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PZT FILMS PREPARED BY TVA AND PLD FROM PbO_2 :TiO_2 : ZrO_2 (1:1:1) NANOCERAMIC TARGETS

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Lead zirconate titanate (PZT) thin films on Si single crystal were prepared by two techniques: a) thermionic vacuum arc (TVA) and b) pulsed laser deposition (PLD), using ceramic targets made of PbO_2, ZrO_2 and TiO_2 nanopowders. Structural characterisation of the samples by XRD, EDS and micro-Raman spectroscopy reveals combinations of PZT and its constituent oxides resulting from either experiment. Morphology studies carried out by SEM and AFM remark a smoother surface for the PLD films than for the TVA ones. A comparison between the ablated and the raw zones of the PLD target leads to the conclusion that the laser-ceramic interaction eases the PZT synthesis.

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1. Introduction

Lead zirconate titanate (PZT) has attracted much attention due to its excellent ferroelectric, piezoelectric, dielectric and pyroelectric properties [1, 2]. In the form of thin/thick films PZT finds a wide range of applications in non-volatile random access memories [3], piezoelectric micro-sensors [4, 5] and intergraded capacitors [6, 7]. A wide range of methods is being used to fabricate PZT films, such as chemical vapour deposition (CVD) [8], pulsed laser deposition (PLD) [9-11], sputtering [12], metal organic decomposition (MOD) [13] and sol–gel [14]. The PZT films studied in this work were prepared from composite targets by two alternative ways: a) the thermionic vacuum arc deposition (TVA) [15] and b) the PLD technique, with the aim to understand the mechanisms involved in the deposition processes of PZT and thus to provide a comparison and eventually a selection criterion for the most appropriate technique between TVA and PLD. Structural characterisation through XRD, EDS and micro-Raman spectroscopy measurements has been done on the films and their originating targets. Morphology studies resulted from SEM and AFM investigations.

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2. Experimental details

2.1 Targets preparation

Identical targets were used with both TVA and PLD deposition techniques. The targets were prepared from high purity (99.9%) oxide powders PbO_2, TiO_2 and ZrO_2 in stoichiometric amounts 1:1:1. The powders were mixed in methanol and milled at high energy for 4h. The resulted blend was stirred dry and then annealed to 900^{o}C for 4h in air. A new milling step followed for 6h and the resulted nanopowders were pressed in pellets at 60MPa and annealed to 1250^{O}C for 6h in sealed ampoules. A final polish was given to the surfaces of the pellets.

2.2 Film deposition

2.2.1 TVA technique

The TVA set-up is shown in the Fig.1. A detailed description of the technique is given elsewhere [15]. The cathode, anode and substrate are set in a stainless steel reaction chamber. The Si substrate-TVA gun distance was 300mm and the substrate temperature was 450^{o}C in all experiments. To achieve a stable discharge during the PZT deposition processes the following parameter values were used: I_{arc} = 1.3A and U_{arc} = 400V. The process evolved in vacuum (3×10^{-6} Torr at the start of the experiment). A quartz oscillator has been used to control the thickness of the film during deposition. The 100nm films thus obtained were removed from the chamber 120min after the deposition, when their temperature reached at room temperature.

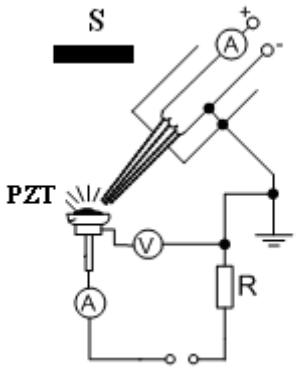


Fig. 1. The experimental set-up containing the tungsten filament, PZT anode, and substrates S.

2.2.2 PLD technique

Widely used with various materials, PLD is described in detail in many papers [9-11]. We employed a common PLD set-up to run the PZT deposition. The films were deposited on Si substrates held at 450 °C, using the third harmonics of a Nd:YAG laser (EKSPLA model NL301) λ=355 nm, τ= 5 nsec/pulse at a repetition rate of 10 Hz. The number of pulses on each sample was 135.000, at a fluence of 2 J/cm^2. The preliminary pressure in the chamber was 4×10^{-5} Torr and the oxygen pressure during the deposition was 130 mTorr. The thickness of the films was 100 nm as calculated from the ablation threshold and the number of pulses delivered on each run.

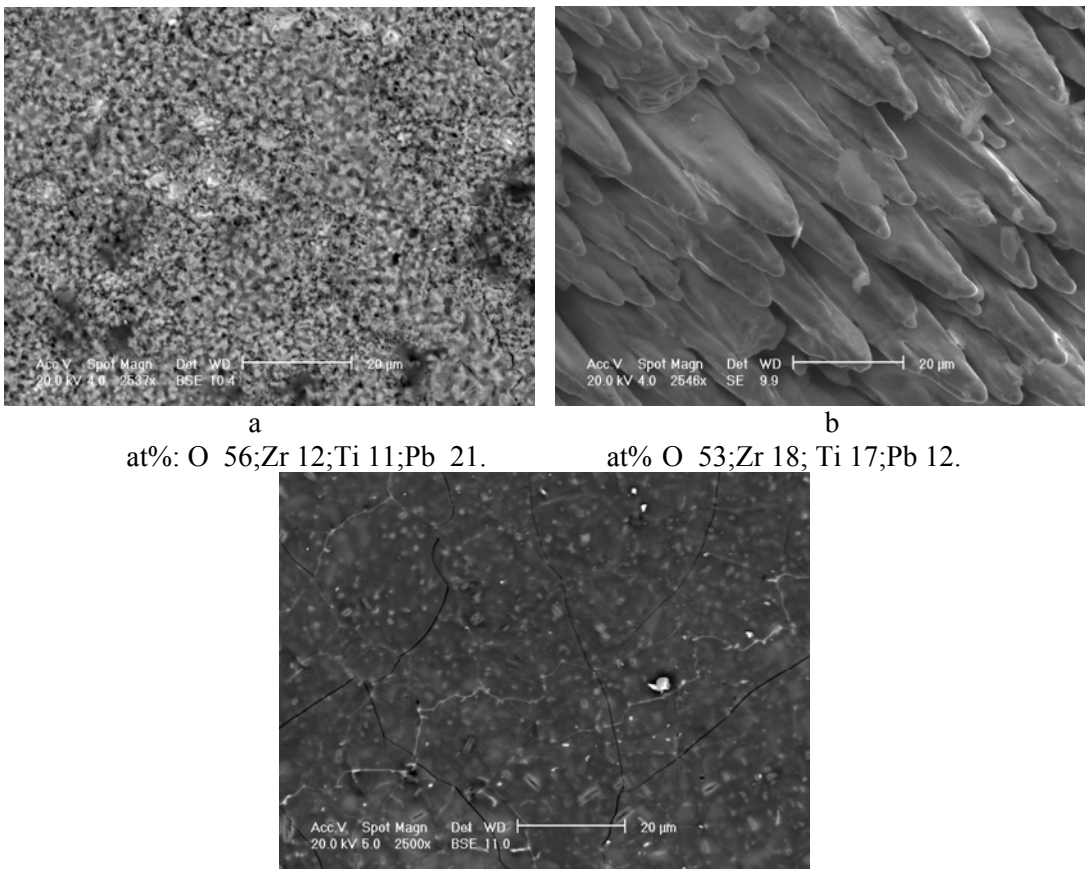
2.3 Characterisation

Targets before TVA evaporation/ laser ablation as well as following the deposition processes were investigated for morphology and structural properties by SEM, EDS and Raman

spectroscopy. The SEM-EDS investigations were performed with a PHILIPS ESEM 30 microscope. The films were characterised by XRD, AFM and Raman spectroscopy. XRD measurements were performed at grazing incidence on all films using the CuK_α radiation (λ =1,5421A^o) of a Szimadzu 6000 X-ray diffractometer. The unpolarised Raman spectra were taken at room temperature with a LABRAM HR 800 micro-Raman spectrometer (Horiba Scientific) in the backscattering geometry using a 632nm laser source (1μm diameter of the spot) in the range 130cm^{-1} to 900cm^{-1}. The resolution of the spectra was 0.5cm^{-1}.

3. Results and discussion

In Fig.2 the morphology of the targets' fresh surface (a), laser ablated surface (b) and TVA evaporated (c) can be observed along with the respective EDS analysis. The concentrations (at. %) were normalized to oxygen.



a

at%: O 56;Zr 12;Ti 11;Pb 21.

b

at% O 53;Zr 18; Ti 17;Pb 12.

c

at% O 62; Zr 17; Ti 15; Pb 6.

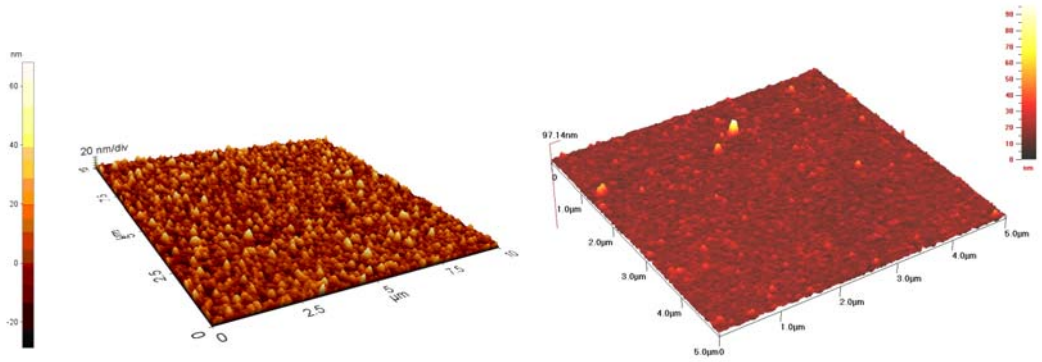
Fig. 2. SEM images of (a) fresh PZT target, (b) laser ablated region of the target and (c) TVA evaporated target. The corresponding EDS analyses over 100μm X 100μm surfaces on each target are displayed, with the concentrations of the elements normalized to oxygen.

The reduced concentration of Pb in the evaporated/ablated targets in comparison with the raw material is normal, knowing that the boiling point of led is quite low. The remaining amount of Pb has contributed to the PZT synthesis, as it will be shown below.

In Fig. 3 the AFM images of two films deposited by TVA (a) and PLD (b) are shown. The higher roughness of the TVA film is easily observed. Still, we suggest droplets arisen on the surface of the PLD film mainly cause the roughness. The grain size of the material is also in close relation with smoothness of the films' surfaces. The XRD patterns (not shown here) correspond to

a mixture of PZT perovskite phase with a clear (110) peak and crystallites of the targets' component oxides.

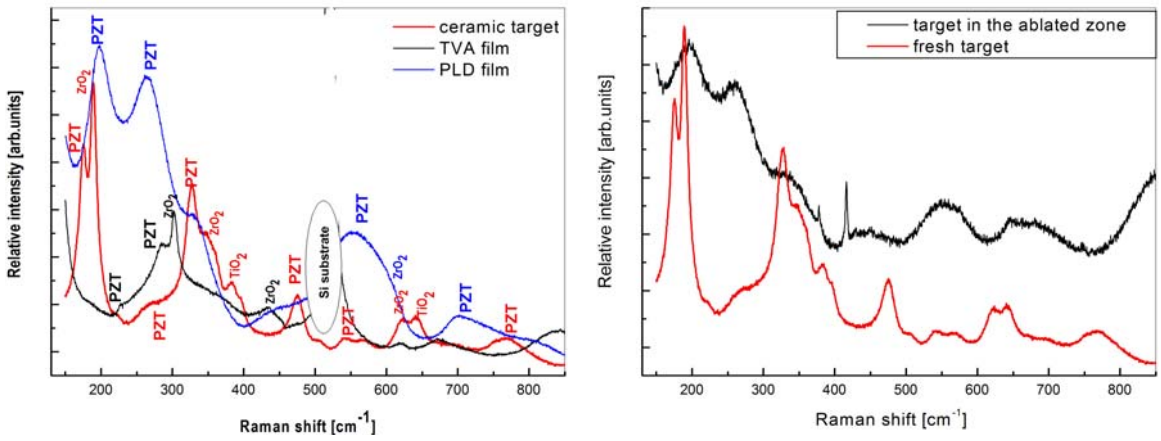
The average crystallite size was calculated from the (110) peak through the Debye-Sherrer formula [16, 17] for films deposited by either techniques and resulted in 20 nm for the PLD samples and 40nm for the TVA ones.



a b

Fig. 3. AFM images of PZT films deposited on Si by (a) PLD and (b) TVA. It is to remark the smoother surface of the PLD film.

The difference between the grain sizes in the films deposited by the two techniques is also obvious from the shapes of the Raman lines. The Raman spectra of the fresh target, TVA and PLD films respectively are shown in fig. 4a and in fig. 4b, the Raman spectra of the fresh target and its ablated region are compared. The Raman lines in fig.4a were identified after curves deconvolution and fit with Lorentz-Gauss functions.



a b

Fig. 4 a) Raman spectra of fresh target, PLD and TVA films. The colours of the Raman lines corresponding to PZT and component oxides are irrespective to the curves' colours b) Comparison between the Raman spectra on the ablated zone of the target and on its fresh surface.

It is obvious that both deposition techniques resulted in films with high PZT contents [18]. However, a shift of the lines toward higher frequency is noticed. This is a consequence of the increase of the force constants owing to the volume contraction within the nanoparticles. Thus, in the TVA samples where the nanoparticle size is larger than in PLD films the Raman shift is slightly greater [19]. The absence of Pb oxides lines in the spectra of fresh targets along with the presence of most PZT lines, ZrO_2 and TiO_2 lines makes witness of an insufficient PbO_2 excess at the target preparation. This affirmation is also supported through the EDS analysis of the raw, evaporated and ablated targets. Raman measurements carried out in the ablated zone of the target

(see fig. 2 b) revealed an interesting effect of the laser-ceramic target interaction as shown in fig.4b: it appears that the ablation process significantly advances the PZT synthesis. Therefore, we believe that an ideal way to obtain homogeneous PZT films would be to prepare ceramic targets from PbO_2, ZrO_2 and TiO_2 nanopowders and laser - anneal them before any deposition process.

4. Conclusions

Films with an average thickness of 100nm were deposited by TVA and PLD techniques on Si substrates held at 450^{o}C, from ceramic targets made of PbO_2, ZrO_2 and TiO_2 nanopowders mixed in stoichiometric amounts 1:1:1. Raman spectroscopy measurements revealed a high content of PZT in samples deposited by either way although lines of ZrO_2 are also present. From XRD measurements crystallites as large as 40nm are found in the TVA films, whereas in the PLD ones the average size touches 20nm. This results in smoother surfaces of the PLD films, although droplets in small amounts can still be observed. The ablation process significantly improves the PZT synthesis at the target's surface. Therefore, we propose ceramic targets to be prepared from PbO_2, ZrO_2 and TiO_2 nanopowders and laser - annealed before any deposition process. A larger excess of led oxide than in this work should be foreseen for the mixture.

Acknowledgments

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