Surface-Controlled Deposition of Sc_2O_3 Thin Films by Atomic Layer Epitaxy Using β-Diketonate and Organometallic Precursors

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Scandium oxide thin film deposition by atomic layer epitaxy was studied at 175−500 °C using $Sc(thd)_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and $(C_5H_5)_3Sc$ as scandium precursors. A constant deposition rate of 0.125 Å $(cycle)^{-1}$ was observed at 335−375 °C on Si(100) and soda lime glass substrates with $Sc(thd)_3$ and O_3. The use of H_2O_2 as an additional oxidizer slightly increased the deposition rate to 0.14 Å $(cycle)^{-1}$. When $(C_5H_5)_3Sc$ and H_2O were used as precursors, the growth rate of Sc_2O_3 was significantly higher, viz., 0.75 Å $(cycle)^{-1}$ at 250−350 °C. The effects of growth parameters such as reactant pulsing times were investigated in detail to confirm the surface-controlled growth mechanism. The crystallinity and surface morphology of the films were characterized by XRD and AFM, while ion-beam analysis (time-of-flight elastic recoil detection analysis) was used to determine the stoichiometry and impurity levels. Crystalline thin films with (111) as the dominant orientation were obtained on Si(100) when depositions were carried out at 300 °C or above from $Sc(thd)_3$ and O_3 precursors, while films deposited from $(C_5H_5)_3Sc$ and H_2O were polycrystalline regardless of the deposition temperature. When films were deposited at 300 °C onto Si(100), the preferred orientation changed from (111) to (100) when the film thickness exceeded 200 nm. Films were stoichiometric when deposited from $Sc(thd)_3/O_3$ below 450 °C or from $(C_5H_5)_3Sc/H_2O$ at 250 °C or above. When the films were deposited from $Sc(thd)_3/O_3$, the carbon content was below 0.1 atom % regardless of the deposition temperature, whereas the hydrogen content decreased to below 0.1 atom % when the deposition temperature was increased to 375 °C. The C and H contents of the films, deposited from $(C_5H_5)_3Sc/H_2O$ at 300−400 °C, were around 0.1 and 0.5−0.3 atom %, respectively.

Introduction

Scandium oxide thin films have been used as damage-resistant,[1] antireflection,[2] and high-reflection multilayer coatings,[3−5] in light-emitting diodes (LEDs) and high-power UV lasers. Other possible applications of Sc_2O_3 films include thin film interference polarizers[6] and inorganic resist material for nanometer-scale electron beam lithography[7] as well as etch-stop layers for multilayer dielectric gratings.[8] The preparation and analysis of dielectric films containing scandium, such as $YScO_3$, have also been reported.[9] Sc_2O_3 has also been used for the stabilization of ZrO_2 thin films[10] and as a dopant in nickel copper oxide based NO_x sensors.[11] The use of Sc_2O_3 in cathodes in high-resolution and high-brightness cathode ray tubes has also been studied.[12,13] In this application Sc_2O_3 together with W improves the cathode emission capability, although better emission characteristics have been obtained by metallic scandium overlayers.[14] Furthermore, Sc_2O_3 has attracted interest as a constituent of ferroelectric thin films, such as

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$Pb[(Sc_{0.5}Nb_{0.5})_{0.57}Ti_{0.43}]O_3$[15] and $Pb(Sc_{0.5}Ta_{0.5})O_3$.[16,17] These materials have been studied for pyroelectric imaging and piezoelectric applications. For the improvement of magnetic properties, Sc_2O_3 has been used as a dopant in barium hexaferrite thin films.[18]

Scandium oxide thin films have been deposited by both physical and chemical gas-phase methods. More recently liquid-phase (sol−gel) techniques have also been applied.[19] The physical gas-phase methods used include electron-beam[2] and laser-beam[1,20] evaporation and sputtering.[7,12] Direct evaporation and condensation[21,22] as well as reactive evaporation[23] of Sc_2O_3 at low pressure have also been employed. Furthermore, Sc_2O_3 films have been prepared by direct evaporation of metallic Sc followed by subsequent oxidation of the resulting scandium film.[24]

Syntheses of several types of volatile scandium compounds have been reported. Alkoxides,[25] aryloxides,[26] and nonfluorinated[27] and fluorinated[28−30] β-diketonates of scandium have been prepared. The nonfluorinated volatile β-diketonate compounds contain ligands such as acetylacetonate (acac),[28−30] 2,2,6,6-tetramethyl-3,5-heptanedione (thd),[31,32] 6-methyl-2,4-heptanedione (mdh),[32] and 2,2,7-trimethyl-3,5-heptanedione (tmod).[32] Other volatile compounds including the organometallic tris(cyclopentadienyl)scandium[33−35] and mixed-ligand cyclooctatetraene compounds[36,37] have also been synthesized. However, according to the best of our knowledge, only $Sc(acac)_3$, $Sc(thd)_3$, $Sc(tmod)_3$, and $Sc(mdh)_3$ have been used in the CVD studies.[32,38] CVD depositions of scandium oxide from $Sc(thd)_3$, $Sc(tmod)_3$, and $Sc(mdh)_3$ have been carried out at 450−600 °C using O_2 as an oxidizer.[32]

Atomic layer epitaxy (ALE),[39,40] also referred to as atomic layer deposition (ALD) or atomic layer CVD (ALCVD), has been successfully employed for the deposition of a variety of thin oxide films.[41,42] Recently we have deposited some representative Group 3 oxides, namely, Y_2O_3[43,44] and La_2O_3.[45] Although Sc_2O_3 thin films have been deposited from β-diketonate precursors by CVD,[32] ALE has not been used nor have volatile organometallic compounds been employed as precursors. Therefore, our interest in Sc_2O_3 films stems from the need to exploit the possibilities of the ALE method for Sc_2O_3 film deposition and also to study the suitability of organometallic scandium compounds as precursors. Furthermore, data on a similar type of β-diketonate precursor for each Group 3 oxide would give some insight into the ALE deposition mechanisms. Here we report the results of a comparative ALE study on the deposition of Sc_2O_3 thin films using both $Sc(thd)_3/O_3$ and $(C_5H_5)_3Sc/H_2O$ precursor combinations. The effect of an additional oxidizer on the growth rate of Sc_2O_3 thin films in the $Sc(thd)_3/O_3$ process is also reported.

Experimental Section

Precursor Preparation and Analysis. $Sc(thd)_3$ was prepared by the method described by Eisentraut and Sievers[46] and purified by sublimation. The volatility of $Sc(thd)_3$ was checked by simultaneous TG/DTA measurements (Seiko SSC 5200) using 2 mbar of pressure and a 99.999% nitrogen atmosphere; this was done to simulate the ALE deposition conditions.[47] Purified $Sc(thd)_3$ was also characterized by mass spectrometry under UHV conditions in a JEOL DX 303/DA 5000 instrument. $(C_5H_5)_3Sc$ was purchased from the Institute of Organometallic Chemistry, Russian Academy of Sciences (Nizhny Novgorod, Russia).

Sc_2O_3 Film Deposition. Scandium oxide thin films were deposited in a commercial flow-type hot-wall ALE reactor (Microchemistry F-120) using $Sc(thd)_3/O_3$ and $(C_5H_5)_3Sc/H_2O$ precursors. In some $Sc(thd)_3/O_3$ depositions, 30% H_2O_2 (Merck, pro analysis, no. 107209) was used as an additional oxidizer. Soda lime glass and Si(100) were used as substrates. $Sc(thd)_3$ and $(C_5H_5)_3Sc$ were evaporated from open crucibles kept at 115 and 105 °C, respectively. O_3 was generated from O_2 (99.999%) in an ozone generator (Fischer model 502). The O_3 concentration as determined by iodometric titration was about 4%. H_2O and H_2O_2 were evaporated from a container kept at 25 °C without any additional bubbling system. Thin film depositions were carried out at 2−3 mbar of pressure with N_2 (>99.999%, Schmidlin UHPN N_2 generator) as a carrier and purge gas. The growth rate as a function of deposition temperature and pulsing times were studied in the temperature range of 175−500 °C.

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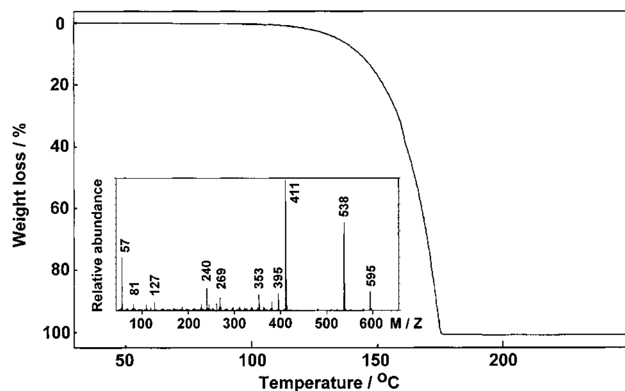

Figure 1. Typical TG curve for a $Sc(thd)_3$ precursor sample (10 mg) showing complete volatilization. The heating rate was 10 °C min^{-1}, and the measuring pressure was 2 mbar. The inset shows ex situ mass spectra of $Sc(thd)_3$ collected under UHV conditions with a 70 eV ionization potential.

Characterization Methods. Film thicknesses were determined by using the fitting of the optical spectra as described by Ylilammi and Ranta-aho.[48] Depending on the substrate type, either reflectance or transmittance spectra were measured by a Hitachi U-2000 dual-beam spectrophotometer. The crystallite orientations of Sc_2O_3 films were determined by X-ray diffraction using Cu Kα radiation in a Philips MPD 1880 instrument. AFM measurements were carried out by a Nanoscope III atomic force microscope (Digital Instruments) operated in tapping mode with a scanning rate of 1−2 Hz. To check the uniformity of the samples, several 10−20 μm wide scans from different parts of the samples were performed. Final images were measured with a scanning area of 2 × 2 μm. Roughness values were calculated as root-mean-square (rms) values. Films deposited were also analyzed by FTIR using a Nicolet Magna-IR 750 instrument equipped with a deuterated triglycine sulfate (DTGS) detector. Transmission spectra were collected from samples deposited onto Si(100) substrates. Silicon substrate peaks were subtracted from the raw spectra obtained.

Elemental concentrations were determined by time-of-flight elastic recoil detection analysis (TOF-ERDA) at the Accelerator Laboratory of the University of Helsinki. In this method[49] heavy ions are used as projectiles which hit the sample at an oblique angle. These high-energy ions eject sample atoms as a result of elastic collisions. Both velocity and energy can be determined for the recoiled atoms using timing gates and a charged particle energy detector, which enables the differentiation of masses. With affected by inaccuracies of the stopping powers and scattering cross sections, elemental depth distributions can be calculated. In this study, elemental concentrations were calculated directly from the energy spectra yields, and therefore the results given are not parametrized values for stopping powers. For our TOF-ERDA studies, a 53 MeV $^{127}I^{10+}$ ion beam was used, generated by 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 recoils, energy spectra were obtained from the TOF signal and hydrogen spectra from the charged particle detector.

Results and Discussion

Precursor Analysis. According to TG measurements, $Sc(thd)_3$ sublimes in a single step at 2 mbar of pressure (Figure 1); the single-step process is consistent with the previously reported TG studies performed under atmospheric pressure.[31] The onset value in our TG curves was 146−150 °C. According to the DTA

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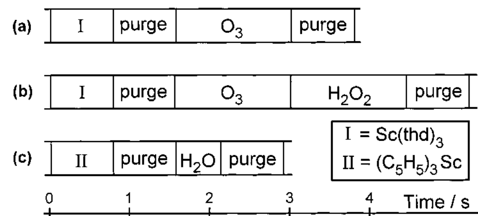

Figure 2. Typical pulsing schemes in the ALE deposition of Sc_2O_3 films using the conventional process ($Sc(thd)_3/O_3$) (a) and that with an additional oxidizer ($Sc(thd)_3/O_3/H_2O_2$) (b) as well as using an organometallic precursor ($(C_5H_5)_3Sc/H_2O$) (c).

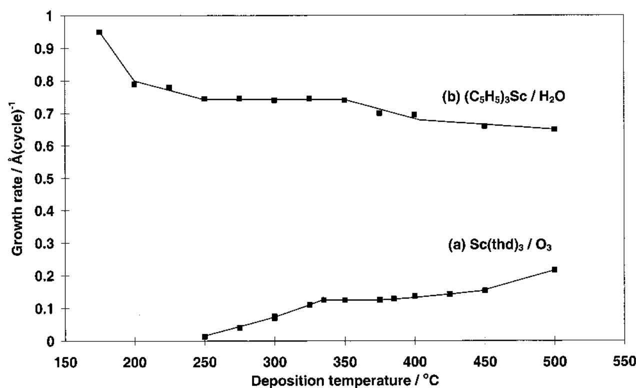

Figure 3. Growth rates of Sc_2O_3 thin films as a function of the deposition temperature from $Sc(thd)_3/O_3$ (a) and $(C_5H_5)_3$-Sc/H_2O (b). The pulsing times for $Sc(thd)_3$ and O_3 were 0.8 and 2.0 s, respectively, while for $(C_5H_5)_3Sc$ and H_2O they were 0.8 and 1.0 s, respectively.

results, no melting occurs below the sublimation temperature. The melting point (155−156 °C) measured at normal pressure was in a good accordance with the published value.[31] The MS spectrum of $Sc(thd)_3$ (Figure 1, inset) resembles the previously published data[50] as well as the results obtained from an analysis of other Group 3 thd compounds.[51,52] It should be noted that the precursor MS data were collected ex situ under UHV conditions while the ALE depositions took place at a higher pressure of approximately 2−3 mbar. Nevertheless, the MS spectra reveal the main gas-phase species of $Sc(thd)_3$. The main intensity peak with mass number $m/z = 411$ can be assigned to $Sc(thd)_2^+$. Other peaks, originating from $Sc(thd)_3^+$ and $Sc(thd)_3^-C(CH_3)_3^+$, were also observed with mass numbers $m/z = 595$ and 538, respectively. Furthermore, a peak at $m/z = 57$ can be assigned to the trimethyl radical $C(CH_3)_3^+$.

ALE Depositions. The deposition rate of the Sc_2O_3 film was investigated as a function of temperature by using $Sc(thd)_3/O_3$ and $(C_5H_5)_3Sc/H_2O$ precursor combinations. The pulsing schemes are shown in Figure 2 a,c. Precursor pulsing times were kept sufficiently long to achieve surface saturation. In the case of $Sc(thd)_3/O_3$, quite low deposition rates were observed throughout the temperature range studied (Figure 3). However, surface-controlled growth with a deposition rate of 0.125 Å $(cycle)^{-1}$ was obtained at 335−375 °C, thus indicating the existence of an ALE window.[53] Films deposited onto

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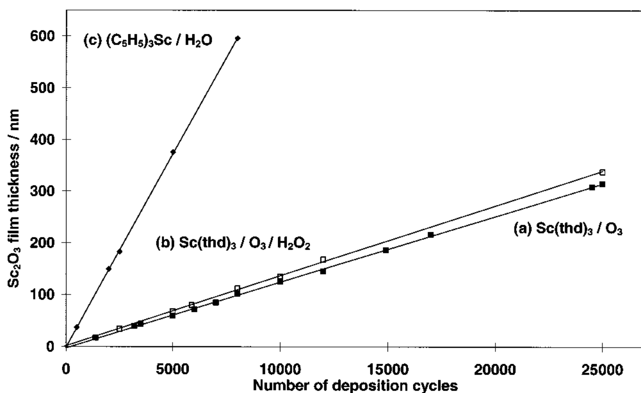

Figure 4. Sc_2O_3 film thickness as a function of the number of deposition cycles. The depositions were carried out from $Sc(thd)_3/O_3$ (a) and $Sc(thd)_3/O_3/H_2O_2$ (b) at 375 °C, while the Sc_2O_3 films from $(C_5H_5)_3Sc/H_2O$ (c) were deposited at 300 °C. The pulsing times for $Sc(thd)_3$ and O_3 were 0.8 and 2.0 s, respectively. A 2.0 s pulsing time was used for the additional H_2O_2 oxidizer, while 0.8 and 1.0 s pulsing times were chosen for $(C_5H_5)_3Sc$ and H_2O, respectively.

Si(100) and soda lime glass substrates were uniform over the substrate area of 10 × 5 cm^2 when deposited at 375 °C or below this temperature. Above 375 °C, the film thickness at the leading edge of the substrate increased, indicating thermal decomposition of $Sc(thd)_3$. At 500 °C, the deposition rates measured at 2 cm from the leading and trailing edges of the substrate were 0.19 and 0.14 Å (cycle)$^{-1}$, respectively.

Depositions from the $(C_5H_5)_3Sc/H_2O$ precursor combination resulted in a significant increase in Sc_2O_3 film growth rate as compared to the $Sc(thd)_3/O_3$ process (Figure 3). A constant growth rate of 0.75 Å (cycle)$^{-1}$ was obtained at 250−350 °C. The growth rate increased when the deposition temperature was decreased below the constant growth region (i.e., below 250 °C). Typically in a β-diketonate process the growth rate decreases when deposition takes place below the ALE window. When organometallic compounds with higher reactivities are used, the growth rate depends mainly on other factors, for example, on the amount of −OH groups on the surface,[54] i.e., the number of adsorption sites available. In the Sc_2O_3 process, the growth rate was observed to decrease when the deposition temperature was increased from 350 to 425 °C. However, the films were still uniform. Films deposited at 450 °C and above had a steep thickness profile, indicating thermal decomposition of $(C_5H_5)_3Sc$.

The effects of pulsing times for the $Sc(thd)_3/O_3$ process at 375 °C as well as those for $(C_5H_5)_3Sc/H_2O$ at 300 °C were studied in detail. Constant growth rates of 0.125 and 0.75 Å (cycle)$^{-1}$ were obtained by using 0.8−3.0 s pulsing times for the scandium precursors. Uniform films were obtained when the O_3 and H_2O pulsing times were 1.0−3.0 and 0.5−3.0 s, respectively. When depositions were carried out using the optimized pulsing times within the ALE window, the thickness of the deposited film could simply be determined by the number of deposition cycles (Figure 4) as should be the case in an ideally behaving ALE process.[53] The refractive indices of the Sc_2O_3 films were measured to be rather constant at 580 nm, i.e., around 1.96. The films were colorless and highly transparent in the visible region when the depositions were carried out from a β-diketonate precursor, viz., $Sc(thd)_3/O_3$, or from $(C_5H_5)_3Sc/H_2O$ below 450 °C. Films deposited from $(C_5H_5)_3Sc/H_2O$ at 450 °C or above were brown-black, indicating a significant carbon contamination. Adhesion of the films was tested by the tape test.[55] The adherence was good as no peeling was observed regardless of the substrate or the deposition process.

When the ALE deposition rate obtained for the $Sc(thd)_3/O_3$ process is compared to the those of other Group 3 oxides, namely, Y_2O_3[43,44] and La_2O_3,[45] it can be noted that the surface-controlled growth rate decreases in the order of diminishing ionic size, viz., La > Y > Sc. Furthermore, the temperature range of the self-controlled deposition region, “ALE window”, shifts toward lower temperatures in the same order. A plausible explanation for the observed lower growth rate and ALE window transition is the enhanced thermal stability of the β-diketonate complexes with decreasing ionic radius of the metal ion.[56] Typically, a low growth rate is attributed to steric hindrances of the bulky precursors.[57] Besides, all Group 3 oxides are basic and tend to absorb CO_2. The basicity decreases in the order La > Y > Sc.[58] This is a possible explanation for the observed increase in carbonate-type contamination. Y_2O_3 thin films deposited within the ALE window (250−375 °C) contained 5.0−1.0 atom % carbon depending on the deposition temperature. The more basic $La(thd)_3$ together with O_3 at the ALE window (225−275 °C) yielded $La_2O_2CO_3$ films corresponding to 11.5 atom % carbon. It should be noted that smooth Sc_2O_3 films were only obtained when deposited at 375 °C or below, whereas ALE depositions of other Group 3 oxides produced smooth films also above the ALE window up to 425 °C. As discussed earlier,[44,45] a partially decomposed precursor, possibly $M(thd)_2$ (M = Y, La),[59] may still be chemisorbed in a surface-controlled manner. Unfortunately, according to the best of our knowledge, gas-phase studies concerning the stability of $Sc(thd)_3$ fragments have not been performed.

To increase the growth rate of Sc_2O_3, an additional oxidizer was used after the O_3 pulse (Figure 2b). The very low ALE growth rate of Sc_2O_3 thin films (0.125 Å (cycle)$^{-1}$) makes the $Sc(thd)_3/O_3$ process unpractical for the deposition of thicker films. Because ALE relies on surface reactions, a controlled process can only be obtained either by quantitative chemisorption or by reaction between the gaseous precursor and the functional surface sites.[60] In oxide thin film deposition processes, reactive surface sites are typically −OH groups and the growth rate can be enhanced by increas-

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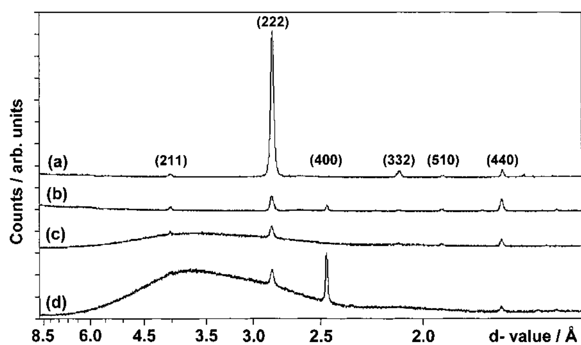

Figure 5. XRD patterns of Sc_2O_3 films deposited from Sc(thd)$_3$/O_3 at 375 °C onto Si(100) (a) and soda lime glass (c). Furthermore, (b) and (d) represent XRD patterns of films deposited from $(C_5H_5)_3Sc/H_2O$ at 300 °C onto Si(100) and soda lime glass, respectively. The thicknesses of all films were 150 nm. Diffraction peaks were identified according to JCPDS card 5-629.

ing the number of isolated −OH groups on the surface.[54] In the processes which use water as an oxidizer, this can be achieved by increasing the water dosage.[61] The increase in growth rate can be 20−100% depending on the metal precursor used and other process parameters.[61] On the other hand, when O_3 is used as an oxidizer, using water as an additional oxidizer may also significantly increase the growth rate as seen in the case of NiO where an increase of 15−20% was observed.[62] In the present study, H_2O_2 was used as an additional oxidizer with 1.0−3.0 s pulsing times. In preliminary experiments H_2O was also used, but no increase in the growth rate was obtained. Purging by nitrogen between the O_3 and H_2O_2 pulses was also attempted, but no effect on the growth rate or film properties was observed. With H_2O_2, the growth rate increased to 0.14 Å (cycle)$^{-1}$, which represents a 12% increase in the deposition rate. No significant differences in the film properties were observed; i.e., the uniformity, crystallinity, and roughness were similar when O_3 was used as such or with H_2O_2 as an additional oxidizer regardless of the H_2O_2 pulsing time.

Sc_2O_3 Thin Film Characteristics. The orientations and degrees of crystallinity in the Sc_2O_3 films were analyzed from samples deposited above 300 °C from Sc(thd)$_3$/O_3 with a thickness of 50−80 nm. At 250−300 °C due to the low growth rate, we were able to deposit within a reasonable time only very thin films (10−20 nm). As expected, the crystallinity of the films deposited on both substrates increased with increasing deposition temperature. Thicker films (>50 nm) were crystalline regardless of the substrate and deposition temperature, with (222) the most intense reflection throughout the deposition temperature range. However, some minor intensity peaks assigned to the (211), (332), (510), and (440) reflections were also observed regardless of the film thickness (Figure 5a,c). Peak widths (fwhm) measured from the (222) reflection were on the order of 2θ = 0.3−0.35° when measured from samples deposited onto Si(100) substrates. Thinner samples (<20 nm) deposited onto both substrates below 325 °C were amorphous, and only the (222) orientation was observed at higher temperatures. Due to a low deposition temperature and a low surface mobility, an amorphous layer in the beginning of an ALE deposition process has previously been observed in ZnS thin films, for instance.[63] The substrate and film thickness also play a significant role in the crystallinity. As expected, Sc_2O_3 films deposited onto Si(100) were more crystalline than those on the soda lime glass substrates. The relative intensity of the (440) orientation of films deposited onto soda lime glass increased with the film thickness, and it was most intense in films having thicknesses over 150 nm.

Sc_2O_3 thin films deposited from $(C_5H_5)_3Sc/H_2O$ onto Si(100) were less crystalline as compared to films deposited from the β-diketonate precursor (Figure 5b). (222), (400), and (440) reflections were the most intense ones when the films were deposited onto Si(100) at 175−300 °C and when the film thickness was kept below 200 nm. Minor-intensity (211), (332), and (510) reflections were also observed regardless of the deposition temperature. When the thickness of the films deposited at 300 °C onto Si(100) was increased above 200 nm, the (400) reflection became dominant. Above 350 °C the intensity of the (222) reflection increased as a function of the deposition temperature, resulting in almost completely (111) oriented films at 500 °C. The (222) reflection the was most intense when the films were deposited onto soda lime substrates below 250 °C or above 350 °C, whereas (100) oriented films were obtained at 275−350 °C (Figure 5d). Only thinner films (<100 nm) were (111) oriented when deposited at 300 °C onto soda lime substrates.

TOF-ERDA analyses were performed for the Sc_2O_3 films deposited onto Si(100) at 175−500 °C. Sc_2O_3 films deposited from Sc(thd)$_3$/O_3 below 325 °C were not analyzed because films with a sufficient thickness could not be prepared due to the very low growth rate discussed above. The carbon content of the films deposited from Sc(thd)$_3$/O_3 was below 0.1 atom % regardless of the deposition temperature. When the films were deposited at 325 °C, the hydrogen and fluorine contents were 0.5 and 1.4 atom %, respectively. The hydrogen content decreased to below 0.1 atom % when the deposition temperature was increased to 375 °C. Furthermore, increasing the deposition temperature from 325 to 500 °C resulted in a decrease in the fluorine content from 1.4 to below 0.2 atom %. In our previous study with the same reactor setup, fluorine contamination was attributed to the Teflon gaskets used and/or perfluorinated vacuum greases.[44] Sc_2O_3 thin films deposited from $(C_5H_5)_3Sc/H_2O$ contained more impurities than films deposited from the β-diketonate precursor. However, only 0.1 atom % carbon and 0.5−0.3 atom % hydrogen were observed when the films were deposited from $(C_5H_5)_3Sc/H_2O$ at 300−400 °C (Figure 6). When the deposition temperature was decreased to 175 °C, the carbon and hydrogen contents increased to 2.7 and 15 atom %, respectively. Furthermore, an increase of the deposition temperature to 500 °C increased the hydrogen content to 3.5 atom %, while the carbon content also increased to 18 atom %, which was seen as a brown-

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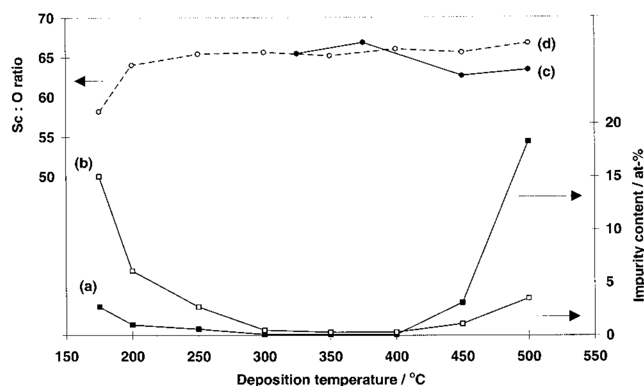

Figure 6. Results of a TOF-ERD analysis for hydrogen (a) and carbon (b) contents in Sc_2O_3 films deposited by the $(C_5H_5)_3$-Sc/H_2O process. The Sc to O ratios of films deposited from Sc(thd)$_3$/O_3 (c) and $(C_5H_5)_3$Sc/H_2O (d) are also given.

black color of the films. This was probably due to the thermal decomposition of $(C_5H_5)_3$Sc as seen in the nonuniformity of the films deposited above 400 °C. Furthermore, 0.3−0.1 atom % chlorine was observed in the films deposited at 175−250 °C, respectively. Chlorine contamination possibly originated from the synthesis of $(C_5H_5)_3$Sc, which involved $ScCl_3$.

The stoichiometry of the deposited Sc_2O_3 films was also analyzed by TOF-ERDA (Figure 6). When Sc_2O_3 films were deposited from Sc(thd)$_3$/O_3 at 325−375 °C, the scandium to oxygen ratio was stoichiometric, i.e., 0.65−0.67. Slightly oxygen deficient films (0.62−0.63) were observed when depositions were carried out at 450−500 °C. Furthermore, no differences in the impurity level or stoichiometry were observed in films where the deposition was assisted by an additional oxidizer at 375 °C as compared to the plain Sc(thd)$_3$/O_3 process. Sc_2O_3 films deposited from $(C_5H_5)_3$Sc/H_2O were stoichiometric (0.65−0.67) when deposited at 250 °C or above. At lower deposition temperatures the amount of oxygen increased, and the Sc to O ratio was only 0.58 when the films were deposited at 175 °C.

Sc_2O_3 films deposited from $(C_5H_5)_3$Sc/H_2O at 175−500 °C and from Sc(thd)$_3$/O_3 at 325−500 °C were also analyzed by FT-IR. Infrared bands at 425 and 630 cm^{-1} were observed regardless of the precursor used or the deposition temperature. These bands can be identified as being due to Sc_2O_3.[64,65] The intensities of the infrared bands were quite constant when the films were deposited from Sc(thd)$_3$/O_3, whereas a maximum in intensity was observed in films deposited from $(C_5H_5)_3$Sc/H_2O at 250−400 °C. When the depositions were carried out below 250 °C, an additional weak intensity band at 3300−3400 cm^{-1} was observed. In this region, absorption bands due to stretching vibrations of water molecules in $Sc(OH)_3 \cdot nH_2O$ as well as bands characteristic of −OH groups in $Sc(OH)_3$ have previously been reported.[66] Therefore, we assume that a low deposition temperature and H_2O as an oxidizer result in films with $Sc(OH)_3$ as an impurity. The intensity of the OH band increased with decreasing deposition temperature, which is consistent with the off-stoichiometry observed by the TOF-ERD analysis.

The surface morphologies of the deposited films were analyzed by AFM, and we found that the Sc_2O_3 films were uniform regardless of the precursor used (Figure 7). Films 70−80 nm thick deposited from Sc(thd)$_3$/O_3 were smooth when deposited within the ALE window (325−450 °C) with only a slightly increasing trend in rms values ranging from 1.3 to 2.1 nm (Figure 8). Above 450 °C or outside the surface-controlled growth regime, an increase in roughness was observed and an rms value of 9.0 nm was obtained for the films deposited at 500 °C. The roughness of the 130−150 nm thick films deposited from $(C_5H_5)_3$Sc/H_2O below 300 °C was quite constant (1.5−2.0 nm). An increase in the roughness was observed when the deposition temperature was 300−400 °C with a maximum rms value around 6 nm. When the deposition temperature was increased to exceed 400 °C, the films again became smoother. A similar change in roughness was observed when MgO films were deposited by ALE from $(C_5H_5)_2$Mg/H_2O.[67]

Conclusions

Scandium oxide thin films can be deposited in a surface-controlled manner using Sc(thd)$_3$/O_3 or $(C_5H_5)_3$-Sc/H_2O as a precursor at 335−375 or 250−350 °C, respectively. The deposition temperatures are significantly lower than those used in CVD experiments.[32] Unfortunately, the deposition rate obtained in the Sc-(thd)$_3$/O_3 process was very low (0.125 Å (cycle)$^{-1}$) compared to the ALE deposition rates of other Group 3 rare earth oxides deposited from β-diketonates and ozone.[44,45] However, an increase in the deposition rate to 0.14 Å (cycle)$^{-1}$ was observed when hydrogen peroxide was used as an additional oxidizer. The slightly higher growth rate is probably due to an increase in the available reactive sites on the surface. On the other hand, a significant increase in growth rate was obtained by using $(C_5H_5)_3$Sc and H_2O as precursors. Thus, surface-controlled ALE growth with a deposition rate of 0.75 Å (cycle)$^{-1}$ was obtained at 250−350 °C. In all cases, the thickness of the deposited Sc_2O_3 films was linearly dependent on the number of deposition cycles, enabling a facile process control.

The crystallinity of the Sc_2O_3 films increased with increasing deposition temperature. The most intense reflection was (222) regardless of the deposition temperature of Sc_2O_3 films deposited from Sc(thd)$_3$/O_3 onto Si(100) substrates, but minor-intensity (211), (332), (510), and (440) reflections were observed as well. On the other hand, the (440) reflection was most intense in films with a thickness over 150 nm deposited on soda lime glass substrates. Thin 10−20 nm films were amorphous on both substrates when deposited below 325 °C. Sc_2O_3 films deposited from $(C_5H_5)_3$Sc/H_2O were less crystalline than films deposited from the β-diketonate precursor. Also in this case, the (222) reflection was most intense in films deposited onto Si(100) substrates, whereas on soda lime glass substrates (400) was the preferred orientation in films deposited at 275−350 °C.

The carbon content in films deposited from Sc(thd)$_3$/O_3 was below 0.1 atom % regardless of the deposition

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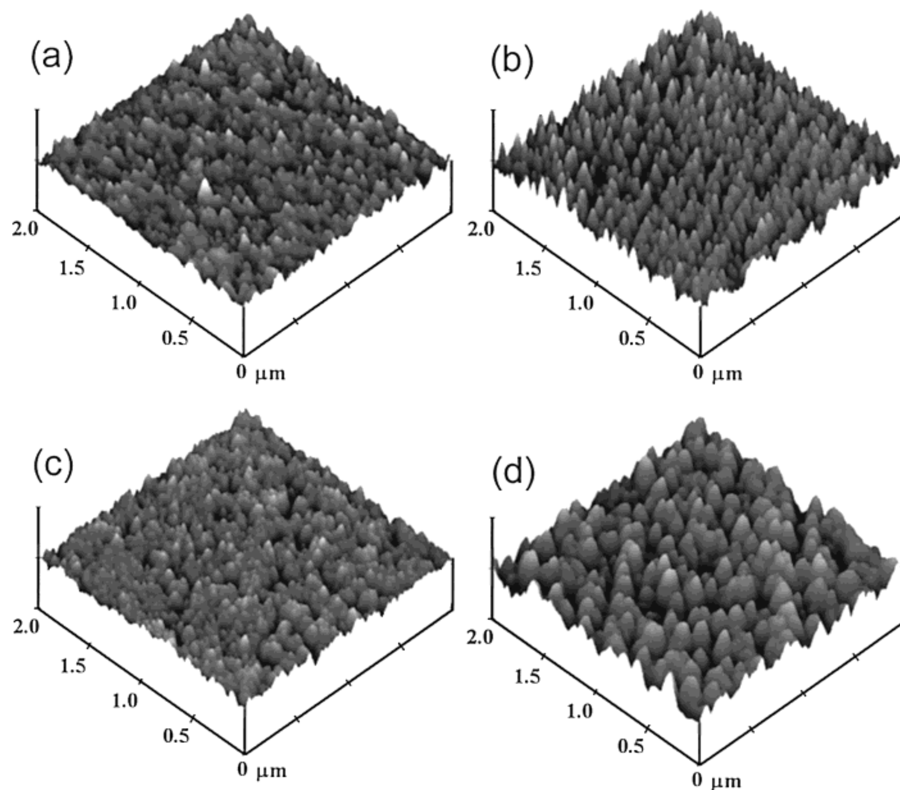

Figure 7. AFM images of Sc_2O_3 films deposited from $Sc(thd)_3/O_3$ at 350 (a) and 400 °C (b) as well as from $(C_5H_5)_3Sc/H_2O$ at 250 (c) and 350 °C (d). The thicknesses of the measured samples were 70 (a, b) and 150 (c, d) nm. The height axes were 40 (a−c) and 100 (d) nm.

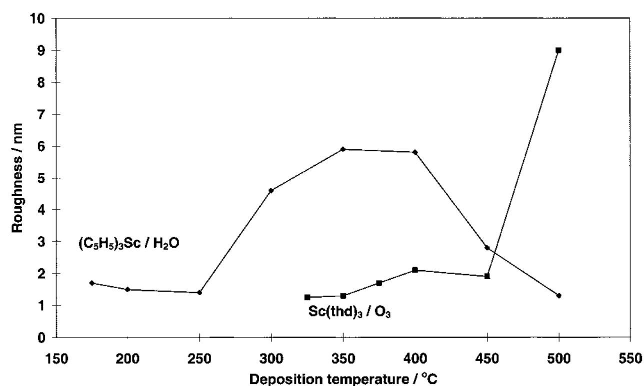

Figure 8. Roughness of the deposited Sc_2O_3 films as a function of the deposition temperature. The film thicknesses were 70−80 and 130−150 nm when the films were deposited from $Sc(thd)_3/O_3$ and $(C_5H_5)_3Sc/H_2O$, respectively.

temperature (325−500 °C). Due to the low growth rate, the impurity levels of the very thin films deposited below 325 °C were not analyzed. The hydrogen content decreased from 0.5 to below 0.1 atom % when the deposition temperature was increased from 325 to 375 °C. As regards the true organometallic precursor, Sc_2O_3 thin films deposited at 300−400 °C from $(C_5H_5)_3Sc/H_2O$ contained 0.1 and 0.5−0.3 atom % carbon and hydrogen, respectively. The impurity levels increased significantly when the deposition temperature was increased or decreased. Sc_2O_3 films deposited from $Sc(thd)_3/O_3$ were stoichiometric with a Sc to O ratio of 0.65−0.67 when deposited at 325−375 °C. An additional oxidizer did not affect the impurity levels or stoichiometries of the films. Sc_2O_3 films deposited from $(C_5H_5)_3Sc/H_2O$ were also stoichiometric with a measured Sc to O ratio of 0.65−0.67 when deposited at 250 °C or above.

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