SiO₂ thin film growth through a pure atomic layer deposition technique at room temperature†

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In this study, less contaminated and porous SiO₂ films were grown via ALD at room temperature. In addition to the well-known catalytic effect of ammonia, the self-limitation of the reaction was demonstrated by tuning the exposure of SiCl₄, NH₃ and H₂O. This pure ALD approach generated porous oxide layers with very low chloride contamination in films. This optimized RT-ALD process could be applied to a wide range of substrates that need to be 3D-coated, similar to mesoporous structured membranes.

Introduction

Silicon dioxide (SiO₂) and more generally ultra-thin oxide films have been extensively described as good components for modern nanotechnologies such as dielectric materials in silicon microelectronic devices, anticorrosion films or non-exhaustive applications of nanoscale films in catalysis. The environment- and human-friendly nature of SiO₂ induces its wide use in protective layers for antisticking, antifogging, self-cleaning or water repellency. Various techniques such as chemical vapor deposition, lithographic patterning, electrochemical deposition or sol-gel were investigated to prepare superhydrophobic SiO₂ by tuning surface roughness or energy. SiO₂ is consistently known for its application in protective or gate insulator coatings and interfacing high-k (ref. 14–19) or surface passivation materials. The increased demand for transparent active materials at the nanoscale justify the need for substrates.

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SiO₂ thin films obtained through ALD have widely been described as binary surface reactions dealing with various types of precursors Si(C₂H₅O)₄ or Si(NCO)₄ (ref. 13 and 30–33) or Si(NCO)₄ (ref. 34) with H₂O; CH₃OSi(NCO)₃ (ref. 35 and 36) with H₂O₂; Si(NH₂)₂ or SiH₂(NEt₂)₂ (ref. 38). Besides the necessity to work at high temperatures (i.e. >100–350 °C), most of the reactions require large reactant exposure of ≥10⁶ L (1 L = 10⁻⁶ Torr s) with a growth rate of ~1–2 Å per cycle. One approach to decrease the deposition temperature and the level of contamination is to use plasma-enhanced-ALD (PE-ALD). It is possible to decrease the temperature below 50 °C, and these SiO₂ films are described as excellent candidates for thin film encapsulation in organic devices or TFT gate insulators due to the absence of impurities and good electrical properties. Currently, the use of amino ligands as precursors leads to promising results, even on large surfaces; however, a final annealing step at 900–1000 °C is required to decrease interface defects or carbon contamination. Many efforts have been done, in terms of parameters and choice of precursors, in order to optimise ALD process, for the growth of SiO₂ coatings at high temperatures. Nevertheless, it is commonly agreed that there is a strong interest in the development of the process at room temperature. George et al. described the atomic layer-controlled growth using SiCl₄ and H₂O many times. They demonstrated that a reaction catalyzed using Lewis bases such as pyridine (C₅H₅N) or ammonia (NH₃) avoids large precursor flow rates and can only occur close to room temperature. Nevertheless, in these studies, C₂H₂N or NH₃ were never really considered as “precursors”. The proposed mechanism, which took into account the hydrogen bonding between the Lewis base and either the SiOH* surface species or the H₂O reactant, was studied by considering the global residual pressure of the continuous flow of the catalyst. Moreover, the secondary reaction of the catalyst reservoir (continuous flow), available in the reactor with HCl as the byproduct, drastically increased the probability of the inclusion of contaminants in the film. Therefore, a sequential approach could enhance the quality of the film and the understanding of the role of the catalyst.

This paper describes a pure ALD study of SiO₂ using the optimized sequential exposure of SiCl₄, H₂O and NH₃ precursors at room temperature. The ALD mode was confirmed by tuning the exposition of each precursor and the related...
purges. The initiation of the exposition was followed by using the residual gas analysis (RGA) mass spectrometer. Atomic growth control was investigated by the in situ Quartz Crystal Microbalance (QCM) and X-ray Photoelectron Spectroscopy (XPS), Dynamic-Secondary Mass Ion Spectroscopy (D-SIMS) and X-ray Diffraction (XRD) post-characterizations. A comparison between our investigation and the state-of-the-art of low temperature ALD SiO2 synthesis revealed the possibility to deposit ultra-thin films with very low contaminations at room temperature. The film conformality is shown and the capability of this optimized binary reaction, to be used on various types of temperature-sensitive supports with high aspect ratios, is confirmed.

Materials and methods

ALD processes were carried out in a TFS200-Beneq reactor in the planar configuration at a base pressure of 0.3 mbar. SiO2 thin films were then deposited on Si substrates, preliminary prepared by a standardized cleaning procedure established by Radio Corporation of America (RCA). The deposition reactor was equipped with a QCM (Neyco) for the gravimetric monitoring of the film growth. The QCM was fixed to the central part of the substrate holder. A quadrupole mass spectrometer, Vision-2000C, MKS-instrument, was assembled at the outlet of the deposition reactor to monitor the exhaust gas composition. SiO2 thin films were obtained at room temperature using SiCl4 and H2O as precursors. The vaporized precursors were transferred to the ALD reaction chamber with N2 as the carrier gas. SiCl4 was purchased from Sigma Aldrich and used as-received. Both canisters containing the precursors were maintained at 19 °C during deposition. NH3 gas (<99.9%), used as a catalyst, was injected into the reactor under 1 bar pressure.

The morphology and thickness of the obtained samples were characterized using a FEI Heliosnanolab 650 Focused Ion Beam Secondary Electron Microscope (FIB-SEM). The structure of the films deposited on dedicated Kapton tape was probed by small-angle X-ray scattering (SAXS) using an X-ray Diffractometer (X’Pert Pro [Panalytical]) equipped with a focusing mirror and a Pixcel 1D detector in the transmission mode. The elemental composition depth profile was assessed using D-SIMS (Cameca, IMSLAM); however, the quantification was performed by XPS (Thermo VG Scientific, MicroLab 350) using Al Kz source.

Results and discussion

Catalytic SiO2 RT-ALD growth

SiO2 films obtained at room temperature have already been prepared by the sequential exposure (ABAB...) of two reactants (A and B). Many well-known precursors require high deposition temperatures, plasma or highly reactive co-reactants such as ozone gas.37 Despite a low enthalpy of reaction, SiCl4 usually reacts with water [oxidant species] at high temperatures (>325 °C).38 The comparison of thermal ALD and room temperature processes reveals a higher growth rate/ALD cycle in favour of room temperature reactions (~2 Å per cycle) (Fig. S1, ESI†).

The amount of contaminants integrated in RT-SiO2 films is inherently dependent on the way of tuning the surface exposure to precursors. Based on studies by George et al.,39 we investigated the growth of SiO2 at room temperature (RT)-ALD by alternatively exposing the surface to SiCl4 and H2O under a constant flow of NH3. The exposure time was fixed at 90 s for SiCl4 with a purge time of 1 min. H2O exposure was fixed at 90 s with a purge time of 5 min to ensure a perfect saturation of the surface.40 The in situ monitoring of the film growth obtained by the QCM is shown in Fig. S2, ESI†. As already described,41 the reduction reaction of SiCl4 with water is depicted through the minimum of SiCl4 weight gain (Fig. S2b, ESI†) and the longer reaction of the NH3–H2O mixture (Fig. S2c–e, ESI†). Then, as shown in Fig. S2b, ESI† the gain of mass that is observed in one ALD cycle is predominantly obtained from the half reaction of H2O. Nevertheless, the growth rate of ~1.5 Å per cycle (297 nm/2000 cycles), experimentally obtained through this process with a constant flow of NH3, tends to reach the 2 Å per cycle value described by George et al.39

XPS elemental analysis of the SiO2 film (deposited on Al2O3/Si) (Fig. 1) shows the presence of carbon, nitrogen and chlorine in addition to silicon and oxygen within the SiO2 deposited film. A depth profiling analysis reveals that the carbon is restricted to the surface of the film.

The asymmetry of the C 1s peak suggests the presence of C–H, C–O–C or C=O bonds at the surface due to air exposure. The Si 2p peak of the Si–O layer appeared at 104.4 eV with a 1.77 eV (broadened up to 2.22 eV due to charge effects during the depth profiling) full width at half maximum (FWHM). The sharp and symmetric Si 2p peak centred at ~104 eV suggests an oxidation state of +4, which was attributed to the presence of SiO2. A high contribution of the byproducts of the reaction is detected through the presence of Cl and N elements in the films. The Si/Cl ratio increased from ~1.3 at the surface to 3.2 in the bulk of the film (Table 1).

Furthermore, the reaction of the lone pair of active –Cl with the hydrogen of water induced a significant formation of HCl. The higher detection limit of D-SIMS was used to screen the chemical elements present in the “bulk” of the film, particularly
Contaminant inclusion mechanism

George et al. described the mechanism of a catalysed binary reaction that spontaneously takes place in the presence of pyridine or NH$_3$ as a Lewis base agent. The hydrogen bonding between the Lewis base and SiOH* (surface species) or H$_2$O allows the reaction to be performed at room temperature (Fig. S3, ESI†). Compared to high temperature processes that use large precursor exposures (>10$^3$ Torr s), SiO$_2$ RT-ALD takes place owing to the strong nucleophilic attack of the oxygen from SiOH* on SiCl$_4$ and that from H$_2$O on SiCl*. Nevertheless, to the best of our knowledge, no specific data have been reported on the variation of the chemical composition and the morphology of such films. Based on the catalytic effect of NH$_3$, it can be clearly deduced that a constant flow of NH$_3$ statistically ensures a maximized reaction of Õ–O–Si–[Cl]$_4$m available sites. Nevertheless, the perfect delimitation of the exposure windows at room temperature could be enhanced by working in a non-conventional high vacuum state (<10$^{-6}$ Torr). As it is not the case for standard ALD reactors, we attempted to understand and control the contaminant inclusion mechanism in the pulsed NH$_3$ regime. Thus, the state-of-the-art production of SiO$_2$ at RT using a constant flow of NH$_3$ has been compared to pulse NH$_3$-catalysed RT-ALD. Inspired by the reactivity of chlorinated precursors described by Damyanov et al., the amount of contamination could be cautiously explained by the functionality $x$ of the adsorbed species at the surface explained hereafter:

\[
x(\equiv\text{Si–OH}) + \text{SiCl}_4 \rightarrow (\equiv\text{Si–O})\text{SiCl}_{4−x} + x\text{HCl}
\]

$x = 1$: monofunctional, $x = 2$: bifunctional and $x = 3$: trifunctional.

The injected precursor SiCl$_4$ reacted with the surface (≡) hydroxyl species. Moreover, the competition between the single bond case ($x = 1$) and multiple bonds ($1 < x < 3$) was directly linked to the stagnancy of precursors in the ALD regime. As far as the concentration of hydroxyl groups on the surface increased, the saturation of H$_2$O directly enhanced the formation of HCl. Along with the constant flow of NH$_3$, the ~2.2 Si/N ratio measured by XPS in the bulk of the film indicates a strong nitrogen contamination exceeding acceptable limits, especially through the inclusion of NH$_4$Cl salt. As indicated by George et al., this salt is formed as a result of the NH$_3$ catalyst complexing with HCl. Because of the vapour pressure of the NH$_4$Cl salt (i.e. 4 × 10$^{-5}$ Torr (ref. 50)), some quantity of the salt remained within the film. In that context, note that compared to an inert gas, using NH$_3$ as a carrier gas may not contribute to a pure ALD process performed at RT. Indeed, a significant contamination of the surface is attributed to the excessive dose of NH$_3$. The contamination depicted here confirms the already described importance of adjusting the quantity of NH$_3$ to limit the reaction with HCl. Thus, we considered that pulsing NH$_3$ similar to the other precursors could minimize unfavourable reactions at room temperature.

Low contamination SiO$_2$ growth under pulsed NH$_3$

Dense oxide under pure ALD regime. Based on the same chemistry used in the previous part, each chemical involved in the following process has been considered as a precursor. This indicates that an adequate separation of each pulsed chemical has been guaranteed. The purge of the reactor has been optimized using the appropriate ratio of carrier gas flow/reactor base pressure (<2 Torr). Any overlap between each precursor purge has been prevented by checking the injection with the integrated RGA. Fig. 3 shows the ALD saturation curves at RT for SiCl$_4$ (a), H$_2$O (b) and NH$_3$ (c) precursors. According to the diagrams, the saturation of all precursors occurs after exposure for 90 s. The N$_2$ purging time between SiCl$_4$ and NH$_3$ precursors has been fixed at 90 s. The appropriate purging time after water exposure was then determined by RGA (H$_2$O: m/z = 18 uma) analysis using a systematic variation process (Fig. S4, ESI†). After 300 s purging time, water was completely removed from the reactor.

Based on the trends observed in Fig. 4, the growth of a SiO$_2$ film in a pure ALD regime at RT has been investigated. SiCl$_4$,
NH₃ and H₂O exposure times were fixed at 90 s and extended purges were applied after NH₃ and H₂O pulses at 180 s and 300 s, respectively. As shown in Fig. S5a, ESI† the 0.02 µg cm⁻² per cycle weight gain is 30 times lower than the process with a constant flow of NH₃ (Fig. S2, ESI†). Nevertheless, the injection of NH₃ and H₂O precursors significantly contributes to a certain gain of mass (Fig. S5 panel b, ESI†), and then a growth rate of 0.5 Å per cycle is obtained for 500 deposition cycles. It can be observed that the high H₂O mass adsorbed during the interaction of H₂O molecules with active complexes at the surface ends through the efficient replacement of chlorine by hydroxyl groups (Fig. S3, ESI†).

The XPS elemental analysis (Fig. 4) still shows the presence of chlorine, nitrogen and carbon in addition to silicon and oxygen. The amount of contaminants (Table 2) is nonetheless substantially decreased. Firstly, the Si/Cl ratio increased from ~4 (surface) to ~8.7 in the bulk of the film. Secondly, compared to the films obtained with a constant flow of ammonia, the Si/Cl ratio improved significantly (threefold). Moreover, the Si/N ratio increased from 1.1 to 3.8 (2.2 to 5.9 inside the film). This indicates a limited reaction between HCl and NH₃ to form NH₄Cl. The best fitting procedure of the high-resolution spectrum of N 1s reveals a single binding energy peak at 401.1 ± 0.3 eV, corresponding to NH₄⁺. This confirms the formation of the NH₄Cl salt, and the small amount of detected Al is attributed to the alumina sub-layer (i.e. SiO₂/Al₂O₃/Si).

The SIMS depth profile of the SiO₂ film is shown in Fig. 5. The intensity of chlorine decreases ~30 times faster than the process performed with the constant NH₃ flow. In fact, less than 100 s sputtering is needed to decrease the intensity below 1 × 10⁵ cnts per s compared to ~2800 s for the NH₃ constant flow process. Moreover, the intensity of nitrogen seems to be in the same range of 10–100 cnts per s. Compared to the XPS results, this corroborates the formation of the NH₄Cl salt. Note that the intensity of Si is higher than that of Al, confirming the coating process of SiO₂ on Al₂O₃. From the depth profile, we can estimate the SiO₂ film thickness to be around 25 nm. Based on the XPS and SIMS results, it can be assumed that this RT process is optimized in terms of surface exposure. Nevertheless, the residual traces of HCl still react with NH₃ because of the difficulties to purge H₂O or NH₃ at RT. Moreover, small quantities of byproducts, such as NH₄Cl, were consequently integrated into the film.

Fig. 6a and b show top-view SEM images of the SiO₂ film. We observed a rough layer with grain sizes of up to 200 nm. This roughness is highlighted in the 45° tilted view (Fig. 6c).

Furthermore, cross-section analyses evidence the presence of a compact film (Fig. 6d). From these pictures, we can conclude that this pulsed NH₃ growth process leads to dense but rough SiO₂ thin films. A thickness of 30 ± 5 nm is measured through the cross-section, close to the 25 nm value deduced from the SIMS analysis. This leads to a lower growth rate of ~0.5 Å per cycle related to the lower weight gain observed with QCM (i.e. 30× lower than the SiO₂ film processed under a constant flow of NH₃). Nevertheless, the irregular surface aspect reveals

**Table 2** XPS quantification of elements present in the SiO₂ thin film obtained with a pure ALD regime

| Name | At% | At% (depth profiling) |
|------|-----|-----------------------|
| Si 2p | 12.9 | 4.1 |
| O 1s | 54.2 | 59.7 |
| N 1s | 3.6 | 0.7 |
| Cl 2p | 3.2 | 0.5 |
| C 1s | 11.4 | <1.0 |
| Al 2p | 14.7 | 34.9 |
that the process does not correspond to a pure ALD growth mode, as expected. This peculiar non-homogeneous growth at RT suggests that the surface reaction is in competition with the integration of contaminants. The self-limiting process actually promotes the deposition of species onto the substrate and onto the deposits (e.g. islands) with equal probability. The inclusion of contaminants at a sub-atomic growth rate (i.e. <1 Å per cycle) could explain the morphology of the obtained film. Moreover, the high amount of –OH surface groups could affect the dehydroxylation/rehydroxylation equilibrium (section: Contaminant inclusion mechanism), leading to the production of a higher quantity of HCl in the case of trifunctional bonds. Nevertheless, the oxide thin film displays a significant density in volume with limited inhomogeneity. This is in line with the sub-atomic growth rate mechanism surrounded by limited contamination. The tailoring of ALD parameters in this RT-SiO2 growth process shows a substantial adaptability in terms of morphology and chemical composition. These results suggest that a tuning of the growth parameters could influence the crystallisation. Hence, different types of SiO2 layers could be processed at RT.

**Porous oxide under limited ALD regime.** As described in the previous section, less contaminated SiO2 can be produced by adjusting the surface exposure of SiCl4, NH3 and H2O precursors. Furthermore, the effect of limited exposure on the composition and the morphology of the film has been investigated. Hence, the process has been tuned to maintain low level of contaminants in an ALD non-saturation regime. The precursor exposure has been decreased to a minimum value for SiCl4 (i.e. 100 ms) in agreement with a low contamination strategy. Then, according to RGA results, the exposure time of NH3 and H2O was fixed to 2 s for both with a purge of only 10 s using 300 sccm of N2.

As shown in Fig. S6, ESI,† a growth rate of 1.54 µg cm⁻² per cycle was obtained. Compared to the process described in the previous section, the exposure reaction used here generates 50 times higher weight gain. In order to disentangle any physicochemical influence from the substrate, silicon oxide films were grown on a pre-characterized barrier layer. Hence, SiO2 growth was investigated on two different sub-layers, i.e. TiO2 deposited by ALD and Si bulk.
Fig. 7 shows the XPS experiment results. As expected, Cl, C, N elements were detected in both samples. For SiO₂ deposited on TiO₂, the detection of Ti 2p before etching confirms the low thickness of the film.

However, the percentage of chlorine was clearly maintained below the limit of 3% (obtained for the previous process with extended exposures) (Table 3). The higher chlorine concentration observed after etching (3.79 at%) was attributed to the chlorine inherent to the TiO₂ ALD process. This was confirmed by the low chlorine concentration for SiO₂ deposited directly on the silicon wafer (Table 3, SiO₂/Si). In order to screen the composition and morphology of the film, thicker SiO₂ layer (2500 cycles) were processed on a chlorine-free material, i.e. Al₂O₃ (50 nm) on Si.

The SIMS depth profiling of the synthesized SiO₂ thick film exhibits a concentration of chlorine that rapidly decreases as a function of sputtering time (Fig. 8). Compared to the previous process, the intensity of Cl is starting a decade less, around 3.5 × 10⁴ cnts per s. Moreover, the amount of C and N is very low, which confirms the low level of NH₄Cl contamination in a thick volume of SiO₂.

Furthermore, the higher concentration of chlorine close to the surface of the film indicated the slow dissociative chemisorption of water, which induced the desorption of HCl. This recombination clearly affected the growth mechanism of SiO₂. As shown in Fig. 9, SEM analyses highlighted the porous state of the oxide film. In addition to the 200–500 nm diameter aggregates on the surface of the layer, the top and tilted view (Fig. 9a) revealed a SiO₂ sponge-like structure. The porosity of the film was confirmed by SAXS where a periodical arrangement of pores could be fitted with an average radius of 130 Å (std dev 30% and most frequent radius ~ 110 Å). The applied FIB cross-section (Fig. 9b) reveals the presence of 20–50 nm cavities (merging pores due to the preparation) and isolated pores of ~15 nm. As explained by Puurunen in the ALD random deposition approach, 56 if the growth per cycle is not constant, the increase in the surface roughness should be fast at the beginning of the growth and slow thereafter. This naturally indicates that a smaller number of ALD reaction cycles are required to fit a conformal deposition in a close-packed array as far as the growth rate is adjacent to an atomic monolayer.

By considering the growth rate of ~0.11 Å per cycle obtained in this process, it could explain why the SiO₂ film is less “closed” as the one processed via the pure ALD approach. The sponge-like porous structure growth may be related to the limited surface diffusion of the by-products (NH₄Cl, HCl) generated during each half cycle. Indeed, the diffusion/desorption of by-products is slower in the case of low reaction temperature.

| Name       | At% (depth profiling) |
|------------|-----------------------|
| SiO₂/TiO₂/Si |                       |
| Si 2p      | 16.4                  |
| O 1s       | 58.8                  |
| N 1s       | 1.4                   |
| Cl 2p      | 1.1                   |
| C 1s       | 14.6                  |
| Ti 2p      | 7.7                   |
| SiO₂/Si    |                       |
| Si 2p      | 25.9                  |
| O 1s       | 60.5                  |
| N 1s       | 1.6                   |
| Cl 2p      | 1.0                   |
| C 1s       | 11.1                  |

Fig. 8 SIMS depth profile of porous SiO₂ film obtained with 100 ms pulse of SiCl₄, 2s of NH₃ and H₂O precursors.

Fig. 9 SEM images of the ~260 nm thick ALD SiO₂ (300 cycles) film at different magnifications: (a) 45° tilted view of the entire oxide film; (b) FIB cross-section that confirms the porous state of the film.
Conclusions

Porous SiO₂ thin films have been produced by ALD using a sequential exposure of SiCl₄, NH₃ and H₂O at room temperature. The catalytic effect of ammonia has been exploited to optimize the saturation of the precursors and the extended purges. A relation between the significant porosity and the chemical saturation of the surface has been indicated using QCM, XPS, SIMS and SEM. It has also been demonstrated that this optimized process exhibited a decrease in the inherent inclusion of contaminants such as NH₄Cl and HCl in the film. As demonstrated on AAO membranes, the transferability of this 2D process to 3D structures could extend the use of SiO₂ films in several domains such as complex or high aspect ratio materials.

Conflicts of interest

The authors disclose that there are no conflicts to declare.

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