



## Influence of atomic layer deposition chemistry on high-*k* dielectrics for charge trapping memories

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### ABSTRACT

In this work we report the performance of the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/HfO<sub>2</sub> and SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/ZrO<sub>2</sub> stacks with emphasis on the influence of atomic layer deposition chemistry used for forming the HfO<sub>2</sub> and ZrO<sub>2</sub> blocking layers. Two Hf precursors were employed – tetrakis(ethylmethylamino)hafnium (TEMAH) and bis(methylcyclopentadienyl)methoxymethyl hafnium (HfD-04). For ZrO<sub>2</sub>, tetrakis(ethylmethylamino)zirconium (TEMAZ) and bis(methylcyclopentadienyl)methoxymethyl zirconium (ZrD-04) were used as metal precursors. Ozone was used as the oxygen source. The structural characteristics of the stacks were examined by transmission electron microscopy and grazing incidence X-ray diffraction. The electrical properties of the stacks were studied using platinum-gated capacitor structures. The memory performance of the stacks was evaluated by write/erase (W/E) measurements, endurance and retention testing. Endurance measurements revealed the most important difference between the stacks. The films grown from TEMAH and TEMAZ could withstand a significantly higher number of W/E pulses (>3 × 10<sup>5</sup> in the 10 V/−11 V, 10 ms regime), in comparison to the stacks made from HfD-04 and ZrD-04 precursors (<5 × 10<sup>3</sup> W/E cycles). This difference in endurance characteristics is attributed mainly to the different deposition temperatures suited for these two precursors and the nature of the layer formed at the Si<sub>3</sub>N<sub>4</sub>/HfO<sub>2</sub> and the Si<sub>3</sub>N<sub>4</sub>/ZrO<sub>2</sub> interfaces.

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### 1. Introduction

The scaling of conventional floating-gate (FG) flash memory cells faces significant challenges mainly due to the scalability limitations for the active dielectrics, typically made of a SiO<sub>2</sub> thin film for the tunnel oxide and of an oxide–nitride–oxide (ONO) stack for the blocking (or control) dielectric [1]. It is projected that these cell limitations together with the FG interference effects between neighboring cells, which increase with the cell density, will not allow flash memory scaling below the 22 nm technology node [1,2].

An alternative approach for the continuation of non-volatile memory cell downscaling is offered by the silicon nitride charge-trap memory technology [1,3]. The typical paradigm of this class of memory cells is the SONOS structure (silicon–oxide–nitride–oxide–silicon) which exploits for charge storage the high density of electron and hole traps that are inherent within the silicon

nitride layer [4]. The main drawbacks of the SONOS structure are the limited speed of the erase operation and the over-erase effect. While the write operation (substrate electron injection and trapping into the nitride layer) is fast, the erase operation (substrate hole injection and trapping into the nitride layer and/or electron ejection) depends strongly on the thickness of the bottom or tunnel oxide [5]. If the tunnel oxide is thicker than 2.5 nm, the erase operation becomes very slow. In turn, if the tunnel oxide is thinner than 2 nm, degradation of the retention characteristics occurs, as the trapped charge carriers leak through the thin tunnel oxide [6]. Furthermore, the use of high negative gate voltages in order to enhance the erase operation combined with the trapped positive charge leads to electron injection via the top electrode, an effect that limits the amount of positive trapped charge (over-erase effect) [5]. The extreme sensitivity of the erase operation to the thickness of the tunnel oxide layer has limited the SONOS memory applications to niche markets such as military, radiation and space applications [7].

The interest in charge trap memory technology re-emerged with the NROM memory cell [8] and the introduction of the high

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permittivity (or high- $k$ ) metal oxides into the mainstream semiconductor logic devices [9]. Simulation and experimental works showed that the replacement of the SiO<sub>2</sub> control oxide in SONOS devices by a high- $k$  oxide (e.g., Al<sub>2</sub>O<sub>3</sub>) leads to a significant electric field redistribution across the structure [10,11]. For a given voltage the use of a high- $k$  control oxide in a tri-layer stack (high- $k$ /N/O) results in an increase of the tunnel oxide electric field, leading to faster write–erase operations. In addition, when the high- $k$  oxide is combined with a high work-function metallic electrode the over-erase effect during the erase operation is significantly suppressed [11]. A typical realization of this approach is the so-called TANOS structure (tantalum nitride, alumina, silicon nitride, silicon oxide, silicon) [11]. Besides Al<sub>2</sub>O<sub>3</sub>, other materials such as HfO<sub>2</sub>, HfAlO, and HfSiO have been tested as blocking oxides [12–16].

The above mentioned efforts constitute alternative routes for the improvement of the charge trap memory technology. However, while the replacement of one or more dielectric layers of the standard ONO gate stack by high- $k$  materials remains an attractive option, the majority of these materials are characterized by a relatively high defect density, and low energy barriers for both electrons and/or holes with respect to Si and metal gates, which in turn leads to defect assisted conduction modes such as the Poole–Frenkel or the trap enhanced carrier tunneling mechanisms [17–21]. As a result the properties of the memory cells may become strongly dependent on the properties of the high- $k$  layers, making their processing very challenging. Furthermore, the high- $k$  metal oxides are refractory materials that may be processed in most controlled way using the atomic layer deposition (ALD) technique. As has been reported in several works the quality of a high- $k$  film produced by ALD depends highly upon the used chemistry, i.e., on the metallic precursors, the oxygen source and the deposition temperature [22,23]. In this work our primary interest is to examine the influence of the HfO<sub>2</sub> and ZrO<sub>2</sub> ALD precursor chemistry on the memory properties of SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/HfO<sub>2</sub> and SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/ZrO<sub>2</sub> memory stacks where HfO<sub>2</sub> and ZrO<sub>2</sub> are used as blocking oxides.

## 2. Experimental procedure

### 2.1. Selection of ALD precursors

Over the last 20 years, several ALD precursor chemistries have been developed for the deposition of HfO<sub>2</sub> and ZrO<sub>2</sub> thin films, which include mainly the hafnium and zirconium halides, the alkoxides, the alkylamides and the cyclopentadienyls [22–24]. The Hf and Zr halides are solid compounds with low volatilities [23]. Although the growing films have no carbon contamination the halogen incorporation affects the integrity of the dielectrics and is a disadvantage of the ALD halide chemistry [23,25]. Furthermore, dust and particle contamination of the film may occur and the production of HCl by-product corrodes the reactor [23]. For these reasons the halides were excluded as precursors in the current study. Similarly, the alkoxide precursors suffer from thermal decomposition which limits the ALD temperature range and result in film contamination by hydrogen and carbon [23].

Common precursors for ALD growth of HfO<sub>2</sub> and ZrO<sub>2</sub> are the Hf and Zr alkylamides which contain metal–nitrogen bonds. These precursors were introduced in order to replace the chloride based Hf and Zr precursors. Hf and Zr alkylamides are volatile with high reactivity towards water and ozone [26]. The major drawback of alkylamides is their thermal instability which limits the deposition temperature below 300 °C [27]. Higher deposition temperatures are usually preferable since they ensure that the chemical reactions are more complete and effective, leaving less residuals which may otherwise weaken the film properties. For example, the tetra-

kisethylmethylamides of hafnium and zirconium, Hf[N(C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>4</sub>] and Zr[N(C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>4</sub>], referred here as to TEMAH and TEMAZ, respectively, decompose thermally at reactor temperatures higher than 275 °C. Despite this fact, HfO<sub>2</sub> films deposited using TEMAH and H<sub>2</sub>O are stoichiometric, while the impurity levels for residual hydrogen and carbon, determined by elastic recoil detection analysis (ERDA), were found to be 1–2 and 0.5 at.%, respectively [28]. On these bases, TEMAH and TEMAZ were selected in the present study as precursors for the deposition of the HfO<sub>2</sub> and ZrO<sub>2</sub> films.

Alternative metal precursors that were introduced recently in ALD processing are the metal cyclopentadienyls. These are organometallic molecules with metal atoms bound to a ligand basically consisting of five-membered carbon ring [22,24]. In addition to their high volatility and chemical reactivity towards water and ozone, these precursors possess higher thermal stability than the alkylamides and can sustain deposition temperatures up to 375 °C [29,30]. This is quite beneficial leading to films with high chemical purity. For example the carbon and hydrogen contents in ZrO<sub>2</sub> films grown by the bis(methylcyclopentadienyl)methoxymethyl zirconium ((CpMe)<sub>2</sub>Zr(OMe)Me, where Cp = C<sub>5</sub>H<sub>5</sub> and Me = CH<sub>3</sub>, further denoted as ZrD-04) is below the detection limits of ERDA (0.5 at.%) [29]. Therefore, other precursors for deposition of ZrO<sub>2</sub> and HfO<sub>2</sub> used in this study were ZrD-04 and also HfD-04 (bis(methylcyclopentadienyl)methoxymethyl hafnium, (CpMe)<sub>2</sub>Hf(OMe)Me). The formation of metal oxide films was provided by the application of ozone, which is a strong oxidizer leading to the formation of dense films with low impurity content [24].

### 2.2. Sample fabrication and experimental methods

In the deposition experiments, n-type silicon substrates with resistivity of 1–2 Ω cm were used after initial oxidation in N<sub>2</sub>O ambient at 800 °C to produce a 2.5 nm thick thermal SiO<sub>2</sub>, followed by the deposition of a 5 nm thick Si<sub>3</sub>N<sub>4</sub> layer by low pressure chemical vapor deposition using NH<sub>3</sub> and dichlorosilane at 800 °C. On top of the SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> stack, hafnium oxide or zirconium oxide thin films were deposited by ALD to a thickness of 10 nm. The HfO<sub>2</sub> layer was formed using either the TEMAH precursor and ozone (O<sub>3</sub>) at 275 °C, or the HfD-04 precursor and O<sub>3</sub> at 350 °C, i.e. at temperatures below the critical limits to thermal decomposition of these precursors. Similarly, the ZrO<sub>2</sub> layer was formed either by TEMAZ and O<sub>3</sub> at 275 °C or by the ZrD-04 and O<sub>3</sub> at 350 °C. Reference dual stacks of SiO<sub>2</sub>/HfO<sub>2</sub> and SiO<sub>2</sub>/ZrO<sub>2</sub> were also fabricated using the alkylamide processes (TEMAH/O<sub>3</sub>, TEMAZ/O<sub>3</sub>). In addition, the effect of oxygen annealing on the gate stack properties was also studied and, for this reason, a part of the samples was subjected to annealing at 600 °C for 2 min in oxygen ambient.

The structural characteristics of the samples were examined by grazing incidence X-ray diffraction (GIXRD) using a Bruker D8 instrument and employing parallel beam optics. Transmission electron microscopy (TEM) studies were performed in cross section and plan view geometry using a Philips CM 20 electron microscope in both TEM and high resolution TEM (HRTEM) modes. Generic type platinum capacitors were fabricated using photolithography and lift-off process for the study of the electrical characteristics including the memory properties of the gate stacks. The current voltage ( $I$ – $V$ ) characteristics were recorded using a HP 4140B picoammeter and the  $C$ – $V$  characteristics using a HP 4284A LCR meter. The electrical pulses were applied to the capacitors using a HP 8110 pulse generator. The capacitor area of the samples under investigation was  $1 \times 10^{-4}$  cm<sup>2</sup>. Table 1 shows the major ALD parameters and the processed samples.

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