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# Preparation and dielectric properties of compositionally graded lead barium zirconate thin films

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ABSTRACT

Both up and down compositionally graded $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) thin films with increasing $x$ from 0.4 to 0.6 were deposited on Pt(1 1 1)-buffer layered silicon substrates through a sol–gel method. The microstructure and dielectric properties of graded PBZ thin films were investigated systemically. X-ray diffraction patterns confirmed that both PBZ films had crystallized into a pure perovskite phase after annealed 700 °C. Electrical measurement results showed that although up graded films had a slightly larger tunability, dielectric loss of down graded films was much lower than that of up graded films. Therefore, the figure of merit of down graded PBZ films was greatly enhanced, as compared with up graded films. Moreover, down graded PBZ thin films also displayed excellent temperature stability with a smaller temperature coefficient of capacitance (TCC) of $-0.59 \times 10^{-3}\,°C^{-1}$ from 20 °C to 80 °C.

## 1. Introduction

Over the last few decades, because of the rapid development of integrated microelectronic devices, there is an urgent need of nonlinear dielectric materials for tunable applications, such as phase shifters, tunable filters, and voltage controlled oscillators. In order to meet the requirement in practice, materials with large tunability, small dielectric loss, enhanced figure of merit (FOM) and good temperature stability, are generally desired. Among the numerous candidates, ferroelectric (FE) thin films with perovskite structure, such as $(Ba,Sr)TiO_3$ (BST) and $Ba(Zr,Ti)O_3$ (BZT), are considered to be the foremost ones and thus have been investigated extensively [1–4]. However, it was found that the oxidation state of titanium ions in these films was easily reduced from +4 to +3 at higher temperature [5]. As a result, the dielectric properties of titanium contained films usually encountered degradation under higher temperature and higher external electric field. Therefore, a kind of tunable dielectric materials without titanium ions would be more favorable.

Recently, it was reported that titanium excluded perovskite $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) materials with higher barium content above 45 mol% were in paraelectric state at room temperature, which possessed excellent dielectric properties comparable to BST and BZT and thus had the potential application in tunable devices [6,7]. In order to optimize the final dielectric properties of PBZ thin films, effects of chemical constituent, nonstoichiometric doping and bottom electrodes on the electrical performance have been investigated in detail [8–11]. However, all of these studies were focused on the compositionally uniform films. In fact, films with compositionally graded structure often displayed improved nonlinear dielectric properties, such as lower dielectric loss, larger dielectric tunability and smaller temperature coefficient of capacitance. And quite a few papers on compositionally graded BZT and BST thin films have been reported [12–15]. But, to the best of our knowledge, compositionally graded PBZ thin films are still not investigated up to now.

Hence, in this work up and down graded $(Pb_{1-x}Ba_x)ZrO_3$ ($x = 0.4$, 0.5 and 0.6) thin films with respect to the substrates were fabricated via a sol–gel technique. And structure and dielectric properties of graded PBZ thin films were explored. It was found that the final dielectric properties of films were strongly dependent on the gradient sequence of the composition.

## 2. Experimental procedures

Three precursor solutions of $(Pb_{1-x}Ba_x)ZrO_3$ with $x = 0.4$, 0.5 and 0.6 were prepared by the sol–gel method. Barium acetate, lead acetate trihydrate and zirconium isopropoxide were used as starting materials. Glacial acetic and deionized water were used as solvents. More detailed synthesis procedure of the sol could be found in our recent work [16]. The final concentration of each sol was 0.2 M. After aged 24 h of the sol, graded PBZ thin films were obtained by sequentially depositing four layers of each composition onto Pt(1 1 1)/$TiO_2$/$SiO_2$/Si(1 0 0) substrates. Each PBZ

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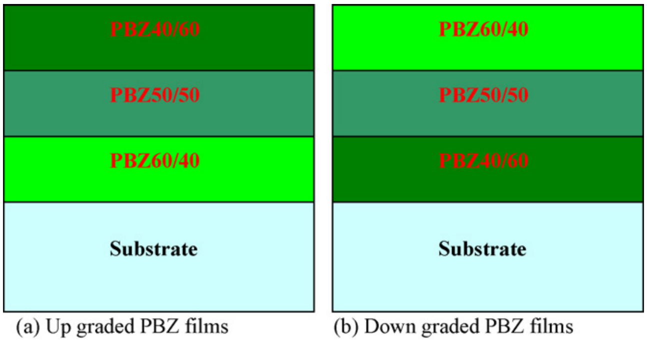

**Fig. 1.** The schematic diagrams of up (a) and down (b) graded PBZ thin films.

layer was spin-coated at 3000 rpm for 20 s and pyrolyzed at 450 °C for 10 min. The spin-coating and heat-treatment were repeated twelve times to obtain the desired thickness. A capping layer of 0.2 M PbO precursor solution, which was prepared from lead acetate trihydrate, was added before the films went through a final anneal at 700 °C for 30 min to form the perovskite phase. This capping layer served the purpose of preventing excessive lead loss, thereby ensuring the formation of a single perovskite phase. The final thickness of both graded PBZ thin films was about 250 nm. For convenience, PBZ films with Pb–Ba ratio varying from $(Pb_{0.6}Ba_{0.4})ZrO_3$ at the Pt bottom electrode to $(Pb_{0.4}Ba_{0.6})ZrO_3$ at the top surface were named “up graded” PBZ films, whereas films with opposite gradient composition were called “down graded” films. The schematic diagrams of both up and down graded PBZ thin films are given in Fig. 1.

The phase structure of graded PBZ films was investigated by using X-ray diffractometer (XRD Bruker D8 Advance diffractometer). For electrical measurements, gold pads 0.50 mm in diameter as top electrodes were coated onto the film surface by dc sputtering. The dc electric-field and temperature-dependent dielectric properties were measured by a computer controlled TH2828 *LCR* analyzer (Tonghui Electronic, China) at 100 kHz with an AC drive amplitude of 50 mV.

## 3. Results and discussion

Fig. 2 gives the XRD patterns of up and down graded PBZ thin films after annealed at 700 °C for 30 min. It is evident that films in both cases display a polycrystalline cubic perovskite phase with a random orientation. There is no evidence of secondary phase formation, as no peaks other than (1 0 0), (1 1 0), (1 1 1), (2 0 0), and (2 1 0) peaks of PBZ films are detected. It is also revealed that no obvious difference in the texture is found in both cases.

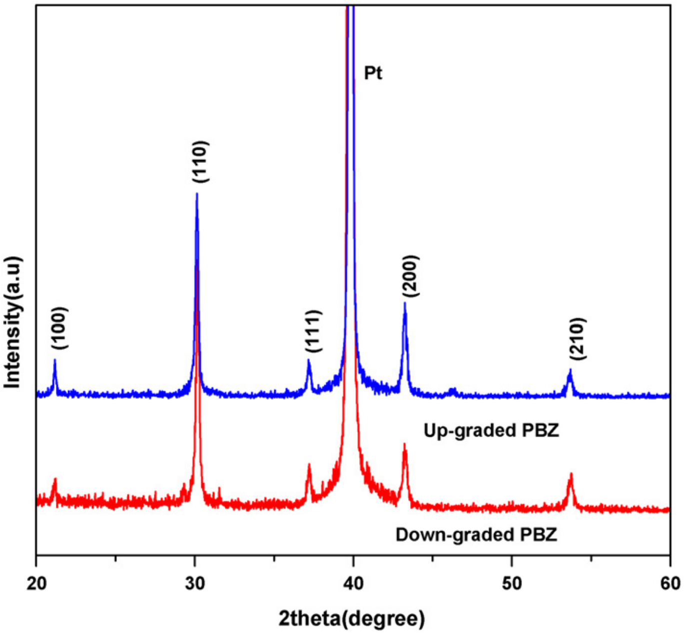

**Fig. 2.** XRD patterns of up and down graded PBZ thin films.

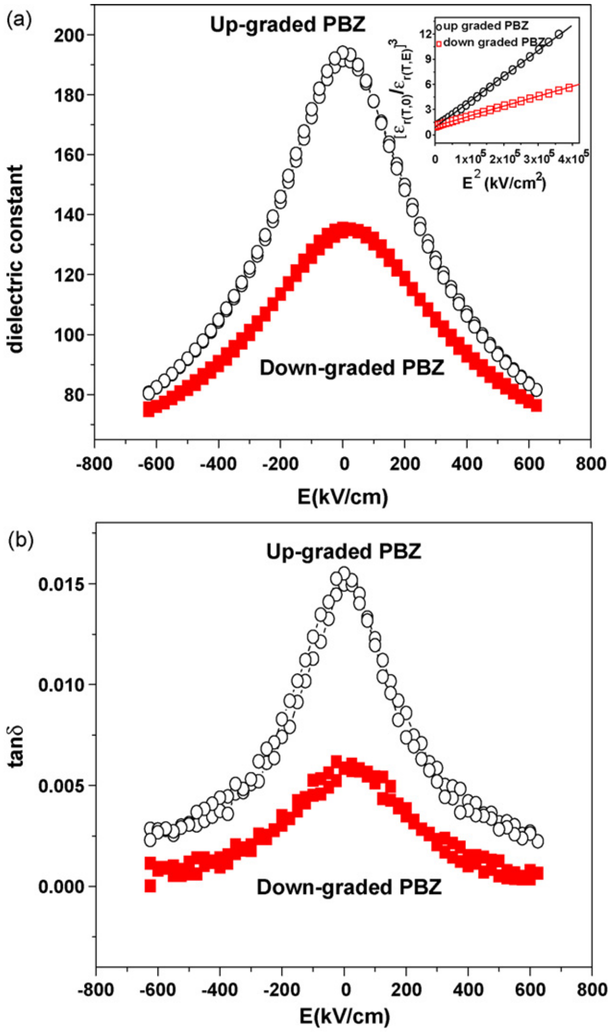

**Fig. 3.** Room temperature electric-field dependence of dielectric constant (a) and dielectric loss (b) of up and down graded PBZ thin films.

The dc electric-field-dependent dielectric constant ($\varepsilon_r$–$E$) and dielectric loss curves of up and down graded PBZ thin films are shown in Fig. 3, which were measured at 100 kHz and at room temperature. It could be found from $\varepsilon_r$–$E$ curves that up graded PBZ thin films have larger dielectric constant, as compared with down graded films. For example, dielectric constant at zero field and at room temperature is 194 and 135, respectively, for up and down graded films. Furthermore, it is seen from Fig. 3(a) that variation of dielectric constant follows the same tendency for up and down graded PBZ films, and that the values are gradually decreased with electric-field increasing. The nonlinear characterization of $\varepsilon_r$–$E$ curves could be explained by phenomenological theory proposed by Johnson. Based this theory, in the case of $\varepsilon_r \gg 1$, the relationship between dielectric constant and the applied electric-field for perovskite-structure ferroelectric materials in paraelectric state was expressed as follows [17,18]:

$$\varepsilon_{r(T,E)} = \frac{\varepsilon_{r(T,0)}}{[1+\varepsilon^3_{r(T,0)}\alpha_{(T)}E^2]^{1/3}}, \tag{1}$$

where $\alpha_{(T)}$ was the temperature-dependent constant which provided the information on the degree of anharmonic contributions of the polarization to the free energy, and $\varepsilon_{r(T,0)}$ and $\varepsilon_{r(T,E)}$ were the dielectric constant at temperature $T$ without and with applied electric-field $E$, respectively. Thus, according to this equation, the

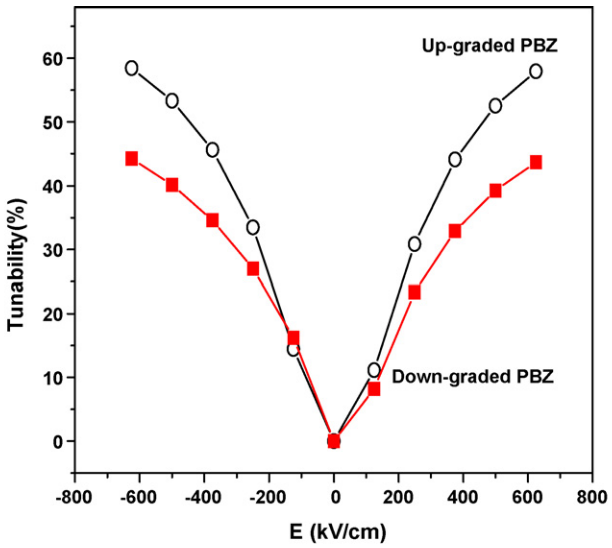

**Fig. 4.** Room temperature tunability as function of electric-field for up and down graded PBZ thin films.

maximum values of dielectric constant for ferroelectric materials in paraelectric state are obtained at zero electric-field. If a filed coefficient was defined as $b = \varepsilon_{\mathrm{r}(T,0)}^{3}\alpha_{(T)}$, Eq. (1) could be re-written as a linear equation about $[\varepsilon_{\mathrm{r}(T,0)}/\varepsilon_{\mathrm{r}(T,E)}]^3$ and $E^2$:

$$\left(\frac{\varepsilon_{\mathrm{r}(T,0)}}{\varepsilon_{\mathrm{r}(T,0)}}\right)^3 = 1 + bE^2. \tag{2}$$

Here, field coefficient $b$ represents the strength of dielectric nonlinearity. According to Eq. (2), the experimental data are well fitted by linear fitting, as shown in the inset of Fig. 3(a). From the fitting parameters, the obtained values of $b$ are $3.048 \times 10^{-5}\,(\mathrm{cm}^2/\mathrm{kV}^2)$ and $1.187 \times 10^{-5}\,(\mathrm{cm}^2/\mathrm{kV}^2)$ for up and down graded PBZ films, respectively. And the corresponding $\alpha_{(T)}$ is $4.341 \times 10^{-12}\,(\mathrm{cm}^2/\mathrm{kV}^2)$ and $4.766 \times 10^{-12}\,(\mathrm{cm}^2/\mathrm{kV}^2)$. Larger $b$ value for up graded films indicates a stronger strength of dielectric nonlinearity, thus the dielectric constant is easier to be reduced by external electric-field. Whereas, bigger $\alpha_{(T)}$ value for down graded films means the increase in anharmonic contributions of the polarization to the free energy.

As shown in Fig. 3(b), the variation of electric-field-dependent dielectric loss curves for both graded films display the similar manners, just as $\varepsilon_\mathrm{r}$–$E$ curves. Obviously, the maximum values of dielectric loss are also obtained at zero electric-field. Moreover, it could be found that dielectric loss of down graded PBZ film is greatly declined, as compared with up graded films. For example, the dielectric loss at zero electric-field is 0.0155 and 0.006 for up and down graded films, respectively. Thus, these results indicate that the final dielectric properties of graded ferroelectric films could be optimized by selecting a proper deposition sequence.

The electric-field dependent-tunability ($T$) results of up and down graded PBZ thin films are displayed in Fig. 4. $T$ is defined as $[\varepsilon_{\mathrm{r}(T,0)} - \varepsilon_{\mathrm{r}(T,E)}]/\varepsilon_{\mathrm{r}(T,0)}$, where $\varepsilon_{\mathrm{r}(T,0)}$ and $\varepsilon_{\mathrm{r}(T,E)}$ are defined as before [19]. As expected, the tunability for both graded films is increased with electric-field increasing. The tighter tunability curve for up graded films implies enhanced tunable ability at the same applied field in contrast to down graded films. For example, the tunability at 625 kV/cm is 58% and 44% for up and down graded PBZ thin films, respectively. The higher dielectric tunability for up graded films is contributed to its bigger dielectric constant. This phenomenon can also be explained by Johnson phenomenological theory. According to Eq. (1) and definition of $T$, $T$ could be written as:

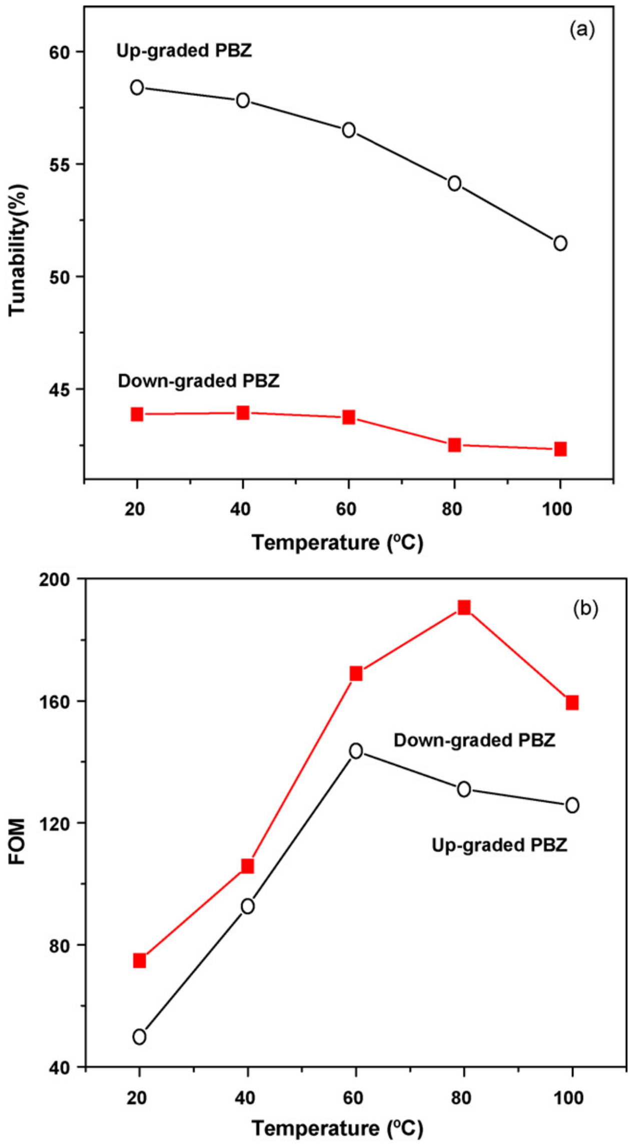

**Fig. 5.** Temperature-dependent tunability (a) and FOM values (b) of up and down graded PBZ thin films.

$$T = 1 - \frac{1}{[1 + \varepsilon_{\mathrm{r}(T,0)}^{3}\alpha_T E^2]^{1/3}}. \tag{3}$$

Clearly, this equation illustrates that higher dielectric constant at $E = 0$ could lead to larger $T$ values. Here, it should be noted that although up graded PBZ films have an elevated tunability in contrast to down graded films, the tunability of down graded films is still higher enough to meet the practical applications.

Fig. 5(a) presents the temperature-dependent tunability curves of up and down graded PBZ thin films, which were measured at 625 kV/cm and at 100 kHz. As the increase of measurement temperature, the tunability for both graded films is declined step by step. As the temperature increasing from 20 °C to 100 °C, the tunability of up graded PBZ thin films is reduced from 58% to 51%, whereas the tunability of down graded films is decreased from 44% to 42%. Thus, this result implies that the down graded PBZ thin films have better temperature stability in contrast to up graded films. The good temperature stability of down graded films is always desired in practical application. In order to evaluate the overall dielectric

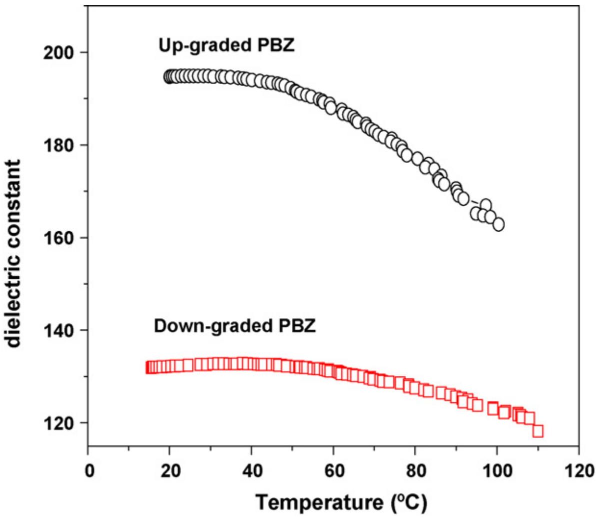

**Fig. 6.** Temperature-dependent dielectric constant of up and down graded PBZ thin films.

performance of graded PBZ films, the figure of merit (FOM), defined as $T/\tan\delta_{(T,0)}$, is introduced [20]. Fig. 5(b) shows FOM values, which was also obtained in the temperature range of 20–100 °C. Clearly, in the whole measurement range, down graded PBZ thin films possess larger FOM values, compared with up graded films. For example, FOM values at 20 °C are 37 and 76 for up and down graded films, respectively. The elevated FOM values for down graded films attribute to its smaller dielectric loss, although its tunability is slightly lower than that of up graded films.

Fig. 6 shows the temperature-dependent dielectric constant curves of up and down graded PBZ films, measured at 100 kHz and on heating process. As expected there is no obviously steep change occurring in the measurement range. With temperature increasing, dielectric constant in both cases is decreased gradually. And the temperature-dependent dielectric constant of down graded PBZ films displays a flatter profile, indicating a better stability over a wide temperature range. For giving a quantitative comparison, the temperature coefficient of capacitance (TCC), defined as $\mathrm{TCC} = \Delta\varepsilon/(\varepsilon_0 \Delta T)$ is introduced, where $\Delta\varepsilon$ is the change in dielectric permittivity with respective to $\varepsilon_0$ at 20 °C and $\Delta T$ is the change in temperature relative to 20 °C [21]. According to this equation, the calculated TCC values in the temperature range from 20 °C to 80 °C are $-1.52 \times 10^{-3}\,{}^{\circ}\mathrm{C}^{-1}$ and $-0.59 \times 10^{-3}\,{}^{\circ}\mathrm{C}^{-1}$ for up and down graded PBZ thin films, respectively. The smaller TCC value further demonstrates that down graded PBZ films possess better temperature stability, compared with up graded PBZ films. It was reported that TCC value for graded BST and BZT films was $0.92 \times 10^{-3}\,{}^{\circ}\mathrm{C}^{-1}$ and $1.20 \times 10^{-3}\,{}^{\circ}\mathrm{C}^{-1}$, which was measured at similar condition as present work [15,21]. Thus, this result means that the temperature-dependent stability of down graded PBZ films is also superior to that of extensively studied graded BST and BZT films.

## 4. Summary

In present work, compositionally graded $(\mathrm{Pb}_{1-x}\mathrm{Ba}_x)\mathrm{ZrO}_3$ thin films with a pure perovskite structure were prepared by the sol–gel technique. As compared with up graded PBZ films, down graded films showed a very lower dielectric loss and displayed an acceptable tunability. Thus, FOM values of down graded PBZ films were improved greatly. Moreover, down graded films also possessed smaller temperature coefficient of capacitance ($-0.59 \times 10^{-3}\,{}^{\circ}\mathrm{C}^{-1}$) than up graded PBZ films ($-1.52 \times 10^{-3}\,{}^{\circ}\mathrm{C}^{-1}$), indicating enhanced temperature stability. It is therefore concluded that down graded PBZ thin films are more likely to be used in tunable devices.

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