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Ferroelectric and Piezoelectric Properties of Nb Doped PZT Films

T. HACCART^a, E. CATTAN^a, D. REMIENS^a, S. HIBOUX^b and
P. MURALT^b

^aLAMAC, Université de Valenciennes et du Hainaut-Cambrésis, Z.I. Champ de l'Abbesse – 59600 Maubeuge – FRANCE and ^bLaboratoire de Céramique, Ecole Polytechnique Fédérale de Lausanne (E.P.F.L.) Lausanne – CH 1015 – SUISSE

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. The Niobium, Nb, concentration varied from 1 to 7 at.% by increment of 1 at.%. The effects of the Nb introduction on the PZT electrical properties, i.e. dielectric, ferroelectric and piezoelectric ones were investigated. The relative dielectric constant (ϵ_r) was very sensitive to the Nb introduction; ϵ_r reaches 1100 for a PNZT film doped at 2 at.% in comparison to 820 for a PZT film. The ferroelectric properties were also dependent of the doping level; in particular the remnant polarization reaches its maximum value for a 2 at.% Nb doped PZT film. The introduction of Nb enhances the piezoelectric properties of the films. The maximum value of d_{33} varied from 55 pm/V for PZT films to 115 pm/V for a 2 at.% Nb doped films. For this doping level, e_{31rem} reaches its maximum value: -4.6 C/m^2 . PNZT thin films, with weak Nb concentration (comprised between 1 to 2 at.%) are suitable for microsystems realization.

Keywords: r.f. sputtering; Nb doped PZT films (PNZT); dielectric; ferroelectric; piezoelectric coefficients (d_{33} and e_{31})

INTRODUCTION

The advent of microsystems (MEMS for MicroElectroMechanical Systems) has allowed Lead Zirconate Titanate ($\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ or PZT) to adopt a leader position of piezoelectric materials. Already largely used in the bulk form, PZT and its derivatives have been naturally required in thin film form thanks to their remarkable ferroelectric, pyroelectric and piezoelectric properties. Applications are numerous : ferroelectric memories, actuators, sensors, infrared detectors,.....

The addition of metals or rare earth allows to modify and especially to increase the performances of these materials in bulk form and thus to strengthen potential applications of PZT. Various dopants have already been introduced [1] :

- the Lanthanum (La-PLZT), which allows to improve piezoelectric (for concentration inferior to 6%) and electro-optic properties.

- the Niobium (Nb-PNZT), which for weak concentrations improves the piezoelectric properties of the bulk ceramics.

Concerning doped PZT thin films, few works have been published [2,3,4]. The effects of the donor dopants, particularly Nb, on the properties relative to ferroelectric memories have been discussed in many recent papers [5,6].

The effect of Nb doping on the piezoelectric properties of PZT films with a composition near the morphotropic phase boundary has not yet been established. For the design of micro-actuators, it is imperative to know the material properties such as the piezoelectric constants. To our knowledge, the piezoelectric coefficients of PNZT are still not widely available.

In this context, we have studied the influence of the Nb substitution on the electrical PZT films properties. More precisely, we have systematically evaluated the dielectric, the ferroelectric and the piezoelectric properties as a function of the Nb concentration. The films were deposited by r.f. magnetron sputtering; the ratio Zr/Ti is fixed near the morphotropic phase boundary.

EXPERIMENTAL

PZT (54/46) and PNZT, with Nb varying from 1 to 7 at.% by increment of 1 at.%, were deposited by r.f. magnetron sputtering on

Si/SiO₂/Ti/Pt-(111) substrates. A description of the equipment is given in reference [7]. The targets are cold pressed powders since they are easy to fabricate and facilitate compositional change and doping. The Pb content in the target was decreased so to achieve electroneutrality (which is modified by niobium substitution).

The sputtering conditions are given in Table I: they have been optimized for PZT (54/46) films [8].

TABLE I Typical sputtering conditions of PZT and PNZT films

Target diameter (mm)	76
r.f. power density (W/cm ²)	3
Gas pressure (mT)	30 (Ar)
Inter-electrodes distance (mm)	60
Substrate temperature (°C)	25 - 140

The same sputtering parameters were used for all PNZT film growth. A weak r.f. power is applied to the target so as to prolong its life duration. The distance target-substrate, close to the diameter of the target, gives thickness homogeneity on the order of 6% on a 2 inches diameter substrate. The growth rate is about 25 to 30 Å/min.

Figure 1 shows the transfer function of the niobium species (measured by E.D.X.) from the target to the film. Typically, 80% of the Nb contained in the targets is present in the film.

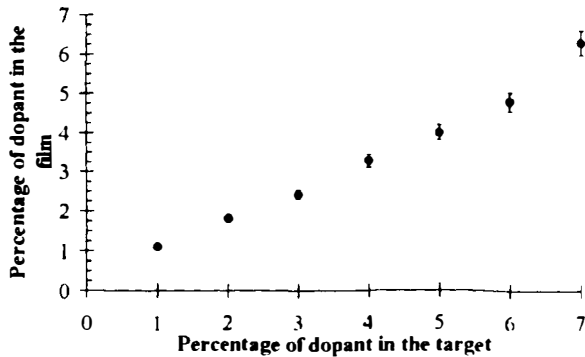


FIGURE 1 Transfer function of niobium species

This result agrees with theoretical forecast, since the sputtering efficiency of the niobium is very close to those of titanium and zirconium [9].

As the films are deposited without substrate heating, they are amorphous and a post-annealing treatment is necessary to crystallize the films in the perovskite phase. Conditions of annealing have been determined for PZT and they have been kept for all PNZT films. It concerns a conventional annealing (diffusion furnace): the annealing is done at ambient atmosphere. The typical annealing conditions are given in Table II.

TABLE II 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

With these conditions of annealing, films are a little rough, without fissure and dense as certifies the SEM photography of the figure 2 for a 2 at.% doped PNZT.

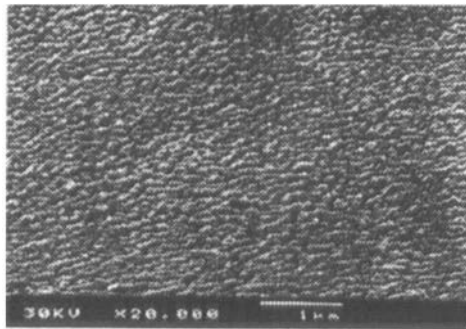


FIGURE 2 SEM photograph of the surface of a PNZT film doped at 2 at.%

The films crystalline structure has systematically been observed by the recording of the diagram of X-ray diffraction in the θ - 2θ configuration ($\text{CuK}\alpha$). A typical example of diffraction diagram is presented figure 3: it concerns a film of PNZT doped to 2 at.%.

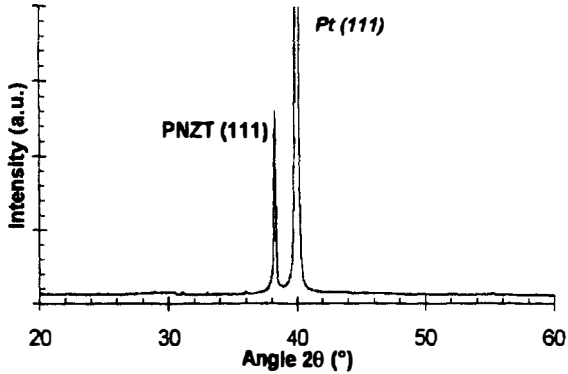


FIGURE 3 Typical example of X.R.D. pattern of a PNZT with Nb = 2 at.%

The film is crystallized in the perovskite phase; no pyrochlore phase is detectable. Films are strongly oriented in the [111] direction. The film preferential orientation is defined by the relationship :

$$\alpha_{(hkl)} = I_{(hkl)} / \sum I_{(hkl)}$$

It is on the order of 90% independent of the percentage of doping.

RESULTS AND DISCUSSION

The electrical properties, that is to say dielectric, ferroelectric and piezoelectric ones, have been systematically evaluated as a function of the percentage of doping and compared to the ones of undoped PZT films with similar thickness.

For each electrical characterization Pt top electrodes, with 1 mm diameter (necessary for piezoelectric evaluation), were deposited on the films by the lift-off process. The films investigated were 0.7 μm thick, in order to eliminate the thickness effect as a variable.

The relative dielectric permittivity, ϵ_r , and the dielectric loss, $\tan \delta$, which are the characteristics of the capacitor samples have been evaluated using an HP 4192A impedance analyzer. All the measurements have been performed using an alternating voltage of weak amplitude (100 mV) in order not to modify the material properties (polarization). The work frequency is fixed at 10 kHz.

Figure 4 shows the evolution of ϵ_r as a function of the Nb concentration.

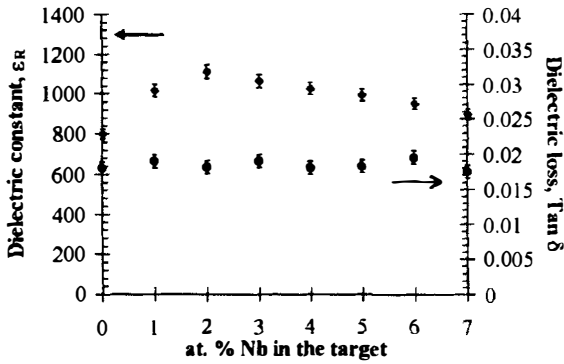


FIGURE 4 Evolution of the dielectric constant, ϵ_R and the dielectric loss, $\tan \delta$ with the niobium concentration.

For the low dopant concentrations (< 2 at.%) ϵ_r increased with the percentage of doping : for the undoped PZT ϵ_r is equal to 800, it reaches a maximal value (1100) for a 2 at.% doping. Then, when the quantity of niobium increases, ϵ_r decreases to reach the value of 950 for a PNZT doped to 7 at.%.

The evolution of the loss factor is presented also figure 4. For undoped films $\tan \delta$ is in the order of 1.8%. Identical values are observed for doped PZT films; the values saturates at 1.8% whatever the doping concentration (in the range 1-7 at.%).

Ferroelectric measurements were made using a Radiant RT6000 at om temperature. The remnant polarization (P_R) is more important for a PNZT than for a PZT : P_R^+ varied between 17 and 20 $\mu C/cm^2$ for a PNZT doped to 2 at.% : it varied between 14 and 16 $\mu C/cm^2$ for a PZT. Increase in the same order of magnitude has been reported by other

group [5]. It is similar for the maximum polarization (P_M) : P_M reaches its maximal value ($34\mu\text{ C/cm}^2$) for a PNZT doped at 2 at.%. For larger doping concentrations (> 2 at.%) polarizations (maximal and remnant) decrease slightly while remaining superior to those of the undoped PZT. Figure 5 (evolution of P_R with Nb concentration) shows this behavior.

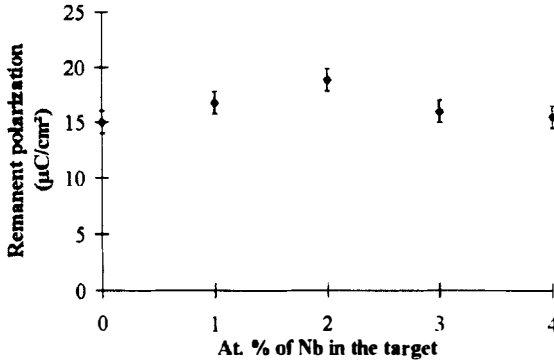


FIGURE 5 Evolution of P_R in function of Nb concentration in the target

The coercive field (E_C) seems to be independent of the doping level, as indicates the figure 6, which shows the evolution of E_C^+ as a function of the niobium concentration.

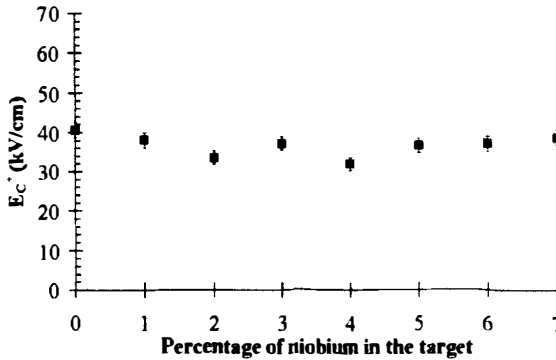


FIGURE 6 Evolution of E_C^+ as a function of Nb concentration in the target

The longitudinal piezoelectric coefficient, d_{33} , of PNZT films has been systematically evaluated and compared to those of undoped PZT films. As the film is clamped to the substrate, it is not easy to measure the piezoelectric constant with the experimental set-up used for bulk ceramics. In this study, a double beam laser interferometer was used to accurately evaluate the film dilatation (by the converse piezoelectric effect) by eliminating the influence of the substrate motion. The interferometer shows a high sensitivity (10^{-4} Å) and stability $< 1\%$ over 6 hours [10]. We measured an effective coefficient ($d_{33\text{eff}}$) since the film is rigidly clamped to the substrate [11].

Figure 7 shows the piezoelectric hysteresis loops as a function of the doping concentration.

The introduction of Nb enhances the PZT film piezoelectric properties as in the bulk ceramics [1]. The maximum values of d_{33} varied from 55 pm/V for undoped PZT to 115 pm/V for 1 at.% doped film. Very little variation was observed between 1 and 2 at.%; for higher doping level, the piezoelectric performance decreases. For example d_{33} is equal to 90 pm/V for a 3 at.% PNZT film.

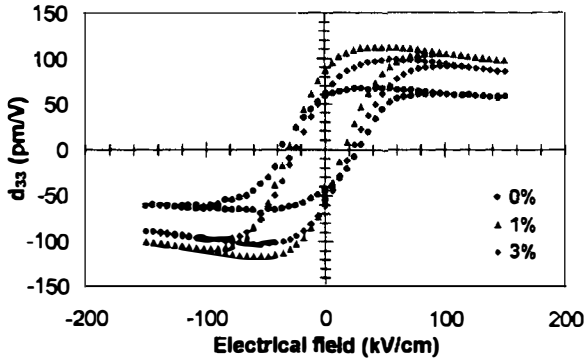


FIGURE 7 Piezoelectric hysteresis loops of PZT and PNZT (1 and 3 at.%)

The variation of the remnant d_{33} ($d_{33\text{rem}}$) as a function of the doping concentration is presented in figure 8. The $d_{33\text{rem}}$ value for undoped films seems weak in comparison with some values recently published [12,13]; but we must take into account some parameters such as the film orientation [14], the surface of the top electrode,... to make a valid comparison.

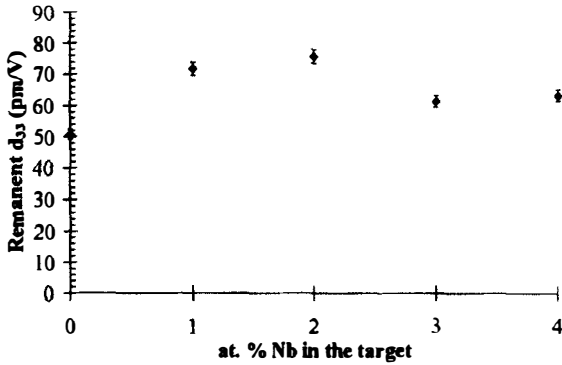


FIGURE 8 Variation of the d_{33rem} function of the Nb concentration in the target

This result confirms that the optimized doping level correspond to 1-2 at.% with d_{33rem} in the order of 80 pm/V.

The variations of d_{33rem} with Nb concentration are perfectly in agreement with the variations of P_R^+ (figure 5); the maximum values are obtained for a 2 at.% PNZT.

We have also evaluated the transverse piezoelectric coefficient, e_{31} , as a function of the doping level. For that, we have used the embedded beam method; a description of this experimental set-up is given in references [15,16].

For an optimized poling treatment [17], applied to PZT as well as to PNZT (the films thickness are similar), we have also observed that the maximum value of e_{31rem} is obtained for a 2 at.% PNZT film. Typically, for a PZT film e_{31rem} is in the order of -3.5 C/m^2 , it reaches -4.6 C/m^2 for a 2 at.% PNZT film.

CONCLUSION

PZT (54/46) and PNZT, with Nb concentration varied from 1 to 7 at.%, were deposited by r.f. sputtering followed by a post-annealing treatment on platinized silicon substrates. The dielectric, ferroelectric and the piezoelectric properties were systematically evaluated as a function of the doping concentration. The introduction of Nb enhances the electrical properties as in the bulk ceramics. The films performance as well as in terms of ϵ_r , P_R (P_M), d_{33} and e_{31} attains its maximum value for a doping level equal to 2 at.%. Typically, $\epsilon_r = 1100$, $d_{33rem} = 80 \text{ pm/V}$ and $e_{31rem} = -4.6 \text{ C/m}^2$. When the doping level is higher than 2 at.% all

the electrical performances decrease. PNZT thin films with Nb concentration in the order of 2 at.% are suitable for the realization of microsystems.

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