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Influence of Crystallization Kinetics on Texture of Sol–Gel PZT and BST Thin Films

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Abstract

The evolution of morphology of sol–gel PZT and BST thin films during rapid thermal annealing (RTA) is investigated by recording of elastic light scattering data in reflected mode. The analysis of film morphology and texture evolution obtained by XRD reveals the dependence of crystallization kinetics on the annealing conditions. The evolution of film morphology during the transition to the perovskite phase is analysed by the time dependence of fractal dimensionality. The parameters characterizing the kinetics of the transformation to the perovskite phase are extracted by mathematical treatment of experimental data. A mechanism for texture formation is proposed. © *1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

The achieved success in application of integrated ferroelectrics stimulates the growth of interest in detail investigations of the main stages of ferroelectric thin film technology. Recently sol–gel processing has emerged as one of the preferred methods for manufacturing of high quality thin films. The high temperature annealing of amorphous sol–gel PZT films is required for formation of perovskite phase having the ferroelectric properties. The strong dependence of ferroelectric parameters on the annealing conditions was pointed out.[1–3] It was shown that the best results are obtained in texture films prepared by Rapid Thermal Annealing (RTA).[4] Nevertheless to our knowledge there are almost no *in-situ* investigations of crystallization kinetics during RTA due to time resolution limits of conventional experimental methods. *In-situ* investigations by X-ray diffraction[5] and spectroscopic ellipsometry[6] have been carried out only for low crystallization rate. We have demonstrated that instantaneous angular dependence of elastic scattered light intensity is rather sensitive to the film morphology. Moreover the time resolution of the light scattering method is considerably high.[7–9] Proposed mathematical treatment of experimental data allows to extract the essential information about crystallization kinetics. In this work we present the detail investigation of the evolution of the film morphology during annealing by light scattering technique. The comparison of this data with XRD data shows that the essential parameters characterizing the formation of the perovskite phase in PZT and the growth of crystallites in BST can be obtained by the analysis of the light scattering data.

2 Experiment

We have investigated the crystallization of sol–gel films of lead zirconate–titanate (PZT) and barium–strontium titanate (BST). The amorphous sol–gel films of PZT $Pb(Zr_{0.53}Ti_{0.47})O_3$ with 10% of excess Pb are prepared by spinning on $Si/SiO_2/Tt/Pt$ substrate. The platinized silicon substrate $Si/SiO_2/Ti/Pt$ [(100) Si/400 nm SiO_2/10 nm Ti/120 nm Pt] is annealed at 650°C for 30 min before the film deposition. The films are pyrolysed for 15 min after each coating at 380–490°C temperature range. The BST films $(Ba_{0.7}Sr_{0.3})Ti_{1.005}O_3$ are prepared from an acetate/methoxyethanol based spin-on solution. The solution concentration is adjusted to obtain a thickness of one crystalline layer of 45–50 nm. The annealed platinized silicon substrate $Si/SiO_2/ZrO_2/$

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Pt (20 nm-thick layer of ZrO_2) is used. The pyrolysis is performed in a diffusion furnace at 450°C for 20 min in oxygen atmosphere.

The wafer is subsequently cut into sections and so the set of the samples with the identical preparation history is used for studying the RTA crystallization at different annealing times and temperatures. The heating rate for RTA process is about 100°C s^{-1} and the heating time never exceeds 10 s. The annealing temperature ranges from 600 to 750°C for PZT and from 650 to 800°C for BST. The main attention is paid to the detail investigation of the crystallization kinetics at short annealing times (from 10 to 200 s).

Differences in refraction index of the perovskite and pyrochlore phases allow to control spatial phase distribution in partially annealed samples by using optical microscope.[10] The evolution of heterophase structure during annealing at different conditions have been video-recorded. The focused beam of low power He–Ne laser ($\lambda = 0{\cdot}63\,\mu$m) is used as a probe for elastic light scattering investigations. The angular dependence of the scattered light intensity is measured in the angular range from 2 to 60° with the resolution about 10 min. We also record independently the total scattered light intensity over whole angular range.

Comparison of scattered light data with film surface images obtained by optical and electron microscopy reveals that: (1) the measured data is determined only by the light scattering at the film surface, as the light scattering by the Pt-film boundary and in film bulk is negligible; (2) investigated angular dependencies are sensitive to surface morphology;[11] (3) the observed wide scale range of surface relief details favors the application of fractal formalism for treatment of angular dependence data.[12,13] The partially annealed samples are examined by X-ray diffraction. We have analyzed the variation of: (1) intensity of the texture perovskite maximum (111) in regime theta-2 theta (CoK_α); (2) integral intensity of the pyrochlore (222) maximum and nontexture perovskite (011) and (002) ones.

Comparison of results deduced from these different experimental methods allowed the finding of the relationship between the evolution of the film morphology and the kinetics of the crystallization process.

3 Annealing of PZT Films

It was shown that the optical methods can be effectively used only for the studying of the transition from the pyrochlore to the perovskite phase[9–11] as the amorphous and pyrochlore phases are indistinguishable when studied by optical microscope observation and light scattering technique. We have obtained the temperature dependence of the texture maximum for constant annealing time ($\Delta t = 60$ s) in temperature range 600–750°C. The $I_{(111)}$ increases for temperatures from 600 to 700°C and decreases at 750°C. Such behavior points to the acceleration of texture growth with the temperature increasing up to 700°C. The decrease at 750°C can be associated with the decay of the perovskite phase at higher temperatures.

For detailed investigation of the crystallization kinetics we have chosen the lowest temperature, $T = 600$°C, in order to gain appropriate time resolution at the beginning stage of the process. The set of the samples has been prepared by partial annealing during different time intervals ranging from 15 s to 16 min. The time dependence of texture perovskite maximum [Fig. 1(a)] and integral intensity of scattered light [Fig. 1(b)] demonstrate the similar behavior with two stages: fast and slow. Fitting of exponential law provides two strongly different time constants. The process starts with the 'fast stage' (time constant $\tau \sim 12$ s) which continues up to 60 s when it is changed drastically to the 'slow stage' ($\tau \sim 880$ s). It is clear that such treatment of the fast stage is too simplified.

For proper description of the fast stage we fit the experimental data by Kolmogorov–Avrami (K–A) formula for α(2D) kinetic process.[14,15]

$$I(t) = I_0 + \Delta I\left\{1 - \exp[-(t - t_d)^3/\tau^3]\right\} \quad (1)$$

where t_d = delay time.

This analysis shows the sufficient difference in kinetic parameters obtained from the time

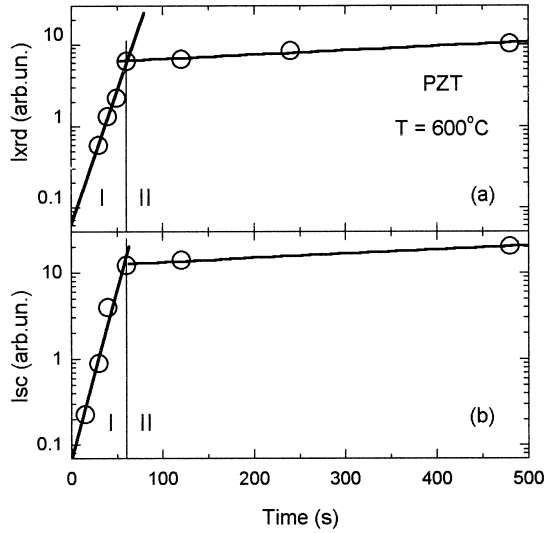

Fig. 1. The time dependence of the intensity of XRD (111) texture maximum (a) and integral scattered light intensity (b) in PZT films. Experimental points are fitted by exponential functions.

dependence of the intensity of the texture maximum I_{sc} and the scattered light intensity $I_{(111)}$ (Fig. 2). The new stage of the process, characterized by delay time, is observed in both time dependencies. The delay time for I_{sc} is much longer ($t_d \sim 40$ s) than for $I_{(111)}$ ($t_d \sim 17$ s). The time constants τ are 14 and 33 s, respectively. So the whole annealing process must be divided into three distinct stages: 'delay', 'fast' and 'slow'.

3.1 Delay stage

XRD measurements show that the pyrochlore phase appears and grows from the first seconds of annealing. Moreover the appearance and slow growth of a small number of perovskite crystallites is observed by optical microscopy. Such behavior can be explained by the local decreasing of activation energy induced by the defects. The existence of these crystallites cannot be recorded by the light scattering technique as lower than the threshold of our equipment.

3.2 Fast stage

Fast growth of intensity of the texture maximum [Figs 1(a) and 2(a)] is accompanied by several pronounced optical effects. The increasing of the scattered light intensity [Figs 1(b) and 2(b)] and strong change of angular dependence of the scattered light intensity are due to the fast development of the surface morphology. This fact can be verified by the optical microscope observations. The increasing of the angle ϕ_{max} corresponding to the scattered light intensity maximum can be attributed to the decreasing of the distances Δr between individual scattered centers due to the increasing of the number of perovskite crystallites [Fig. 3(a)]. The fitting of $\Delta r(t) \sim 1/\phi_{max}$ data by exponential law provides $\tau = 22$ s. The nucleation, growth and coalescence of individual perovskite crystallites are observed during the whole stage. The end of the fast stage corresponds to the qualitative change of the patterns (geometrical transformation of percolation type).

The above mentioned difference in time constants and delay times for $I_{(111)}(t)$ [Fig. 2(a)] and $I_{sc}(t)$ [Fig. 2(b)] can be explained as follows. The XRD measurements allow to distinguish between growth of the texture and nontexture perovskite structures while the light scattering is sensitive only to the variations of the surface morphology. So observed difference demonstrates that growth of the texture crystallites nucleating on the substrate[16] starts later and occurs faster than the growth of the nontexture crystallites appearing in the bulk.

Nevertheless the fractal analysis of the angular dependence of scattered light intensity can reveal the growth of texture perovskite structure. It is well-known that the dependence of light intensity scattered from mass fractal objects on the wave vector is[17]

$$I(q) \sim q^{-D} \tag{2}$$

where $q = 4\pi/\lambda \sin(\phi/2)$ = wave vector, λ = light wavelength, ϕ = scattering angle, D = fractal dimension.

Time dependence of momentary value of D during RTA ($T = 650$°C) is presented in Fig. 4. Obtained results are fitted by K–A formula describing the decrease of pyrochlore phase fraction by α process:

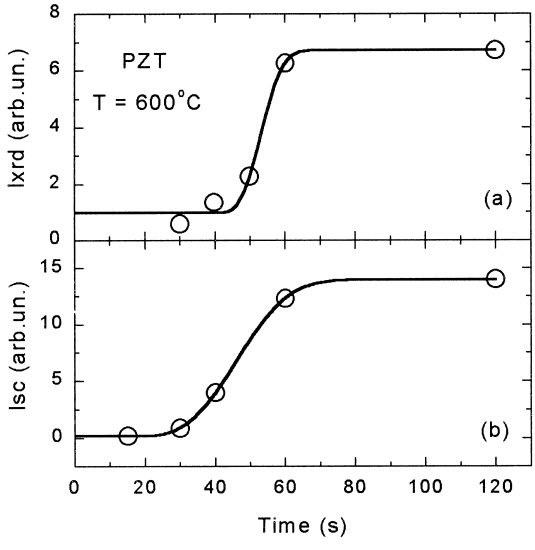

Fig. 2. The time dependence of the intensity of XRD (111) texture maximum (a) and the integral scattered light intensity (b) during fast growth of the perovskite phase in PZT films. Experimental points are fitted by eqn (1).

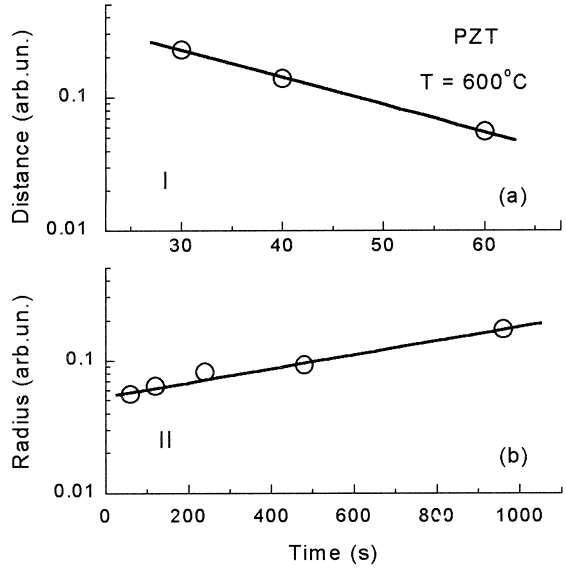

Fig. 3. The time dependence of the distance between the crystallites of the perovskite, phase during fast stage (a) and increasing of their average size during slow stage (b) in PZT films. Experimental points are fitted by exponential functions.

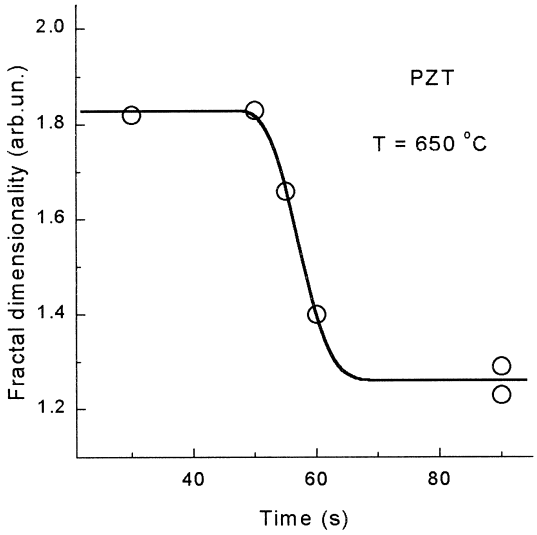

Fig. 4. The time dependence of fractal dimensionality in PZT films. Experimental points are fitted by eqn (3).

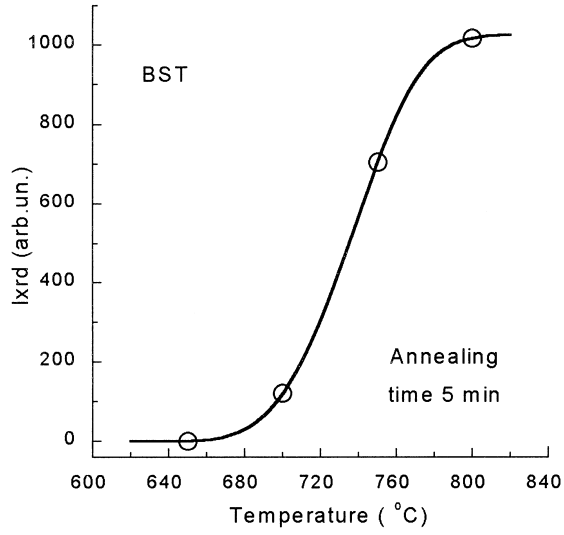

Fig. 5. The temperature dependence of the intensity of XRD (110) maximum in SBT films. Experimental points are fitted by eqn (4).

$$D(t) = D_0 + \Delta D \exp[-(t - t_d)^3/\tau^3] \qquad (3)$$

where D_0 = fractal dimension of the film completely transforming to perovskite phase.

It is important that the best fitted parameters ($\tau = 12$ s, $t_d = 47$ s) are close to ones obtained for $I_{(111)}(t)$. Such coincidence can be explained assuming that the fractal objects with wide scale range are forming only during growth of the texture perovskite structure.

3.3 Slow stage

The slow growth of the intensity of the texture maximum [Figs 1(a) and 2(a)] observed from 60 to 600 s ($\tau = 850$ s) is correlated with the optical data. The change of surface morphology leads to increasing of the scattered light intensity [Figs 1(b) and 2(b)] ($\tau = 890$ s) and decreasing of the angle $\phi_{\max}$ corresponding to angular dependence maximum due to the growth of the average sizes of the crystallites R [Fig. 3(b)]. The fitting of $R(t) \sim 1/\phi_{\max}$ data by exponential law provides $\tau = 850$ s. The obtained results demonstrate that the slow stage corresponds to the slow recrystallization accompanied by the raise of texture quality and by the decrease of the fraction of the pyrochlore phase. It is confirmed also by the decreasing of the pyrochlore phase detected by XRD.

4 Annealing of BST Films

The similar approach is used for studying of the crystallization kinetics in sol–gel BST films. We have prepared the set of samples by RTA at different temperatures from 650 to 800°C with constant annealing time (5 min). Temperature dependence of intensity of XRD peak (110) is presented at Fig. 5.

The experimental points are fitted by proposed modification of K–A formula for $\beta(2D)$ kinetic process with constant heating rate[8,9]

$$I(T) = I_0\left\{1 - \exp[-(T - T_{\mathrm{st}})^4/T_0^4]\right\} \qquad (4)$$

where T_{st} = the start temperature of crystallization process, T_0 = the rate constant.

The successful fitting confirms that crystallization kinetics is defined by the growth of the nuclei raised during pyrolysis and allows to extract the essential kinetic parameters $T_{\mathrm{st}} = 633$°C, $T_0 = 112$°C.

5 Conclusion

It was shown that the light scattering and XRD data with subsequent mathematical treatment can give quantitative description of the crystallization process kinetics. As a result one can obtain the parameters characterizing nucleation and growth of crystallites, and the development of the fractal objects. It must be pointed out that the proposed universal method can be used for the investigation of the crystallization kinetics of various films on any substrates with any bottom electrodes. It can be applied for the optimization of the annealing conditions during manufacturing of various integrated ferroelectric devices.

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