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Processing of Y_2O_3 Thin Films by Atomic Layer Deposition from Cyclopentadienyl-Type Compounds and Water as Precursors

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Y_2O_3 thin films were grown onto Si(100) substrates by atomic layer deposition (ALD) using organometallic precursors, viz. tris(cyclopentadienyl)yttrium, Cp_3Y, and tris(methylcyclopentadienyl)yttrium, $(CpCH_3)_3Y$ (Cp = cyclopentadienyl). Water was used as oxygen source. The deposition rate of yttria in the Cp_3Y/H_2O process slightly increased as a function of the deposition temperature, viz. from 1.5 to 1.8 Å/cycle at temperatures from 250 to 400 °C. With the $(CpCH_3)_3Y/H_2O$ process, a constant growth rate of 1.2−1.3 Å/cycle was achieved in a wide deposition temperature range of 200−400 °C. The ALD-type growth mode was corroborated in both processes at 250 and 300 °C. The deposited films were characterized by XRD, AFM, and TOF-ERDA for crystallinity, morphology, and chemical composition, respectively. Carbon impurity levels for films deposited at 300 °C from $(CpCH_3)Y$ and Cp_3Y were 0.2 and 0.5 atom %, respectively. $(CpCH_3)_3Y/H_2O$-processed film contained 3.1 atom % of hydrogen, whereas the Cp_3Y/H_2O-processed film contained 1.8 atom %. With both processes the smoothest films were obtained at or below the deposition temperature of 250 °C.

Introduction

Y_2O_3 is an attractive material for microelectronic and optoelectronic applications. In microelectronics, it is a promising material for applications due to its permittivity (10−15), wide band gap, high refractive index, high thermal stability, and low lattice-mismatch with Si ($a(Y_2O_3) = 10.60$ Å vs $a(\mathrm{Si}) \times 2 = 10.86$ Å). Thus, Y_2O_3 has been considered as an alternative high permittivity (high-*k*) oxide to replace SiO_2 in complementary metal oxide semiconductor (CMOS) devices.[1] In addition, Y_2O_3 thin films have been employed in various other applications such as optical[2] and protective[3] coatings, buffer layers in ferroelectrics[4] and superconductors,[5] as well as dielectric insulators in electroluminescent devices.[6] Yttrium oxide is also used to produce yttria-stabilized zirconia (YSZ).[7] For other applications, Y_2O_3 is a well-known host matrix for rare-earth ions, e.g. when doped with Eu, yttrium oxide is a red-emitting phosphor.[8]

Y_2O_3 thin films have been mainly deposited by physical vapor deposition methods, but chemical vapor deposition (CVD) methods also have been employed. Thermal CVD processes of Y_2O_3 films have been carried out at relatively high deposition temperatures of 500−800 °C.[9−11] To decrease the deposition temperature to around 350 °C attempts to use plasma[12] or catalyst[13,14] assisted CVD processes have been reported. As a metal precursor tris(2,2,6,6-tetramethyl-3,5-heptanedione) yttrium, (Y(thd)$_3$) has been the most frequently used precursor, but other β-diketonates[15,16] and YCl_3 [17] also have been employed. Weber et al.[18] applied plasma-enhanced CVD for Y_2O_3 thin films using a true organometallic precursor of the cyclopentadienyl-type, namely cyclooctatetraenyl-pentamethylcyclopentadienyl yttrium. The deposition rate was 5−6 times higher than that with the thd precursor.

Atomic layer deposition (ALD), originally known as atomic layer epitaxy, has been frequently employed for the deposition of oxide thin films,[19] including Y_2O_3.[20−22]

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ALD is a chemical vapor deposition method in which the thin film is deposited by alternating, saturating pulses of the precursor gases separated by inert gas purging.[23−25] With elements as precursors, a monolayer growth per cycle is possible. In practice, due to steric hindrances, one reaction cycle usually produces only a distinct fraction of a monolayer. Self-limiting growth mode of ALD enables processing of high-quality thin films on large area substrates with high conformality and thus ALD has gained the attention of the microelectronics industry. ALD is a low-thermal-budget process where deposition temperatures are usually in the range of 200−500 °C. Within the so-called ALD window[23] the process, in contrast to conventional CVD, is usually rather insensitive to temperature. In ALD processing of Y_2O_3, $Y(thd)_3$ has been employed as metal source and ozone has been used as an oxygen source, resulting in a constant growth rate of 0.23 Å/cycle within the deposition temperature range of 250−375 °C.[21] When β-diketonate type precursors for yttrium are used a highly reactive oxygen source, such as ozone, is required to produce films with low impurity contents. Formation of a SiO_x interfacial layer between Y_2O_3 and Si-substrate has been observed with ozone, however.[22,26] Ozone oxidizes the HF-etched silicon substrate and creates a 1.1−1.4-nm-thick interfacial SiO_2 layer between the Si substrate and Y_2O_3 film.[22,26] This interfacial layer increases the equivalent oxide thickness. Thus, ozone-based processes may not be suitable for the deposition of alternative gate insulators, and other more reactive metal precursors are needed. Another problem in the use of $Y(thd)_3$ is the relatively low growth rate obtained[21] which excludes the process for some applications where thicker films are needed. However, another group of suitable volatile rare-earth and transition metal compounds exists, namely the cyclopentadienyl ($Cp = C_5H_5$) compounds, which are typically highly reactive toward water thus forming an interesting alternative to the β-diketonate/ozone-based processes. Recently, cyclopentadienyl-type compounds, viz. Cp_3Sc[27] and $Cp_2Zr(CH_3)_2$,[28] have been used as metal-containing precursors, together with water as an oxygen source, for depositing Sc_2O_3 and ZrO_2 thin films by ALD, respectively. In these studies, the impurity contents under optimized conditions remained extremely low; for Sc_2O_3 films deposited at 300 °C from Cp_3Sc and water, the impurity levels were only 0.1 and 0.5 atom % for carbon and hydrogen, respectively.[27] On the basis of these encouraging results, it seemed that the growth rate and quality of Y_2O_3 thin films can be significantly enhanced by using organometallic precursors. In the present paper, we have exploited the cyclopentadienyl-type organometallic precursors, namely Cp_3Y and $(CpCH_3)_3Y$ for low-temperature deposition of Y_2O_3 thin films by ALD without the need of aggressive oxidants, such as ozone.

Experimental Section

Y_2O_3 Film Deposition. For the deposition of Y_2O_3 thin films, n-type Si(100) (Okmetic, Vantaa, Finland) was used as substrate. The substrate area was 10 × 5 cm^2. Si substrates covered by the native oxide were ultrasonically cleaned in ethanol and distilled water. The air- and moisture-sensitive precursors Cp_3Y and $(CpCH_3)_3Y$ were obtained from the Institute of Organometallic Chemistry, Russian Academy of Sciences (Nizhny Novgorod, Russia). Y_2O_3 films were deposited in a flow-type hot-wall ALD reactor MC-120 manufactured by ASM Microchemistry Ltd (Espoo, Finland). The metal precursors Cp_3Y and $(CpCH_3)_3Y$ were handled in a glovebox and inertly inserted into the reactor and evaporated from open crucibles kept at 150 and 110 °C, respectively. Distilled water was evaporated from a container kept at 25 °C. The chamber pressure was 2−3 mbar during the depositions. Nitrogen (>99.999%, Schmidlin UHPN 3000 N_2 generator) was used as a carrier and purging gas. Growth rate as a function of the deposition temperature was studied in the temperature range of 175−450 °C for the $(CpCH_3)_3Y$ precursor and at 175−500 °C in the case of Cp_3Y. Standard pulsing sequence (ALD growth cycle) was the following: 0.7-s pulse of metal precursor, followed by 1 s of nitrogen purge, 0.7 s of water, and finally 1.2 s of nitrogen purge. To verify the ALD-type growth, the metal precursor pulsing time was varied from 0.7 to 3 s at the deposition temperatures of 250 and 300 °C.

Characterization Methods. Reflectance spectra were measured in a Hitachi U-2000 double beam spectrophotometer. The film thicknesses of the deposited films were determined by measuring the optical reflectance spectrum between wavelengths of 190 and 1100 nm and fitting a theoretical spectrum to the measured spectrum.[29] Crystallite orientations and crystallinity of the deposited films were determined by X-ray diffraction with Cu Kα radiation in a Philips MPD 1880 diffractometer. Surface morphology was studied with a Nanoscope III atomic force microscope (Digital Instruments) operated in tapping mode. Samples were measured with a scanning frequency of 1.5 Hz. Several wide scans (10−20 μm) were performed from different parts of the samples to check the uniformity of the sample. Final images were measured from a scanning area of 2 × 2 μm^2. Roughness values were calculated as root-mean-square values (rms).

Impurity levels, as well as the Y to O ratio, were measured from films deposited with $(CpCH_3)_3Y$ or Cp_3Y at 300 °C, by time-of-flight elastic recoil detection analysis (TOF-ERDA) at the Accelerator Laboratory of the University of Helsinki. In addition, the effect of deposition temperature on the chemical composition of the $(CpCH_3)_3Y$ processed yttria films was studied. In the TOF-ERDA method,[30,31] heavy ions are projected into the sample and the resulting signal consists of forward recoiling sample atoms ejected by the ion beam. Both velocity and energy for recoiled atoms are 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

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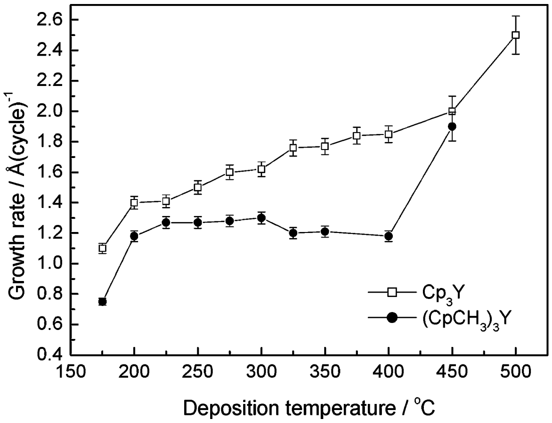

Figure 1. Growth rates of Y_2O_3 films deposited by the $(CpCH_3)_3Y/H_2O$ or Cp_3Y/H_2O process as a function of the deposition temperature.

53 MeV $^{127}I^{10+}$ ion beam was used, obtained from a 5 MV tandem accelerator EGP-10-II. For heavy recoil, energy spectra were obtained from the TOF signals and hydrogen spectra were obtained from the charged particle detector. In TOF-ERD analysis the uncertainties of the impurity contents are due to statistical and possible systematic errors in the stopping power values. The uncertainties fall below 0.1 atom % units for contents below 1 atom % and below 0.2 atom % for contents above 1 atom %.

For the electrical characterization, Y_2O_3 was deposited onto n-type Si(100)-substrates at 300 °C using both cyclopentadienyl-type precursors. Prior to the depositions, the substrates had a native SiO_2 layer which was not removed. The Y_2O_3 layer thickness was 55 and 88 nm when using Cp_3Y and 68 nm with $(CpCH_3)_3Y$. Aluminum gate electrodes with an effective area of 0.204 mm^2 were e-beam evaporated onto the Y_2O_3 film surface. The backsides of the Si substrates were HF-etched before evaporating the 100-nm-thick aluminum electrodes to create an ohmic contact. Thus, the capacitance−voltage (C−V) and current−voltage (I−V) measurements were carried out on Al/Y_2O_3/native SiO_2/n-Si(100)/Al capacitor structures. C−V characteristics were measured with a HP 4284A precision LCR-meter. The voltage step was 0.05 V and the frequency of ac signal was 500 kHz. The I−V voltage curves were measured with a Keithley 2400 Source Meter with a voltage step of 0.05 V. All measurements were carried out at room temperature and without any postdeposition annealing.

Results and Discussion

ALD Depositions. The growth rate of the Y_2O_3 thin films was investigated as a function of the deposition temperature using $(CpCH_3)_3Y$ or Cp_3Y as metal sources and water as an oxygen source (Figure 1). For the $(CpCH_3)_3Y$ precursor, a constant growth rate of 1.2−1.3 Å/cycle was achieved in the temperature range of 200−400 °C. The growth rate obtained was about five times higher than that observed with the $Y(thd)_3/O_3$ precursor combination.[21] At higher deposition temperatures (>400 °C), the decomposition of the $(CpCH_3)_3Y$ precursor destroys the self-limiting growth mode leading to nonuniform films. When applying the unsubstituted Cp_3Y precursor with water even higher growth rates were observed, e.g. the measured growth rate at 300 °C was 1.62 Å/cycle. The growth rate increased with the increasing deposition temperature and a plateau of constant growth rate as a function of the temperature was not observed, however. The larger size leading to steric hindrance of the precursor molecules on the substrate surface may decrease the growth rate in the case of $(CpCH_3)_3Y$ compared to Cp_3Y. With both precursors, the obtained Y_2O_3 films were uniform over the substrate area of 10 × 5 cm^2 when the deposition temperature was 400 °C or below. To corroborate the self-limiting ALD growth mode, pulse times of the metal precursor were varied at the deposition temperatures of 250 and 300 °C. As seen in Figure 2, saturation of the growth rate was achieved already with a 0.7-s metal precursor pulse duration, and a further increase of the pulse length had no effect on the growth rate which confirms the self-controlled ALD-type growth. Furthermore, increasing the water pulse duration from 1 to 2 s resulted in films with the same thickness. The dependence of the film thickness on the number of reaction cycles at 300 °C is plotted in Figure 3. A linear dependency was obtained with both yttrium precursors thus giving additional evidence for an ALD-type growth mode.

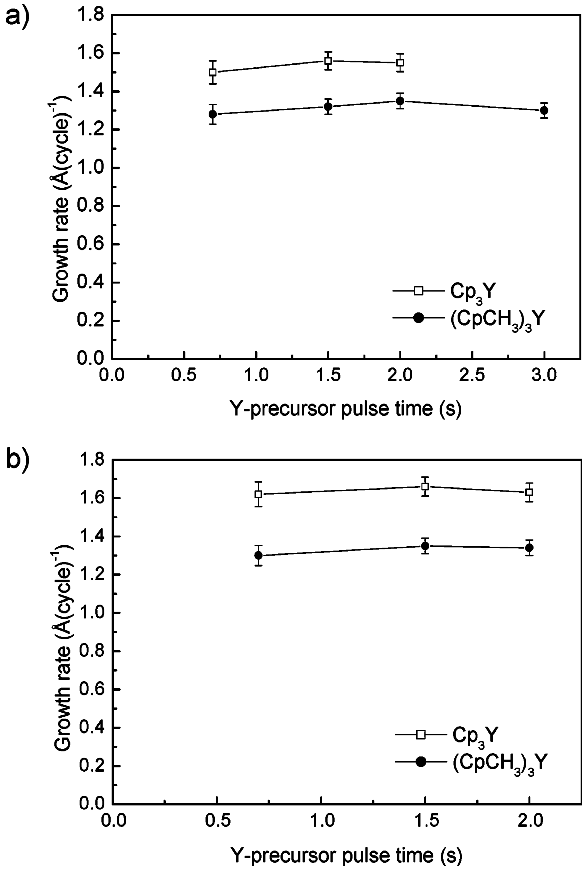

Figure 2. Y_2O_3 growth rates, as a function of the Y-precursor pulse length, deposited at 250 °C (a) and 300 °C (b). Lines are guides for the eye.

Y_2O_3 Film Characteristics. The TOF-ERD analysis confirmed that stoichiometric films with low carbon levels had been obtained (Table 1). However, the Y/O ratio in the $(CpCH_3)_3Y$ processed films increased slightly with the increasing deposition temperature, increasing from 0.65 to 0.67 at the deposition temperatures of 200 and 300 °C, respectively. At the deposition temperature of 400 °C, the ratio was 0.68, or slightly higher than the stoichiometric ratio of 0.67. The Cp_3Y/H_2O processed film deposited at 300 °C exhibited also a nearly ideal stoichiometry with a Y/O ratio of 0.68. When comparing the cyclopentadienyl/H_2O processes with the previously reported $Y(thd)_3/O_3$ process, a clear improvement in the

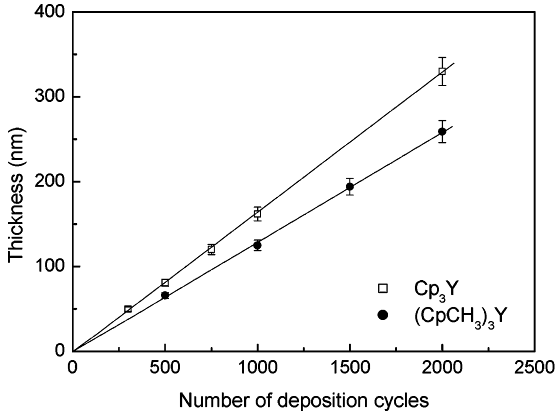

Figure 3. Thickness of Y_2O_3 films deposited by the $(CpCH_3)_3Y/H_2O$ or Cp_3Y/H_2O process as a function of number of deposition cycles. The deposition temperature was 300 °C in both cases.

Table 1. Composition of Y_2O_3 Films Grown on Silicon as Measured by TOF-ERDA

T_{growth}, °C	precursor	Y/O ratio	H, atom %	C, atom %
200	$(CpCH_3)_3Y$	0.65	6.8	0.5
300	$(CpCH_3)_3Y$	0.67	3.1	0.2
400	$(CpCH_3)_3Y$	0.68	0.9	0.2
300	Cp_3Y	0.68	1.8	0.5

Y/O ratios toward stoichiometry was observed. The Y/O ratio in the yttrium oxide films deposited in the $Y(thd)_3/O_3$ process at temperature range of 200 to 350 °C increased from 0.39 to 0.62 but remained below the ideal stoichiometry.[21] The carbon impurities in the $(CpCH_3)_3Y$ processed films were in the order of 0.5 atom % in the film deposited at 200 °C but they were further reduced to only 0.2 atom % when the films were deposited at 300 and 400 °C. Increasing the deposition temperature in the $(CpCH_3)_3Y/H_2O$ process from 200 to 300 °C resulted in a significant decrease in the hydrogen impurity level, viz. from 6.8 to 3.1 atom %. And finally the film deposited at 400 °C had only 0.9 atom % of hydrogen. Also, the Cp_3Y/H_2O-processed films deposited at 300 °C contained low impurity concentrations, viz. 0.5 and 1.8 atom % for carbon and hydrogen, respectively. In the yttria film deposited by the $Y(thd)_3/O_3$ process at a very low temperature of 200 °C the carbon content was considerably higher, or about 10 atom % but it was reduced to 1.0−1.4 atom % at the optimized deposition temperature of 350 °C.[21] Also, a clear decrease in the hydrogen level as a function of deposition temperature was detected, as an increase of the deposition temperature from 200 to 350 °C reduced the hydrogen content from 6 to 1.5 atom %.[21]

With strong oxidizers the C_5H_5-ligand is completely decomposed, leading to carbon contamination. In the present case, using a mild oxidizer such as water only the metal−carbon bond is broken. Thus, the carbon contamination remains rather low in the Y_2O_3 films deposited at 300 °C with both yttrium precursors and the CH_3-ligand seems not to be affecting the carbon content. However, the larger size of $(CpCH_3)_3Y$ molecule decreases the growth rate and increases the thermal stability while Cp_3Y is more reactive toward water.

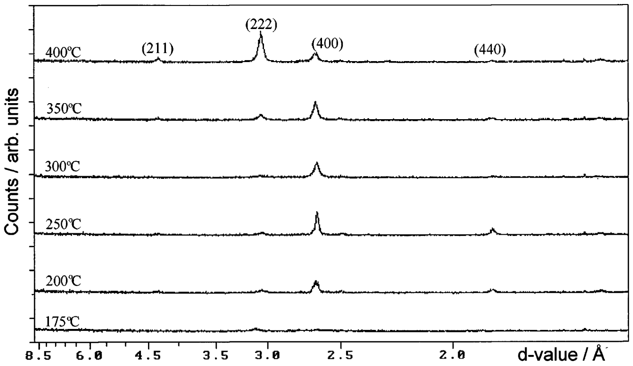

Figure 4. XRD patterns of the Y_2O_3 films deposited on Si(100) from $(CpCH_3)_3Y$ and H_2O at different temperatures. Thicknesses of the films deposited at 200−400 °C were 120−130 nm, whereasthe thickness of the film deposited at 175 °C was 75 nm. Diffraction peaks were identified and indexed according to JCPDS card 25-1200.

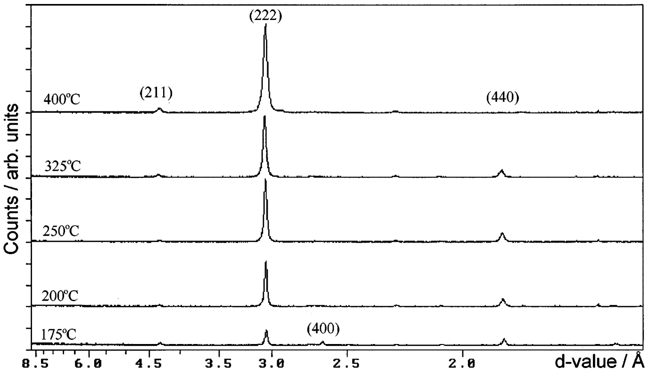

Figure 5. XRD patterns of Y_2O_3 films deposited on Si(100) from Cp_3Y and H_2O at different temperatures. Thicknesses of the films deposited at 200−400 °C were 140−180 nm, whereas thickness of the film deposited at 175 °C was 110 nm. Diffraction peaks were identified according to JCPDS card 25-1200.

Crystallinity and crystallite orientation of the films grown onto Si(100) were studied with XRD. For films with thicknesses in the 120−130 nm range deposited by the $(CpCH_3)_3Y/H_2O$ process at 350 °C or below, the preferred orientation of the cubic phase was (400) but also some minor intensity peaks originating from the (222) and (440) reflections were visible (Figure 4). When the deposition temperature was increased to 400 °C a change in the preferred orientation to (222) was observed. In the case of Y_2O_3 films deposited with the Cp_3Y process, the (222) reflection was the most intense one independent of the deposition temperature. Polycrystalline films with this orientation were obtained even at the low deposition temperature of 175 °C (Figure 5). It is assumed that although Cp_3Y is the more reactive precursor, the nucleation process occurs at a higher rate even at low temperatures resulting in (222) oriented films, while in the case of $(CpCH_3)_3Y$ more thermal energy is needed to achieve the (222) as dominant orientation. The previously deposited Y_2O_3 films, using $Y(thd)_3$ and O_3 as precursors, were observed to be polycrystalline with (400) as the most intense reflection, but at higher temperatures the preferred orientation changed to (222).[21] In addition, it should be noted that with both precursors the crystallinity of the films increased with increasing film thickness.

The surface morphology of the as-deposited films was studied by AFM. The deposition temperature had a considerable effect on the surface roughness of the 100−150-nm-thick films processed with both precursors. When Cp_3Y was used as a precursor, smooth and

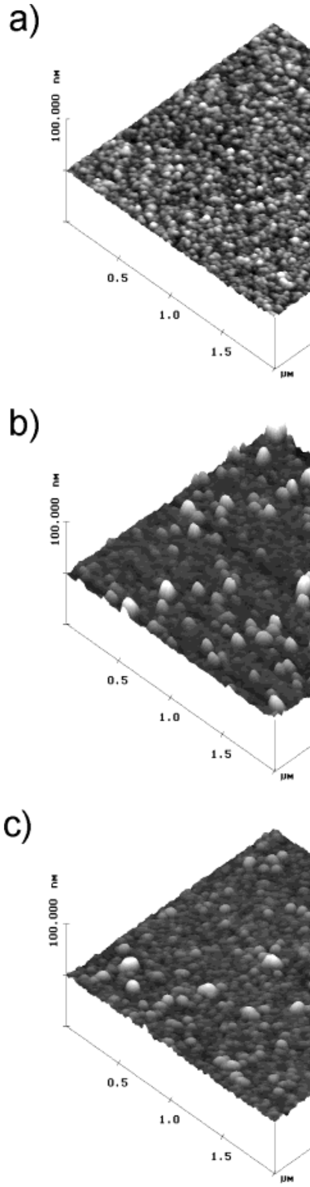

Figure 6. AFM images of Y_2O_3 films deposited from Cp_3Y/H_2O at 250 °C (a) and 300 °C (b) as well as that for Y_2O_3 film deposited from $(CpCH_3)_3Y/H_2O$ at 250 °C (c). The thicknesses of the samples were 150 (a), 80 (b), and 125 nm (c) and the corresponding rms values were 0.8 (a), 2.2 (b), and 1.5 nm (c). Image size: 2 × 2 μm^2. Depth scale: 50 nm from black to white.

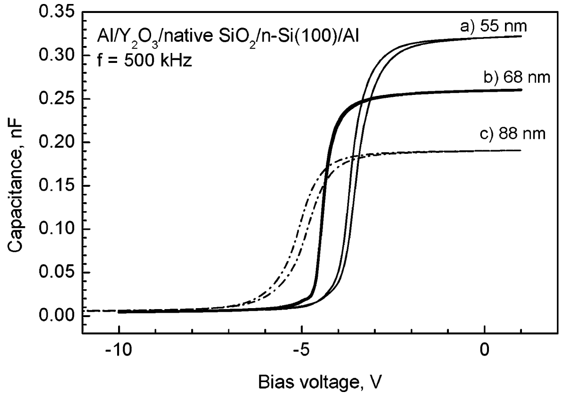

Figure 7. Capacitance−voltage curves of $Al/Y_2O_3/Si$ structures with Y_2O_3 deposited onto native SiO_2 covered Si substrate using Cp_3Y/H_2O (a and c) or $(CpCH_3)_3Y/H_2O$ (b) process. Labels indicate the Y_2O_3 layer thickness. The deposition temperature of the Y_2O_3 layer was 300 °C.

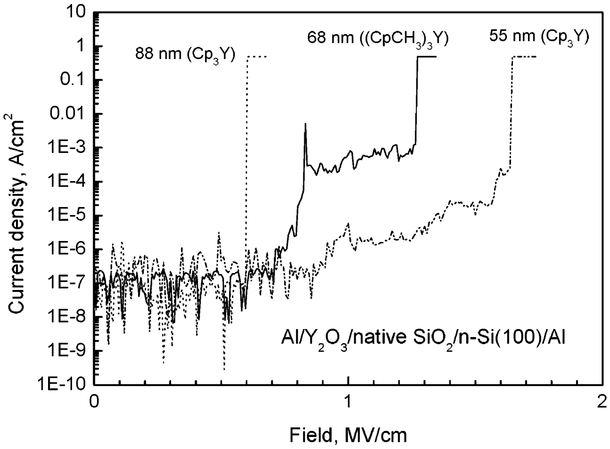

Figure 8. Leakage current density vs electric field strength curves for $Al/Y_2O_3/Si$ structures with Y_2O_3 deposited onto native SiO_2 covered Si substrate. Labels indicate the Y_2O_3 thickness and the yttrium precursor used. The measurements were carried out under forward bias, i.e., the electrons were injected into oxide from substrate.

uniform films were obtained at the deposition temperature of 250 °C or below. Figure 6a shows the surface of a 150-nm-thick Y_2O_3 film grown at 250 °C (rms 0.8 nm). The roughness increased (rms 2.2 nm) when the deposition temperature was raised to 300 °C (Figure 6b). Similar behavior was observed when the $(CpCH_3)_3Y/H_2O$ process was used. Typical rms-roughness value was about 1.5 nm for a 125-nm-thick film grown at 250 °C (Figure 6c) but it was increased 3-fold to around 4−5 nm for films with same thickness when grown at 300 °C. Independently of the precursor used, a further roughening of the films was observed when the deposition temperature was 350 °C or above. The increase in roughness with increasing deposition temperature is probably caused by crystallization of the films and at higher temperatures also by a partial decomposition of the precursor molecule. A similar increase in roughness even inside the ALD-window temperature regime has also been observed for MgO[32] and Sc_2O_3 [27] thin films processed with Cp compounds.

Figure 7 depicts the capacitance−voltage curves for the Al/Y_2O_3/native SiO_2/n-Si(100)/Al structure where the Y_2O_3 layer was grown by ALD at a deposition temperature of 300 °C using $(CpCH_3)_3Y$ or Cp_3Y as metal precursors. The flatband voltage for an Al/insulator/n-Si(100) structure should be around −0.2 V.[33,34] As shown in Figure 7, a significant amount of positive fixed charge in the films was observed as the flatband voltage strongly shifts toward negative bias. The accumulation capacitance decreases with increasing insulator thickness yielding an effective permittivity value of 10, as calculated from the accumulation capacitance. Hysteresis was low for the $(CpCH_3)_3Y$-processed film, whereas hysteresis width was considerably higher for the Cp_3Y-processed films. This is indicative of the charge being

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trapped at disorder-induced, rechargeable oxide traps. Current−voltage behavior, depicted in Figure 8, was studied for the above-mentioned capacitor structures with various thicknesses of the yttria layer. The breakdown field increased with decreasing insulator thickness. With both precursors, the polycrystalline structure of the films offers pathways to leakage current along grain boundaries. The leakage current in a 0.5 MV cm^{-1} field was in the order of 10^{-7} A cm^{-2}.

Conclusions

The results reported here show that the cyclopentadienyl-type compounds of yttrium can be successfully employed as precursors in atomic layer deposition of Y_2O_3 thin films. By using $(CpCH_3)_3Y$ and water as precursors, Y_2O_3 growth rate of 1.2−1.3 Å/cycle was achieved in a wide deposition temperature range of 200−400 °C. This growth rate is about five times higher than achieved previously with the $Y(thd)_3/O_3$ combination.[21] The growth rate was further increased to 1.6 Å/cycle by using the Cp_3Y/H_2O process at 300 °C. The deposited films at 300 °C were stoichiometric and they contained only small amounts of impurities. The crystallinity of the obtained films increased with the increasing deposition temperature for both precursor combinations tested. From the morphological point of view, the smoothest films in both processes were deposited at deposition temperatures of 250 °C or below. The electrical measurements revealed positive fixed charge in the Y_2O_3 films deposited at 300 °C.

The advantageous features of the present Cp-based ALD-processes, as compared to the previously reported β-diketonate-based process for yttria,[21] include, besides the low deposition temperature of stoichiometric films, also significantly higher growth rate and crystallinity as well as low impurity levels in the films. Furthermore, the reactive Cp-compounds allow for the use of simply water as oxygen source instead of more aggressive ozone.

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