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Chen C. Li and Seshu B. Desu[a]
Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Stress relaxation in PbTiO$_3$ films was investigated by the *in situ* stress measurement technique. A simple viscous flow model was successfully used to interpret the kinetics and behavior of stress relaxation of PbTiO$_3$ thin films. The activation energy responsible for stress relaxation was estimated to be 190 kJ/mole, which was accounted for by the lattice diffusion of vacancies. A Nabarro–Herring creep model was successfully employed to correlate the relationships among the viscosity, lattice diffusion coefficient, and grain size of the PbTiO$_3$ films, and an estimate of the lattice diffusion coefficient of vacancy motion during relaxation was obtained. Also, the observed time required for complete relaxation was found to be in accord with theoretical values. Hillock formation resulting from grain boundary sliding is believed to contribute to stress relaxation in its early stage. Thereafter, grain growth resulting from lattice diffusion is believed to play a major role in the stress relaxation. © *1996 American Vacuum Society.*

I. INTRODUCTION

Unlike bulk materials, thin films condensed onto substrates are in an extremely nonequilibrium state characterized by a high level of stress. This nonequilibrium is caused by a number of factors associated with both the preparation techniques and the physicochemical properties of substrates and film materials. Stress can be introduced into a thin film due to, among other factors, differential thermal expansion between the film and its substrate, lattice misfit with the substrate, or chemical reaction within the film or with the substrate.

The tendency of a thin film to move towards equilibrium brings about relaxation of the internal stress in the film. Stress relaxation in thin films can take place during their thermal treatment. The relaxation in thin films often causes the formation of hillocks, whiskers, voids, and cracks and, in certain cases, the film breaks down into separate islands and peels off the substrate[1] which obviously is deterimental to the performance of the corresponding thin film devices. Accordingly, in order to understand and therefore control the effect of stress on the performance of thin film devices, it is of great importance to investigate the mechanisms of stress relaxation in the materials of interest.

Deformation mechanisms[2] such as defectless flow, dislocation glide, dislocation creep, diffusional creep, and grain boundary sliding have been proposed to explain the stress relaxation in a number of thin film materials including metals,[3] alloys,[4] silicides,[5] and simple oxides.[6] At present, it is generally accepted that stress relaxation in most thin films is the result of the plastic deformation by diffusional creep.[7] However, it is essential to mention that relaxation mechanisms in thin films are greatly influenced by many factors such as film stress level, temperature, film thickness, and grain size. Thin films often contain extremely high concentrations of excess vacancies which are built in during depo-

sition. The stress level may be affected considerably by the flow of vacancies to the film surface and by structural defects.[8] It has also been suggested that, during thin film grain growth, the removal of grain boundaries—and hence the reduction of excess volume in the grain boundaries—will induce stress in the film when it is constrained by the substrate.[8]

Little work has been done, to the best of our knowledge, on the stress relaxation of multicomponent oxide thin films.[9] In this work, an *in situ* stress measurement technique was employed to investigate the kinetics and mechanisms of stress relaxation in PbTiO$_3$ thin films. It was assumed that the stress relaxation of thin films could be described by creep phenomena in bulk materials. An attempt was made to correlate stress relaxation with creep behavior using a simple viscous flow model and diffusional creep mechanisms. Using this technique, the diffusion coefficient responsible for the relaxation mechanism was estimated. Furthermore, the kinetics of stress relaxation were also found to be in excellent agreement with experimental and theoretical values.

II. ANALYSIS

In order to understand the stress–relaxation phenomena of PbTiO$_3$ films at elevated temperatures, a viscous flow model, depicted in Fig. 1, was considered. For simplicity, only uniaxial compressive stress was assumed to act on a slab of PbTiO$_3$ that was free to flow vertically [Fig. 1(a)]. The PbTiO$_3$ film was modeled as a Maxwellian element whose overall mechanical response reflects a series combination of an elastic spring and a viscous dashpot [Fig. 1(b)] that incorporates the various relaxation mechanisms of the film. Upon loading, there is an instantaneous deformation of the spring elastically. With increasing time, the elastic strain, ϵ_e, will be accommodated by the development of a plastic strain, ϵ_p, in a time-dependent viscous fashion. The total strain ϵ_t, however, remains a constant. Since the value of the net stress, σ, acting on the film is dictated by the level of the elastic strain,
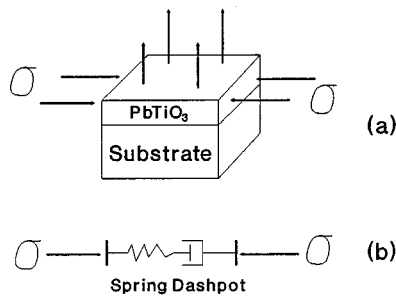

FIG. 1. The viscous flow model for stress relaxation. (a) Slab of PbTiO₃ on a substrate; (b) model of the PbTiO₂ as a Maxwellian element.

$$\sigma = E\epsilon_e/(1-\nu) \tag{1}$$

(E is Young's modulus and ν is the Poisson ratio), film stress will relax as time proceeds.

The same compressive stress, σ, will concurrently act on both the spring and dashpot so that

$$\epsilon_e = \sigma/E$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2)$

$$\dot{\epsilon}_p = \sigma/\eta,$$

where $\dot{\epsilon}_p = d\epsilon_p/dt$ and η is viscosity. For constant ϵ_t, $\dot{\epsilon}_e = -\dot{\epsilon}_p$ or $(1/E)d\sigma/dt = -\sigma/\eta$. Upon integration, we obtain

$$\sigma = \sigma_0 \exp(-Et/\eta) = \sigma_0 \exp(-t/\tau), \tag{3}$$

where the time constant $\tau = \eta/E$. The initial stress in the film, σ_0, therefore relaxes by decaying exponentially with time.

This stress, σ_0, is equivalent to the stress σ_{ab} [Eq. (5) in Ref. 10], the stress level upon the completion of PbTiO₃ formation. Therefore, in connection with the stress curve developed during PbTiO₃ formation, we can obtain a full schematic of the stress–time curve as shown in Fig. 2, assuming time constant $t = 50$ min.

III. EXPERIMENTAL PROCEDURE

The films were grown in a conventional cryopumped electron beam evaporator.[10] Two-in.-diam sapphire substrates
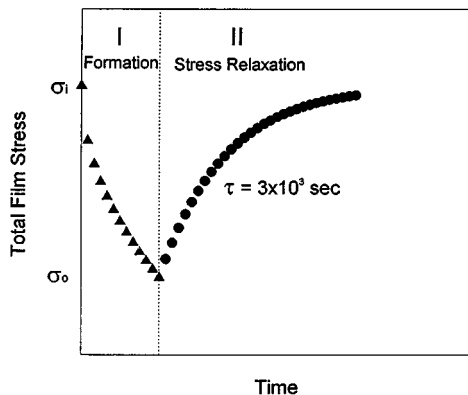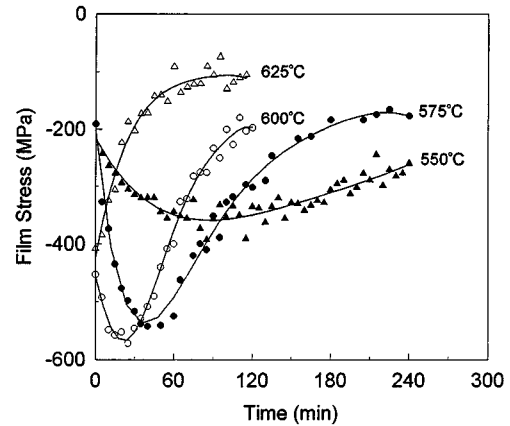

FIG. 2. A modeled stress–time curve.

FIG. 3. Experimental stress–time plots for PbTiO₃ thin films.

were mounted 34 cm above the electron beam evaporation source. Before deposition, the system was pumped down to 4×10^{-8} Torr, rising to 2–3×10^{-7} Torr during deposition. 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 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. Based on this technique, stress–temperature and stress–time plots of the PbO/TiO/sapphire specimens were obtained.

IV. RESULTS AND DISCUSSION

Figure 3 shows the typical stress–time plots of PbTiO₃ thin films for four different temperatures. These plots were found to be very similar to the schematic in Fig. 2. However, the cusp in Fig. 2 was not seen in Fig. 3. The absence of the cusps in Fig. 3 could be attributed to the initial stress relaxation as the multilayer approached the completion of PbTiO₃ formation.

The absolute value of the data in the region of relaxation was replotted in a semilog scale of stress against time as shown in Fig. 4. The data showed very good linearity for temperatures up to 600 °C. The deviation from the straight line at a temperature of 625 °C could likely have been caused by a change in the relaxation mechanism. From the slopes of
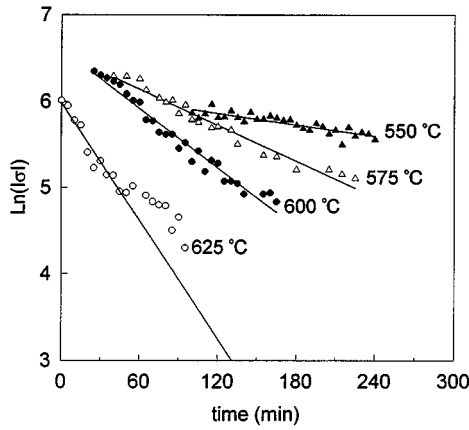
FIG. 4. Ln($|\sigma|$) as a function of time.

the straight lines in Fig. 4 the viscosity, η, was obtained (as shown in Fig. 5) by taking the Young's modulus of PbTiO₃ films as 13.1×10^{11} dyn/cm².[11] Since the viscosity decreases with increasing temperature and is governed by the following formula,

$$\eta = \eta_0 \exp(\Delta E/kT). \qquad (4)$$

The activation energy of the stress relaxation was estimated to be 190 kJ/mole. This value is 1.76 times greater than the activation energy for PbTiO₃ formation in which the mechanism was believed to be grain-boundary diffusion.[10]

A. Mechanism of stress relaxation

Although, in general, it is accepted that diffusional creep is the main cause of relaxation in thin films, several concurrent processes are expected to contribute to the relaxation of a film. The mechanisms that dominate stress relaxation in thin films depend on the stress level, film thickness, and temperature.[12] If we assume the grains in thin films are circular disks, to a first approximation, with radius r and thickness h, we have the following relationship between the surface area (including grain boundary and interface area) and volume:
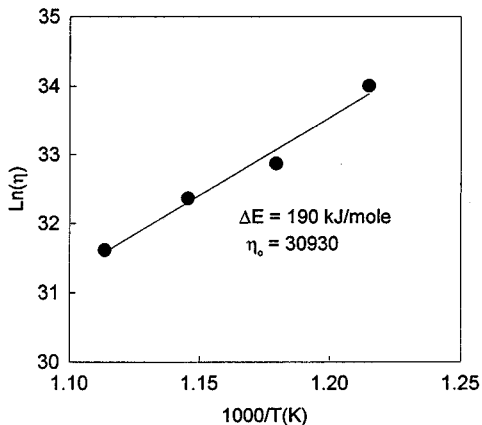

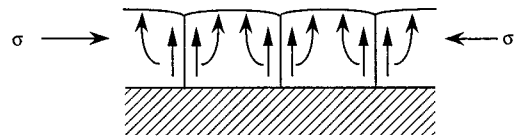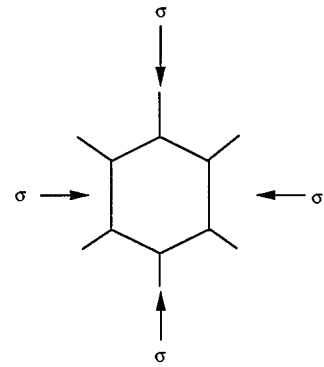FIG. 5. The Arrhenius behavior of viscosity of PbTiO₃ films.

FIG. 6. Schematic illustrations of possible paths along which atoms diffuse to relax stress.

$$S_v = (1/2)(2\pi rh + 2\pi r^2)/(\pi r^2 h) = (1/r) + (1/h)$$
$$= (2/d) + (1/h), \qquad (5)$$

where d is the average grain diameter, i.e., the average grain size. The factor 1/2 was introduced in the expression above because each surface is shared between two grains. From the dimensions of film thickness and average grain size, we can have the following relationships,

$$S_v = 1/h, \quad d \gg h,$$

$$S_v = 3h \quad \text{or} \quad 3/d, \quad d \sim h,$$

$$S_v = 2/d, \quad d \ll h.$$

It is believed that the predominant mechanism is lattice diffusion when $d \gg h$, whereas it is grain-boundary diffusion when $d \ll h$. When $d \sim h$, as it is in our case, it is likely that lattice diffusion dominates the mechanism of stress relaxation in the temperature range around 0.55 Tm (melting temperature). However, we believe that grain-boundary diffusion could be essential in the early stage of stress relaxation when the grain size is still very small.

In the original formulation of Coble and in Nabarro–Herring creep, atoms and vacancies were assumed to flow between neighboring grain boundaries subjected to different normal stress when the film is loaded in a nonbiaxial fashion. For an equibiaxially compressed film, as shown in Fig. 6, the atoms should flow between the grain boundaries and the free surface rather than between neighboring boundaries. However, possible paths along which atoms can diffuse to relax stress are the grain boundaries and the grains.

B. Stress relaxation by the diffusional creep mechanism

Diffusional creep or Nabarro–Herring creep occurs by the movement of point defects (usually vacancies) under a concentration gradient generated by the applied stress.[13] In thin films under biaxial stress this concentration gradient is present between grain boundaries both parallel and perpendicular to the direction of film stress. A simplified analysis of diffusional creep in thin films under uniaxial stress has been done in the past.

The viscous flow model that has been widely used in the stress relaxation of metallic glass[14] was successfully employed to interpret the annealing kinetics of the films. In a crystal, assuming that lattice diffusion dominates stress relaxation in PbTiO₃ thin films, viscous flow also occurs through the movement of vacancies. This is the Nabarro–Herring creep, in which the viscosity is given by[14]

$$\eta = (kTd^2)/(4\Omega D_1),\qquad(6)$$

where Ω is the atomic volume, d is the average grain size, k is the Boltzmann constant, η is the viscosity, T is the absolute temperature, and D_1 is the lattice diffusion constant. The viscosity was derived from Fig. 5 as $\eta = 30\,930\,\exp(190\,000/kT)$. Since the mechanisms are the same both for lattice diffusion and for viscous flow, lattice diffusion constants were deduced as $D_1 = D_{10}\exp(-190\,000/kT)$, where D_{10} is the pre-exponential factor. Equation (6) was used to correlate the viscosity and lattice diffusion constant of PbTiO₃ films with their grain size. Taking $\Omega = 12.6 \times 10^{-24}$ cm³, the average grain size, d, of PbTiO₃ films was measured to be 0.2 μm for the PbTiO₃ film annealed at 600 °C and D_{10} was calculated to be $\approx 3 \times 10^{-5}$ cm²/s. This value is two orders of magnitude greater than the pre-exponential factor for the grain-boundary diffusion constant shown previously. It may be noted that this magnitude of difference is comparable to that for alloys.[15] From this analysis, the estimation of lattice diffusion through vacancies was calculated as

$$D_1 = 3 \times 10^{-5}\,\exp(-190\,000/kT)\quad \text{cm}^2/\text{s}.\qquad(7)$$

C. Estimation of relaxation time

During annealing, the morphology (e.g., grain size) of the films can change with time and therefore vacancy flow or ionic flow can predominantly take different paths for different regimes of relaxation. It is difficult to precisely evaluate the relative contributions of diffusional flow by lattice diffusion and grain-boundary diffusion in the predicting kinetic behavior of stress relaxation. The present experimental observations and previous discussions suggest that both processes probably contribute to stress relaxation in the PbTiO₃ films.

Assuming that the sum of the elastic (ϵ_e) and plastic (ϵ_p) strains remains constant and that film stress, as observed in the stress–time plots in Fig. 3, cease to relax when the stress–time plots are leveling off, it can be shown for diffusional creep[16] that, when $\epsilon_p = K\sigma$, (where K is a factor char-

TABLE I. Time required for complete stress relaxation of PbTiO₃ films.

Temperature (°C)	625	600	575	550
t_v (min)	52	104	219	482
t_{gb} (min)	53	78	117	181
T (min)	41	87	144	446

acteristic of a different creep mechanism) the time, t, required for essentially complete stress relaxation is given by the relation

$$t = \beta(1-\nu)/KE,\qquad(8)$$

where $\beta = 2.3$, ν is the Poisson ratio, and E is the Young's modulus. If grain boundaries act as vacancy sinks and grain growth is due to diffusional creep with lattice diffusion predominating,[16,17]

$$K \sim 10(D_1/dh)(\Omega/kT),\qquad(9)$$

where D_1 is the lattice diffusion constant, Ω is the atomic volume, h is the film thickness, d is the average grain size, k is the Boltzmann constant, and T is the absolute temperature. By taking $D_1 = 3 \times 10^{-5}\exp(-190\,000/kT)$, $d = 0.2 \times 10^{-4}$ cm, $\Omega = 12.6 \times 10^{-24}$ cm³, $\nu = 0.2$, and $E = 13.1 \times 10^{11}$ dyn/cm², the time, t_v, required for complete stress relaxation was calculated and is listed in Table I. For comparison, the time constants, $\tau\,(=\eta/E)$, required for the initial film stress to fall to $1/e$ of its initial value were also calculated and are listed in Table I.

The calculated times of relaxation agree with the experimentally observed values. For instance, at 625 °C, the stress–time curve started leveling off when the annealing time reached 50 min, as shown in Fig. 3. The data are in excellent agreement with the experimental value at other temperatures also. It follows, therefore, that the diffusional flow of vacancies by lattice diffusion is the mechanism for stress relaxation in PbTiO₃ films.

One may argue that stress relaxation is likely to be dominated by grain-boundary diffusion only. If this is the case, K would then be given by

$$K \sim 10(D_{gb}\,a/dh^2)(\Omega/kT),\qquad(10)$$

where a is grain boundary width and D_{gb} is given by $3 \times 10^{-7}\exp(-108\,000/kT)$.[10] The t_{gb} values were calculated for various temperatures by taking $a = 0.25$ nm, $d = 0.2 \times 10^{-4}$ cm, $h = 0.2 \times 10^{-4}$ cm, and $\Omega = 12.6 \times 10^{-24}$ cm³; the calculated values are listed in Table I. It was found that t_{gb} is smaller than the experimental values and even smaller than τ. This indicated that grain-boundary diffusion was not likely the dominant mechanism for stress relaxation. t_{gb} was also found to be approximately two orders of magnitude smaller than t_v for Pb (Ref. 18) and Cu (Ref. 12) thin films when the temperature was around 0.5 Tm. These results
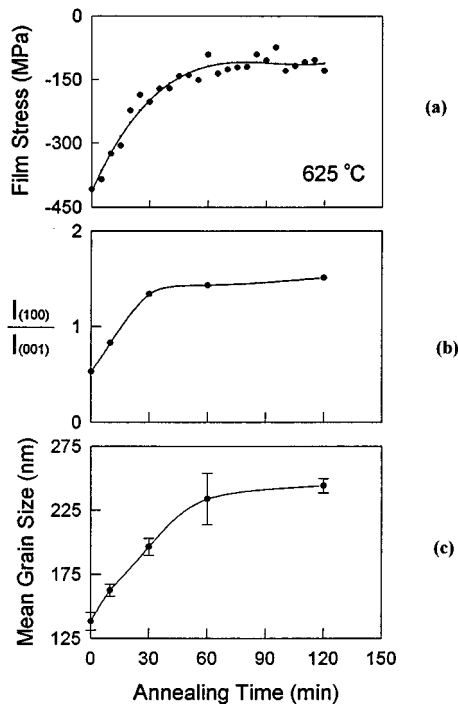
FIG. 7. The effects of both orientation and size of grains on film stress. (a) Film stress as a function of annealing time; (b) change in orientation as a function of annealing time; (c) change in grain size as a function of annealing time.
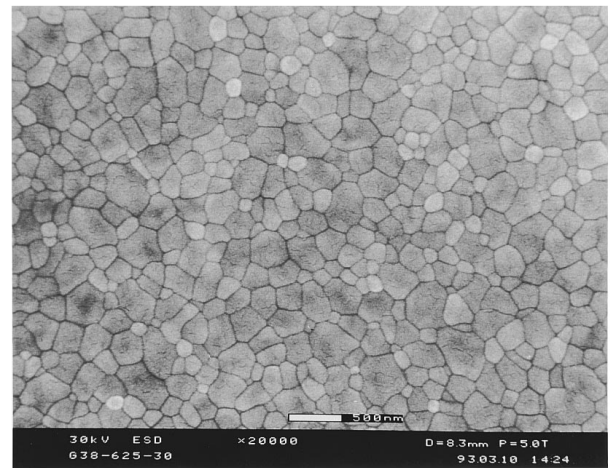

FIG. 8. SEM microstructure of the PbTiO₃ films annealed at 625 °C for 30 min.

croscopy (SEM) microstructure of PbTiO₃ films annealed at 625 °C for 30 min. From Fig. 8, it is clear that grain growth has taken place by the consumption of smaller grains. Since reorientation of small grains is a part of the grain growth process, grain growth can be considered to be the predominating mechanism.

E. Hillock formation by grain-boundary sliding

In previous discussions, it was understood that lattice diffusion plays the dominant role in stress relaxation. However, from morphological observations we believe that grain boundaries are of great importance in the early stages of stress relaxation. Figure 9 illustrates hillock formation in PbTiO₃ thin films annealed at 600 °C for 30 min. Hillocks were also found in the films annealed at other temperatures. It was noticed that the number density of the hillocks remained relatively constant as the anneal time increased. This behavior suggested that hillocks only formed at the beginning of relaxation while the grain size was still very small. At this stage, vacancy diffusion (mainly via grain boundaries) could have caused grain boundary sliding (shown in

clearly indicate that the grain-boundary diffusion coefficient obtained from formation kinetics cannot be used for stress relaxation.

Since PbTiO₃ thin films were exposed to elevated temperatures, they displayed a number of interesting time-dependent deformation processes characterized by the thermally activated motion of ions and defects. As a result, changes in the film morphology occurred and stress levels were reduced.

D. Morphology development during stress relaxation

Figure 7 depicts the effects of grain orientation and mean grain size on film stress. Several points were selected from the stress–time plots [Fig. 7(a)] and the corresponding microstructures were examined. It was found that recrystallization in the films played a major role in stress relaxation. Recrystallization concurrent with deformation is believed to occur by two different mechanisms that result in rather different microstructures. The first mechanism is identified by the rotation of the misorientation of the small grains or sub-cell microstructure, eventually causing the subboundaries to be indistinguishable from high angle grain boundaries. This mechanism could account for the change of the $I_{100}:I_{001}$ ratio associated with film stress levels [Fig. 7(b)]. The second mechanism is characterized by the migration of pre-existing high angle grain boundaries, i.e., grain growth. This mechanism could contribute to the reduction of stress levels as well [Fig. 7(c)]. Figure 8 shows a typical scanning electron mi-
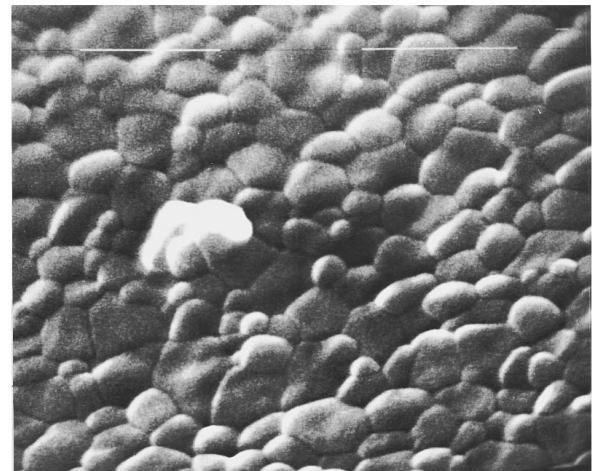

FIG. 9. Hillock formation in the PbTiO₃ film annealed at 600 °C for 30 min.
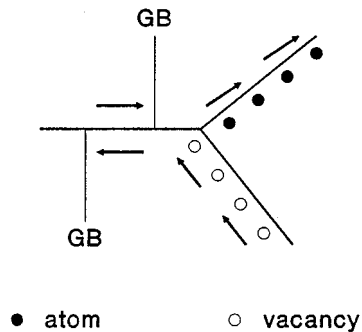
FIG. 10. Grain-boundary sliding by diffusion along the grain boundary around the triple edge.

Fig. 10) which usually occurs at grain boundary junctions.[19] In some instances, it is possible for a grain to be squeezed, and as a result, form a protrusion in the films. As relaxation proceeded, the grain size increased, the effect of grain boundary sliding diminished, and the lattice diffusion mechanism prevailed.

Hillock formation has been found in some other thin film systems such as lead,[20] gold,[21] copper,[22] tin,[23] silver,[24] aluminum,[25] and TiSi₂.[26] The formation in these cases was caused by localized surface growth at high temperatures which resulted from compressive stress in the films.[13] In the case of Al films, it is often observed upon cooling that a groove[25] surrounding the hillocks is formed. However, this phenomenon was not significant in PbTiO₃ films. Hillocks may result not only from uniformly distributed strains but also from localized electromigration effects.[27]

V. SUMMARY

Stress relaxation in PbTiO₃ films was investigated by an *in situ* stress measurement technique. A simple viscous flow model was successfully employed to interpret the behavior of stress relaxation in the PbTiO₃ thin films. Using this model, the estimation of the effective viscosity (η) of PbTiO₃ films was made possible. The activation energy responsible for stress relaxation was estimated to be 190 kJ/mole. The relaxation of film stress was dominated by lattice diffusion through the vacancy movement.

In order to microscopically understand stress relaxation in the PbTiO₃ thin films, the Nabarro–Herring creep model was employed to correlate the viscosity (η), lattice diffusion coefficient (D_1), and grain size of the films. Based on this model, the lattice diffusion coefficient of the vacancy motion was estimated to be $3 \times 10^{-5} \exp(-190\,000/kT)$. Using this

data, the time required for complete relaxation of the PbTiO₃ thin films was calculated and was compared with the experimental values. It was found that the experimental values observed from stress–time plots matched very well with the calculated values. Therefore, it follows that this stress relaxation process is dominated by the lattice diffusion of the vacancies. Hillock formation caused by grain-boundary sliding could partially relax the film stress in its early stage. Thereafter, grain growth resulting from lattice diffusion mainly accounted for the stress relaxation.

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