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Cerium dioxide buffer layers at low temperature by atomic layer deposition

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Thin films of cerium dioxide were deposited by atomic layer deposition (ALD). Temperature ranges studied in detail were 175–375 °C and 225–350 °C for the Ce(thd)$_4$ and Ce(thd)$_3$phen (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate, phen = 1,10-phenanthroline) precursors, respectively. Ozone was used in both cases as oxygen source. Thickness, crystallinity and morphology of the CeO$_2$ films were determined by UV-VIS spectroscopic, XRD and AFM measurements, respectively. Narrow ALD windows, *i.e.* temperature ranges with constant growth rate, were observed at temperatures 175–250 °C for Ce(thd)$_4$ and 225–275 °C for Ce(thd)$_3$phen. The growth rates of CeO$_2$ inside the ALD windows were 0.32 Å (cycle)$^{-1}$ and 0.42 Å (cycle)$^{-1}$ for Ce(thd)$_4$ and Ce(thd)$_3$phen, respectively. CeO$_2$ films grown on soda lime glass and Si(100) were polycrystalline and slightly oriented with the (200) and (111) peaks as the strongest reflections. TOF-ERD analysis of the Ce : O ratio showed that the films were nearly stoichiometric but that they contained hydrogen (7–10 atom%), as well as some carbon and fluorine, as impurities.

1. Introduction

Cerium dioxide has a number of attractive properties for applications in electronics and optics such as durability and high refractive index as well as high transparency in the visible and near-infrared region.[1,2] Applications currently under development include thin film optical waveguides[1] and solid oxide fuel cells (SOFC)[3] where about 10% of the cerium is substituted by gadolinium. Other applications of CeO$_2$ stem from its advantageous properties, too. The large relative permittivity ($\varepsilon_r = 26$) makes CeO$_2$ a possible choice for high-ε_r (high-k) dielectric gate material in ULSI technology.[4] CeO$_2$ has also been used in resistive type oxygen gas sensors for combustion gases[5] as well as in H$_2$S sensors.[6]

However, probably the highest application potential of cerium dioxide thin films lies in their use as buffer layers for high-temperature superconductors[7] and ferroelectric Pb(Zr,Ti)O$_3$ (PZT)[8] films deposited on silicon or sapphire. Buffer layers are needed in order to avoid chemical reactions at the film/substrate interface.[7,9] CeO$_2$ has a fluorite structure with lattice parameter $a = 5.41$ Å which provides an excellent match with Si ($a = 5.43$ Å) and a rather good one with R-sapphire ($a = 5.12$ Å).[9,10] YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) has an orthorombic structure with smaller lattice parameters ($a = 3.82$ Å; $b = 3.89$ Å) but by rotating 45° in the CeO$_2$ basal plane the lattice mismatch between YBCO and CeO$_2$ will be less than 1%.[7] As regards PZT, this can be epitaxially grown on CeO$_2$(111)/Si(111) substrates where the CeO$_2$ layer is effective in suppressing interdiffusion between the PZT film and Si.[8] In addition to the buffer layers, CeO$_2$ can be used as a compatible intermediate material in the fabrication of superconductor–insulator–superconductor (SIS) multilayer structures.[11] Further more, cerium is one of the constituents of the Nd–Ce–Cu–O superconductor.[12]

Cerium dioxide thin films have been deposited by many different techniques. Physical methods include electron beam evaporation (EBE),[13] sputtering,[14] laser ablation[15–17] and molecular beam epitaxy (MBE).[18] Several chemical methods have been applied as well, among them sol–gel techniques,[19] catalyst-enhanced chemical vapour deposition (CECVD),[20] metalorganic CVD (MOCVD),[21–24] aerosol-assisted CVD,[25] plasma-enhanced CVD (PECVD)[26] and atomic layer deposition (ALD).[27] In CVD methods the precursors most often used have been β-diketonates and their derivatives. Especially tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium, *i.e.* Ce(thd)$_4$, has frequently been employed.[9,21,22,27,28] Ce(thd)$_4$ is one of the best-characterized cerium precursors available and its crystal structure and mass spectra are known.[29] The deposition temperatures in the CVD methods have been in the range 300–900 °C,[21,22] and as low as 250 °C in the PECVD method.[20]

ALD, also referred to as Atomic Layer Epitaxy (ALE) and Atomic Layer CVD (ALCVD), can be considered as an advanced modification of the CVD method.[30,31] In ALD the thin film growth is self limiting, and the precursor pulses are alternately introduced onto the substrates to avoid gas phase reactions. The substrate area is purged with inert gas between the precursor pulses. ALD can also be used to deposit conformal and uniform thin films in a reproducible way.[32] Thickness control by the number of deposition cycles is accurate and easy when the deposition is carried out within the 'ALD window', *i.e.* the temperature range where a constant growth rate is achieved by a self limiting growth mechanism.[30,31] Previously, ALD has been used to deposit CeO$_2$ at relatively high temperatures (350–600 °C) from Ce(thd)$_4$ and ozone precursors and the results were reported in a brief conference paper only.[27] In addition, both Ce(thd)$_4$ and Ce(thd)$_3$phen have been used as cerium precursors in an ALD process for doping of electroluminescent SrS:Ce thin films.[28]

2. Experimental

As part of our ongoing investigation into superconducting thin films by ALD,[10] we have also studied the deposition of binary and complex oxides, such as MgO,[33,34] yttria-stabilized ZrO$_2$ (YSZ),[35] LaAlO$_3$,[36] LaGaO$_3$[37] and SrTiO$_3$[38] for use as possible substrate and buffer materials. Here we report the deposition of cerium dioxide at relatively low temperatures, *i.e.* even below 250 °C, using (1,10-phenanthroline)tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium (Ce(thd)$_3$phen) and Ce(thd)$_4$ as precursors.

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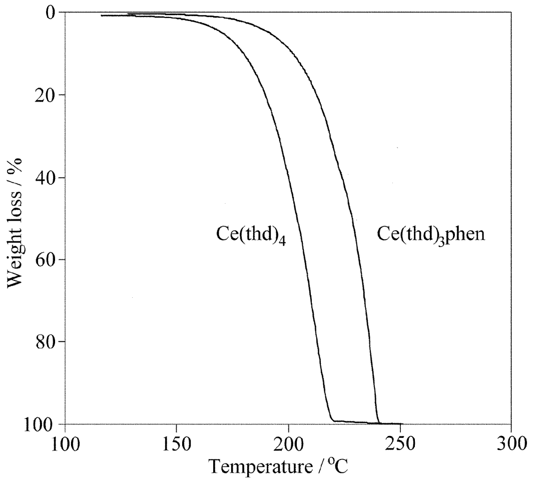

Fig. 1 TG/DTA curves of $Ce(thd)_4$ and $Ce(thd)_3phen$. Measurements were carried out in a dynamic nitrogen flow under a reduced pressure (2 mbar).

$Ce(thd)_4$ and $Ce(thd)_3phen$ were synthesized according to published methods[28,29,39] and purified by sublimation. Simultaneous TG/DTA measurements were used to verify the purity of the precursors and to establish appropriate evaporation temperatures. The measurements were done under vacuum in a Seiko Instruments SSC/5200 thermobalance. Furthermore, in order to simulate the ALD growth conditions, the TG/DTA measurements were performed in a dynamic nitrogen atmosphere under a reduced pressure (2 mbar).

Cerium dioxide thin films were deposited in an F-120 ALD reactor (ASM Microchemistry Ltd., Espoo, Finland). Based on the TG/DTA data (Fig. 1), evaporation temperatures for the precursors $Ce(thd)_4$ and $Ce(thd)_3phen$ were chosen as 140 °C and 175–180 °C, respectively. Cerium precursors and ozone were transported onto the substrates with nitrogen carrier gas ($>99.999\%$). N_2 was also used to purge the substrate area between the precursor pulses. N_2 was prepared in a nitrogen generator (Nitrox UHPN 3000-1). Ozone (10%) was employed for oxidation and was produced from oxygen ($>99.999\%$) in an ozone generator (Fischer Model 502). Pulse times for $Ce(thd)_4$, $Ce(thd)_3phen$ and ozone were varied between 1.0–1.5 s, 0.5–3.75 s and 0.5–5.0 s, respectively. The purge time for nitrogen was 1.5–2.5 s.

Soda lime glass and silicon(100) (Okmetic, Espoo, Finland) were used as substrates (5×10 cm^2). Silicon substrates were ultrasonically cleaned without removing the native oxide. The deposition temperature ranges studied were 175–375 °C and 225–350 °C for $Ce(thd)_4$ and $Ce(thd)_3phen$, respectively. The pressure in the reactor was about 2 mbar.

Thickness, structure and morphology of the CeO_2 films obtained were determined *ex situ*. Thickness was determined by a spectrophotometric method.[40] Transmittance spectra were recorded in the wavelength region 370–1100 nm for soda lime glass substrates and reflectance spectra in the region 190–1100 nm for the Si(100) substrates. The spectra were fitted to obtain geometric thickness. Measurements were performed in a Hitachi U-2000 spectrophotometer. A Philips MPD 1880 powder diffractometer with Cu $K\alpha$ radiation was used for the X-ray diffraction studies to determine crystal structure and crystallite orientation. Atomic force microscopy (AFM) measurements were routinely carried out to determine the surface morphologies of the films. All AFM images were recorded with a Nanoscope III Multimode SPM instrument operating in tapping mode with a scanning rate 1–2 Hz.

Stoichiometry and impurities of the CeO_2 thin films were measured by time-of-flight elastic recoil detection analysis (TOF-ERDA) at the Accelerator Laboratory of the University of Helsinki.[41] In these measurements, an EGP-10-II 5 MV tandem accelerator was used to obtain a 53 MeV $^{127}I^{10+}$ ion beam, which was projected into the sample generating forward recoiling sample atoms. Both the velocity and the energy of the recoiling atoms were measured using timing gates and a charged particle detector, respectively, which made it possible to separate different masses. The sample surface was tilted 20° and the recoils were determined at 40° with respect to the incoming beam. The given concentration results were obtained directly from total recoil yields using Rutherford scattering cross sections. Due to the small film thicknesses some hydrogen and carbon loss was observed during the TOF-ERD measurements caused by heavy ion irradiation. Together with indistinguishable surface and interface impurities this resulted in quite high uncertainties in the hydrogen and carbon concentrations. FTIR was used for qualitative analysis of impurities in the thin films deposited onto the Si(100) substrates. Silicon substrate peaks were subtracted from the raw transmittance spectra obtained. FTIR spectra were recorded with a Nicolet Magna-IR 750 spectrometer.

3. Results and discussion

As a first step, the influence of $Ce(thd)_3phen$ and ozone pulse times was examined at 275 °C with focus on the silicon substrate. The duration of the $Ce(thd)_3phen$ pulse was varied between 0–3.75 s while the ozone pulse time was held constant at 2.5 s. Judging from Fig. 2 it was obvious that in the case of silicon substrates much shorter pulse times were sufficient to achieve constant growth rate. In order to keep the precursor consumption at a relatively low level the pulse time was chosen as low as 1.0 s. However, with soda lime glass substrates this was obviously somewhat too short a pulsing time because the saturative (constant growth) region was not reached. Consequently the growth rates obtained on soda lime glass were not completely reproducible and therefore the main emphasis was focused on the Si(100) substrates. It can be noted that the small increase in growth rates obtained with longer pulse times and with both substrates (Fig. 2) is due to partial thermal decomposition of the precursor, which leads to the formation of more reactive and less bulky species such as $Ce(thd)_3$ and $Ce(thd)_2$ as verified by mass spectrometric studies on $Ce(thd)_4$.[29]

The duration of the ozone pulse was varied between 0.5–5.0 s while the Ce-precursor pulse time was kept constant at 1.0 s and the substrate temperature at 275 °C. It was observed that at least a 2.0 s pulse time is needed under these experimental conditions to achieve saturated surface reaction. For ozone, a pulse time of 2.5 s was considered sufficient and it was kept as such in all growth experiments.

Secondly, the growth rates were determined as a function of the substrate temperature. Precursor pulse times and purging

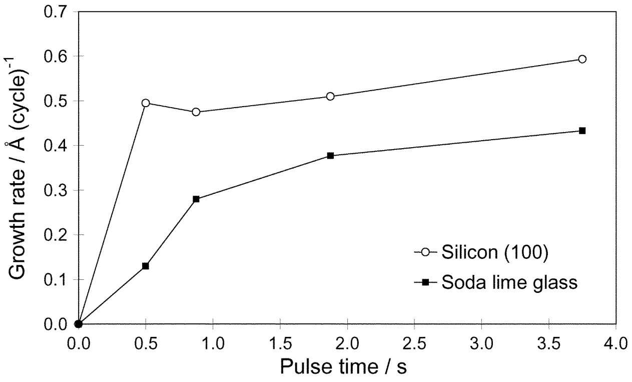

Fig. 2 The influence of $Ce(thd)_3phen$ pulse times on the growth rate of CeO_2 at 275 °C. Ozone pulse duration was 2.5 s. Thickness was measured at 4 cm from the leading edge of the substrates.

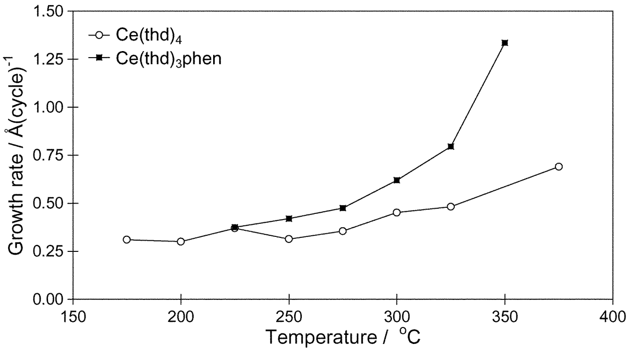

Fig. 3 The growth rate of CeO_2 from $Ce(thd)_4$ and $Ce(thd)_3phen$ on silicon(100) substrate as a function of the substrate temperature.

times were long enough to obtain surface saturation. The temperature ranges studied were 175–375 °C and 225–350 °C for $Ce(thd)_4$ and $Ce(thd)_3phen$, respectively. Narrow ALD windows were found at 175–250 °C for $Ce(thd)_4$ and 225–275 °C for $Ce(thd)_3phen$. It may be noted that the differences in the growth rates were quite small in these temperature regions. Above the ALD window, the growth rate increased in both cases (Fig. 3), which was most likely due to the thermal decomposition of the Ce-precursor. However, at 250 °C the decomposition rate of the precursor was almost negligible, which was verified by pulsing solely $Ce(thd)_3phen$. As seen in Fig. 3, the increase in growth rate above the ALD window ($>$275 °C) was more pronounced with $Ce(thd)_3phen$ than with $Ce(thd)_4$. This indicates that $Ce(thd)_4$ is thermally more stable than $Ce(thd)_3phen$ under similar experimental conditions. Results from our earlier TG/DTA studies are in agreement with this observation.[27–29]

After the required pulse lengths and the temperature limits had been determined, additional depositions were carried out within the ALD window. The growth rates were determined by depositing CeO_2 thin films of different thicknesses, *e.g.* by altering the number of cycles (Fig. 4). A linear relationship was observed between the number of deposition cycles and the film thickness, as should be the case in an ideal ALD process. The growth rate of CeO_2 with $Ce(thd)_3phen$ was 0.42 Å/cycle (at 250 °C), while with $Ce(thd)_4$ it was about 25% lower (0.32 Å/cycle).

The films on silicon substrates were very uniform (Fig. 5), but on soda lime glass a clear thickness profile was observed as films were getting thinner towards the tailing edge. This was an expected phenomenon, because the pulsing times used, as discussed earlier in the text, were somewhat too short in this case (*cf.* Fig. 2).

The crystallinity and orientation of the crystallites were examined by X-ray diffraction. XRD measurements showed that, regardless of the precursor, the deposited CeO_2 films on Si(100) were polycrystalline in the temperature range studied (Fig. 6). The crystallinity increased as the temperature was raised, as judged from the XRD peak intensities and their FWHM values. In the case of depositions with $Ce(thd)_3phen$ at temperatures 250–325 °C, the (200) reflection was slightly more intense than the others, *viz.* (111), (220) and (311). At lower temperatures, on the other hand, the (111) reflection was the strongest but the difference was small. With $Ce(thd)_4$ precursor at 200 °C, the (111) peak was also the strongest one by only a narrow margin before the (200) reflection. When the substrate temperature was increased, the (200) reflection became more dominant but films were still polycrystalline. Previously, it has been observed that CeO_2 films grown by ALD at higher temperatures ($>$375 °C) are polycrystalline with (111) or (110) reflections dominating depending on the deposition temperature.[27] For CeO_2 films grown by laser ablation the (111) reflection has been reported to be the strongest one.[17]

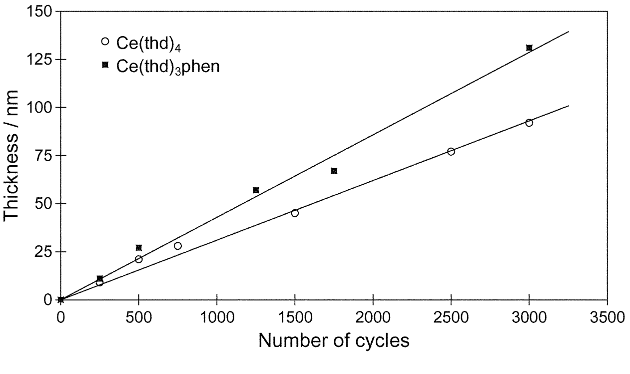

Fig. 4 CeO_2 film thickness on Si(100) as a function of the number of deposition cycles. Depositions with $Ce(thd)_3phen$ were carried out at 250 °C and those with $Ce(thd)_4$ at 200 °C.

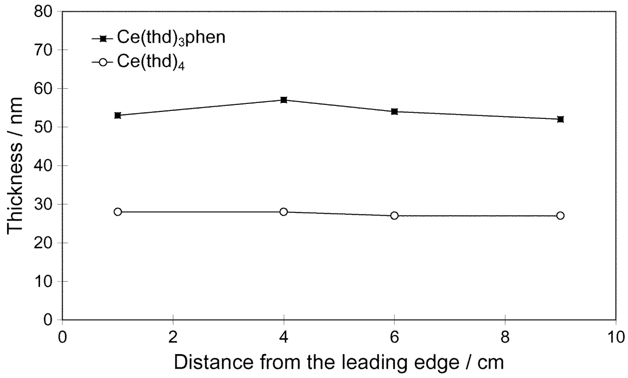

Fig. 5 Thickness uniformity of the CeO_2 films on silicon deposited onto Si(100) at 250 °C and 200 °C using $Ce(thd)_3phen$ and $Ce(thd)_4$, respectively.

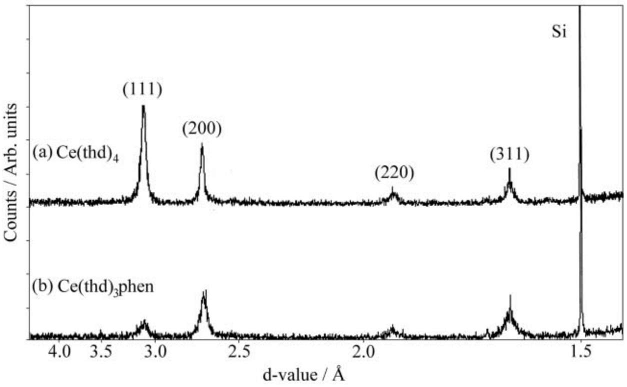

Fig. 6 XRD patterns of CeO_2 thin films deposited onto Si(100) (a) at 200 °C from $Ce(thd)_4/O_3$ and (b) at 250 °C from $Ce(thd)_3phen/O_3$. Film thicknesses were (a) 90 nm and (b) 150 nm.

Atomic force microscopy (AFM) was used to study the morphology of the CeO_2 films deposited on Si(100). The films were smooth and uniform regardless of the precursor used (Fig. 7). Rms values for 50–75 nm thick CeO_2 films deposited within the ALD window varied between 0.6 and 1.2 nm. The roughness of the CeO_2 films was found to increase slightly when the deposition temperature was raised above the ALD window.

TOF-ERD analyses were carried out to determine the stoichiometry and the impurity levels of the CeO_2 thin films (Table 1). The analysed CeO_2 thin films were deposited onto the Si(100) substrates at temperatures within the ALD window. The Ce : O ratios of the films studied were around 0.46, which means that the films must have oxygen also as an impurity, because otherwise the Ce : O ratio cannot lie under the stoichiometric value of 0.50. Other major impurities were

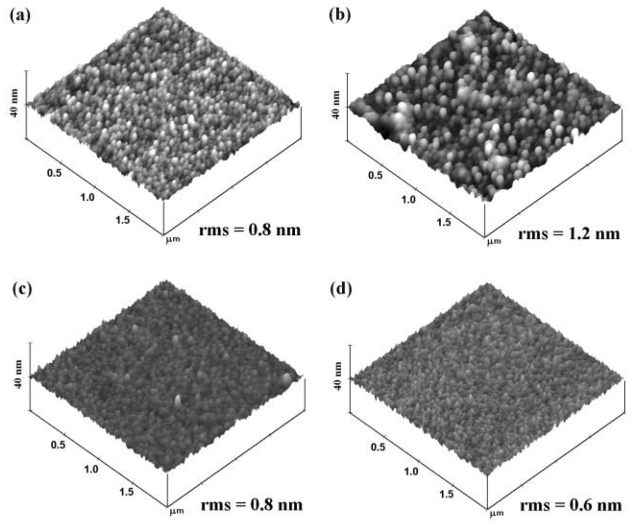

Fig. 7 AFM images of the CeO_2 films deposited onto Si(100) substrates from $Ce(thd)_3phen$ or $Ce(thd)_4$ and ozone at different temperatures: (a) $Ce(thd)_3phen/O_3$, 225 °C, (b) $Ce(thd)_3phen/O_3$, 275 °C, (c) $Ce(thd)_4/O_3$, 200 °C and (d) $Ce(thd)_4/O_3$, 225 °C. Film thicknesses were 75 nm for (a) and (c) and 50 nm for (b) and (d).

hydrogen, carbon and fluorine. In addition, CeO_2 thin films deposited from $Ce(thd)_3phen/O_3$ contained also 0.4 atom% sodium, which was most probably originating from NaOH used in the synthesis.[39] Also the carbon level was highest in the CeO_2 sample deposited from $Ce(thd)_3phen/O_3$. Samples contained 4 atom% and 0.8–1.1 atom% carbon, when deposited from $Ce(thd)_3phen/O_3$ and $Ce(thd)_4/O_3$, respectively. Hydrogen levels in all samples were quite high, *viz.* between 7 and 10 atom%, and they probably were distributed evenly throughout the films. Previously, in the case of Y_2O_3 deposited from $Y(thd)_3$ and ozone by ALD, it has been observed that at low deposition temperatures the carbon and hydrogen impurity levels of the thin films remain high.[42] Fluorine levels detected were between 0.6 and 2.0 atom% and these were most probably originating from the vacuum grease or Teflon gaskets used.[42]

FTIR measurements of CeO_2 films were carried out to determine the type of hydrogen and carbon impurities. Previously, hydroxide and carbonate impurities have been found in the ALD-grown Sc_2O_3, Y_2O_3 and La_2O_3 thin films.[42–44] An IR band around 1500 cm^{-1} typical for a carbonate group was observed in the FTIR spectra of the samples.[43–46] This is presumably due to the carbon-containing precursor. In addition, a broad band between 3000 and 3500 cm^{-1} was observed, most likely originating from the stretching vibrations of water molecules.[45–47]

4. Conclusions

CeO_2 thin films can be deposited at relatively low temperatures or even below 250 °C by using the cerium β-diketonate precursors, *viz.* either $Ce(thd)_4$ or $Ce(thd)_3phen$, together with ozone as an oxidant. The growth rates of CeO_2 were 0.32 Å $(cycle)^{-1}$ and 0.42 Å $(cycle)^{-1}$ from $Ce(thd)_4/O_3$ and $Ce(thd)_3/O_3$, respectively. The growth rates obtained, especially with the $Ce(thd)_3phen$ precursor, were similar to those obtained in the previous ALD experiments at higher temperatures but with a different reactor design.[27] We also observed narrow ALD windows, which provide an easy and accurate way to control the thickness of CeO_2 films. The ALD windows were located at 175–275 °C and 225–275 °C for $Ce(thd)_4$ and $Ce(thd)_3phen$, respectively. The use of $Ce(thd)_4$ appears to be more practical than applying $Ce(thd)_3phen$. This is partly because of the sensitivity of the growth rate to the precursor synthesis, *i.e.* low reproducibility in synthesis. In order to obtain reproducible results, larger precursor batches should be synthesized to guarantee uniformity of the precursor. Unfortunately, $Ce(thd)_3phen$ has been observed to decompose in air within a few weeks,[21] so prolonged storage cannot be applied. Also the ALD window obtained with $Ce(thd)_4$ is wider than that with $Ce(thd)_3phen$. Furthermore, CeO_2 thin films deposited from $Ce(thd)_4/O_3$ contained lower impurity levels of hydrogen, carbon and sodium. It remains to be seen if the *in situ* synthesis of ALD precursors could solve the problem and provide a fresh and reproducible supply of the precursor.[48] This might be, however, difficult in the case of an adducted precursor such as $Ce(thd)_3phen$. On the other hand, the presence of trivalent cerium in the precursor, as in $Ce(thd)_3phen$, does not prevent the conversion of the precursor to CeO_2 provided that a powerful enough oxidant is used. Because of the difficulty in oxidizing trivalent cerium to the tetravalent state, which is seen in the rather high standard potential (Ce^{3+}/Ce^{4+} E° = 1.72 V),[49] ozone was used as oxidizer in the present study. A comparison of the precursors for the ALD growth of CeO_2 is presented in Table 2. Apart from a slightly higher growth rate, the adducted precursor, $Ce(thd)_3phen$, does not appear to bring any advantages compared to the use of $Ce(thd)_4$.

Films were polycrystalline with no orientation dominating (Fig. 6). For superconducting thin film structures the (100) orientation of CeO_2 should be favourable.[10] However, it appears not to be possible to obtain the (100) orientation of CeO_2 films by a direct deposition on Si(100).[16] For this reason different buffer layers between the Si(100) substrate and the CeO_2 layer have been studied, *e.g.* yttria-stabilized ZrO_2 (YSZ),[9,16,22,50–54] $SrTiO_3$ (STO)[9,22] and MgO.[9,22] The most promising material appears to be YSZ, which has been reported to favour the (100) orientation of CeO_2 on YSZ(100)/Si(100).[9,16,22,50–54] Following the successful deposition of ZrO_2 thin films by ALD,[55,56] work on YSZ has been initiated and will be shortly reported.[35]

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Table 2 A comparison of $Ce(thd)_4$ and $Ce(thd)_3phen$ as precursors for the atomic layer deposition of CeO_2 thin films

Property	$Ce(thd)_4$	$Ce(thd)_3phen$
Facile synthesis	yes	yes
Commercially available	yes	no
Stability under prolonged storage	good	poor
In situ synthesis possible	yes	no
Growth temperature (ALD window) using ozone/°C	175–275	225–275
Growth rate at 250 °C/Å $(cycle)^{-1}$	0.32	0.42

Table 1 Stoichiometry and impurity levels of the CeO_2 thin films on Si(100) substrates quantitatively evaluated by TOF-ERDA

Process	Deposition temp./°C	Ce : O ratio	C/atom%	H/atom%	F/atom%	Na/atom%
$Ce(thd)_3phen/O_3$	225	0.46 ± 0.03	4.0 ± 1.0	9.0 ± 2.0	0.6 ± 0.2	0.4 ± 0.2
$Ce(thd)_4/O_3$	200	0.45 ± 0.03	1.1 ± 0.3	10 ± 4.0	1.3 ± 0.3	—
$Ce(thd)_4/O_3$	225	0.47 ± 0.03	0.8 ± 0.2	7.0 ± 2.0	2.0 ± 0.2	—

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