



## Plasma-enhanced atomic layer deposition of BaTiO<sub>3</sub>



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### ABSTRACT

Among high-*k* thin films, perovskite BaTiO<sub>3</sub> (BTO) is an attractive candidate due to its exceptionally high dielectric constant. In contrast to conventional atomic layer deposition (ALD), plasma-enhanced ALD (PEALD) has several advantages such as lower process temperature, improved film quality and the deposition of a wider spectrum of materials. We report the successful deposition of high-*k* BTO thin films by PEALD. Compositional, morphological, and crystallographic characterizations of PEALD BTO are presented. The electrical performance of PEALD BTO thin films as a function of Ba-to-Ti-ratio is shown. Slightly Ti-rich BTO has the lowest equivalent oxide thickness while Ba-rich films show the lowest leakage current.

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The use of high-*k* thin films that exhibit a low leakage current is essential in realizing dynamic random access memory (DRAM) capacitors with high charge storage density and long storage lifetime [1,2]. Among high-*k* thin films, perovskites such as BaTiO<sub>3</sub> (BTO), SrTiO<sub>3</sub> (STO), or (Ba,Sr)TiO<sub>3</sub> (BST) are attractive candidates due to their exceptionally high dielectric constants maintained even for thin films (>100) [2–7]. Recent development of DRAM structures have necessitated the down-scaling of features to smaller dimensions (<30 nm), i.e. higher aspect-ratios, for enhanced information storage densities. Therefore, the conformal coating of high-*k* thin films over the inner surface of high aspect-ratio trenches is of great importance.

In this regard, atomic layer deposition (ALD), which is dominated by unique self-limiting surface reactions, is an attractive tool to fabricate DRAM capacitors. ALD enables the deposition of conformal films over complex 3-dimensional geometries with precise thickness control. Additionally, one can minimize the thermal damage of the device in the process of the deposition due to the relatively low process temperature (<400 °C) during ALD [8]. Plasma-enhanced ALD (PEALD), in which excited species (such as ions and radicals) generated by a plasma are used to react with ligands of the precursor during the second half-step, has several advantages compared to the conventional thermal ALD [9]; for

example, the highly reactive plasma species give more flexibility in processing conditions and materials properties. PEALD films are also known to possess higher density and less contamination originated from unreacted ligands, which potentially results in the lowered electrical leakage current of dielectric oxide films [9].

In this report, we demonstrate for the first time the successful deposition of PEALD BTO films using cyclopentadienyl(Cp<sup>\*</sup>)-type barium precursor, Ba(iPr<sub>3</sub>Cp<sup>\*</sup>)<sub>2</sub> (iPr<sub>3</sub>Cp<sup>\*</sup> = 1,2,4-trisopropyl-cyclopentadienyl). The growth behaviors of the individual oxides (i.e., BaO and TiO<sub>2</sub>) and of BaTiO<sub>3</sub> have been tested and the ALD growth-mode was confirmed. The detailed compositional, morphological, and crystallographic characteristics of the PEALD BTO are presented, and compared to those of thermal ALD BTO films previously reported [10]. PEALD of BTO films showed to result in more uniform and denser films with more crystallites dispersed in the amorphous BTO matrix, compared to thermal ALD BTO. Lastly, the electrical performance of PEALD BTO films is shown as a function of Ba-to-Ti cation ratio for the possible application in charge storage capacitors.

BTO films were deposited in a commercial PEALD reactor (FlexAL, Oxford Instruments). Ba(iPr<sub>3</sub>Cp)<sub>2</sub> (Air Liquide) and Ti (OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (TTIP, Sigma Aldrich) were utilized as the Ba and Ti precursors, respectively. The precursor canisters of the Ba and Ti precursors were heated to 180 and 55 °C, respectively. Oxygen plasma was generated from an inductively coupled plasma system (plasma power, 250 W; operating pressure, 15 mTorr). The BaO PEALD process consisted of (i) Ba precursor injection (3 s) followed by (ii) Ba precursor exposure (60 s) to enhance diffusion and

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adsorption of the precursor molecules, (iii) precursor purging by Ar (60 s), (iv) plasma stabilization (2 s), (v) O<sub>2</sub> plasma injection (10 s) and (vi) Ar purging (2 s). In case of the TiO<sub>2</sub> PEALD process, (i) TTIP injection (5 s), (ii) precursor purging by Ar (5 s), (iii) plasma stabilization (2 s), (iv) O<sub>2</sub> plasma injection (3 s) and (v) Ar purging (2 s) were employed. The BTO films with different cation composition ratios ( $[\text{Ti}]/([\text{Ba}] + [\text{Ti}]) = 0.26\text{--}0.76$ ) were fabricated by alternately depositing one BaO cycle and several TiO<sub>2</sub> cycles, which together form one super-cycle.

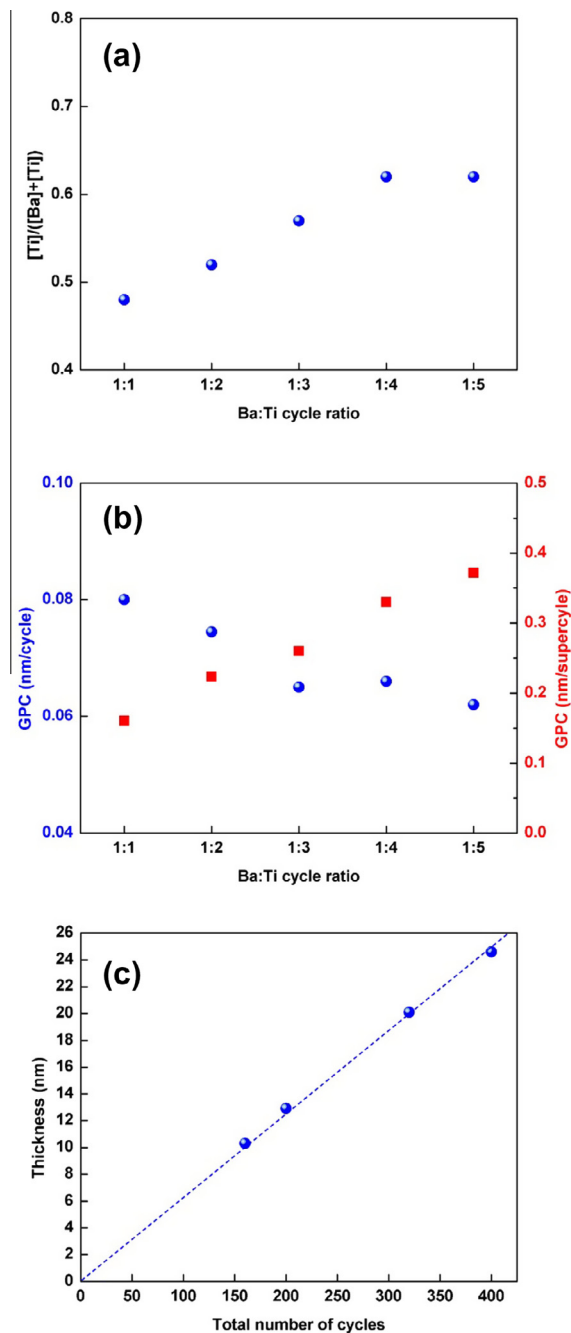
The film thickness ( $t_{\text{BTO}}$ ), roughness and density were measured by X-ray reflectivity (XRR) measurements (X'Pert Pro, PANalytical). The film thickness was also confirmed by a spectroscopic ellipsometer (Woollam M2000). High-resolution transmission electron microscopy (HRTEM) at an acceleration voltage of 300 kV was employed to analyze the crystallization of the samples (FEI Titan ETEM 300 kV). The composition analysis was conducted by X-ray photoelectron spectroscopy (XPS, PHI VersaProbe Scanning XPS Microscope) with Al (K $\alpha$ ) radiation (1486 eV). Atomic force microscopy (AFM, JEOL 5200) was used to characterize the surface morphology of the films. For the electrical measurement, Pt/BTO/p-doped Si metal–insulator–semiconductor capacitors were fabricated using highly p-doped Si wafers (a sheet resistance of 0.008  $\Omega$  cm) as substrates and a DC-sputtered Pt (200 nm) film as the top electrode. The electrical properties, (i) capacitance at 1 kHz and (ii) current density–voltage ( $J$ – $V$ ) curves (0 to +2 V) were measured by an LCR meter (Agilent, model No. E4980A) and a Keithley SourceMeter (2636A), respectively. The detailed process to obtain dielectric constants of BTO ( $\epsilon_{\text{BTO}}$ ) as well as the equivalent oxide thickness (EOT), i.e.  $t_{\text{BTO}}(3.9/\epsilon_{\text{BTO}})$ , were reported elsewhere [10–12].

We first investigated the basic ALD characteristics of the individual oxides BaO and TiO<sub>2</sub> in order to be able to deposit stoichiometric BTO. Fig. S1a and b show the growth per cycle (GPC) of BaO as a function of substrate temperature (200–350 °C) and Ba precursor pulse time, respectively. The GPC of PEALD BaO in the range of 250–300 °C was nearly constant at 0.25–0.26 nm/cycle with 4–7% non-uniformity on a 4-inch wafer. Furthermore, the GPC values of PEALD BaO at 250 °C were saturated with a precursor pulse time longer than 3 s. However, the GPC of BaO was significantly increased to  $7.6 \pm 0.02$  nm/cycle at 350 °C. Similarly, the measured GPC values of PEALD TiO<sub>2</sub> were  $\sim 0.045$  nm/cycle with 2% non-uniformity at substrate temperatures of 200–300 °C (Fig. S1c). Further, the GPC of PEALD TiO<sub>2</sub> showed to be saturated with a precursor pulse time greater than 3 s as seen in Fig. S1d.

The saturation of the GPC with increasing precursor pulse time (in the range of 250–300 °C) implies that the deposition of BaO using Ba(<sup>i</sup>Pr<sub>3</sub>Cp)<sub>2</sub> and O<sub>2</sub> plasma lies within the ALD window. The high GPC even at a relatively low deposition temperature (250 °C) clearly shows the benefit of using oxygen plasma as an oxidant over water or ozone. Furthermore, the deposition at 250 °C is appropriate to sustain thermal stability of the Ti-alkoxide-type precursor, TTIP, a key parameter for TiO<sub>2</sub> ALD growth [13]. The significant increase in GPC of BaO at 350 °C may be ascribed to the partial decomposition of Ba(<sup>i</sup>Pr<sub>3</sub>Cp)<sub>2</sub> to smaller alkyl-substituted Cp\* complexes [2]. Lee et al. [2,13] also reported the chemical vapor deposition like growth of SrO when Sr(<sup>i</sup>Pr<sub>3</sub>Cp)<sub>2</sub> was initially supplied to fresh substrates which readily provide oxygen (e.g. IrO<sub>2</sub> and RuO<sub>2</sub>). Hence, these substrates show to be unfavorable for depositing films with a uniform Ba-to-Ti ratio in the direction of growth. In our work, this is not the case due to higher bond dissociation energies of Si–O and Ti–O bonds over the Ba–O bond (bond dissociation energies Hf<sub>298</sub> (kJ/mol); Si–O: 798; Ti–O: 662; Ba–O: 563) [14]. The observed GPC values of TiO<sub>2</sub> are consistent with the previously reported GPC values, 0.04–0.05 nm/cycle at similar deposition conditions [15]. These results imply that the ALD mode deposition of BTO, which is

fabricated by repeating BaO and TiO<sub>2</sub> layers alternately, is possible at the temperature range where both of them show a constant GPC, i.e. 250–300 °C.

Fig. 1a shows the cation ratio ( $[\text{Ti}]/([\text{Ba}] + [\text{Ti}])$ ) inside the film depending on the ALD cycle ratio (i.e., the number of TiO<sub>2</sub> cycles per one BaO cycle). The cation ratios were controllable by simply changing the Ba:Ti cycle ratio: the film becomes slightly Ba-rich ( $[\text{Ti}]/([\text{Ba}] + [\text{Ti}]) = 0.48$ ) when the Ba:Ti cycle ratio is 1:1, and becomes slightly Ti-rich ( $[\text{Ti}]/([\text{Ba}] + [\text{Ti}]) = 0.52$ ) when the cycle ratio is 1:2. Fig. 1b shows the GPC versus the Ba:Ti cycle ratio: the GPC per supercycle is increased with increasing number of Ti



**Fig. 1.** (a) Composition ratio ( $[\text{Ti}]/([\text{Ba}] + [\text{Ti}])$ ) and (b) GPC (blue for per individual cycles, red for per super-cycle) vs. Ba:Ti cycle ratio. (c) Thickness of the BTO film vs. total number of individual ALD cycles for BTO with the Ba:Ti cycle ratio of 1:3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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