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Jyrki Lappalainen, Sergey A. Ivanov, and Vilho Lantto



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Secondary grain growth and surface morphology of post-annealed nanocrystalline $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$ thin films

Jyrki Lappalainen^{a)}

Microelectronics and Materials Physics Laboratory, P.O. Box 4500, FIN-90014 University of Oulu, Finland

Sergey A. Ivanov

X-ray Laboratory, Karpov' Institute of Physical Chemistry, 103064, ulica Vorontsovo pole 10, Moscow, Russia

Vilho Lantto

Microelectronics and Materials Physics Laboratory, P.O. Box 4500, FIN-90014 University of Oulu, Finland

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Nd-modified PZT [PNZT,Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O₃] thin films were deposited using a pulsed XeCl-excimer laser on single-crystal MgO(100) substrate at room temperature. After deposition, the PNZT thin-film samples were post-annealed at three different temperatures of 700, 800, and 900 °C. The crystal structure and crystallite size distribution were measured using conventional x-ray diffraction methods. Atomic force microscopy was used for the surface morphology characterization of both amorphous and polycrystalline films. Detailed grain structure of annealed PNZT films was studied in perpendicular film-substrate cross sections using field-emission scanning electron microscopy (FESEM). When annealing temperature increased from 700 to 900 °C, an orientation of growing grains in the film with (001) planes parallel to the film surface took place. The mean crystallite size increased from 210 to 330 Å, respectively. FESEM micrographs revealed a subpopulation of columnar grains in the films growing downward from the upper surface of the film as a result of secondary grain growth due to minimization of the surface, strain, and ferroelectric depolarization energies. At the same time, the surface roughness was considerably decreased. © 2002 American Institute of Physics. [DOI: 10.1063/1.1515954]

I. INTRODUCTION

Miniaturization of both active and passive components like conductors, resistors, capacitors, and different semiconductor devices is needed in today's integrated circuits and other microelectronics applications. For the fabrication, for example, of microelectromechanical systems, electro-optical devices, and solid-state transducers, a proper deposition of different functional materials like ferroelectric leadzirconate-titanate $[PZT,Pb(Zr_rTi_{1-r})O_3]$ thin films is very important.¹⁻³ Depending on the deposition and processing conditions, PZT thin films may have amorphous, polycrystalline, columnar, or epitaxial structure. Several properties, such as dielectric and polarization responses, leakage conduction, and optical transmission and reflection are influenced to a large extent by the grain structure of the film.^{4,5} In the case of chemical vapor deposition, sputtering, and pulsed laser deposition (PLD) techniques, PZT films, grown in situ on heated substrates, usually have a highly oriented columnar or epitaxial grain structure, and they possess, for example, rectangular ferroelectric hysteresis loops with remanent polarization $P_r \approx 40 \ \mu \text{C/cm}^2$ and relative dielectric constant $\varepsilon \approx 800$. On the other hand, the resistivity of films due to the columnar structure can be low with ρ $\approx 10^6 - 10^8 \ \Omega \ cm$ as compared to values in polycrystalline PZT films with $\rho \approx 10^{11} - 10^{12} \Omega$ cm.⁶⁻⁸ In the case of *in situ*

deposition on heated substrates, the growth of grains starts from the substrate surface, where thermally activated atomic species move by surface diffusion, nucleate to form a thermal equilibrium structure with a specific critical size, and subsequently form a grain. In such a system, there are three different energies acting: substrate surface energy, isotropic surface energy of the grain, and interface energy between the grain and substrate. Precise size, structure, and orientation of the nucleated grains depend on the minimization of these energies, and the configuration having the lowest free energy is favored. Later, after the growing grains have coalesced, grain boundary energy and strain energy due to the macroscopic stress might also have significant influence on the orientation and grain growth of the film.9 In the case of room-temperature deposition of films similar to the case here with the laser deposition of PZT films, oxide films are typically amorphous after deposition, and form a polycrystalline film structure with small crystallite size below 150 nm during post-annealing heat treatment. If the grain size is much smaller than the film thickness, as is the case in this study, the nucleation of the grains inevitably occurs throughout the as-deposited film. Thus, a nucleation process and grain growth different from that described above has to be considered. In addition, the post-annealing heat treatment can be used to control the grain growth, orientation, and the surface morphology of the films.

Here we present some results of the grain growth and orientation of Nd-modified PZT (PNZT) thin films deposited

^{a)}Electronic mail: jyla@ee.oulu.fi

by the PLD process on MgO(100) substrate at room temperature during post-annealing heat treatment at different temperatures. When the composition of the ceramic PNZT target was near the morphotropic phase boundary (MPB) of PZTs (Zr/Ti ratio ≈ 0.53), the laser-beam fluence could be used to adjust the chemical composition of the as-grown amorphous PNZT films. A unique property of the PLD process is the generation of particulates or droplets in the film.¹⁰ This is typically seen as one of the main disadvantages of the PLD process, seeing that it impairs the film surface morphology, but can actually be a benefit when initial stages of grain growth are considered. In this case, however, the grain growth and orientation during the post-annealing treatment determines mainly the quality of the PNZT film surface. Since the Rayleigh scattering of light from the film surface plays a very important role in different optical applications, as in electro-optic modulators and waveguides,¹¹ the surface roughness of PNZT films studied here was also measured and analyzed carefully.

II. EXPERIMENTAL PROCEDURE

A pulsed XeCl-excimer laser with a wavelength of 308 nm was used to deposit amorphous PNZT thin films with thickness of 300 nm on MgO(100) substrate. The deposition was carried out at room temperature at a base pressure of 6 $\times 10^{-5}$ mbar. The substrate and the target were placed parallel at a distance of 30 mm, and the angle between the normal of the target and the incident laser beam was 45°. The laser beam was scanned over the rotating target surface so that the selected fluence was kept constant during the deposition process. The repetition rate of the laser pulses was 25 Hz and the duration of a single pulse was 30 ns. The laserbeam fluence was 2.0 J/cm² and a $Pb_{0.97}Nd_{0.02}$ \times (Zr_{0.55}Ti_{0.45})O₃ target with a density of 7.4 \times 10³ kg/m³ was used. The post-annealing process of the films was carried out under an inverted zirconia crucible together with some extra PNZT powder in order to prevent an excess loss of lead during annealing at temperatures of 700, 800, or 900 °C for 20 min at the maximum temperature. A heating and cooling rate of 400 °C/h was used in all temperature profiles.

Crystal structure and crystallite size distribution of the PNZT films after annealing were studied by x-ray diffraction (XRD) measurements. In order to study the crystallite-size distribution function (see Fig. 2), x-ray diffraction experiments [URD-63 diffractometer, (Germany), Cu K_{α} radiation, step-scanning technique] were performed on strain-free samples. Tikhonov's regularization procedure to Fourier x-ray profile analysis was applied for calculations of the crystallite-size distribution.¹² The instrumental broadening was obtained from a perfect standard specimen. All calculations were performed with a special computer program.¹³ It was shown that the broadening of all tested diffraction reflections was more likely to be due to size effects, and the stress in the films was mainly macroscopic thermal stress, introducing only some shift of the reflections.¹⁴

Atomic force microscopy (AFM) was used to study the surface morphology of both amorphous and annealed thin



FIG. 1. X-ray diffraction patterns (Cu K_{α} radiation) from three PNZT thin films deposited at a laser-beam fluence of 2.0 J/cm² and post-annealed at (a) 700, (b) 800, and (c) 900 °C. The thickness of the film was about 300 nm.

films. The field emission scanning electron microscopy (FESEM) (Jeol JSM-6300F) was used to study the crystallite size and structure of PNZT film cross sections. AFM pictures were analyzed using Image SXM v. 1.61 software. Amplitude distribution functions (ADF) representing the statistical distribution of the film surface height data were generated for picture profiles, and the values of rms roughness R_q (the variance of the ADF) were calculated. Based on these data, bearing area curves (BAC) were calculated in order to further evaluate the morphology of the PNZT thin films. Basically, BAC shows the cumulative fraction of the studied film area which is covered by a certain height of the surface compared to the maximum value of the ADF.

III. RESULTS

A. XRD measurements

Three XRD patterns from PNZT films with thickness of about 300 nm, annealed at 700, 800, and 900 °C, respectively, are shown in Fig. 1. In the case of the film annealed at 700 °C, the XRD pattern in Fig. 1 is very similar to that measured from the target with random grain orientation. The intensity of the pattern is very weak and a possible indication of the pyrochlore phase is seen at 2θ angle of 30°. Although the overall intensity in the XRD pattern of the PNZT film annealed at 800 °C in Fig. 1 is still low, the intensities of (001) and (002) reflections are clearly pronounced as compared to the corresponding intensities in the XRD pattern of the PNZT film annealed at 700 °C. The increase is an indication of the orientation of grains with the $\langle 001 \rangle$ crystal direction perpendicular to the film surface in consequence of the increasing annealing temperature. The XRD pattern in Fig. 1 from the PNZT film annealed at 900 °C reveals a much more pronounced orientation where the majority of grains in the film are (001) oriented. For the tetragonal crystal structure, values of the lattice constants a = 4.02 Å and c = 4.08 Å were calculated from the peak positions of the (001), (002), and (011) reflections in the XRD pattern in Fig. 1(c). The value of the ratio c/a = 1.015 for the degree of the tetragonal distortion is obtained from the lattice constants. This value and the value of the lattice constant c are actually smaller than the values c/a = 1.023 and c = 4.13 Å (a) =4.04 Å) obtained from bulk ceramic PNZT samples with similar Nd-modified composition near the MPB.¹⁵ From the XRD patterns of PNZT films annealed at 700 and 800 °C in Fig. 1, even smaller ratio values c/a = 1.0128 and c/a= 1.0067 were calculated, respectively, although an accurate determination of the peak positions was now more difficult due to the weak intensity of the reflections.

In order to quantify the degree of the grain orientation of the PNZT films, the sum of intensities of (001) and (002) reflections [I(001)+I(002)], was compared to the sum of all peak intensities of the XRD pattern, $\Sigma I(hkl)$, using the ratio¹⁶

$$p = \frac{I(001) + I(002)}{\Sigma I(hkl)}.$$
(1)

The *p* values were compared to those values calculated from XRD patterns from bulk ceramic PNZT samples, such as the ablation target itself, having the same composition and small crystallite size with random orientation. For the film annealed at 700 °C in Fig. 1, a value p = 0.379 was calculated, a comparison with the value p = 0.168 for bulk PNZT ceramics with random orientation suggests that the film annealed at 700 °C already is slightly oriented to the (001) direction. This observation confirms our earlier results indicating that post-annealed PNZT films on MgO(100) substrate are typically oriented with the c-axis perpendicular to the film surface.^{8,17} In the case of films annealed at 800 and 900 °C in Fig. 1, values of p = 0.621 and 0.933 were obtained, respectively. As shown in Fig. 1(c), other peaks than those from the (001), (002), and (011) reflections are hardly observable in the XRD pattern from the PNZT film annealed at 900 °C. The obtained results indicate an increasing orientation of the films in the (001) direction with increasing post-annealing temperature. In addition to the perovskite phases of PNZT, these films contained also a small quantity of the phyroclore phase, which gives a small peak to the XRD patterns at 2θ angle a bit above 30° at the base of the (011) reflection of PNZT.

The volume-weighted crystallite-size distributions of the PNZT films in Fig. 1 are shown in Fig. 2. A broadening of peak profiles in the x-ray diffraction patterns due to structure and size of crystallites was studied from the (011) reflection of the samples annealed at the three different temperatures. The crystallite size distributions of the films were calculated using the Fourier analysis method.¹² The mean crystallite size of the films increased from 208 to 330 Å with an increase in post-annealing temperature from 700 to 900 °C. The maximum of the crystallite-size distribution shifted to higher crystallite-size values with increasing annealing temperature.



FIG. 2. Volume-weighted crystallite-size distribution functions of the three PNZT thin films in Fig. 1, annealed at 700, 800, and 900 °C, respectively. The vertical line at \approx 70 Å indicates the critical crystallite size for PbTiO₃ measured by Chattopadhyay *et al.* (Ref. 19).

perature, and, furthermore, a bimodal two-peak structure is seen in the distribution of the film annealed at 900 °C. The shape of this distribution suggests that the film contains many large crystallites with size between 600 and 1300 Å, although the mean crystallite size is 330 Å.

B. SEM and AFM analyses

Three FESEM micrographs of PNZT thin-film cross sections are shown in Fig. 3. The development of the grain structure in the films with increasing post-annealing temperature is evident from the micrographs. The film annealed at 700 °C in Fig. 3(a) clearly has a dense polycrystalline structure of small uniformly distributed grains. Although the crystallite-size distribution curve in Fig. 2 reveals that there are some large crystallites even in the films annealed at 700 °C, it is clear that the vast majority of the grains are equiaxial as a consequence of a normal, "bulk" type, grain growth. However, a cross section of the PNZT film annealed at 800 °C [Fig. 3(b)] shows a double layer structure with large grains at the top of the film, and an underlying layer with a grain structure similar to that of the PNZT film annealed at 700 °C [Fig. 3(a)]. The top layer of the film consisted of large columnar grains with a length of about 130 nm and width between 20 and 50 nm, oriented with the longer side perpendicular to the film surface and resulting in an average grain aspect ratio of 3.71. This secondary grain growth leads to the columnar layer structure, which is typical





100 nm





FIG. 3. FESEM micrographs of cross sections of PNZT films annealed at (a) 700, (b) 800, and (c) 900 $^{\circ}$ C. Columnar crystal growth starting from the upper surface of the film is clearly seen in (b) and (c).

also for *in situ* deposited thin films. The PNZT film in Fig. 3(c) annealed at 900 °C has columnar grains already reaching through the whole film, and the stagnation of the grain growth is attained. There are, in fact, columnar grains that are responsible for the increased intensities of the (001) and (002) reflections in Figs. 1(b) and (c). Thus, the information from the cross-sectional FESEM micrographs is very consistent with the results from XRD measurements.

The changes in the grain structure and crystallite size distribution with increasing post-annealing temperature were found also to strongly affect the surface morphology of the films. In addition to increased crystallite size, which means a decreased number of light scattering grain boundaries, the



FIG. 4. AFM micrographs of PNZT film surfaces after annealing at (a) 700 and (b) 800 °C. The rms roughness R_q values of the surfaces are 39.17 and 11.97 nm, respectively.

surface quality of the films is very important for optical applications of the films in order to avoid Rayleigh scattering and losses. Two AFM micrographs of surfaces of PNZT films annealed at 700 and 800 °C are shown in Figs. 4(a) and 4(b), respectively. The PNZT film annealed at 800 °C with rms roughness $R_q = 11.9$ nm has better surface morphology than the film annealed at 700 °C, for which $R_q = 39.2$ nm. Corresponding roughness value for the film annealed at 900 °C in Figs. 1–3 was $R_q = 20.4$. In general, the annealing of the PNZT films at 700 °C impaired the surface morphology of the films, with an average $R_q \approx 41$ nm, compared to that of the as-deposited amorphous films with an average $R_q \approx 22$ nm, but annealing at 800 °C [Fig. 4(b)] improved the surface quality of the films, so that the average R_q was 10 nm. The average roughness of the PNZT films annealed at 900 °C was 18 nm. The grain orientation in the film is obvious also from the AFM micrograph in Fig. 4(b), where a rectangular grain texture aligned nearly parallel to the frame



FIG. 5. Typical bearing area curves with corresponding values of rms roughness R_q (in nanometers) of five PNZT thin films annealed at 700, 800, and 900 °C, respectively.

of the micrograph is clearly seen on the film surface. In fact, the grain size in Fig. 4(a) looks bigger than that in Fig. 4(b), in contradiction to the data presented in Fig. 2. However, the x-ray diffraction technique reveals the crystallite-size distribution of the coherently diffracting domains, and the grains in the surface of the film annealed at 700 °C, to most likely consist of several domains. This is due the development of the ferroelectric perovskite phase during heating via paraelectric pyrochlore phase with a much larger unit cell. Initial development of the pyrochlore phase is most likely also responsible for the rough surface of the films annealed at 700 °C. In Fig. 5, there are five BAC curves shown for PNZT films describing the cumulative change in the surface height distribution after annealing process. For comparison, a totally flat surface with a height difference of 0 nm gives a step-like transition from 0% to 100%, as shown in Fig. 5. Films annealed at 800 °C have clearly the steepest BAC curves, whereas the films annealed at 700 °C have the gentlest ones. In the films annealed at 900 °C, the surface roughness starts to increase again, and the BAC curve starts to become gentle again. From this data it is also evident that the PNZT films annealed at 800 °C have the best surface quality due to the secondary growth of the columnar layer of oriented grains at the top of the film. The observed improvement in the surface morphology was also confirmed by optical transmission and reflection measurements.¹⁸ The values of the parameter *p* introduced in Eq. (1), the ratio $p_{\rm film}/p_{\rm bulk}$, rms roughness R_q , and of the mean crystallite size of different PNZT thin-film and bulk samples are collected in Table I.

IV. DISCUSSION

From the XRD patterns in Fig. 1 and FESEM micrographs in Fig. 3, it is possible to conclude that the grain growth and orientation process in as-deposited amorphous PNZT thin films is strongly activated by the post-annealing temperature. Although the x-ray diffraction technique gives information only on the average crystal structure and lattice constants, and typical compositional and structural fluctuations of alloy ceramics in the scale of few nanometers are not revealed, it can be effectively used for the crystallite-size analysis of ceramic samples. The nanometer-scale crystallitesize distributions in Fig. 2, increasing mean values from 20 to 33 nm with increasing annealing temperature, were calculated. The structure of the ferroelectric PNZT films with crystallite size similar to that in Fig. 2 is affected by the size effect, since the range of long-range Coulomb forces in the crystal structure is of the same order as the crystallite size. This situation leads to a decrease in the ferroelectric lattice distortion, and the ratio c/a decreases with decreasing crystallite size until the crystal structure of the grains transforms to the cubic symmetry with the value c/a = 1. For PbTiO₃ nanocrystallites, Chattopadhyay et al.¹⁹ have defined the critical crystallite size for this cubic transformation to be $d_c \approx 70$ Å. They also showed that for PbTiO₃ grains with the diameter below 100 nm, the ratio c/a starts to decrease from its nominal bulk value, and the decrease is very rapid below the diameter size $d \approx 60$ nm. An exponential dependence of the ratio c/a on the grain size d, $(c/a)_d$, was given also by Jiang et al.,²⁰ using

$$\left(\frac{c}{a}\right)_{d} = \left(\frac{c}{a}\right)_{\infty} - \left\{ \left[\left(\frac{c}{a}\right)_{\infty} - 1 \right] \exp\left[-C(d-d_{c})\right] \right\}, \quad (2)$$

where $(c/a)_{\infty}$ stands for the bulk value of the ratio c/a and C is a constant. Since the dielectric and polarization properties, such as remanent polarization P_r and dielectric constant ε , of ferroelectric materials are directly related to the degree of the ferroelectric distortion, they are also expected to decrease with decreasing grain size. Although the exact values of the

TABLE I. Comparison of the values of the parameter p, ratio $p_{\text{film}}/p_{\text{bulk}}$, rms roughness R_q , and mean crystallite size between amorphous and post-annealed PNZT films and bulk ceramics.

PNZT sample	р	$p_{ m film}/p_{ m bulk}$	R_q [nm]	Mean crystallite size [nm]
Bulk ceramic	0.168	1		750 ^a
Amorphous film			15.8	
Film: 700 °C	0.375	2.256	39.2	20.8
800 °C	0.621	3.696	11.9	25.2
900 °C	0.933	5.554	20.4	33.0

^aDetermined from SEM micrographs.

critical grain size for PNZT ceramics with compositions near the MPB are not known, it is possible to conclude from Fig. 2 that the laser-deposited and post-annealed PNZT films contain a large portion of grains below the critical grain size, and they do not have any ferroelectric response under an applied external electric field. According to the low measured values of the ferroelectric distortion c/a = 1.0128, 1.0067, and 1.015 for the PNZT films annealed at 700, 800, and 900 °C, respectively, in comparison with the bulk value c/a = 1.023, the films are expected to have impaired ferroelectric properties. Actually, the electrical properties of the post-annealed polycrystalline PNZT thin films in capacitor structures with platinum electrodes on MgO(100) substrate,^{8,17} with remanent polarization $P_r \approx 25 \ \mu \text{C/cm}^2$ and relative dielectric constant $\varepsilon_r \approx 560$, are slightly weaker than the properties of *in situ* grown PZT films with a columnar structure. Polarization response of the paraelectric phase as a function of electric field is linear, and it should sum to the overall polarization response and cause tilting of the hysteresis loop which is, actually, the case in these films.¹⁷ On the other hand, due to several blocking grain boundaries with electrical barriers in nanocrystalline films, high values of the low-field resistivity $\rho \approx 10^{11} - 10^{12} \ \Omega \ cm$ (two orders of magnitude higher than typical values in highly oriented columnar PZT films) were measured.^{8,17} Thus, these changes in the electrical properties are, to some extent, a consequence of the size effect due to the reduced grain size of post-annealed PNZT films. Also, for bulk PZT ceramics with grain size above 0.1 μ m, the dielectric constant ε_r , remanent polarization P_r , and piezoelectric constants d_{33} and d_{31} decrease, and the coercive field E_c increases with decreasing grain size.²¹

The nucleation and growth of this kind dense nanocrystalline grain structure throughout the film is probably assisted by the particulates formed in the PLD process.¹⁰ Nanometer scale particulates are generated during and after every laser pulse in the molten phase of the target surface, and then swept to the substrate in the form of droplets instead of plume of atomic species, like the vast majority of the material. Although these particulates do not necessarily have a perovskite crystal structure or the right kind of chemical composition, they might serve as nucleation centers for the amorphous phase, mainly composing the as-deposited film. Later, these particulates are merged to the grains of the film through the coalescence and coarsening processes.

In order to qualitatively analyze the tendency of the post-annealed PNZT films to have an orientation with the *c*-axis perpendicular to the film surface, the heat treatment procedure and thermally induced strains in the film-substrate structure has to be considered. PNZT films in Pt/PNZT/Pt/MgO capacitor structures were found to have a similar *c*-axis orientation in earlier studies.¹⁷ On the other hand, PNZT films in a corresponding capacitor structure on silicon substrate (Pt/PNZT/Pt/SiO₂/Si) were found to have an orientation with the *a*-axis perpendicular to the film surface, that is, parallel to the external electric field, and the *c*-axis lying parallel to the surface plane of the film.¹⁷ This is an example of the case in which the film orientation follows from the stress. The cooling run of a heat treatment procedure generates thermal stresses that are proportional to the integral

$$\sigma_{th} = \frac{E_f}{(1 - \nu_f)} \int_{T_{\text{high}}}^{T_{\text{low}}} (\alpha_s - \alpha_f) dT, \qquad (3)$$

where E_f , v_f , α_s , α_f , and T are the Young's modulus and Poisson ratio of the film, the linear thermal expansion coefficients of the substrate and film, and temperature, respectively. In the temperature range discussed here, the thermal expansion coefficients α are typically independent of temperature, and for the PNZT/MgO structure $\Delta \alpha = (\alpha_s - \alpha_f)$ $=6.7 \times 10^{-6} \circ C^{-1}$, which leads to a compressive stress, whereas for the PNZT/Si structure $\Delta \alpha = -1.5 \times 10^{-6} \circ \text{C}^{-1}$, leading to a tensile stress in the PNZT film.^{17,22-24} As discussed in the Introduction, the grain structure with shape and orientation minimizing the overall energy of the system most effectively will be favored, thus leading to the secondary grain growth of this specific subpopulation at the expense of the other grains. The strain energy minimization typically dominates over the surface energy minimization in the films with grain size much smaller than film thickness.⁹ Thus, it is now possible to conclude that in post-annealed PNZT films on MgO substrate, the c-axis orientation is most probably due to the compressive stress in the film, whereas on the silicon substrate, the a-axis orientation is present due to the tensile stress generated during heattreatment procedures. When the maximum temperature of the post-annealing process increases from 700 to 900 °C, not only an increased crystal growth producing larger grains in the film is expected, but the thermal stress also increases, causing a clear orientation of the PNZT film, as shown in Fig. 1.

From the FESEM micrographs in Fig. 3, it is evident that, in these post-annealed PNZT thin films, the growth of the columnar (001) oriented grains starts from the film surface and continues downward into the thin-film structure. The surface morphology of the films also improved considerably during the heat treatment, so that it appeared to be flatter than the surface of the as-deposited amorphous films. In addition to the strain energy minimization, the flattening of the film surface at higher post-annealing temperatures supports the idea that the strong orientation and columnar grain growth in the upper surface of the film is also related to the minimization of the energy of the depolarization field through the formation of domains in the film surface. The favored orientation of the domain configuration should also follow the structure shown in Fig. 3, with the longer side of the domains perpendicular to film surface, although there was no evidence of single domain grains in this study.²⁵ Wang et al.²⁶ have also shown in their theoretical studies that the formation of 180°-domain structure in c-axis oriented films is favored in order to minimize the surface and depolarization free energy. They considered c-axis oriented epitaxial or single-crystal films, for which internal stress was expected to be small and the effect of the depolarization field to be dominant. It is suggested that the compressive stress here also favors the minimization of the total free energy by domain formation. Thus, together with the effect of the depolarization field, the macroscopic compressive stress further promotes the discovered tendency for grain growth and surface flattening of PNZT films. If the films are annealed at higher temperatures, such as 900 °C, grain growth can be stagnated and grains reach through the film, and further coarsening of the grains typically leads to increased surface roughness.

V. CONCLUSIONS

Ferroelectric PNZT thin films were deposited on MgO(100) substrates without heating using pulsed laser deposition. Afterwards, the films were post-annealed at three different temperatures of 700, 800, and 900 °C. Grain structure and crystallite size distribution, together with the surface morphology of the films, were studied. PNZT films annealed at 700 °C had actually a nanosized equiaxial grain structure with a low amount of grain orientation and quite poor surface morphology. However, after annealing at higher temperatures, the films had a subpopulation of columnar grains with an orientation of the (001) crystal direction perpendicular to film surface. This columnar grain structure started to grow from the upper surface of the film and continued through the film when the annealing temperature increased. Surface morphology of the films also improved during annealing, so that the surface appeared to be flatter than that of the as-deposited amorphous PNZT films. The tetragonal distortion c/a was found to increase as annealing temperature increased, together with a strong increase in the intensity of (001) reflections. It was found from the crystallite-size distributions that the films have a portion of grains with diameters below the critical size, thus impairing the dielectric and ferroelectric polarization properties of the films. Two different reasons for the observed columnar grain structure with the *c*-axis orientation perpendicular to the film surface were proposed: (i) a large difference of the thermal expansion coefficients $\Delta \alpha$ between the film and substrate generates a compressive stress into the film which favors the orientation, and (ii) the structure is enhanced by the minimization of the ferroelectric depolarization energy at the film surface.

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