



# Atomic layer deposition of zirconium dioxide from zirconium tetrachloride and ozone



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## ABSTRACT

ZrO<sub>2</sub> films were grown by atomic layer deposition using ZrCl<sub>4</sub> and O<sub>3</sub> as precursors. The films were grown on silicon substrates in the temperature range of 220–500 °C. The ALD rate was monotonously decreasing from 0.085 to 0.060 nm/cycle in this temperature range towards the highest temperatures studied. The content of chlorine in the films did not exceed 0.2 at.% as measured by elastic recoil detection analysis. The content of hydrogen was 0.30 and 0.14 at.% in the films grown at 300 and 400 °C, respectively. Structural studies revealed the films consisting of mixtures of stable monoclinic and metastable tetragonal/cubic polymorphs of ZrO<sub>2</sub>, and dominantly metastable phases of ZrO<sub>2</sub> below and above 300 °C, respectively. Permittivity of dielectric layers in Al/Ti/ZrO<sub>2</sub>/(TiN)/Si capacitors with 15–40 nm thick ZrO<sub>2</sub> ranged between 12 and 25 at 100 kHz and the dielectric breakdown fields were in the range of 1.5–3.0 MV/cm.

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## 1. Introduction

Metal oxide, such as ZrO<sub>2</sub> thin films, has been of a continuous research interest for micro- and nanoelectronics. As a dielectric metal oxide, ZrO<sub>2</sub> has been of interest at first as a potential candidate for gate dielectrics in transistors [1–5]. ZrO<sub>2</sub> has found, in nanoelectronics, an application as a memory capacitor dielectric [6–10], and is investigated also as a potential dielectric for resistive random-access memories [11]. In addition, ZrO<sub>2</sub> has been considered as a host ion conductor material for solid oxide fuel cells [12,13] or encapsulation material layer for organic electronic devices [14]. In relation to different applications, energetically enhanced growth mechanisms of metal oxides, incl. ZrO<sub>2</sub> [15] as well as structural development of ZrO<sub>2</sub> layers [10,16] have been research directions of interest.

In general, the layered materials, e.g., metal oxides, should be prepared in processes providing the maximum purity and structural perfection of the layers. Especially in chemical deposition processes commonly ensuring laterally uniform growth over large and arbitrarily shaped areas, the chemical purity of the materials synthesized is a common issue. One of the main residual elements contaminating the films is hydrogen, a common contributor to the chemical composition of the precursor chemicals. Hydrogen is capable to enhance proton conduction in the solids, drifting towards interfaces, distorting the capacitance

values and inducing electronic defects and broken metal–oxygen bonds, thus also enhancing leakage currents [17,18]. If the accompanying impurity in the films is chlorine, then certain amounts of hydrogen chloride may form, which may etch the host metal oxide structure. For this reason, hydrogen-free processes could be sought. For instance, regarding gate oxide deposition processes, ZrO<sub>2</sub> films have been fabricated either by sputtering [3,4] or electron-beam evaporation [5] of thin metallic Zr films, followed by ozone-assisted oxidation in order to form insulating ZrO<sub>2</sub> layers. In addition, carbon — i.e., another light element also often contributing to the composition of the metal precursor ligands, is known as a source of electronic trap states [19] in dielectric films.

Atomic layer deposition (ALD) of metal oxides is most commonly based on sequential surface reactions between metal and oxygen precursors, therewith in the case of ZrO<sub>2</sub> between, e.g., Zr[N(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> and H<sub>2</sub>O [12] or Zr[(CH<sub>3</sub>)<sub>2</sub>N]<sub>4</sub> and H<sub>2</sub>O [20]. Often, both precursors contain hydrogen and thus the residual hydrogen content could be diminished after substituting either one or both precursors by hydrogen-free ones. ZrO<sub>2</sub> films have been grown by several water-free ALD processes [21], such as in those based on (C<sub>5</sub>H<sub>5</sub>)Zr(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub> and oxygen plasma [7,22], Zr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> and O<sub>3</sub> [14], Zr[N(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> and O<sub>3</sub> [6,9,11,23], Cp<sub>2</sub>ZrCl<sub>2</sub> and O<sub>3</sub> [13,24], or Zr(NEtMe)<sub>3</sub>(guanEtMe) and O<sub>3</sub> [25]. Regarding metal halide based and hydrogen-free ALD processes, depositions of Al<sub>2</sub>O<sub>3</sub> from AlCl<sub>3</sub> and O<sub>3</sub> [26], TiO<sub>2</sub> from TiCl<sub>4</sub> and O<sub>3</sub> [27], Ta<sub>2</sub>O<sub>5</sub> from TaCl<sub>5</sub> and O<sub>3</sub> [28], HfO<sub>2</sub> from HfCl<sub>4</sub> and O<sub>3</sub> [29], and HfO<sub>2</sub> from HfI<sub>4</sub> and O<sub>2</sub> [30] have been reported. There is also an implication about the possibility to atomic layer deposition of

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ZrO<sub>2</sub> from ZrCl<sub>4</sub> and O<sub>3</sub> [29], although the details of the process have remained beyond the scope of that study. ZrO<sub>2</sub> films have been grown on electrodes assumptionally most relevant to the particular applications, such as on silicon under potential gate dielectrics [20,22] or titanium nitride for memory capacitors [7–9,23]. Certain issues related to the increment of leakage currents due to the roughness of TiN electrodes have been pointed out [31].

This study is to prove the possibility to deposit ZrO<sub>2</sub> thin films in a hydrogen-free and carbon-free ALD process. The films were grown in a water-free and hydrogen-free process from zirconium tetrachloride and ozone as precursors. The aim of the study is not in the thorough and direct comparison with the films deposited in more traditional and scaled up ALD processes, e.g., in that using ZrCl<sub>4</sub> and H<sub>2</sub>O but rather in the examination of the average growth rate, and effect of the main deposition parameters on the film structure and electrical behavior. During the work, the films were characterized structurally and electrically.

## 2. Experimental details

The films were grown in a commercial flow-type hot-wall reactor F120 (ASM Microchemistry, Ltd.) [32]. The reactor was operated under a pressure of about 1000 Pa using nitrogen as a carrier and purging gas. ZrO<sub>2</sub> was deposited using the process based on zirconium tetrachloride, ZrCl<sub>4</sub> in the substrate temperature range of 220–500 °C. Ozone, O<sub>3</sub>, was used as an oxygen precursor. Ozone was produced with a Wedeco Ozomatic Modular 4 HC ozone generator from oxygen (99.999%, Linde Gas). The estimated ozone concentration output of the generator was about 100 g/m<sup>3</sup>. ZrCl<sub>4</sub> was evaporated at 170–180 °C from an open boat inside the reactor and transported to the substrates by the carrier gas flow. The cycle times used did not exceed 1.5–0.5–6.0–0.5 s, denoting the sequence metal precursor pulse–purge–O<sub>3</sub> pulse–purge. The substrates were cut as 5 × 5 cm × cm pieces out of undoped Si(100) covered with a 1.5–2.0 nm thick wet chemically grown SiO<sub>2</sub>. Selected samples were annealed at 900 °C in N<sub>2</sub> flow for 30 min. At 300 and 400 °C thinner films were grown using cycle numbers varied between 200 and 300. In addition, in a special experiment, the ozone pulse length was varied between 2.0 s and 12.0 s. In the latter experiments, also conducting electrode substrates were used for the deposition of ZrO<sub>2</sub>. These substrates were based on (100) silicon with resistivity 0.014–0.020 Ω · cm, i.e., boron-doped to concentration up to 5 × 10<sup>18</sup>–1 × 10<sup>19</sup>/cm<sup>3</sup>, and coated with 10 nm thick chemical vapor deposited titanium nitride layer. The films were grown to thicknesses ranging from 15 to 40 nm, in order to make the structural and compositional measurements more convenient.

The thicknesses of the films were evaluated either by X-ray reflectometry (XRR) or by energy dispersive X-ray (EDX) spectroscopy. The XRR was performed using a PANalytical X'Pert PRO X-ray diffractometer with Cu K<sub>α</sub> source. In the GIXRD, the incidence angle was 1°. Specimens for transmission electron microscopy (TEM) were prepared with the lift-out method [33] in a FEI Quanta 3D 200i focused ion beam (FIB)-scanning electron microscope (SEM), i.e., FIB-SEM dual beam microscope. Bright-field TEM images were taken with a FEI Tecnai F-20 microscope operated at 200 kV. EDX was also applied for the measurements on the residual chlorine content in the solid films by a Hitachi S-4800 scanning electron microscope (SEM) equipped with an Oxford INCA 350 EDX spectrometer. The EDX spectra were measured at 30 keV. The beam current and spectrometer gain were determined from a calibration measurement performed under the same beam conditions. The film thicknesses and ratios of the different elements were calculated from the k ratios of Zr and Cl K<sub>α</sub> X-ray lines measured with the calibrated beam. The calculations were done with a GMRFILM program [34], assuming a density of 5 g/cm<sup>3</sup> for ZrO<sub>2</sub>. Surface morphology was monitored using the same SEM apparatus. In addition, the thicknesses of the films were determined from reflectance spectra measured within a wavelength range of 380–1100 nm using a Hitachi U2000 spectrophotometer and applying a fitting method developed by Ylilammi

and Ranta-aho [35]. The composition of selected as-deposited and annealed samples was determined by Time-of-Flight Elastic Recoil Analysis (ToF-ERDA), using 35 MeV <sup>127</sup>I<sup>7+</sup> beam. The measurement geometry was 15 ± 25° (scattering/detection angle 40°, incident angle 15° from sample surface). For depth scales, 5.0 g/cm<sup>3</sup> sample density was considered.

For electrical measurements, Al/Ti/ZrO<sub>2</sub>/TiN/Si/Al and Al/Ti/ZrO<sub>2</sub>/Si/Al capacitors were constructed with the capacitor area of 0.204 mm<sup>2</sup>. Double-layer >110 nm/>50 nm thick Al/Ti dot electrodes were evaporated through a shadow mask on the ZrO<sub>2</sub> films by electron beam evaporation, the Ti layer being in direct contact to ZrO<sub>2</sub>. Backside ohmic contact was provided by evaporating 100–120 nm thick Al layer on etched Si. The capacitance–voltage (C–V) curves were measured using an HP4284A precision LCR meter in the a.c. frequency range of 1 kHz–1 MHz, applying a series capacitance–dissipation (Cs–D) measurement mode with a bias voltage step of 0.1 V and a trigger delay of 0.5 s. For current–voltage measurements a Keithley 2400 source meter was used applying stair step voltage with a voltage step of 0.1 V and 0.5 s delay.

## 3. Results and discussion

### 3.1. Film growth

Growth of ZrO<sub>2</sub> from ZrCl<sub>4</sub> and O<sub>3</sub> is energetically favored in the whole temperature range studied and may proceed in accord with the following equation:



for which the changes in enthalpy, ΔH, entropy, ΔS, and Gibbs free energy, ΔG, are –409 kJ/mol, 236 J/K mol, and –545 kJ/mol, respectively, at 300 °C (HSC Chemistry for Windows, version 5.1, Outokumpu Ltd.).

The growth rate, measured at approximately equal distances from the edges of substrates, demonstrated moderate, but firm decrease with the increase in the growth temperature (Fig. 1) The decrease in the growth rate in the substrate temperature range of 200–500 °C by about 1.4–1.5 times is analogous to that observed earlier in the case of ALD of ZrO<sub>2</sub> from ZrCl<sub>4</sub> and H<sub>2</sub>O [36,37]. In the case of water-based ALD, one can consider the contribution of surface OH-groups as active adsorption sites in the process: the density of the OH-groups decreases with the increase in the substrate temperature and, consequently, suppresses the deposition rate. An additional reason to the decrease in the

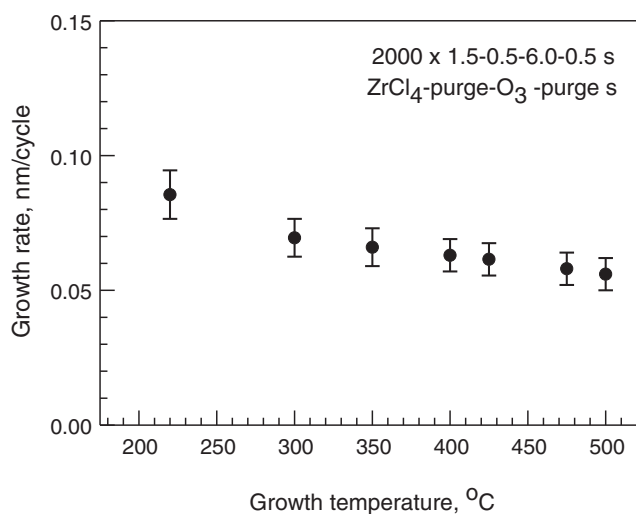


Fig. 1. Growth rate against growth temperature for ZrO<sub>2</sub> films grown from ZrCl<sub>4</sub> and O<sub>3</sub>, measured by EDX. The amounts of cycles, cycle times and reactor conditions were kept constant in the series given.

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