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Analysis of thin-film PZT/LNO stacks on an encapsulated TiN electrode

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ABSTRACT

We realized metal-ferroelectric-metal (MFM) capacitors comprising high-quality ferroelectric lead zirconate titanate ($Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT) thin films on an $LaNiO_3$/poly-Si/titanium nitride (TiN)/SiO_2 integrated on a 100 mm Si wafer. Promising effective piezoelectric coefficient and remnant polarization of 53 pm/V and 19.2 $\mu C/cm^2$, respectively, are obtained for the 100 nm-PZT/20 nm-LNO stack. Further analysis of the samples indicates the presence of a passive layer, possibly near the Ti/PZT interface at the top electrode. A leakage current model has been used to explain the obtained current density–electric field curves. In this model, diffusion limited transport has been assumed in which the injection is interface-controlled. Based on the capacitance and the leakage current measurements, the thickness and dielectric constant values of the passive layer are estimated to be 2.1 nm and 23, respectively. The observed apparent low barrier height value of 0.32 eV is attributed to ferroelectric polarization related phenomena. A good agreement between measurement and leakage current model is obtained.

1. Introduction

Ferroelectric films attract much interest for their applications in high density capacitors [1], sensors and micromechanical systems [2,3], and nonvolatile memories [4,5]. Lead zirconate titanate ($Pb(Zr,Ti)O_3$, or PZT) is of particular relevance for its high piezoelectric and high dielectric constant. Miniaturization and integration of devices based on ferroelectric/piezoelectric action requires the reduction of the PZT layer thickness as well as the thickness of its encapsulating electrodes [6–10]. In addition, uniform films on larger substrates are desired for the same purpose.

The properties of PZT films are strongly dependent on the surrounding layers and the fabrication conditions. Since the film/electrode interface becomes more prominent with scaling, thickness reduction may lead to a reduced piezoelectric performance.

In earlier work on scaling of PZT, small substrates and a buffer/electrode layer thicker than one hundred nanometer were used [11,12]. These buffer/electrode layers were generally grown to relatively thick dimensions to keep control of the PZT growth orientation and to avoid the ferroelectric performance degradation [13–15]. In this work, however, we focus on the investigation of sub-100 nm thick $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) films on 100 mm Si wafers with the use of an $LaNiO_3$ (LNO) buffer layer and an encapsulated-TiN bottom electrode down to 25 nm thicknesses.

2. Processing

Test structures were realized on 100 mm Si wafers to characterize the thin PZT/LNO stacks. The processing started with a 5 nm TiN layer deposition by atomic layer deposition (ALD). The TiN thickness was controlled *in situ* with a spectroscopic ellipsometer. Subsequently, a 10 nm amorphous-Si (a-Si) layer was deposited in the same reactor without vacuum break to prevent the oxidation of TiN. The deposition of a-Si was done at 350 °C by low pressure chemical vapor deposition (LPCVD) at 1 mbar process pressure using trisilane (Si_3H_8) as precursor. This encapsulated TiN, a widely employed gate metal in advanced Si technology [16], was used as a bottom electrode for the PZT thin film capacitors. Then, the wafers were annealed in an N_2 environment at 900 °C for 30 s using rapid thermal annealing system. During the RTA step, the system ramped-up at a rate of 25 °C/s and ramped-down at a rate of 55 °C/s rate. As a result, the amorphous-Si layer is crystallized. The LNO buffer layer and PZT film were deposited using a KrF excimer laser source (Lambda Physik, 248 nm wavelength) at 2.5 J/cm^2 fluence and 10 Hz repetition rate in a large-area pulsed laser deposition (LAPLD) system at SolMateS B.V., The Netherlands. The target-substrate distance was kept at 6.0 cm. The LNO and PZT films were grown at substrate temperature of 600 °C and ambient oxygen pressure of 0.1 mbar. The used tool reaches 92–95% thickness uniformity across a 100 mm Si wafers for PZT and LNO depositions. After deposition, the films were cooled down to room temperature in oxygen atmosphere with a ramp rate of

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20 °C/min. Finally, the PZT as well as the LNO film were patterned by wet etching (using a solution of BHF:HNO_3 followed by HCl) and a top electrode stack of 10 nm Ti and 100 nm Pt was sputtered through a shadow mask to fabricate 200 × 200 μm^2 capacitors.

3. Characterization and analysis

To analyze the crystal orientation, PZT bulk (target) and thin films were characterized by X-ray θ–2θ diffraction (XRD: Philips X'PERT MPD) as shown in Fig. 1. All PZT films have been crystallized corresponding to the perovskite structure and no other phases are observed. The (100) preferred orientation is dominant for all films, and the minor (110) peak is decreased with an increase in LNO seed-layer thickness.

The polarization hysteresis (*P–E*) loop measurements were performed in the ferroelectric mode of the aixACCT TF-2000 Analyzer adopting a triangular ac electric field of ±1000 kV/cm at 1 kHz frequency and at room temperature. Fig. 2 shows the difference in ferroelectric polarization loops of PZT thin films for different film thicknesses and LNO-layer thicknesses. A schematic cross section of the test structures is shown in the inset of Fig. 2.

An improvement of the average remnant polarization (P_r = 19.2 $\mu C/cm^2$; $P_r = (P_{r+} - P_{r-})/2$) is observed for the 100 nm-PZT/20 nm-LNO stack in comparison with that of 100 nm-PZT/10 nm-LNO stack (P_r = 15.3 $\mu C/cm^2$). The average coercive field of these structures is approximately 195 kV/cm. Because of the relatively high leakage current through the 75 nm-PZT/10 nm-LNO stack an opening of the *P–E* loop at high electric fields is formed and also an increase in both the remnant polarization (18.4 $\mu C/cm^2$) and coercive field (243.3 kV/cm) is obtained. Moreover, the ferroelectric signal is lost for structures with a 5-nm-thick LNO layer, as can be seen from the further opening of the *P–E* loop. The asymmetry in the presented *P–E* loops can be attributed to the use of different metals, hence work functions, for the top and bottom electrodes.

There have been other studies reporting coercive fields of 100 and 125 kV/cm for 100 nm thick PZT layers on $LaNiO_3$/Si [17] and $SrRuO_3$/$SrTiO_3$ [18] substrates, respectively, values which are in the same range as presented in this work. The relatively high E_c values can be explained by the use of a small film thickness *d*: $E_c(d) \propto d^{-2/3}$ [19].

The piezoelectric coefficient ($d_{33,f}$) was measured using a Polytech MSA-400 scanning laser Doppler vibrometer (LDV) method with a precision below 1 pm. In this study, the piezoelectric capacitor was excited with an 8 kHz sinusoidal ac-voltage of 3 V amplitude. Under these measurement conditions, a $d_{33,f}$ coefficient of 53 pm/V was measured. This value is very close to reported values obtained from relatively bulky PZT layers [20]. A high $d_{33,f}$ value favors the application of the PZT films as a stressor [8–10].

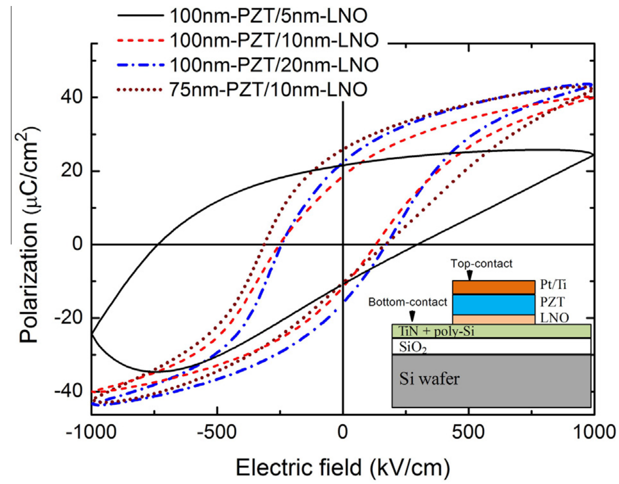

Fig. 2. Thickness dependence of polarization hysteresis (*P–E*) loops. The *P–E* loops were performed at an applied ac electric field of ±1000 kV/cm and 1 kHz frequency. The inset shows the schematic cross section of the test structure.

The electrical performance of the PZT layer in terms of leakage current and capacitance is also of major importance for device applications. High-frequency capacitance–electric field (*C–E*) and temperature dependent leakage current density-field (*J–E*) measurements were performed using a SÜSS Microtech probe station equipped with a Keithley 4200 semiconductor characterization system. The bias voltage was applied to the top electrode while the bottom electrode was grounded. The electric field (*E*) is determined by dividing the bias voltage (*V*) to the PZT film thickness. The dielectric constants were obtained from *C–E* measurements at an ac amplitude of 30 mV at 1 kHz frequency. Fig. 3 shows the dielectric constant–electric field curves, which were calculated from the corresponding *C–E* curves.

We observe typical butterfly shaped dielectric constant curves indicating dielectric response variation with the dc-bias due to the domain re-orientation process [21,22]. However, as observed in the polarization loop experiments (Fig. 2), the center of the hysteresis loops shifts towards a negative bias. In addition, there

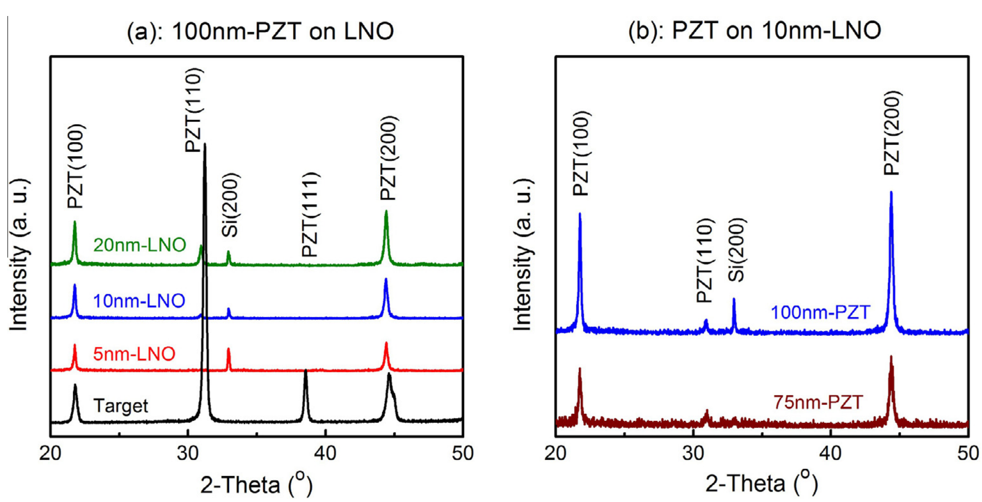

Fig. 1. XRD graphs of (a) a 100 nm-thick PZT film on different LNO layer thicknesses and (b) a 75 nm and a 100 nm PZT film on a 10 nm-thick LNO layer.