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Original Article

Electric field-induced phase transition and energy storage performance of highly-textured $PbZrO_3$ antiferroelectric films with a deposition temperature dependence

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ABSTRACT

Thin $PbZrO_3$ (PZO) antiferroelectric films with (001)-preferred orientation were deposited on $SrRuO_3$/$Ca_2Nb_3O_{10}$-nanosheet/Si substrates using pulsed laser deposition. Variation of the deposition temperature was found to play a key role in the control of the microstructure and strongly influence the energy storage performance of the thin film. The critical phase switching field, where the aligned antiferroelectric (AFE) domains start to transform into the ferroelectric (FE) state, decreased with increasing temperature. On the other hand, the content of the FE phase in the AFE PZO thin films increased with increasing deposition temperature. A large recoverable energy-storage density of 16.8 J/cm^3 and high energy-storage efficiency of 69.2% under an electric field of 1000 kV/cm were achieved in the films deposited at 525 °C. This performance was due to the high forward switching field and backward switching field values and the low difference between these two fields. Moreover, the PZO thin films showed great charge-discharge cycling life with fatigue-free performance up to 10^{10} cycles and good thermal stability from room temperature to 100 °C.

1. Introduction

Antiferroelectric (AFE) materials have attracted great interest due to their attractive features for pulse-power energy storage [1–3], digital displacement transducers [4,5], and electro-optic devices [6,7]. Antiferroelectric materials consist of an ordered array of electric dipoles, but the adjacent dipoles are oriented in opposite directions, leading to a zero spontaneous polarization [8]. Under an external electric field, however, these antiparallel dipoles can be forced to be parallel, corresponding to an electric field-induced antiferroelectric-to-ferroelectric (AFE–FE) phase transition, which is shown by the characteristic double polarization-electric field (*P–E*) hysteresis loop [9–11]. Hence, AFE materials usually display high energy storage density, fast charge-discharge speed, and large electric field-induced piezoelectric strain. There are many AFE $PbZrO_3$ (PZO)-based materials, such as pure $PbZrO_3$ [12–15], $(Pb,Ba)ZrO_3$ [16,17], $(Pb,Sr)ZrO_3$ [16], $(Pb,La)ZrO_3$ [18], $(Pb,La)(Zr,Ti)O_3$ [19], $(Pb,La)(Zr,Ti,Sn)O_3$ [20,21], $(Pb,Y)(Zr,Ti,Sn)O_3$ [2], and $(Pb,Nb)(Zr,Ti,Sn)O_3$ [22]. These materials have been investigated and considered for applications in high-power density energy storage. One of the most widely studied AFE compositions is $PbZrO_3$ (PZO). It has an orthorhombic perovskite structure below the Curie temperature of 230 °C (antiferroelectric-paraelectric phase transition) [2,23], and is commonly represented as a pseudocubic unit cell with a_{pc} = 4.15 Å [1].

Recently, the study of AFE thin film energy storage performance is attracting increased attention due to the larger energy storage density obtained at higher electric breakdown field, as compared to the values for corresponding bulk ceramics. Several deposition techniques, such as pulsed laser deposition (PLD) [24], sputtering [13,15], and sol-gel spin-coating [12,14] have been used for the deposition of the PZO thin films. Each deposition technique has its intrinsic advantages and disadvantages. Pulsed laser deposition has been demonstrated to be a versatile method for the fabrication of high quality thin films. The main advantage of PLD is the possibility to transfer stoichiometrically multicomponent target materials, especially containing volatile components such as lead (Pb), to the layer. Moreover, PLD is a powerful method that allows a thicker film to be fabricated in a short time due to the high deposition rate and the ability to incorporate the process directly into a Si-production line [25,26], such as for MEMS manufacturing. However, a limited number of studies have been carried out

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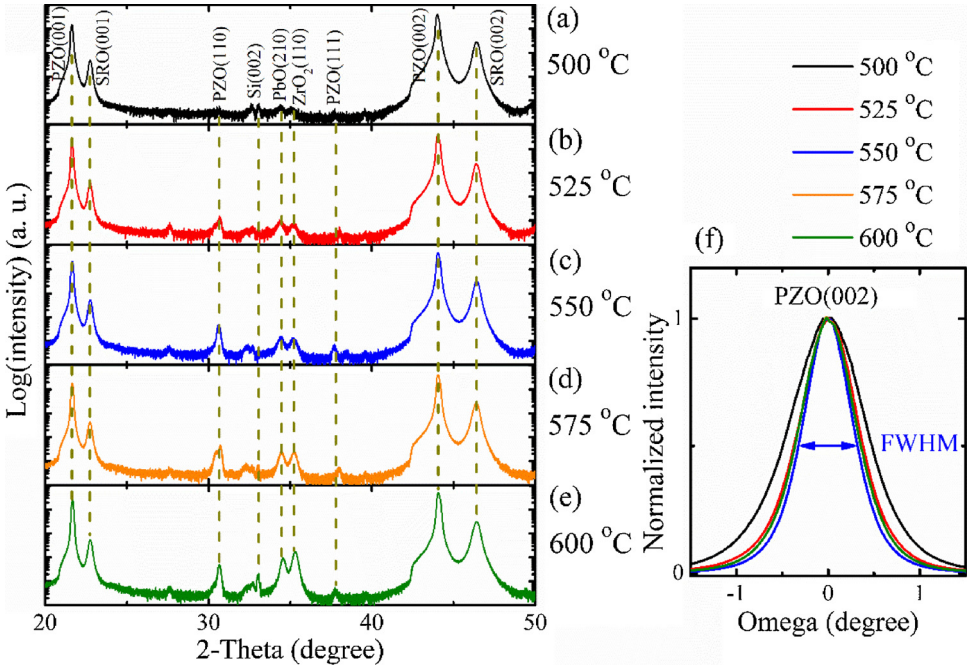

Fig. 1. XRD patterns of PZO thin films deposited at different temperatures: (a) 500 °C, (b) 525 °C, (c) 550 °C, (d) 575 °C and (e) 600 °C. (f) Corresponding rocking curves of the PZO(002) reflection peaks.

to optimize PZO thin film properties (and AFE thin films in general) using the PLD method.

The subject of the present study is the deposition of highly-textured PZO thin films on conductive-oxide $SrRuO_3$ electrode-buffered $Ca_2Nb_3O_{10}$ nanosheet/Si substrates by controlling the deposition temperature in order to change and maximize the energy storage performance. Their microstructure, electric field-induced AFE-FE phase transition, and charge-discharge cycling life have been also investigated. The main result is that the optimal deposition temperature is 525 °C to gain the highest energy storage performance in PZO thin films. This temperature is significantly lower than for ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) thin films (600 °C). Moreover, the energy storage performance of the PZO thin films remained unchanged for up to 10^{10} charge-discharge cycles.

2. Experiment

2.1. Nanosheet deposition

$Ca_2Nb_3O_{10}$ (CNO) nanosheets were fabricated on Si substrates by the exfoliation of layered protonated calcium niobate ($HCa_2Nb_3O_{10}{\cdot}1.5H_2O$) using the Langmuir-Blodgett deposition method [27]. The thickness of the CNO monolayers was approximately 2.7 nm.

2.2. Pulsed laser deposition

Thin film stacks of $SrRuO_3/PbZrO_3/SrRuO_3$ were grown CNO/Si substrates using pulsed laser deposition (PLD) with a KrF excimer laser source (Lambda Physik, 248 nm wavelength). The deposition conditions for the $PbZrO_3$ (PZO) films included a 10 Hz laser repetition frequency, 500–600 °C substrate temperature, 2.5 J/cm^2 energy density, and 0.1 mbar O_2 pressure. The deposition conditions for $SrRuO_3$ (SRO) top- and bottom-electrodes were 4 Hz, 600 °C, 2.5 J/cm^2 and 0.13 mbar O_2. All layers were deposited successively without breaking the vacuum. After deposition, the films were cooled down to room temperature in a 1 bar oxygen atmosphere and at a ramp rate of 8 °C/ minute. The thickness of PZO layers is about 1000 nm, while the thickness of SRO electrodes is about 100 nm.

2.3. Fabrication of thin-film capacitors

The film capacitor structures (100 × 100 μm^2) were patterned by a standard photolithography process and structured by argon-ion beam etching of the SRO top-electrodes and wet-chemical etching (HF − HCl solution) of the PZO films.

2.4. Analysis and characterization

Crystallographic properties of the thin films were analyzed by x-ray diffraction (XRD) θ–2θ and omega (ω)-scans using a PANalytical X-*ray*diffractometer (PANalytical, Almelo, The Netherlands) with Cu-*Ka*radiation (1.5405 Å wavelength). The normal operating power is 1.8 kW (45 kV and 40 mA). Cross-sectional high-resolution scanning electron microscopy (HRSEM: Zeiss-1550, Carl Zeiss Microscopy GmbH, Jena, Germany) and energy-selective backscattering (EsB) were performed to investigate the microstructure and thickness of the as-grown thin films.

The polarization-electric field (P-E) hysteresis loop and switching current (I_S-E) were performed with dynamic hysteresis measurement (DHM) in ferroelectric module of the aixACCT TF-2000 Analyzer (aixACCT Systems GmbH, Aachen, Germany). The aixACCT TF-2000 Analyzer was also used for the capacitance measurement. The capacitance-electric field (C–E) curves were measured using a slowly sweeping *dc*-electric field of up to 600 kV/cm amplitude with on top a 1 kHz *ac*-voltage of 0.2 V A Keithley 4200 semiconductor characterization system (Tektronix, Beaverton-Oregon, United States) was used for the leakage current measurement.

3. Results and discussion

The XRD θ–2θ patterns for the PZO thin films as a function of deposition temperature (T_d) are shown in Fig. 1. All samples show strong (001) and (002) diffraction peaks, indicating that they are highly oriented along the (001) direction. It was found that the 2θ value is almost unchanged with increasing T_d. The out-of-plane lattice constant for the PZO thin films was calculated to be about 4.12 Å. This is slightly lower than that for the orthorhombic unit cell of PZO bulk ceramics