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Characterization of PZT films prepared using pulsed laser ablation with a magnetic field

J. Frantti, H. Moilanen, S. Leppävuori and J. Vaara

Microelectronics and Material Physics Laboratories, University of Oulu,
P.O. Box 400, FIN-90571 Oulu, Finland

A static magnetic field has been used to concentrate the plasma generated during the laser ablation deposition process. The main purpose in using the field was to investigate the composition and the thickness distribution of a PZT film.

The field was induced by permanent magnets (B ≈0,5 T) situated inside the ablation chamber. The plasma ions were moved by the magnetic field on to the substrate. PZT films were deposited on sapphire substrates using a XeCl-excimer laser (pulse energy ≈50mJ and wavelength 308nm, fluence ≈0.8J/cm^2).

Neodymium doped PZT films were characterised by Raman spectroscopy, EDS and XRD. Raman and EDS spectra were measured as a function of position on the substrate. According to EDS analysis the composition of the ablated film differed from that of the target and there was significant thickness variation as a function of the position on the substrate. Measuring the thickness and composition of the film it was possible to calculate distributions of the different species of PZT films without and with the magnetic field. Measured Raman spectra were typical of PZT throughout the substrate.

1. INTRODUCTION

Lead zirconate titanate (PZT) materials are widely used with various titananium-zirconium ratios in ferro-, pyro- and piezoelectric applications. In our experiments the composition of the Nd-doped PZT was $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$, which is a composition having high piezoelectrical coefficients and almost equal amount of tetragonal and rhombohedral phases [1,2]. There is no clear morphological boundary between these two phases at that composition because of the very fine particle size [3]. Laser ablation is a suitable method for producing stoichiometric dense ferroelectric PZT films when the fluence is correct for the used target-substrate distance. It has been find out that too high laser beam fluence causes lead deficiency, probably partly due to a resputtering process on the ablated film [4]. In this work the distributions of elements of PZT film have been calculated by measuring the thickness and composition of the films. The effect of a static magnetic field to these distributions has been analysed.

2. EXPERIMENTAL

Laser ablation was carried out using an XeCl excimer laser with pulse energy ≈50mJ and fluence ≈ 0.8 J/cm^2 with pulse repetition rate 25 Hz. A fluence of ≈0.8 J/cm^2 was found to be suitable for producing stoichiometric PZT thin films with target-substrate distance 32±1 mm after annealing at a temperature of 750°C. The target and 1"x1" single crystal sapphire substrates were situated in the static magnetic field, which was generated using a u-shaped permanent magnet. The laser beam was focused on to the rotating target by a quartz lense situated outside the ablation chamber. The angle between the laser beam and the normal of the surface of the target was 9.5° as shown in Figure 1. Ablation was carried out using two direction of the magnetic field, which were opposite to each other and parallel to the substrate. The pressure during the laser ablation was ≈5x10^{-5}mbar. An ablation geometry is shown in Figure 1.

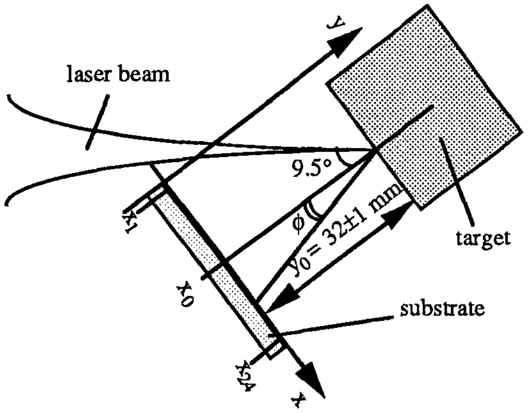

Figure 1. Schematic picture of the ablation geometry. A static magnetic field (B ≈0.5T) is perpendicular to the plane of the paper.

3. THEORETICAL CONSIDERATION

In the pulsed laser ablation process short time (in these experiments the pulse duration was ≈20ns) high energy pulses heat the surface of the target typically to a temperature of several thousand Kelvins. It is possible to estimate the temperature on the surface using heat flow equations and after that estimate the amount of ionized particles by Langmuir-Saha equation [5]. In this work the ablation geometry was measured carefully and the thickness and the composition of the films were measured (before annealing) as a function of position on the substrate using EDS system. A special thin film calculation program TFOS/FLS was used to carry out ZAF and film thickness calculations [6]. The amount of lead, titanium and zirconium was measured as a function of position on the substrate. Estimation of the distributions is based on equations 1-3 showed below. Equation 1 determines the distribution profile of the form $\cos^n\phi$ [7,8] in the case of Figure 1.

$$\sigma(x) = A\cos^n\phi = A\left[1+\left(\frac{x_0-x}{y_0}\right)^2\right]^{-n/2} \quad (1)$$

The total distribution $\sigma^k(x)$ of k:th species which here are atoms of lead, titanium or zirconium, and $\sigma^k{}_{ion}(x)$ and $\sigma^k{}_{neutral}(x)$ are respectively the distribution of the k:th species caused originally by ions and neutral particles is

$$\sigma^k(x) = \sigma^k_{ion}(x)+\sigma^k_{neutral}(x) \quad (2)$$

A neutral distribution is symmetric

$$\sigma^k_{neutral}(x_0-x) = \sigma^k_{neutral}(x_0+x) \quad (3)$$

By measuring film composition and thickness with and without a magnetic field it is possible to calculate empirical discrete distribution of the ions and neutral particles. It should be noted that the equations are only approximate, because the calculus is based on the assumption that ions are moving in a static, homogeneous magnetic field independently from other particles and that most of the ions have a charge of one Coulomb.

4. RESULTS AND DISCUSSION

For the case where B =0 the measured and calculated distribution of lead, zirconium and titanium are shown in Figure 2a, b and c, respectively. Theoretical distribution was achieved determining parameters A, x_0 and n in the equation (1) in such a way so that the calculated distribution correlates with the measured values.

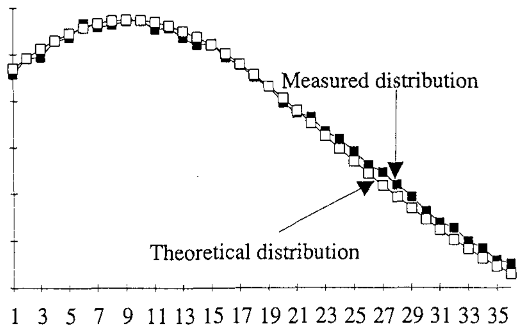

Figure 2a. The measured and calculated distribution of lead when the field is zero. The vertical scale is in arbitrary units. The horizontal scale is 1.06 mm/div. n =4.6.

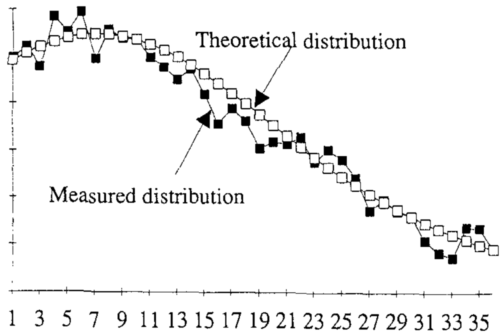

Figure 2b. The measured and calculated distribution of zirconium when the field is zero. The vertical scale is in arbitrary units. The horizontal scale is 1.06 mm/div. n =6.

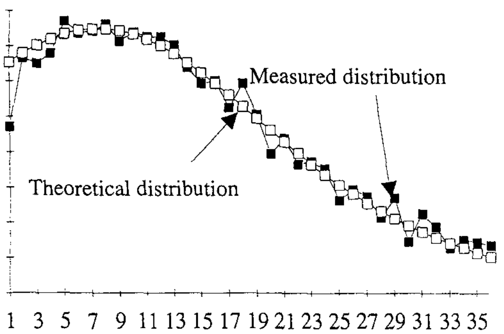

Figure 2c. The measured and calculated distribution of titanium when the field is zero. The vertical scale is in arbitrary units. The horizontal scale is 1.06 mm/div. n =6.8.

For the case of B =0 the measured and calculated distributions correspond correctly. In the case of a magnetic field the distributions were not of the form of the equation (3).

A clear thickness and slight composition variation on the substrates was found. Figures 3a and 3b show amounts of lead, titanium and zirconium as a function of position with two opposite directions of the magnetic field (when the angle between target and laser beam was 9.5°). In case (a) the field guides the ions in the direction of positive x-axis and in case (b) the field guides ions in the direction of negative x-axis of Figure 1. It was found that before the annealing procedure there was lead excess, which was evaporated during annealing procedure.

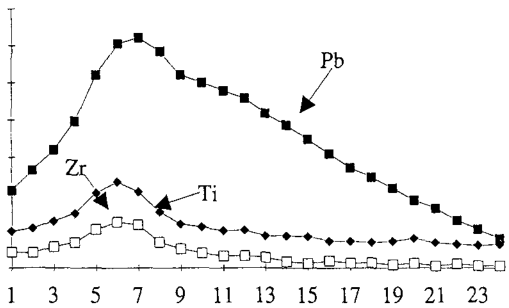

Figure 3a. Amount of lead, zirconium and titanium as a function of position on the substrate. The vertical scale is in arbitrary units. The horizontal scale is 1.06 mm/div. Magnetic field guides particles to the direction of the positive x-axis.

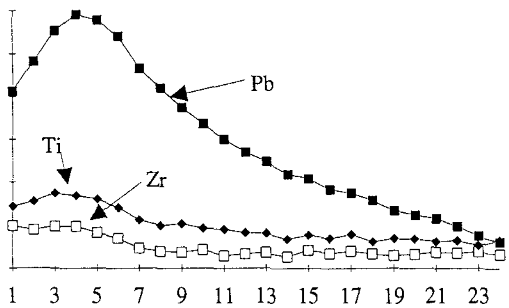

Figure 3b. Amount of lead, zirconium and titanium as a function of position on the substrate. The vertical scale is in arbitrary units. The horizontal scale is 1.06 mm/div. Magnetic field guides particles to the direction of the negative x-axis.

Also Raman and XRD spectra were measured as a function of position, but nothing special was found and spectra were typical to PZT throughout the substrate. That was mainly because during annealing (750°C, 2 hours) the extra amount of lead was lost and the compostion of the film was homogeneous after annealing treatment. Both XRD and Raman techniques are quite insensitive to sligth composition variation of the film.

Generally used the thin film calculus program of EDS seems to give sometimes uncorrect values of composition. During annealing the composition of the ablated film is changing drastically, if there was before heat treatment an excess of lead. It was found, that the composition of the thin PZT films with excess lead were stoichiometric after annealing. Also unhomogeneouties of the magnetic field that is concentrating the plasma is making error to the results.

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