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Zirconia thin films by atomic layer epitaxy. A comparative study on the use of novel precursors with ozone

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Zirconium oxide thin films have been deposited by atomic layer epitaxy (ALE) using $Zr(thd)_4$, $Cp_2Zr(CH_3)_2$ and Cp_2ZrCl_2 (thd = 3,3,5,5-tetramethylheptane-3,5-dionate, Cp = cyclopentadienyl) as zirconium precursors and ozone as the oxygen source. A plateau of constant growth rate (ALE window) was observed for the $Zr(thd)_4/O_3$ process at 375–400 °C, for $Cp_2Zr(CH_3)_2/O_3$ at 310–365 °C and for Cp_2ZrCl_2/O_3 at 275–350 °C. Within these temperature ranges constant deposition rates of 0.24, 0.55 and 0.53 Å $(cycle)^{-1}$ were obtained, respectively. Deposited films were characterised by XRD and AFM for crystallinity and surface morphology, while TOF-ERDA was used to analyse the ZrO_2 film stoichiometry and possible impurities. Films deposited by optimised parameters from $Cp_2Zr(CH_3)_2/O_3$ and Cp_2ZrCl_2/O_3 were crystalline showing the preferred (-111) orientation of monoclinic ZrO_2. In all films, the orthorhombic zirconia phase was also present, although at higher temperatures its relative amount decreased. $Zr(thd)_4/O_3$ process produced films with lowest crystallinity consisting of both orthorhombic and monoclinic phases. According to TOF-ERDA, films were nearly stoichiometric with less than 0.5 atom% hydrogen and carbon. Outside the ALE window, a small chlorine contamination (0.1–0.3 wt%) was observed by XRF when the ZrO_2 films were deposited from Cp_2ZrCl_2/O_3 at 200–275 °C.

Introduction

Zirconium dioxide is a thermally and chemically stable material used for optical and electrical applications. For example, ZrO_2 has attracted interest as mirrors and antireflective coatings, thermal barriers and hard protective layers.[1–5] Due to its high permittivity ($\varepsilon = 17–22$),[6,7] ZrO_2 thin films have also been used as dielectrics in microelectronics.[8,9] The use of ZrO_2 as a buffer layer for high T_c-superconductors[10] and high temperature insulating shields[11] has also been studied. Preparation of complex dielectric films containing zirconium, such as $ZrTiO_4$,[12] has been reported as well.

ZrO_2 has three different structural polymorphs, of which the monoclinic (M) phase is the thermodynamically stable one at room temperature. High temperature forms of ZrO_2, namely the cubic (C) and tetragonal (T) polymorphs, can be stabilised at room temperature by several ways. The mechanism of phase transformation has frequently been studied and different routes have been suggested.[13,14] Physical properties, such as strain, film thickness and crystallite size, affect the stabilisation and phase transformation of ZrO_2. The cubic form of ZrO_2 is usually stabilized in thin films by adding other oxides, typically Y_2O_3,[15] but also Sc_2O_3,[16] CaO,[17] CeO_2,[18–20] In_2O_3,[21] Gd_2O_3,[15] MgO,[15,17] Al_2O_3[16,22] and $MgAl_2O_4$[23] have been used. Yttria stabilised zirconium oxide (YSZ),[24–26] has been used as a buffer layer for high-T_c superconducting films as such or together with CeO_2 or Y_2O_3,[27–29] as well as in solid electrolyte applications for oxygen pumps,[30] sensors[31] and catalysts.[19] Furthermore, relatively thick (>2 μm), stabilised ZrO_2 films have been utilised in solid-oxide fuel cells[32] and oxygen membranes.[33] Other than yttrium stabilised ZrO_2 compounds have been suggested for certain applications, for example, in high temperature[22] and corrosion protection layers[18] as well as in transparent conductive oxides.[21] ZrO_2 is also a constituent of several interesting oxide thin films of complex composition, such as $Pb(Zr,Ti)O_3$[34,35] and $Pb(Zr,Ti,Nb)O_3$.[35] The application potential of these ferroelectric oxides has been studied for capacitors in integrated circuits for dynamic random access (DRAMs) and non-volatile memories.[36]

Atomic layer epitaxy (ALE),[37] also referred to as atomic layer deposition (ALD) or atomic layer CVD (ALCVD), has been successfully employed for the deposition of a variety of oxide films.[38–40] It is based on alternating saturative reactions on the substrate surface, which makes the thin film growth process self-limiting and easy to control.[41] ALE has been used for the deposition of amorphous and nanocrystalline ZrO_2 films from zirconium tetrachloride[42] and $ZrO[C(CH_3)_3]_4$,[43] respectively. ZrO_2 thin films were deposited at 500 °C from $ZrCl_4/H_2O$ precursors but more recently the depositions have also been successfully carried out at a much lower temperature, *viz.* 300 °C.[44,45] Furthermore, the ALE deposition of ZrO_2 for catalyst preparation and surface-controlled precursor chemisorption has been studied on high surface area silica substrates with $ZrCl_4$[46] and Cp_2ZrCl_2[47] precursors, respectively, in an attempt to quantitatively establish the stoichiometry and mechanism of the surface reactions.

ALE/ALD can be compared to the other major chemical deposition method, *viz.* CVD which has frequently been used for the deposition of ZrO_2. Different types of precursors have been utilised in the CVD depositions of ZrO_2 including pure inorganics,[42,48,49] β-diketonates[2,25,50] and alkoxides[51,52] as well as mixed-ligand[53–55] and amido complex[56] compounds of zirconium. In addition, the CVD deposition of ZrO_2 has been reported from volatile organo-zirconium compounds,[1] including $Cp_2Zr(CH_3)_2$.[57] According to the best of our knowledge, Cp_2ZrCl_2 has not yet been used as a precursor in CVD processes. However, it is a sufficiently volatile compound with thermal stability up to 500 °C.[58]

Generally speaking, precursors similar to those used in CVD are also applicable to an ALE process provided that certain requirements, such as thermal stability and sufficiently high reactivity, are met. The properties of different types of ALE precursors have recently been discussed.[59] Typically, β-diketonate and inorganic compounds have been employed as

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ALE precursors, but interest towards deposition of oxide thin films also from true organometallic compounds has increased, because lower deposition temperatures and higher rates can be achieved. For example, ALE processes utilizing organometallic precursors for Al_2O_3,[60] MgO,[61] $BaTiO_3$[62] and $SrTiO_3$[62] have recently been developed. In this paper we report the results of ZrO_2 deposition by atomic layer epitaxy using organometallic compounds, namely $Cp_2Zr(CH_3)_2$ and Cp_2ZrCl_2. For comparison, we report the results of ZrO_2 film depositions from a β-diketonate type precursor, $Zr(thd)_4$. In all cases ozone was used as the oxygen source.

Experimental

Commercial Cp_2ZrCl_2 (Strem Chemicals, #93-4002, 99%) (Cp = cyclopentadienyl, C_5H_5) was used without purification while the two other zirconium precursors were synthesised by published methods. Thus, $Cp_2Zr(CH_3)_2$ was synthesised by the method described by Samuel and Rausch[63] while $Zr(thd)_4$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) was prepared according to Morozova *et al.*[64] After the synthesis, the precursors were purified by sublimation and their volatility was checked by simultaneous TG/DTA in a Seiko SSC 5200 thermobalance. 2 mbar pressure and nitrogen (99.999%) carrier gas were used in order to simulate the ALE deposition conditions.[65]

Zirconium oxide thin films were deposited in a commercial flow-type hot-wall atomic layer epitaxy (ALE) reactor (F-120 by ASM Microchemistry Ltd.) using $Zr(thd)_4$, $Cp_2Zr(CH_3)_2$ and Cp_2ZrCl_2 as zirconium precursors and ozone as oxidising agent. O_3 was generated from O_2 (99.999%) in an ozone generator (Fischer model 502). Nitrogen (>99.999%, Schmidlin UHPN 3000 N_2 generator) was used as a carrier and purging gas. Thin film depositions were carried out under a 2–3 mbar pressure onto (100) oriented silicon and soda lime glass substrates measuring 10×5 cm^2. All substrates used were cleaned ultrasonically in ethanol and water before use. Zirconium precursors were evaporated from open glass crucibles. The deposition rate of ZrO_2 was studied as a function of the deposition temperature at 275–500 °C ($Zr(thd)_4/O_3$), 250–500 °C ($Cp_2Zr(CH_3)_2/O_3$) and 200–500 °C (Cp_2ZrCl_2/O_3).

Reflectance and transmittance spectra were measured in a Hitachi U-2000 double beam spectrophotometer. Thicknesses of the deposited films were calculated by the optical fitting method described by Ylilammi and Ranta-aho.[66] Crystallite orientations and crystallinity of the deposited films were determined by X-ray diffraction using Cu Kα radiation in a Philips MPD 1880 diffractometer. Surface morphology was studied by a Nanoscope III atomic force microscope (Digital Instruments) operated in tapping mode. Samples were measured with a scanning frequency of 1–2 Hz. Several wide scans (10–20 μm) were performed from different parts of samples to check the uniformity of the sample. Final images were measured from a scanning area of 2×2 μm. Roughness values were calculated as root mean square values (rms).

Impurity levels were analysed by X-ray fluorescence (XRF) and time-of-flight elastic recoil detection analysis (TOF-ERDA). Chlorine impurities in the samples were measured by a Philips PW 1480 WDS X-ray spectrometer equipped with a Rh anode. The chlorine impurity levels were then quantitatively estimated using the Uniquant 4.34 program (Omega Data Systems, Netherlands), which is based on fundamental parameters and experimentally determined instrumental sensitivity factors.[67]

TOF-ERDA measurements for other impurities than chlorine and for the Zr/O ratio were carried out at the Accelerator Laboratory of the University of Helsinki. In this method[68] heavy ions are projected into the sample and the signal consists of forward recoiling sample atoms ejected by the ion beam. Both velocity and energy for recoiled atoms were determined using timing gates and a charged particle detector, which enables the differentiation of different masses. With known stopping power and scattering cross sections, elemental depth distributions can also be calculated. For these TOF-ERDA studies, a 53 MeV $^{127}I^{10+}$ ion beam was used, obtained from a 5 MV tandem accelerator EGP-10-II. Samples were measured at 20° tilt and the recoils were detected at 40°, with respect to the incoming beam. For heavy recoil, energy spectra were obtained from the TOF signals and hydrogen spectra from the charged particle detector. In TOF ERD analysis the uncertainties of the impurity contents are due to statistical and possible systematic errors on the stopping powers. The uncertainties fall below 0.1 atom% units for contents below 1 atom% and below 0.2 atom% for contents above 1 atom%.

Results and discussion

Precursor analysis and ZrO_2 film growth

Precursors were analysed by TG/DTA which indicated a complete volatility except in the case of $Cp_2Zr(CH_3)_2$ where a few percent residue was left unvolatilised (Fig. 1). Onset values for volatilisation at 2–3 mbar pressure were 200–205 °C for $Zr(thd)_4$, 100–105 °C for $Cp_2Zr(CH_3)_2$ and 155–160 °C for Cp_2ZrCl_2. As we were unable to transfer the samples in a completely inert atmosphere into the TG/DTA apparatus, a slight decomposition of $Cp_2Zr(CH_3)_2$ was observed. For this particular precursor the amount of the weight loss at 170–190 °C and the amount of sublimation residue increased when samples were stored for longer periods in ambient atmosphere. Finally, after 60 hours of storing, no weight loss due to original $Cp_2Zr(CH_3)_2$ was detected. However, when $Cp_2Zr(CH_3)_2$ was transferred inertly into the ALE reactor, a complete volatility was observed. According to DTA results, no melting of the precursors took place before sublimation. Source material temperatures for the ALE depositions were estimated from the TG results. Thus, $Zr(thd)_4$, $Cp_2Zr(CH_3)_2$ and Cp_2ZrCl_2 were evaporated from open crucibles kept at 170, 70 and 140 °C, respectively.

The deposition rate of ZrO_2 as a function of deposition temperature was studied with different precursors. Pulse times for reactants were kept constant and sufficiently long in order to obtain a complete surface saturation on the substrate. Precursor pulse times were 0.8–1.0 s depending on the precursor selected; the ozone pulse time was kept constant at 1.5 s. Purge times of 1.0–3.0 s between reactive pulses were compared but no differences in growth rates were observed and therefore 1 s was chosen for all experiments. A plateau in the growth rate was observed for each of the precursors. As expected, the observed growth rate with $Zr(thd)_4/O_3$ was low due to the bulky size of the precursor. Previously in CVD

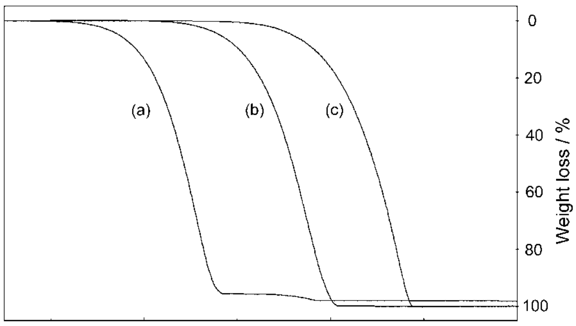

Fig. 1 TG curves of the precursors used; $Cp_2Zr(CH_3)_2$ (a), Cp_2ZrCl_2 (b) and $Zr(thd)_4$ (c). Heating rate was 10 °C min^{-1} and sample weight ~10 mg. This measuring pressure was 2 mbar.

experiments[50] observed high thermal stability of $Zr(thd)_4$ was the probable reason for the unusually high deposition temperature required as compared to the other ALE processes based on β-diketonate precursors and ozone.[38] A constant growth rate of 0.24 Å (cycle)$^{-1}$ was obtained in a narrow temperature range of 375–400 °C (Fig. 2). A slightly lower growth rate (0.22 Å (cycle)$^{-1}$) was observed at 350 °C. At still lower temperatures the growth rate slowly decreased down to 0.08 Å (cycle)$^{-1}$, which was the value obtained at 275 °C. When the deposition temperature was increased above the plateau region up to 500 °C, the growth rate increased significantly to 0.41 Å (cycle)$^{-1}$, but at the same time the thickness profile at the leading edge of the films increased, indicating precursor decomposition. This is a typical phenomenon in the ALE deposition of oxides, although the heavier Group 3 β-diketonates (*e.g.* the rare earths) appear to produce uniform films also above the ALE window.[69,70] Likewise, uniform ZrO_2 films can be deposited by CVD from $Zr(thd)_4$ at 540–575 °C,[50] which is about 150–200 °C higher than the temperature used in the present ALE depositions.

ZrO_2 thin films deposited from $Cp_2Zr(CH_3)_2/O_3$ were uniform when prepared below 365 °C and a constant growth rate of 0.55 Å (cycle)$^{-1}$ was obtained in the region of 310–365 °C (Fig. 2). Below this, the deposition rate decreased to 0.22 Å (cycle)$^{-1}$, obtained at 250 °C. The maximum growth rate of 1.04 Å (cycle)$^{-1}$ was reached at 500 °C. Unlike the other two precursors, where the growth rate increases only slightly above the constant growth rate plateau, there was for the $Cp_2Zr(CH_3)_2/O_3$ process a sudden increase in the growth rate and thickness profile above 365 °C. For comparison, it can be noted that CVD depositions from $Cp_2Zr(CH_3)_2$ have been performed at 400–550 °C, although it has also been possible to carry out depositions at 300 °C in the presence of O_2/H_2O producing ZrO_2 films with, however, 5% carbon.[57]

ZrO_2 films were prepared from Cp_2ZrCl_2/O_3 in a similar manner. Below 400 °C the deposited films were uniform with only a minor thickness profile within the substrate length of 10 cm. A constant growth rate of 0.53 Å (cycle)$^{-1}$ was observed at 275–350 °C (Fig. 2). Above 350 °C the growth rate slowly increased with increasing temperature. Maximum growth rate of 0.64 Å (cycle)$^{-1}$ was obtained at 500 °C, measured 2 cm from the leading edge of the substrate. Compared to the depositions performed on high surface area silica,[47] where uniform samples were obtained at 300–350 °C, controlled thin film deposition appears to occur here over a slightly wider temperature region. This may be due to different experimental conditions, mainly pressure.

Existence of an ALE window, *i.e.* temperature region where the deposition is surface-controlled, was checked for each process by increasing the reactive pulsing times (Fig. 3). Both $Zr(thd)_4/O_3$ and Cp_2ZrCl_2/O_3 processes produced uniform films when precursor pulsing times were 0.8–3.0 s at 375 and 300 °C, respectively. A slightly longer pulsing time (1.0 s) was needed to obtain a complete surface saturation in the $Cp_2Zr(CH_3)_2/O_3$ process at 350 °C. Regardless of the process used, ozone pulse times of 1.5–3.5 s resulted in uniform films. Another characteristic and beneficial feature of an ALE-type process is the facile control of the film thickness by the number of deposition cycles. A linear dependency was obtained when ZrO_2 was deposited by optimised pulsing parameters (Fig. 4).

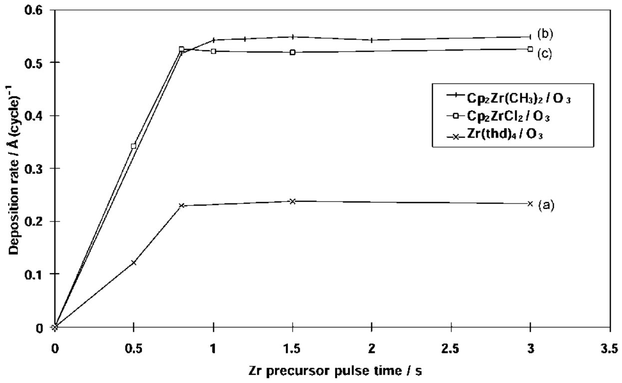

Fig. 3 Deposition rates of ZrO_2 thin films as a function of Zr precursor pulsing times. Deposition temperatures were 375 °C ($Zr(thd)_4/O_3$) (a), 350 °C ($Cp_2Zr(CH_3)_2/O_3$) (b) and 300 °C (Cp_2ZrCl_2/O_3) (c). Pulsing time was 2.0 s for O_3 and purging times 1.5–2.0 s depending on the Zr precursor pulsing time.

Characterisation of the ZrO_2 films

ZrO_2 films from the $Zr(thd)_4/O_3$ process were only slightly crystalline regardless of the deposition temperature and the substrate used. Broad diffraction peaks (FWHM values 0.5–0.65° 2θ of M(002) peak on Si(100) substrate) also indicated low crystallinity, which together with the several structural polymorphs of ZrO_2 complicates an interpretation of the diffraction diagrams. Thus, a straightforward identification of all peaks was not possible because of the monoclinic (200) and orthorhombic (O) (002) reflections overlapping at a *d*-value of 2.62 Å. The strongest peak, albeit still low in intensity, was identified as belonging either to the M(200) or O(002) reflection and was observed in films deposited at 300–500 °C (Fig. 5a, d). Very low intensity M(−221) and M(−203) reflections were also observed in all samples. Regardless of the deposition temperature, a reflection at $d = 2.96$ Å, identified as O(111), was also observed. The intensities of the M(−111) and O(111) reflections increased only slightly when the deposition temperature was increased (Fig. 6a).

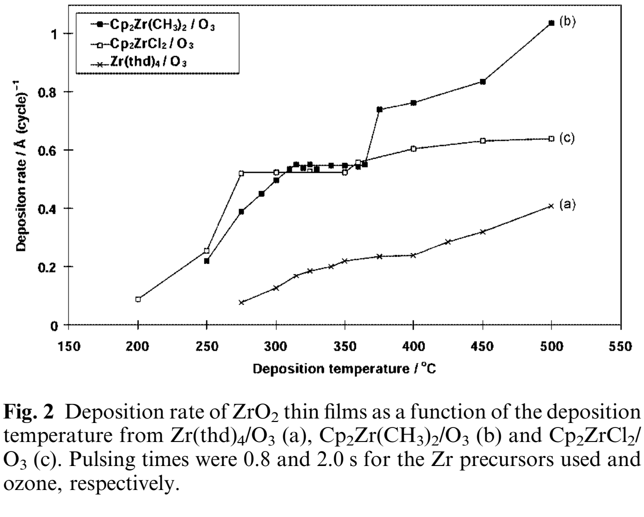

Fig. 2 Deposition rate of ZrO_2 thin films as a function of the deposition temperature from $Zr(thd)_4/O_3$ (a), $Cp_2Zr(CH_3)_2/O_3$ (b) and Cp_2ZrCl_2/O_3 (c). Pulsing times were 0.8 and 2.0 s for the Zr precursors used and ozone, respectively.

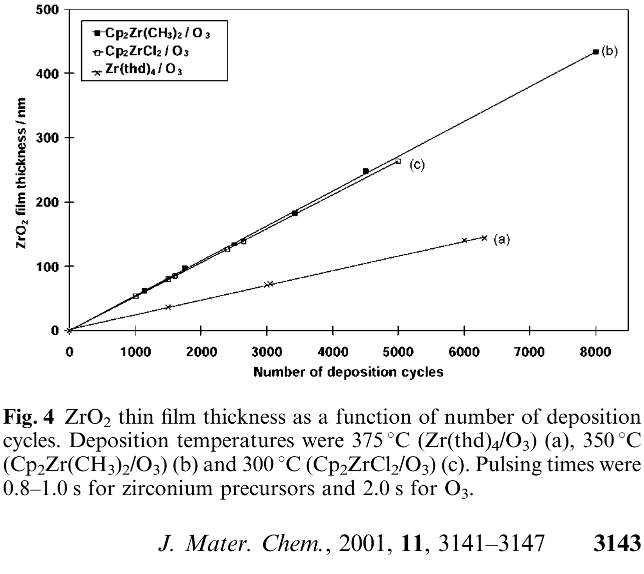

Fig. 4 ZrO_2 thin film thickness as a function of number of deposition cycles. Deposition temperatures were 375 °C ($Zr(thd)_4/O_3$) (a), 350 °C ($Cp_2Zr(CH_3)_2/O_3$) (b) and 300 °C (Cp_2ZrCl_2/O_3) (c). Pulsing times were 0.8–1.0 s for zirconium precursors and 2.0 s for O_3.

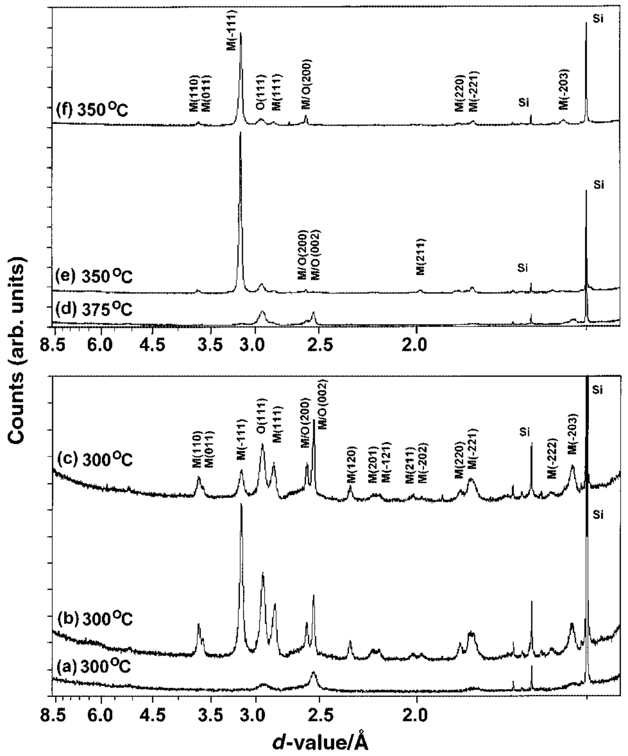

Fig. 5 X-Ray diffraction patterns of the ZrO_2 films deposited from $Zr(thd)_4/O_3$ (a, d), $Cp_2Zr(CH_3)_2/O_3$ (b, e) and Cp_2ZrCl_2/O_3 (c, f). Si(100) was used as a substrate. Diffraction peaks were identified according to JCPDS reference values (cards 37-1413 and 37-1484 for orthorhombic (O) and monoclinic (M) phases, respectively). M/O(002) notation corresponds to overlapping M(200) and O(002) reflections.

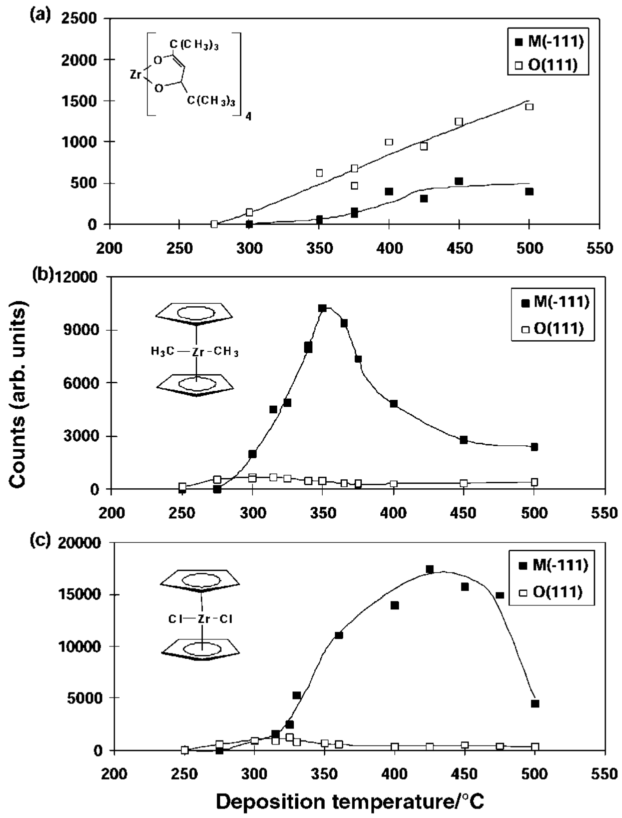

Fig. 6 XRD peak intensities of monoclinic (−111) and orthorhombic (111) reflections of the deposited ZrO_2 thin films onto Si(100). Depositions were carried out from $Zr(thd)_4/O_3$ (a), $Cp_2Zr(CH_3)_2/O_3$ (b) and Cp_2ZrCl_2/O_3 (c). Si(100) was used as substrate. Film thicknesses were 130–170 nm.

Depositions carried out by the $Cp_2Zr(CH_3)_2/O_3$ process resulted in weakly crystalline ZrO_2 films when deposited below 300 °C; the M(−111) reflection was barely observable. M(−111) became the most intense reflection in films deposited at 300 °C, but several other peaks were identified as well, when films were deposited onto Si(100) (Fig. 5b). At higher deposition temperatures, the intensity of the M(−111) orientation increased rapidly, exhibiting a maximum value at 350 °C (Fig. 6b). The weaker O(111) reflection was observed to be present in the whole temperature range of 250–500 °C. Generally, the film crystallinity decreased when deposition temperature was increased above 350 °C, however, FWHM value of the M(111) reflection was in the range of 0.25–0.30° 2θ, and a certain minimum value was seen in films deposited at 350 °C.

The third process, *i.e.* that based on Cp_2ZrCl_2/O_3, produced slightly crystalline ZrO_2 with monoclinic and orthorhombic phases at lower temperatures (250–300 °C). By increasing the deposition temperature the crystallinity of the films deposited onto Si(100) could be enhanced, thus producing almost completely (−111) oriented monoclinic ZrO_2 films above 350 °C (Figs. 5c, f and 6c). The O(111) reflection was also observed in the crystalline films (275–500 °C) being strongest in films deposited around 300 °C (Fig. 6c). Maximum crystallinity was observed in films deposited around 425–450 °C. Measured M(111) peak widths expressed in terms of FWHM values were in the range of 0.25–0.35° 2θ, exact values depending on the deposition temperature.

In the present study, in addition to the monoclinic phase an orthorhombic phase was also observed regardless of the zirconium precursor used. Typically while the tetragonal and monoclinic phases have been observed in CVD-deposited thin films, the metastable orthorhombic phase of ZrO_2 has been only seldom reported in thin films[71] and in bulk material only when the grain size is very fine (below 30 nm).[72] Recently, ALE-deposited nanocrystalline films from various precursors have been identified as being either monoclinic or metastable tetragonal ZrO_2, but not orthorhombic.[43]

Stoichiometry and impurity levels of ZrO_2 films were examined by TOF-ERDA from films deposited onto Si(100) substrates within the ALE window of each process. The zirconium to oxygen ratio was nearly stoichiometric (Table 1) but a slight excess of oxygen of the order of a few percent was observed regardless of the precursor used. Carbon and hydrogen impurity levels were quite low in each case. Fluorine content was around 0.1 atom% regardless of the precursor used. This is probably a contamination caused by the materials used in the reactor set-up with Teflon gaskets and perfluorinated vacuum greases. In addition, possible chlorine impurities

Table 1 Stoichiometry and impurity levels of the ZrO_2 thin films deposited from different precursors onto Si(100) substrates analysed by TOF-ERDA

Process	Deposition temperature/°C	Zr : O ratio	Carbon/atom%	Hydrogen/atom%	Fluorine/atom%
$Zr(thd)_4/O_3$	375	0.46 ± 0.03	0.20	0.3	< 0.1
Cp_2ZrCl_2/O_3	300	0.47 ± 0.03	0.54	0.5	0.1
$Cp_2Zr(CH_3)_2/O_3$	315	0.48 ± 0.03	0.16	0.1	0.1

in ZrO_2 films originating from Cp_2ZrCl_2/O_3 were studied by XRF. In earlier studies, it has been observed that at lower temperatures, ALE deposition of oxide materials from chlorine-containing precursors may lead to Cl impurities being incorporated into the deposited films. For example, chlorine contaminations in other Group 4 oxide films, namely TiO_2 and HfO_2, have been observed when deposited from $TiCl_4/H_2O$ [73] and $HfCl_2/H_2O$,[74] respectively. However, no similar data are available in the literature for low temperature deposition from $ZrCl_4/H_2O$ precursors. We found that chlorine from Cp_2ZrCl_2/O_3 was not incorporated into the ZrO_2 films when they were deposited above 275 °C. However, below 275 °C, 0.1–0.3 wt% Cl was observed depending on the deposition temperature. According to TOF-ERDA results, chlorine content was below the detection limit (0.07 atom%) when ZrO_2 films were deposited at 300 °C or above.

ZrO_2 film surface morphology was analysed by AFM as a function of the deposition temperature and film thickness (Fig. 7). In the first set of samples, the thickness of the films was kept at 100–140 nm while the deposition temperature was varied. When the $Zr(thd)_4/O_3$ process was used, the ZrO_2 film roughness increased from 1.7 to 5.3 nm with increasing deposition temperature from 315 to 450 °C. On the other hand, the roughness of ZrO_2 films was quite constant, 2.8–3.3 nm, when deposited by the $Cp_2Zr(CH_3)_2/O_3$ process at 275–400 °C. However, the roughness increased when the deposition temperature was increased above 400 °C. The third process, *i.e.* that based on Cp_2ZrCl_2/O_3, produced ZrO_2 films with roughness of 3.0–5.0 nm when deposited at 275–450 °C. A second set of samples with different thicknesses of 40–400 nm was deposited by the $Zr(thd)_4/O_3$ process at 375 °C, by $Cp_2Zr(CH_3)_2/O_3$ at 350 °C and by Cp_2ZrCl_2/O_3 at 300 °C and an increase in the roughness was observed regardless of the process used (Fig. 8). However, compared to previous ZrO_2 depositions by ALE using $ZrCl_4$ and H_2O as precursors,[42] where agglomeration of the films was observed, increases in roughness and grain size were much smaller. This indicates, as expected, that ALE deposition of ZrO_2 using β-diketonate or organometallic precursors proceeds by a different mechanism from that observed with $ZrCl_4$ as a precursor.

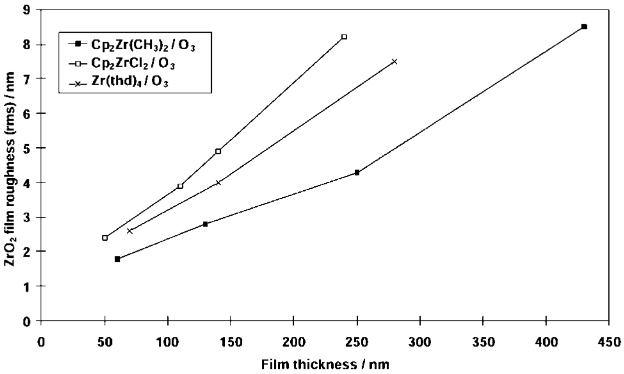

Fig. 8 Roughness of the ZrO_2 films on Si(100) substrates as a function of the film thickness measured by AFM. The film deposition temperature was 375 °C for $Zr(thd)_4/O_3$, 350 °C for $Cp_2Zr(CH_3)_2/O_3$ and 300 °C for Cp_2ZrCl_2/O_3.

Conclusions

ALE deposition of ZrO_2 thin films was successfully performed from organometallic and β-diketonate type precursors using ozone as oxidizer. A surface-controlled deposition region (ALE window) was observed for the $Zr(thd)_4/O_3$ process at 375–400 °C and for $Cp_2Zr(CH_3)_2/O_3$ at 310–365 °C while this was at 275–350 °C for the Cp_2ZrCl_2/O_3 system. Constant growth rates of 0.24, 0.55 and 0.53 Å $(cycle)^{-1}$, respectively, were measured for these processes. Saturation of growth rate as a function of reactive pulses together with a linear dependency of film thickness as a function of the number of deposition cycles indicate a controlled ALE-type growth which enables a straightforward control of the deposition process.

The crystallinity of the ZrO_2 films depends on the precursors used as well as on the deposition temperature. Low

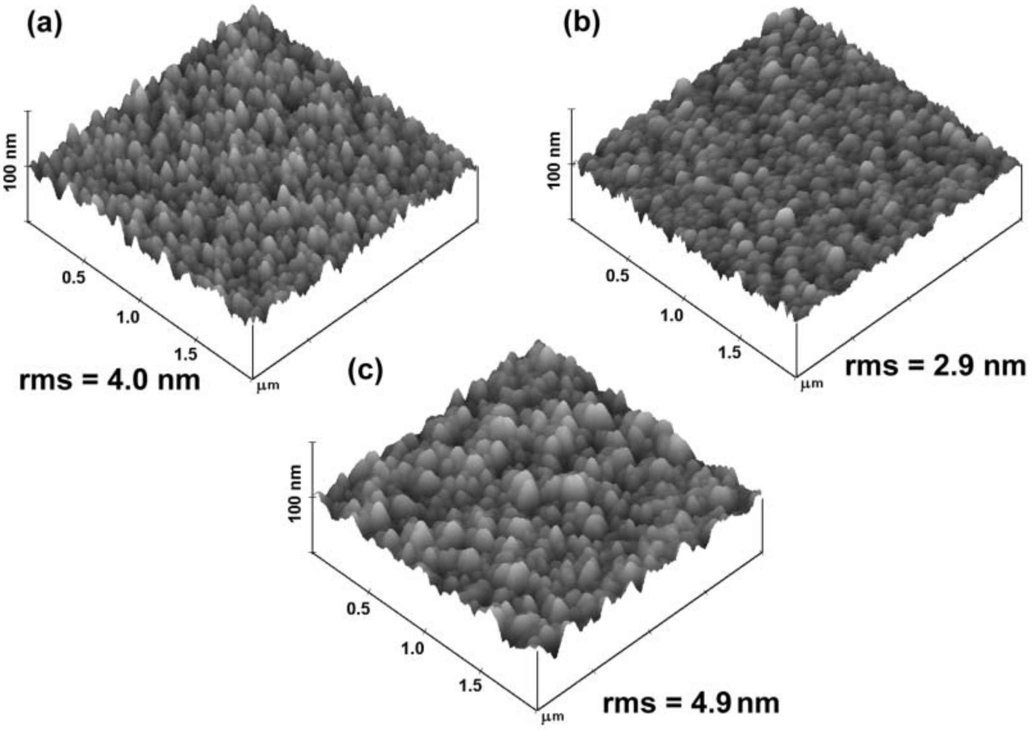

Fig. 7 AFM images of ZrO_2 films deposited onto Si(100) substrates (a) by $Zr(thd)_4/O_3$ at 375 °C, (b) by $Cp_2Zr(CH_3)_2/O_3$ at 350 °C and (c) by Cp_2ZrCl_2/O_3 at 300 °C. Film thickness was 130–140 nm. Depth scale: 50 nm from black to white.

temperature depositions resulted in films with low crystallinity containing both the orthorhombic and monoclinic phases. For each precursor, as expected, the crystallinity increased with increasing deposition temperature. The $Zr(thd)_4/O_3$ process produced films with the lowest crystallinity. The orientation and crystallinity of the films deposited from Cp_2ZrCl_2/O_3 and $Cp_2Zr(CH_3)_2/O_3$ were quite similar. However, ZrO_2 films deposited from $Cp_2Zr(CH_3)_2/O_3$ exhibited maximum crystallinity at a 75–100 °C lower temperature than films deposited by the Cp_2ZrCl_2/O_3 process. In the latter case, maximum values were obtained above the ALE window, whereas films of highest crystallinity were obtained from the $Cp_2Zr(CH_3)_2/O_3$ precursors when deposited within the ALE window.

AFM results indicate that the ZrO_2 film roughness was dependent on the deposition temperature when deposited by the $Zr(thd)_4/O_3$ process. The rms roughness of 100–140 nm thick films remained quite constant (2.8–4 nm) when $Cp_2Zr(CH_3)_2$ or Cp_2ZrCl_2 were used as zirconium precursors. An increase in roughness as function of film thickness was observed regardless of the process used.

According to TOF-ERDA results, nearly stoichiometric films were obtained in all cases. Impurity levels were dependent on the selected precursor but they were quite low in each case, *i.e.* 0.1–0.5 and 0.2–0.5 atom% for H and C, respectively. ZrO_2 films deposited from Cp_2ZrCl_2/O_3 below the ALE window contained chlorine as an impurity. According to XRF data the chlorine content decreased with increasing temperature being 0.3 wt% at 200 °C and 0.1 wt% at 275 °C. At 300 °C chlorine was no longer detected by TOF-ERD analysis.

The present study clearly demonstrates the suitability of novel precursors, previously used only in CVD, also for ALE depositions of ZrO_2 thin films. For future applications, volatile organometallic precursors seem to outperform the conventional volatile β-diketonate complexes. Although in the case of zirconium the growth rates obtained with Cp_2ZrCl_2/O_3 and $Cp_2Zr(CH_3)_2/O_3$ were comparable to the conventional $ZrCl_4/H_2O$ process, the better crystallinity may be advantageous in some applications. The level of chlorine and other residues remaining in the films depend on the selected process and its parameters but the impurity level was generally low. Thus, from the wide range of ALE processes now available for the processing of ZrO_2 thin films it is possible to choose the optimum one for ZrO_2-containing thin film materials depending on the application aimed at.

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