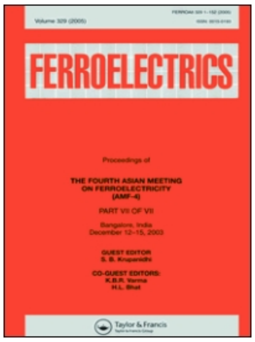

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GRAIN GROWTH AND ORIENTATION OF NANO-CRYSTALLINE LASER-DEPOSITED $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$ THIN FILMS

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Nd-modified PZT (PNZT, $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$) thin films were deposited using a pulsed XeCl-excimer laser on single-crystal MgO(100) substrates at room temperature. Samples were post-annealed at 700, 800, and 900 °C. X-ray diffraction (XRD), atomic force microscopy (AFM), and field-emission electron microscopy (FESEM) were used for the film structure characterization. With increasing annealing temperature from 700 to 900 °C, a film orientation with (00l) planes parallel to the film surface took place. The mean crystallite size increased from 210 to 330 Å, respectively. FESEM micrographs revealed large columnar grains growing downwards from the upper surface of the film.

Keywords: lead zirconate titanate, pulsed laser deposition, thin films

INTRODUCTION

A proper deposition of different functional materials like ferroelectric lead-zirconate-titanate (PZT, $Pb(Zr_xTi_{1-x})O_3$) thin films is very important for the fabrication, *e.g.*, of micro-electro-mechanical systems (MEMS), electro-optical devices, and solid-state transducers [1,2]. Several properties, such as dielectric and polarization responses, leakage conduction, and optical transmission and reflection, are influenced to a large extent by the grain growth and structure of the film [3]. PZT films, grown *in situ* on heated substrates, have usually a highly oriented columnar or epitaxial grain structure, and they possess good ferroelectric properties with remanent polarization $P_r \approx 40$ $\mu C/cm^2$ and relative dielectric constant $\varepsilon \approx 800$. In polycrystalline PZT films these properties are typically found in the range of $P_r \approx 20$ $\mu C/cm^2$ and $\varepsilon \approx 500$, respectively. On the other hand, polycrystalline PZT films have very high resisitivity with the values of $\rho \approx 10^{11}$-10^{12} Ωcm [4-6]. These properties are dependent on the microstructure of the films. In this paper we describe some effects of the post-annealing process on the PNZT thin-film structure.

EXPERIMENTAL

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 (12 mm × 5 mm × 0.5 mm). The deposition was carried out at room temperature at a base pressure of 6×10^{-5} mbar. The deposition distance was 30 mm. The laser-beam fluence was 2.0 J/cm^2 and a $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$ target with a density of 7.4×10^3 kg/m^3 was used. The post-annealing process of the films was carried out in a lead- rich atmosphere in order to prevent an excess loss of lead during annealing at temperatures of 700, 800 or 900 °C for 20 minutes at the maximum temperature [6]. Crystal structure and crystallite-size distribution of the PNZT films after annealing were studied by x-ray diffraction measurements. In order to study the crystallite-size distribution function x-ray diffraction experiments (URD-63 diffractometer, CuKα radiation, step-scanning technique) were performed on the strain-free samples. The Tikhonov's regularization procedure to Fourier x-ray profile analysis and a special computer program were applied for calculations of the crystallite-size distribution [7,8]. An instrumental broadening was obtained from a perfect standard specimen. Atomic force microscopy (Nanoscope II) and field-emission electron microscopy (Jeol JSM-6300F) were used to study the surface morphology, crystallite size and structure of PNZT films.

RESULTS AND DISCUSSION

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 is very similar to that measured from the target with random grain orientation. 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 from that of the PNZT film annealed at 700 °C. The increase is an indication of the orientation of grains with the <001> crystal direction perpendicular to the film surface in consequence of the increasing annealing temperature. The XRD pattern from the PNZT film annealed at 900 °C reveals that already 93 % 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 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 to the MPB [9].

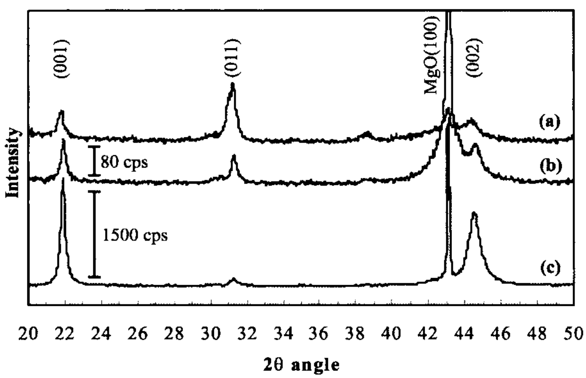

FIGURE 1. X-ray diffraction patterns (CuKα radiation) from three PNZT thin films deposited at a laser-beam fluence of 2.0 J/cm^2 and post-annealed at (a) 700, (b) 800, and (c) 900 °C. The thickness of the films was about 300 nm.

The volume-weighted crystallite-size distributions of the PNZT films in Fig.1 are shown in Fig.2. The maximum of the crystallite-size distribution shifted to higher values with increasing annealing temperature, and, furthermore, a 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 plenty of large crystallites (roughly ~80 % of the volume of the film) with size between 600 and 1300 Å. Three FESEM micrographs of PNZT thin-film cross sections are shown in Fig.3. The film annealed at 700 °C in Fig.3(a) has clearly a dense polycrystalline structure of small uniformly distributed grains (~25 nm measured from Fig.3(a)). A cross section of the PNZT film annealed at 800 °C in Fig.3(b) shows a double layer structure with large grains at the top of the film (~130 nm long, ~20-50 nm wide), and an underlying layer with a grain structure similar to that of the PNZT film annealed at 700 °C in Fig.3(a). The top layer of the film consisted of large columnar grains with the longer side perpendicular to the film surface, which is typical also for *in situ* deposited columnar thin films. The PNZT film in Fig.3(c) annealed at 900 °C has columnar grains reaching already through the whole film. There are, in fact, these columnar grains that are responsible for the increased intensities of the (001) and (002) reflections in Figs.1(b) and (c).

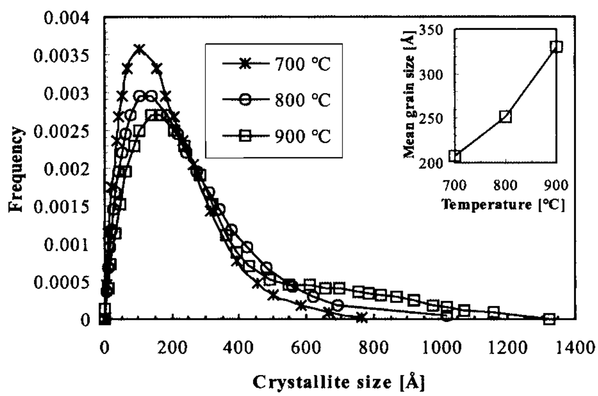

FIGURE 2. Volume-weighted crystallite-size distribution functions of the three PNZT thin films in Fig.1, annealed at 700, 800, and 900 °C, respectively. The increase of the mean grain size with increasing annealing temperature is also shown.

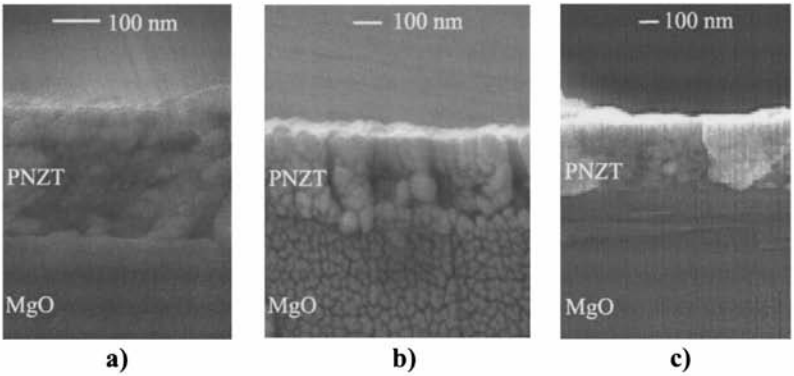

FIGURE 3. FESEM micrographs of cross sections of 300 nm-thick PNZT films annealed at (a) 700, (b) 800, and (c) 900 °C. (Grainy structure in figure (b) on very flat cross section of MgO substrate is due to the agglomeration of Au/Pd film necessary for FESEM. Obviously, this does not obscure the structure of the PNZT film.)

The changes in the grain structure and crystallite-size distribution with increasing post-annealing temperature were found also to affect strongly on the surface morphology of the films. The PNZT films annealed at 800 °C with the rms roughness R_q = 11.9 nm has better surface morphology than the film annealed at 700 °C with a value of R_q = 39.2 nm. The observed improvement in the surface morphology was confirmed by optical transmission and reflection measurements [10].

Two different phenomena both favoring the observed columnar grain structure with the *c-axis* orientation perpendicular to the film surface were proposed. First of all, a large difference of the thermal expansion coefficients, $\Delta\alpha$, between the PNZT film and MgO substrate generates a compressive stress into the film during the cooling period of the post-annealing cycle [6,11]. Secondly, the minimization of the ferroelectric depolarization energy at the film surface further enhances the effect [12].

As a consequence of the nanosized grain structure of the polycrystalline PNZT films, the ferroelectric and piezoelectric properties of the films are somewhat depressed due to decreased tetragonal distortion. On the other hand, in the polycrystalline PZT films, leakage conduction is very low compared to the epitaxial and highly oriented columnar films [8,9]. The low conduction clearly indicates the existence of numerous blocking grain boundaries typical for oxide ceramics, which decrease the leakage conduction. At such a grain boundary, an extra electric field and corresponding energy barrier generated by trapped surface charge has to be overcome by electrons in order to activate the corresponding conduction mechanism and, thus, the leakage current is reduced.

CONCLUSIONS

Ferroelectric PNZT thin films were deposited on the MgO(100) substrate without heating using pulsed laser deposition. Afterwards, the films were post-annealed at three different temperatures of 700, 800, and 900 °C. The films annealed at 700 °C had a nanograin structure with low amount of grain orientation and quite poor surface morphology. The films annealed at higher temperatures had an increased columnar grain structure with an orientation of the <001> crystal direction perpendicular to the film surface. This columnar structure started to grow from the upper surface of the film and continued through the film when the annealing temperature increased. The tetragonal distortion *c/a* and the intensity of the (00l) reflection were found to increase with increasing annealing temperature.

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