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Atomic layer deposition of Al_2O_3 films using $AlCl_3$ and $Al(O^iPr)_3$ as precursors

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Al_2O_3 films have been grown by atomic layer deposition (ALD) using reactions between $AlCl_3$ and $Al(O^iPr)_3$. In this process the aluminium alkoxide serves as both a metal and an oxygen source. No separate oxygen source is required. With this approach an Al_2O_3 film has been deposited on silicon without an interfacial silicon oxide layer. The film growth rate was 0.8 Å cycle^{-1}. The residual contents of chlorine, hydrogen and carbon in the film deposited at 300 °C were 1.8, 0.7 and <0.1 at.%, respectively. The chlorine content diminished rapidly with increasing growth temperature. The permittivities and leakage current densities were comparable to the conventional Al_2O_3 ALD processes for thick films, but the permittivity decreased for very thin films. Post deposition annealing is required to improve electrical properties of thin films.

1 Introduction

The growth of aluminium oxide films has received increasing attention becauce of their applications in electronic and optoelectronic devices and in protective and ion barrier layers, for example.[1–6] Al_2O_3 is an attractive dielectric because it has a large band gap (9 eV) and large band offsets with silicon, and it serves also as a good diffusion barrier. Though Al_2O_3 has relatively low permittivity (*ca.* 9) this is more than twice that (3.9) of the widely used SiO_2.[7]

The scaling of the metal-oxide-semiconductor field effect transistor (MOSFET) channel length to submicron feature sizes requires a corresponding reduction in the gate dielectric thickness to achieve high performance. Although SiO_2 remains the gate dielecric material of choice, SiO_2 is fast approaching its thickness limit. There are several challenging requirements for the alternative gate dielectrics which are essential for achieving devices with controlled characteristics.[8] In practice this means a well-defined low threshold voltage and a high transconductance obtained by having a minimum amount of charge trapped in the gate dielectric and at the semiconductor–dielectric interface.[9] It is known that a native oxide layer on the Si surface limits full exploitation of the high permittivity materials in very thin gate oxide films. Etching of Si in HF solutions results in hydrogen-terminated surfaces containing small amounts of adsorbed fluorine. Such surfaces are protective enough towards reoxidation during short air exposures.[10] On the HF-etched surface the interfacial SiO_2 layer may form by two mechanisms: (i) a reaction between silicon and high permittivity oxide, and (ii) oxidation of the silicon surface during the oxide deposition. The first mechanism can be avoided by choosing oxides which are more stable than SiO_2, like Al_2O_3.[11] The second mechanism requires careful control of the oxidation properties of the deposition environment, but even then often forces one to accept a thin interfacial layer.

One promising technique for controlled growth of very thin films is atomic layer deposition (ALD).[12] The basic idea of ALD, previously known also as atomic layer epitaxy (ALE), is an exploitation of sequential surface reactions resulting in a saturating monolayer or submonolayer growth during each step. This growth proceeds by exposing the substrate surface alternately to the precursors and, accordingly, the deposition process is based on alternate chemisorption of the precursors, surface reactions and desorption of the gaseous side-products. ALD offers self-limiting film growth ensuring large area uniformity, excellent conformality and simple film thickness control.[13–17]

Conventional ALD oxide processes are based on alternate metal and oxygen source pulses.[12] Especially in microelectronic devices where silicon is used as a substrate material the oxidation of the silicon surface may occur when the silicon surface is exposed for the first time to the oxygen source, normally water, hydrogen peroxide, ozone or oxygen.[12] During this first oxygen source pulse there is only a single monolayer of the metal compound on the silicon surface, which is usually not enough to prevent the silicon surface from oxidizing and an interfacial SiO_2 layer may easily form.

Aluminium oxide is maybe the most studied material in ALD. Many different precursor combinations have been examined. The Al precursors include $AlCl_3$,[4,18–20] $Al(CH_3)_3$,[16,21–27] $Al(C_2H_5)_3$,[28] $Al(CH)_2Cl$,[29] $Al(OEt)_3$[20] and $Al(O^iPr)_3$.[20] All can be combined with one of the separate oxygen sources mentioned above. Recently, a new chemical approach to ALD of metal oxides has been developed. In these processes the separate oxygen source was replaced with a metal alkoxide which reacted with a metal halide.[30] Reactions between metal halides and metal alkoxides are familiar already from solution studies where they have been used as a non-hydrolytic sol–gel route to oxides. These reactions involve thermally activated condensation between the halide and alkoxide groups, and lead to the formation of metal–oxygen–metal bridges and an alkyl halide as a by-product.[31–33] The film growth between $AlCl_3$ and $Al(O^iPr)_3$ to Al_2O_3 can be presented similarly

$$AlCl_3 + Al(OCH(CH_3)_2)_3 \rightarrow Al_2O_3 + 3((CH_3)_2CH)Cl \quad (1)$$

Reactions in non-hydrolytic sol–gel prosesses are typically rather slow, but at growth temperatures used in ALD the reactions can be accelerated. Another favorable reaction in solution, especially at low temperatures, is the redistribution of ligands leading to a mixture of halogenoalkoxides.[31]

In the metal alkoxides of highest interest for gate oxide

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deposition, the oxygen is strongly bonded to a metal that has a higher free energy of oxide formation than silicon, and thus it is reasonable to expect that such metal alkoxides would be less oxidizing towards silicon than the conventional oxygen sources. The main purpose of these water-free processes is to avoid the use of strong oxidants, especially in the beginning of the ALD growth process, and thereby prevent the formation of SiO_2. Recently, we demonstrated that with this new chemistry it is possible to deposit binary oxides like Ta_2O_5,[34] TiO_2 and Al_2O_3,[30] and also many different mixed oxides with various precursor combinations.[30,35,36] In this paper we examine the growth of Al_2O_3 using $AlCl_3$ and $Al(O^iPr)_3$ as precursors. Growth rate, film composition, and electrical properties are studied.

2 Experimental

A commercial F-120 ALD reactor (ASM Microchemistry Ltd) operated under a nitrogen pressure of about 10 mbar was used in the growth experiments. Nitrogen was used as the carrier and purging gas. The Al_2O_3 films were deposited on 535 cm^2 soda lime glass or silicon wafer pieces using $AlCl_3$ (Aldrich, 99.9%) and $Al(O^iPr)_3$ (Strem, +98%) as precursors. In some experiments $Al(OEt)_3$ (Strem, 99%) was also used. Before deposition, silicon wafer pieces were dipped into a dilute (1%) HF solution for 30 s and then dipped into water to remove the native oxide. Finally the silicon wafer pieces were blown dry with nitrogen. The precursors were evaporated inside the reactor and pulsed onto the substrates by means of inert gas valving. $AlCl_3$ was evaporated from an open boat held at 80 °C and $Al(O^iPr)_3$ at 110 °C. The pulse times were varied between 0.2 and 1.0 s. The purging time was constant at 0.5 s. The number of deposition cycles was varied between 64 and 2000 and the growth temperature from 150 to 375 °C.

Film thicknesses and refractive indexes were evaluated by fitting transmittance or reflectance spectra using a program developed and described by Ylilammi and Ranta-aho.[37] Spectra of the films grown were measured within a wavelength range of 370–1100 nm using a Hitachi U-2000 spectrophotometer. Thicknesses of very thin films were measured using a Bruker T8 Advance X-ray diffractometer/reflectometer by fitting reflectance spectra. Structural analysis was carried out with a Philips MPD 1880 powder X-ray diffractometer using Cu Kα radiation. The depth profiling of the film composition and residual contaminants was carried out using time-of-flight elastic recoil detection analysis (TOF-ERDA). A 34 MeV I^{9+} beam for TOF-ERDA was obtained from a 5 MV tandem accelerator EGP-10-II at the Accelerator Laboratory at the University of Helsinki. Averaged at.% concentrations were evaluated from depths of 40–120 nm. The chlorine contamination level was measured also by a Link ISIS Energy Dispersive X-ray spectrometer (EDX) installed to a Zeiss DSM 962 scanning electron microscope.

For the electrical measurements, MOS capacitors were defined by electron beam evaporating circular platinum electrodes through a shadow mask ($A = 3.14 \times 10^{-2}$ cm^2). Platinum back contacts completed the test devices. Electrical properties were measured using a Keithley 2400 SourceMeter and an HP4275A Precision LCR meter. Capacitances were measured at a frequency of 500 kHz. Heat treatments were carried out in a tubular furnace under a nitrogen atmosphere at 600 and 800 °C for 15 min.

3 Results and discussion

As is typical for Al_2O_3 deposited at moderate temperatures, the films grown were amorphous. The saturation of the growth rate at 0.8 Å cycle^{-1} with $Al(O^iPr)_3$ pulse times longer than 0.2 s is evident and thus no self-decomposition of $Al(O^iPr)_3$ appears to take place. This was confirmed by separate self-decomposition tests where only $Al(O^iPr)_3$ was pulsed onto substrates at 300 °C. However, when the pulse length of $Al(O^iPr)_3$ was increased in the growth experiments, thickness non-uniformity also increased. The refractive index sligthly increases from 1.62 to 1.65 with increasing $Al(O^iPr)_3$ pulse length from 0.2 to 1.0 s. The purge time, when varied from 0.5 to 1.0 s, had no effect on the deposition rate. The effect of $AlCl_3$ pulse length on the growth rate was also studied keeping the $Al(O^iPr)_3$ pulse length constant at 0.5 s. Increasing the $AlCl_3$ pulse length from 0.2 to 1.0 s led to a nearly linear increase in growth rate from 0.74 to 0.93 Å cycle^{-1}, indicating a slow reaction which is not fully saturated. The $AlCl_3$ precursor pulse length was chosen for later experiments as 0.2 s, *i.e.* as short as possible to reduce chlorine residues.

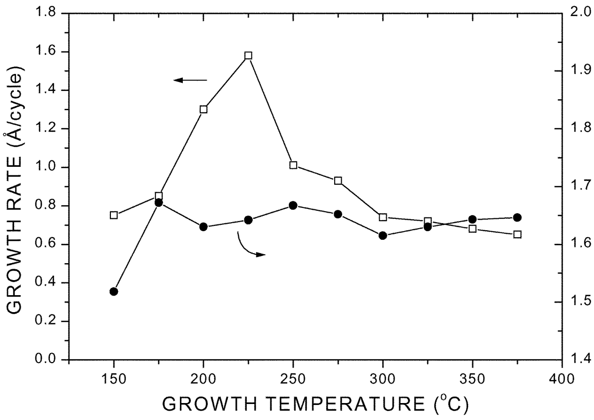

Fig. 1 Dependence of the Al_2O_3 growth rate (□) and refractive index (●) on growth temperature. The pulse lengths were 0.2 s for $AlCl_3$ and 0.5 s for $Al(O^iPr)_3$.

Fig. 1 shows the dependence of growth rate and refractive index on the deposition temperature. A maximum growth rate of *ca.* 1.6 Å cycle^{-1} is observed at 225 °C. At this temperature the chlorine content is higher than 11 at.%, but with increasing temperature the chlorine content decreased to 1 at.%. Possible formation of aluminium oxochlorides at low temperatures can explain why the chlorine content decreases suddenly within a narrow growth temperature region from 225 to 275 °C. Below 225 °C the decrease in the growth rate can be explained by incomplete, kinetically limited surface reactions. It was also observed that the films deposited below 225 °C were not stable in air. Within a temperature range of 225–375 °C the growth rate decreases with an increase in temperature. This is probably caused by a reduction in the amount of reactive surface sites, for example through –OR decomposition, or by a transformation of precursor species from dimers to monomers with increasing reactor temperature. The increase in the deposition temperature improves the purity and uniformity of the films. The optimum growth temperature seems to be 300 °C because at 250 °C strong thickness non-uniformity is measured across the substrate, probably due to the formation of oxochlorides. Similar film thickness non-uniformity is observed at 350 °C where $Al(O^iPr)_3$ starts to decompose thermally.

The growth seems to start somewhat slowly on HF-etched silicon. After about 150 cycles the growth behaviour is linear and film thickness is easy to control *via* the number of reaction cycles.

The growth rate is higher in this new process as compared with the traditional $AlCl_3$–H_2O ALD oxide process.[38] This can be explained in that both precursors deposit aluminium, whereas in the $AlCl_3$–H_2O system only one of the precursors deposits aluminium. The growth temperature region is narrower in the new process because $Al(O^iPr)_3$ starts to decompose at temperatures above 300 °C.

Some experiments were carried out also with the

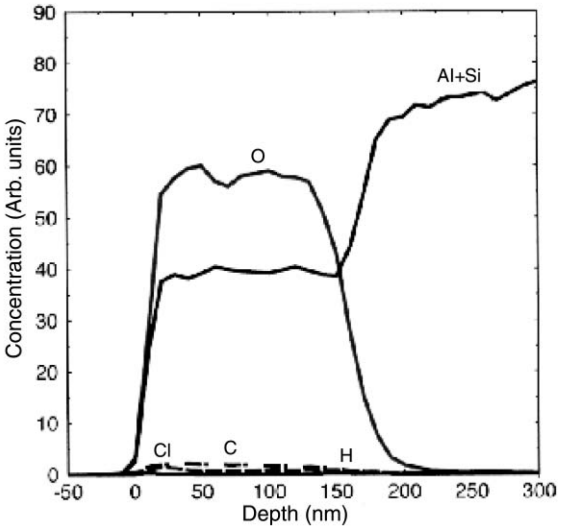

Fig. 2 Composition depth profile in the Al_2O_3 film deposited at 300 °C (TOF-ERDA). The $AlCl_3$ and $Al(O^iPr)_3$ pulse lengths were 0.2 and 0.5 s, respectively. The film thickness was 147 nm.

$AlCl_3$–$Al(OEt)_3$ combination. With this process, growth occured just at 400 °C, whereas with $Al(O^iPr)_3$ the reactions took place and growth already occurred at 150 °C. Because these reactions are based on the ability of the O–R bond to split, they are governed by the nature of both the carbon group and the halogen. Reactions are promoted if the alkyl group R is able to stabilize a positive charge. Therefore a more branched R leads to more facile reactions. A similar trend was also noticed in non-hydrolytic sol–gel studies.[31,39]

An example of the TOF-ERDA depth profile is depicted in Fig. 2. The film composition is relatively homogeneous through the film. The contents of hydrogen, chlorine and carbon are high in the films deposited below 300 °C, but the impurity contents decrease rapidly when the temperature increases. The chlorine contents measured by EDX and TOF-ERDA compare well. Under the optimized conditions at 300 °C, the film contains 1.8 at.% chlorine, 0.7 at.% hydrogen and <0.1 at.% carbon.

Because one important application for Al_2O_3 is the gate oxide in MOSFETs, the Si–Al_2O_3 interface is important. One result of this work is that there is no discernable interfacial layer between silicon and aluminium oxide (Fig. 3). Even if the bright zone was oxidized silicon, it is only a monolayer thick and thus represents an atomic level interface. This indicates that with this new approach of the ALD method it is possible to avoid oxidizing the silicon surface during the growth process.

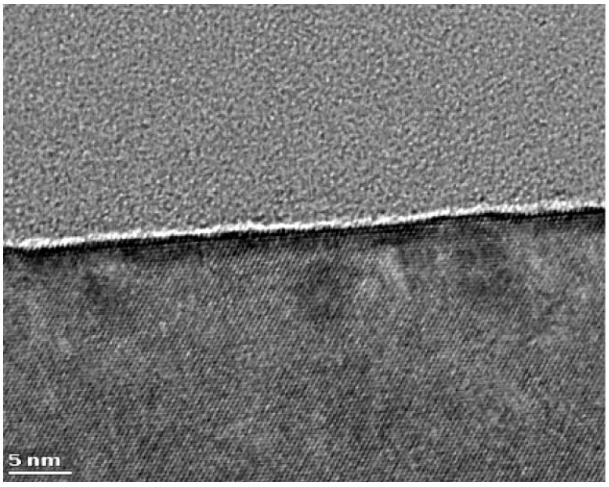

Fig. 3 High-resolution transmission electron microscope image of the interface between a silicon substrate and Al_2O_3 film grown at 300 °C. The $AlCl_3$ and $Al(O^iPr)_3$ pulse lengths were 0.2 and 0.5 s, respectively.

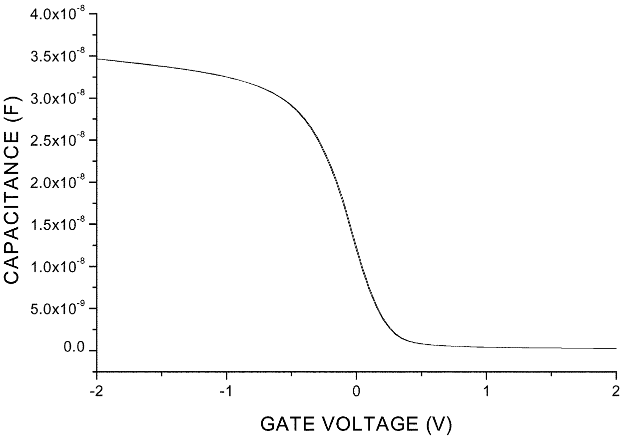

Fig. 4 Capacitance–voltage characteristics of a 4.4 nm Al_2O_3 film grown at 300 °C, and annealed at 600 °C. The measurement frequency was 500 kHz. The data were recorded from accumulation to inversion, and back to accumulation.

The capacitance–voltage characteristics of a 4.4 nm thick Al_2O_3 film grown at 300 °C and annealed at 600 °C for 15 min in nitrogen is presented in Fig. 4. The flatband voltage V_{FB} is *ca.* −0.1 V. There is no detectable hysteresis in the films. Anomalous dielectric permittivity behaviour is observed with different film thicknesses. With sufficiently thick Al_2O_3 films (>30 nm) the permittivities seemed to saturate to a level of 8–9. For thin films (<30 nm) the permittivity decreased to 5–7. Similar phenomena have been noticed earlier and different explanations have been considered.[40–42] Strong capacitance and permittivity dependence is observed as a function of frequency. Leakage current is quite high for Al_2O_3 with this kind of thickness [4.4 nm (10^{-4} A cm^{-2} at an electric field 2 MV cm^{-1})] and obviously affects the capacitance dispersion. For films thicker than 100 nm, leakage current densities of 10^{-7} A cm^{-2} were measured at an electric field of 2.0 MV cm^{-1} with In_2O_3:Sn–insulator–Al structure. The dielectric properties of the films deposited at higher temperatures were generally better than those of the films grown at low temperature. This is probably due to the higher residual content and lower density of the films deposited at lower temperatures.

Heat treatment at 600 °C improved electrical properties remarkably compared to as-deposited films, which is probably caused mainly by a decrease of impurities. Annealing at 800 °C for 15 min leads to a significant decrease of permittivity. The measured X-ray diffraction pattern indicated the crystallization of Al_2O_3.

4 Conclusions

Al_2O_3 thin films were deposited by atomic layer deposition *via* sequential surface reactions of $AlCl_3$ and $Al(O^iPr)_3$ in the temperature range of 150–375 °C. The metal chloride–metal alkoxide chemistry is an effective way to deposit films without water or other rather oxidizing oxygen sources, which is important especially in microelectronic devices where silicon is used as a substrate material. With this approach an Al_2O_3 film was deposited without forming an interfacial layer. The structure of the metal alkoxide has a crucial effect on growth onset temperature and rate. In the case of $AlCl_3$ and $Al(O^iPr)_3$ at optimum precursor pulse lengths, a growth rate of *ca.* 0.8 Å $cycle^{-1}$ was determined at 300 °C. The film compositions were homogenous throughout the film. The residual contents of chlorine, hydrogen and carbon in the films deposited at 300 °C were 1.8, 0.7 and <0.1 at.%, respectively. Anomalous dielectric permittivity behaviour with different film thicknesses was observed. For films thicker than 30 nm the permittivities were 8–9 and leakage current densities were typically 10^{-6} A cm^{-2} at an electric field strength of 2 MV cm^{-1}. Permittivities of very thin films were remarkably lower[5–7] compared to thicker films and bulk values. Strong frequency dependence was observed for the capacitance/permittivity values. Also, leakage current densities were rather high for the thin films. Optimized post-deposition heat treatment is necessary to improve the electrical properties and to reduce the amount of residual contaminants.

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