Materials Research Bulletin 44 (2009) 2152–2154

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Short communication

# Sol–gel derived PZT films doped with vanadium pentoxide

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ARTICLE INFO

*Article history:*
Received 4 July 2009
Accepted 7 July 2009
Available online 15 July 2009

*Keywords:*
B. sol-gel chemistry
C. X-ray diffraction
D. dielectric properties
D. ferroelectricity

ABSTRACT

The present research investigated the sol–gel preparation, dielectric and ferroelectric properties of PZT films doped with 5 mol% vanadium oxide. Stable PZTV sols can be readily formed, and homogeneous, micrometer thick and pinhole-free PZTV films were obtained by using spin coating followed with rapid annealing. The X-ray diffraction patterns revealed that no parasitic or secondary phases were formed in the sol–gel PZT films with the addition of vanadium oxide. The material doped with vanadium pentoxide showed enhanced dielectric constant and remanent polarization with reduced loss tangent and coercive field.

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## 1. Introduction

Lead zirconate titanate (PZT) thin films have been extensively investigated due to their excellent ferroelectric and piezoelectric properties [1–3] for various applications such as nonvolatile ferroelectric random access memories (NvFeRAMs) and microelectromechanical systems (MEMS) [4,5]. It is, however, difficult to use bulk PZT in most microscale devices; most of their devices requires the use of thin films. There are two general methods for the fabrication of PZT films: vapor phase deposition including chemical vapor deposition [6–8], pulsed laser ablation [9,10], and sputtering [11,12], and solution based deposition such as tape casting [13–15] and sol–gel processing [16–19]. PZT films grown by means of vapor phase deposition offer better dielectric, ferroelectric, and piezoelectric properties as the desired columnar structure can be obtained when the deposition process is appropriately controlled [6,20]. However, it is a great challenge to control the chemical stoichiometry of such a complex oxide with PbO, a volatile component, at elevated temperatures under vacuum. Solution methods permit the precise control of chemical composition of complex oxide systems; however, the resultant films typically have poorer dielectric, ferroelectric and piezoelectric properties due to the uniaxial grain microstructure formed during post-deposition annealing [16]. In addition, post-annealing at elevated temperatures imposes a challenge to the bottom electrodes [21,22]. Reduction of annealing temperature comprises the dielectric, ferroelectric and piezoelectric properties as a result of poor PZT crystallinity and small grain [16]. Doping is one effective method to improve the properties of PZT thin films with reduced processing temperature. Many physical properties of materials vary significantly with a subtle change of chemical composition through doping or substituting by a desired impurity, although the change of physical properties may be due to completely different mechanisms and the doping level can vary substantially from material to material [23]. A lot of effort have been made to dope PZT; for example, donor dopants, such as Nb, have been found to enhance the dielectric constants, increase the bulk resistivity, reduce the coercive field, as well as to improve the fatigue property of PZT [2,24,25].

In this letter, we studied the influence of vanadium doping on sol–gel derived PZT films, and demonstrated enhanced dielectric and ferroelectric properties. From an empirical point of view, two primary conditions should be satisfied by these dopants. Firstly, they should have higher valence states than 4+; and secondly, their radii should be comparable with that of the original B-site Ti ion. Our approach is to substitute $Ti^{4+}$ and/or $Zr^{4+}$ with a smaller cation $V^{5+}$ to enhance the dielectric and ferroelectric properties through increasing “the rattling space” and, thus the polarizability in PZT. Most research groups used similar-sized niobium ion to substitute zirconium and titanium to improve the fatigue resistance of PZT ceramics or thin films so far [26,27]. Wu et al. [23,28] studied vanadium as a dopant to improve the dielectric and ferroelectric properties of strontium bismuth niobate ceramics with reduced sintering temperature. Computational investigation also proved that vanadium can be used as a B-site donor in PZT [29].

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0025-5408/$ – see front matter. Published by Elsevier Ltd.
doi:10.1016/j.materresbull.2009.07.006

## 2. Experimental and procedures

High-purity lead acetate trihydrate [$Pb(C_2H_3O_2)_2{\cdot}3H_2O$, ≥99%], zirconium n-propoxide solution [$C_{12}H_{28}O_4Zr$, 70 wt% in propanol], titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$, 97%], and vanadium triisopropoxide oxide [$VO[CHO(CH_3)_2]_3$, 95–99%] were used as precursors. Acetic acid was used as solvent as well as stabilizing agent; isopropanol was used as solvent of vanadium triisopropoxide oxide [30], and deionized water (DI-$H_2O$), lactic acid, glycerol, ethylene glycol were used to stabilize the sol and to adjust viscosity of the sols. Sols with chemical formula $Pb_{1.05}Zr_{0.52}Ti_{0.48}O_3$ (referred to as PZT) and $Pb_{1.05}(Zr_{0.52}Ti_{0.48})_{0.95}V_{0.05}O_{(3-\delta)}$ (denoted as PZTV) were synthesized according to the procedure reported in literature [16]. For the synthesis of PZTV sol, 0.2 M vanadium solution were added to PZT mixture solution prior to admixing with DI-$H_2O$, lactic acid, glycerol and ethylene glycol at room temperature under vigorous stirring. The resultant PZT and PZTV sols were stable at room temperature for more than 2 months. $Pt/Ti/SiN_x/SiO_2/Si$ substrates were used as bottom electrode for thin film deposition. Before spinning coating, the substrates were ultrasonic cleaned in acetone and acetic acid separately for 5 min. The sols were firstly filtered through a 0.2 μm membrane and then spin-coated. The coated film was dried in air for 15 min, followed with rapid annealing at 650 °C (for PZT films) or 630 °C (for PZTV films) for 15 min. Three coatings were prepared by repeating the spin-coating–drying–rapid annealing processing to get a final thickness ~1.0 μm.

Phase characterization was carried out by means of X-ray diffraction (XRD, Philips 1820 X-ray diffractometer with Cu/K-alpha1 (40 kV, 120 mA, $\lambda$ = 1.5418 Å), step size (0.02), sweep speed ($0.25^\circ\ s^{-1}$), 43-pts/Parabolic Filter, Threshold = 3.0) and scanning electron microscopy (SEM, Philips, JEOL JSM7000). The dielectric properties of the PZT and PZTV films were measured at room temperature using a Hewlett Packard Precision 4284A LCR Meter with an oscillating amplitude of ~100 mV and a frequency of 100 kHz. Au top electrodes of 100–150 nm thick and 1 mm in radius were grown using DC magnetron sputter-deposition. The *P–E* hysteresis loops were obtained using a Radiant Technology RT 6000HVA with a frequency of 8 Hz at room temperature.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of PZT and PZTV films and reveals a well-formed polycrystalline perovskite structure for both films. No pyrochlore phase or other parasitic or secondary phase was detectable in both samples. The XRD patterns of the PZT and PZTV films revealed that both films were polycrystalline with random oriented grains. The XRD patterns also showed that the decreased sintering temperature did not have a noticeable negative effect on the crystallization of PZTV. The lowered sintering temperature in this study is partly due to the low melting point of vanadium oxide, which can be used as one effective sintering aid for low-firing ceramics and partly due to the possible formation of a eutectic liquid phase in this multiple oxide system [28]. It was also found that the incorporation of vanadium did not have any apparent influence on the crystal lattice constants of the perovskite structure, though pentovalent vanadium ion is much smaller than tetravalent titanium and zirconium ions. It is not exactly clear why there is no detectable change of lattice constant when smaller pentovalent vanadium ions are incorporated into PZT structure. However, considering the radius and coordination of vanadium ions [31], it is most likely that vanadium ions take the places of tetravalent titanium or zirconium ions or the B-sites in $ABO_3$ perovskite structure. It is known that $ABO_3$ perovskite does not have a close packing anion lattice and there is a so-called "rattling space" for B ions inside the oxygen octohedra. The perovskite structure is stable within a certain range of rattling space. No change of lattice constants with B-site doping has been reported earlier in layer structured $SrBi_2Nb_2O_9$ [28,32]. The relatively poor XRD pattern is due to the small amount of films used for the measurement, relatively large Pt peak, and low sintering temperatures used which resulted in so small grains and poor crystallinity in the XRD pattern. The lack of any evidence of V doping is probably due to the fact that the doping content is low and the resulting lattice constants change is small if there is any [28]. It is not anticipated to form new crystalline phase. However, it is possible that vanadium oxide reacted with other oxides to form an amorphous phase at the grain boundaries, resulting in a composite effect in the samples studied.

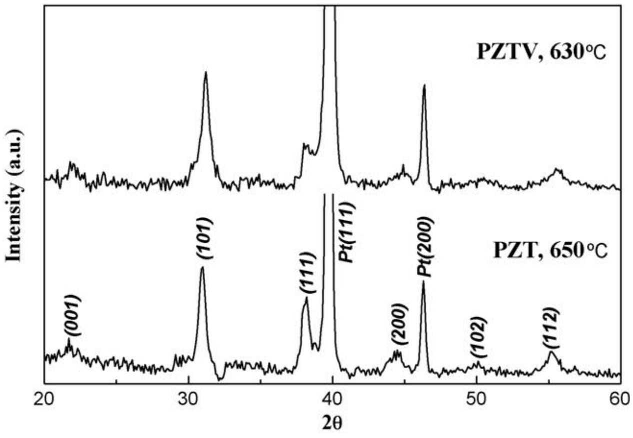

**Fig. 1.** XRD patterns of PZT and PZTV films deposited on $Pt/Ti/SiN_x/SiO_2/Si$ substrates.

Fig. 2 shows the SEM images of PZT and PZTV films. Top morphology views reveal that both films are homogeneous and crack free. The cross-section images demonstrated uniaxial grains of ~100 nm in diameter with a narrow size distribution. The thickness is ~0.97 μm for PZT film and ~1.0 μm for PZTV film. The images were comparable with those published in the literatures of PZT thin films [17–19,26].

Fig. 3 compares the *P–E* hysteresis of PZT and PZTV films and clearly demonstrates that doping with vanadium has a significant influence on the ferroelectric properties. The coercive field reduced from $2E_c = (E_{c+} - E_{c-})$ = 148 kV/cm for PZT films to 134 kV/cm for PZTV films. The remanent polarization increased significantly from approximately $2P_r = (P_{r+} - P_{r-})$ = 13 μC/cm$^2$ for PZT films to $2P_r$ = 21 μC/cm$^2$ for PZTV films. Although the remanent polarization value in this experiment was not large compared to that reported in the literature for sol–gel derived PZT film with approximately the same Zr/Ti ratio [26,33,34], the *P–E* properties were greatly improved due to the incorporation of vanadium. One possible reason for this improvement can be explained that the "rattling space" inside the oxygen octahedron was increased due to the partial substitution zirconium and titanium by vanadium. The polarizability in isotropic perovskites ($ABO_3$) has been a subject of intensive study, and it has been found that polarizability is largely determined by the size of A and B cations [35]. In general, a size decrease of B cations (located inside an oxygen octahedron) results in an increase in polarizability duo to "a larger rattling space" available for B cations, provide that the perovskite structure is preserved. Table 1 shows the dielectric constant ($\varepsilon_r$) and loss tangent (tan $\delta$) at a frequency of 100 kHz, the remanent polarization ($P_r$) and the coercive electric field ($E_c$) of the sol–gel derived PZT and PZTV films. The table shows that the vanadium doping results in an appreciable increase in dielectric constant and reduction in loss tangent. It should be noted that the increase of dielectric constant, reduction of loss tangent, and improved ferroelectric properties reported in this study are only based on

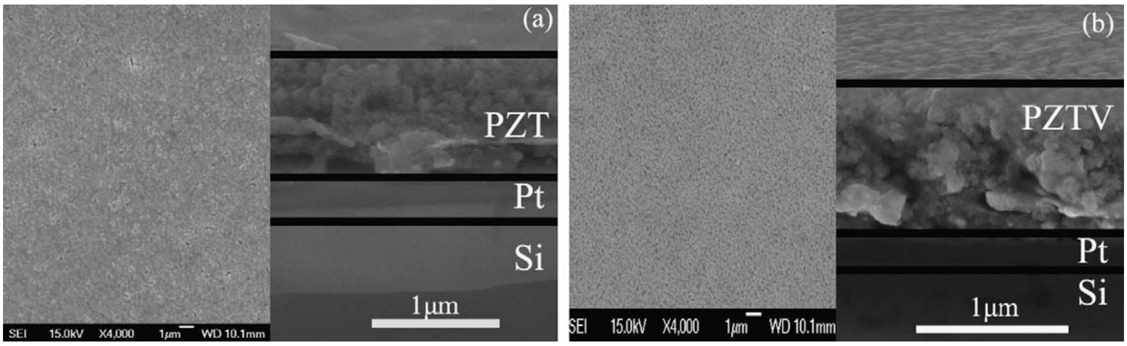

**Fig. 2.** SEM top morphology and cross-sectional images (inset) for (a) PZT and (b) PZTV films.

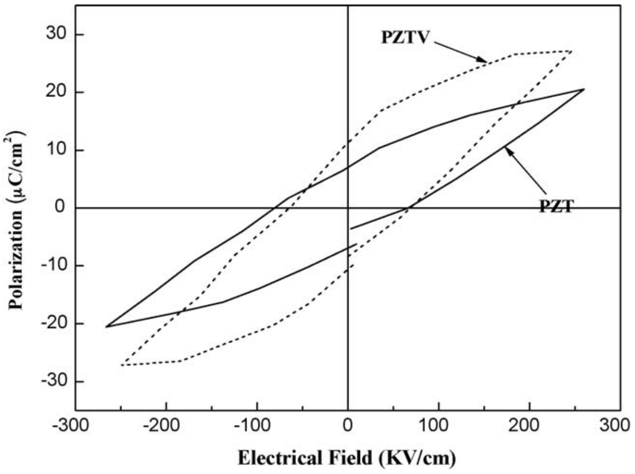

**Fig. 3.** *P–E* hysteresis loop of sol–gel derived PZT and PZTV films.

**Table 1**
Dielectric and ferroelectric properties of sol–gel derived PZT and PZTV films.

| Sample | $\varepsilon_r$ | tan $\delta$ | $P_r$ | $E_c$ |
|---|---|---|---|---|
| PZT | 430 | 0.26 | 6.6 | 74 |
| PZTV | 594 | 0.16 | 10.3 | 67 |

comparison of pure PZT and PZTV with 5% vanadium doping. Excessive doping is likely to result in a significant increase in leakage current and loss tangent, and/or lead to the formation of parasitic phase. It is not known what is the best composition (or optimal doping level) and the optimal processing conditions, more research is required.

## 4. Conclusions

Sol–gel derived PZTV films of ∼1.0 μm thickness were prepared. Substitution of zirconium and titanium by much smaller vanadium cations (5 mol%) resulted in a significantly higher remanent polarization from ∼6.6 μC/cm$^2$ to ∼10.3 μC/cm$^2$, and a lower coercive field from ∼74 kV/cm to ∼66 kV/cm. Experiments also revealed that the incorporation of vanadium did not increase the loss tangent while the dielectric constant of the PZT thin films increased. However, future research is necessary to understand the mechanism of vanadium doping on the ferroelectric properties of the perovskite PZT and the limit of vanadium doping in the perovskite structure.

## Acknowledgments

The authors would like to thank Dr. Lei Zhang and Dr. Su Huang for the dielectric constant and *P–E* hysteresis measurements. Shen would also like to thank China Scholarship Council (CSC) for the financial support.

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