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Control of the Composition of $(Pb,Ti)O_3$ and $Pb(Zr,Ti)O_3$ Thin Films Obtained by RF Magnetron Sputtering Using a New Design of Target

Valérie Lefort-Courtois,* Denis Remiens, Michel Descamps and Bernard Thierry

Laboratoire des Matériaux Avancés Céramiques (LAMAC), Université de Valenciennes et du Hainaut-Cambrésis,
Route de Mairieux, Z.I. Champ de l'abbesse, 59600 Maubeuge, France

Abstract

A new generation of target has been identified to deposit lead based perovskite films through the RF magnetron sputtering method. $PbTiO_3$ *and* $Pb(Zr,Ti)O_3$ *thin films were sputtered from* (PbO,TiO_2) *and* (PbO,TiO_2,ZrO_2) *targets. The film composition was controlled by simply modifying the thickness of each oxide layer. The sputtered area of each oxide is also well-defined and allows to achieve reliable compositions of the film deposited. Relations were established between the compositions of the target and the films. The evaluation of each oxide area could also be calculated corresponding to any desired film composition whatever the element. Better distribution of the doping agent was also achieved with this multilayer target. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: target, films, tape casting, PZT.

1 Introduction

Lead based perovskite thin films are widely studied for their interesting properties as part of microelectronic applications. The range of these extend from Surface Acoustic Wave devices, electroacoustic transducers, ferroelectric memory devices to pyroelectric sensors.[1,2]

For these applications RF magnetron sputtering was employed for PZT films deposition starting from oxide targets. Multicomponent oxide targets often consist of mixed and pressed oxide powders but many problems are met during their fabrication and use. For example, pressing large diameter disks is often difficult and leads to their cracking. This has been overcome by Ghosh *et al.*[3] with a mosaic target composed of a certain number of square pellets. The shape of this mosaic target can be easily modified as desired, the size that can be achieved is 5 inches, the fabrication cost is reduced and the preparation process remains simple.

The determination of the target chemical composition is in fact the main difficulty encountered with these multicomponent oxide targets. Using a target where composition is the same as the composition of the thin film is not enough. The yield sputtering of a monoxide differs from the yield sputtering of a multicomponent target, and the knowledge of this parameter has been little developed. For a desired chemical composition thin film, the target composition is often determined by trial and error, and is only valid for certain sputtering conditions. The large range of oxide targets proposed by many authors shows that there is still a need for new target design.[4,5]

In the case of metallic targets, an evaluation of the target composition was proposed by Sreenivas *et al.* but this has not been yet reported in the case of oxide targets.[6] In that frame, we have developed a multilayer target. It is obtained starting from several oxide sheets cast using the doctor blade method. The thickness of each oxide tape governs the compositions of the target and so of the sputtered film. Two tape-casting methods are applied: one based on a monolayer system, for the (PbO,TiO_2) targets, and one based on a multilayer system, for the (PbO,ZrO_2,TiO_2) targets. In the first case, one PbO tape and one TiO_2 tape were cast separately and stacked. In the second case, three layers

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*To whom correspondence should be addressed. Fax: +33-03-2764-6654; e-mail: valerie.courtois@univ-valenciennes.fr containing, respectively, PbO, TiO_2 and ZrO_2 powders, were simultaneously cast one on the other. Whatever the case, the as-obtained multilayer tape was wound around itself, released from organic additives, cold isostatic pressed and cut into disks (2 mm thickness, 30 mm diameter). It was used in this state as a target.

In this study, for some given sputtering conditions, the modifications of the thickness of the oxide tapes are discussed relative to the film composition.

2 Experimental

Figure 1 presents a diagram of a multilayer target for which the complete forming process has been described in a previous paper.[7] Its development had needed a complete study of the powder dispersion, of the tape casting then of the target forming process and more particularly the critical debinding step. The (PbO,TiO_2, ZrO_2) target could not be made starting from stacked monolayer tapes and a multilayer tape one has been developed. For that case, the composition of oxide slurries has been optimised (to be published). Various target compositions were obtained by modifying the thickness of the oxide tapes and so the gap of the casting blade. The erosion area and the layer thickness of each target were determined by means of Scanning Electron Microscopy (30 kV, Jeol, JSM-T 330A) and the sputtered target profile was observed using a surface scan (Surfascan 2 D, Somicronics).

PT and PZT thin films were prepared on Si/SiO_2 substrates by RF magnetron sputtering without any substrate heating. The system has already been described elsewhere.[7,8] Sputtering conditions are summarised in Table 1. The sputtering chamber was evacuated to a pressure of about 10^{-7} mBar using a molecular pump before argon was introduced. Before the film deposition, the substrates were cleaned with organic solvents (acetone, ethyl-alcohol and trichloroethylene). The chemical composition was analysed by Energy Dispersion Spectroscopy (E.D.S., 1 nA, Princeton Gama Tech, OS19-JO14, 2200).

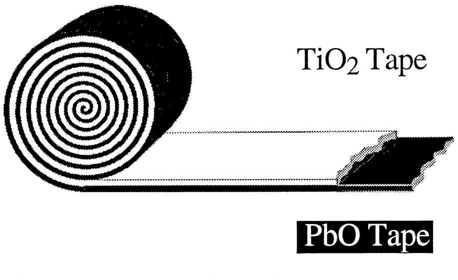

Fig. 1. Schematic diagram of a (PbO,TiO_2) multilayer target with a powder center.

Table 1. Sputtering conditions for preparation of $PbTiO_3$ and $PbZrTiO_3$ thin films

Target		*Sputtering parameters*	
Diameter	25·4 mm	RF power density	2·36 W cm^{-2}
Thickness	2 mm	Gas pressure	100 mTorr
Presputtering time	15 h	Gas process	Argon
Sputtering time	6 h	Inter-electrode distance	35 mm
		Substrate temperature	Ambient
		Substrate	Si/SiO_2

3 Results and Discussion

3.1 Determination of the surface composition of the target

The observation of scanning profiles of sputtered targets, in the conditions defined in Table 1, has allowed the location of the eroded zone with regard to the target centre and the determination of its width. An example of scanning profile obtained is presented in Fig. 2. The width of the eroded zone was estimated at about 7210 μm and its depth is not taken into account because we have compared targets sputtered in the same conditions. The target centre was supposed not to be sputtered. Moreover the thickness of the oxide layers were measured from SEM micrographs. The determination of an oxide area A_x is based on the calculation of the concentric ring areas. The iterative equations are as follows:

$$A_x = \sum_{i=1}^{n} \pi(R_{i\text{ext}}^2 - R_{i\text{int}}^2) \qquad (1)$$

where $R_{1\text{int}}$ is the radius of the target centre and is related to the interior boundary of the eroded zone ($R_{1\text{int}} = R_{\text{centre}} = 1500\ \mu m$), $R_{1\text{ext}}$ is equal to R_{centre} plus e_1 which is the thickness of the first layer closed to the centre, $R_{n\text{ ext}}$ is equal to R_{centre} plus the width of the eroded zone W_{eroded} (1500 +7210 μm = 8710 μm) and is defined as the exterior boundary of the eroded zone.

3.2 Target–film composition relations

Relations between the calculated PbO and TiO_2 eroded areas for various (PbO,TiO_2) targets and the observed atomic composition of the $PbTiO_3$ thin films have been established from Fig. 3. Linear relations are observed and are given by the following equations:

$$A_{\text{PbO}} = 4{\cdot}26 \times 10^6 \times \text{Pb\%} \qquad (2)$$

$$A_{\text{TiO}_2} = 6{\cdot}90 \times 10^6 \times \text{Ti\%} \qquad (3)$$

From these relations, a reliable evaluation of the target composition is now possible whatever the desired film composition for some given sputtering parameters (Fig. 1).

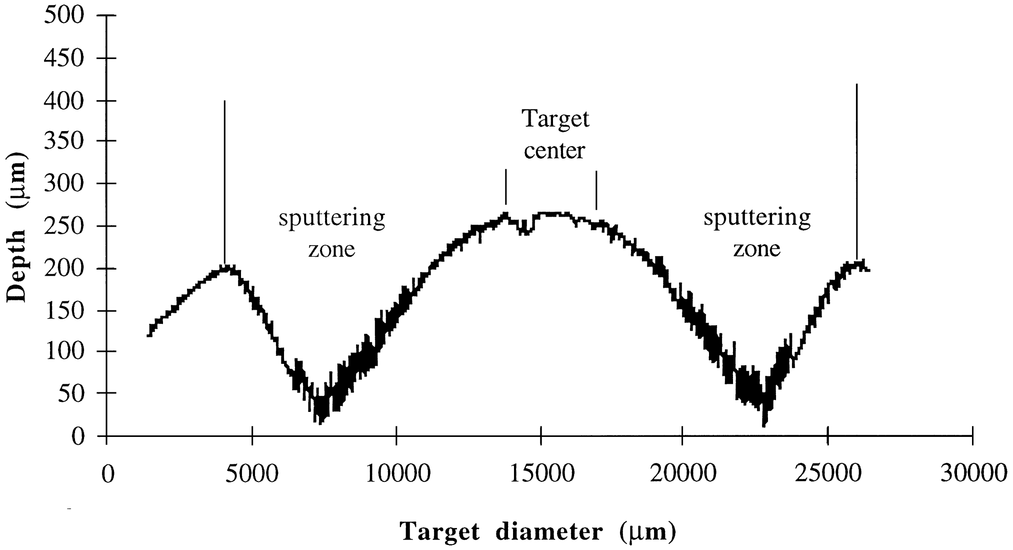

Fig. 2. Scanning profile of a (PbO,TiO_2) multilayer target which has undergone a presputtering of 15 h and a sputtering of 4 h.

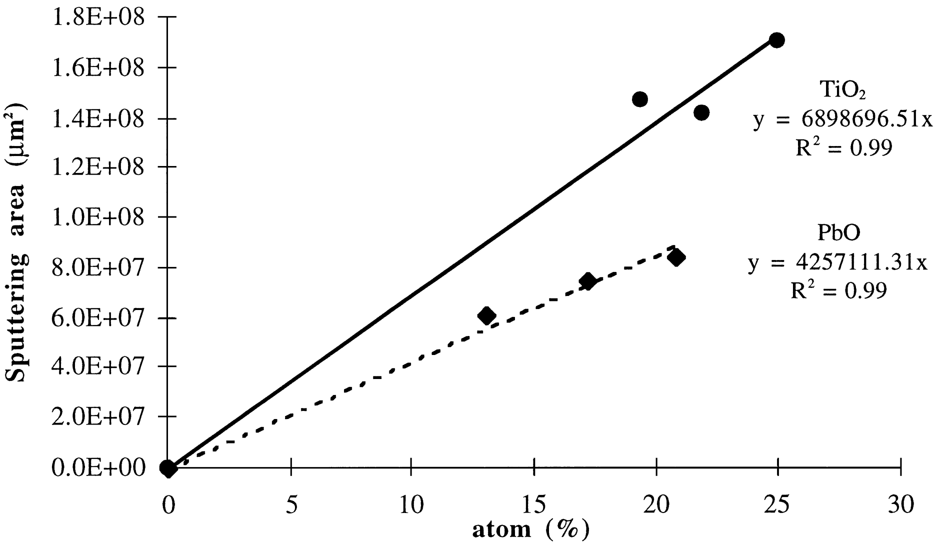

Fig. 3. Sputtered areas of PbO and TiO_2 as a function of film composition expressed as at% of Pb and Ti, respectively.

These relations would be easily established whatever these parameters. For example, a stoichiometric $PbTiO_3$ thin film can be obtained by sputtering with a (PbO,TiO_2) target in which PbO and TiO_2 areas were estimated at, respectively, $85{\cdot}14 \times 10^6 \times 2$ and $13{\cdot}79 \times 10^7$ μm^2 [eqns (2) and (3)]. These areas corresponded to a mean layer thickness of 73 and 127 μm for the PbO and TiO_2, respectively.

In addition, the sputtering rate for this stoichiometric film achieves 30 against 20 Å min^{-1} starting from a standard non-calcined target despite their equivalent non-sintered state.[9] This can be attributed to their different densities, due to different forming processes used (dry and liquid routes). Moreover the debinding state of the multilayer targets avoids some possible contamination.[10] Eventually last, the sputtering rate corresponding to a $PbTiO_3$ sintered target also achieves 30 Å min^{-1} but the multilayer targets present a higher life-time (Table 2).

On the same principle, linear relations have been established for the $Pb(Zr,Ti)O_3$ thin films and are given by the following equations (Fig. 4):

$$A_{PbO} = 4{\cdot}38 \times 10^6 \times Pb\% \qquad (4)$$

$$A_{ZrO_2} = 6{\cdot}55 \times 10^6 \times Zr\% \qquad (5)$$

$$A_{TiO_2} = 7{\cdot}90 \times 10^6 \times Ti\% \qquad (6)$$

Table 2. Characteristics of the standard oxide target and of the (PbO, TiO_2) multilayer oxide target used to obtain stoichiometric $PbTiO_3$ films

	Standard targets[9]			*Multilayer targets*
	Non-calcined	*Calcined*	*Sintered*	
Density ($g\,cm^{-3}$)	3·29	4·26	7·03	5·6
Sputtering rate (Å min^{-1})	20	29	31	30
Life-time (h)	43	7–15	7	86

The PbO eqns (2) and (4), established for the $PbTiO_3$ and $PbZrTiO_3$ films are virtually equivalent. This shows that Zr addition in $PbTiO_3$ films did not result in any modification of the lead concentration. Moreover the area of TiO_2 needed to obtain a stoichiometric $PbTiO_3$ film is almost equal to the sum of the ZrO_2 area and TiO_2 area needed for a $Pb(Zr,Ti)O_3$ film with an atomic ratio Zr/Ti equal to 50/50. These trends demonstrate independence between the different elements which is not observed when a standard oxide target is used. This property constitutes an additional advantage since knowing the relations between the target and the film compositions for each element and for some given sputtering conditions, it is possible to evaluate the area of each oxide necessary to obtain a desired film composition whatever the elements combined.

3.3 Doped thin films

We have supposed above that the target centre was not sputtered since this is classically observed with a magnetron sputtering system. However 1% atom of Zr has been detected when films were sputtered from a (PbO,TiO_2) target with a centre of ZrO_2 powder. So some part of the target centre is eroded and this may be attributed to some defects in our sputtering system (magnetron fields seem to be not strong enough). This can be used in a positive way. Indeed the variation of the diameter of the target center makes it entered more or less in the eroded zone (Fig. 5). This trend can be useful for doped films for which the low proportion of the doping element must be finely controlled by changing the nature of the area center with doping oxide powder. The area centre of a multilayer target is well-defined

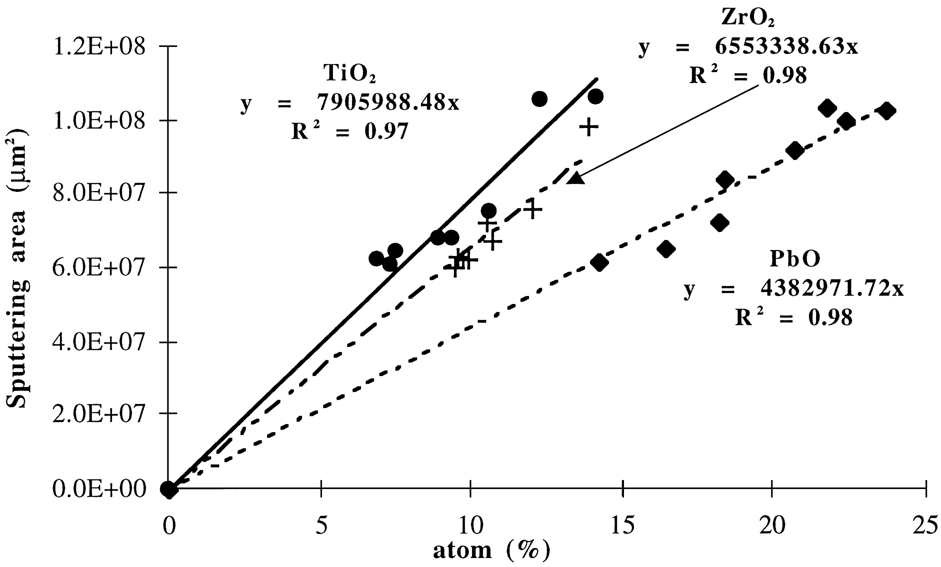

Fig. 4. Sputtered areas of PbO, ZrO_2 and TiO_2 as a function of film composition expressed as at% of Pb, Zr and Ti, respectively.

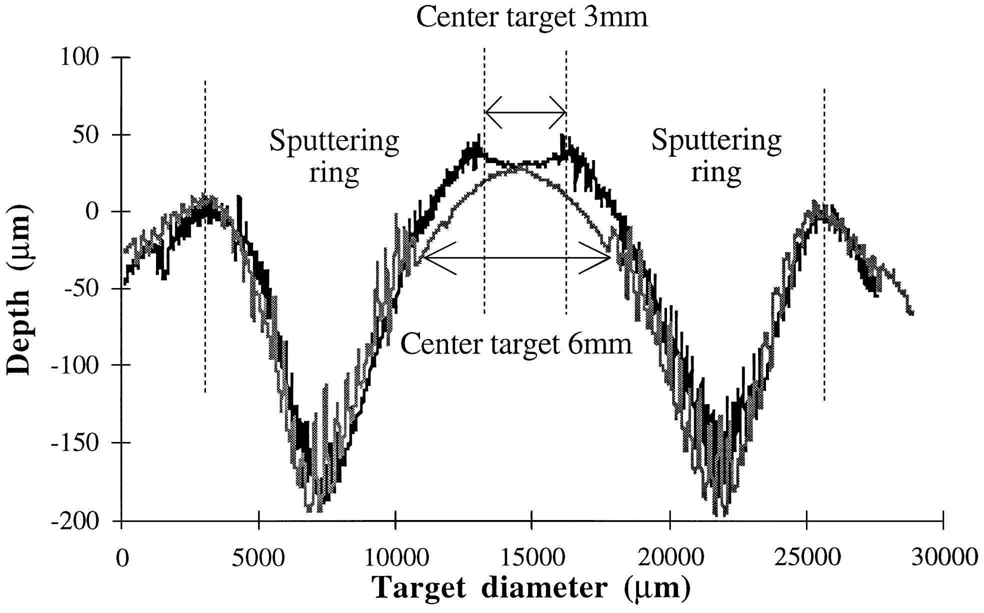

Fig. 5. Scanning profile of (PbO,TiO_2) targets with a ZrO_2 center, 3 and 6 mm in diameter.

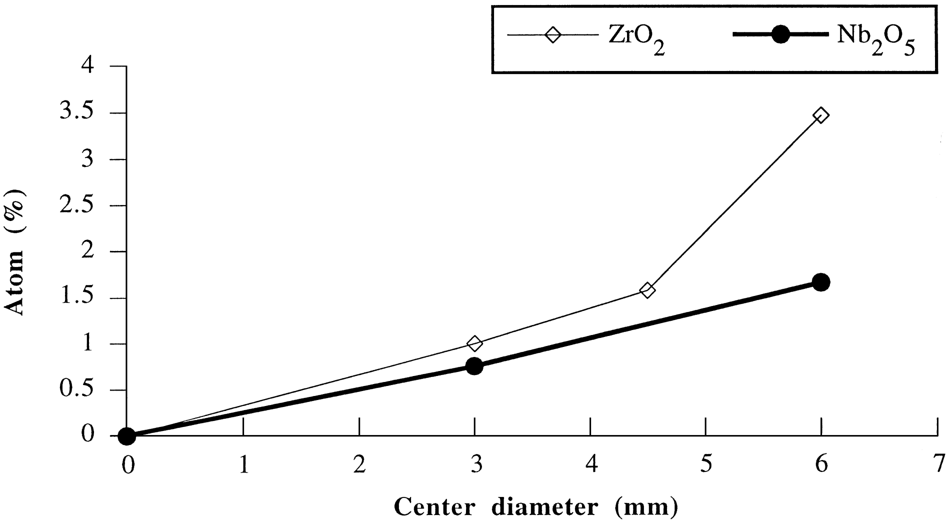

Fig. 6. Doping element (at%) in the thin film as a function of the ZrO_2 and Nb_2O_5 center diameter of the target.

so this ensures an homogeneous distribution of a doping element. Moreover its location in the eroded zone permits the achievement of low atomic percentages. This is not easily achieved with targets based on mixed powders. To confirm that, trials of doping have been investigated and the first results obtained are presented in Fig. 6. $(Pb,Ti)O_3$ films doped with various Zr contents have been obtained by sputtering (PbO,TiO_2) targets with ZrO_2 centres of various diameters. The nature of the centre powder has also been changed. In that way $Pb(Ti,Zr)O_3$ films doped with Nb were deposited. A linear relation is obtained between the atomic percentage of doping element in the films and the size of the target centre.

4 Conclusion

Multilayer targets lead to high sputtering rates, are less sensible to contamination and present a higher life-time than any standard target studied in our laboratory.[8] Apart from these intrinsic characteristics, this new design offers surface and bulk homogeneity of the target chemical composition. For given layer thickness and center diameter of the target, the sputtered area is the same. Relations established between the compositions of the target and of the film for given sputtering conditions, have shown an independence between the elements. They allow the estimation of the target composition to obtain a desired composition film and this may be easily determined whatever the sputtering conditions. This possibility is one of the most important aspects of the multilayer targets. The homogeneous distribution of a doping element, ensured by a well-defined sputtered area, is also a main advantage. A multilayer target allows reliability of the doped-film composition whatever the element content.

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