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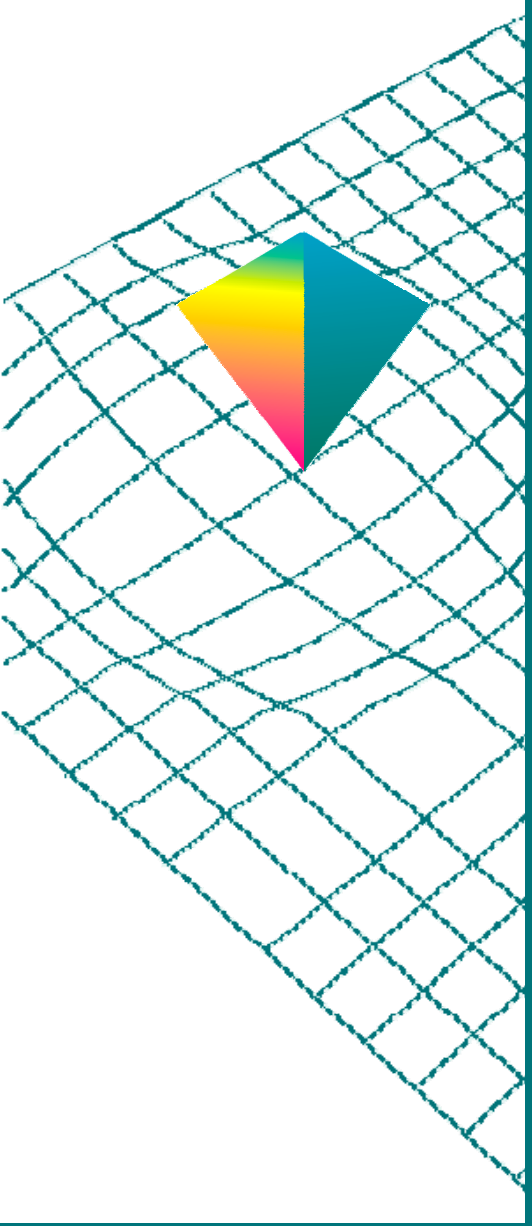

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50. Internationales Wissenschaftliches Kolloquium
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MICRO AND NANO FILMS OBTAINED BY MSD AND PLD FROM GLASS AND GLASSCERAMIC MATERIALS

Abstract

Thin films can be obtain by sol-gel and pulsed laser deposition PLD, magnetron sputtering deposition (radio frequency) MSD and vapor deposition methods.

The targets were obtained as vitreous and crystallized materials. For glass materials the melting and cooling techniques were used. $BaCO_3$, B_2O_3 and TiO_2 rutil were mix and melt at 1200°C for 2 hours in platin crucibles. Differential thermal analyze and x-ray diffraction were used for glass characterization.

Crystallized materials were obtained by thermal treatments. Were obtained $BaTiO_3$ and other barium polititanates.

The layers were obtained by pulsed laser deposition and magnetron sputtering deposition. Atomic Force Microscopy Optic digital and Electron microscopy were used to characterize the micro and nano films.

Introduction

Glass and glass ceramics were obtained in the BaO-TiO_2-B_2O_3 system [1] using up to 50 mol% more B_2O_3. $BaTi(BO_3)_2$ ternary compound was identified and the fact that TiO_2 in high quantities may occupy network positions [2]. Millet, J. and coworkers [3] also mentioned a ternary

compound $Ba_2Ti_2B_2O_9$. Compositions with less then 40mol% TiO_2 and more then 20mol% B_2O_3, were studied and with more then 50mol% TiO_2 and 5-40mol% B_2O_3 [4] too. Glass ceramic materials were obtained by controlled thermal treatment in which BaTiO3 was identified [5]. Ferroelectric nanostructures were obtained by pulsed laser [6] deposition using a BaTiO3 target. The switching properties of dense $BaTiO_3$ ceramics with 50 nm average grain size [7] were investigated at local scale by piezoresponse force microscopy. It results that 50 nm $BaTiO_3$ ceramics retain ferroelectricity at a local scale. Columnar and highly oriented (100) BaTiO3 and SrTiO3 thin films were prepared by a chelate-type chemical solution deposition (CSD) process [8] by manipulation of film deposition conditions and seeded growth techniques on LaAlO3. It has been illustrated that grain size and orientation of the perovskite films can be manipulated by changes in precursor chemistry. The misfit relaxation mechanism of $BaTiO_3$ thin films of different thicknesses grown two-dimensionally on $SrTiO_3$(100) substrates by pulsed laser deposition was analysed using X-ray diffraction and transmission electron microscopy[9]. Iron-doped BaTiO 3 composite thin films were fabricated by pulsed-laser deposition from pure metallic Fe and ceramic BaTiO 3 targets [10]. $BaTiO_3$ target of 50 mm diameter were obtained by press/ sinterization and hot press as presented in micrographs figure 1 a and b. The films showed that the tetragonal phase disappeared at thickness less then 55 nm [11]. Dense $BaTiO_3$ ceramics consisting of submicrometer grains were prepared using the spark plasma sintering (SPS) method. Hydrothermally prepared $BaTiO_3$ (0.1 and 0.5 μm) was used as starting powders [12]. Conditions for thin film growth by PLD [13] were the following: HrF excimer laser, λ=248nm, energy density:1.5-2J/cm^2, background pressure; 10^{-7}Torr, O_2 presure: 100m Torr, deposition rate 0.5-1.5 Å/s. The tetragonal-orthorhombic-rhombohedral phase transitions, characteristic of bulk BaTiO3, are completely absent in the epitaxial films due to the presence of tensile strain.

2 Experiments

2.1 Target preparation

Vitreous materials were obtained by melting at 1200°C for 2 hours. Composition was the following 40mol%B_2O_3 35 mol%TiO_2 and 25mil % BaO from p.a. reagents.

The materials obtained by melting were used as target for PLD and MSD. They were analyzed by DTA and x-ray diffraction. Results are presented in table1.

Table 1. Specific temperatures obtained by Differential Thermal Analyze (using a MOM device) for samples obtained by different ways (cooled on metallic plate* / ultra fast quenching**

Code sample	Transformation temp. Tg ^{O}C	Loss weight %	Exothermal ^{O}C	Endothermic ^{O}C
B4*	536	0	694; 884; 946	984
B4**	561,0	-0,1	672,7; 683,2	947,4; 991,4; 1008,8; 1033,4

The vitreous materials were crystallized in bulk [15] at different temperatures for 2 hours in an electric fournace with controller. The material was opac, cream to yellow. The XRD analised put into evidence the presence of titante cristaline phases as presented in fig 1, 2 and table 2.

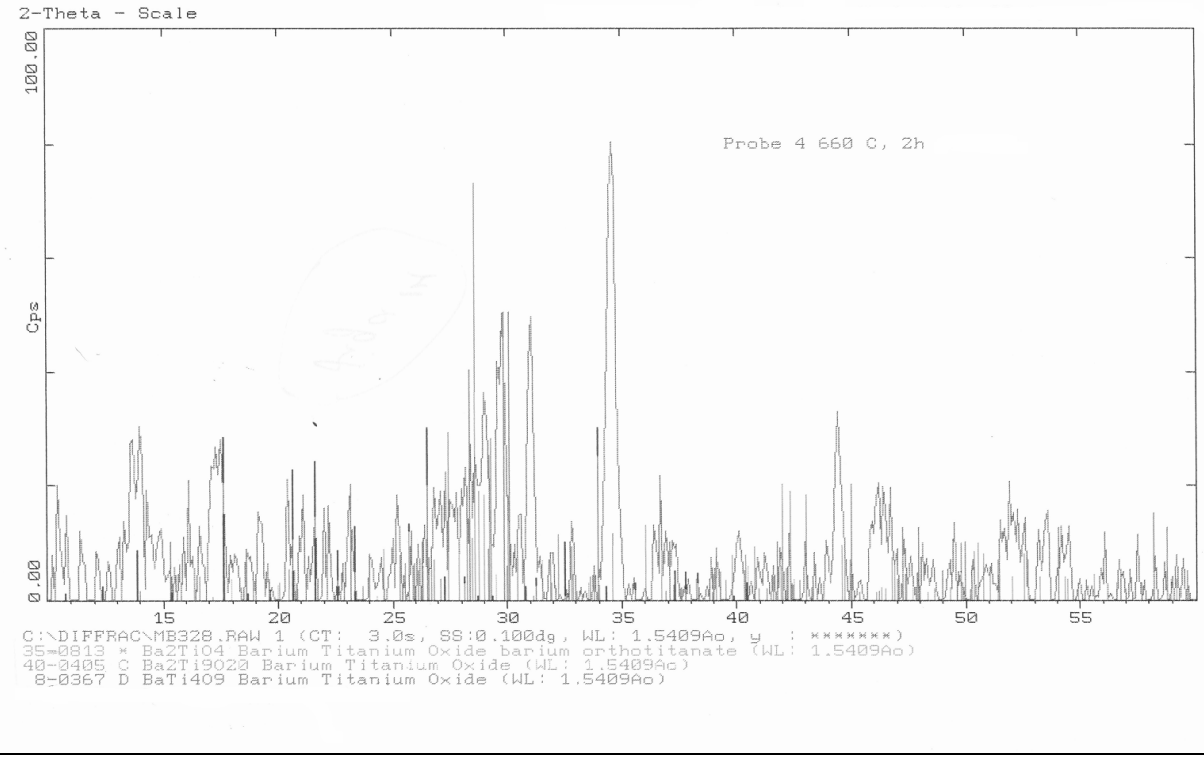


Fig 1 XRD of sample 4 treated at 660°C for 2 h (analized in TUI)

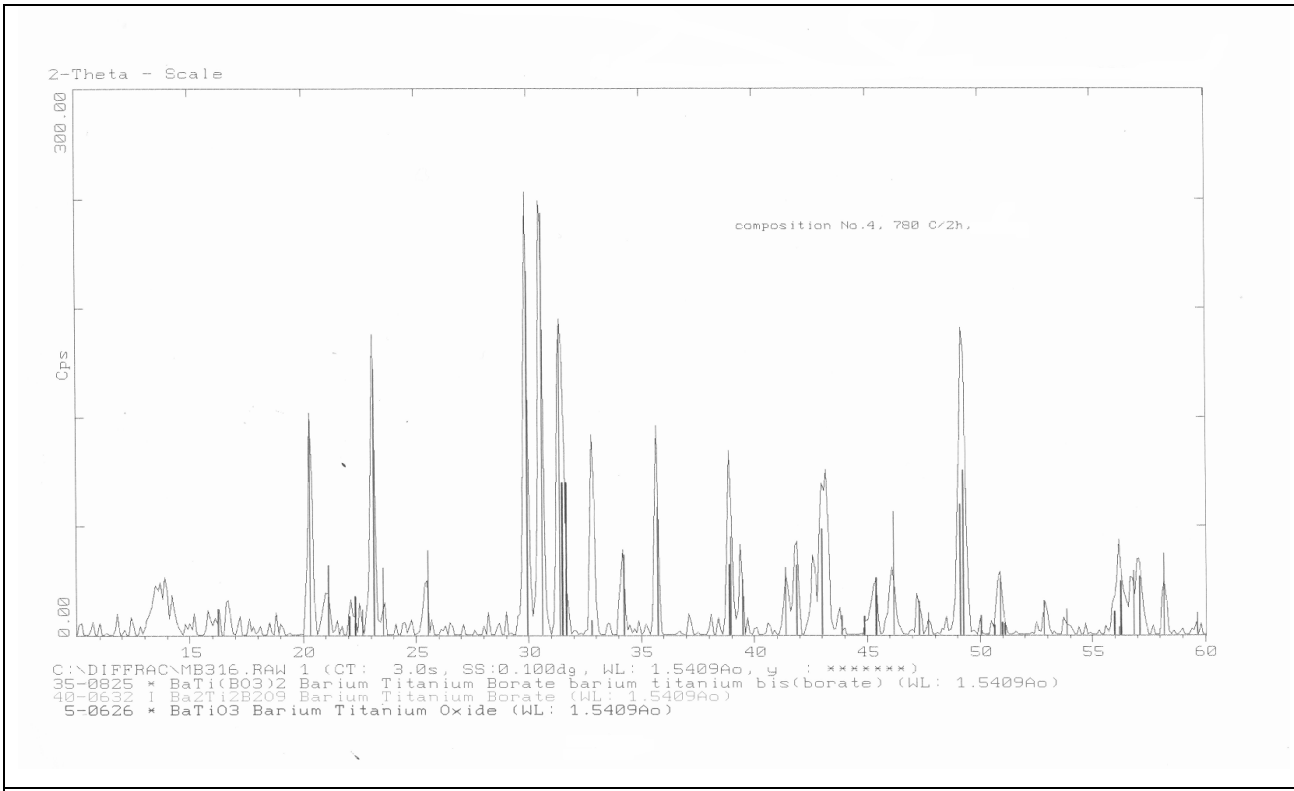


Fig 2 XRD of sample 4 treated at 780°C for 2 h (analized in TUI)

Table 2 XRD results

Cod sample	Crystalization temp. ^{O}C	coloure	Crystaline Compound
4	660	crem	Ba_2TiO_4 , $Ba_2Ti_9O_{20,}$ $BaTi_4O_9$
4	690	crem	$Ba_2Ti_2B_2O_9$, Ba_2TiO_4, $BaTi_4O_9$, BaO Ti $(BO_3)_2$
4	780	crem	BaO Ti $(BO_3)_{2,}$ $Ba_2Ti_2B_2O_9$, $BaTiO_3$
4	800	yellow	2BaO $2TiO_2$ B_2O_3; BaO TiO_2 B_2O_3

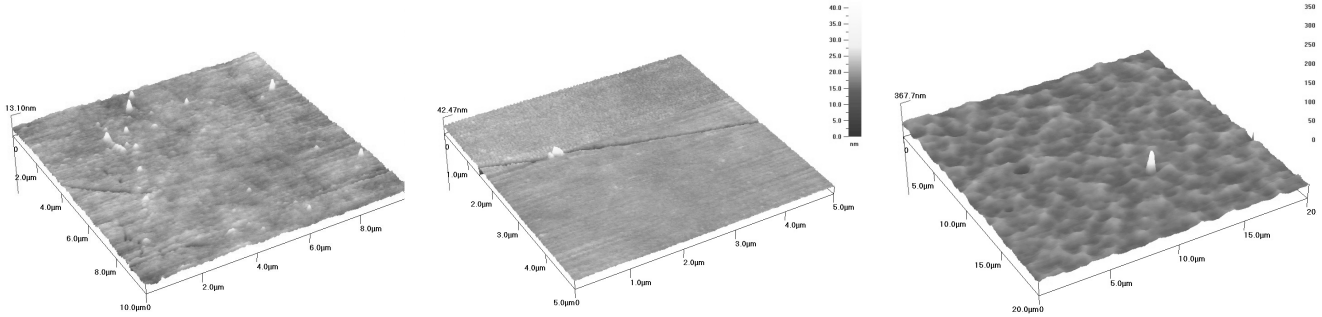
2.2. Thin film preparation

Films were obtained by MSD and PLD techniques. Were used MSD (radio frequency assisted magnetron sputtering deposition equipment) type Varian ER3119. The working pressure was 3 x 10^{-5}torr -5 x 10^{-5}torr in Ar atmosphere (30 s.c.cm) and the evaporation rate used was 0.3 Å/s -0.4 Å/s. The distance target and source was 10cm±0.2cm. Substrates were Si (type p for electronics)

and quartz glass polished laser quality. For PLD the evaporation rate was 0.7-1.1 Å/s and energy pulse 300mJ/ns.

3. Results

The films thickness and aspects were different function of substrate and time of deposition. AFM was used to characterize the quality of substrates and deposited films. In case of MSD the thickness was up to 370nm on Si and the films smooth. AFM of films obtained by MSD and PLD on Si and Q substrate are presented in fig 3-4. After PLD the films were more rogues and thick up to 6900nm on Si the uniformity can not be controlled.



substrate Si MSD after 10 min MSD after 40 min

PLD Si after 10 min

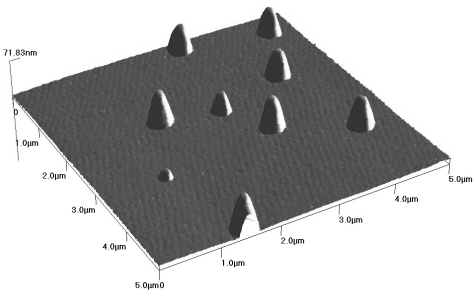
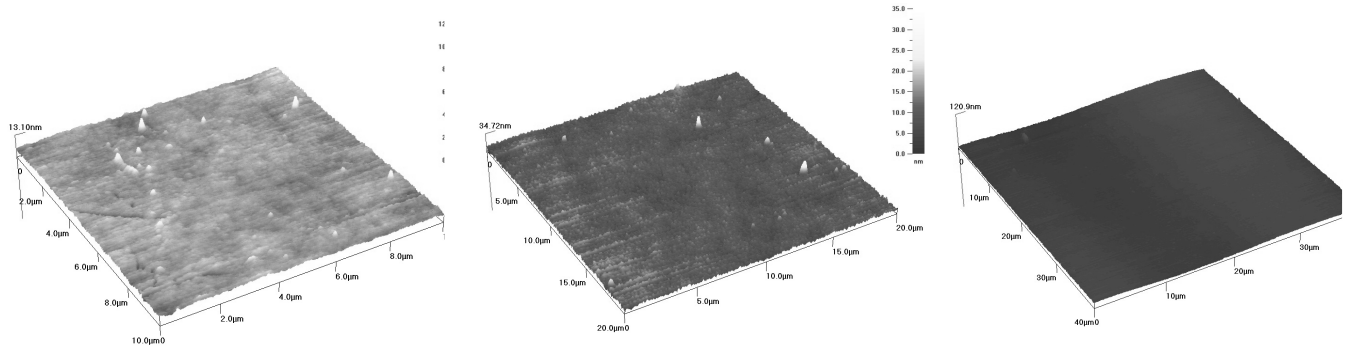
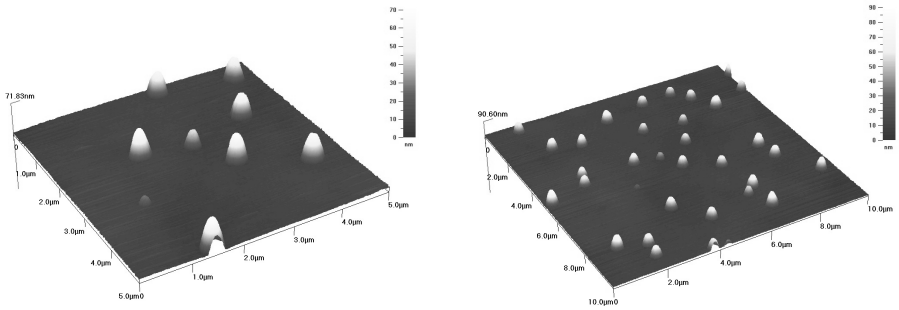


Fig 3 AFM of films obtain at different deposition time by MSD and PLD on Si substrate

AFM of films obtained by MSD and PLD on Q substrate are presented in fig 4.



Substrate Q (quartz) | MSD Q after 10 min | MSD Q after 40 min



PLD Q after 5 min | PLD Q after 10 min

Fig 4 AFM of films obtain at different deposition time by MSD and PLD on Q

4. Conclusions

By different deposition techniques were obtained micro and nano films using glass and glassceramic targets. The thickness and aspects were different as a function of substarate and time of deposition.

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