Int. J. Nanoelectronics and Materials **3** (2010) 9-21

Lead free ferroelectric films deposited by sol-gel for electronic applications

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Abstract

Lead in electronic components is prohibited by the RoHS directive since july 2006. Nevertheless, there are some exceptions for example $PbZr_XTi_{1-X}O_3$ (PZT) materials because they present exceptional piezoelectric properties. PZT is used as sensors and actuators in numerous applications such in sonar, echography, alarm, etc…Up to now, neither in ceramic form nor in film form, it have been surpassed by lead free materials. At present, many studies are devoted to find a substitute to PZT as it will be probably banned in five years or so. Our work is in this objective and concerns the study of the electrical properties at low frequency, from DC to 1MHz, of ferroelectric films with thickness inferior or equal to 1µm. The starting material is $BaTiO_3$ in which Ba is exchanged by Sr at different levels and also doped with various cations (monovalent, divalent, trivalent…). This permits us to improve the dielectric and ferroelectric properties: for example to decrease the losses and to increase the tunability. Another method to optimize the electrical properties is to study the annealing conditions: very high temperature applied a short time (950°C@15mn) should be favoured. This leads to both higher dielectric constant and polarization. The pyroelectric and piezoelectric coefficients have also been improved but as concerns the

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piezoelectric performance, our lead free films are still inferior to the PZT one. Further optimization is needed.

Keywords: Ferroelectrics, Thin films, Lead free, Sol gel.
PACS: 77.22-d, 77.22.Gm, 77.84-s, 77.84.Dy, 81.20.Fw.

1. Introduction

The RoHS European directive (Restriction on Hazardous Substances) has prohibited lead in electric and electronic applications since july 2006. However lead oxide based ferroelectrics materials are still used for their superior piezoelectric properties, but in the near future, they will be banned. In fact they are mainly used for sensors, actuators and transducers. The most popular lead oxide material is $Pb(Zr,Ti)O_3$, a lead zirconate titanate (PZT). It is used in ceramic and film forms which depends upon the application. The search to find an alternative to PZT began before the RoHS directive, but that mainly concerns the ceramic form. To the best of our knowledge, up to now, no lead free ferroelectric ceramic has superior or even equal piezoelectric performances to PZT. Nevertheless, interesting results have been achieved with different families such alkaline niobates, bismuth titanates and their derivatives [1]. Usually these materials are doped and so their chemical compositions are quite complex [2]. Then, it is difficult to deposit them in film form. In this view, we have deposited ferroelectric films with a simple chemical formula, doped and non doped in order to optimize their electrical properties. The starting material is the well-known $BaTiO_3$ in which we have substituted some barium and/or titanium atoms by other ones. $BaTiO_3$ is interesting in view of electronic applications as its Curie Temperature T_C is above 100 °C and could be decreased by the substitution of Ba or Ti ions. The objective of this study being the realization of electronic components such as sensors with a low cost, we have used a sol-gel deposition process on silicon substrates. Then, we have improved the electrical properties of the films by varying the annealing conditions.

2. Material

The materials synthesized in this study were deposited on various substrates by a classical sol-gel process [3]. Barium and strontium acetates were used as starting material in order to deposit $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films. The dopants such as bismuth, magnesium, manganese, potassium and tin were added also as acetates but in low concentration from 2.5% to 10% (molar) and dissolved in acetic acid. Titanium isopropoxide is then added to obtain the precursor solution. After dissolution, ethylene glycol was added as proposed by Adikary et al. [4]. The solution is then spin-coated on a substrate by a spinner at 3000 rpm during 30s. After that, the sample is heated 30s on a hot plate at 350°C to evaporate the solvent. These operations are repeated 15 times to obtain a film with a thickness of about 500nm. At last, the film is annealed in air at 750°C during 1h in order to crystallize in the perovskite phase [5]. For electrical characterizations, gold pads have been evaporated through a shadow mask to realize the upper electrode with diameter ranging from 150µm to 2mm. The bottom electrode is in platinum deposited on silicon substrates. Alternatively, we also used other substrates such as steel, sapphire, MgO and bare silicon.

Numerous films have been deposited to this work in order to study their electrical properties as a function of the doping both in the ferroelectric state and in the paraelectric one:

- Ferroelectric films: $Ba_{0.9}Sr_{0.1}TiO_3$, (BST90/10) in which strontium atoms replace barium in A site and $BaSn_{0.02}Ti_{0.98}O_3$ (BTS) in which tin replaces titanium in B sites. The electrical properties will be optimized and compared with those of PZT films.
- Paraelectric films: $Ba_{0.5}Sr_{0.5}TiO_3$ (BST50/50) which is paraelectric at ambient temperature. These films were doped with Bi, Mg, Mn in A site [6] and K in B site [7] in order to decrease the losses in radiofrequencies and to increase the tunability.

The films were characterized by X-ray diffraction (XRD) using a RIGAKU Miniflex$^+$. The morphology of the films was determined with a Scanning electron microscope (SEM) LEO438VP. The thickness of the film was measured with a TALYSURF INTRA 150

profilometer. The dielectrical properties were determined in low frequencies (20 Hz - 1 MHz) with an HP4284A impedance analyzer and in high frequencies (10 MHz - 60 GHz) with a vectorial network analyzer E8364A-PNA as a function of a DC bias from – 40 volts to +40 volts. Pyroelectric and piezoelectric properties were determined with home made set-up.

3. Influence of the doping

The study of the doping of the paraelectric BST50/50 film at room temperature is in view of electronic applications in radiofrequencies and microwaves. The main properties to be tested are: the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ with the loss tangent $tg\delta = \varepsilon''/\varepsilon'$ and the tunability n_r which is the relative variation of the dielectric constant ε' as a function of a DC voltage V such as $n_r = 1 - \varepsilon'(V)/\varepsilon'(0)$. The surface morphology and cross-section of an undoped BST50/50 film are shown on figure 1. The film is relatively dense, smooth and without cracks. It is polycrystalline with a mean size of the grains of about 50 nm. This grain size decreases slightly when doping with Mn and Mg whereas it increases with Bi and K doping. This is in relation with the size of the corresponding ions: Mn^{2+} and Mg^{2+} are smaller mthan K^+ and Bi^{3+}. The thickness of the film is about 250 nm.

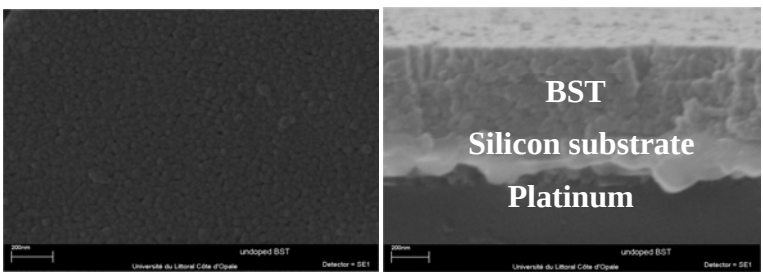

Fig.1: SEM photography of $Ba_{0.5}Sr_{0.5}TiO_3$ thin film

The dielectric constant and the loss tangent of the undoped and the doped films are given in figure 2 as a function of frequency at room temperature. For all the films, ε' shows a small decrease with frequency up to 1 MHz. This dispersion in low frequency is usually

ascribed to the existence of oxygen vacancies, impurities and grain boundaries [8]. It can be seen that although the doping level is small (5 mol%) the effect on the dielectric constant is to decrease ε' whatever the dopant. It is admitted that the value of the dielectric constant is strongly affected by the microstructure and the grain size [9]. We think also, that in our case, the effect of the dopants is to reduce the polarization associated with the oxygen vacancies. The formation of non ferroelectric phases such as oxides can also largely reduce ε'. This is probably the case with the doping with Mg giving MgO as ε' at 1 MHz is only 110 which is 2.5 times less than the undoped film value. However this smaller value of ε' is favourable in perspective of applications in microwaves.

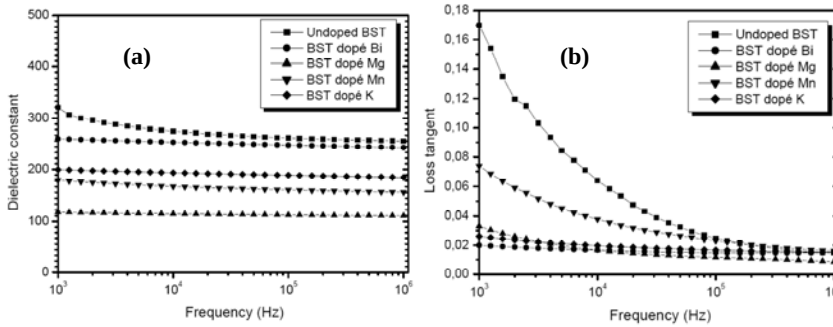

Fig. 2: Dielectric constant (a) and loss tangent (b) of undoped and 5% mol. doped $Ba_{0.5}Sr_{0.5}TiO_3$ thin films.

As concern the losses, they are smaller for all the doped films than for the undoped ones (see figure 2b). This confirms our hypothesis of the decrease of the oxygen vacancies number in the doped films. The smallest loss tangent is obtained with the Mg doped film: for example $tg\delta = 8 \times 10^{-3}$ at 1 MHz. This value is encouraging for RF and microwaves applications as it is known either from a theoretical point of view [10] or from an experimental one [11] that the losses increase as a function of frequency from the MHz frequencies up to the THz frequencies.

The tunability n_r of all the films has been determined from the measurement at low frequency of C(V), the capacitance of planar

capacitors as a function of the DC voltage applied. The C(V) curves measured at 1MHz are presented in figure 3a. The corresponding tunability versus the applied DC electrical field is given in figure 3b. It can be seen that the doping with K gives the highest tunability: typically n_r = 36% with a DC field of 20 V/µm. This could be linked to the grain size of the film [12]: this will be confirmed in the following paragraph. On the other hand, the lower tunability with Mn or Mg doping could be linked to the existence of non ferroelectric phases, for example oxides phases such as MgO (with Mg doping), MnO_2 and Mn_2O_3 (with Mn doping).

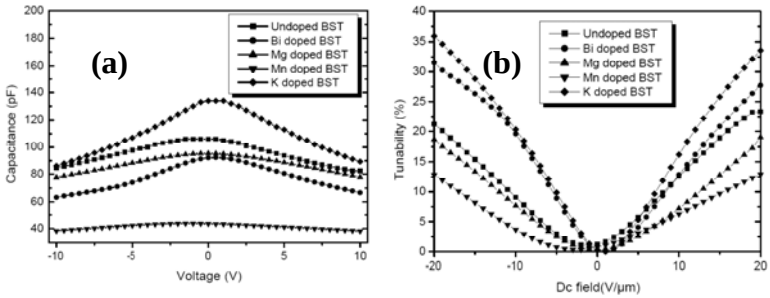

Fig. 3: C(V) curves (a) and tunability (b) at 1MHz of undoped and doped BST50/50 films.

4. Influence of the annealing

The study concerns both the ferroelectric and the paraelectric states. Here we have studied $Ba_{0.9}Sr_{0.1}TiO_3$ (BST90/10) films which are ferroelectric at room temperature. The objective is also to compare the electrical properties with lead based PZT films of composition $PbZr_{0.5}Ti_{0.5}0_3$ also ferroelectric at room temperature. All the films were deposited by sol-gel on platinized silicon substrates of the same commercial batch (CRYSTAL GmbH).

4.1 Annealing temperature

BST90/10 thin films were annealed at 3 temperatures: 750°C, 850°C and 950°C during 1 hour in air. From XRD, it can be said that the films are all polycrystalline with a (111) preferential orientation

which is the orientation of the platinum electrode. From SEM, the surface is smooth without cracks: the mean size of grains increased with the annealing temperature from 60 nm at 750°C to 110 nm at 950°C. The thickness of the films is about 400 nm. In figure 4, We give 3 annealing temperatures, and the evolution in low frequency of the dielectric is constant and there is a sign of loss tangent. It can be seen that ε' increases with the annealing temperature: for example at 1 MHz, ε'= 330 at 750°C and ε'= 520 at 950°C. This is in link with the size increase of grains, in agreement with B. Malic et al. [13]. Concerning the losses, tgδ is very close for the 3 films at frequencies higher than 10 kHz: at 1 MHz, tgδ is inferior to 0.01. So, from the dielectric results, the optimum temperature is 950°C. As the dielectric constant increases, the tunability also increases: 30% at 750°C, 35% at 850°C and 60% at 950°C for a DC field of 12 V/µm. This is also linked to the increase of the grain size.

We have made several measurements and simulations in the paraelectric state, at t= +100°C, which showed that the increase of the tunability follows the model of Ginzbourg-Landau-Devonshire [14]. The tunability is characterized by $C_3*\varepsilon'(0)^3$ were C_3 is a constant. In our case, $C_3*\varepsilon'(0)^3$ increases from 1.26 x 10^{18} m^5/C^2F with an annealing temperature of 750°C to 4.4 x 10^{18} m^5/C^2F at 950°C.

In the same way the hysteresis cycle increases drastically with the annealing temperature. This is shown figure 5 on the polarization curves measured at 1 kHz versus the DC electrical field.

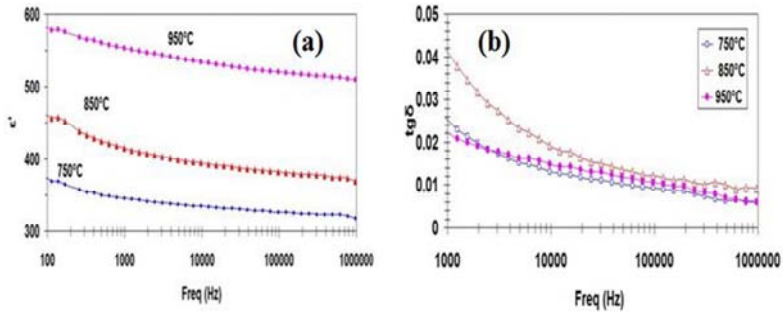

Fig. 4: Dielectric constant (a) and loss tangent (b) for BST90/10 thin films annealed at 750°C, 850°C and 950°C

It can be noticed that these curves show that the BST90/10 films are in the ferroelectric state. The remanent polarization P_r is 1 μC/cm^2 at 750°C and increases to 4.2μC/cm^2 at 950°C (see figure 5b). This is certainly linked to the increase of the grain size.

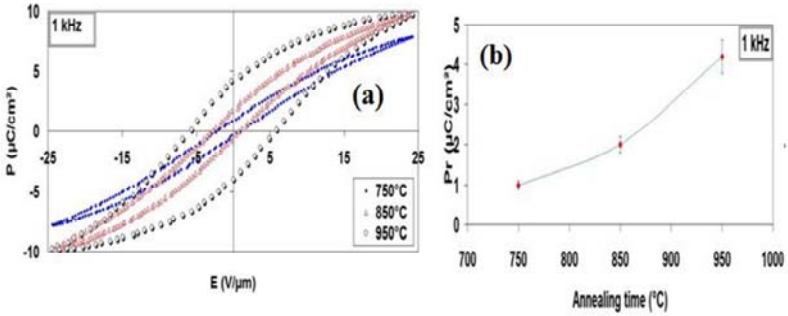

Fig. 5: Hysteresis cycle (a) and remanent polarization (b) at 1kHz for BST90/10 thin films annealed at 750°C, 850°C and 950°C during 1 hour.

4.2 Annealing duration

The duration of the annealing was varied from 15 min to 60 min at the optimized temperature of 950°C. It can be noted that the mean grain size of the films remains constant at about 110 nm. However the dielectric constant increases largely when the annealing duration decreases as shown on figure 6. At 20°C@10kHz, ε' increases from 560 to 710 and to 780 for an annealing duration of 60 min, 30 min and 15 min, respectively. This increase of ε' is not due to an increase of the intrinsic polarization of the BST material but probably to a decrease of the non ferroelectric "dead layer" effect when the duration decreases. The measurement of the dielectric constant up to 110°C shows that the ferroelectric to paraelectric transition is at about 70°C. This Curie temperature is lower than the corresponding BST90/10 ceramic one which is 84°C [14]. Studies on ceramics have shown that a lower grain size can induce a lower Curie temperature [15, 16]. This behaviour has been also observed on $KNbO_3$ powders with different particle sizes [17]. So, the shift of the phase transition at T_c observed on our film can be attributed most probably to the grain size and the domains' structure. On the other hand, strains and

essentially compressive strain that could be considered here, are generally reported to contribute to an increase of the transition temperature [18, 19], whereas it was shown that T_c can decrease with tensile stress in the films [20]. Another effect is that the dielectric constant of films in the ferroelectric state is quite constant up to T_C = 70°C. This difference with ferroelectric ceramic behaviour is very interesting in view of realizing electronic components such as sensors.

As concerns the tunability, there is a small decrease from 60% to 55% when the annealing duration at 950°C decreases from 60 min to 15 min. At present this variation is not well understood. The hysteresis cycle evolves in the opposite manner: it increases when the annealing duration decreases. Then, the remanent polarization P_r = 4.2 μC/cm^2 with 60 min of annealing increases to 5μC/cm^2 with only 15 min of annealing. This increase is in relation with the decrease of the dead layer effect as the electric field is only applied to the ferroelectric film in this case.

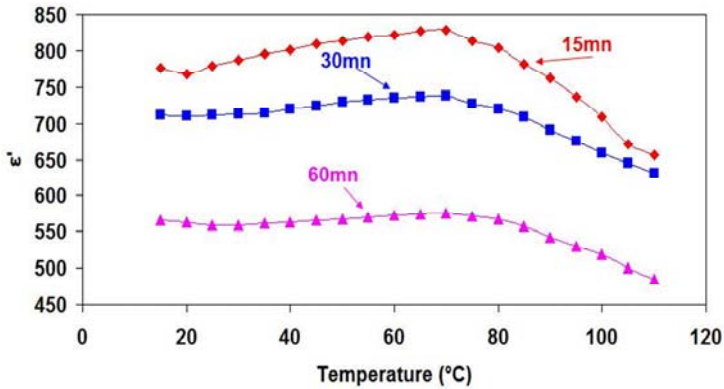

Fig. 6: Thermal evolution of the dielectric constant at 10 kHz of BST90/10 films annealed at 950°C for different annealing durations.

In the ferroelectric state, contrary to the paraelectric state, it is possible to test the pyroelectric and piezoelectric properties: this is important to realize sensors and actuators. The pyroelectric coefficient γ has been determined from the measurement of the pyroelectric current I_p following the Bayer-Roundy method [21] leading to $\gamma = I_p dt/SdT$ (S=electrode area; dT/dt=rate of change of the temperature). We have obtained a value $\gamma = 3.4 \times 10^{-4}$C/m^2/K for a

BST90/10 thin film annealed at 950°C during 15 min. This value is the same as the one obtained with a Mn doped PZT film [22]. It is encouraging in view of realizing an infrared sensor as the figure of merit of this type of sensor is proportional to γ. The piezoelectric properties are determined by tensors with terms d_{ij}. In the case of our BST90/10 films which have a tetragonal crystalline structure, the piezoelectric matrix is mainly characterized by the terms d_{31} and d_{33}. We have developed a set-up to measure d_{33} with a modified method proposed by Lefki et al. [23]. It consists in applying a variable force on the film to measure the resulting electrical charge. For a BST90/10 film of thickness 1µm we have obtained at room temperature d_{33} = 19 pC/N. This value is low compared with 100 pC/N obtained from the same measurement method for a PZT film [24]. In the following table we compare at room temperature the dielectric and the ferroelectric properties obtained in this work with BST90/10 and PZT films of the same thicknesses (400 nm) and deposited on the same platinized silicon substrate.

Table 1: The dielectric and the ferroelectric properties obtained in this work with BST90/10 and PZT at room temperature

	ε' @ 1MHz	tgδ @ 1MHz	Pr (µC/cm²)	E_c (V/µm)	Tunability @12V/µm
BST90/10	830	0.015	5	4.3	55%
PZT	950	0.05	15	5	53%

The BST90/10 film optimized by an annealing at 950°C during 15 min exhibits electrical properties comparable to the PZT film except for the remanent polarization P_r which is 3 times less for the BST film. It has been shown recently on a BST50/50 ceramic doped with 20% of tin that the value of P_r could be doubled [25]. So we began to dope a $BaTiO_3$ film with a low level of tin (2 mol%) to obtain $BaSn_{0.02}Ti_{0.98}O_3$ (BTS). In this case, we did not observe a modification of P_r but a drastic increase of the tunability up to 76% for an electric field of 12V/µm. In fact, the film capacitance has varied by a factor 4 with a DC voltage of only 4.8 volts. This can be used in electronic components agile in radiofrequencies such as filters, antennas, phase shifters, etc... A drawback with a doping using tin is that the Curie temperature is largely shifted towards low

temperature: with our BTS film, T_C = 70°C. That is why we did not dope $BaTiO_3$ films with higher levels of tin.

5. Conclusion

Ferroelectrics are very interesting materials for applications in electronic, in particular the BST family. We have shown that by doping it is possible to improve their electrical properties namely dielectric, ferroelectric, pyroelectric and piezoelectric. This need a systematic study of many dopants and of the doping level in view of the application aimed. Another improvement of the electrical properties is to optimize the annealing conditions: we have found that the increase of the temperature up to 950°C during a short time, typically 15 min, has a favourable effect on the dielectric and ferroelectric properties. For the radiofrequencies and microwaves applications, the BST films should be in the paraelectric state and doped with Mg: they are good candidates as the loss tangent may be as low as 8.10^{-3} at 1 MHz. As concerns applications requiring high tunability, doping with K should be favoured. For the applications in DC or in low frequencies such as infrared sensors the BST should be in the ferroelectric state. A doping with a very low level of tin gives a high yield of usable films and a good reproducibility of their electrical properties. Finally the electrical properties of our optimized lead free ferroelectric films are comparable to those of PZT ones, except for the piezoelectric and ferroelectrics performances. Work is in progress at present to deal with this problem.

Acknowledgements

We would like to thank ADEME and the Conseil Régional Nord-Pas de Calais for giving a grant to one of us (M. Mascot). P. Belleville from CEA Le Ripault (France) is also thanked for the deposition of PZT films by sol-gel.

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