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Effect of nanoparticles on ferroelectric and electrical properties of novel PMNT thin-films

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ABSTRACT

This work studies the impact of adding nanoparticles to high-k PMNT (lead magnesium niobate–lead titanate, $Pb(Mg_{0.33}Nb_{0.67})_{0.65}Ti_{0.35}O_3$) thin films. PMNT thin films were grown on Pt(111)/TiO_2/SiO_2/Si substrate using a sol–gel technique. Ligand stabilised PMNT nanoparticles were added to the sol–gel material with the aim of seeding the crystallization process. The measurements show that use of nanoparticles in PMNT thin films influences the remanent polarization, coercive field and dielectric constant. These characterization results support the ongoing investigation of the material ferroelectric and electrical properties which are necessary before the novel dielectric can be used in silicon applications.

1. Introduction

High-k PMNT (*lead magnesium niobate–lead titanate, Pb(Mg,Nb)TiO_3*) ferroelectric material has shown promising performance characteristics [1,2]. PMNT has potential for realising high-performance and low-cost application which is suitable for high-density, low-power, portable silicon electronic systems. Before these high-k materials can be used in conjunction with modern Si processes, the materials must be extensively and accurately characterised.

This paper describes the impact of adding nanoparticles to high-k PMNT ($Pb(Mg_{0.33}Nb_{0.67})_{0.65}Ti_{0.35}O_3$) thin films. An advanced test structure design methodology for dielectric characterization of novel high-k materials has been developed previously [3]. It was also observed that the measurements could be implemented between small square pads which had originally been placed on the test mask to serve as open de-embedding structures for S-parameter measurements.

2. Samples fabrication

PMNT thin films were grown on Pt(111)/TiO_2/SiO_2/Si substrate using a sol–gel technique. Some of the sol–gel mixtures used added nanoparticles of the same material as potential nucleation seeds. These perovskite crystallites were prepared by high energy milling of a mixture of PbO, MgO, TiO_2 and Nb_2O_5 powders in the molar ratio corresponding to the stoichiometry $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ with 2 mol% of excess PbO [4]. The sol–gel was spin-coated using a WS-400A-6NPP/LITE Spin-Coater (Laurell Technologies) at a spin rate of 3000 rpm for 30 s at room temperature (RT). The coated wafers were then transferred onto a hot-plate, which had been set to 300 °C, and kept at this temperature for ~1 min. The wafers were then allowed to rest at RT for ~30 s. The spin-coating and subsequent heating were repeated with the required times for the multi-layer films. The resultant films were annealed using a Jipelec Jetfirst 150 model rapid thermal processor at two temperatures of 450 °C and 750 °C in O_2 atmosphere respectively [5]. The samples are distinguished by different anneal temperatures (450 °C or 750 °C) and by the presence of nanoparticles (np) or not. The nanoparticles were prepared by high energy milling [4]. The average particle size of the nanoparticles is 50 nm. The film thicknesses are as follows: PMNT_450 (475 nm, estimated), PMNT_np_450 (475 nm, estimated), PMNT_750 (380 nm) and PMNT_np_750 (250 nm). The films all appear dense and compact. There is no evidence of porosity. Figs. 1 and 2 show the SEM images of the 750 °C samples without nanoparticles and with nanoparticles, respectively.

Fig. 3 shows the flowchart of the synthesis.

100 nm Pt was used as a top electrode for the PMNT thin film. 200 nm Au was also deposited on the top Pt layer to improve the electrical contact. The composite film was patterned to form a series of square pad test structures by photolithography. The measurements were performed using a set of 3 square pads on each sample. The edge-to-edge distance between the adjacent pads is 25 μm, and the pad dimensions are 125 μm × 125 μm. The ferroelectric and electrical characteristics for various samples are presented in the next section.

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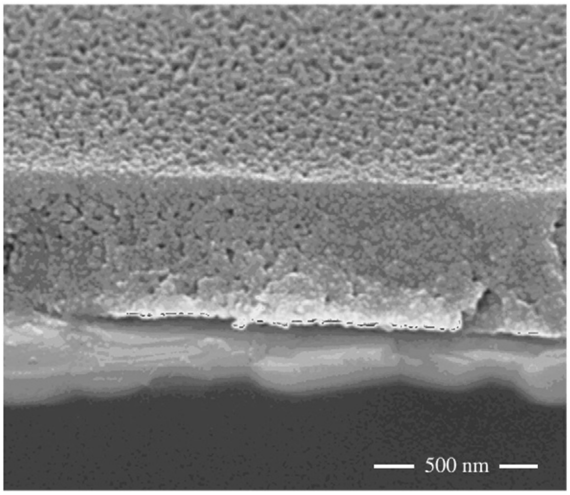

Fig. 1. SEM images of the 750 °C sample without nanoparticles.

3. Ferroelectric properties

Ferroelectric properties of the Pt/PMNT/Pt capacitors were measured using a standard ferroelectric test system (Radiant Technologies RT66B) with the samples mounted on a Cascade probe station. The two samples both exhibited ferroelectric properties as seen in the ferroelectric polarization vs. applied voltage (P–V) hysteresis loop.

3.1. Samples annealed at 750 °C

Fig. 4 shows the hysteresis loops of the PMNT_750 thin film capacitor at six different applied voltages. The Pt/PMNT/Pt capacitor exhibits well-saturated P–V switching curves. The remanent polarization (P_r) at room temperature is 7.43 μC/cm^2 at an applied voltage of 10 V and is larger

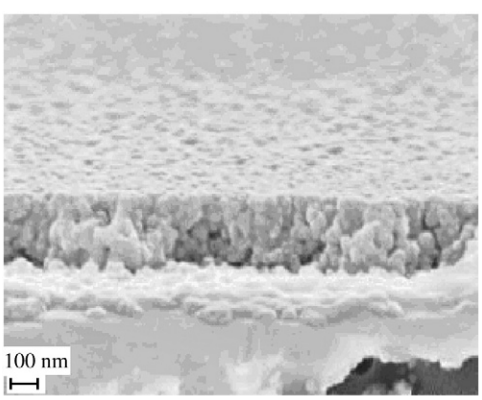

Fig. 2. SEM images of the 750 °C sample with nanoparticles.

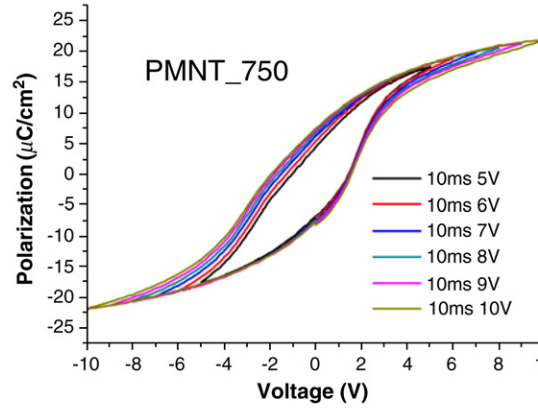

Fig. 4. Ferroelectric hysteresis loops of the PMNT_750 thin film capacitor.

than 4.36 μC/cm^2 at an applied voltage of 5 V. The coercive field (E_c) of the PMNT film capacitor is about 41.97 kV/cm. Fig. 5 shows the hysteresis loops of the PMNT_np_750 thin film capacitor at two different applied voltages. The P_r is 2.50 μC/cm^2 at an applied voltage of 10 V. The E_c of the PMNT film capacitor is about 111.77 kV/cm.

3.2. Samples annealed at 450 °C

Fig. 6 shows the hysteresis loops of the PMNT_450 thin film capacitor at four different applied voltages. The Pt/PMNT/Pt capacitor exhibits well-saturated P–V switching curves. The P_r at room temperature is 2.63 μC/cm^2 at an applied voltage of 10 V while it has a value of over 0.469 μC/cm^2 at an applied voltage of 4 V. The E_c of the PMNT film capacitor is about 20.84 kV/cm. Fig. 7 shows the hysteresis loops of the PMNT_np_450 thin film capacitor at four different applied voltages. The P_r is also 2.63 μC/cm^2 at an applied voltage of 10 V. The E_c of the PMNT film capacitor is about 33.47 kV/cm.

4. Electrical properties

The capacitance at zero-bias for frequencies up to 1 MHz was measured using a HP 4285A precision LCR meter. The dielectric constant as a function of voltage at 1 MHz was measured with a Hewlett Packard (HP) 4280A C–V meter.

4.1. Samples annealed at 750 °C

Figs. 8 and 9 show the variation of the dielectric constant of the 750 °C PMNT thin-films as a function of frequency from 100 kHz to 1 MHz and voltage, respectively. The PMNT_750 shows higher ε_r than PMNT_np_750 at all the frequency points [6]; it might be because PMNT_750 is perovskite and PMNT_np_750 is pyrochlore. The PMNT_np_750 has an ε_r of approximately 73. Therefore, we can conclude that this sample has not formed the perovskite phase and is still in the pyrochlore phase. This is confirmed by XRD measurements for these

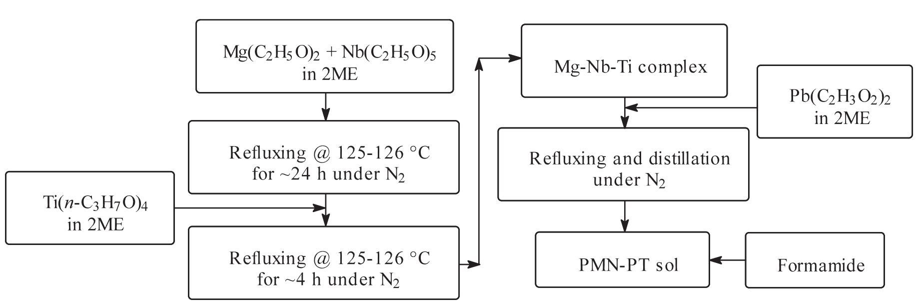

Fig. 3. Flowchart of the synthesis for the PMNT samples.