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# Electrical property evaluation of manganese-fluorine codoping of lead zirconate titanate thin films: Compatibility between hard material and piezoelectric activity

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For some microelectromechanical system (MEMS) applications, the conditions of operation, high temperature, high stress, etc., can be very severe. Under these conditions the piezoelectric performance of polar material can decrease due to a partial (or a total) depoling induced by external excitations. So, it is important to have a piezoelectric active material that presents a good stability versus external parameters which can modify the spatial distribution of the dipolar moment and so the macroscopic polarization state (temperature, stress, etc.). In this context, we have studied the influence of some dopant introduction on barium (Ba)-strontium (Sr) lead zirconate titanate (PZT) thin films: manganese (Mn) and fluorine-manganese (F-Mn) codoped. (Ba, Sr) doping is used to increase the PZT piezoelectric activities; Mn doping, depending on the Mn content, can induce hardening effect that leads to an increase of stability but a decrease of piezoelectric activities and (Mn, F) codoping to keep the piezoelectric performances with low nonlinear and low hysteretic behavior versus external excitations. Thin films have been deposited by rf magnetron sputtering on platinized silicon substrates. Their dielectric, ferroelectric, and piezoelectric properties have been systematically measured as a function of Mn and F contents. The best composition in order to have a hard material without degradation of the piezoelectric activity is Mn(1%)–F(1%) (Ba, Sr) PZT. With this material, MEMS applications in special environment can be developed. © 2006 American Institute of Physics. [DOI: [10.1063/1.2369542](https://doi.org/10.1063/1.2369542)]

## I. INTRODUCTION

Due to their high level of piezoelectricity, bulk lead zirconate titanate (PZT) ceramics are widely used as active materials in actuators and sensors. In thin film form, microelectronic and microelectromechanical system (MEMS) technologies have been developed essentially for the realization of devices on silicon substrate such as ferroelectric random access memory<sup>1</sup> (FRAM) for memory applications and piezoelectric micromachined ultrasonic transducers (PMUTs) for medical or wireless telecommunication applications.<sup>2,3</sup>

The selected compositions with Zr content around 48 mol % are generally located near the morphotropic phase boundary (MPB) where the piezoelectric properties reach an optimum.<sup>4</sup> One of the main interest of PZT material is that the macroscopic characteristics can be easily modified by the addition of small amount of dopants leading to soft (highly active materials but very sensitive to external excitations) or hard materials (medium activity but good stability of characteristics versus stress, temperature, or electrical fields).<sup>5,6</sup> In parallel, there is a need of small active material volume in order to develop microsystems leading to film technology development.<sup>7</sup> In thin film form there is a limited number of papers concerning the introduction of dopants (such as Nb,

Mn, etc.) on PZT and their associated electrical evaluations.<sup>8,9</sup> The number of dopants is limited and the introduction of codopant (introduction of simultaneously two chemical elements in the structure) in PZT films is very exceptional.

Our study is devoted to the fabrication, evaluation, and comparison of the electrical properties of PZT thin films with introduction of dopants in the material. The main objective is to realize hard PZT thin film (high coercive field) which presents excellent piezoelectric activity. Several doped or codoped compositions have been studied including (Ba, Sr)-doped PZT, Mn-doped (Ba, Sr) PZT, and (Mn, F)-codoped (Ba, Sr) PZT.

In bulk form pure PZT is rarely used as active materials because the piezoelectric activity is not optimum; in thin film form the undoped PZT is frequently used may be due to the fact that it is easy to fabricate. It is well known that when the number of chemical elements which compose the material increases it is more complicated to control the film composition (except by sol gel), but the piezoelectric properties of doped PZT are largely improved with the introduction of dopants.

(Ba, Sr) doping is well known to increase the ionicity of the chemical bonding in perovskite structures leading to higher piezoelectric activity. In bulk form (ceramic) this property has been verified, but no work on (Ba, Sr) PZT thin film has been published. Besides, ionic radii of Ba (1.34 Å)

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and Sr (1.12 Å) are, respectively, a little higher and a little smaller than this one of Pb (1.20 Å) and consequently the simultaneous use of these two dopants makes the lattice accommodation easier.<sup>10</sup> So, we have chosen to dope the PZT films with (Ba, Sr) (substitution in the A site); more precisely the concentrations are fixed to 6 mol % barium and 5 mol % strontium. These values come directly from results obtained on bulk ceramic studies. The (Ba, Sr)-doped PZT is not hardened as a consequence it is imperative to introduce other elements in the perovskite structure in order to attain our main objective: fabrication of hard PZT thin films. Previous works on Mn and (Mn, F) codoping have shown that these elements could be a solution to obtain a hard PZT material (in bulk form).

In this paper, we have fabricated (Ba, Sr)-doped PZT and (Ba, Sr)-Mn and (Mn, F) codoping PZT targets and deposit these materials in thin film form by sputtering. Systematically the electrical properties of the films are evaluated in order to determine the optimum (Mn, F) contents to have a good hard PZT material which presents good piezoelectric properties.

## II. DEPOSITION OF PZT AND CODOPED PZT THIN FILMS

### A. PZT and (Ba, Sr)-doped PZT films

The PZT and the codoped PZT films have been deposited by radio frequency magnetron sputtering; the system has been described previously.<sup>11</sup> All the materials, pure PZT, (Ba, Sr)-doped PZT, and (Ba, Sr, Mn, F)-doped PZT, deposited in this study, are obtained with the same sputtering conditions in terms of pressure, radio frequency power density, etc. These conditions are those optimized for PZT films<sup>12</sup> and we have shown recently that the same conditions can also be applied to doped PZT material such as Nb-doped PZT films.<sup>13</sup> We can generalize these properties when the sputtering yield and the thermalization distance of the different chemical species which compose the material are nearly the same. This is the case for all the atoms contained in the material used in this study,<sup>14,15</sup> typically the transfer function is in the order of 70%–80% [measured by energy dispersion spectroscopy (EDS)]. The single oxide targets have been elaborated by uniaxial cold press of the ceramic powders used for the fabrication of the bulk material; no lead excess, as is currently observed for the realization of PZT thin films, is used. The Ba and Sr contents are fixed by the concentration used in the bulk ceramic: 6 mol % barium and 5 mol % strontium. The ceramic powders have been prepared by a dry process based on a selective coprecipitation of hydroxide and oxalates following with a 600 °C calcination described elsewhere.<sup>16</sup> The obtained powder has been pressed in pellets of 10 cm in diameter and 10 cm in height. The pellets have been sintered in sealed alumina crucible with a PZT source in order to prevent PbO evaporation. The target diameter and thickness have been fixed to 7.5 cm and 3 mm, respectively. The films were grown without substrate heating and so a postannealing treatment is necessary to obtain the perovskite phase. The annealing parameters are listed in Table I (with the sputtering conditions); we used the same annealing treat-

TABLE I. Sputtering and annealing conditions of the different PZT films deposited on this study.

Parameters	
Target diameter (mm)	76
rf power density (W/cm <sup>2</sup> )	3
Gas pressure (mTorr)	30 (Ar)
Interelectrode distance (mm)	60
Substrate temperature (°C)	170 (ion bombardment)
Annealing temperature (°C)	625
Annealing time (min)	30
Atmosphere	Air

ment as for PZT films. The films are deposited on Si/SiO<sub>2</sub>/TiO<sub>x</sub>/Pt substrates. The Pt film presents a (111) preferred orientation. A typical x-ray diffraction pattern of a (Ba, Sr)-doped PZT and pure PZT films is presented in Fig. 1; only the perovskite phase is present. The films have a strong (111) preferred orientation.

### B. Mn and (Mn, F)-codoped (Ba, Sr) PZT films

The number of chemical elements in these materials becomes important and so the control of the film composition could become more complicated. But since the chemical elements of this material present similar physicochemical properties, the plasma effects (dispersion, collision, etc.) during the transfer from the target to the substrate are nearly the same for all the species. The target fabrication steps are described previously; the Mn contents are fixed to 0.5%, 1%, 1.5%, and 2% and F varied in the range of 1%–7%. The sputtering and annealing conditions are the same than those used for the growth of (Ba, Sr) PZT films. Some examples of x-ray diffraction patterns of Mn and (Mn, F)-doped PZT films are also shown in Fig. 1; no structural modification is observed and no second phase (pyrochlore) is present.

## III. ELECTRICAL EVALUATION AND HARDENING EFFECT

### A. Introduction

For electrical measurements, Pt top electrodes of 150 μm diameter have been deposited by sputtering and lift-

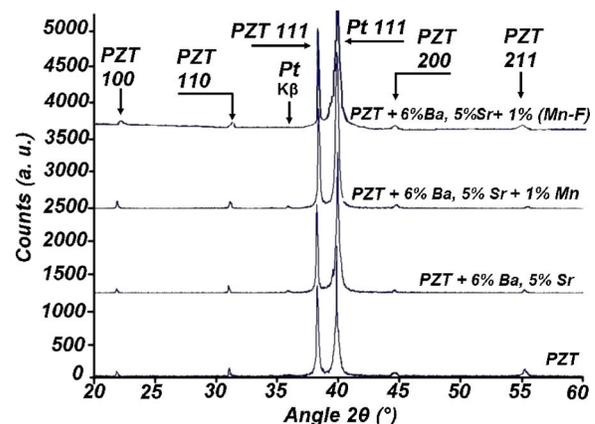


FIG. 1. Typical examples of XRD patterns of pure PZT, (Ba, Sr)-doped PZT films, Mn-doped (Ba, Sr) PZT films, and (Mn-F)-(Ba, Sr) PZT films deposited on Si/SiO<sub>2</sub>/TiO<sub>x</sub>/Pt substrates.

TABLE II. Comparison of the electrical properties of pure PZT and (Ba, Sr)-codoped PZT thin films.

PZT type	$\epsilon_r$	$\tan \delta$	$P_r$	$P_m$	$E_c$	$d_{33}$
Pure PZT	720	1.4	14	37	51	47
(Ba, Sr) PZT	840	1.3	20	41	45	60

off process. The relative dielectric constant ( $\epsilon_r$ ) and the dielectric loss ( $\tan \delta$ ) have been evaluated at room temperature using an HP 4692A multi frequency LCR meter. All the measurements have been performed using an alternative voltage of 100 mV for which no modification of the PZT (and codoped) material polarization state has been observed. The frequency has been fixed to 10 kHz. The ferroelectric properties (maximum and remanent polarizations, coercive field, etc.) are determined with an automatic system (AIXacct TF 2000 Analyzer). The piezoelectric coefficient  $d_{33}$  is evaluated with a modified laser Doppler vibrometer (LDV); this alternative method is required to overcome the complexity of using a double beam interferometer. If the substrate can be constrained, or its mass used to minimize bending effects, then versatile instruments such as the LDV can be used. Our system consists initially of a Polytec laser Doppler vibrometer (OV512/DFE650) which is combined with a Nikon optical microscope for beam delivery to the sample. The vibrometer delivers the measurement beam and the reference beam via a fiber optic link. An adjustment stage facilitates positioning and focusing of the measurement beam on the sample surface. The probing focused laser spot has a typical size of around 10  $\mu\text{m}$ ; the resolution is in the order of 2 pm and the frequency bandwidth varied between a few hertz to 10 MHz. Details of the experimental setup are described elsewhere.<sup>17-19</sup> All the results are summarized in Table II; the improvement of the properties by the introduction of (Ba, Sr) is clearly shown. The doped film permittivity increases but the value is lower than the value measured on bulk material (1100 and 1400 for, respectively, undoped and doped PZTs). The main reasons are well known: a little difference in material composition between the film and the bulk. The EDS measurements confirm these variations: the Ba and Sr contents in the films are, respectively, 4.7 mol % and 3.8 mol %, the grain size, the microstructure, and the existence of an interface between the film and the electrode which are constituted of a low dielectric constant material. An important result is, as expected, an improvement of the piezoelectric

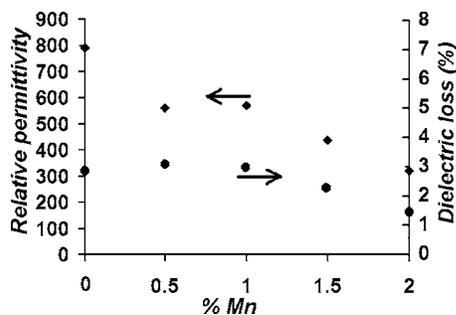


FIG. 2. Evolution of the relative permittivity and loss factor of the (Ba, Sr) PZT films as a function of the Mn content (in the target).

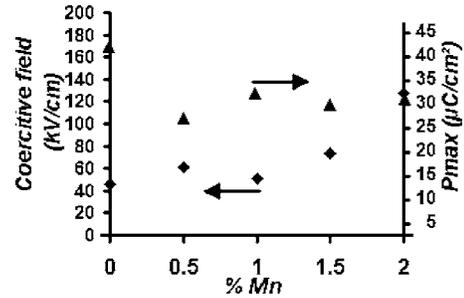
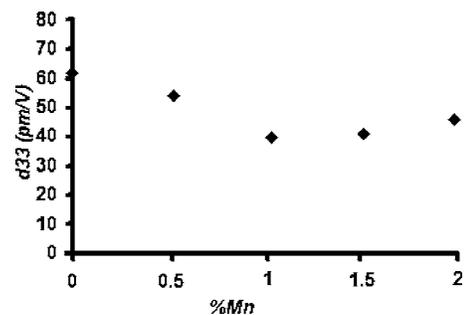


FIG. 3. Variation of the coercive field and the maximum polarization of the (Ba, Sr) PZT films as a function of Mn content (in the target).

activity of the (Ba, Sr)-doped PZT; the  $d_{33}$  coefficient varied from 47 to 60 pm/V for an undoped and a codoped material, respectively. Unfortunately, the introduction of (Ba, Sr) induces a decrease of the coercive field: 51–45 kV/cm for pure and doped PZTs, respectively. This behavior is in total contradiction with our main objective to fabricate hard PZT films. It is well known that the hardening effect on PZT bulk ceramics can be induced by the introduction of acceptor dopants such as Mn, Fe, Mg, etc. In this work we decide to introduce Mn atoms in the perovskite structure; the Mn content varied between 0.5% and 2%. Identical works are now in progress with Mg dopant, but it appears that the hardening effect is very important; for some Mg content we can not modify the dipole orientation. We will present these results in another paper.

## B. Electrical properties of Mn-doped (Ba, Sr) PZT films

The electrical properties of Mn-doped (Ba, Sr) PZT films are completely evaluated as well in terms of dielectric (Fig. 2), ferroelectric (Fig. 3), and piezoelectric (Fig. 4) performances. The introduction of Mn induces a decrease of  $\epsilon_r$  and  $\tan \delta$ ; this is the consequence of the preferentially  $180^\circ$  domain pinning. The evolution of the ferroelectric properties as a function of the Mn content is shown Fig. 3 for the coercive field ( $E_c$ ) and for the maximum polarization ( $P_m$ ). It is clear that the introduction of Mn induces a strong hardening effect of the material:  $E_c$  varied between 48 and 122 kV/cm for undoped and 2% Mn doped (in the target), respectively. The ferroelectric performance decreases rapidly with the introduction of Mn; without Mn,  $P_m$  is equal to 40  $\mu\text{C}/\text{cm}^2$  and for 0.5% of Mn,  $P_m$  is in the order of 25  $\mu\text{C}/\text{cm}^2$ . Above 0.5% (in the target),  $P_m$  is kept constant (around

FIG. 4. Evolution of  $d_{33}$  as a function of the Mn content (in the target).

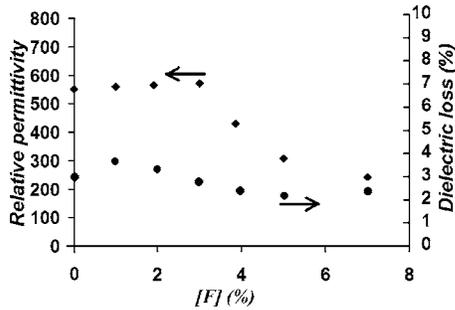


FIG. 5. Evolution of  $\epsilon_r$  and  $\tan \delta$  on (Ba, Sr) PZT-1% Mn-doped films as a function of F concentration in the target.

$25 \mu\text{C}/\text{cm}^2$ ). This degradation is the consequence of the hardening effect directly related to the pinning effect. A large decrease of the  $d_{33}$  coefficient is observed. Figure 4 shows the  $d_{33}$  variation with the Mn content. The  $d_{33}$  reaches a minimum value of  $30 \text{ pm}/\text{V}$  for a Mn content of 2% in the target.

In conclusion of this part of the study, we observe that the presence of very small quantity of manganese in the film (typically the EDS measurements show that 1% and 2% of Mn in the target correspond, respectively, to 0.08% and 1.5% in the films) induces a hardening effect of the material but the piezoelectric performances are largely affected. So, the Mn-doped (Ba, Sr) PZT material is not the solution to have a hardening material which presents important piezoelectric activity.

In order to have a hard material with good piezoelectric properties or more precisely to maintain the properties of the (Ba, Sr) PZT, we have introduced fluorine in substitution of oxygen in the Mn-codoped PZT. As we will see later, Mn dopant acts only as a hardener leading to a decrease of piezoelectric activities due to the pinning of domain walls by oxygen vacancies; (Mn, F) codoping both improve piezoelectric activities and stability versus external excitations. This original behavior seems to be linked to the Mn valency distribution in the structure and the dipole defect pattern controlled by the fluorine dopant. Fluorine would both allow several ionization degrees of Mn leading to electron exchange between them and the creation of (Mn, F) or (oxygen vacancy, F) dipole defects.<sup>10</sup> The electron exchange would increase the piezoelectric activities by modulating the polarization value within domains, whereas the dipole defects would limit the hysteresis and the nonlinearity.

### C. Electrical properties of (Mn, F)-codoped (Ba, Sr) PZT films

The fluorine concentration in the target varied between 1% and 7%. The variation of  $\epsilon_r$  as a function of the fluorine content in the target is shown in Fig. 5; the Mn concentration is fixed to 1%.  $\epsilon_r$  increases with F content and reaches a maximum value of 600 for a fluorine threshold concentration of about 1.5%, for higher values,  $\epsilon_r$  decreases. The  $\epsilon_r$  initial value [840 measured on (Ba, Sr) PZT] is not attained; the same behavior is observed for  $\tan \delta$  and the losses are maximum for the same F concentration. The ferroelectric properties are systematically evaluated; the results are shown in

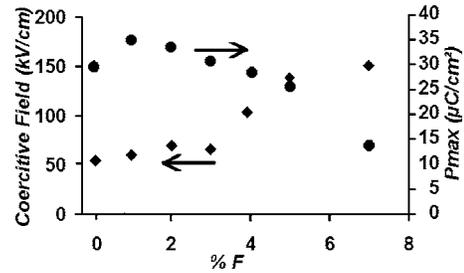


FIG. 6. Evolution of  $E_c$  and  $P_m$  as a function of fluorine content in the target.

Fig. 6. The introduction of small quantity of F (lower than 1%) enhances the maximum polarization. The coercive field varied rapidly with F content, and  $E_c$  varied between 50 and 150 kV/cm when the F content varied between 0% and 7%. So, the F content controls the hardening effect of the material. Figure 7, relative to the  $d_{33}$  evolution versus F content, shows that the best concentration of dopant is in the order of 1% and  $d_{33}$  is equal to  $70 \text{ pm}/\text{V}$ . This value of  $d_{33}$  is higher to this one initially obtained on (Ba, Sr) PZT film. This result is clearly the demonstration that it is possible to have a hard material without introducing a degradation of their piezoelectric performance. The pinning effect acts essentially on the  $180^\circ$  domain wall motion; so the electrical degradation is more pronounced on the dielectric properties rather than piezoelectric activity.<sup>20</sup>

The electrical evolutions are very sensitive to the F content in the films; a F content of 1% in the target corresponds approximately to 0.08% in the film (EDS measurement). The simultaneous substitution of Mn/F allows the creation of donor and acceptor sites and as a consequence the exchange of electrons between them which induces a decrease of the space charges accumulated at the domain wall. This decrease of the space charge density induces an increase of the domain wall mobility and so an improvement of the piezoelectric activity. Identical behavior and explanation have been observed for bulk ceramics;<sup>21</sup> this result is not surprising. The physical properties and their origin observed in bulk ceramics are also observed in thin film form. So, the properties of the bulk material can be considered as a reference.

We have found a PZT film composition for which it is possible to have simultaneously a good piezoelectric response and a hardening material; this composition is 1 mol % Mn-1 mol % F (6% Ba, 5% Sr). These values cor-

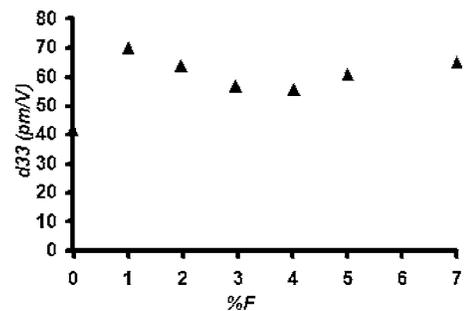


FIG. 7. Evolution of  $d_{33}$  as a function of F.

respond to the doping concentration in the target; in the films the content are lower due to the transfer function (typically 80%).

#### IV. CONCLUSION

In conclusion, this paper shows that the introduction of Mn/F on PZT [or more precisely on (Ba, Sr)-codoped PZT] is a solution to produce a “hard” material which presents good piezoelectric properties. This type of polar material is necessary for some MEMS applications where the environment is strong and could induce a depolarization of the material. The mechanism which can explain the results seems to be linked to the Mn valency distribution and the dipole defect pattern controlled by the fluorine dopant. Fluorine would both allow several ionization degrees of Mn leading to electron exchange and the creation of (Mn, F) or (oxygen vacancy, F) dipole defects. The electron exchange would increase the piezoelectric activities by modulating the polarization value within domains, whereas the dipole defects would limit the hysteresis and the nonlinearity. In thin film form, by using sputtering deposition with a single ceramic target (homemade), the best (Mn, F) doping level is (1%, 1%); these values correspond to the doping concentration in the target. These PZT thin films should open MEMS device applications in extreme environment.

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