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Ceramic dielectric film capacitors fabricated on aluminum foils by chemical solution deposition

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ABSTRACT

Integration of oxides onto base metal substrates offers great advantages in cost and weight reduction, device miniaturization, and flexibility in packaging. In this work, we report the deposition of dielectric $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_{3-\delta}$ (PLZT 8/52/48) films on aluminum foils by an in-air crystallization process. Film-on-foil structures with and without conductive oxide $LaNiO_3$ (LNO) buffer layer between PLZT film and aluminum foil were tested. Utilization of LNO buffer layer dramatically improved the dielectric and ferroelectric properties of the overlying PLZT compared with those for films deposited directly on aluminum. The improvements in electrical properties were attributed to the suppression of cubic non-ferroelectric layer at the metal/dielectric interface by LNO buffer layer. This work can be extended to the integration of other functional oxide materials with light, conductive, and inexpensive aluminum substrates for a broad range of applications.

1. Introduction

Functional oxide materials have been traditionally deposited on single crystalline substrates with noble metal electrodes (e.g., platinized silicon) [1,2]. Because the deposition process usually requires high temperature annealing in relatively oxidizing atmospheres, base metals cannot be used since they would oxidize and/or react with the oxides. However, there has been an increasing desire to integrate oxides onto base metal substrates, since this combination offers great advantages in cost and weight reduction, device miniaturization, and flexibility in packaging. For example, $YBa_2Cu_3O_7$ (YBCO), $BaTiO_3$, and $Pb(Zr,Ti)O_3$ (PZT) thin films have been processed on base metal tapes/foils for superconducting, ferroelectric, dielectric, and piezoelectric applications [3–6]. Among them, ceramic dielectric films deposited on base metals can be potentially useful for high power capacitors in hybrid electric vehicles, actuators and sensors in consumer electronics, DC/AC inverters in distributed energy systems, flexible micro-electromechanical systems (MEMS), 3D memory stacks, etc.

Table 1 summarizes the physical properties of commercially viable base metals. The most-studied metals for oxide integration are Cu and Ni, primarily due to their low electrical resistivity and high melting temperature [7–10]. As one of the most abundant base metals on earth, aluminum (Al) and its alloys have a low resistivity (high conductivity), are significantly lower in price (one-fourth the price of Cu, one-ninth of Ni), and have the lowest density, the latter two properties being beneficial for cost and weight reduction in device applications. In addition, because Al is paramagnetic (with a relative magnetic permeability $\mu_r = 1.000022$), it exhibits much lower ac loss than that of ferromagnetic Ni or Fe and therefore is more advantageous for radio frequency (RF) application. Besides, the melting point of Al is higher than the temperature required to crystallize the most-studied dielectrics, such as PZT and lanthanum-doped PZT (PLZT) (typically $> 600\ ^\circ C$). These characteristics make Al suitable as a substrate for deposition of dielectric oxides.

In 1967, Pechini demonstrated the chemical solution deposition of $BaTiO_3$ thin films directly on Al foil in air to form a dielectric capacitor [11]. In the 1990s, the deposition of PZT and PLZT on Al was also reported [12–14]. However, testing of these films indicated poor ferroelectric hysteresis loops and a low dielectric constant (≈64), indicating significant degradation of electrical properties [12,13]. For comparison, PZT on platinized silicon (PtSi) usually displays a dielectric constant of ≈1000 [15,16]. This degraded dielectric behavior was attributed to the formation of a low-*k* parasitic layer, such as an insulating aluminum oxide layer [12], or a cubic non-ferroelectric layer at the metal/dielectric interface [14].

Recently, two approaches have been developed to eliminate the deleterious effects of a low-*k* interfacial layer. The first is to

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Table 1
Physical properties of candidate base metals.

Base metal	Density (g/cm^3)	Melting point (°C)	Electrical resistivity (nΩ m)	Thermal expansion coefficient (10^{-6}/°C)	Price[a] (USD/MT)
Cu	8.96	1085	16.8	16.5	7273
Ni	8.91	1455	69.3	13.4	14,725
Zn	7.14	420	59.0	30.2	1903
Al	2.70	660	28.2	23.1	1835
Al alloy	–	–	–	–	1785

[a] Price from London Metal Exchange, August 14, 2013.

carefully maintain a low oxygen partial pressure (pO_2) during the thermodynamic equilibrium process. This step avoids the formation of the parasitic layer while maintaining the high quality and phase integrity of the perovskite dielectrics. This approach has been demonstrated in the coating of dielectrics on base metal Cu and Ni [4,5,17]. However, it is not suitable for Al due to its strong propensity to be oxidized even under highly reducing conditions ($pO_2 \leq 10^{-50}$ atm at 600 °C) according to the Ellingham–Richardson diagram [18]. The second approach is to negate the influence of the interfacial layer by interposing a conductive oxide buffer layer between the dielectric ceramic films and the metal substrates [19,20]. The conductive oxide buffer layer acts as the bottom electrode. This approach can also enable the freedom of in-air processing without the intricacies of low pO_2 conditions.

In this work, we prepared $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_{3-\delta}$ (PLZT 8/52/48) films on Al foils by chemical solution deposition (CSD) in air. Tests of this coated material were conducted with and without a conductive oxide $LaNiO_3$ (LNO) layer, which can serve as both bottom electrode and buffer layer between film and foil. We found that the electrical properties of the PLZT films on Al foils are significantly enhanced with LNO buffer layer and comparable to those of PLZT deposited on platinized silicon (PtSi). This work demonstrated the feasibility of depositing oxide dielectrics on light, conductive, inexpensive Al foils by an in-air process. PLZT films on Al foils can be useful for embedding into printed circuit boards, or for making various devices including piezoelectric sensors, micro-electromechanical systems, electro-optical components, and decoupling capacitors.

2. Experimental

A 0.5 M PLZT solution was prepared by dissolving appropriate amounts of lead acetate trihydrate, lanthanum nitrate hexahydrate, zirconium propoxide, and titanium isopropoxide in 2-methoxyethanol. 20 mol% excess lead was used in the starting solution to compensate for the lead lost during the high-temperature crystallization. Stock solutions (0.3 M) of LNO were prepared by dissolving lanthanum nitrate and nickel acetate in 2-methoxyethanol and refluxing for 2 h inside a glove box.

Aluminum foils (from Alcan Foil with a thickness of ≈36 μm) were ultrasonically cleaned in acetone and methanol prior to the deposition. LNO solution was spin coated onto the substrate at 3000 rpm for 30 s, pyrolyzed at 450 °C for 10 min, and crystallized at 630 °C for 2 min in air. This process was repeated five times to build the desired thickness with a final annealing at 630 °C for 5 min in air. PLZT stock solution was spin coated onto LNO-buffered aluminum foils at 3000 rpm for 30 s. Films were then pyrolyzed at 450 °C for 10 min and crystallized at 630 °C for 5 min, with a final annealing of 630 °C for 15 min in air after nine layers. The final thicknesses of the LNO and PLZT films were about 0.4 and 1 μm, respectively. Platinum top electrodes (diameter of 250 mm and thickness of 100 nm) were then deposited by electron beam evaporation using a shadow mask.

Dielectric measurements were made as a function of temperature with an Agilent E4980A LCR meter using an oscillator level of 0.1 V and 10 kHz in conjunction with a Signatone QuieTemp1 probe station with hot stage (Lucas Signatone Corp., Gilroy, CA). Radiant Technologies Precision Premier II Tester was used to measure the polarization-field hysteresis loops, the leakage current, and the polarization fatigue behavior.

3. Results and discussion

The crystalline phases of the PLZT films deposited on Al foils with and without LNO buffer layer were identified by X-ray diffraction (XRD), as shown in Fig. 1. Well-crystallized, randomly oriented PLZT phases are observed in both samples, in addition to the peaks from Al substrates and Pt top electrodes. No aluminum oxide or other secondary phase is detectable, even for the samples of PLZT films deposited directly on Al foils. However, the formation of a thin layer of amorphous aluminum oxide cannot be ruled out, because amorphous oxide cannot be detected by conventional XRD measurement.

The dielectric constant and dielectric loss as a function of bias field for PLZT films on Al foils with and without LNO buffer layer were measured at 10 kHz and room temperature, as shown in Fig. 2. During the measurement, the voltages were applied using a top electrode (Pt) to bottom electrode (Al) configuration. The PLZT films directly deposited on Al foil exhibit poor hysteresis with very low dielectric constant (≈197) and poor tunability. Although the dielectric loss at zero voltage bias is also low (≈0.02), it increases rapidly with increasing electric field. The LNO-buffered PLZT films display a butterfly-shaped hysteresis, saturation at high field, and good dielectric tunability. Dielectric constant of ≈1150, dielectric loss of ≈0.09, and dielectric tunability of ≈68% were typically observed at 10 kHz for PLZT films with LNO buffer layer. These measured dielectric constant values are lower than those reported for PLZT on PtSi and LNO-buffered Ni (≈1350) processed in air at the same frequency [21], but higher than those for PLZT on Cu substrates (≈1000) processed in low pO_2 [4,7,8].

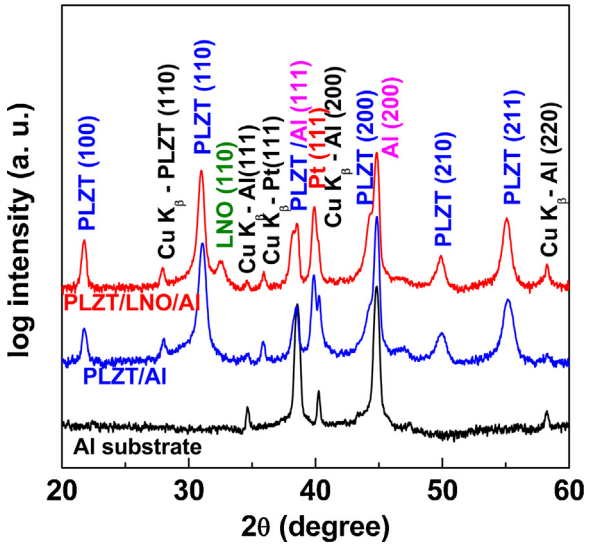

Fig. 1. XRD pattern of the PLZT films on Al with and without LNO buffer layer.