

Atomic Layer Deposition and Characterization of Aluminum Silicate Thin Films for Optical Applications

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Optical multilayer interference coatings rely on the refractive index differences and specific thicknesses of the low and high refractive index materials used in optical multilayer structures. An accurate control of important parameters such as film thicknesses, uniformities, and refractive indexes is demanding. Atomic layer deposition (ALD) inherently possesses many characteristics beneficial for obtaining fully conformal and uniform films of specific thicknesses with excellent repeatability. Additionally, the layer-by-layer deposition of the films allows tuning of the film stack properties, such as refractive index, which is an advantage when designing optical filters. By now, Al_2O_3 has been most often used as a low refractive index from that of Al_2O_3 , we have developed and examined various ALD processes of aluminum silicate thin films. We concentrate on reporting the refractive indexes, growth rates, and compositions of the films as these parameters are vital for screening suitable ALD processes for optical applications. By varying the amount of silicon in the $Al_XSi_YO_Z$ thin films, the refractive indexes between 1.47 and 1.59 were obtained in this study.

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Atomic layer deposition $(ALD)^{1-4}$ is one of the most attractive thin film deposition methods in applications where film conformality, uniformity, thickness controllability, and repeatability are crucial. These characteristics make ALD a potential technique for the deposition of optical multilayer interference coatings, such as antireflection coatings, neutral beam splitters, high-reflection coatings, and Fabry–Perot filters.⁵

In general, optical multilayer structures consist of stacks of alternating high and low refractive index materials of specific thicknesses. TiO₂, Ta₂O₅, and Nb₂O₅ are commonly applied for the high refractive index layers, while SiO₂ and MgF₂ are common material choices for the low refractive index layers. The development of appropriate, robust SiO₂ processes has been challenging in ALD for a long time because of the lack of proper silicon precursors, in particular for processes using water as an oxygen source. The use of H₂O₂ as an oxidant instead of H₂O produces better results.⁶ However, several water based processes have been developed which rely on the use of catalysts, e.g., pyridine and ammonia,⁷⁻⁹ but these processes work only at low temperatures close to room temperature where metal oxide processes typically cannot be used for the multilayer growth. With ozone as an oxygen source, SiO_2 films have been deposited using aminosilane based precursors.^{T0,11} Ozone based processes can be combined with additional H_2O exposures to facilitate Si precursor adsorption on hydroxyl sites.¹²⁻¹⁴ Also Si₂Cl₆ can be used with ozone, but the film growth requires higher deposition temperatures.¹⁵ Despite the recent advances in ALD SiO₂, there is still need for studies on alternative approaches to low refractive index materials. While the development of binary SiO₂ processes has been difficult for ALD, ternary mixtures containing SiO₂ have been much easier to deposit with ALD. Therefore, to approach the refractive index level of pure SiO_2 (n = 1.45), mixing SiO_2 with other low refractive index ALD materials, Al_2O_3 (n = 1.65) in particular, may be employed.

Because of the layer-by-layer deposition scheme in ALD, process controllability is generally considered superior compared to many other thin film deposition methods.¹ Not only binary compounds can be deposited, but processes for mixed oxides and nanolaminates have also been developed.¹⁶⁻²¹ Ritala et al.²² described an ALD pro-

cess group where a metal alkoxide serves as both an oxygen and a metal source compared to water or ozone as a plain oxygen source in common ALD oxide processes. Therefore, by employing alternating pulses of a metal alkoxide with another metal source, such as a metal halide or a metal alkyl, mixed oxides can be deposited. This also allows silicon to be incorporated into the oxide materials.

Hausmann et al.²³ introduced an $Al_XSi_YO_Z$ ALD process where alternating tris(*tert*-butoxy)silanol and trimethylaluminum pulses produced the growth rates up to 12 nm/cycle by a catalytic reaction between the precursors. However, with these unprecedentedly high growth rates, film thicknesses cannot be adjusted with a precision desired in optical multilayers. Likewise, using AlCl₃ instead of trimethylaluminum produced the growth rates of 0.8 and 7.8 nm/cycle depending on the length of the tris(*tert*-butoxy)silanol pulse.²⁴ The aluminum silicate films have also been deposited using AlCl₃, tetramethoxysilane, and water as the precursors.²⁵ Plasma-enhanced ALD has been employed using TMA and tetraethoxysilane with O₂ plasma.^{26,27}

The present paper summarizes some of the key properties of the $Al_XSi_YO_Z$ films obtained by ALD from various precursor combinations derived and modified from the previously developed metal alkoxide–metal halide/alkyl chemistries. As the motivation arises from optical applications, the emphasis is on refractive index, growth rate, and film composition; even though the $Al_XSi_YO_Z$ films may also be adapted for insulating and protective film applications.²⁸

Experimental

The $Al_x Si_y O_z$ thin films were deposited in a hot-wall flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Helsinki, Finland) operated under about 10 mbar of nitrogen pressure. Nitrogen (99.9995%) was produced with a NITROX UHPN 3000 nitrogen generator and used as a carrier and a purging gas. The thin films were grown on 5×5 cm² borosilicate glass and unpolished silicon substrates between 150 and 500°C. Approximately 100 nm thick layers of Ta_2O_5 were deposited from tantalum ethoxide and water²⁹⁻³¹ prior to the Al-Si-O₂ films to allow an accurate refractive water prior to the $Al_xSi_yO_7$ films to allow an accurate refractive index measurement of films on glass. High vapor pressure precursors were held in source bottles outside the reactor and delivered through a needle and solenoid valves into the reactor. Contrary, low vapor pressure precursors were vaporized inside the reactor and pulsed with an inert gas valving. A summary of the precursors used in the processes is presented in Table I.

The thicknesses and refractive indexes of the films were evaluated by fitting transmittance spectra.³² The spectra were measured in

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| Table I. | Summary | of the | precursors | used in | this study. |
|-----------|---------|--------|------------|---------|-------------|
| I unit II | Summary | or the | precuisors | ubeu m | uns study. |

| Precursor | Abbreviation | Manufacturer | Purity (%) | Source location | Sublimation/ evaporation temperature (°C) |
|--|---------------------------------------|-----------------|---------------|--------------------|--|
| tetrachlorosilane | SiCl ₄ | Fluka Chemika | ≥99 | external | -20 |
| SiCl ₄ | 7 | | | | |
| tetramethylsilane $Si(CH_3)_4$ | SiMe ₄ | Fluka Chemika | ≥99 | external | -20 to -23 |
| tetraethoxysilane Si $(OC_2H_5)_4$ | Si(OEt) ₄ | | | external | 45 |
| tetrabutoxysilane Si $(OC_4H_9)_4$ | $\mathrm{Si}(\mathrm{OBu})_4$ | Strem Chemicals | ≥97 | internal | 55-60 |
| tri-t-butoxysilanol Si[OC(CH ₃) ₃] ₃ OH | (^t BuO) ₃ SiOH | Gelest | | internal | 32–35 |
| aluminum chloride AlCl ₃ | AlCl ₃ | Riedel-de Haën | 98 | internal | 90 |
| dimethylaluminum chloride Al(CH ₂) ₂ Cl | AlMe ₂ Cl | Witco | | external | RT ^a |
| trimethylaluminum Al(CH ₂) ₂ | AlMe ₃ | Witco | | external | RT |
| aluminum ethoxide Al(OC ₂ H ₅) ₂ | Al(OEt) ₃ | Strem Chemicals | 99 | internal | 135 |
| aluminum isopropoxide | Al(O ⁱ Pr) ₃ | Strem Chemicals | 98+ | internal | 100–110 |
| All OCH(CH ₃) ₂] ₃ deionized water H_2O | H ₂ O | | | external | RT |

^a RT denotes room temperature.

the wavelength region of 370–1100 nm by a Hitachi U-2000 spectrophotometer. The refractive indexes are reported at the wavelength of 580 nm. Elemental compositions of the Al_XSi_YO_Z films were determined with a time-of-flight elastic recoil detection analysis (TOF-ERDA) using a beam of 53 MeV ¹²⁵I¹⁰⁺ or 58 MeV ¹²⁷I¹¹⁺ ions.³³ Crystallinity of the films was examined using grazing incidence X-ray diffraction (GIXRD) patterns measured with a PANalytical X'Pert Pro X-ray diffractometer.

Results and Discussion

The precursor combinations tested for $Al_XSi_YO_Z$ processes are presented in Table II. In many cases, alternating pulses of silicon alkoxide and aluminum precursors did not result in the film growth. However, when water pulses were added to the processes, it was possible to obtain films that had lower refractive indexes than the films obtained using only an aluminum precursor and water (n_{580}

| Process | Dep. temp. (°C) | Growth rate (Å cycle ⁻¹) | Refractive index (n ₅₈₀) |
|---|--------------------|---|--------------------------------------|
| Si(OBu) ₄ –AlCl ₃ | 150-500 | 1.47-4.56 | 1.48-1.54 |
| Si(OBu) ₄ -AlCl ₃ -H ₂ O | 250, 300 | 1.24-2.75 | 1.52-1.62 |
| Si(OBu) ₄ -AlMe ₂ Cl | 200-400 | a | |
| Si(OBu) ₄ -AlMe ₂ Cl-H ₂ O | 150-400 | 0.57-0.93 | 1.50-1.62 |
| Si(OBu) ₄ -AlMe ₃ | 200-500 | | |
| Si(OBu) ₄ -AlMe ₃ -H ₂ O | 150–350 | 0.50-1.21 | 1.53-1.64 |
| Si(OBu) ₄ -Al(OEt) ₃ | 300 | _ | |
| Si(OEt) ₄ -AlCl ₃ -H ₂ O | 200-500 | 1.20 (300°C) | 1.56 (300°C) |
| Si(OEt) ₄ -AlMe ₂ Cl-H ₂ O | 200-500 | 0.58-0.88 | 1.58-1.60 |
| Si(OEt) ₄ -AlMe ₃ -H ₂ O | 200-400 | 0.57-0.86 | 1.58-1.61 |
| $SiCl_4-Al(OEt)_3$ | 300–500 | | |
| $SiCl_4$ -Al(O ⁱ Pr) ₃ | 200-500 | | |
| $SiMe_4$ -Al(OEt) ₃ | 200–500 | _ | |
| SiMe ₄ -Al(OEt) ₃ -H ₂ O | 200, 500 | | |
| (^t BuO) ₃ SiOH–AlCl ₃ | 200-400 | 8.16-9.14 | 1.47 |
| (^t BuO) ₃ SiOH–AlCl ₃ –H ₂ O | 200-500 | 7.90-11.22 | 1.45-1.48 |
| (^t BuO) ₃ SiOH–AlMe ₃ | 250, 300 | 8.50-11.20 | 1.48-1.51 |
| (^t BuO) ₃ SiOH–AlMe ₃ –H ₂ O | 300 | 8.18-8.52 | 1.49 |

Table II. The deposition temperatures, refractive indexes, and growth rates of the studied $Al_X Si_Y O_Z$ processes.

^a Sign [--] means that film deposition was unsuccessful.

Table III. SiO₂ deposition tests with different Si precursors. None of the precursor combinations or self-decomposition tests resulted in the film growth.

Table IV. The elemental compositions and refractive indexes of the Al_xSi_yO_z films deposited with Si(OBu)₄-AlCl₃ and Si(OBu)₄-H₂O-AlCl₃-H₂O pulse sequences. The Si(OBu)₄ pulse length was 1 s (3 s at 3).

| Process | Dep. temp. (°C) | Pulse sequence | 1 | 2 | 3 | 4 |
|---|--------------------|------------------|----------------------|----------------------|----------------------|-------------------|
| Si(OBu) ₄ | 500 | | | | | Si(OBu |
| Si(OBu) ₄ -H ₂ O | 300, 500 | | | | | H ₂ O |
| Si(OBu) ₄ -SiMe ₄ | 200-500 | | Si(OBu) ₄ | Si(OBu) ₄ | Si(OBu) ₄ | AlCl ₃ |
| Si(OBu) ₄ -SiMe ₄ -H ₂ O | 200, 500 | | AlCl ₃ | AlCl ₃ | AlCl ₃ | H ₂ O |
| Si(OEt) ₄ -H ₂ O | 300, 500 | | | | | |
| (^t BuO) ₃ SiOH | 500 | dep. temp. (°C) | 200 | 300 | 500 | 300 |
| (^t BuO) ₂ SiOH–H ₂ O | 300, 500 | n ₅₈₀ | 1.51 | 1.49 | 1.49 | 1.57 |
| (= = =)3===== ==2= | , | O (atom %) | 51 | 56 | 55 | 60 |

 \sim 1.65), hence implying that silicon was incorporated into the films. Table III shows deposition tests where growth of SiO₂ was attempted from different silicon precursors. However, none of the precursor combinations or self-decomposition tests resulted in the film growth. This implies that an aluminum precursor was always needed for the successful film growth. But even then, only the silicon alkoxides resulted in the film growth, while SiCl₄ and SiMe₄ did not.

 $Si(OBu)_4$ precursor.— $Si(OBu)_4$ -AlCl₃.— The Si(OBu)_4-AlCl₃ process was studied at the deposition temperatures between 150 and 500°C. At 200°C and higher temperatures, the films were uniform over the substrate. The pulse length of Si(OBu)₄ had a strong effect on both the growth rate and the refractive index at 200 and 300°C (Fig. 1). The growth rates and refractive indexes of over 2 Å/cycle and about 1.50 were achieved at 300°C, respectively, when the $Si(OBu)_4$ pulse length was 0.5 s or more. Longer $Si(OBu)_4$ pulses were needed for the similar growth rates and refractive indexes at 200°C. However, it seems that the saturation of growth rates was not achieved with these pulse lengths, which indicates slow surface reactions on the substrates.

The elemental analysis (Table IV) reveals that the Si/(Si + Al)ratio increases with increasing the deposition temperature. The high amount of chlorine (6 atom %) in the film deposited at 300°C may be an additional reason for the low refractive index. At 500°C, 20 atom % of Si has been incorporated into the film, which is four times the amount of Al (5 atom %). As expected, higher deposition temperatures decrease the carbon and chlorine impurity contents in the films. Conversely, hydrogen contents are remarkably high compared to the other impurities at low and high deposition temperatures. The low carbon content indicates that hydrogen impurity does not originate from the butoxide ligands, so the high hydrogen content may be related to hydroxyl groups. As H2O has not been used in



Figure 1. The growth rate (\Box, \blacksquare) and refractive index (\bigcirc, \bullet) of the $Al_XSi_YO_Z$ films as a function of Si(OBu)₄ pulse length. The deposition temperatures were 200 (\Box , \bigcirc) and 300°C (\blacksquare , \bullet).

| | Si(OBu) ₄ AlCl ₃ | Si(OBu) ₄ AlCl ₃ | Si(OBu) ₄ AlCl ₃ | Si(OBu) H ₂ O AlCl ₃ H ₂ O |
|--------------------|---|---|---|--|
| dep. temp. (°C) | 200 | 300 | 500 | 300 |
| n ₅₈₀ | 1.51 | 1.49 | 1.49 | 1.57 |
| O (atom %) | 51 | 56 | 55 | 60 |
| Si (atom %) | 10 | 17 | 20 | 12 |
| Al (atom %) | 16 | 17 | 5 | 23 |
| H (atom %) | >18 | 4 | 17 | 3 |
| C (atom %) | 0.9 | 0.7 | < 0.1 | 0.3 |
| Cl (atom %) | 4 | 6 | 0.7 | 1.6 |
| Si/(Si + Al) ratio | 0.38 | 0.50 | 0.80 | 0.34 |
| | | | | |

these depositions, the high hydrogen impurities result presumably from the air exposures of the films after deposition.

 $Si(OBu)_4$ -AlCl₃-H₂O. Adding a water pulse after the AlCl₃ pulse decreased the growth rate and increased refractive index substantially compared to the water-free process (Fig. 2). Similarly, adding water pulses after the Si(OBu)₄ and the AlCl₃ precursors increased the refractive index, however, the H₂O pulse after the AlCl₃ pulse had more a decisive effect on the refractive index. The process exploiting water pulses produces $Al_x Si_y O_z$ film with lower silicon content (12 atom %) and higher Al content (23 atom %) than the process without water pulses (Table IV). The impurity content is considerably lower in the film deposited with the water containing process. The carbon content decreases to less than half (0.3 atom %)and the chlorine content decreases to almost one-fourth (1.6 atom %) compared to the water-free process at the same deposition temperature. Increasing the Si(OBu)₄ pulse length increases the growth rate and decreases the refractive index, as can be seen in Fig. 3. However, the growth rates are lower and the refractive indexes are higher than in the water-free process (Fig. 2). While the effect of the water pulses is to drive the process toward Al₂O₃, the growth rate is still substantially higher and the refractive index is lower than in the AlCl₃-H₂O process of an undoped AlCl₃-H₂O (0.77-0.97 Å/cycle and 1.64-1.67).

 $Si(OBu)_4$ -AlMe₂Cl-H₂O.— In order to decrease the chlorine content in the Al_xSi_yO_z films, AlMe₂Cl precursor was used in place of AlCl₃. The water-free process did not result in the film growth at the



Figure 2. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_XSi_YO_Z films with different pulsing sequences. The deposition temperature was 300°C and pulse length of the Si(OBu)₄ was 1 s.



Figure 3. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_XSi_YO_Z films as a function of the Si(OBu)₄ pulse length when H₂O was pulsed after the AlCl₃ pulse. The deposition temperature was 300°C.

deposition temperatures between 200 and 400°C (Table II). The highest growth rates were obtained with the Si(OBu)₄ + H₂O + AlMe₂Cl and Si(OBu)₄ + H₂O + AlMe₂Cl + H₂O pulse sequences, but the Si(OBu)₄ + H₂O + AlMe₂Cl + H₂O pulse sequence resulted in the lowest refractive index as can be seen in Fig. 4. Doubling the Si(OBu)₄ pulse length to 2 s did not have a significant effect on the growth rates and refractive indexes. Table V shows that the chlorine content (1.1 atom %) of the film deposited at 300°C is lower than the films deposited using AlCl₃ and water pulses (1.6 atom %) (Table IV). The carbon content of the films is 2.9–3.5 atom % (Table V), whereas in the processes using AlCl₃ (Table IV) the carbon content is substantially lower (0.1–0.9 atom %).

The growth rate and refractive index are shown in Fig. 5 as a function of the deposition temperature when water was pulsed after both the Si(OBu)₄ and AlMe₂Cl precursors. The growth rates and refractive indexes increase with increasing the deposition temperature and reach up to 0.9 Å/cycle and 1.58 at 300°C, respectively. The amount of silicon incorporated into the films increases as a function of the deposition temperature (Table V). The refractive index also increases along with the temperature, which may result from the lower amount of impurities. Although AlMe₂Cl precursor produces lower chlorine content (1.1 atom %) than AlCl₃ (1.6 atom



Figure 4. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_xSi_yO_z films with different pulse sequences. The deposition temperature was 300°C. The pulse length of Si(OBu)₄ was 1 s; in the two right-sided sequences it was 2 s.

Table V. The elemental compositions of the $Al_xSi_yO_z$ films deposited with $Si(OBu)_4 + H_2O + AlMe_2Cl + H_2O$ and $Si(OBu)_4 + AlMe_2Cl + H_2O$ pulse sequences. The $Si(OBu)_4$ pulse length was 1 s.

| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | Pulse sequence | 5 | 6 | 7 | 8 |
|--|--|--|--|--|--|
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | $Si(OBu)_4 \\ H_2O \\ AlMe_2Cl \\ H_2O \\ H_2O$ | $\begin{array}{c} \text{Si(OBu)}_4\\ \text{H}_2\text{O}\\ \text{AlMe}_2\text{Cl}\\ \text{H}_2\text{O} \end{array}$ | $\begin{array}{c} \text{Si(OBu)}_4\\ \text{H}_2\text{O}\\ \text{AlMe}_2\text{Cl}\\ \text{H}_2\text{O} \end{array}$ | Si(OBu) ₄ AlMe ₂ Cl H ₂ O |
| Cl (atom %) 2.3 1.2 1.1 1.2 | dep. temp. (°C) n ₅₈₀ O (atom %) Si (atom %) Al (atom %) H (atom %) C (atom %) Cl (atom %) | 200 1.53 50 3 28 13 3.5 2.3 | 250 1.57 52 5 29 10 2.9 1.2 | 300 1.58 60 6 21 9 3.1 1.1 | 300 1.56 53 7 25 10 3.5 1.2 |

%), less silicon is incorporated into the film. Additionally, hydrogen and carbon contents are higher with AlMe₂Cl (9 and 3.1 atom %) than with AlCl₃ (3 and 0.3 atom %).

 $Si(OBu)_4$ - $AlMe_3$ - H_2O .— The water-free Si(OBu)_4-AlMe_3 process did not produce any film growth between the deposition temperatures of 200 and 500°C, but by adding water pulses, films were successfully grown. The growth rates and refractive indexes of the $Al_XSi_YO_Z$ films deposited by different pulse sequences are shown in Table VI. The refractive indexes seem to correspond with the refractive indexes of the Si(OBu)_4-AlMe_2Cl-H_2O processes (Fig. 5). The growth rates of the films in the Si(OBu)_4-AlMe_3-H_2O processes have a similar tendency as in the Si(OBu)_4-AlMe_2Cl-H_2O pro-



Figure 5. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_XSi_YO_Z films as a function of the deposition temperature. The pulse length of the Si(OBu)₄ was 1 s.

| Table VI. The growth rates and refractive indexes of | the |
|--|------|
| Al _x Si _y O _z films deposited with different pulse sequences. | Гhe |
| deposition temperature was 300°C. Si(OBu) ₄ pulse length wa | is 1 |
| or 2 s. | |

| Pulse sequence | Growth rate (Å/cycle) | Refractive index (n_{580}) |
|------------------------------------|-----------------------|------------------------------|
| $Si(OBu)_4 + H_2O + AlMe_3$ | 0.99 | 1.64 |
| $Si(OBu)_4 + AlMe_3 + H_2O$ | 0.47 | 1.59 |
| $Si(OBu)_4(2 s) + AlMe_3 + H_2O$ | 0.55 | 1.57 |
| $Si(OBu)_4 + H_2O + AlMe_3 + H_2O$ | 0.68 | 1.58 |



Figure 6. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_XSi_YO_Z films as a function of the deposition temperature. The pulse length of Si(OBu)₄ was 1 s.

cesses: If the H_2O pulse was given after the Al precursor, the growth rate was considerably lower than if the H_2O pulse was given after the Si precursor.

The pulse sequence $Si(OBu)_4 + H_2O + AlMe_3 + H_2O$ was studied at a deposition temperature range between 150 and 350°C (Fig. 6). The growth rate is almost constant (~ 0.7 Å/cycle) between 200 and 350°C, but the refractive index increases from 1.50 to 1.60 while the temperature increases from 150 to 325°C. At the same time, the amount of silicon in the films increases with the deposition temperature (Table VII). Therefore, the increase in the refractive indexes must be due to the decrease of the hydrogen and carbon impurity contents in the films (Table VII). A comparison of the Si(OBu)_4 + H_2O + AlMe_3 + H_2O pulse sequence to the corresponding pulse sequence using the AlMe_2Cl precursor reveals that the processes are very similar.

 $Si(OEt)_4$ precursor.— $Si(OEt)_4$ — $AlCl_3$ — H_2O .— Some experiments were performed using Si(OEt)_4, AlCl_3, and water as precursors between 200 and 500°C. The water pulse was added after both the precursors. The growth rates of the films deposited at 200 and 300°C were 1.2 Å/cycle, while the refractive index was 1.56 at 300°C. The films deposited at higher temperatures (400 and 500°C) could not be measured due to nonuniformity of the films.

 $Si(OEt)_4$ - $AlMe_2Cl-H_2O$.— The growth rate of the films as a function of the deposition temperature is shown in Fig. 7. The water pulse was added after both the Si(OEt)_4 and AlMe_2Cl precursors. The growth rate decreases as the deposition temperature is in-

Table VII. The elemental compositions of the $Al_{x}Si_{y}O_{z}$ films deposited with $Si(OBu)_{4}$ + $H_{2}O$ + $AlMe_{3}$ + $H_{2}O$ pulse sequence. The $Si(OBu)_{4}$ pulse length was 1 s.

| Pulse sequence | 9 | 10 | 11 |
|--------------------|----------------------|----------------------|----------------------|
| | Si(OBu) ₄ | Si(OBu) ₄ | Si(OBu) ₄ |
| | H ₂ O | H ₂ O | H ₂ O |
| | AlMe ₃ | AlMe ₃ | AlMe ₃ |
| | H ₂ O | H ₂ O | H ₂ O |
| dep. temp. (°C) | 200 | 250 | 300 |
| n ₅₈₀ | 1.52 | 1.56 | 1.58 |
| O (atom %) | 49 | 52 | 52 |
| Si (atom %) | 4 | 5 | 6 |
| Al (atom %) | 27 | 27 | 27 |
| H (atom %) | >15 | 12 | 11 |
| C (atom %) | 5 | 3.5 | 3.2 |
| Cl (atom %) | ≪0.1 | ≪0.1 | ≪0.1 |
| Si/(Si + Al) ratio | 0.13 | 0.16 | 0.18 |



Figure 7. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_xSi_yO_z films as a function of the deposition temperature. The pulse lengths of Si(OEt)₄ were 1 and 3 s.

creased, but the refractive index remains constant. Increasing the $Si(OEt)_4$ pulse from 1 to 3 s did not have an effect on the growth rates or the refractive indexes.

 $Si(OEt)_4$ - $AlMe_3$ - H_2O .— The $Si(OEt)_4$ + H_2O + $AlMe_3$ + H_2O pulsing sequence resulted in the same growth rate (0.8 Å/cycle) and the refractive index (1.59) when the films were deposited between 200 and 300°C. At 400°C, the growth rate and refractive index were a bit lower. Increasing the length of the Si(OEt)_4 pulse from 1 to 3 s at 300°C did not cause any significant changes to the refractive index or to the growth rate. The Si(OEt)_4 + H_2O + AlMe_3 + H_2O pulsing sequence produces almost the same refractive indexes and growth rates as the Si(OEt)_4 + H_2O + AlMe_2Cl + H_2O pulsing sequence. The TOF-ERDA results of the films deposited at 300 and 400°C are shown in Table VIII and it can be seen that the differences in the elemental contents are small.

 $({}^{t}BuO)_{3}SiOH$ precursor.— $({}^{t}BuO)_{3}SiOH$ —AlCl₃.— He et al.²⁴ studied the film growth by alternating pulses of $({}^{t}BuO)_{3}SiOH$ and AlCl₃ on H-terminated Si(100) at 240°C. They found that with the $({}^{t}BuO)_{3}SiOH$ pulse lengths of 0.8 s and 15 s, the growth rates were 8 and 78 Å/cycle, respectively. The 78 Å/cycle growth rate implies that the process deposits more than one molecular layer per cycle and that it is not possible to control the film thickness with a nanometer-level accuracy. In our study, the growth rate was 9.1 Å/cycle at 300°C with 4 s (${}^{t}BuO)_{3}SiOH$ pulse length and the refractive index was 1.47.

| Table | VIII. | The | elemental | compositions | of the | Al _X Si _Y | O _Z films |
|--------|---------|--------|----------------|-----------------|--------------------|---------------------------------|----------------------|
| deposi | ited wi | ith Si | $i(OEt)_4 + 1$ | $H_2O + AlMe_3$ | + H ₂ O | pulse s | equence. |
| The S | i(OEt) | 4 pul | se length v | was 1 s. | | | |

| Pulse sequence | 12 | 13 |
|--------------------|----------------------|----------------------|
| | Si(OEt) ₄ | Si(OEt) ₄ |
| | H ₂ O | H_2O |
| | AlMe ₃ | AlMe ₃ |
| | H ₂ O | H ₂ O |
| dep. temp. (°C) | 300 | 400 |
| n ₅₈₀ | 1.59 | 1.58 |
| O (atom %) | 53 | 56 |
| Si (atom %) | 6 | 5 |
| Al (atom %) | 27 | 29 |
| H (atom %) | 10 | 8 |
| C (atom %) | 4 | 2 |
| Cl (atom %) | _ | _ |
| Si/(Si + Al) ratio | 0.18 | 0.15 |



Figure 8. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_xSi_yO_z films as a function of (^tBuO)₃SiOH pulse length. The deposition temperature was 300°C.

 $({}^{t}BuO)_{3}SiOH-AlCl_{3}-H_{2}O$.— The $({}^{t}BuO)_{3}SiOH-AlCl_{3}-H_{2}O$ process was examined at a deposition temperature range between 200 and 500°C. Different pulse sequences with H₂O pulses added did not have a significant effect on the refractive indexes (1.48) and the growth rates (9 Å/cycle) as compared to the water-free process. Longer (${}^{t}BuO)_{3}SiOH$ pulses increase growth rate, but the refractive index seems to be almost constant (Fig. 8). However, the growth rate starts to saturate at longest pulse length examined. At the deposition temperatures over 300°C both the growth rates and refractive indexes are constant: about 9 Å/cycle and 1.47, respectively (Fig. 9). Table IX shows the elemental compositions of the films and it seems that the AlCl₃ pulse length does not have an effect on the composition.

 $({}^{t}BuO)_{3}SiOH-AlMe_{3}$.— The reaction between alternating exposures of (${}^{t}BuO)_{3}SiOH$ and AlMe₃ has been studied previously by Hausmann et al.²³ They were able to grow conformal Al_xSi_yO_Z films between 200 and 300°C with processing cycles consisting of less than 30 s. In our study, the deposition temperatures between 250 and 300°C were used. Figure 10 shows that very long and untypical precursor pulse lengths do not affect the growth rate and the refractive index of the films. However, very long pulse lengths increase the overall deposition time and exhaust of (${}^{t}BuO)_{3}SiOH$ precursor from the source boat may cause problems (Fig. 10; 40 s (${}^{t}BuO)_{3}SiOH$ pulse length).

In the earlier study²³ the growth rates saturated to about 120 Å/cycle at the deposition temperatures of 225 and 250°C. How-



Figure 9. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_xSi_yO_z films as a function of the deposition temperature. The pulse length of the Al_xSi_yO_z was 4 s.

| Table IX. The elemental compositions of the $Al_X Si_Y O_Z$ films de | | | | | | |
|--|------|---|--------------|---------------|-----|--|
| posited | with | (^t BuO) ₃ SiOH + H | $_{2}O + Al$ | $Cl_3 + H_2O$ | and | |
| $(^{t}BuO)_{3}SiOH + H_{2}O + AlMe_{3} + H_{2}O$ pu | | | | sequences. | The | |
| (^t BuO) ₃ SiOH pulse length was 4 s. | | | | | | |

| | 0 |
|--|--|
| $\begin{array}{cccc} ({}^{t}BuO)_{3}SiOH & ({}^{t}BuO)_{3}SiOH & ({}^{t}BuO \\ H_{2}O & H_{2}O & H \\ AlCl_{3} \ (0.5 \ s) & AlCl_{3} \ (0.2 \ s) & AlMe_{3} \\ H_{2}O & H_{2}O & H \end{array}$ |) ₃ SiOH 2O (0.5 s) 2O |
| dep. temp. (°C) 300 300 30 | 00 |
| n ₅₈₀ 1.48 1.47 1. | 49 |
| O (atom %) 63 63 5 | 3 |
| Si (atom %) 29 27 2 | 20 |
| Al (atom %) 6 5 | 5 |
| H (atom %) 3.5 3.7 2 | 20 |
| C (atom %] <0.1 <0.1 2 | .5 |
| Cl (atom %) 1.0 0.8 | _ |
| Si/(Si + Al) ratio 0.83 0.84 0. | 80 |

ever, this is over ten times more than was obtained in this study. The $({}^{t}BuO)_{3}SiOH$ dose for an optimum growth rate was about 70 nmol/cm² in the earlier study,²³ while we estimated the dose to be between 50 and 150 nmol/cm² in our experiments. Clearly, the dosage of $({}^{t}BuO)_{3}SiOH$ is not the reason for the tenfold difference in the growth rates between the experiments. The explanation may lie in the differences in the ALD reactor design. In the ALD reactor used by Hausmann et al.,²³ the reaction chamber was closed during the precursor exposures while our ALD reactor equipped with quartz cassette substrate holder is a cross flow-type reactor, and thus a continuous carrier gas flow instantly transports excess precursor molecules and volatile reaction by-products away from the reaction site.

 $({}^{t}BuO)_{3}SiOH-AlMe_{3}-H_{2}O$.— Different pulsing sequences of $({}^{t}BuO)_{3}SiOH$, AlMe₃, and H₂O precursors do not have an effect on the growth rates or refractive indexes at 300°C (Fig. 11). Adding water pulses seems to decrease the refractive indexes, but this may also be related to the inaccuracies in the refractive index determination. The results are in a good agreement with the results of Hausmann et al.²³ as they reported that there were no differences between films deposited without water dose and films deposited with the (${}^{t}BuO$)₃SiOH + AlMe₃ + H₂O pulse sequence.

Comparison of the processes.— Figure 12 summarizes the dependence of the refractive index on Si/(Si + Al) ratio, which was



Figure 10. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_xSi_yO_Z films as a function of (¹BuO)₃SiOH pulse length. The deposition temperature was 250 °C.



Figure 11. The growth rate (\blacksquare) and refractive index (\bigcirc) of the Al_xSi_yO_Z films with different pulse sequences. The deposition temperature was 300°C. The pulse length of (^tBuO)₃SiOH was 4 s.

analyzed by TOF-ERDA. The films were prepared using different processes described above. Because the refractive index of Al₂O₃ is about 1.65, even the small amounts of SiO₂ incorporated into Al_2O_2 decrease the refractive indexes of the films well below that of Al₂O₃. Using Si(OBu)₄ and (^tBuO)₃SiOH as precursors, the refractive indexes of 1.50 and below were reached. (^tBuO)₃SiOH (Fig. 12, #14–16) seems to produce high growth rates (7–11 Å/cycle) and low refractive index films when AlCl₃ or AlMe₃ is used as the Al precursor. Additionally, water pulses do not have an effect on the growth rates and refractive indexes. Si(OBu)₄ produces thin films with a refractive index below 1.50 only with AlCl₃ and without water pulses (Fig. 12, #2, and #3). The growth rates between 1 to 4 Å/cycle were achieved depending on the pulse length of Si(OBu)₄. As a full saturation of the growth rate was not observed with $Si(OBu)_4$ pulse lengths up to 2 s, longer pulses could result in even higher growth rates than reported in this paper. Among the processes using H_2O , the Si(OBu)₄ and Si(OEt)₄ precursors resulted in considerably lower amounts of Si in the films and therefore higher refractive indexes compared to (^tBuO)₃SiOH. All the films were amorphous according to GIXRD measurements and thus they can be expected to exhibit a smooth and featureless morphology as always found in amorphous ALD oxide thin films. Therefore differences in a morphology or microstructure should not have an influence on the refractive indexes.



Figure 12. A summary of the refractive indexes and Si/(Si + Al) ratios. The numbers denote the processes in Tables IV, V, and VII-IX. Open symbols (numbers 1, 5, and 9) indicate films, in which the impurities may have contributed for the low refractive indexes.

Conclusions

Several precursor combinations were successfully used to incorporate SiO₂ into the Al₂O₃ films to decrease the refractive index of Al₂O₃ relatively close to the refractive index of SiO₂. Using Si(OBu)₄ and (^tBuO)₃SiOH as precursors, the refractive index of 1.50 and below was reached. (^tBuO)₃SiOH seems to produce the high growth rate and low refractive index films when AlCl₃ or AlMe3 is used as the Al precursor. Additionally, water pulses did not have an effect on the growth rates and refractive indexes when (^tBuO)₃SiOH was used as the Si precursor. Si(OBu)₄ produced thin films with a refractive index below 1.50 only with AlCl₃ and without water pulses. However, the process with Si(OBu)₄ and AlCl₃ produced lower growth rates than the processes involving (^tBuO)₃SiOH, which may be important for an accurate film thickness control in optical applications.

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