Nanostructured Dense ZrO_2 Thin Films from Nanoparticles Obtained by Emulsion Precipitation

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Nonagglomerated spherical ZrO_2 particles of 5–8 nm size were made by emulsion precipitation. Their crystallization and film-forming characteristics were investigated and compared with nanosized ZrO_2 powders obtained by sol–gel precipitation. High-temperature X-ray diffraction indicated that the emulsion-derived particles are amorphous and crystallize at 500°C into tetragonal zirconia, which is stable up to 1000°C. Crystallite growth from 5–20 nm occurred between 500°–900°C. Films of 6–75 nm thickness were made by spreading, spin coating, and controlled deposition techniques and annealed at 500°–600°C. The occurrence of *t*- ZrO_2 in the emulsion-precipitated powder is explained by the low degree of agglomeration and the corresponding low coarsening on heating to 500°–800°C, whereas the agglomerated state of the sol–gel precipitate powder favors the occurrence of the monoclinic form of zirconia under similar conditions.

I. Introduction

ZIRCONIA coatings are of special interest for several high-performance applications, such as high- k dielectrics, wear-resistant insulating coatings, sensors, and electrolytes. Thin homogeneous nanocrystalline zirconia films with grain sizes <20 nm have been prepared by reactive sputter deposition^{1–3} and sol–gel methods.⁴ Dense layers made by deposition of nonagglomerated nanoparticle dispersions may lead to systems with substantially reduced sintering temperature and minimal grain growth.⁵

Several techniques for the synthesis of nano- ZrO_2 have been reported, such as inert gas condensation,^{6–8} forced hydrolysis,^{9–11} alkoxide hydrolysis,^{12,13} hydrothermal processes¹⁴ and other techniques.^{15–17} ZrO_2 nanoparticles obtained by sol–gel-based processes are often highly agglomerated,⁹ whereas more elaborate methods to obtain monodisperse ZrO_2 resulted in particle sizes >30 nm.¹⁸ ZrO_2 precursor particles have also been synthesized in heterogeneous media, such as emulsions, micellar systems, and microemulsions.^{19,20} Typical problems encountered in emulsion precipitation are particle growth beyond the dimensions of the aqueous droplets, and strong and uncontrolled aggregation, in particular during the water-removal step.²¹

Bulk zirconia has three polymorphs, i.e., monoclinic (*m*- ZrO_2) at room temperature, tetragonal (*t*- ZrO_2) at 1200°C and higher, and

cubic (*c*- ZrO_2) at temperatures >2400°C.²² The presence of small amounts of certain ionic species such as sulfate⁴ may stabilize the tetragonal phase down to lower temperatures. Garvie²³ observed that *t*-zirconia is present at room temperature when the particle size of the tetragonal phase is smaller than a certain critical value. When the particles grew to be >30 nm, a complete conversion from the tetragonal into the monoclinic phase occurred. A simple thermodynamic model has been proposed to describe the free energy of an unconstrained spherical crystal, from which the critical particle radius (r_c) for the tetragonal to monoclinic transformation can be correlated with the phase-transformation temperature:^{24,25}

$$r_c = \frac{3.79 \text{ nm}}{\left(1 - \frac{T}{1448}\right)} \quad (1)$$

where T (K) is the transformation temperature. Recent high-resolution transmission electron microscopy studies on ZrO_2 also revealed a critical upper size for ultrapure tetragonal grains.^{3,25,26} Aita *et al.*³ determined a critical layer thickness of 6.2 nm at 564 K for nanolaminates made from polycrystalline zirconia and amorphous alumina, which agrees well with the predictions of Eq. (1).

In several other studies, it has been suggested that the pH of the solution from which the zirconia precursor precipitates determines the predominant phase. Davis²⁷ investigated zirconia gels, precipitated from a zirconyl nitrate solution at pH values between 0–14. Relatively high fractions of tetragonal ZrO_2 were found in calcined powders synthesized at pH <5 or >12. In powders prepared from nitrate,²⁸ chloride,¹⁸ and sulfate⁴ based zirconia precursors the tetragonal and monoclinic phases were found to coexist at >600°C when the grains had grown larger than 25 nm.

Clearfield²⁹ explained the occurrence of tetragonal ZrO_2 at low temperatures by assuming two precipitation mechanisms, slow and rapid precipitation. Slow precipitation is thought to dominate at pH <2 and >13, where aqueous tetrameric Zr(IV) species form an ordered network that acts as a template for the formation of the tetragonal phase. Rapid precipitation, on the other hand, promotes the formation of a random network that crystallizes into a mixture of *m*- and *t*- ZrO_2 (pH 2–6), or almost pure monoclinic ZrO_2 (pH 7–11) on heating.

In the present study, ZrO_2 precursor particle dispersions in decane are made by a modified emulsion precipitation method. The particle morphology, crystallization behavior and phase evolution on annealing are investigated and compared with similar sized ZrO_2 powders obtained by sol–gel precipitation method. Three methods are applied to deposit thin films from dispersions of ZrO_2 precursor nanoparticles in decane. The film formation characteristics, morphology, and phase evolution on annealing are characterized.

II. Experimental Procedures

(1) Emulsion Precipitation Synthesis

A 0.02M ZrCl_4 (Merck, Darmstadt, Germany) solution was used as aqueous precursor phase for emulsion precipitation. As

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precipitation agent, a 0.025M hexamethylenetetramine (HMTA; Fluka Chemical, Ronkonkoma, NY) solution was used. Thermally stable (20°–80°C) water in oil emulsions was prepared from 40 g of one of the above-mentioned aqueous solutions, 60 g decane (Fluka), 1 g nonyl phenol tetra-ethyleneglycol ether (Arkopal 40; Hoechst, Frankfurt, Germany), and 1 g didodecyl-dimethyl-ammonium bromide (DiDAB; Fluka). An Ultra-Turrax (IKA T25 basic, Dijkstra Vereenigde, Netherlands) was used to produce emulsions of the aqueous solutions in decane at a rotation speed of 20 000 rpm. The emulsion containing the precursor solution was mixed with one of the emulsions containing a precipitation agent, stirred for 5 min at room temperature, followed by stirring for 10–15 min at 50°–60°C to induce precipitation. The pH during precipitation was monitored with a pH electrode for emulsions (Inlab 420, Mettler-Toledo, Highstown, NJ). After precipitation, a poly-(octadecyl methacrylate) solution (PODMA; 25 wt% solution in toluene, Aldrich, Milwaukee, WI) was added for particle stabilization. The amount of PODMA added was 10 wt% with respect to the theoretical amount of oxide formed. The water phase was removed by azeotropic distillation. Because DiDAB is soluble only at the water/decane interface, the excess of DiDAB not needed for particle stabilization precipitated after water removal and was removed with a filter paper. The remaining soluble surface-active agents were washed out with decane in a cross-flow filtration device.³⁰

(2) Sol-Gel Synthesis

Sol-gel derived ZrO₂ nanoparticles were obtained from a 50 mL precursor solution containing 0.4M ZrCl₄ and 0.2M HCl (Merck). Precipitation was induced by adding the precursor solution dropwise to 80 mL of 25% ammonia (Merck) under stirring.³¹ The precipitate was kept in the solution overnight, collected and washed with doubly distilled water until the chloride concentration was below the detection limit (tested with AgNO₃). After washing twice with ethanol, the precipitate was dried at 80°C and calcined in air at 400°C.

(3) Thin Film Formation

Thin films were deposited by spin coating, spreading, and controlled deposition of the dispersions on polished [100]-oriented silicon wafers (76 mm diameter, MEMC Electronic Materials, St. Peters, MO) under class 1000 clean-room conditions. Before use, the wafers were chemically etched with concentrated HF.

The spin-coating procedure consisted of covering the substrate with a few drops of dispersion at low-spinning speed, after which the rotation frequency was increased to 2000 rpm for ~20 s. This procedure was repeated four times.

Dispersion spreading was done by placing a few droplets of the dispersion between the polished sides of two wafers and horizontal sliding of one wafer relative to the other.

The controlled-deposition procedure consisted of attaching the substrate to a Peltier element (Model L 100, LC-Electronics, Germany) that was placed under a tilt angle of 9°, and cooling down the substrate to 10°C. The dispersion was added dropwise to the top of the substrate, after which the substrate was left for 7 d in a water vapor-free glove box to allow slow drying.

Any residual organics were removed by subsequent heat treatment for 3 h at 200°C, and oxygen plasma treatment at 45°C for 1.5 h. The oxygen-plasma treatment was conducted with an (Model ET Plasmab 508 Electrotech, Ulm, Germany; 49.5 mL/min O₂, 0.17 mbar, 250 W rf power). To study the temperature evolution of the films, samples were annealed in air for 3 h at different temperatures. The heating rate was 5°C/min between room temperature and 50°C below the final temperature, and 2°C/min in the last 50°C temperature interval.

(4) Characterization

High-temperature X-ray diffraction (HTXRD) measurements were performed on particle dispersions using a diffractometer (Model X'pert-MPD, Philips, Eindhoven, Netherlands) with CuKα

radiation ($\lambda = 0.15418$ nm). The particle dispersions were applied directly as concentrated films on platinum strips. The spectra were recorded in the range 2 θ 15°–95° between room temperature and 1300°C (heating/cooling rates 2°C). Every 100°C, the temperature was kept constant for 1 h to anneal the samples before *in situ* XRD spectra were recorded. The average crystallite size D was calculated using the Scherrer formula $D = 0.9\lambda/B\cos(\theta)$, where B is the full-peak width at half of the maximum intensity after correction for instrument broadening contributions.

The morphology of nanoparticles was characterized by high-resolution transmission electron microscopy (HRTEM; Model CM30 Twin STEM, Philips; 300 kV, 0.23 nm resolution). TEM was performed on unfiltered particles, whereas HRTEM was performed after removal of organic residuals as described above. Zirconia thin films were characterized by field emission scanning electron microscopy (FESEM; Model XL30 SFEG-SEM, Philips, voltage 1–30 kV, 2 nm lateral resolution) and HRTEM on cross sections of thin films.

III. Results and Discussion

(1) Zirconia Nanoparticles

The yield of ZrO₂ precursor particle dispersions was 70%–80%. These dispersions were stable and could be concentrated reversibly, whereas the solvent could be exchanged with hexane or octane. Figure 1(a) shows an HRTEM micrograph of unfiltered emulsion-derived ZrO₂ precursor particles. The particles are not agglomerated, and some organic residuals are visible in the upper part of the picture. Most particles have a diameter between 5–8 nm, but some particles with a diameter of up to 12 nm are present as well. Figure 1(b) shows TEM images of the sol-gel-derived powder at two magnifications. In contrast to the nonagglomerated state of the emulsion-precipitated powder, the sol-gel powder consists of large agglomerates of 50–100 nm or larger size. As shown in the inset, the primary grain size is 4–9 nm, i.e., in the same range as the precipitated powder.

The phase evolution of these two types of precursor nanoparticles on heat treatment was investigated with HTXRD. The emulsion-derived particles made were amorphous and crystallised into *t*-ZrO₂ after annealing for 1 h at 500°C, as shown in Fig. 2(a). Line broadening analysis indicated that the initial crystallite size at 500°C is similar to that of the precursor particles. On further heating the tetragonal phase remained stable till 1000°C. At 1100°C the monoclinic phase formed, although the intensities of the monoclinic ($\bar{1}11$) and (111) reflections were <2% of the intensity of the tetragonal (111) reflection. At 1300°C, the monoclinic phase was present only in trace amounts. On cooling *m*-ZrO₂ was detected at temperatures <800°C, and became the predominant phase at <400°C. The volume fraction of the tetragonal phase x_t was calculated from the peak intensity ratio,³² i.e.:

$$x_t = \frac{I(111)_t}{I(111)_t + I(111)_m + I(111)_m} \quad (2)$$

where $I(abc)_x$ is the intensity of the (abc) reflection of phase “x.” At room temperature, x_t was found to be ~35%. Figure 3 shows the entire HTXRD pattern at 900°C. Although it is assumed that the amorphous particles crystallize into *t*-ZrO₂, no distinction between *t*- and *c*-ZrO₂ can be made by XRD only. However, the weak (112) reflection at 2 θ 42.6° can be assigned only to *t*-ZrO₂, which suggests that the material is at least predominantly tetragonal. Samples heated to temperatures <1000°C remained tetragonal after cooling down to room temperature. The average crystallite size of the *t*-phase remained 5–7 nm until 700°C, and was <20 nm until 900°C. Significant growth occurred from 1000°C onward, reaching an estimated size of ~80 nm when the monoclinic phase appeared. On further heating to 1300°C, further particle growth of the tetragonal phase to 100–120 nm occurred. When the monoclinic phase reappeared from 400°C downward, the particle size of the tetragonal phase decreased to ~30 nm at room temperature. The average size of the monoclinic phase is also ~30 nm. Similar

Fig. 1. (a) TEM image of precipitated 5–8 nm ZrO_2 precursor particles. Some organic residuals are also visible; (b) TEM image of sol-gel-derived ZrO_2 powder. The inset shows the same powder at higher magnification. The primary particle size is 4–9 nm.

sizes were found when the particles were heated to 1000°C and subsequently cooled. The decrease in particle size during the cooling part of the temperature cycle may possibly be explained by crystal breakup or the formation of hybrid $t\text{-ZrO}_2/m\text{-ZrO}_2$ crystals from larger tetragonal crystals due to internal stresses.

In the sol-gel-derived powders $m\text{-ZrO}_2$ already formed at much lower temperatures, i.e., 600°–700°C, as illustrated in Fig. 2(b). At 1100°C, the volume fraction of $t\text{-ZrO}_2$ was ~37%. At higher temperatures, the monoclinic phase diminished and disappeared completely at 1300°C. On cooling the powder remained tetragonal until the monoclinic phase re-emerged below 1000°C. Initially, the initial crystallite size of the sol-gel powders was ~9 nm, as estimated from line broadening analysis, and they had grown to 12–15 nm when the monoclinic phase started to form. The crystal size of the monoclinic phase was similar. The crystallites of both phases grew to ~70 nm at 1200°C. During cooling the monoclinic phase reappeared at 900°C with crystal sizes of ~70 nm. The shape of the tetragonal peak during cooling was highly asymmetric between 900° and 500°C, which may be explained by strain occurring during phase transformation.³³ As the volume fraction of the monoclinic phase increased, the monoclinic crystal size decreased until it reached values of ~55 nm at room temperature.

The crystalline phase that forms from both types of amorphous powders is the metastable low-temperature t -zirconia phase that is often observed in nanopowders.²³ A special feature of the powder prepared by emulsion precipitation is that the tetragonal phase remains stable in a broad temperature range up to 1000°C. Powders prepared by other techniques such as sol-gel synthesis form a mixture of m - and $t\text{-ZrO}_2$ already at much lower temperatures.^{34,35} The martensitic transition from the monoclinic to the high-temperature tetragonal phase at 1200°–1300°C exhibited by both types of powders is also observed in conventional bulk zirconia.^{22,36}

Partial transformation to $m\text{-ZrO}_2$ occurs between 1000°–1100°C and 500°–600°C in both the emulsion and sol-gel-derived powders, respectively. According to Eq. (1), these temperatures correspond with critical particle radii $r_c \sim 31$ nm (1000°C) and ~8 nm (500°C). Although the experimental data did not show a distinct transformation temperature above which only the monoclinic phase is stable, these calculated values correspond well with the experimental tetragonal particle sizes of 32 and 6.3 nm that are found in these two systems at the same temperatures.

However, the monoclinic grain size was found to be smaller than the coexisting tetragonal grain size under various conditions, which contradicts the assumptions underlying Eq. (1). This suggests that phase development is more strongly related to parameters, such as preparation conditions, material purity, and/or the influence of constraint effects due to a relatively dense packing of particles. Especially, the latter effect can explain the observed differences in the tetragonal/monoclinic compositions of emulsion and sol-gel-derived powders between 500° and 1000°C. The low degree of agglomeration and the corresponding low coarsening on heating to 500°–800°C of the emulsion-precipitated powder explains the occurrence of $t\text{-ZrO}_2$, whereas the high coarsening of the sol-gel precipitate powder on calcination favors the occurrence of the monoclinic form of zirconia.

(2) ZrO_2 Thin Films

When the nanoparticle dispersions were deposited as thin films, very similar results were obtained for the spin coating and spreading techniques. Both methods led to thin layers with thicknesses of 6–30 nm. This corresponds roughly to 1–5 layers of grains. The coated wafers became transparent after heat treatment in air at 500°C or higher. The TEM image in Fig. 4(a) shows a cross section of a spin-coated ZrO_2 film after annealing at 500°C for 3 h. A smooth and continuous ZrO_2 layer with a thickness of 6–10 nm that is attached to an amorphous SiO_x layer can be seen. Although the native oxide layer of the wafer had been removed by chemical etching before film deposition, it reappears during annealing. The spin-coated film shown in Fig. 4(b) was annealed at 1000°C. The thickness of 9–10 nm is similar to the thickness before annealing, but the grains appear to have become flatter. The SiO_x layer in between the zirconia film and the silicon wafer grew considerably to a thickness of ~130 nm, and was found to be independent of the thickness of the zirconia layer.

The usual layer thickness obtained with spin coating was 4–8 nm, which corresponds to 1–2 monolayers. HRTEM measurements were performed on cross sections of samples after annealing at 200°–600°C for 3 h to study the structural development of these layers on heat treatment. The coatings shown in Fig. 5 (annealed at 200, 400° and 600°C, respectively) appeared dense even below the crystallization temperature, and showed no signs of significant shrinkage. A native silicon oxide layer formed between the silicon

Fig. 2. Temperature evolution of the t -(111), m -($\bar{1}11$), and m -(111) reflections by HTXRD: (a) emulsion-derived ZrO_2 particles; (b) sol-gel-derived ZrO_2 particles.

wafer and the zirconia film as a result of the high-temperature treatment. Between 200° and 500°C the ZrO_2 layers are mainly amorphous, although they have some crystalline grains with visible lattice fringes. The latter grains probably developed under the electron beam. Coatings annealed between 200° and 500°C are very similar to the coating shown in Figs. 5(a) and (b). A fully crystallized layer is formed at 600°C, as shown in Fig. 5(c). The crystallites are randomly orientated with sizes of 5–12 nm.

Considerably thicker ZrO_2 layers were prepared using the controlled deposition technique. Typically, the thickness of a single layer was 40–50 nm, although the final films did not have a similar thickness over the entire substrate. Further layer buildup by multiple deposition steps without detectable boundaries between layers was possible, provided that each layer was heat-treated before deposition of the next layer. Up to four deposition steps were applied. Samples for HRTEM characterization were usually taken from the thinnest part of the coating.

Figure 6 displays a cross section and a planar view of a singly coated film after annealing at 600°C. The surface of the coating appears to be very smooth and the thickness is ~45 nm. The densely packed grains have a random orientation and are 5–10 nm in size, as estimated from their lattice fringes. A thin film is visible on top of the coating in Fig. 6(a) that is due to thickness variations of the layer.

IV. Conclusions

Nonagglomerated spherical ZrO_2 particles of 5–8 nm size were made by an emulsion-precipitation method. The precipitated nanoparticles are amorphous and crystallize at 500°C into tetragonal (t) zirconia, which is the only phase present up to 1000°C. In other studies on zirconia nanoparticles reported to date, the monoclinic (m) and tetragonal phases were found to coexist already at

Fig. 3. HTXRD pattern of emulsion-derived ZrO_2 at 900°C . The marked reflections can be attributed to the tetragonal phase.

temperatures of $100^\circ\text{--}150^\circ\text{C}$ above the amorphous-to-tetragonal phase transition temperature. Sol-gel-derived ZrO_2 nanoparticles that were investigated for the sake of comparison, were partly monoclinic at 600°C and higher temperature. Both types of powders exhibit the well-known martensitic transition from the monoclinic to the high-temperature tetragonal phase at $>1200^\circ\text{C}$.

The crystallites obtained by emulsion precipitation grew slightly from 5–20 nm between 500° and 900°C , and grew significantly from 1000°C onward to ~ 100 nm at 1300°C . The low degree of agglomeration and the corresponding low coarsening on heating to $500^\circ\text{--}800^\circ\text{C}$ of the emulsion-precipitated powder explains the occurrence of $t\text{-ZrO}_2$, whereas the high coarsening of the sol-gel precipitate powder on calcination favors the occurrence of the monoclinic form of zirconia. Because of the enhanced thermal stability of the low-temperature tetragonal phase, the particle size at the onset of the tetragonal-to-monoclinic phase transition was much larger than reported elsewhere. On cooling the tetragonal crystals transformed into monoclinic, yielding a final size of $\sim 30\text{--}40$ nm at room temperature for both the t - and $m\text{-ZrO}_2$ grains. This suggests that the crystals either broke up during cooling, or that hybrid $t\text{-ZrO}_2/m\text{-ZrO}_2$ crystals were

Fig. 4. Cross-sectional images of ZrO_2 films prepared by spin-coating. (a) TEM image of layer after annealing at 500°C ; (b) HRTEM images of layer after annealing at 1000°C .

Fig. 5. Thermal evolution of the microstructure of ZrO_2 layers prepared via spin-coating; (a) annealed at 200°C ; (b) annealed at 400°C ; (c) annealed at 600°C .

Fig. 6. HRTEM images of cross sections of a ZrO_2 film prepared by film coating after annealing at 600°C .

formed from the larger tetragonal crystals because of large internal stresses.

Thin films were prepared by spreading, spin coating, and controlled deposition and annealed at $500^\circ\text{--}600^\circ\text{C}$. Spreading and spin coating led to thin layers with a thickness of 6–30 nm. Deposition by controlled deposition led to films with an average thickness of 45–75 nm. After annealing the densely packed grains were randomly orientated and were only 5–10 nm in size. HTXRD and HRTEM showed that the powders and films were tetragonal up to at least 1000°C , although the presence of cubic zirconia cannot be excluded.

Homogeneous mono- or multilayers of nanocrystalline zirconia with grain sizes <20 nm have been made so far only by reactive sputter deposition and sol-gel methods. In particular, the latter method yields very similar zirconia films to those obtained here. However, layer deposition from premade particle dispersions offers the advantage of milder deposition conditions and may therefore be more adequate to coat certain substrates.

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