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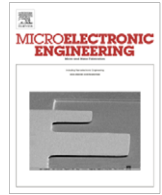

Improved manufacturability of ZrO_2 MIM capacitors by process stabilizing HfO_2 addition

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ABSTRACT

A broad compositional range of the dielectric material $Zr_{1-x}Hf_xO_2$ was evaluated with respect to its applicability in DRAM storage capacitors. The paper reports on phase composition, crystallization behavior, and electrical properties of the mixed system in planar metal-insulator-metal (MIM) capacitors. Admixture of HfO_2 into ZrO_2 proved to stabilize the deposition process at high temperatures without degrading the dielectric properties of the film. Compared to pure ZrO_2 the 30–40% HfO_2 containing films showed improved scalability (capacitance equivalent thickness 0.73 nm at $8 * 10^{-9}$ A/cm^2) as well as improved reliability.

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1. Introduction

Tetragonal crystallized ZrO_2 is currently a widely used dielectric for DRAM capacitors [1–3]. In order to meet stringent leakage current requirements for memory applications, dielectric films with low impurity content are needed. For atomic layer deposited (ALD) ZrO_2, this can be achieved by operating the process close to the thermal decomposition temperature of the precursor and by using long ozone feeding times [1]. However, these process conditions may provoke crystallization of pure ZrO_2 already during deposition leading to process instabilities and reliability issues [2,3]. This problem has been addressed by Al_2O_3 doping which increases the crystallization temperature, but causes a loss of capacitance due to the low permittivity of the dopant [2,3]. Therefore, stabilizers with higher *k* values than Al_2O_3 would be highly desirable.

In this paper, we propose the addition of HfO_2 to ZrO_2 as an alternative solution without loss of *k*. HfO_2 has a higher crystallization temperature than ZrO_2, but instead of forming the high-*k* tetragonal phase in pure form, it predominantly crystallizes in the lower *k* monoclinic phase [4]. Recently, it was shown that the phase composition of the ZrO_2–HfO_2 system can be controlled by the mixing ratio [5].

2. Experimental

All pure and mixed films of the material system $Zr_{1-x}Hf_xO_2$ were grown in a 300 mm single wafer ALD reactor using TEMAZ and TEMAH as precursor. Ozone was used as an oxidant and argon as a purge and carrier gas.

To determine the ALD growth window for TEMAH and TEMAZ, 20, 40, and 60 cycles were grown on Si-wafers at substrate temperatures ranging from 95 to 395 °C. Film thickness of this cycle variation was then determined by spectral ellipsometry (SE) and linearly fitted to obtain the growth per cycle (GPC). The GPC for the mixed system (ZrO_2, 3:1, 1:1, 1:3, HfO_2) was evaluated on TiN at a constant growth temperature of 295 °C.

For a parallel physical and electrical characterization of the mixed system, 7–9 nm thick $Zr_{1-x}Hf_xO_2$ films were deposited on planar TiN coated substrates as well as on structured wafers.

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MIM capacitors were formed using chemical vapor deposited (CVD) TiN (450 °C) as top electrode. Stoichiometry of the films ranged from pure ZrO_2 to pure HfO_2. The growth of all mixed films was started and completed with at least three cycles of TEMAH.

Grazing incidence X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) were performed for as-deposited films to gain insight on structure, composition, and film morphology. Additional GIXRD spectra were collected after top electrode formation. *I–V* and *C–V* measurements were performed using standard measurement equipment.

3. Results and discussion

The ALD growth windows of TEMAZ and TEMAH indicate that both precursors exhibit ALD-type behavior for the maximum temperature of 295 °C which was used to grow $Zr_{1-x}Hf_xO_2$ layers (Fig. 1, bottom). Solely based on this planar growth experiments even higher deposition temperatures up to 350 °C might be possible to further improve impurity level and film quality. For temperatures above 350 °C, the drastic increase of growth rate indicates enhanced thermal decomposition of the precursor resulting in CVD-like growth. For future application in 3D DRAM structures, the process window and the tolerable CVD fraction needs to be evaluated in terms of step coverage in stack or trench structures.

The growth per cycle for $Zr_{1-x}Hf_xO_2$ at 295 °C was found to follow a linear trend expected for chemically similar precursors like TEMAZ and TEMAH (Fig. 1, top). For directly alternating precursor pulses, however, the GPC drops below the theoretical value as estimated from the individual growth rates of the precursors. Further indication for deviation from growth behavior of the single precursors is reflected in an increased surface roughness for as-deposited films close to the 1:1 mixing ratio (Fig. 2, inset).

As a result of the high deposition temperature, which is necessary to improve leakage current properties, the as-deposited 9 nm ZrO_2 film shows a fully crystallized tetragonal structure (Fig. 2). However, for an admixture of 29% HfO_2, onset of crystallization during deposition is being suppressed, whereas films remain completely amorphous for higher HfO_2 contents. The inhibition of crystallization by HfO_2 addition is further reflected in a decreasing surface roughness which generally suggests improved electrical properties due to a higher interface quality (Fig. 2 inset) [2].

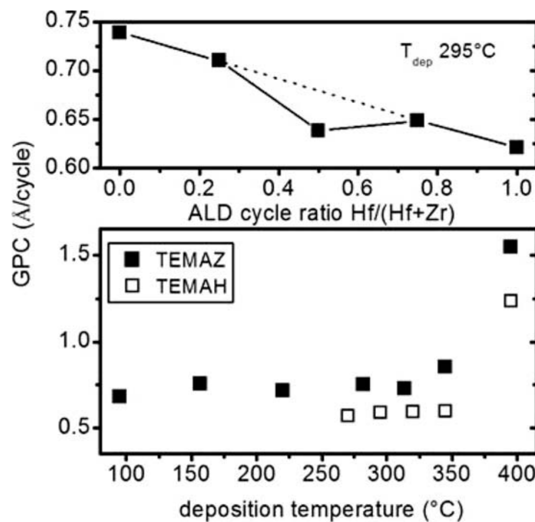

Fig. 1. Growth per cycle (GPC) for the mixed system HfO_2–ZrO_2 at 295 °C deposition temperature (top). ALD growth window for TEMAZ and TEMAH (bottom).

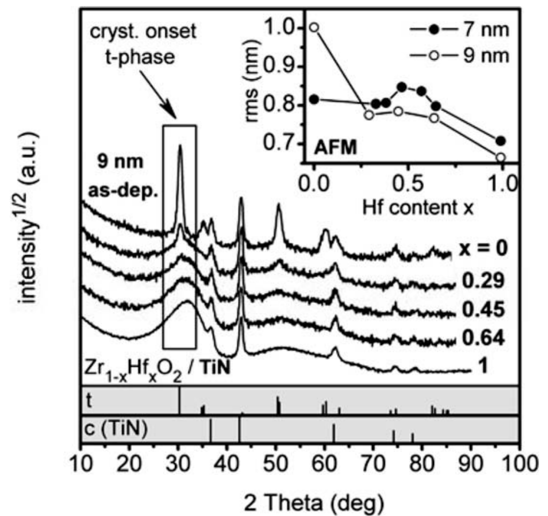

Fig. 2. GIXRD and AFM for as dep. 9 nm $Zr_{1-x}Hf_xO_2$ on TiN show suppression of crystallization by HfO_2 addition.

The thermal budget of top electrode deposition leads to the crystallization of all films (Fig. 3). Thereby, the onset of monoclinic phase formation is observed at around 45% HfO_2. Comparing the XRD spectra of the 7 and 9 nm films for this composition, the dependence of phase stability on film thickness becomes apparent. Due to reduced surface energy contribution, the tetragonal phase is destabilized with increasing thickness and higher HfO_2 content (Fig. 4) [6–8].

Coinciding with the appearance of the monoclinic phase, the *k* value drops sharply and strong leakage current degradation can be observed (Fig. 5). The dependence of current density on capacitance area suggests a statistically distributed void formation in the spatial range of the measured devices (Fig. 6). We attribute this effect to defect formation driven by the monoclinic phase formation [4,9].

However, for HfO_2 contents below the critical concentration, films showed improved electrical properties compared to pure ZrO_2 and achieved a CET of 0.73 nm within the specified leakage current of 10^{-8} A/cm^2 (Fig. 5). The lower CET of films with low HfO_2 content simply result from a slightly lower physical thickness caused by the not perfectly compensated change in GPC for mixed

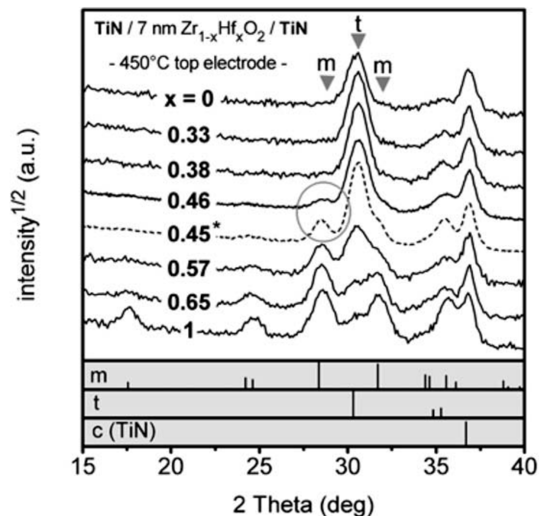

Fig. 3. GIXRD of 7 nm $Zr_{1-x}Hf_xO_2$ (MIM) reveal tetragonal to monoclinic phase transition with HfO_2 content (* 9 nm).

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