be influenced not only by the aforementioned factors but also by interaction between A and B. Let us assume that the film stresses of individual layers are constant at a given temperature, and that a product layer of AB is formed at the interface between A and B, then the total stress of the multilayer will be influenced by the thickness of the AB film. Since the extent of reaction is time dependent at a given temperature, the total stress of the multilayer is also time dependent.

Therefore, the formation kinetics of multicomponent thin films can be studied by using the *in situ* stress measurement technique.

The *in situ* stress measurement technique was applied by Ablett *et al.* on a Cu/Ti multilayer alloy system.⁴ In their study, the origin of these stresses was attributed to the formation of compounds such as TiCu and TiCu₃. The formation of TiCu resulted in compressive stresses and TiCu₃ resulted in tensile stresses. However, neither semiquantitative nor quantitative relations between total stress and reaction kinetics have been documented. In addition, the unavoidable phenomenon of stress relaxation in thin films was not discussed either.

In this article, we demonstrate the use of the *in situ* stress measurement technique for studying the formation kinetics of PbTiO₃ from PbO/TiO₂ multilayers. Our kinetic data matched very well with the reported data obtained for the PbO and TiO₂ powder mixtures. Using this technique, the grain boundary diffusion coefficient was deduced. In Part II we will discuss the phenomenon of stress relaxation in PbTiO₃ thin films.

II. METHODOLOGY

The formation of PbTiO₃ thin films takes place via the reaction between PbO and TiO₂ films. The reaction product separates the reactants from one another, and the reaction proceeds by diffusion of the participating components through the reaction product. For very low solubilities of the reactants in the reaction product (i.e., for a product with a very low range of homogeneity, as shown in the PbO–TiO₂ phase diagram⁵) the particle fluxes are locally constant and, as long as local thermodynamic equilibrium is maintained at the phase boundary, a planar growth mode is made possible and a parabolic growth law results.

When sequentially deposited films are all very thin compared to the substrate, each film imposes a separate bending moment and separate curvature. Since moments are additive, so are the curvatures.

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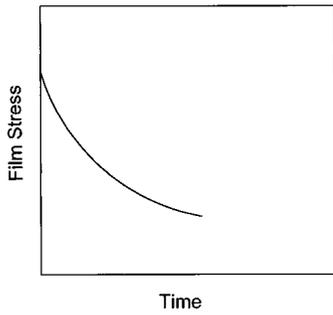


FIG. 1. Schematic stress–time plot for PbTiO₃ thin film reaction.

$$1/R_1 + 1/R_2 + \dots = (1 - \nu_s/E_s)(6/d_s^2)(\sigma_1 d_1 + \sigma_2 d_2 + \dots),$$

$$\sigma d = \sum \sigma_i d_i, \quad i=1 \text{ to } n, \tag{3}$$

where R_i denotes the radius of curvature of the layer i , ν_s and E_s are the elastic constants of the substrate, and σ and d denote total film stress and thickness, respectively.

For a PbO/TiO₂ multilayer on a sapphire substrate, the total film stress can be expressed as

$$\sigma d_{ab} = \sigma_a d_a + \sigma_b d_b, \tag{5}$$

where (a) and (b) denote PbO and TiO₂ and later (ab) is PbTiO₃.

Assuming that (i) stresses of the PbO, TiO₂, and PbTiO₃ layers (σ_a , σ_b , and σ_{ab}) are constant during the formation of PbTiO₃, (ii) the total thickness (d) of the multilayer is constant, and (iii) initial stress is defined as $\sigma_i = (\sigma_a d_a + \sigma_b d_b)/d$, where $d_a/d_b \sim 2/1$, this ratio is close to the ratio of density of the participating materials. Accordingly, the consumption of the PbO layer should be twice as fast as that of the TiO₂ layer. The value of σ_i is obtained from the stress–temperature plot where the temperature is 500 °C, which will be explained later in this article.

At a certain fraction of reaction where a layer of PbTiO₃ (d_{ab}) is formed, the total film stress becomes [using Eq. (5) and the relation $d_a/d_b \sim 2/1$]:

$$\sigma d = \{\sigma_a [d_a - (2/3)d_{ab}] + \sigma_b [d_b - (1/3)d_{ab}] + \sigma_{ab} d_{ab}\},$$

$$\sigma = (1/d)\{(\sigma_a d_a + \sigma_b d_b) + d_{ab}[\sigma_{ab} - (2\sigma_a + \sigma_b)/3]\}$$

$$= [(\sigma_a d_a + \sigma_b d_b)/d] + [\sigma_{ab} - (2\sigma_a + \sigma_b)/3](d_{ab}/d)$$

$$= \sigma_i + (\sigma_{ab} - \sigma_i)(d_{ab}/d). \tag{6}$$

Therefore,

$$d_{ab}/d = (\sigma - \sigma_i)/(\sigma_{ab} - \sigma_i) = f(T, t). \tag{7}$$

From Eq. (6) and the parabolic law, the film stress–time relationship can be plotted as shown in Fig. 1.

III. EXPERIMENTAL PROCEDURE

The film deposition system was a conventional cryo-pumped electron beam evaporator. The 2 in. sapphire substrates were mounted 34 cm above the electron beam evaporation source. Before deposition, the system was pumped down to 4×10^{-8} Torr, rising to $2\text{--}3 \times 10^{-7}$ Torr during depo-

200nm PbO
100nm TiO
Sapphire

FIG. 2. Configuration of the multilayer.

sition. All the depositions were performed at ambient temperature with a deposition rate of 0.2–0.5 nm/s. Total film thickness was kept constant at 300 nm.

High purity, vapor deposition grade oxides (PbO and TiO) were used as the evaporation sources. TiO₂ was not used due to its decomposition during deposition. Based on theoretical calculations and taking into account the loss of Pb (10 mol % of PbO was added), the thickness of the PbO and TiO layers was approximately 200 and 100 nm, respectively. The configuration of the multilayer is shown in Fig. 2. The substrates were cleaned by a series of organic solutions and de-ionized water, followed by drying in N₂ gas.

Film stress measurements as a function of temperature and time were performed for the PbO/TiO oxide multilayers, on 2 in.-diam sapphire substrates in air. The heating rate was 5 °C/min. The sample curvature was calculated from the change in position of a reflected laser beam. The position was measured by a position sensitive detector while the beam was scanned across the sample. The total film stress was calculated by comparing the substrate curvature before and after film deposition using Stoney’s Equation,⁶ which yields the biaxial stress in the thin films parallel to the substrate:

$$\sigma = [E_s/6(1 - \nu_s)](t_s^2/t_f)(1/R), \tag{8}$$

where E_s , ν_s , and t_s are Young’s modulus, the Poisson ratio, and the thickness of the substrate, respectively, and t_f is the film thickness. R is an effective radius of curvature of the substrate determined by $R = 1/(1/R_2 - 1/R_1)$, where R_1 and R_2 are the substrate radii of the curvature before and after film deposition. This formula is applicable when t_f is far smaller than t_s and the central wafer deflection is much smaller than the diameter of the wafer. Both conditions are met in the present work.

Based on this technique, stress–temperature and stress–time plots of the PbO/TiO/sapphire specimens were obtained. In order to quantify the extent of the reaction and the morphological change associated with film stress development, separate tests such as x-ray diffraction analysis for phase determination and scanning electron microscopy for morphology observation were carried out.

IV. RESULTS AND DISCUSSION

Electron spectroscopy for chemical analysis (ESCA) of as-deposited individual PbO and TiO layers indicated that Pb:O and Ti:O ratios are near unity (1.03 for PbO and 1.0 for TiO). A similar analysis was also carried out for the films subjected to annealing at temperatures lower than 500 °C. The Pb:O ratio quickly became 1:1 upon heating, whereas the Ti:O ratio gradually reached 1:2 in the temperature range

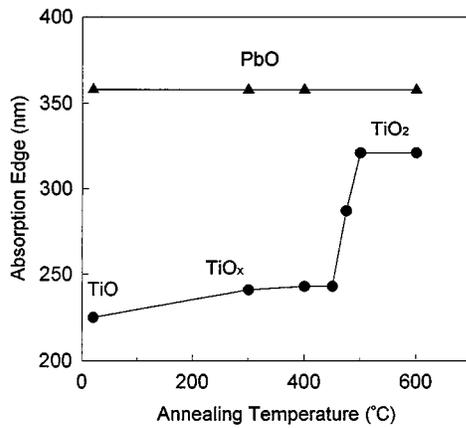


Fig. 3. Absorption edge of PbO and TiO_x films as a function of temperature.

from 400 to 500 °C. No PbTiO₃ formation was found from x-ray diffraction analysis in this temperature range.

Since ESCA can only analyze the film composition of the surface layers, the transmittance method was used to detect oxidation of the bulk films. Here the absorption edges of both PbO and TiO layers were used as an indication of the extent of their oxidation. An independent experiment was conducted to study the oxidation of both 200 nm PbO and 100 nm TiO layers on sapphire substrates as a function of temperature. Both films were subjected to transmittance versus wavelength measurement. It was found that (Fig. 3) the absorption edge for both oxide layers was temperature dependent. For the PbO layer, since it was nearly stoichiometric, its oxidation was complete upon heating. Therefore its absorption edge remained constant throughout the temperature range examined. For the TiO layer, incorporation of oxygen was slow at temperatures of less than 450 °C and became active above 450 °C. The TiO layer completely transformed into TiO₂ when the temperature reached 500 °C.

It was reported⁷ that no reaction between lead oxide and titanium oxide could take place below 400 °C and that reaction was very slow at temperatures around 500 °C. In accord with earlier reports, our data also showed that when the temperature reached 500 °C, the PbO/TiO multilayer would become a PbO/TiO₂ multilayer, and the extent of the reaction between PbO and TiO₂ could be neglected. This will be confirmed later in the article. The formation of PbTiO₃ from the PbO/TiO₂ multilayers was thus activated at temperatures greater than 500 °C.

A. In situ study of PbTiO₃ formation by stress measurement

Figure 4 depicts a typical stress–temperature plot of the PbO/TiO multilayer on a sapphire substrate that was subjected to annealing in air at 575 °C for 4 h with a heating rate of 5 °C/min. The as-deposited multilayer is under tension with a film stress of approximately 100 MPa. It was found that the as-deposited film stress was very sensitive to the deposition rate. For a better understanding, Fig. 4 was divided into three regions. As the temperature rose, the film

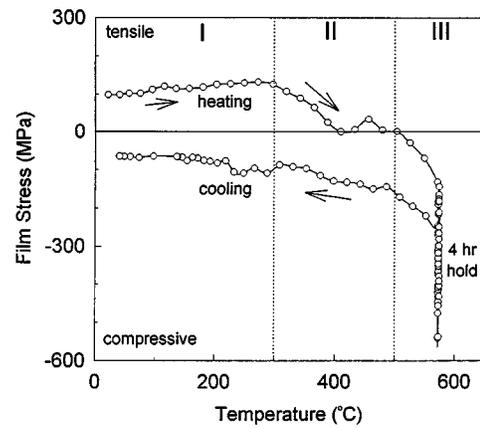


Fig. 4. A typical film stress–temperature plot during formation of a PbTiO₃ thin film.

stress did not change much, as shown in region I. The tensile stresses in the film decreased as the curve entered region II at around 300 °C and reached a local minimum at around 400 °C; it then increased slightly and decreased to a state where the film was nearly stress free at 500 °C. The stress development in region II was attributed to the oxidation of TiO to TiO₂. This was confirmed by a separate study which showed that the stress of an individual PbO layer remained constant throughout the temperature range examined. The intake of oxygen into the films could result in increased film volume, thereby generating compressive stresses. A reasonable explanation for the local stress surge at around 450 °C is that it is due to crystallization in the titanium oxide layer which generates tensile stress. In region III, the stress–temperature curve fell entirely into the compressive state. Compressive stress continued developing in the films when the temperature was above 500 °C and reached a local minimum in the isothermal region; then the tensile stress started building up. This region of the curve was attributed to the formation of the PbTiO₃ phase in the film and to stress relaxation.

Film stress during cooling showed very good linearity only against temperature. Therefore thermal stress (σ_{th}) could be calculated as

$$\sigma_{th} = (E_f / (1 - \nu_f)) (1 \alpha_f - \alpha_s) (T_a - T), \quad (9)$$

where T_a is the annealing temperature, $E_f / (1 - \nu_f)$ is the biaxial modulus of the PbTiO₃ film, and α_f and α_s are thermal expansion coefficients of the film and substrate. Taking the α_s of sapphire as $8.8 \times 10^{-6} / ^\circ\text{C}$,⁸ the thermal expansion coefficient of the PbTiO₃ film was calculated as $10.6 \times 10^{-6} / ^\circ\text{C}$. This value was found to be higher than that of $7.1 \times 10^{-6} / ^\circ\text{C}$ for PbTiO₃ ceramics,⁹ which is considered to be stress free in the temperature range below Curie point.

With increasing temperature, the interaction between the lead oxide and the titanium oxide layers is depicted schematically in Fig. 5. In region III, stress development involves two kinetic processes, PbTiO₃ formation and stress relax-

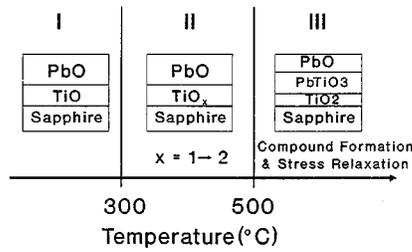


FIG. 5. Interaction between PbO and TiO_x layers as a function of temperature.

ation. In this article, the authors try to establish a basic understanding of the kinetics of PbTiO₃ formation **only** using the *in situ* stress measurement technique. From this point on this article concentrates on the temperature regime from 550 to 625 °C.

The isothermal region for several different annealing temperatures was replotted in Fig. 6. The development of compressive stress in the early stage of the stress–time plots can be attributed to the growth of the PbTiO₃ layer. During the growth process, the absorption of vacancies from a free surface by the product layer can bring about a compressive stress because of “swelling” of the deposit. As the growth process was completed, the film stress reached an extreme, that is, the local minima in the plots as shown in Fig. 6.

Using this *in situ* stress measurement technique, one can monitor the kinetics of compound formation step by step even if the reaction is reasonably fast. For instance, the minimum was found at around 40 min for 575 °C. Lowering the annealing temperature increased the time to achieve a minimum, e.g., around 100 min for 550 °C. Conversely, raising the annealing temperature decreased the time to achieve a minimum, e.g., around 20 min for 600 °C. By annealing at 625 °C, the minimum occurred too fast to appear on the plot.

Intuitively, the stress plots (Fig. 6) can be divided into two different regions as shown in Fig. 7. The asymmetry of the curve implied two different mechanisms for the two distinct regions. During formation, a large amount of vacancies and grain boundaries were generated. Accordingly, the strain en-

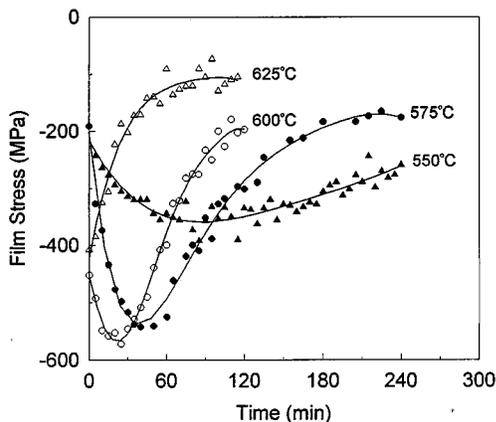


FIG. 6. Stress–time plots for PbTiO₃ thin films.

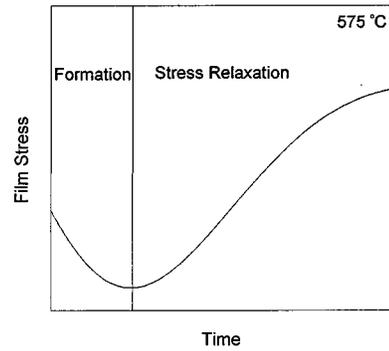


FIG. 7. Implications in a stress–time plot.

ergy stored in the vacancies and grain boundaries needed to be released. Tensile stress was generated by the elimination of vacancies and grain boundaries, therefore, film stress relaxed.

B. Formation kinetics

Figure 8 shows the fraction of the PbTiO₃ formation, *f*, determined using x-ray diffraction as a function of annealing time for the temperature ranging from 550 to 600 °C. From Fig. 8 the thickness of the PbTiO₃ layer formed can be deduced using

$$d_{ab} = (d) \cdot (f) \tag{10}$$

The growth of the PbTiO₃ layer is governed by the parabolic law, i.e.,

$$(d_{ab})^2 = kt, \tag{11}$$

where *k* is the rate constant. Figure 9 illustrates the kinetics of PbTiO₃ growth for three different temperatures. Since the data of Fig. 8 represent a diffusion-controlled growth process, the chemical interdiffusion coefficient (*D*) can be determined from the rate constant $k = 4D$. The rate constant, *k*, has an Arrhenius behavior as shown in Fig. 10. The straight line fit points to a thermally activated growth of PbTiO₃ on

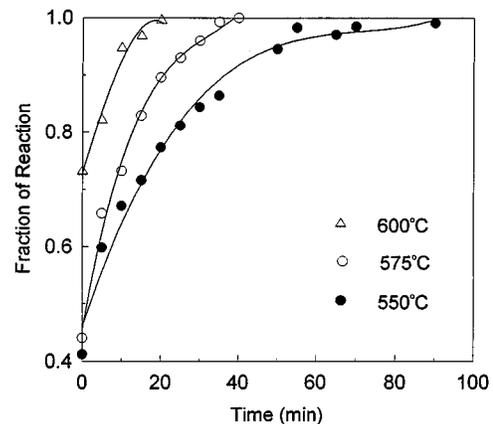


FIG. 8. Fraction of PbTiO₃ formed as a function of time as determined by the x-ray diffraction technique.

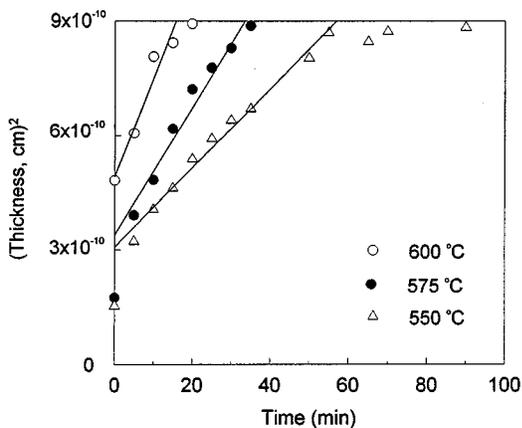


FIG. 9. Time dependence of the thickness of PbTiO₃ films.

sapphire. The activation was estimated to be 108 kJ/mole. This value is in excellent agreement with the literature values as shown in Table I.

C. Mechanism of PbTiO₃ formation

From PbO and TiO₂ layers, a polycrystalline PbTiO₃ phase is formed. During reaction, the fluxes of the components in the product layer, which are responsible for the advancement of the reaction, are the moving ions. Therefore, in order to preserve local electrical neutrality, the fluxes of the different ions must always be coupled with each other. Consequently, the following combinations are possible: either oppositely charged ions flow in the same direction, or ions with like charges flow in opposite directions through the reaction product. These simple considerations give the possible limiting cases of a solid state reaction between ionic crystals. For the formation of ionic crystals such as PbTiO₃, it is the slower partner that essentially determines the reaction rate. From the rate constants, the chemical diffusion constant of PbTiO₃ formation in this work could be calculated as 6.8×10^{-14} cm²/s at 575 °C. The chemical diffusion constants at this temperature were estimated to be 1×10^{-12} cm²/s for PbO (Ref. 13) and 7.4×10^{-16} cm²/s for TiO₂.¹³

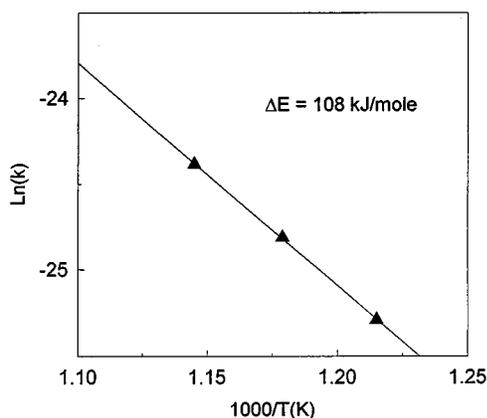


FIG. 10. The Arrhenius behavior of rate constants of PbTiO₃ formation.

TABLE I. Kinetic data of PbTiO₃ formation.

Activation energy (kJ/mole)	Reference	Process
108, 122	7	PbO+TiO ₂ powders
151	10	Pb+TiO ₂ powders
77	11	Pb(OH) ₂ +Ti(OH) ₄ PbCO ₃ +Ti(OH) ₄
81, 69	12	TiO ₂ ×nH ₂ O+PbCO ₃ ×nH ₂ O
108	This work (1993)	PbO/TiO ₂ thin films

Our experimental value is approximately an order lower than that for PbO and two orders higher than that for TiO₂. This could suggest that transport of Ti⁴⁺ ions through the product layer is the rate-determining step. Furthermore, it is believed that the participating components diffuse mainly through grain boundaries. It is then reasonable to write the grain-boundary diffusion constant as

$$D_{gb} = 3 \times 10^{-7} \exp(-108000/kT) \text{ cm}^2/\text{s}. \quad (12)$$

It is well known that the effect of compressive stress on atomic or molecular diffusion in a constrained solid is to reduce the diffusivity because of the enhancement of steric hindrance in the lattice.¹⁴ Therefore, one can expect a lower grain boundary diffusion constant for a stress-free PbTiO₃ formation.

From Eq. (12), one can extrapolate the rate constant of the PbTiO₃ formation at 500 °C. The amount of reaction between PbO and TiO₂ films annealed at 500 °C for 0.1 min was calculated to be 2%. This is self-consistent with the assumptions.

V. SUMMARY

A novel *in situ* stress measurement technique has been successfully developed to study the formation kinetics of multicomponent thin films such as PbTiO₃. Using the multilayer approach, film composition can be simply controlled by the thickness of the individual layers. The formation of the PbTiO₃ layer at the interface of PbO/TiO₂ altered the total stress of the multilayers. By monitoring stress changes in the multilayers, the *in situ* formation kinetics of PbTiO₃ film was successfully examined and quantitatively documented. The activation energy of PbTiO₃ formation was estimated to be 108 kJ/mole which is in excellent agreement with the value in the literature. It is believed that the formation of the PbTiO₃ phase was dominated by the grain-boundary diffusion mechanism because of the very fine grain size in the films. The grain-boundary diffusivity responsible for this reaction was also deduced.

ACKNOWLEDGMENTS

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