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Electric field and temperature scaling of polarization reversal in silicon doped hafnium oxide ferroelectric thin films

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ABSTRACT

HfO_2-based binary lead-free ferroelectrics show promising properties for non-volatile memory applications, providing that their polarization reversal behavior is fully understood. In this work, temperature-dependent polarization hysteresis measured over a wide applied field range has been investigated for Si-doped HfO_2 ferroelectric thin films. Our study indicates that in the low and medium electric field regimes ($E <$ twofold coercive field, $2E_c$), the reversal process is dominated by the thermal activation on domain wall motion and domain nucleation; while in the high-field regime ($E > 2E_c$), a non-equilibrium nucleation-limited-switching mechanism dominates the reversal process. The optimum field for ferroelectric random access memory (FeRAM) applications was determined to be around 2.0 MV/cm, which translates into a 2.0 V potential applied across the 10 nm thick films.

1. Introduction

Recent studies show that pronounced ferroelectricity can be induced in hafnium oxide thin films when incorporated with various dopants (Si, Al, Y, Gd, La, and Sr) and annealed under certain conditions. The impacts of dopant type and concentration on the ferroelectric switching properties have been reviewed by Schroeder et al. [1]. Furthermore, ferroelectricity can also be achieved in HfO_2–ZrO_2 solid-solution [2]. Apart from macroscopic polarization/strain hysteresis measurements and micro-structural analyses of the phase transition, conclusive evidences for the existence of intrinsic ferroic behavior have also been provided by mesoscopic piezoresponse force microscopy (PFM) experiments [3] and first principles calculation [4–7].

Non-volatile ferroelectric memory would be one of the most attractive applications for this new type of lead-free and CMOS process compatible binary oxide ferroelectric material with comparatively low dielectric constant. When using it to replace conventional perovskite structure oxides, e.g. $Pb(Zr,Ti)O_3$ (PZT), a number of current integration and scaling issues in ferroelectric memory development can be eliminated [8]. Recent report of ferroelectric field effect transistors (FeFET) fabricated using Si-doped HfO_2 (Si:HfO_2) in 28 nm technology has evidenced this expectation [9].

The operation principle of nonvolatile ferroelectric memories is based on the ability of ferroelectrics to store digital information represented by their negative or positive remanent polarization states, which are also switchable via the application of external electric fields. A wealth of studies have shown that the polarization switching behavior of ferroelectrics depends strongly on the choice of materials, internal defects, interface properties, and external loads such as electric field, temperature, and stress [10,11]. For instance, PZT displays higher switchable polarization than $SrBi_2Ta_2O_9$ (SBT), but suffers severe fatigue if no oxide electrodes are used; while SBT films sandwiched between two platinum electrodes are known as “fatigue-free” [12,13]. An insufficient applied field will lead to a sub-loop, and the resultant incomplete writing should be avoided in ferroelectric random access memories

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(FeRAMs). Moreover, there is experimental evidence that the coercive field shows also a temperature and time dependency. This affects the proper selection of write/read voltages over the operation temperature range of the device [14]. Of course, the polarization switching kinetics and reliability properties are highly desirable information for a successful introduction of HfO_2-based ferroelectric thin films in applications.

Thermal stability of the remanent polarization measured at high field levels has already been reported for Si:HfO_2 ferroelectric thin films [15]. In this work, we detail the experimental investigation for the same compound in terms of its temperature dependent polarization hysteresis behavior measured over a wide range of applied fields from 0.5 to 4.0 MV/cm. In addition, the switching endurance properties were studied preliminarily at various bipolar stressing fields. The collected results are of huge technical importance for optimizing device operation conditions, as well as are scientifically interesting for the understanding of domain switching dynamics in ultra-thin ferroelectric films.

2. Experimental techniques

Metal-ferroelectric-metal (MFM) planar capacitor structures consisting of Pt (50 nm)/TiN (10 nm)/Si:HfO_2 (10 nm)/TiN (10 nm) film stack were grown onto silicon substrates. In detail, the TiN electrodes were formed by atomic layer deposition (ALD) using $TiCl_4$ and NH_3 precursors at 450 °C. The Si:HfO_2 thin films were grown by ALD at 280 °C with $Hf[N(CH_3)C_2H_5]_4$ (TEMAH) and $Si[N(CH_3)_2]_4$ (4DMAS) as precursors, and ozone (O_3) was used as an oxygen source. Sub-cycles of 4DMAS during HfO_2 deposition resulted in a silicon dopant content of ~5.0 mol. %. Crystallization of the Si:HfO_2 films was induced by a 800 °C/20s RTP anneal in N_2 after top TiN electrode deposition. Evaporated platinum dots served as electrical contacts and as a hard mask in chemical etching of the top TiN layer.

Janis ST-500 probe station was used for electrical probing of the capacitor array with the Pt dots (100 μm radius) being stressed and the common bottom TiN electrode being grounded. The polarization–electric field (*P*–*E*) hysteresis curves and endurance properties were characterized using an aixACCT TF Analyzer 2000 system. For *P*–*E* hysteresis measurements in a wide temperature range from 100 K to 400 K, the triangular waveform electric field was applied at a frequency of 1.0 kHz, and the maximum field amplitude (E_{max}) was varied from 0.5 to 4.0 MV/cm. Before performing the measurements presented in this work, each capacitor was first subjected to a ±3.0 MV/cm bipolar high field cycling at a frequency of 1.0 kHz for 5 s. Such a "wake-up" or de-ageing treatment was deployed to minimize the asymmetry and distortion of the polarization hysteresis loop [16].

3. Results and discussion

3.1. Electric field and temperature scaling of polarization hysteresis

Fig. 1 shows the polarization hysteresis loops measured at room temperature (RT), from which three categories of polarization reversal behavior can be identified depending on the amplitude of the applied field.

Well-saturated *P*–*E* loops can be obtained in the high-field region ($E_{max} \geqslant 2.0$ MV/cm), where an increasing field amplitude causes only very slight increases in the remanent polarization (P_r) and coercive field (E_c). At $E_{max} = 4.0$ MV/cm, the measurement gives a $2P_r$ ($2P_r = P_r^+ - P_r^-$) of ~43.7 μC/cm^2 and an average coercive field ($(E_c^+ - E_c^-)/2$) of ~1.0 MV/cm. In contrast to PZT films, which are normally thicker than 70 nm in integrated ferroelectric memory products, the $2P_r$ value of our 10 nm thick Si:HfO_2 thin films is comparable (30–45 μC/cm^2 for PZT), but the coercive field is roughly one order of magnitude higher [14,17]. The Si:HfO_2 thin film can withstand extremely high electric field strength mainly due to its relatively low dielectric constant, and therefore lower local electric-field that distorts and weakens the molecular bond [18].

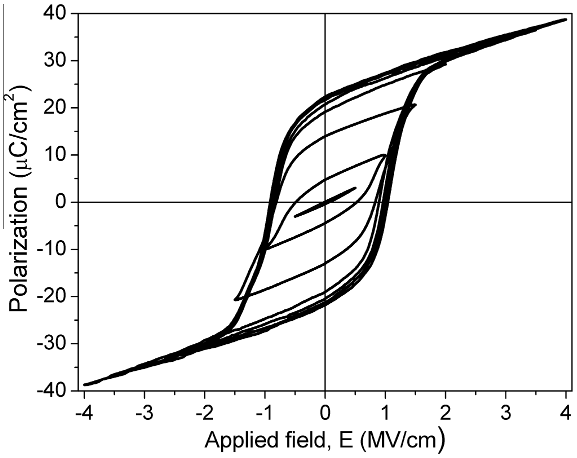

Fig. 1. Evolution of *P*–*E* hysteresis loops with increasing external applied field amplitude. The measurements were performed at room temperature and 1.0 kHz.

In the medium-field regime ($E_c \leqslant E_{max} < 2E_c$), minor loops resulting from partial switching of domains in the material can be observed. The portion of switched domains, which is represented by the remanent polarization and loop area, is very sensitive to the field amplitude applied in this regime. For PZT films used in FeRAM application, the write operation requires twofold coercive voltage ($2V_c$) to ensure sufficient and stable nonvolatile switching charge that can be read by subsequent applied voltage pulse [14]. Our measurements show that the same conclusion applies to the use of Si:HfO_2 ferroelectric thin films in FeRAM. When the applied field is further reduced into the low-field region ($E_{max} < E_c$), almost linear *P*–*E* curve can be seen in Fig. 1. The slope represents the DC dielectric permittivity.

Fig. 2 displays temperature dependent *P*–*E* loops measured at $E_{max} = 0.5$, 1.0, 2.0 and 3.5 MV/cm, which were selected as representative applied fields in aforementioned low-, medium-, and high-field regions. It is demonstrated that, depending on the field regions where the measurements were performed in, temperature scaling of the polarization hystereses differs significantly in terms of the area, shape, remanent polarization as well as coercive field. The evolution of the latter two characteristic parameters was depicted in Fig. 3. In subsections 3.2 and 3.3, we summarize the main experimental findings in three measured field regions, and discuss the mechanisms underlying the differences in thermal effects on polarization reversal behavior.

3.2. Kinetics of polarization reversal in low ($E_{max} < E_c$) and medium ($E_c \leqslant E_{max} < 2E_c$) electric field regimes

When measured in low-field region, domain-wall displacement is regarded as the main source of the weak hysteresis observed in *P*–*E* curves. In such a non-switching condition, the domain structure remains on average the same, while a low electric field will cause translation of existing domain walls across periodic potential wells created by an array of pining defects [11,19]. Contribution of domain-wall displacement to the electromechanical properties has been studied intensively for $BaTiO_3$ and PZT ceramics, which the dielectric and piezoelectric non-linearity and hysteresis can be