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Piezoelectric Properties of PZT: Influence of (Zr/Ti) Ratio and Niobium Substitution

T. HACCART, C. SOYER, E. CATTAN and D. REMIENS

*LAMAC, Université de Valenciennes et du Hainaut-Cambrésis
Z.I. Champ de l'Abbesse-59600-MAUBEUGE-France*

Pb(Zr,Ti)O₃ (PZT) and Pb(Zr,Ti,Nb)O₃ (PNZT) thin films were grown on platinized silicon substrates by r.f. magnetron sputtering followed by a post-annealing treatment. PZT films with various Zr/Ti compositions ranging from 15/85 to 70/30 were grown; for PNZT films (the ratio Zr/Ti is fixed to 54/46) the Niobium concentration varied from 1 to 7 at.% by increment of 1 at.%.

The main objective of this work is to determine the effects of the Zr/Ti ratio and the Nb concentration on the electrical properties of PZT thin films. The dielectric, ferroelectric and piezoelectric properties of the films were systematically evaluated. In particular, the piezoelectric properties were very sensitive to the Nb substitution and the Zr/Ti ratio.

Keywords: r.f.sputtering; Pb(Zr_xTi_{1-x})O₃; various Zr/Ti; Nb doped; dielectric; ferroelectric; piezoelectric

INTRODUCTION

Lead Zirconate Titanate thin films Pb(Zr_x Ti_{1-x})O₃ (namely PZT) is a widely studied ferroelectric material. Its interesting properties, dielectric, ferroelectric, pyroelectric and piezoelectric ones are attractive for numerous applications such as ferroelectric memories and Micro-Electro-Mechanical Systems (MEMS) [1,2].

It is well known in bulk ceramics that the electrical properties are very dependent on the Zr/Ti ratio. The addition of metals or rare earths allows also to modify (and specially to increase) the performances of this material. Several dopants have already been introduced :

-the Lanthanum (La), substituted in site A of the perovskite, to form $(\text{Pb,L a})(\text{Zr,Ti})\text{O}_3$ (PLZT) ceramics. The piezoelectric performances of the material are improved for La concentration inferior to 6 at. %.

-the Niobium (Nb), substituted in site B of the perovskite, to form $\text{Pb}(\text{Zr,Ti,Nb})\text{O}_3$ (PNZT) ceramics. A weak concentration of Nb (typically 1-2%) improves the piezoelectric properties of PZT.

Concerning doped PZT thin films, few works have been published [3,4]. In particular, the influence of Nb doping on the ferroelectric properties of PZT films have been discussed in many recent papers [5,6].

Some papers have also described the influence of the Zr/Ti ratio on the dielectric and ferroelectric properties [7].

The effect of Nb doping and the Zr/Ti ratio on the piezoelectric properties of PZT films have not yet well established. To our knowledge, the piezoelectric coefficients of PNZT are still not widely available.

The aim of this work is thus to study the evolution of the electrical properties and in particular the piezoelectric coefficients of PZT films in a wide range of chemical composition and PNZT films with composition near the morphotropic phase boundary.

EXPERIMENTAL

PNZT (54/46) with Nb ranging from 1 to 7at.% by increment of 1 at.% and PZT with Zr content ranging from $x=0.15$ to $x=0.7$ were deposited by r.f. magnetron sputtering on Si/SiO₂/Ti/Pt (111) substrates. A description of the equipment is given in the reference [8]. The targets were cold pressed powders since they are easy to fabricate and facilitate compositional changes and doping. For PNZT, we have decreased the Pb content in the target to achieve electroneutrality, which is modified with Niobium substitution.

The sputtering parameters are given in table 1; they have been optimized for PZT (54/46) films [9]. We have used the same sputtering parameters for PNZT growth whatever is the doping level and for PZT films whatever the Zr/Ti composition. The compositional changes of PZT films with sputtering parameters (gas pressure, rf power...) were

investigated. It was found that the Zr/Ti ratio remains relatively constant whereas the Pb/Zr+Ti ratio was clearly dependent on the sputtering conditions. So, using of targets with various Zr and Ti contents do not require changing the sputtering parameters.

TABLE 1 Sputtering deposition conditions of PZT thin films

Target diameter	76.2mm
RF power density	2.36W/cm ²
Target - substrate distance	60mm
Sputtering gas	Ar
Working gas pressure	30mTorr
Substrate temperature	25°C - 160°C

We have estimated by EDS (Energy Dispersive Spectroscopy) the transfer function of the Niobium species. Typically, 80% of the Nb contained in the target is present in the film.

As the films are deposited without substrate heating, they are amorphous and a post-annealing treatment is required to crystallize the films in the perovskite phase. Conditions of annealing have been determined within the framework of the study of the PZT (54/46) and have been applied for PNZT (whatever is the percentage of doping) and for PZT with various Zr/Ti ratio. It concerns a conventional annealing (diffusion furnace); the annealing is performed at ambient atmosphere. The typical annealing conditions are also given in table 2.

TABLE 2 Typical annealing conditions of PZT and PNZT films

Speed of heating	3°C/min.
Temperature of annealing	625°C
Annealing time	30min.
Speed of cooling	1°C/min.
Atmosphere	Air

The films crystalline structure has systematically been observed by the recording of the diagram of X-ray diffraction in the configuration $\Theta - 2\Theta$ ($\text{CuK}\alpha$). The films are perfectly crystallized in the perovskite phase; no pyrochlore phase is detected.

For example, figure 1 shows the diffraction diagram of PZT films with Zr/Ti equal to 25/75, 30/70, 35/65, 45/55, 54/46, 70/30. All the films exhibit a perovskite structure.

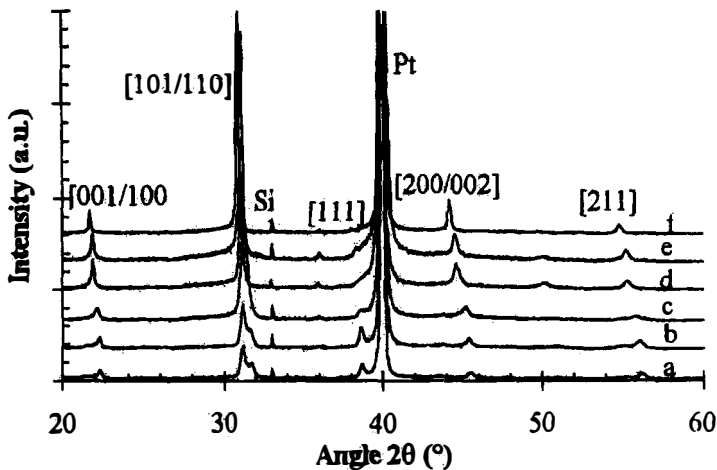


FIGURE 1 Evolution of XRD pattern for PZT films with various Zr content a) $x=25$, b) $x=30$, c) $x=35$, d) $x=45$, e) $x=54$ and f) $x=70$

Due to the various Zr/Ti ratios, changes in position of (100), (110), (111), (200) and (211) peaks of diffraction are observed. When $x < 0.30$, the diffractograms display split peaks for the (101/110) doublet relative to the tetragonal composition. When Zr/Ti=35/65 and 45/65, a single peak is observed. This behavior is in contradiction with result of bulk ceramics where the peaks splitting is systematically observed for Zr/Ti $< 54/46$. This is probably due to the stress present in the films. A more complete study is necessary to understand this point.

The morphologies of the films are crack-free and uniform as observed in figure 2 which shows a SEM cross-section of PZT (45/55 in this example).

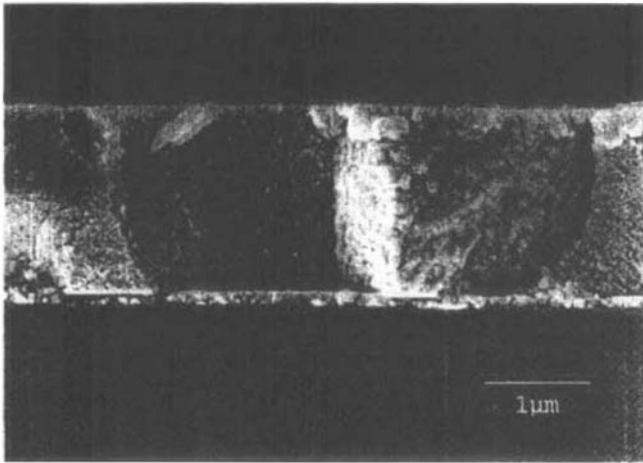


FIGURE 2 SEM cross-sectional view of PZT(45/55) thin film (the film thickness is 1,8 μ m)

RESULT AND DISCUSSION

The electrical properties, i.e. dielectric, ferroelectric and piezoelectric ones have been systematically evaluated as a function of the percentage of doping and of the (Zr/Ti) ratio and compared to the ones of undoped PZT(54/46) films with similar thickness.

For each electrical characterization, Pt top electrodes with 1 mm diameter (necessary for piezoelectric evaluation), were deposited on the film by lift-off process.

The relative dielectric constant ϵ_r was deduced from capacity measurement (HP4192A impedance analyzer) All the measurements have been performed using an alternative voltage of weak amplitude (100 mV) in order to not modify the material properties (polarization). The work frequency is fixed to 10 kHz.

Figure 3a shows the evolution of ϵ_r as a function of the Nb concentration. For the weak quantities of doping (< 2 at.%), ϵ_r increased with the percentage of doping; for the undoped PZT(54/46), ϵ_r is equal to 850, it reaches a maximum value (1100) for a quantity of doping equal to 2 at.%.

When the quantity of niobium is superior to 2 at.%, ϵ_r decreases to reach the value of 950 for a PNZT. The variation of the dielectric loss is also presented in figure 3a. For undoped PZT(54/46), $\tan\delta$ is in the order of 1,8%. Identical values are observed for doped PZT films.

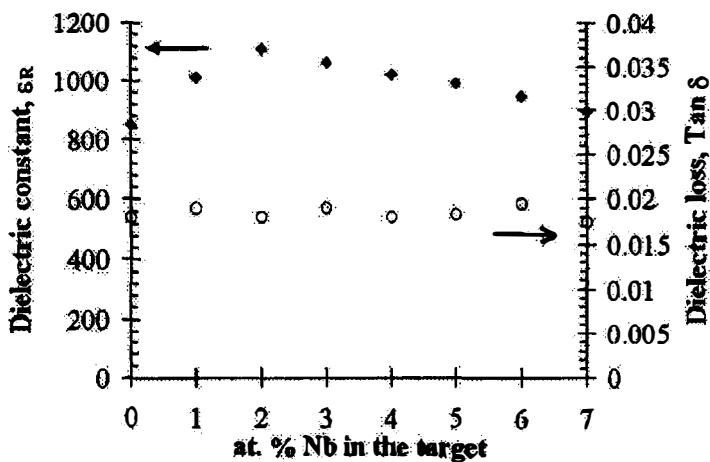


FIGURE 3a Evolution of the dielectric constant and the dielectric loss as a function of the Nb concentration in the target

Figure 3b shows the evolution of ϵ_r as a function of Zr/Ti ratio. The maximum value is obtained near the morphotropic phase. This result is comparable to those reported for bulk ceramics [10], but the measured values are higher than for the ceramics. This feature is also observed for PZT thin films grown by different techniques [11,12]. The dielectric losses seem to be independent on the composition.

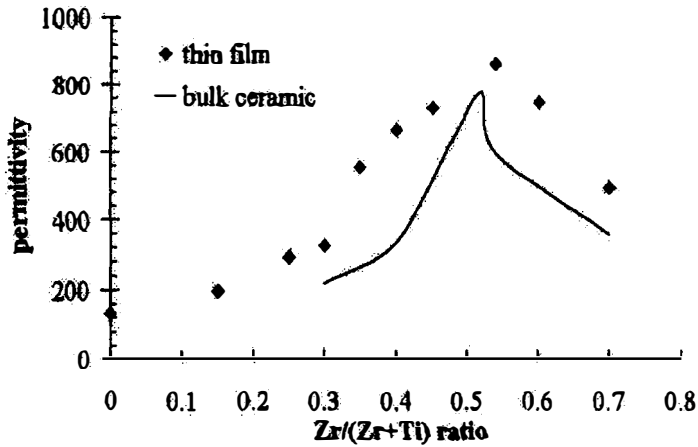


FIGURE 3b Evolution of ϵ_r as a function of Zr/Ti ratio

Ferroelectric measures are undertaken on a Radiant RT6000 at room temperature. A typical example of an hysteresis loop for a PNZT (2 at.% doped) is presented in figure 4a.

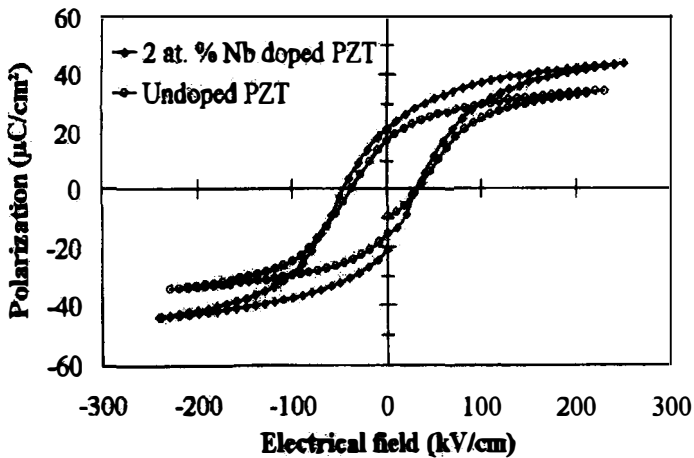


FIGURE 4a (P-E) hysteresis loop of PZT(54/46) and PNZT (Nb=2 at.%) films

The maximum polarization (P_M) is larger for a PNZT than for a PZT; P_M reaches its maximal value at $44 \mu\text{C}/\text{cm}^2$. It is similar for the remnant polarization: P_r is in the order of $21 \mu\text{C}/\text{cm}^2$ in comparison to $17 \mu\text{C}/\text{cm}^2$ for an undoped PZT(54/46) film.

For larger concentration of doping (> 2 at.%), polarizations (maximal and remnant) decrease slightly while remaining superior to those of the undoped PZT.

The coercive field seems independent of the doping level.

Different hysteresis loops measured on PZT with various Zr/Ti ratio ($Zr/Ti = 35/65$ for the tetragonal phase and $Zr/Ti = 70/30$ for the rhombohedral phase) are presented in figure 4b with systematical comparison with the hysteresis loop of a 54/46 PZT film.

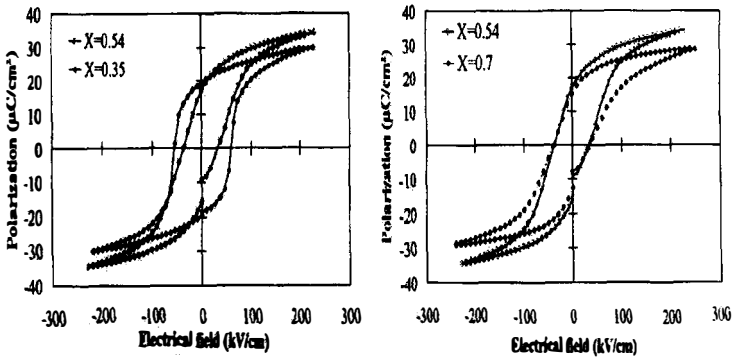


FIGURE 4b (P-E) hysteresis loop of PZT thin film with $x=0.35$, $x=0.54$, $x=0.7$

For $x=0.35$, the hysteresis loop appears to be more squared, and exhibits a higher coercive field than for the $x=0.54$ composition. The ratio P_r^+/P_M is approximately equal to 0,64. By increasing the Zr/Ti ratio, P_r^+/P_M decreases. For $x=0.54$, P_r^+/P_M reaches 0,51 and the hysteresis loop is slimmer. Finally, for the rhombohedral composition, the ratio P_r^+/P_M is still closed to 0,5. Both remnant and maximum polarizations decrease and the hysteresis loop seems to be more tilted.

The piezoelectric coefficients, the longitudinal (d_{33}) and the transversal (e_{31}) ones were evaluated by a double beam laser interferometer [13] and the embedded beam method [14] respectively. Since the films are clamped to the substrates, we measure an effective coefficient ($d_{33 \text{ eff}}$ and $e_{31 \text{ eff}}$) [15]. Figure 5 shows the evolution of remnant

e_{31} as a function of the Zr/Ti ratio. The experimental details (such as the film polarization) are described elsewhere [16].

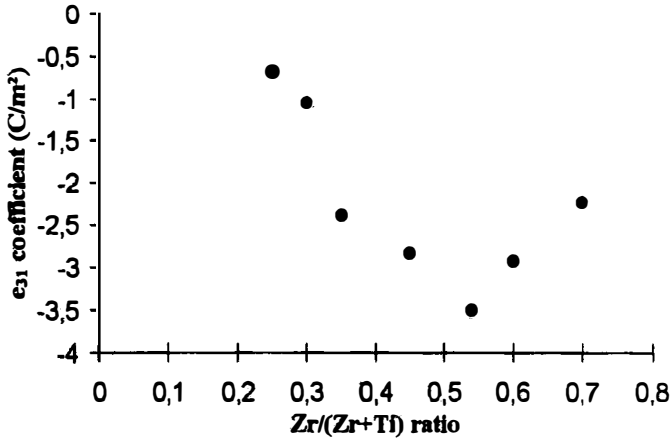


FIGURE 5 Evolution of the remnant e_{31} as a function of Zr/Ti ratio

The maximum value of e_{31} is obtained at the morphotropic phase boundary; e_{31} is equal to $-3,5 \text{ C/m}^2$.

Figure 6 shows the evolution with the niobium concentration of e_{31} coefficient

The introduction of Nb enhances the PZT film properties as in the bulk ceramics. The maximum value of e_{31} is $-4,6 \text{ C/cm}^2$ and it is relative to a PNZT with Nb concentration of 1 at. %.

Very little variation was observed between 1 and 2 at. % ; for higher doping level, the piezoelectric performances decrease.

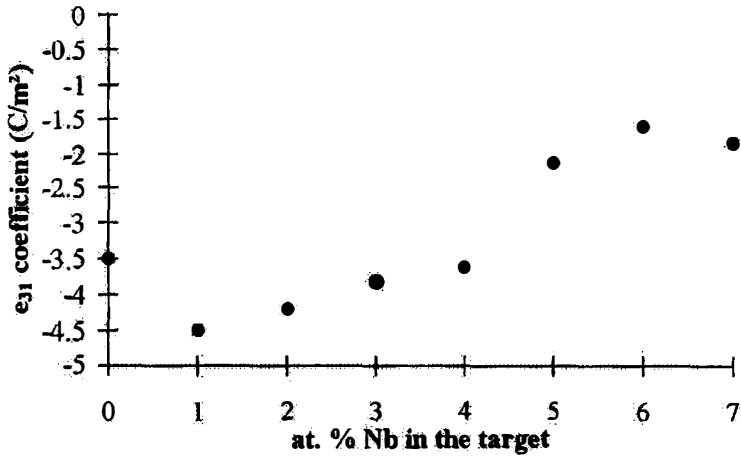


FIGURE 6 Evolution of the remnant e_{31} as a function of the Niobium concentration in the target

The variation of d_{33} as a function of the doping concentration is presented figure 7.

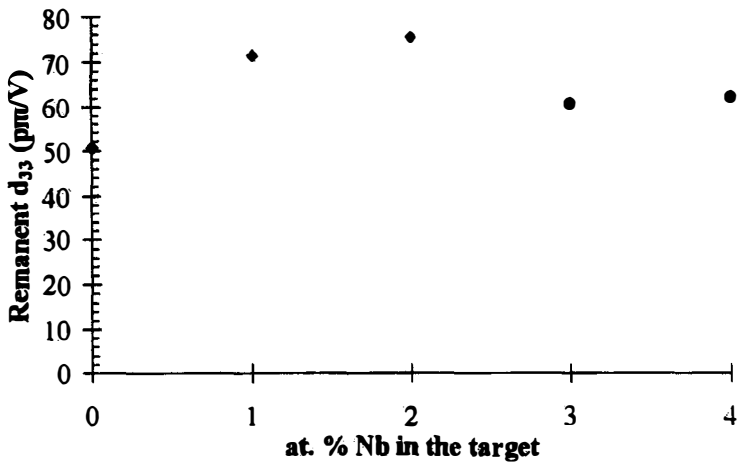


FIGURE 7 Variation of the d_{33} remnant function with the Nb concentration in the target

The results are very similar to the ϵ_{31} variations; d_{33} reaches its maximum value for a 1-2 at.% PNZT film. The maximum remnant d_{33} value is in the order of 80 pm/V in comparison to 50 pm/V for an undoped PZT(54/46) film.

CONCLUSION

PZT thin films covering the full compositional range of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ with $0 < x < 0,8$ and PNZT with Nb concentration varied from 1 to 7 at.% were deposited by r.f. magnetron sputtering followed by a post-annealing treatment. The electrical (dielectric, ferroelectric and piezoelectric) properties of all the samples were systematically characterized.

In term of piezoelectric properties, which are the most important parameters for microsystem applications, it appears that:

- For PZT films, the most convenient composition is the morphotropic phase $x=0,54$
- For PNZT films, the best results are obtained for a low Nb concentration in the order of 1-2 at.%

The behaviors are very similar to those observed on PZT bulk ceramics.

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