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Atomic layer deposition and properties of mixed Ta₂O₅ and ZrO₂ films

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Thin solid films consisting of ZrO₂ and Ta₂O₅ were grown by atomic layer deposition at 300 °C. Ta₂O₅ films doped with ZrO₂, TaZr₂.75O₈ ternary phase, or ZrO₂ doped with Ta₂O₅ were grown to thickness and composition depending on the number and ratio of alternating ZrO₂ and Ta₂O₅ deposition cycles. All the films grown exhibited resistive switching characteristics between TiN and Pt electrodes, expressed by repetitive current-voltage loops. The most reliable windows between high and low resistive states were observed in Ta₂O₅ films mixed with relatively low amounts of ZrO₂, providing Zr to Ta cation ratio of 0.2. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4975928]

INTRODUCTION

Artificially combined and structured metal oxides have gained interest as materials exhibiting interesting and advanced physical and chemical properties. Herewith Ta₂O₅ and ZrO₂ composites mixed within a variable range of tantalum to zirconium cation ratios have been studied as materials of possible interest towards several applications. Ta₂O₅-ZrO₂ mixtures produced by the sol-gel technique have been characterized in terms of their structure, surface acidity, and catalytic properties.1 Tantalum doped zirconia has been of interest due to its thermomechanical behavior.2 Corrosion resistance of structurally and mechanically stable, mostly orthorhombic, ZrO₂–Ta₂O₅,3,4 or ZrO₂–Nb₂O₅–Ta₂O₅5,6 pellets and powders have been examined and described.

Electronic and structural properties of tantalum-doped monoclinic ZrO₂ have both been characterized theoretically.7 Zirconia nanocrystals have been stabilized in the tetragonal phase of ZrO₂ by tantalum doping.8 Phase diagrams for the Ta₂O₅-ZrO₂ system, including ternary zirconate phases,9 have been described. Ta₂O₅-ZrO₂ composite polycrystalline powders have been described as materials possessing dielectric permittivity values up to 50.10 Dielectric properties of TaZr₆O₁₇ films obtained by composition-combinatorial approach through the sol-gel technique were characterized.11 In zirconium doped tantalum oxide films, sputtered on nitride electrodes, leakage current densities lower than those in undoped tantalum oxide, were measured.12 Sputtered Ta₂O₅–ZrO₂ high-k gate dielectric films have been studied for potential applications in metal-oxide-semiconductor (MOS) devices.13,14 Zr-doped TaOₓ high dielectric constant (high-k) films were deposited on silicon wafer pre-covered with tantalum nitride to hinder the formation of the SiOₓ interface layer during the subsequent high-temperature annealing step.15 A large variety of metal oxides has exhibited resistive switching behavior.16–22 Tantalum oxide has, however, been one of the most prominent candidate material in the field of memristor technology. Mostly sputtered, but also atomic layer deposited tantalum

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oxide films with variable stoichiometry have been investigated as materials suitable for the application in resistance switching memory cell capacitors.17,19,20,23–27 TiN/Ta2O5/Ta,28,29 Pt/TaOx/HfNx,30 Al/Cu/Ti/TaOx/W,31 Pd/(TiO2)Ta2O5−x/TaOy/Pd27 and Pt/TaOx/Ta26 resistive switching memory cells have been fabricated. Concentration of defects in the Ta2O5 layers and, in particular, the existence and tunability of the content of oxygen vacancies has been considered and studied as an important factor affecting the memristive performance of TaOx-based cells.32,33 The switching, as observed, has been dependent on the choice of electrode materials in direct contact to the oxide layer. Highly reactive metals, such as Ti and Zr, have produced low yields for switchable TaOx based devices, whereas Ni and noble metals (Pd, Pt, Au) did not create sufficiently oxygen vacancies at the top metal–oxide interface via chemical reactions resulting in unipolar switching dominated by thermal effects.34 Stable bipolar resistive switching has been observed in structures containing one electrode acting as a basis for cation-oxygen exchange (reactive metals) and non-reacting (noble) metals as the second electrode. Regarding the useful thickness of the oxide based memristive devices, one can apply TaOx layers with thickness below 1-2 nm, still exhibiting reliable resistive switching properties.29

ZrO2 has also been frequently described as a thin film material exhibiting resistive switching. The effect was observed when deposited, e. g., between Pt and TiN electrodes either in the form of undoped ZrO2 alone,35 or together with HfO2.36 Furthermore, resistive switching has been described in ZrO2 films containing implanted Zr+ in Au/Cr/Zr+–ZrO2/n+-Si,37 indium-tin-oxide/ZrO2/Ag,38 Ag/ZrO2/Ag,39 Ti/ZrO2/Pt,40–42 Cu/ZrO2/Pt,44 and Ni/ZrO2/TaN45 stacks. ZrO2 has therewith been deposited by sputtering,42,43,45 spin coating,39 electron beam evaporation44,46,47 and laser ablation.40,41 It is to be noted that resistive switching has been observed and evaluated in amorphous ZrO2 films as well.52 It has also been found that embedding an amorphous ZrO2 layer in Pt/ZrO2/TiO2/Pt structure can result in excellent bipolar switch in comparison with Pt/TiO2/Pt device.38 In a few cases, ZrO2 layers have artificially formed as defective host materials, prone to filamentary switching, after distribution of metallic (i.e. not intentionally oxidized) implants in the oxide, exemplified by Cu/ZrO2:Cu/Pt,47 Ti/ZrO2 with embedded Mo layer/Pt,48 and Cu/ZrO2:Ti/Pt,30 and Cu/TiOx−ZrO2/Pt30 based ReRAM stacks. In the latter case, 20 nm thick ZrO2 films were deposited by electron beam evaporation, followed by atomic layer deposition of TiO2 layer.

It may occur challenging to keep strict control over the defect density and the suitable degree of stoichiometry in metal oxides subjected to resistance switching. For instance, artificially defective TaOx/Ta2O5 films have been created by implanting oxygen ions into pre-sputtered 50 nm thick Ta films.51 Controlled fabrication of resistive switching stacks by atomic layer deposition has been considered as a complicated process, due to the difficulties related to feasible formation of medium rich of oxygen vacancies, in which the filament forms, as well as an O vacancy deficient layers to control the filament rupture.52 However, there are recent works devoted to atomic layer deposition of memristive TaOx based switches built on TiN/Ta2O5/Ta/TaN stacks with 1-4 nm thick tantalum oxide films.29 In another study, 7 nm thick Ta2O5 layers in TiN/Ta2O5/TiN and TiN/Ta2O5/Al2O3/TiN stacks were grown by ALD from Ta(OC2H5)5, and H2O.53

ALD of zirconium oxide doped tantalum oxide films with the purpose to use the material in transistor gate dielectric films has been claimed.54 Ta2O5 thin films have been grown in a water-free ALD process from Ta(OC2H5)5 and TaCl5.55,56 ZrO2-Ta2O5 nanolaminates with improved dielectric characteristics were grown by atomic layer deposition using Ta(OC2H5)5, ZrCl4 and H2O as precursors.57,58 Enhanced dielectric constant was also measured in ZrO2-Ta2O5 nanolaminates grown by ALD and heat treated after the deposition.59 However, in the latter study the precursors used were not reported. ZrO2 films were grown earlier by ALD from ZrCl4 and O3.60 It seems that mixed tantalum zirconium oxide films have not yet been grown in water-free ALD process from Ta(OC2H5)5 and ZrCl4. However, ALD of zirconium doped tantalum oxide films with the purpose to use the material in transistor gate dielectric has been claimed,54 whereby the films were grown using alternate cycling of metal precursors Ta(OC2H5)5, TaCl5, ZrI2 (and/or ZrCl4), and H2O or H2O2 as oxygen precursors. Kärkkänen et al.61 have investigated the ALD of ZrO2 thin films from Zr[N(CH3)(C2H5)]4 and O3, and studied their resistive switching behavior.

In this study, thin solid films of mixed Ta2O5 and ZrO2 layers were grown by ALD from Ta(OC2H5)5 and ZrCl4 as metal precursors. O3 has optionally been applied as an oxygen source. The oxide films were, alternatively, also grown in direct reactions between halide and alkoxide
precursors along with the so-called water-free hydrolysis route. The study was aimed at the evaluation of the effect of relative content of both cations on the resulting film structure and resistive switching characteristics.

EXPERIMENTAL DETAILS

Ta$_2$O$_5$-ZrO$_2$ films were grown in a flow-type hot-wall ALD reactor F120 (ASM Microchemistry, Ltd.) at a substrate temperature of 300 °C. Zirconium tetrachloride, ZrCl$_4$ (Aldrich, 99.99 %), and tantalum pentaethoxide, Ta(O)$_2$H$_5$ (Strem Chemicals, 99.9 %), further also denoted as Ta(OEt)$_5$, were used as zirconium and tantalum precursors, respectively. Nitrogen, N$_2$, was applied as the carrier and purging gas. ZrCl$_4$ and Ta(O)$_2$H$_5$ were evaporated at 170–185 and 95 °C, respectively, from open boats inside the reactor and transported to the substrates by inert gas valving of the carrier gas flow. Ozone, O$_3$, used as an additional oxygen precursor, was produced in a Wedeco Ozomatic Modular 4 HC ozone generator from oxygen (99.999 %, Linde Gas). The estimated ozone flow rate from the generator during the ozone pulsing was about 220 sccm, while the carrier gas flow rate in the ALD reactor was kept at 400 sccm.

The films were grown via alternate exposure of the substrate surface to either sequential ZrCl$_4$ and Ta(O)$_2$H$_5$ flows separated by purge periods, or to sequential ZrCl$_4$, Ta(O)$_2$H$_5$, and O$_3$ flows separated by purge periods. For example, and further in this paper, the cycle sequencing written as 750 × 0.5-0.5-1.0-0.5 s, TaOEt-p.-ZrCl$_4$-p., will denote 750 ALD cycles, each consisting of 0.5 s long Ta(O)$_2$H$_5$ pulse, 0.5 s long ZrCl$_4$ pulse, and 0.5 s long purge. Analogously, the cycle sequencing written as 100 × [6 × 0.5-0.5-1.0-0.5 s, TaOEt-p.-ZrCl$_4$-p.] + 6 × 0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p.] denotes 100 Ta$_2$O$_5$-ZrO$_2$ supercycles, each consisting of 6 ALD cycles for Ta$_2$O$_5$ constituent layers grown with 0.5 s Ta(O)$_2$H$_5$ pulse, 0.5 s purge, 1.0 s O$_3$ pulse, and 1 ALD cycle for ZrO$_2$ constituent layers grown with 0.5 s Ta(O)$_2$H$_5$ pulse, 0.5 s purge, 1.5 s O$_3$ pulse, and 0.5 s purge. These 6 Ta$_2$O$_5$-ZrO$_2$ supercycles were followed by 6 ALD cycles for Ta$_2$O$_5$, closing the stack of the layers, and making the film symmetrical from electrode to electrode in terms of the chemical composition. The growth cycles and some essential characteristics of selected films grown in this study are given in Table I.

The substrates were cut as 5 cm × 5 cm pieces out of undoped Si(100) covered with a 1.5–2.0 nm thick wet chemically grown SiO$_2$. Selected samples were annealed at 900 °C in N$_2$ flow for 30 min. Also conducting substrates were used, based on (100) silicon with resistivity 0.014–0.020 Ω·cm, i.e., boron-doped to concentration up to 5 × 10$^{18}$–1 × 10$^{19}$/cm$^3$, and coated with 10 nm thick chemical vapor deposited titanium nitride layer. The films were grown to thicknesses ranging from 1 to 100 nm, in order to make the structural and compositional measurements more convenient. Spectroscopic ellipsometer model GES5-E, equipped with a 75 W xenon lamp as a light source emitting a continuous spectrum ranging from ultraviolet to infrared (185 – 2000 nm), was used for the evaluation of the films thicknesses and refractive indexes. The incident light was focused with a microspot with dimensions 365 × 270 µm under 75° incidence angle. 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. Grazing incidence X-ray diffractometry (GIXRD) was performed using a PANalytical X’Pert PRO X-ray diffractometer with Cu Kα source at the incidence angle of 1°. Specimens for transmission electron microscopy (TEM) were prepared with the lift-out method 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.

Energy dispersive X-ray spectrometry (EDX) was applied for the measurements of the zirconium to tantalum atomic ratio, and also for the estimation of the film thicknesses, using 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 under the same beam conditions. The film thicknesses and ratios of the different elements were calculated from the k ratios of Zr, Ta, and Cl Kα X-ray lines measured with the calibrated beam. The calculations were done with a GMRFILM program.
TABLE I. Sequences of the growth cycles, thickness variations, refractive indexes, Zr:Ta atomic ratios by EDX and contents of constituting elements by ToF-ERDA for Ta$_2$O$_5$-ZrO$_2$ films as-deposited at 300 °C from Ta(OEt)$_5$, ZrCl$_4$, and O$_3$. Precursor pulse lengths are indicated within the cycle sequences. All the precursor pulses were separated by 0.5 s long purge times.

<table>
<thead>
<tr>
<th>Growth cycle sequences</th>
<th>thickness</th>
<th>refractive index</th>
<th>Zr:Ta</th>
<th>Zr, Ta, and Cl at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 × [1 5 × 0.5/1.5 s, TaOEt/O$_3$ + 1 × 0.5/0.5/1.5 s, TaOEt/ZrCl$_4$/O$_3$] + 15 × 0.5/1.5 s, TaOEt/O$_3$</td>
<td>27-35 nm</td>
<td>2.202 ± 0.001</td>
<td>&lt;0.2</td>
<td></td>
</tr>
<tr>
<td>160 × [3 × 0.5/1.5 s, TaOEt/O$_3$ + 1 × 0.5/0.5/1.5 s, TaOEt/ZrCl$_4$/O$_3$] + 10 × 0.5/1.5 s, TaOEt/O$_3$</td>
<td>32-40 nm</td>
<td>2.213 ± 0.006</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>250 × [5 × 0.5/1.0 s, TaOEt/O$_3$ + 1 × 0.5/1.0/1.5 s, TaOEt/ZrCl$_4$/O$_3$] + 5 × 0.5/1.0 s, TaOEt/O$_3$</td>
<td>73 nm</td>
<td>2.27 ± 0.03</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>100 × [6 × 0.5/1.0 s, TaOEt/O$_3$ + 1 × 0.5/1.5 s, ZrCl$_4$/O$_3$] + 6 × 0.5/1.0 s, TaOEt/O$_3$</td>
<td>27-32 nm</td>
<td>2.224 ± 0.002</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1500 × 0.5/1.0/1.5 s, TaOEt/ZrCl$_4$/O$_3$</td>
<td>100-113 nm</td>
<td>2.52 ± 0.05</td>
<td>0.8</td>
<td>12.8 ± 0.2 Ta 16.7 ± 0.3 Zr 0.2 ± 0.1 Cl</td>
</tr>
<tr>
<td>280 × 0.5/1.0/1.5 s, TaOEt/ZrCl$_4$/O$_3$.</td>
<td>24-30 nm</td>
<td>2.203 ± 0.004</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>750 × 0.5/1.0 s, TaOEt/ZrCl$_4$</td>
<td>25-34 nm</td>
<td>2.113 ± 0.001</td>
<td>0.9</td>
<td>12.5 ± 0.4 Ta 15.7 ± 0.6 Zr 4.6 ± 0.4 Cl</td>
</tr>
<tr>
<td>2 × 0.5/1.5 s, ZrCl$_4$/O$_3$ + 50 × [4 × 0.5/1.0/1.5 s, TaOEt/ZrCl$_4$/O$_3$] + 2 × 0.5/1.5 s, ZrCl$_4$/O$_3$</td>
<td>20-30 nm</td>
<td>2.186 ± 0.004</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>250 × [5 × 0.5/1.5 s, ZrCl$_4$/O$_3$ + 1 × 0.5/1.5/0.5 s, ZrCl$_4$/O$_3$/TaOEt] + 6 × 0.5/1.5 s, ZrCl$_4$/O$_3$</td>
<td>120 nm</td>
<td>2.27 ± 0.03</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

assuming a density of 5 g/cm$^3$ for ZrO$_2$. Surface morphology was monitored using the same SEM apparatus. The composition profile in selected as-deposited and annealed samples was determined by time-of-flight elastic recoil detection analysis (ToF-ERDA), using 35 MeV $^{127}$I$^{7+}$ beam. The measurement geometry was 15 ± 25° (scattering/detection angle 40°, incident angle 15° from sample surface). For depth scales, 5.0 g/cm$^3$ film density was considered.

For electrical measurements, Au/Pt/Ta$_2$O$_5$-ZrO$_2$/TiN/Si stacks were formed. Square shaped top electrodes with lateral dimensions of 100–300 µm were electron beam evaporated through a shadow mask. The electrodes consisted of 30 nm thick platinum layer in direct contact to Ta$_2$O$_5$-ZrO$_2$ film, followed by the topmost 30 nm thick Au layer. Electrical characterization of the prepared structures was performed using a Keithley 4200 Semiconductor Characterization System. During the measurement the top electrode was biased and the bottom TiN electrode was grounded.$^{66}$

RESULTS AND DISCUSSION

Film growth and composition

In regard with the elemental composition, in a 33.5 ± 1.0 nm thick film as-deposited using 750 cycles consisting of sequential pulses of Ta(OEt)$_5$ and ZrCl$_4$ separated by purge periods, the
ToF-ERDA revealed 12.5 ± 0.4 at.% Ta, 15.7 ± 0.6 at.% Zr, 63.8 ± 1.7 at.% O, 2.5 ± 0.5 at.% H, 1.0 ± 0.2 at.% C, and 4.6 ± 0.4 at.% Cl (Fig. 1). In accord with EDX, the Zr:Ta cation ratio in this sample was 0.9. The amounts of metal cations in the film were almost equal, which may also be expected due to the equal amounts of the metal precursor pulses. After 30 min annealing in nitrogen at 800 °C, the elemental contents were 12.8 ± 0.4 at.% Ta, 14.5 ± 0.5 at.% Zr, 69.2 ± 1.4 at.% O, 2.3 ± 0.4 at.% H, 1.1 ± 0.2 at.% C, 0.2 ± 0.1 at.% Cl. One can see, that the atomic contents of the metals were the same, within the error limits, before and after heat-treatment. One can also see that the content of lighter and residual elements was not essentially affected by the annealing, except that of chlorine with the content noticeably decreasing from 4.6 to 0.2 at.%. Certain overlap visible in depth profiles of the film and substrate at the interface is due to the measurement technique.

In heavy ion techniques, multiple scattering is essential issue, causing angular and energy broadening of the probing beam and detected particles detected after scattering or recoil processes. Because of multiple scattering and energy straggling, by energy loss for the particles, the depth resolution weakens deeper in the sample, especially in samples containing heavy elements like tantalum. In addition, issues related to the roughness of film surface and interfaces can interfere in the determination of the exact borderlines between distinct layers, especially considering the low incidence angle, 15°. Effects of multiple scattering and energy straggling are not corrected in the Figure 1.
Application of ozone did not noticeably influence the composition of the metal oxide films, in terms of the cation ratio. ToF-ERDA carried out on a 113 nm thick film deposited using 1500 cycles consisting of sequential pulses of Ta(OEt)$_5$, ZrCl$_4$, and O$_3$, separated by purge periods, contained 12.8 ± 0.2 at.% Ta, 16.7 ± 0.3 at.% Zr, 69.2 ± 1.4 at.% O, 2.3 ± 0.4 at.% H, 1.1 ± 0.2 at.% C, and 0.2 ± 0.1 at.% Cl (Fig. 1). In accord with the EDX analysis, although taken from a different location on the sample, the Zr:Ta cation ratio in this film was 0.83. One could see, that the application of ozone has not strongly affected the composition of the films, compared to the films grown using alternate pulsing of Ta(OEt) and ZrCl$_4$ without ozone. The contents of hydrogen and carbon were not affected by the additional exposure to ozone. However, there was certain decrement in the content of chlorine detected, compared to those measured in the film deposited without ozone. This can plausibly be explained by the fact that the ozone was applied after the ZrCl$_4$ pulse, thus probably assisting in the completion of the oxidation of the Zr layer and more effective removal of chlorine species terminating the underlying tantalum zirconium oxide film.

The refractive index values measured by spectroscopic ellipsometry (Table I) were close to those commonly characterizing Ta$_2$O$_5$ and ZrO$_2$. No clear correlation between the refractive index and relative cation contents in the films was observed, which is plausibly due to the similarity of the refractive indexes of these materials. However, the values obtained are indicative of the formation of optically dense solid layers.

Fig. 2 demonstrates selected cross-sectional transmission electron microscopy images from an as-deposited film grown with the Ta$_2$O$_5$:ZrO$_2$ cycle ratio of 6:1 (Fig. 2, top panel), an annealed film grown with the Ta$_2$O$_5$:TaZrO$_4$ cycle ratio of 3:1 (Fig. 2, 2nd panel from top), an as-deposited films grown in exchange reactions between Ta(OEt)$_5$ and ZrCl$_4$ assisted with O$_3$ (Fig. 2, 3rd and 4th panels from top). Here the Ta$_2$O$_5$:TaZrO$_4$ cycle ratio 3:1 is used to denote ALD cycle sequences of 160 × [ 3 × 0.5-0.5-1.5-0.5 s, TaOEt-p.-O$_3$-p. + 1 × 0.5-0.5-0.5-0.5-1.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p.], i.e. deposition of alternate layers of non-doped Ta$_2$O$_5$ and mixed Ta$_2$O$_5$:ZrO$_2$. One can see that the as-deposited layers are amorphous, uniform, smooth and with sharp interface with the underlying TiN. Also the image taken from an annealed sample represents an uniformly crystallized and well adhered region of the film. It is, however, to be noted, that the films often tended to be detached from the TiN, possibly due to the mismatch between elastic properties as well as the zirconate and titanium nitride lattice parameters, and differences in thermal expansion coefficients.

Regarding the film growth rate, the film deposited using 750 ALD cycles consisting of sequential pulses of Ta(OEt)$_5$ and ZrCl$_4$ separated by purge periods without ozone grew with the rate of 0.045 nm/cycle. The 113 and 21 nm thick films deposited using 1500 and 280 ALD cycles consisting of sequential pulses of Ta(OEt)$_5$, ZrCl$_4$, and O$_3$ grew with the rate of 0.075 nm/cycle. The growth rate per cycle has remarkably increased upon the application of ozone pulses. On the other hand, the additional ozone pulses have naturally increased the length of single ALD cycles, and, in this regard, the absolute growth rates for these three films remained similar, 0.017-0.018 nm/s. For comparison, reference Ta$_2$O$_5$ and ZrO$_2$ films grown from Ta(OEt)$_5$-O$_3$ and ZrCl$_4$-O$_3$ precursor systems, respectively, grew with rates 0.035 and 0.07 nm/cycle. The films with the Ta$_2$O$_5$:ZrO$_2$ cycle ratio of 6:1 were grown to different thicknesses using general cycle sequence N × [6 × Ta$_2$O$_5$ + 1 × ZrO$_2$] + 6 × Ta$_2$O$_5$. The thicknesses were 4.2 ± 0.1, 5.6 ± 0.2, 32.2 ± 0.4, and 106 nm for the N values of 6, 10, 100, and 300, respectively. One can see, that the film thickness increased, in practice, proportionally to the total number of the constituent oxide cycles. This was also expected as one of the characteristic features of a pulsed deposition process.

In a 106 nm thick film deposited using O$_3$ pulse after each metal precursor pulse with reduced relative amount of zirconium and with reduced relative amount of zirconium, i.e. with a cycle sequence 300 × [6 × Ta$_2$O$_5$ + 1 × Zr$_2$O$_3$] + 6 × Ta$_2$O$_5$, the ToF-ERDA revealed 23.3 ± 0.2 at.% Ta, 7.4 ± 0.1 at.% Zr, 69.1 ± 0.9 at.% O, and. The amounts of carbon and chlorine were not detectable. One can see that the application of ozone pulses after each metal precursor pulse resulted in higher purity in terms of residual contamination, compared to the films deposited with ozone pulse applied only after the ZrCl$_4$ pulses. This was somewhat expected, because also in earlier reports on water-free ALD using surface reactions between metal precursors only, the contents of residues have been relatively high. Annealing at 800 °C did not change the composition of the film, as verified by ToF-ERDA, as they still contained 0.2 ± 0.1 at.% H. The fact that the hydrogen was not quite removed by annealing,
FIG. 2. Transmission electron microscopy images from a Ta$_2$O$_5$:ZrO$_2$ film as-deposited on TiN electrode using Ta$_2$O$_5$:ZrO$_2$ cycle ratio of 6:1 with cycle sequences of 100 $\times$ [6 $\times$ 0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p. + 1 $\times$ 0.5-0.5-1.5-0.5 s, ZrCl$_4$-p.-O$_3$-p.] $+$ 6 $\times$ 0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p. (top panel); a film annealed on TiN and deposited using cycle sequence of 160 $\times$ [3 $\times$ 0.5-0.5-1.5-0.5 s, TaOEt-p.-O$_3$-p. + 1 $\times$ 0.5-0.5-0.5-0.5-1.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p.] $+$ 10 $\times$ 0.5-0.5-1.5-0.5 s, TaOEt-p.-O$_3$-p. (2nd panel from top); 750 $\times$ 0.5-0.5-1.0-0.5 s, TaOEt-p.-ZrCl$_4$-p. (3rd panel from top); and 2 $\times$ 0.5-0.5-1.5-0.5 s, ZrCl$_4$-p.-O$_3$-p. $+$ 50 $\times$ [4 $\times$ 0.5-0.5-1.0-0.5-1.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p.] $+$ 2 $\times$ 0.5-0.5-1.5-0.5 s, ZrCl$_4$-p.-O$_3$-p. (bottom panel). The inset in the bottom panel shows a cross-section from the same sample in larger scale in order to illustrate the lateral uniformity of the film thickness.
may be explained by the probable diffusion of environmental water/hydrogen back into the material upon storage in the air.

It has been observed earlier that the thin films formed by the water-free ALD process tend to contain relatively high amounts of residual impurities compared to the films grown by ALD processes using water.\(^{55}\) Also, the Ta\(_2\)O\(_5\) films grown from Ta(O\(_{2}\)C\(_3\)H\(_5\))\(_3\) and TaCl\(_5\)\(^{56}\) contained higher amounts of hydrogen and carbon compared to the Ta\(_2\)O\(_5\) films grown from Ta(O\(_{2}\)C\(_3\)H\(_5\))\(_3\) and H\(_2\)O\(^{67}\) or Ta\(_2\)O\(_5\) films grown from TaCl\(_5\) and H\(_2\)O.\(^{58}\) The carbon impurities in tantalum oxide are found to be preferentially located in the neighborhood of the oxygen vacancies, and they reduce the oxygen-vacancy formation energy, which is predicted to have an influence on lowering the forming voltage.\(^{69}\) Oxygen deficiency in Ta\(_2\)O\(_5\) and its effect to the band gap energetics has been characterized thoroughly.\(^{70}\)

**Structural analysis**

Ta\(_2\)O\(_5\) films grown by ALD from Ta(O\(_{2}\)C\(_3\)H\(_5\))\(_3\) and H\(_2\)O or from Ta(O\(_{2}\)C\(_3\)H\(_5\))\(_3\) and TaCl\(_5\) were all amorphous, as has also been observed in earlier works with the same process chemistries.\(^{66,67}\) The Ta\(_2\)O\(_5\) films not mixed with ZrO\(_2\) or mixed with low amounts of ZrO\(_2\) in the present study were crystallized upon annealing to the dominating hexagonal phase (Fig. 3, top panel) similarly to that observed in the earlier studies on crystallized Ta\(_2\)O\(_5\) thin films.\(^{67}\)

The Ta\(_2\)O\(_5\) films doped with low amounts (Zr:Ta atomic ratio ca. 0.2) of zirconium (oxide) crystallized quite laboriously, showing only rather weak XRD peaks after 30 minutes annealing at 800 °C, whereas tantalum oxide grown without mixing it with zirconium oxide was crystallized quite intensely into the hexagonal δ-Ta\(_2\)O\(_5\). This is consistent with results by Tewg et al.\(^{51}\) reporting suppression of the crystallization of Ta\(_2\)O\(_5\) with zirconium oxide doping.

The films deposited using equal amounts of sequential Ta(O\(_{2}\)Et)\(_3\) and ZrCl\(_4\) pulses, separated either only by purge times or additionally by intermediate ozone pulses, were also amorphous in the as-deposited state. Such films contained approximately equal amounts of zirconium and tantalum, and were crystallized after annealing at 800 °C, quite independently of the film thickness (Fig. 3, middle panel). The main phase recognized was evidently TaZr\(_{2.75}\)O\(_8\) (PDF-042-0060) which also seems to be the only defined ternary tantalum zirconium oxide phase. Some minor peaks could be attributed to the reflections from ZrO\(_2\), in addition.

The films with zirconium to tantalum atomic ratio above 1.0-1.6, dominantly consisting of ZrO\(_2\), became crystallized already in the as-deposited state (Fig. 3, bottom panel), to structures characteristic of stable and metastable zirconium oxide polymorphs. Notably, the phase composition in terms of the major contributing polymorphs was not altered after annealing. The degree of crystallization, however, was enhanced, as decided on the basis of the intensity of the reflection peaks increasing upon the annealing.

Undoped ZrO\(_2\) films grown by ALD from ZrCl\(_4\) and O\(_3\) were strongly polycrystalline with a rather large contribution from metastable cubic or tetragonal phase, similarly to that observed before.\(^{60}\) Unambiguous and exact determination of phase composition of the ZrO\(_2\) films containing amounts of additive tantalum relatively low compared to zirconium is not straightforward. One could see, that the films can be regarded as polycrystalline mixtures of stable monoclinic polymorph with characteristic -111 and 111 reflections at 28.3 and 31.8°, respectively, and metastable polymorphs with the most characteristic peak at ca. 30.3°. It occurred, however, quite complicated to attribute this peak distinctively to 111 cubic, 101 tetragonal or 101 orthorhombic phase reflections. Due to the width of the peaks as well as possible shifts in the peak positions caused by internal stresses, also the appearance of the reflections at larger angles did not make the phase determination much more feasible. There appeared, however, a few minor peaks attributable only to the orthorhombic polymorph, such as 211, 220, 212, and 113 reflections at 43.5, 51.0, 53.4 and 58.6°, respectively (not shown). It is to be noted that the orthorhombic phase (PDF Card 037-1413) is metastable under atmospheric pressure and reverts to the monoclinic phase on heating above 300 °C. It seems that the orthorhombic phase was the first one trying to form upon deposition and most of it was transformed into the monoclinic during the film growth already. There were also some peaks attributable only to the monoclinic polymorph. Somewhat surprisingly, there were no obvious peaks attributable only to the otherwise more-known and more often considered cubic phase.
FIG. 3. High-temperature X-ray diffractograms from Ta$_2$O$_5$:ZrO$_2$ films deposited using cycle sequences 250 × [ 5 × 0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p. + 1 × 0.5-0.5-1.0-0.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p. ] + 5 × 0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p. (top panel), 1500 × 0.5-0.5-1.0-0.5 s, TaOEt-p.-ZrCl$_4$-p. (middle panel), and 250 × [ 5 × 0.5-0.5-1.5-0.5 s, ZrCl$_4$-p.-O$_3$-p. + 1 × 0.5-0.5-0.5-0.5 s, ZrCl$_4$-p.-O$_3$-p.-TaOEt ] + 6 × 0.5-0.5-1.0-0.5 s, ZrCl$_4$-p.-O$_3$-p. (bottom panel). The film thicknesses were 73 nm, 42 nm, and 120 nm, respectively. Zr:Ta atomic ratios measured by EDX, dominant crystallographic phases identified, and Miller indexes assigned to the main reflections from the dominant phases are indicated by labels.

RESISTIVE SWITCHING CHARACTERISTICS

Resistive switching characteristics were studied by repeatedly forming and resetting conduction current paths through the oxide layer by applying external voltages of alternating polarity on TiN/Ta$_2$O$_5$:ZrO$_2$/Pt stacks. All the Ta$_2$O$_5$:ZrO$_2$ films deposited in this study demonstrated resistive switching characteristics when measured in as-deposited and mostly amorphous states. Resistive switching could not be observed after increment of long-range ordering, i.e. crystallization, of the
films by annealing at 800 °C for 10-30 min in N₂. Figure 4 depicts resistive switching characteristics of the as-deposited 20-35 nm thick Ta₂O₅:ZrO₂ films.

The film containing zirconium in the amounts below the detection level of EDX required rather high electroforming voltages up to 4 V to the ca. 30 nm thick film (Fig. 4, top panel). The range of the set/reset voltages required for switching between low and high resistance states remained between -2 and +2.5 V, approximately. The window between low and high resistance states was not very stable against the increasing number of voltage cycles, and reached two orders of magnitude in the current density scale, at maximum. These films were amorphous in the as-deposited state, and were crystallized after annealing into hexagonal Ta₂O₅ phase as described above.

The tantalum oxide films containing low, but still measurable amounts of zirconium (0.2 at. %) exhibited the most clearly defined resistive switching memory windows ranging over 4 orders of magnitude in the current scale (Fig. 4, 2nd panel from top). The forming voltage was at around 2.5 V in the ca. 30 nm thick film and did not noticeably exceed the working voltage in the filament setting current regime. Such kinds of films were amorphous in the as-deposited state, and crystallized relatively weakly after annealing at 800 °C, revealing only one rather low diffraction peak attributable to the 011 reflection from hexagonal δ-Ta₂O₅ as described above.

The films grown using direct surface reaction cycles between only Ta(OEt)₅ and ZrCl₄ (Fig. 4, 3rd panel from top), as well as those grown completing the same reaction cycles with O₂ pulse (Fig. 4, 4th panel from top) also demonstrated resistive switching behavior. In these films, the contents of tantalum and zirconium were comparable, i.e. the tantalum to zirconium cation ratios were 0.9 and 0.8, respectively, measured by EDX. One could see, however, that the stability of the switching loops was somewhat worsened again, compared to the loops recorded from the film with the Zr:Ta atomic ratio of 0.2. The width of the memory window in terms of the difference between low and high resistance states was noticeably more scattered during the subsequent voltage cycles, between one to two orders of magnitude in the current scale. The forming voltage for the ca. 30 nm thick films was at around 2 V, being comparable to the set/reset switching voltages. These films were, similarly to the others, amorphous in the as-deposited states. These films were crystallized rather intensely upon annealing, possessing polycrystalline nature and contained the TaZr₂.₇₅O₈ ternary phase.

In the films containing ZrO₂ in amounts exceeding that of Ta₂O₅ (Fig. 4, bottom panel), the resistive switching became rather unstable in terms of the width of the gap between the low and high resistance states. For ca. 20 nm thick film, the difference between these states could vary between two and four orders of magnitude.

The annealing procedure resulted in the crystal growth in the initially highly disordered, i.e. amorphous, films. The annealing also suppressed the appearance of the resistive switching effect, regardless of the chemical composition of the films. The films measured after annealing demonstrated rather high leakage currents already in their virgin states, i.e. were conductive and thus already in the low resistance states. Electroforming of filamentary current channels occurred impossible. This may plausibly arise from the polycrystalline nature of the films, with defective and electronically leaky grain boundary networks extending from bottom to top electrodes. In addition, TEM studies revealed, in several cases, also possible intermixing of the TiN and metal oxide films as well as delamination of the oxide layers from the electrode (not shown). These distortions in layered metal-oxide-metal stacks have evidently caused permanent short circuits between the bottom and top electrodes.

The series of metal-dielectric-metal stacks formed in this study comprised the first resistive switching results on ALD Ta₂O₅:ZrO₂ films grown to thicknesses exceeding 20 nm and with variable chemical composition. It is complicated and yet premature to directly compare their performance to the behavior of reference stacks described in the literature. It has been emphasized, that electroforming step voltages, if considerably higher than that of switching voltage, need to be reduced in order to produce technologically relevant ReRAM devices. Also, low operation voltages are desirable for sub-20 nm CMOS devices. It has also been stated, that the electroforming conditions may strongly depend on the dimensions of the sample, especially, on the switching material thickness. Tantalum oxide based ReRAM structures have mostly been grown by physical vapor deposition to thicknesses ranging from 5-20 nm, and, partially, using nonstoichiometric targets in relation to the pentoxide, as a feature related to the deposition process parameters.
FIG. 4. Resistive switching current-voltage loops from Ta$_2$O$_5$:ZrO$_2$ films grown using cycle sequences of 40× [15×0.5-0.5-1.5-0.5 s, TaOEt-p.-O$_3$-p. + 1×0.5-0.5-0.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p.] + 15×0.5-0.5-1.5-0.5 s, TaOEt-p.-O$_3$-p. (top panel); 100× [6×0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p. + 1×0.5-0.5-1.5-0.5 s, ZrCl$_4$-p.-O$_3$-p.] + 6×0.5-0.5-1.0-0.5 s, TaOEt-p.-O$_3$-p. (2nd panel from top); 750×0.5-0.5-1.0-0.5 s, TaOEt-p.-ZrCl$_4$-p. (3rd panel from top); 280×0.5-0.5-1.0-0.5-1.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p. (the 4th panel), and 2×0.5-0.5-1.0-0.5-1.5-0.5 s, TaOEt-p.-ZrCl$_4$-p.-O$_3$-p.] + 50×[4×0.5-0.5-1.0-0.5-1.5-0.5 s, ZrCl$_4$-p.-O$_3$-p.] (bottom panel). Film thicknesses, Zr:Ta atomic ratios measured by EDX, and growth cycle sequences expressed either in Ta$_2$O$_5$:ZrO$_2$ cycle ratios or amounts of cycles consisting of subsequent TaOEt, ZrCl$_4$ and O$_3$ pulses are given by labels.
For instance, Pt/TaO$_x$/HfN$_x$ structures with 20 nm thick TaO$_x$ films were made by Zhou and Zhai\textsuperscript{30} by magnetron sputtering TaO$_x$ (purity 99.9\%) ceramic targets and using a substrate temperature of 200 °C. In these stacks, the forming voltage was $-3.7$ V, larger than the set voltage, $-2$ V, between the high and low resistance states, and also the initial leakage current was much smaller compared with the leakage current in the high resistance state after forming, rather similarly to the behavior observed in our samples.

In another study by Prakash \textit{et al.},\textsuperscript{30} W/TaO$_x$/W and/or Pt/TaO$_x$/Pt structures were constructed or referred to, with thin TaO$_x$ films comprising, e.g. Ta$_2$O$_{5-x}$ insulating layer and a TaO$_{2.5}$ base layer, with 6-30 nm total thicknesses for the TaO$_x$ films. All the devices with different sizes from 50 $\times$ 50 $\mu$m$^2$ to 30 $\times$ 30 nm$^2$ showed self-compliant bipolar switching with small set/reset voltages of $-1.0/2.0$ V. The switching currents for, e.g., 50 $\times$ 50 $\mu$m$^2$ and 30 $\times$ 30 nm$^2$ devices were $>200$ µA and 40 µA, respectively.

Furthermore, Ta/TaO$_x$/Pt stacks have been formed by Yang \textit{et al.},\textsuperscript{26} containing 7-18 nm thick TaO$_{1.7}$ layers sputtered from a target with nominal stoichiometry of TaO$_2$. These devices could be switched at rather low voltages, and the switching current was less than 100 µA insensitively to the device area. The forming voltage for the first set operation was ca. 0.8 V, only slightly larger than the subsequent normal set voltage, 0.6 V. Window between high and low resistance state currents ranged from 10 to 100 µA. Regarding the downscaling of the functional layer thicknesses, Park \textit{et al.}\textsuperscript{29} have described TiN/Ta$_2$O$_x$/Ta/TaN based switching stacks containing only 0.5-2.0 nm thick Ta$_2$O$_5$ layers grown by ALD with the active memory cell diameter of 28 nm. All the devices showed high resistance values of $\sim 10^4$--$10^5$ Ω, displaying bipolar resistance switching behavior after the electroforming steps. All the devices showed a limited maximum current of $\sim 100$ µA at $-1.0$ V.

In addition, Ta/Ta$_2$O$_5$/TiN stacks with lateral size of 100 nm x 100 nm have been described [Chen \textit{et al.}\textsuperscript{28}], containing amorphous 6 nm thick Ta$_2$O$_5$ layers grown by ALD at 250 °C using TaCl$_5$ and H$_2$O as precursors. The switching current was fixed at 50 µA. The devices were effectively set and reset using pulse amplitudes lower than 1.5 V.

It has been established, that the successful development of ReRAM structures is dependent on the possibility to scale down the switching material layer thickness together with the concurrent decrement of the filament forming voltage to the level comparable to that of the operational set/reset voltages. This research direction would be most appropriate after the determination of the layer composition optimized in terms of both structural and electrical stability. In the present work, the analysis results on Ta$_2$O$_5$ films doped with low amounts of ZrO$_2$ were indicative of the most stable structural and resistive behavior. Further studies on such material layers can be planned accordingly.

**SUMMARY**

Tantalum zirconium oxide mixture films were grown to thicknesses ranging from 20 to 100 nm by atomic layer deposition of either alternating layers of Ta$_2$O$_5$ and ZrO$_2$ from Ta(OC$_2$H$_5$)$_3$, ZrCl$_4$, and O$_3$, or using direct surface reactions between the same metal precursors. The cation ratio in the films could be varied with the sequence and ratio between deposition cycles of the single constituent oxides. Ozone pulses were optionally applied either after both Ta(OC$_2$H$_5$)$_3$ and ZrCl$_4$, or only after the ZrCl$_4$ pulses, in order to complete the oxidation reactions. Application of ozone assisted in the decrement of chlorine residues, as well as in the enhancement of the film growth rate.

Resistive switching properties were recorded in all the films in their as-deposited states, whereas annealing procedure at 800 °C, although crystallizing the films, occurred destructive regarding the switching behaviour. The major factor affecting the resistive switching properties the in as-deposited state was, evidently, the zirconium to tantalum cation ratio. Ta$_2$O$_5$ doped moderately with ZrO$_2$, i.e. with Zr:Ta ratio of 0.2, occurred the most hard to crystallize. At the same time, this material exhibited the most well defined resistive switching properties with the most symmetric and stable current-voltage loops against the repetitive switching voltage cycle. The films containing lower and higher amounts of Zr crystallized relatively strongly, i.e. more easily, but exhibited either more scattered or narrower current-voltage loops already in the as-deposited states.

The films containing Zr and Ta cations in the ratios close to unity were crystallized quite intensely upon annealing, indicating the formation of ternary TaZr$_{2.75}$O$_8$ phase. The films containing relatively...
low amounts of Zr were crystallized as hexagonal Ta$_2$O$_5$. The films containing higher amounts of Zr were dominantly crystallized into metastable cubic/tetragonal or orthorhombic ZrO$_2$ phases. The annealed and crystallized films did not exhibit resistive switching probably due to the dominant grain boundary conduction and/or destruction/delamination of the electrode-metal oxide-electrode stack. The fact that good device switching results are achieved with smooth amorphous films can be a clear advantage for applications, as low-roughness amorphous ALD films are easier to integrate than polycrystalline films. Further investigations are to be directed towards lowering the electroforming voltage, decreasing film thickness and studying the possibilities to densify the films by adjustment of appropriate annealing parameters.

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