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Abstract

Zirconia ultrathin films were deposited by aqueous chemical solution deposition, using citratoperoxo-Zr(IV) precursors with different citric acid content. The precursor synthesis, thermal decomposition and crystallization of oxide powders was studied. This showed an effect of the citric acid content in every stage. The precursors were applied for the deposition of uniform, ultrathin films (< 30 nm thickness) as well. Tetragonal ZrO_2 crystallized starting from 500°C for thin films with a thickness of 10 nm. This was independent of the citric acid content in the precursor. The topography after annealing at 600°C was also similar. However, annealing at higher temperatures led to coarser grain size. The dielectric constant was high (~21-22) and comparable to ZrO_2 deposited by atomic layer deposition.

1. *Introduction*

The miniaturization of integrated circuits has led to continuous downscaling of gate dielectric oxide thicknesses in MOSFETS (metal oxide semiconductor field effect transistor). Currently the conventional dielectric, SiO_2 or $SiON$, is being replaced by alternative materials to suppress high leakage currents which are observed for low thicknesses. These materials, such as hafnium and zirconium based dielectrics, have a higher dielectric constant or k value than SiO_2. Therefore, they can be applied with a higher physical thickness, leading to leakage current reduction while maintaining the same high specific capacitance. For future applications however, the search for even higher k materials continues. For material evaluation purposes, fabrication techniques which allow relatively fast material synthesis are advantageous.

The use of sol-gel for exploration of gate materials e.g. ZrO_2, $SrZrO_3$ has been reported in literature before [1,2], but has been limited to relatively thick films (>180 nm). It was stated that due to the inherent shortcoming of the sol-gel method, it is not possible to prepare ultrathin films [2]. Recently, however, we demonstrated the possibility of depositing ultrathin neodymia and praseodymia films by spin-coating of aqueous solution-gel precursors. Thicknesses down to 3.3 nm, functioning as MOS devices [3,4] were achieved. However, exploration of the route to other metal oxide materials, is necessary to demonstrate wide applicability. This will also allow to address the discrepancy between our findings and the cited "inherent shortcoming" of sol-gel method(s) to produce ultrathin films. The possibility of depositing functional metal oxide films with thickness below 30 nm by non-aqueous chemical solution deposition (CSD) methods has been shown simultaneously with our work e.g. ultrathin piezoelectric $PbTiO_3$ (down to 13 nm) [5] or sol-gel derived HfO_2 (20 nm) [6].

However, film thicknesses remain above 10 nm in contrast with the results obtained from our aqueous route. The results may be correlated to the substrate, its pretreatment, multilayer deposition method, heat treatment, specific precursor composition etc. which have an effect on the films' microstructural stability [7].

For aqueous chemical solution deposition (CSD), an interfacial SiO_2 layer is inevitable: the use of aqueous precursor solutions requires a hydrophilic substrate in order to obtain good wetting and uniform film deposition. Therefore, deposition is carried out on SiO_2/Si substrates. To eliminate the influence of the SiO_2 on the dielectric constant which is measured, film thickness series are prepared. These allow extraction of the dielectric constant of the high-*k* material itself.

In the present work, ZrO_2 films were prepared by aqueous CSD and thicknesses down to less than 5 nm were achieved. ZrO_2 ultrathin film properties are well documented. By comparison of the dielectric properties with those obtained by more conventional deposition techniques, such as atomic layer deposition (ALD), aqueous CSD can be evaluated as a fast fabrication method for dielectric ultrathin oxide films. Here, the effect of the citric acid content in the Zr(IV) precursor on the precursor chemistry, gelation, the oxide formation during thermal treatment and the ultrathin film properties will be discussed in detail.

2. *Experimental details*

An aqueous Zr(IV) precursor solution was synthesized by modifying the route reported earlier by our group [8,9]. The starting materials were zirconium(IV)-n-propanolate ($Zr(C_3H_7O)_4$, Fluka 70% in propanol), citric acid (abbreviated as CA, $C_6H_8O_7$, Aldrich,

99%), hydrogen peroxide (H_2O_2(aq) stabilized p.a., Acros Organics, 35%) and ammonia ($NH_{3(aq)}$ extra pure, Merck, 32%). As ZrO_2 itself is unreactive [10], a freshly prepared hydroxide precipitate was used as the starting product in this synthesis route. The hydroxide is obtained through hydrolysis of the appropriate amount of zirconium(IV)-propanolate in vigorously stirred water. The fresh precipitate is washed with water to remove isopropanol. Next, a solution of citric acid and hydrogen peroxide (molar ratio 20:1 H_2O_2:Zr^{4+}) is added to the precipitate and the mixture is refluxed (120°C/2h). Subsequently, the pH is adjusted to 7.5 with ammonia, followed by a second reflux step (120°C/2h). Finally, the solution is filtered (0.1 µm pore size) to remove remaining particles.

The concentration of the as-prepared solutions is determined by Inductively Coupled Plasma-Atomic Emission Spectrometry, Perkin Elmer, Optima 3000 DV. The solutions were characterized further by means of PCS (Photon Correlation Spectroscopy, Brookhaven Instruments, 90Plus/BI-MAS) and cryogenic TEM (Transmission Electron Microscopy, Philips, CM12). TEM sample preparation consists of freezing the precursor at a high rate in liquid ethane. This prevents artificial precipitation or other structural changes.

These precursors were used for the fabrication of bulk gels as well as for the deposition of thin films. To obtain solid gels the solution was dried in a Petri dish (furnace, 60°C). The gels' chemical structure was characterized by FTIR (Fourier Transform Infra-Red spectrometry, Bruker, IFS 48) and their thermal decomposition was studied by TGA (Thermogravimetric analysis, TA Instruments, TGA 2950). Intermediate decomposition products were characterized by FTIR (KBr pellets, 32 scans per

spectrum) and FT-Raman (Fourier Transform Raman spectrometry, Bruker, FRA 106, excitation wavelength 1064 nm, 2000 scans per spectrum).

To deposit thin films, 4 layers are spin-coated (3000 rpm, 30 s) onto square pieces (~2.5x2.5 cm^2) of p-type 1.2 nm SiO_2/Si (100), cleaned in a sulfuric acid peroxide mixture and ammonia peroxide mixture [11]. Hot plate treatments are carried out for each layer to decompose the organic components (260°C/2', 480°C/2'). Optionally, thermal annealing was carried out by inserting the four-layered film into a preheated tube furnace in dynamic dry air (0.5 l min^{-1}).

The crystal structure of the films was characterized by coupled θ-2θ XRD (X-ray diffraction, Siemens, D5000, Cu Kα). The evolution of this crystal structure with temperature was studied in-situ by HT-XRD (high-temperature X-ray diffraction, Bruker, D8; counting 3 s per step, step size 0.04°2θ). For HT-XRD 4-layered films were deposited, including hot plate treatment, from 0.05 M precursor solutions containing 4, 2 and 1.2 : 1 CA : Zr(IV) so that the expected oxide thickness at 600°C is ~ 10 nm. For the 4:1 CA:Zr(IV) precursor the effect of the film's thickness was evaluated based on films deposited from 0.1 (~20 nm) and 0.2 M (~40 nm) precursor solutions. The HT-XRD measurements were carried out between 10-60°2θ at a heating rate of 10°C/min, with intervals of 100°C from 500 to 900°C. The collection of each pattern requires approximately 50 minutes.

Film thicknesses were determined ellipsometrically (Plasmos, single wavelength) using a refractive index of 1.75 for a single layer model, and calibrated by XRR (X-ray reflectometry). The film's topography was characterized by tapping mode AFM (Atomic Force Microscopy, Veeco, etched Si probe) and scanning electron microscopy (FEI Quanta 200FEG SEM). C-V (Capacitance-Voltage) curves were measured on Pt

top electrodes (areas $\sim 1.10^{-4} - 8.10^{-4}$ cm^2) by using a semiconductor characterization system (Keithley 4200). The Pt top electrodes were evaporated onto the film's surface using a shadow mask for patterning and their surface areas were determined by optical microscopy (Nikon). Finally, the MOS devices are subjected to a Forming Gas Anneal step (ambient = 5% H$_2$, 95% N$_2$), for 20 minutes at 520°C.

3. Results and discussion

3.1 Aqueous precursor solutions and gels

The synthesis route of the Zr(IV) precursor [8,12] was modified in order to reduce the amount of citric acid present. Clear solutions were obtained for a citric acid : Zr molar ratio of 4:1, 3:1, 2:1 but not for a 1:1 ratio where a precipitate remained after the second reflux step. It was concluded from further experiments that the minimal ratio for obtaining macroscopically clear solutions was 1.2:1 citric acid : Zr^{4+}. However, colloidal dispersions or sols can also have a macroscopically clear aspect, yet still contain nanoparticulate material [13]. To give evidence whether the precursors synthesized with different CA:Zr(IV) ratios are truely solutions, particle size measurements were carried out using PCS (Figure 1) and cryogenic TEM. For all the different citric acid to Zr(IV) ratios the particle sizes obtained for the majority of the "particles" present in the solutions are below 2 nm, which is the detection limit of the apparatus. From intensity – diameter plots (not shown) it became clear that the solutions also contain larger particles, up to approximately 500 nm which are present in negligibly small numbers (Figure 1). To give further evidence, cryogenic TEM was carried out for the precursor containing 1.2:1 CA:Zr. This precursor has the highest probability of containing colloidal species formed by hydrolysis and condensation, due

to its smallest concentration of stabilizing ligands. A representative cryogenic TEM image is shown in Figure 2a. It was impossible to discern any particles, apart from ice crystals that are formed as an artefact during the electron microscopic analysis (Figure 2b). The virtual absence of particles larger than 2 nm (Figure 1) as well as the cryogenic TEM images (Figure 2) lead to the conclusion that the precursors are truely solutions for all the citric acid to Zr(IV) ratios studied, without the presence of any colloidal particles.

However, the behavior of the precursor solutions does differ upon gelation via evaporation. For the highest CA:Zr ratios (4:1 – 2:1) a clear, glassy gel was obtained. For the CA: Zr 1.2:1 precursor, an opaque white precipitate is observed in the gel. Powder diffraction of this solid showed the presence of an unidentified crystalline compound (Figure 3). This could be due to precipitation of the excess ammonium citrate, which has reflections below $30°2\theta$ [14]. On the other hand, since there is only a very small excess of ammonium citrate present, it is also possible that the reflections are due to the precipitation of a citrato(peroxo)-zirconium complex. It is concluded that the minimum CA:Zr ratio for gelation is 2:1.

The FTIR spectra of the 4:1 and 1.2:1 Zr(IV) solid precursors are highly similar (Figure 4). This can be ascribed to the fact that both Zr(IV) precursors contain ammonium citrate from the excess of citric acid, albeit in different amounts, and a citratoperoxo-Zr(IV) complex. This complex is assumed to have a structure similar to citratoperoxo-Ti(IV), Nb(V) or V(V) complexes [15-17]. They are characterized by the presence of citrato- and side-on coordinated peroxo ligands. O-H, N-H and C-H vibrations, which show broadening due to hydrogen bonding are observed between 3600 and 2750 cm^{-1}. Typical asymmetric and symmetric carboxylate stretching bands

are situated at 1590 and 1400 cm^{-1} respectively. A shift of the ν(C-O) is observed from 1051 cm^{-1} in ammonium citrate to 1066 cm^{-1} in the Zr(IV) gel. This can be explained by coordination of the citrato ligand's α-hydroxy to the metal ion, similar to what was observed for the citratoperoxo-Nb(V) [16] and citratoperoxo-Ti(IV) complexes [15]. In the fingerprint region of the spectrum the presence of the ν(O$_2$) stretch (900-800 cm^{-1}) and the symmetric and asymmetric ν(MO$_2$) (650-430 cm^{-1}) [18] of the peroxoligand are expected. The spectra of the Zr(IV) gels were compared with ammonium citrate, prepared by evaporation of a citric acid solution neutralized with ammonia to pH 7.6. It becomes clear that the latter also shows similar peaks in this region, at shifted positions (e.g. 840 cm^{-1} in stead of 860 cm^{-1} for the Zr(IV) gels). The peak at 780 cm^{-1} which is seen for the CA 1.2:1 Zr(IV) precursor could be ascribed to a bridging peroxogroup. Its absence in the CA 4:1 Zr(IV) gel might indicate a difference in the structure of the two Zr(IV) precursors. Furthermore, the δ(O-C=O) of the carboxylato groups are found between 700-600 cm^{-1}.

The precursors contain ammonium groups linking the excess citrate as well as the complexed citrato ions into a three dimensional carboxylate structure [19]. Possibly, the Zr(IV) precursor with CA 1.2:1 Zr(IV) is supplementary characterized by the presence of bridging -Zr-O-O-Zr- units, contributing to the structure.

3.2   Thermo-oxidative precursor gel decomposition and bulk metal oxide phase
        formation

The precursors' decomposition profiles were taken as an aid in choosing the anneal treatment of the films (Figure 5). The thermo-oxidative decomposition of

citratoperoxo-gels has been studied in detail by our group for different multimetal ion gel precursors [20-22]. The decomposition scheme with increasing temperature generally consists of a drying step (~100°C), followed by decomposition of the excess of ammonium citrate (~190°C), the pyrolysis of the complex (~350°C) and finally the removal of an organic rest fraction or carbonates (> 450°C).

For the CA 1.2:1 Zr(IV) precursor the first step is observed with maximal rate at ~70°C. Next three overlapping decomposition processes take place from 220-545°C with maximal rates at 275°C, 370°C and 435°C. Finally there is a small weight loss observed around 615°C. For the CA 4:1 Zr(IV) gel overlapping steps are observed from room temperature to 280°C, with the highest rate at 190°C. It is followed by steps at 345°C, 450°C and a small weight loss at 660°C. The difference between the two precursors in the temperature range around 190°C, where there is only a small gradual weight loss for the 1.2:1 solid precursor, is due to the presence of only a very small amount of excess ammonium citrate compared to the 4:1 gel. The pyrolysis of the complex occurs in the same temperature region, around 350°C for the 4:1 gel and around 370°C for the 1.2:1 solid precursor. The slight difference could indicate that the crystallization affects the thermal stability of the solid precursor. At 490°C a large peak in the DTG of the 4:1 precursor is observed. According to the general decomposition scheme of aqueous citrato(peroxo) gels [19-21], at this temperature organic rest fractions are decomposed. These rest fractions are formed from the decomposition of excess ammonium citrate and consist of nitrogen containing organic compounds with a high thermal stability [20]. These compounds are present in a larger amount for the 4:1 than for the 1.2:1 precursor, since it contained a larger amount of excess ammonium citrate. The final decomposition step has a maximal rate at 615°C for the CA 1.2:1

Zr(IV) precursor and at 660°C for the CA 4:1 Zr(IV) precursor. The higher final decomposition temperature of the Zr(IV) gel with a higher CA content, can also be explained by the presence of a larger amount of excess ammonium citrate. The larger amount of organic material in the CA 4:1 Zr(IV) gel also leads to the lower final weight percentage after complete decomposition (15%) compared to the lower CA content (40%). The presence of a smaller amount of organic material, which becomes redundant as soon as the film is deposited, may be considered as an advantage of the CA 1.2:1 Zr(IV) precursor.

FTIR (Figure 6) and FT-Raman (Figure 7) spectra were recorded of (partially) decomposed precursors, heat treated up to different temperatures (heating and cooling at 10°C/min in dynamic dry air, 30 min isothermal). After heating up to 600°C brown powders were obtained, after heating up to 650°C a light brown powder was obtained from the 1.2:1 and a white powder from the 4:1 precursor. At 700°C white powders were obtained from both precursors.

FTIR is highly sensitive to the presence of organic material or carbonates, and is used here to check that phase pure zirconia is obtained in the high temperature region where the TGA is a flat line. The FTIR spectra (Figure 6) show hydroxide stretching vibrations around 3400 cm^{-1}, even though the annealing temperature was 700°C. This may be caused by adsorption of water during storage and sample handling in ambient conditions. The band at 2340 cm^{-1} was not observed for commercial ZrO_2, but can be ascribed here to trapped CO_2, which is evolved during the decomposition of the precursor [23]. After annealing the CA 4:1 Zr(IV) gel at 600°C a vibration is present at 2200 cm^{-1}, which can be ascribed to nitriles formed from ammonium citrate by

dehydration to amides and subsequently to nitriles [24]. This band disappears after annealing at 650°C, which indicates that the final, small weight loss that was observed in the TGA around 660°C is due to the decomposition of these thermostable organics. The broad band centered around 1500 cm^{-1} also indicates the presence of an organic rest fraction and/or ionic carbonates [25]. The intensity of this band decreases as the annealing temperature is increased, but even after heating up to 700°C features can still be distinguished in the same wavenumber range. The peaks at 1630, 1570 and 1420 cm^{-1} can be ascribed to adsorbed H_2O, M-OH and carbonate or organic rest fractions respectively [1]. Sharp, weak bands are observed at 1385 and 1355 cm^{-1}. These are observed in the FTIR spectrum of commercial ZrO_2 as well (not shown), but the band at 1420 cm^{-1} is not. The presence of M-O vibrations is clear below 1000 cm^{-1} and the shape of this band differs for the precursor gels with different CA content, indicative of a difference in the oxide phase present.

Using Raman spectrometry (Figure 7), the tetragonal, cubic and monoclinic ZrO_2 phase can be distinguished [26] and small sample volumes suffice. Raman spectrometry is suited to the distinction of these phases even more than XRD, where the difference between the tetragonal and cubic phase is not so clear. After heating to 600°C, it is impossible to distinguish any oxide peaks, as there is a strong background fluorescence present. The fluorescence may be due to an organic rest fraction causing the high Raman intensity over a broad range of wavenumbers. For CA 1.2:1 Zr(IV) the fluorescent background remains more pronounced up to higher temperatures than for the CA 4:1 Zr(IV) gel, indicating a stronger persistence of the organic rest fraction. After annealing at 650°C and even clearer at 700°C, the oxide phases obtained from the CA 4:1 Zr(IV) gel can be identified as being a mixture of the monoclinic and the

tetragonal phase, while for the CA 1.2:1 Zr(IV) there is quasi pure, tetragonal phase obtained. The tetragonal phase is not thermodynamically stable at room temperature, normally the monoclinic phase is. However, when zirconia is formed with small particle sizes, the tetragonal phase can be stabilized [27]. The formation of tetragonal ZrO_2 (JCPDS 50-1089 [28]) was confirmed for both precursors by electron diffraction and transmission electron microscopy indeed showed an estimated grain size in the order of 5-10 nm (650°C anneal).

3.3   Ultra-thin film crystallization behavior

The crystallization behavior of ultrathin films was studied using high-temperature XRD, allowing in-situ study of the phase (trans)formation during heating (10°C/min, static air). The crystal structure or amorphous nature of the high-k dielectric is important: It may influence its leakage current, expected to be higher in case of crystalline materials due to the presence of grain boundaries, as well as its dielectric constant, which is dependent on the crystallographic phase [29,30].

The relevant part of the HT-XRD diffractograms is presented in Figure 8 (for the CA:Zr 2:1 and 1.2:1 the results are not shown as they were very similar to the result of the 4:1 precursor of 0.05 mol/L). After hot plate treatment, the films are all amorphous. Starting from 500°C crystalline ZrO_2 characterized by a diffraction peak at $2\theta=30.3°$ is present, and it remains up to 900°C independent of the thickness or citric acid content in the precursor. It is clear that the crystal phase formed, is not the thermodynamically stable monoclinic phase. The phase identification is tedious due to the preferential orientation, the high temperature and residual stress in the films shifting the peaks compared to a powder reference at room temperature, and also because of the low peak

intensity due to the low thickness. However, the peak at $30.3°2\theta$ may be ascribed to the (101) peak of a tetragonal ZrO_2 phase, as the (111) peak of cubic ZrO_2 (JCPDS 49-1642) would have been expected at a slightly lower 2θ of 30.1°. After cooling down to room temperature the observed peak is shifted to $30.4°2\theta$ compared to 30.3° for the reference, which indicates the presence of residual stress in the film [31]. Similar to the powders, the crystal phase in the thin films is thus identified as a metastable tetragonal phase. This is in agreement with the increasing stability of tetragonal compared to monoclinic ZrO_2 with decreasing film thickness as described in literature [32,33].

Furthermore, from the XRD patterns after cooling down from 900°C to room temperature, it becomes clear that the tetragonal phase partially transforms to monoclinic ZrO_2 only for the thickest film (~40 nm). This leads to two new peaks at 2θ=28.3 and 31.4°. In contrast with this result, the stability of the pure tetragonal phase at room temperature in ZrO_2 films of 45 nm thickness was demonstrated by off-line XRD at room temperature (not shown): After annealing up to 500, 600, 700 and 800°C in a furnace and quench cooling, all these films only showed the presence of tetragonal ZrO_2 phase. This discrepancy is ascribed to the different thermal history for the furnace anneal and HT-XRD treatment.

At increasing temperatures, there is an increase of the tetragonal (101) peak's integrated intensity, which indicates that the volume of crystalline phase increases. Comparing 10 nm, 20 nm and 40 nm thick films, the peak intensity increases due to the increasing volume of crystallites.

There is no evidence in the XRD patterns for the formation of crystalline zirconium carbonates, although time of flight – secondary ion mass spectrometry measurements demonstrated the presence of residual carbon in the films (not shown).

The absence of a difference in the crystallization temperature and phase formation for precursors containing different amounts of citric acid, differs from the observations made on powders (§2.2) and literature for other material systems [34], where a higher organic content led to a lower crystallinity. This might indicate that in the case of CSD deposited zirconia, the low film thickness is controlling the oxide phase formation to the tetragonal phase, rather than the precursor composition.

3.4   Film thickness and topography

The film thickness was controlled by changing the precursor solution's concentration, as shown in Figure 9 for precursor solutions with different CA:Zr ratio's (1.2, 2 and 4:1). It is clear that after the thermal treatment the film thicknesses are similar, independent of the citric acid content of the precursor solution. The variations observed between the different precursors, are not larger than the variation within one precursor used for replicate depositions and is limited to a few nanometers.

As the crystallization of the ZrO_2 films may lead to local variations in film thickness, it is important to check their topography by AFM. Films deposited from precursors containing CA 1.2 and 4:1 Zr with concentrations of 0.05 and 0.005 mol/L, and annealed to temperatures from 500°C to 800°C in dry air were studied. Representative examples of height images are shown in Figure 10 and 11. The root mean square (RMS) roughness values are very low (0.14-0.58 nm) indicating that the films have very smooth surfaces. For most of the samples the RMS roughness is in the same range as the SiO_2/Si substrate (0.23 nm), that was cleaned and heat treated the same way as the substrates that were used for the deposition [35]. Generally, the RMS roughness increases upon increasing the annealing temperature. This is accompanied by

grain growth that is observed with increasing annealing temperature for the different film thicknesses and precursors studied here. After annealing the thinnest films (0.005 M) up to 800°C, an onset of microstructural stability becomes clear. This can be explained by the increase of the relative grain size compared to the film thickness (Figure 11) [7].

From the AFM images no pronounced, consistent effect of the precursor composition on the film topography can be confirmed. This may be related to the analogy in the crystallization behavior of the films deposited from the different precursors. Furthermore, the topography does not vary strongly with film thickness for both precursors. It is concluded that smooth, uniform ultrathin films can be deposited from the different precursor solutions. This is corroborated by SEM images for the thicker films (0.05 M) as shown in Figure 10.

3.5   Dielectric properties

The dielectric properties were characterized by C-V measurements. As an example, in Figure 12 C-V curves are shown for films with similar thickness ($t_{XRR} \sim 5$ nm) deposited from precursors containing CA 1.2, 2 and 4:1 Zr(IV). The C-V curves for the ZrO_2 films are well behaved after forming gas anneal, which is carried out to reduce the number of interface states [36]. The C-V curves were fitted by the Hauser model to extract equivalent oxide thickness (EOT) values for the different precursors. The EOTs are plotted as a function of physical film thickness in Figure 13 in order to determine the films' k value, which was calculated from the slope. In this way, it was determined that a high k value of 21-22 is obtained, independent of the citric acid content of the precursor. This value is comparable to the dielectric constant (k=21.6) obtained for

zirconia films deposited by ALD [38], which is the widely accepted deposition method for high k films. The good agreement of the k values for the different deposition methods, is an indication that the aqueous CSD method can be put to use for the evaluation of high k materials. Furthermore, the similar k value for the different precursors can be explained by the similarity of the films deposited from them, which are characterized by the same crystallographic phase and similar topography.

Leakage current measurements were carried out to further evaluate the CSD films' dielectric quality as a function of the citric acid content of the precursor (Figure 14). The leakage current obtained here is higher than the leakage for films deposited by ALD [38]. Moreover, the leakage current is independent of the citric acid content of the precursors within experimental error. This is in contrast with expectations based on prior results obtained for lanthanide oxides deposited by aqueous CSD. In a first approach, the leakage current is regarded as being controlled by the carbon content of the film, which could be expected to be lower in case of a precursor with a lower citric acid content. It is clear that this assumption does not suffice to explain the lack of an effect which is observed here. Besides this background leakage, also a contribution of weak spots with different possible origins, such as grain boundaries [37] can be taken into account, which might be affected by the citric acid content in the precursor. Most likely however for the anneal conditions chosen, the carbon content is still at a level that is too high to observe the difference between precursors [38]. In agreement with the latter, further optimization of the annealing conditions allowed to obtain leakage currents of the same order of magnitude as ALD, which is discussed in detail elsewhere [38]. Moreover, with optimal annealing conditions the leakage current was lower for the precursor containing the lowest citric acid content. The low CA content precursor

thus shows an advantage when considering leakage under optimized annealing conditions [38]. All different annealing conditions led to a similar k value.

It can be concluded that after optimization of the anneal treatment, ultrathin zirconia films of good dielectric quality can be obtained from aqueous CSD using precursors with different citric acid contents. Accurate k value extraction is relatively easily achieved, while for leakage reduction an optimization of the anneal treatment is necessary.

4. Conclusions

It is possible to synthesize citratoperoxo-Zr(IV) precursor solutions with different molar ratios of citric acid to Zr(IV), down to CA:Zr(IV) 1.2:1. The precursor solutions are characterized by different gelation behavior, thermal decomposition profiles and oxide formation behavior, as far as the powders are concerned. The differences are related to the amount of excess citric acid, which is needed to build up the amorphous gel structure. The excess also plays a role in the thermal decomposition pathway of the gel that finally leads to the formation of the oxide. Even though the ZrO_2 is in principle simply formed from the Zr(IV) complex, the excess of ammonium citrate influences the secondary reactions, e.g. leading to formation of thermally resistant nitrogen containing organics, as well as the heat generated. In this way, the excess ammonium citrate also influences the oxide's phase purity and formation.

In contrast with the differences observed for the different powder precursors, little or no effect is seen on the crystallization, topography or dielectric constant of ultrathin films

deposited from the different precursor solutions. This demonstrates that a Zr(IV) precursor which did not gel due to its low citric acid content, still allows deposition of functional zirconia films. This may be related to the different drying kinetics during bulk gelation and thin film formation.

The most important advantage in thin films demonstrated here is the large decrease of the amount of carbon containing species that have to be decomposed for the low citric acid content precursor (25% less in weight). This improves the economy and ecologic impact of the whole process, while at the same time allowing to maintain the same k value as for precursors with a higher citric acid content.

5. *Acknowledgements*

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