Thin films and nanotubes of iron oxide are deposited using atomic layer deposition (ALD) on Si(100) and anodic aluminum oxide (AAO), respectively. Ferrocene, Fe(Cp)₂, and oxygen are used as precursors. Successful depositions are carried out in the temperature range 350–500°C on Si(100), while all depositions on AAO are made at 400°C. The growth per cycle values are around 0.14 nm on Si(100) in the temperature range 350–500°C and 0.06 nm on AAO. Below 500°C, the iron oxide crystallizes as a phase mixture on both types of substrates. One of the phases is identified as the rhombohedral Fe₂O₃ phase (hematite), but the second phase cannot be unambiguously identified. Above 500°C, only phase pure hematite is detected. For deposition of nanotubes, in-house-made AAO membranes are used, having an aspect ratio of 30. By etching of the AAO membranes after deposition, free-standing nanotubes retaining the order of the AAO template can be fabricated.

**Keywords:** Anodic aluminum oxide, Atomic layer deposition, Iron oxide, Nanotubes, Thin films

1. Introduction

The transition metals and their oxides are of great interest in numerous scientific fields and applications, both as bulk materials and thin films. One of the more interesting compounds is iron oxide. Amongst the many applications and properties of this material photo catalysis,[1–3] sensors,[4,5] and an interesting magnetic behavior[6,7] can be mentioned. A variety of different methods has been used to deposit iron oxide thin films, e.g., sputtering,[4] sol-gel,[5] aqueous chemical growth,[3] molecular beam epitaxy (MBE),[8] CVD,[9,10] and ALD.[11–14] There are also numerous reports of nanostructured iron oxide.[3,15–18]

Despite all reports of nanostructured materials, it is inherently difficult to fabricate arrays in a well-ordered pattern. One route to obtain well-ordered arrays is to use a template and transfer the pattern to a desired material.[18,19] This can be made in several ways. One method is to deposit a thin film of the desired material on the template as a surface modification.[20,21] Another method is to etch away the template after the deposition of the desired material; this results in a negative projection of the structure.[22,23] A suitable template for this method is anodic aluminum oxide (AAO). The oxide can be electrochemically grown and exhibits a high degree of order over large areas. This approach however excludes many of the thin film techniques used to deposit iron oxide, since most techniques are not able to conformally cover the pore walls of the AAO. One technique that is very well-suited for the template deposition method is ALD. In ALD, reactant gas pulses saturate the surface of the substrate during each pulse, and growth is achieved through self-limiting surface reactions.[24] The reaction gas pulses are separated by purging pulses, i.e., to deposit a metal oxide four pulses are usually needed. The first pulse (t₁) is the metal-source pulse, the second pulse (t₂) is a purging pulse, the third pulse (t₃) is an oxygen-containing pulse, and the fourth and final pulse (t₄) is a second purging pulse. The series of pulses are referred to as a cycle. If the process parameters are properly chosen, the number of cycles used rather than the concentrations of precursors in the gas phase determines the film thickness. This results in the excellent thickness control for which the ALD technique is known.

In this study, ferrocene and oxygen have been used to deposit iron oxide on both Si(100) and along the pore walls of AAO membranes. Ferrocene was chosen as the iron source due to its high thermal stability (above 500°C) in the gas phase.[25] An alternative oxygen source, H₂O, was also tried, but no successful depositions could be made with this precursor. The AAO templates used in this study were both commercial membranes and in-house-made membranes, fabricated using oxalic acid as the electrolyte. The in-house-made membranes were etched away after the iron oxide deposition to make free-standing and parallel nanotubes that retained the order of the AAO template.
2. Results and Discussion

A quartz crystal microbalance (QCM) was used to study the ALD characteristics of the process. Initial experiments indicated that purge times of 2 s were sufficient to prevent overlap of the precursor pulses. The data for the ferrocene and oxygen pulses are given in Figure 1. It can be seen that the growth per cycle values saturate at longer precursor pulses, and such behavior would not be observed if the precursor decomposed at the surface. This suggests that the surface reaction of ferrocene and oxygen was self limiting at 350 °C. A self-limiting process is a criterion for successful depositions, especially in the pores of AAO. If the precursor decomposes on the surface, the pore openings will close rapidly and no material will be deposited inside the pores. In the following experiments the pulse durations $t_1$-$t_2$-$t_3$-$t_4$ were set at 2-2-7-2 s, respectively.

Depositions were made on Si in the temperature range 350–600 °C. The growth per cycle values for these films (Fig. 2) were derived from cross-sectional scanning electron microscopy (SEM) images. As can be seen, the growth per cycle values were found to have both a temperature-independent and a temperature-dependent region. The growth per cycle value in the temperature-independent region was found to be about 0.14 nm per cycle. At high temperatures this value increases with temperature, due to decomposition of the precursor on the surface.

The presence of possible contaminants (i.e. carbon) was investigated using X-ray photoelectron spectroscopy (XPS) on all samples deposited on Si(100). It was found that the carbon content in the films decreased with increasing deposition temperature, being the highest at 350 °C, with a carbon content of 3 at.-%. For deposition temperatures of 425 °C and above, the carbon content was about 1 at.-%. After sputter cleaning of the surface, no variation in the carbon content could be seen upon depth profiling of the deposited films. No other contaminants were found in any of the deposited films. However, the films most likely also contain hydrogen, but the presence of hydrogen can not be detected by XPS.

Grazing incidence X-ray diffraction (GIXRD) showed that all samples were crystalline (Fig. 3). Although the thickness values of the samples deposited at 350–500 °C were of the same magnitude, the diffraction pattern of the sample deposited at the lowest temperature had weaker peaks indicating that the film was partially amorphous. Only hematite, the rhombohedral phase of Fe$_2$O$_3$, could be found in samples deposited at 500 °C and above. At temperatures below 500 °C, another phase was also present. The reflections belonging to the second phase were in agreement with the diffraction patterns of both magnetite (Fe$_3$O$_4$) and maghemite (Fe$_2$O$_3$). The two possible alternatives are both cubic with similar cell parameters. Although only magnetite has a close packed lattice, the reflections from planes containing both odd and even indices in maghemite are very weak. Since these reflections could not be seen in any of the diffraction patterns, it was not possible to distinguish between the two phases. If any of these reflections had been observed, the second phase could have been identified as maghemite. In contrast, the absence of these reflections does not necessarily imply that magnetite is present. The
XRD data therefore does not provide enough information to unambiguously identify the second phase.

Further investigations of the unidentified phase were made using XPS in an attempt to find the oxidation state of the iron in this phase. It should be possible to distinguish between the XPS spectra of the two possible candidates since maghemite contains only Fe$^{3+}$, but magnetite is a mixed-valence compound containing both Fe$^{2+}$ and Fe$^{3+}$. However, due to preferential sputtering, this was not possible. It can be mentioned that magnetic measurements should be able to distinguish between the two phases but this was not attempted in this study.

Using AAO substrates, hollow nanotubes of iron oxide were successfully deposited using in-house-made membranes as templates. The membranes used had a pore diameter of ~70 nm and pore length of 2 μm. The growth per cycle values for the films deposited in the pores of the templates were derived from SEM images such as the one shown in Figure 4. These samples contained the same phase mixture according to XRD (not shown) as the films deposited on Si(100) at 400 °C and the samples had a bright orange color. The growth per cycle values in the pores were determined to be 0.06 nm per cycle, which is considerably lower compared to the corresponding values for flat Si(100) substrates. A reduced growth rate inside the pores has also been observed in earlier studies. One possible explanation for this behavior can be the lower partial pressure of oxygen inside the pores. It has been shown by Sundqvist et al. that a reduced partial pressure of oxygen decreases the growth rate. It can be mentioned that no thickness gradients could be observed along the pore walls by SEM. This conformal coverage of the pore walls indicates that pulse lengths of 30 s were sufficient to saturate the entire surface of the pore walls.

The aspect ratio for the iron oxide nanotubes deposited in the in-house-made AAO templates was ~30. In some experiments the alumina was etched away to make free-standing nanotubes. NaOH was used to selectively etch the alumina since the more commonly employed etchant, phosphoric acid, also etched the iron oxide. The free-standing nanotubes retained the order of the AAO template over large areas, as can be seen in Figure 5.

Some of the samples deposited on AAO were coated with glue on the backside to stabilize the structure when the alumina was etched away. Other samples were filled with silver using electroless deposition. A silver rod deposited in iron oxide-coated pores can be seen in Figure 6. The silver rods act as a support and can also be used to electrically contact the sample.

3. Summary and Concluding Remarks

The growth of iron oxide using ferrocene and oxygen exhibited typical ALD characteristics, with growth per cycle values of 0.14 nm on Si(100) and 0.06 nm on AAO. Below 500 °C, the films consisted of a mixture of hematite and another phase which could not be unambiguously identified, while above this temperature phase-pure hematite was deposited. The carbon-contamination level was in the range 1–3 at.-%, and no other contaminants were found. Free-standing nanotubes that retained the order of the template, with aspect ratios of 30, were fabricated using...
in-house-made AAO. Free-standing iron oxide nanotubes supported by silver rods were also successfully deposited.

4. Experimental

**Anodization:** The fabrication of AAO was performed by applying the well-known, two-step anodization process described by Masuda and Fukuda [27], so only a brief summary of the anodization process will be described here. Aluminum foils (99.999%, Goodfellow Cambridge Ltd.) were electropolished in an electrolysate to obtain a mirror surface. Anodization was performed for 24 h in an oxalic acid (0.3 M) electrolyte, held at a temperature of 1 °C, and a constant potential of 40 V. The AAO formed was stripped in a chromic acid/phosphoric acid solution, and the anodization was performed once more under the same conditions. The same reactor was employed to grow films on Si(100) substrates for another hot-wall, flow-type ALD reactor. A more detailed description of this reactor is given in the Experimental section.

**ALD and QCM on Si(100):** The effects of ALD process parameters on the growth of iron oxide films were studied using a QCM in a flow-type, low-pressure ALD reactor described earlier [28]. The precursors (Fe(Cp)2 of 99% purity and O2 of 99.999% purity) were carried to the substrates in a flow of N2 (99.999% purity). An evaporation temperature of 55 °C for the Fe(Cp)2 yielded a sufficient partial pressure and was used in subsequent experiments. O2 was supplied through needle and solenoid valves that allowed control of the precursor pressure and pulse duration. The partial pressure of O2 was around 30 Pa in the reaction zone during the O2 pulse. The total pressure of the carrier gas and precursors measured at the reactor outlet was kept at 230–270 Pa.

Two series of depositions were made to study the ALD characteristics of the process. In the first series the ferrocene pulse length (t1) was varied between 1 s and 10 s, and the O2 pulse length to to maintain it at 8 s. In the second series the oxygen pulse length (t2) was varied between 2 and 8 s, and the Fe(Cp)2 pulse length was maintained at 2 s. In both series the purging pulses (t3 and t4) were set at 2 s, the deposition temperature was 350 °C, and all other process parameters were kept constant. The same reactor was employed to grow films on Si(100) substrates for post-growth measurements. In these experiments, the temperature of the Fe(Cp)2 source was stabilized at 55 °C, and the durations of the Fe(Cp)2 and O2 pulses were set at 3 and 7 s, respectively. After every precursor pulse the reaction zone was purged with nitrogen for 2 s to avoid overlapping of precursor pulses and to remove gaseous reaction products from the reactor. Thus, the duration of a complete deposition cycle was 14 s. The number of deposition cycles was varied from 200 to 700. The substrate temperatures, T substrate, used ranged from 350 to 600 °C.

**ALD on AAO:** Deposition of iron oxide on AAO was carried out in another hot-wall, flow-type ALD reactor. A more detailed description of this reactor can be found elsewhere [29]. The same precursors as earlier were employed in these experiments. All depositions were made under a total pressure of 260 Pa, with a total linear gas flow velocity of 1 m s⁻¹ and at a deposition temperature of 450 °C. The lengths of all the pulses, t1–t4, were set at 5 s and 150 deposition cycles were used to deposit an iron oxide film on the pore walls of the in-house-made AAO. The ALD process was followed by either a wet chemical process where silver rods were deposited [30] in the pores or a coating of glue on the film side of the samples. The last step was the removal of the template and the aluminum foil. The remaining aluminum foil was etched away using a solution consisting of 0.4 M CuCl₂ and 2.4 M HCl. The alumina membrane was then etched for 10 h in a 0.5 M sodium hydroxide solution, leaving free-standing iron oxide nanotubes supported by either silver rods or glue.

**Characterization:** The morphology of the samples was analyzed using high-resolution SEM (LEO 1530). The phase content was determined by GIXRD (Philips X’pert X-ray diffractometer) using Cu Kα radiation. The carbon residue in the deposited films and other possible contaminants as well as the oxidation state of iron were investigated using XPS (Perkin-Elmer PHI 5500 multi-technique system).

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