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TEM study of PZT crystallization behaviour in multilayer heterostructures

O. Zhigalina[1], D. Khmelenin[1], K. Vorotilov[2], A. Sigov[2], I. Lebo[2]

[1] Shubnikov Institute of Crystallography, Electron microscopy, Leninskiy prospekt 59, 119333 Moscow, Russia, Russian Federation
[2]Moscow State Technical University of Radioengineering, Electronics and Automation, Vernadskiy prospekt 78, 119454 Moscow, Russia, Russian Federation

zhigal@ns.crys.ras.ru
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Thin PZT ($PbZr_{0.53}Ti_{0.47}O_3$) films are one of the prominent materials for ferroelectric random access memory (FRAM), MEMS and other integrated ferroelectric devices [1, 2]. Chemical solution deposition (including sol-gel techniques) is widely used for formation of multicomponent thin film oxides due to good stoichiometric control and a relatively low temperature of oxide phase formation [3, 4]. The main strategy of the annealing procedure during the formation of ferroelectric film is to achieve an optimal crystalline structure at the minimum temperature of the heat treatment. Laser annealing has a number of advantages and can effectively influence the crystallization of multilayer heterostructures based on ferroelectric films [5,6].

In this work we have investigated and tried to compare PZT crystallization processes after traditional isothermal heat threatments at different temperatures and laser annealing.

Films 100—150 nm thick were deposited on Si— $Si0_2$(300 nm)—TiO_2(10 nm)—Pt(100 nm) wafers 100 mm in diameter by the chemical solution deposition method. After deposition of five layers the films were annealed at 550, 600, 650, 700, 750 and 900°C for 20 min. The PZT film thickness was about 160 nm. Laser annealing was performed using a KrF-excimer laser emitting light at the wavelength of λ=248nm. The pulse energies and the number of pulses within one crystallization process were varied over a range of 0.18-0.35 J/cm^2 and 100-500 pulses.

The study of film structure, phase and element composition was performed by TEM (FEI Tecnai G^2 30ST, equipped by HAADF STEM detector and EDX spectrometer, at accelerating voltage of 300 kV) and X-Ray diffraction.

Perovskite grain nucleation in PZT films occurs at about 550 °C: rounded (111) grains grow on the platinum surface with the same (111) orientation in this case. The height of perovskite grains comprises a half of the films thickness. Disordered perovskite grains (to the order of smaller size) and pyrochlore grains (2 ...15 nm) are formed in the bulk of the film as well. At annealing temperature of 600 °C the perovskite grains grow through the whole films thickness, the amount of pyrochlore phase is significantly reduced and practically disappears when the annealing temperature increases to 700 °C. At the same time the amount of (100) oriented perovskite grains increases and dominates over (111) oriented ones after annealing at 900 °C. The reason is the activation of diffusion processes in the layers of the heterostructure that leads in particular to the formation of TiO_2 inclusions on the Pt surface.

In the case of laser annealing it has been found that, in contrast to isothermal annealing, where nucleation on the platinum layer dominates, crystallization and the growth of spherical perovskite crystals occur in the film bulk. The perovskite phase crystals' size increases from 10 to 120 nm with increasing laser beam energy (Figure 1a-d).

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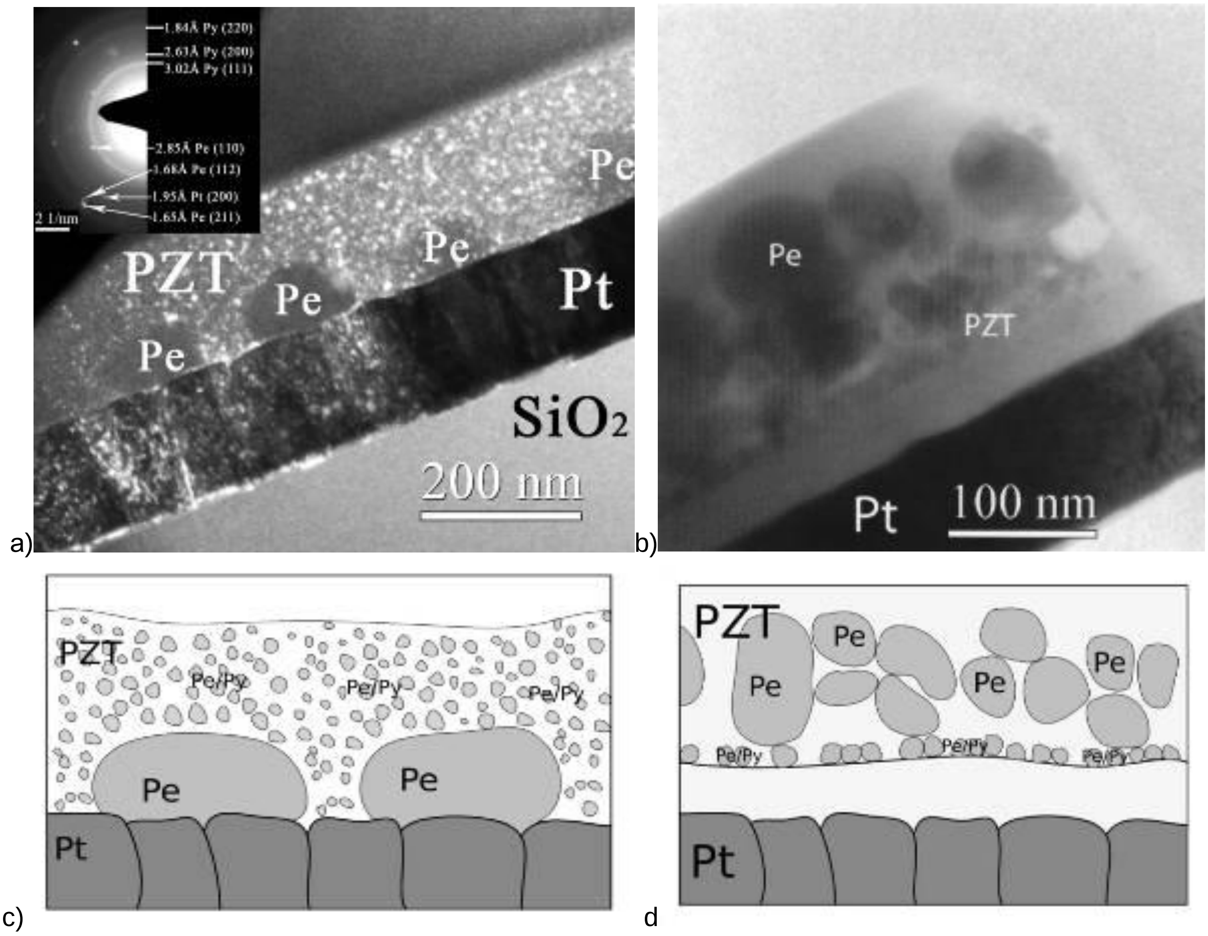

Figure 1. Cross sectional view of PZT/Pt/TiO_2/SiO_2/Si heterostructures:
a) dark field image and corresponding SAED pattern (crystallization at 550 °C),
b) bright field image (laser annealing with the energy preposition of 0.35 J/cm^2)
c), d) corresponding schemes of TEM images a), b).