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(54) **SIO2 thin film produced by atomic layer deposition at room temperature.**

(57) Abstract: The invention is directed to a process of atomic layer deposition for the deposition of silicon oxide on a substrate, performed at room temperature, involving at least three precursors, being silicon tetrachloride, water and one Lewis base agent, being preferentially ammonia. Said process comprises the steps of exposing on said substrate during an exposure time (a) said one Lewis base agent, (b) said silicon tetrachloride, and (c) said water. Said process is remarkable in that at least one step of purge with nitrogen gas is performed after each of the steps (a), (b) and (c) during a purge time. The invention is further directed to a film of silicon oxide which is remarkable in that it comprises a low level of chlorine contaminant and a significant degree of porosity with pores, said pores being preferentially micropores, mesopores or nanopores. (Fig. 1)

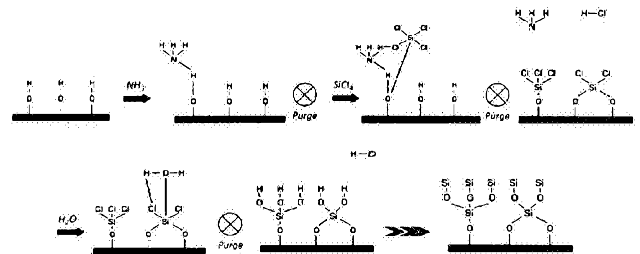


Fig. 1

SiO_2 thin film produced by atomic layer deposition at room temperature

№92795

Description

Technical field

[0001] The invention is directed to the field of deposition of silicon oxide on a substrate, notably an inorganic material.

Background art

[0002] Silicon dioxide (SiO_2) and more generally oxide ultrathin films have been widely described as good components in modern nanotechnologies like dielectric material in silicon microelectronic devices [Frosch C.J., *et al.*, *J. Electrochem. Soc.*, **1957**, *104*, 547-552], anticorrosion films [Olsson C.O.A., *et al.*, *Electrochim. Acta*, **2003**, *48*, 1093-1104] or non-exhaustive applications of nanoscale films in catalysis. The environmentally and human safe state of SiO_2 induces its wide use in protective layers for antisticking, antifogging, self-cleaning or water repellency. For instance, various techniques such as chemical vapor deposition [Ragesh P., *et al.*, *J. Mater. Chem. A.*, **2014**, *2*, 14773-14797], lithographic patterning [Park H.K., *et al.*, *J. Mat. Chem.*, **2012**, *22*, 14035-14041], electrochemical deposition [Gao Y., *et al.*, *ACS App. Mat.&Inter.*, **2014**, *6*, 2219-2223] or sol-gel [Xu B., *et al.*, *Surf. Coat. Techno.*, **2010**, *204*, 1556-1561] are investigated to elaborate superhydrophobic SiO_2 through the tuning of surface roughness or energy. SiO_2 is consistently known for protective or gate insulator coatings [Klaus J.W., *et al.*, *Science*, **1997**, *278*, 1934-1936], interfacing high-κ materials [Wang X., *et al.*, *Appl. Phys. Lett.*, **2010**, *97*, 062901-062903] or surface passivation [Dingemans G., *et al.*, *J. Appl. Phys.*, **2011**, *110*, 09371-093716].

[0003] The increasing demand for transparent active materials in the nanoscale justify the need of a deposition technique compatible with sensitive pre-deposited underlying layer, flexible plastic devices or high aspect ratio substrates. Therefore, Atomic Layer Deposition (ALD) is considered as one of the most suitable technique for its performances in terms of sub-

nanometer thickness control and penetration coating into deep trenches or mesoporous structures.

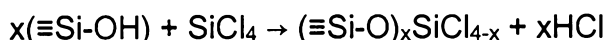
[0004] Although the improvement SiO_2 coatings obtained at high temperatures engaged a lot of efforts towards ALD parameters or precursors, the question of the deposition at room temperature nevertheless emerged. George *et al.* described many times this atomic layer–controlled growth using $SiCl_4$ and H_2O [Du Y., *et al.*, *Thin Solid Films*, **2005**, *491*, 43-53]. They demonstrated that a catalysed reaction using Lewis bases such as pyridine or ammonia avoid large precursor fluxes and can only occur close to room temperature. Nevertheless, in these reported studies, pyridine or ammonia was never really considered as a "precursor". The proposed mechanism that considered the hydrogen bonding between the Lewis base and either the SiOH* surface species or the H_2O reactant was studied by considering the global residual pressure of a continuous flow of catalyst. Moreover, since a pollution of the film through the inclusion of contaminants arise through the secondary reaction of pyridine or ammonia with the byproduct HCl, a sequential approach could enhance the quality of the film and the understanding of the role of the catalyst.

[0005] Silicium oxide (SiO_2) films made at room temperature have been described as feasible by the exposition of two reactants (A and B) through a sequential exposition (ABAB...). Many well-known precursors require high deposition temperatures, plasma or highly reactive co-reactant such as ozone gas [Kim H.-U., *et al.*, *J. Electrochem. Soc.,* **2000**, *147*, 1473-1476]. Nearly correlated to CVD-based processes and despite a low enthalpy of reaction, silicium tetrachloride ($SiCl_4$) usually reacts with water (oxidant specie) at high temperatures (>325°C) [Klaus J.W., *et al.*, *Science*, **1997**, *278*, 1934-1936]. A comparison of thermal ALD and room temperature processes reveal a higher growth rate/ALD cycle in favour of room temperature reactions (~2Å/cycle).

[0006] George *et al.* described the mechanism that spontaneously takes place through a catalysed binary reactions using pyridine or ammonia as a Lewis base agent [Klaus J.W., *et al.*, *Surf. Rev. Lett.*, **1999**, *6*, 435-448]. The hydrogen bonding between the Lewis base and SiOH* (surface specie) or

H_2O allows the reaction to be performed at room temperature. Compared to high temperature processes that use large exposures (>103 Torr.s), SiO_2 room temperature ALD is permitted trough the strong nucleophile attack of the oxygen from (i) SiOH* on $SiCl_4$ and (ii) from H_2O on SiCl* [Du Y., *et al.*, *Thin Solid Films*, **2005**, *491*, 43-53]. Nevertheless, according to our knowledge, no specific data have been described regarding 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 –O on all –O-Si-$(Cl)_n$ available sites. Nonetheless, 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 may not be the case for standard ALD reactors like in our case, we tried to understand and control the mechanism of contaminants inclusion in this regime. Thus, the state-of-the-art production of SiO_2 at room temperature (~25°C) using a constant flow of NH_3 has been compared to pulse NH_3-catalysed RT-ALD.

[0007] Inspired by the reactivity of chlorinated precursors described in the literature [Damyanov D., *et al., J. Non-Cryst. Solids*, **1988**, *105*, 107-113], the amount of contamination could be cautiously explained by the functionality x of the adsorbed 137 specie at the surface explained hereafter:



$$x(\equiv Si\text{-}OH) + SiCl_4 \rightarrow (\equiv Si\text{-}O)_x SiCl_{4-x} + xHCl$$

x = 1 : monofunctional

x = 2 : bifunctional

X = 3 : trifunctional

The injected precursor $SiCl_4$ reacts with the surface hydroxyl species. The competition between the single bond case (x = 1) and multiple bonds ($1 < x \leq 3$) is directly linked to the stagnancy of precursors in the ALD regime. As far as the concentration of hydroxyl groups on the surface is increased, the saturation of H_2O will directly enhance the formation of HCl. Concurrently with the constant flow of ammonia, the ~2.2 Si/N ratio

measured by XPS in the bulk of the film also indicates that strong nitrogen contamination exceed acceptable limits, especially through the inclusion of NH_4Cl salts. As indicated by George *et al.* [Klaus J.W., *et al.*, *Surf. Sci.*, **2000**, *447*, 81-90], this salt is formed as a result of the NH_3 catalyst complexing with the HCl reaction product. Due to the vapour pressure of NH_4Cl salt (*i.e.* 4.10^{-5} Torr), some quantity of salts are remained inside the film. In that context, it is noteworthy that compared to an inert gas, using NH_3 in a carrier gas mode may not contribute to a pure ALD process performed at room temperature.

Summary of invention

Technical Problem

[0008] The invention has for technical problem to provide porous silicon oxide layers with a significant decrease of the amount of contaminants, such as chlorine, included in the film.

Technical solution

[0009] The invention is directed to a process of atomic layer deposition for the coating of silicon oxide on a substrate, notably an inorganic material, performed at room temperature, involving at least three precursors, said at least three precursors being silicon tetrachloride, water and one Lewis base agent, said one Lewis base agent being preferentially ammonia. Said process comprises the steps of (a) exposing on said substrate during an exposure time said one Lewis base agent, (b) exposing on said substrate during an exposure time said silicon tetrachloride, and (c) exposing on said substrate during an exposure time said water. Said process is remarkable in that at least one step of purge with nitrogen gas is performed after each of the steps (a), (b) and (c) during a purge time.

[0010] In one embodiment, said at least one step of purge with nitrogen gas presents a ratio of nitrogen gas flow/total pressure which is inferior to 5 Torr, 4 Torr, 3 Torr, 2 Torr or 1 Torr, preferentially inferior to 2 Torr.

[0011] In one embodiment, said exposure time of the precursors is comprised between 50 milliseconds and 200 seconds.

[0012] In one embodiment, the exposure time of the silicon tetrachloride is comprised between 50 milliseconds and 200 milliseconds, preferentially comprised between 80 milliseconds and 120 milliseconds, more preferentially of 100 milliseconds; and the exposure time of said Lewis base agent and of said water is comprised between 1 second and 3 seconds, preferentially comprised between 1.8 seconds and 2.2 seconds, more preferentially of 2.0 seconds.

[0013] In one embodiment, said exposure time of the precursors is comprised between 50 seconds and 200 seconds, preferentially comprised between 70 seconds and 99 seconds, more preferentially of 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97 or 98 seconds, even more preferentially of 90 seconds.

[0014] In one embodiment, said purge time with nitrogen gas is comprised between 1 second and 20 seconds, preferentially comprised between 5 seconds and 15 seconds, more preferentially of 10 seconds.

[0015] In one embodiment, the purge time with nitrogen gas after step (a) is comprised between 100 seconds and 240 seconds, preferentially comprised between 160 seconds and 200 seconds, more preferentially of 180 seconds; the purge time with nitrogen gas after step (b) is comprised between 10 seconds and 100 seconds, preferentially comprised between 40 seconds and 80 seconds, more preferentially of 60 seconds; and the purge time with nitrogen gas after step (c) is comprised between 200 seconds and 360 seconds, preferentially comprised between 280 seconds and 320 seconds, more preferentially of 300 seconds.

[0016] In one embodiment, said steps (a), (b) and (c) with concomitant purge steps are repeated between 50 and 5000 times, preferentially between 500 and 2500 times.

[0017] In one embodiment, said inorganic material is composed of silicon, silicon oxide, titanium, titanium oxide, aluminium, aluminium oxide, zinc, zinc oxide or any combinations thereof, or any other, preferentially silicon.

[0018] In one embodiment, said silicon materials are cleaned in accordance with RCA procedure before the steps of exposing.

[0019] In one embodiment, said process is carried out in a reactor which is equipped with a residual gas analyser adapted for determining said exposure time and said purge time.

[0020] In one embodiment, said reactor is further equipped with a quartz crystal microbalance adapted for the gravimetric monitoring of the film growth and/or a mass spectrometer adapted for monitoring the gas composition.

[0021] The invention is further directed to a film of silicon oxide obtained by the process as described in the first part of the present invention. Said film of silicon oxide is remarkable in that it comprises a level of chlorine contaminant which is inferior to 5%, 4%, 3%, 2% or 1% of the total mass of said film of silicon oxide, preferably inferior to 3% of the total mass of said film of silicon oxide.

[0022] In one embodiment, said film of silicon oxide comprises pores, said pores being preferentially micropores, mesopores or nanopores (*i.e.* < 50 nm).

[0023] In one embodiment, said film of silicon oxide comprises superhydrophilic properties, anti-reflective properties and/or insulating properties.

Advantages of the invention

[0024] The invention is particularly interesting in that the correlation of the high aspect ratio and the oxygen concentration exhibits a super-hydrophilic behaviour. The silicon oxide thin films of the present invention further manifest a weak conductivity. The optimized room temperature ALD (RT-ALD) process can further be applied on a wide range of substrates that need to be 3D-coated with a low-κ porous silicon oxide layer or any 3D temperature-sensitive materials requiring super-hydrophilic treatments.

Brief description of the drawings

[0025] Figure 1: ALD room temperature growth of SiO_2 under NH_3 catalytic regime.

[0026] Figure 2: Saturation curves of $SiCl_4$, H_2O and NH_3 along the SiO_2 thin film growth. The growth kinetic is shown for 5 cycles sequential exposure of the surface.

[0027] Figure 3: Growth kinetics of pure ALD SiO_2 growth with sequential exposure of the surface to 90s of $SiCl_4$, 90s of NH_3 and 90s of H_2O. A typical zoom of the *in situ* monitoring of 500 loops deposition shown in panel (a) corresponds to a growth rate of 0.02 $\mu g/cm^2$. The panel (b) represents a zoom of the 60% advanced deposition. Lower panels represent the programmed exposures of $SiCl_4$, NH_3 and H_2O, respectively.

[0028] Figure 4: Growth kinetics of SiO_2 for sequential exposure of the surface to 90s of $SiCl_4$, and 90s of H_2O, indicating a growth rate of 0.6 $\mu g/cm^3$ per cycle. Panel (a) shows a typical zoom on 10 cycles of the total 2000 cycles deposited film. Panel (b) corresponds to the view of 2 cycles deposition. Lower panel represent the programmed exposure of H_2O, $SiCl_4$ and NH_3, respectively.

[0029] Figure 5: *In-situ* RGA mass spectrometric monitoring of successive 90s H_2O pulses alternated with 300s N_2 purge. The panel corresponds to the measured intensity of H_2O (m/z = 18 uam) (uam = unified atomic mass).

[0030] Figure 6: XPS spectra of SiO_2 thin film obtained with a sequential 90s exposure of $SiCl_4$, NH_3 and H_2O precursors. Upper panel corresponds to the signal of the raw film and lower panel to the film after surface cleaning.

[0031] Figure 7: SIMS depth profile of pure ALD SiO_2 film obtained with 90s pulse of $SiCl_4$, NH_3 and H_2O precursors and extended N_2 purges, respectively 60, 180 and 300s. Fast and slow sputtering rate are shown respectively in panels (a) and (b).

[0032] Figure 8: SEM images of the 500 cycles processed pure ALD SiO_2 film at different magnifications: (a) top and (b) 45° tilted view of the entire oxide film; (c, d) FIB cross-section images reveal a dense state of the SiO_2 film with an inhomogeneous crystallisation due to the unescapable inclusion of contaminants and the low growth rate of 0.5 Å/cycle.

[0033] Figure 9: Growth kinetics of porous SiO_2 growth with sequential exposure of the surface to 100ms of $SiCl_4$, 2s of NH_3 and 2s of H_2O. The *in situ*

monitoring of 300 loops deposition corresponds to a growth rate of 1.5 µg/cm² per cycle. The insert represents a zoom of 10 cycles process.

[0034] Figure 10: XPS spectra of SiO_2 thin film obtained with a sequential exposure of $SiCl_4$, NH_3 and H_2O precursors. SiO_2 film deposited on (a) Si wafer, (b, c) TiO_2/Si (80 nm) before and after surface cleaning respectively.

[0035] Figure 11: XPS quantification of the suitable element of the SiO_2 thin film obtained with an optimized ALD regime on a TiO_2/Si substrate (above) and a Si substrate (below).

[0036] Figure 12: SIMS depth profile of porous SiO_2 film obtained with 100ms pulse of $SiCl_4$, 2s of NH_3, and H_2O precursors.

[0037] Figure 13: SEM images of the ~260 nm thick ALD SiO_2 (300 loops) film at different magnifications: (a) top and (b) 45° tilted view of the entire oxide film; (c, d) FIB cross-section confirms the porous state of the film.

[0038] Figure 14: Conductivity measurements of the porous SiO_2 film compared to a standard thermal oxide made by rapid thermal CVD (100 nm).

[0039] Figure 15: Water contact angle images of (a) Si wafer, (b) porous SiO_2 and (c) top view of the substrate after depositing the water drop.

[0040] Figure 16: Schematic of the reflection ellipsometric measurements. The variable maximum angle θ_m is set at two different effective grazing angles θ_e = 75 and 81°. Data were acquired in the full wavelength range 350-1000 nm. The spatial reflectance has been measured by counterclockwise rotating the sample as a function of the planar angle τ_R. Z-axis is fixed at zero to maximise the reflected intensity.

[0041] Figure 17: Reflection results obtained by using the ellipsometer at two different grazing angles (respectively 75° and 81°). The reflectance percentage has been measured for SiO_2 deposited on glass (a ,d) and silicon (b, e). The spatial reflection (c, f) confirms the homogeneity of the film with a limited variation of the signal as a function of the τ_R angle.

[0042] Figure 18: SEM images of various thickness ALD SiO_2 (100-300 loops) deposited on anodic aluminium oxide (AAO) membranes.

Description of an embodiment

[0043] ALD processes were performed in a TFS200-Beneq reactor in the planar configuration at a base pressure of 0.3 mbar. SiO_2 thin films were deposited on silicon substrates preliminary cleaned with a standard RCA procedure. The deposition reactor is equipped with a quartz crystal microbalance, QCM, (Neyco) for the gravimetric monitoring of the film growth. The QCM was fixed at the central part of the substrate holder. A quadrupole mass spectrometer, Vision-2000C, MKS-instrument, was mounted at the outlet of the deposition reactor to monitor the exhaust gas composition. SiO_2 thin films were obtained at room temperature using silicon tetrachloride ($SiCl_4$) and water (H_2O) as precursors. Vaporized precursors were transferred to the ALD reaction chamber with nitrogen (N_2) carrier gas. $SiCl_4$ precursor was purchased from Sigma Aldrich and used as received. Both canisters containing the precursors were maintained at 19 °C during deposition.

[0044] Morphology and thickness of the obtained samples were obtained on FEI Heliosnanolab 650 Focused Ion Beam Secondary Electron Microscope (FIB-SEM). The elemental composition depth profile was assessed by Dynamic Secondary Ion Mass Spectrometry (D-SIMS) (Cameca IMSLAM) while the quantification was performed by X-ray photoelectron spectroscopy (XPS) (Thermo VG Scientific, MicroLab 350) using an Al X-Ray source. The thickness, refractive index and reflectance were determined using the UVISEL spectroscopic phase modulated ellipsometer, Horiba scientific using a Cauchy function for analysis. The hydrophobic behaviors of the deposited films were determined by water contact angle (WCA) measurements using drops of water. Additionally, the dielectric properties of the films were determined using a Novolab broadband dielectric spectrometer.

[0045] As described by Klaus *et al.* [Klaus J.W., *et al.*, *Surf. Rev. Lett.*, **1999**, *6*, 435-448], the process described here above confirms that NH_3 gas molecule acts as a catalyst for the deposition of SiO_2 at room temperature (between 20°c and 26°C). Nevertheless, a significant contamination of the surface is coming from the excessive dose of ammonia. The

contamination depicted here confirms the already described importance of adjusting the quantity of NH_3 to limit the reaction between HCl and NH_3. Thus, we considered that tuning the pulses of NH_3 like the other precursors could minimize unfavourable reactions at room temperature.

[0046] Based on the same chemistry used in the previous part, each chemical involved in the following process has been considered as a precursor. This means 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 / total pressure (<2 Torr). Any overlapping between each precursor pulse has been prevented by checking the injection with the integrated Residual Gas Analyser (RGA).

[0047] Figure 1 depicts the growing of a SiO_2 monolayer. Through the injection of NH_3 (under catalytic regime), the O–H bond becomes weaker, –Si can easily react with –O at the surface to form –O-Si-$(Cl)_3$ or –O-Si$(Cl)_2$-O– ligands at the surface. –O coming from water injection directly react with –Si to finally form a SiO_2 monolayer.

[0048] Figure 2 shows the ALD saturation curves at room temperature for $SiCl_4$, H_2O and NH_3 precursors. In our reactor configuration, primary experiments demonstrated that the saturation time for all precursors occurred between 60s and 100s. The timing sequence of the experiment starts with a variable $SiCl_4$ exposure followed by a 90s N_2 purge. Next, a 90s NH_3 exposure was followed by a 180s N_2 purge. Lastly, the cycle was ended by a 90s H_2O pulse and a longer N_2 purge of 300s to ensure a complete release of the subsequent unadsorbed water. This value of 300s has been validated by the RGA.

Figure 2a shows the mass gain versus exposure time for various $SiCl_4$ pulses switched from 500ms to 150s. The profile presents a saturation over t = 90s. A subsequent $SiCl_4$ exposure, not shown here for clarity, produce a smaller mass gain even no gain. This can be observed through the saturation of the curve over 90s. The total weight gain resulting from 5 cycles is about 0.13 $\mu g/cm^2$.

Figure 2b shows the mass gain versus exposure time for various H_20 pulses switched from 500ms to 150s. Starting with the previously obtained

value for $SiCl_4$ (*i.e.* 90s), the cycle is kept identical and a various H_2O exposure time is applied. A maximum weight gain of 0.18 µg/cm² is reached for 90s and the saturation regime is reached over this value.

Figure 2b shows the mass gain versus exposure time for various NH_3 pulses switched from 500ms to 150s. $SiCl_4$ and H_2O are both maintained at 90s, a maximum of 0.17 µg/cm² gain of mass is observed over 90s NH_3 exposure.

The trends observed in figure 2 were used to investigate the growth of a SiO_2 film in a pure ALD regime at room temperature. $SiCl_4$, NH_3 and H_2O exposure times were fixed at 90s and extended purges were applied after NH_3 and H_2O pulses, respectively 180s and 300s. A purge for $SiCl_4$ lasting 60s was applied.

[0049] Those finely tuned fluxes of precursors allow the surface reactions to perform smoothly and in particular, it allows a significant decrease of the amount of contaminants, such as chlorine, but also nitrogen, carbon and any others, which might be included in the silicon oxide thin film.

[0050] As shown in figure 3, the 0.02 µg/cm² per cycle weight gain is 30 times lower than the process done with a constant flow of NH_3 (which is depicted in figure 4). Nevertheless, the injection of NH_3 and H_2O precursors noteworthy contributes to a certain gain of mass (see figure 3b) and a growth rate of 0.5 Å/cycle is obtained for 500 cycles deposition (*i.e.* a higher mass is depicted for H_2O). This confirms that the interaction of H_2O molecules with active complex of the surface ends through the efficient replacement of chlorine by hydroxyl groups (as shown in figure 1).

[0051] In our case, the appropriate purging time of water has been determined by using a systematic variation using the RGA (H_2O: m/z = 18 uam). The trend shown in figure 5 reveals a 300s purge time needed to decrease down to the base line.

[0052] The XPS elemental analysis (figure 6) still shows the presence of chlorine, nitrogen and Carbon in addition of silicon and oxygen. The amount of contaminants is nonetheless substantially decreased. First, the Si/Cl ratio is going 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 is significantly improved (8.7 versus 3). Moreover, the Si/N ratio is heightened from 1.1 to 3.8 (resp. 2.2 to 5.9 inside the film). This indicates a limited reaction between hydrogen chloride with ammonia to form ammonium chloride. High resolution fitting of N1s reveals a single binding energy at 401.1± 0.3 eV corresponding to NH_3^+. This confirms the formation of ammonium chloride salt. The small amount of detected Al is attributed to the alumina sub-layer (*i.e.* $SiO_2/Al_2O_3/Si$).

[0053] The SIMS depth profile of the SiO_2 film is shown in figure 7. The intensity of chlorine is decreasing ~30 times faster than the process done with the constant NH_3 flow. In fact, less than 100s sputtering are needed to decrease the intensity below 1e5 cnts/s compared to ~2800s for the NH_3 constant flow process. Additionally, the intensity of nitrogen seems to be in the same range of 10 to 100 cnts/s. Related to XPS results, this corroborates the formation of NH_4Cl salt. The intensity of Si is nonetheless higher than Al, confirming the coating process of SiO_2 on Al_2O_3. Based on XPS and SIMS results, it can be assumed that this room-temperature process is optimized in terms of surface exposure. Nevertheless, residual traces of hydrochloric acid still react with ammonia due to the difficulties to purge water or ammonia at room temperature. Tittle by-products quantities, such as ammonium chloride, are consequently integrated into the film.

[0054] Figure 8 shows the top-view and cross-section SEM images of the SiO_2 film. We observe a porous layer with grains size up to 200nm. A significant roughness is observed in the 45° tilted view (figure 8c). Additionally, cross-section analyses evidence an inhomogeneous crystallisation into the film (figure 8d). A thickness of ~30nm±5nm is measured through the cross-section, also confirming the ~25nm value deduced from the SIMS pulverisation speed of silicon oxide. This lead to a low growth rate of ~0.5 Å/cycle related to the lower weight gain observed with the QCM (*i.e.* 30x lower than the SiO_2 film processed under a constant flow of ammonia). Nevertheless, the type of crystallisation reveals that the process is not corresponding to a pure ALD growth mode as expected [Ritala M., *et al.*, *Chem. Vap. Depos.*, **1999**, *5*, 7-9]. This peculiar non-homogeneous growth

at room temperature suggests that the surface reaction is in competition with the integration of contaminants. The self-limiting process actually promote the deposition of species onto the substrate and onto the deposits (*e.g.* islands, ...) with equal probability, if we consider that no particles can be produced in a CVD mode, then the inclusion of contaminants at a sub-atomic growth rate (*i.e.* < 1 Å/cycle) could explain the morphology of the obtained film. Moreover, the high amount of hydrogen bonded terminal -OH groups could affect the dehydroxylation-rehydroxylation equilibrium leading to a higher quantity of HCl produced in the case of trifunctional bonds. Nevertheless, the oxide layer display a significant density in volume and the amount of inhomogeneous crystallites is limited. This is in line with the sub-atomic growth rate mechanism surrounded by a limited contamination. The tailoring of the ALD parameters in this RT-SiO_2 growth process manifests a substantial adaptability in terms of morphology and chemical composition. These results let suggest that a tuning of the growth parameters could influence the crystallisation that occurs. Hence, different type of SiO_2 layers could be processed at room temperature.

[0055] Low contaminants SiO_2 can be produced by adjusting the surface exposure of $SiCl_4$, NH_3 and H_2O precursors. Furthermore, the impact of a limited exposition to the composition and the morphology of the film has been carried out. Hence, the process has been tuned to maintain the low level of contaminants in an ALD non-saturation regime. The precursor exposure has been decreased to a minimum value for $SiCl_4$ (*i.e.* 100 ms) in agreement with a low contamination strategy. Then, according to RGA results, the exposure time of NH_3 and H_2O has been fixed to 2s for both with a purge of 10s using 300 sccm of nitrogen.

[0056] As shown in figure 9, a growth rate of 1.54 μg/cm² per cycle is obtained. Compared to the previous processes, the exposure reaction used here generates a ~50 times higher weight gain. In order to screen any physico-chemical influence from the substrate, silicon oxide films were performed by intercalating a pre-characterized barrier layer. Hence *SiO_2* growth has

been investigated on two different sub-layers, *i.e.* TiO_2 deposited by ALD and Si bulk.

[0057] Figure 10 shows the XPS experiment results. As expected, Cl, C, N elements are detected for both samples. In the case of the oxide deposited on TiO_2, the detection of Ti-2p before cleaning confirms the low thickness of the film. However the percentage of chlorine is clearly maintained below the limit of 3% obtained for the previous process with extended exposures likewise N and C (figure 11). Nevertheless, chlorine concentration is increasing as far as the titanium oxide layer is reached through the sputtering. Since chlorine is inherent to the TiO_2 ALD elaboration, the chlorine concentration is effectively lower in the film as indicated by the deposit on Si directly (figure 11 - SiO_2/Si). In order to screen the composition and the porous structure of the film, thicker SiO_2 (2500 loops) has been processed on a layer without chlorine contamination, *i.e.* Al_2O_3 on Si (50 nm).

[0058] The SIMS depth profiling exhibits a concentration of chlorine that is rapidly decreasing as a function of the sputtering time (figure 12). Compared to the previous process, the intensity of Cl is starting a decade less, around 3.5e4 cnts/s. The amount of C is moreover comparable but the N concentration is slightly increasing inside the film (~750s sputtering time). This confirms the low level of NH_4Cl contamination included in a thick volume of SiO_2. Additionally, the higher concentration of chlorine close to the surface of the film hint the slow dissociative chemisorption of water that induces the desorption of HCl. This recombination clearly affects the growth mechanism of silicon dioxide.

[0059] As shown in figure 13, SEM analyses establish the porous state of the oxide film. Except the presence of 200 nm to 500 nm diameter aggregates on the surface of the layer, the top and tilted views (resp. figure 13a and 13b) reveals directly a SiO_2 spongy nature. The applied FIB cross-section (figures 13c and 13d) reveals also the presence of 20-50nm cavities related to a porous film. Compared to the film obtained through the pure ALD process, it is worth notable that the mechanisms involved in this growth process generate alternatively hollow volume on behalf of the

migration into surface crystallites. As explained in the ALD random deposition approach [Puurunen R.L., *Chem. Vap. Dep.*, **2004**, *10*, 159-170], if the growth per cycle is not constant, the surface roughness should increase faster at the beginning of growth and slowly thereafter. This implies naturally that a smaller number of ALD reaction cycles are needed to fit a conformal deposition in a close-packed array as far as the growth rate is adjacent to an atomic monolayer.

[0060] By considering the growth rate of ~0.11 Å/cycle obtained in this process, this could explain why the SiO_2 film is much closed as the one processed under the pure ALD approach. Nevertheless, its spongy state may be related to surface diffusion that are (i) on one hand limited due to the room temperature reaction and (ii) on the other hand widely promote during extended purges during the pure ALD process. In that case, residual water or byproducts (NH_4Cl, HCl) are considered as surface fractions where the supplementary amount of injected precursor will be adsorbed, leading to a non-uniform film. This peculiar structure is nonetheless attractive for some applications that need to be processed at room temperature.

[0061] The performances have been checked for both SiO_2 dense and porous film.

[0062] We investigated the dielectric characterizations on the SiO_2 films obtained in this work and we compared it to a standard thermal oxide (RTO; 1100°C; 1h). As shown in figure 14, the conductivity of the dense SiO_2 film obtained through the pure ALD is in the range of a 50nm thermal oxide (10^{-7} - 10^{-8} S/cm). The conductivity measured for the dense SiO_2 is anyway ~10^3 higher than the standard oxide produced with a constant flow of NH_3 (~10^{-11} S/cm). Furthermore, the thick porous SiO_2 exhibits a low conductivity of 200 µS/cm. This could be attributed to the amount of -OH groups associated to a specific area that is higher than in a compact film.

[0063] Despite its low-κ state, this porous SiO_2 layer could be used as transparent backside coating or as a first passivation layer. No additional transparent, such as Al_2O_3 for instance, layer has been added in order to demonstrate the inherent properties of the as-developed film.

[0064] The versatility of the ALD process allows the production of a tunable low-κ layer at room temperature. This could be in line with many temperature-sensitive hybrid applications.

[0065] Hydrophilic or superhydrophilic surfaces can be created by tuning the roughness at the nanoscale or the porosity of a film. This is peculiar in various applications such as antibacterium, heat transfer or biomedical applications. Hence, the wettability of the film has been analysed by water contact angle (WCA) and results are shown in figure 15. Compared to the untreated silicon surface (figure 15a), the porous SiO_2 layer demonstrates a remarkable super-hydrophilic behaviour (<5°). According to the XPS analyses, this could be attributed to the high concentration of oxygen in the porous film which presents a significant aspect ratio. The interest of hydrophilic behaviour commonly based on TiO_2 for instance [Huang T., *et al.*, *Surf. Coat. Techno.*, **2012**, *213*, 126-132) could be transposed to a standalone porous SiO_2 layer.

[0066] One of the other aspects of porous layer applications is the possibility to create anti-reflective coatings (ARC). The main advantage to add an anti-reflective layer on optically active device (*i.e.* solar cells) is to improve the efficiency [Mazur M., *et al.*, *Opto-Electron. Rev.*, **2013**, *21*, 233-238]. The reflectivity has been checked by ellipsometry with two grazing angles, *i.e.* 75 and 81 degrees (see figure 16). The specular reflection has been surrounded by a spatial reflectance analysis in order to validate the anisotropy of the film and the results are shown in figure 17. A remarkable decrease of the reflectance percentage is observed in both cases of coating glass or silicon. The signal is constantly decreasing as a function of the thickness of the film but only extreme results are shown here for clarity. As the reflectance reduction is about ~10-15% for Si, the scaling down for glass is maintained in the region of ~50% especially for high reflection at grazing angle for glass. The combination of the maintain of substantial reflection percentage at various incident angles with less than 200nm coating gives a good opportunity to use this room temperature process in a wide range of transparent applications. Furthermore, the

possibility to tailor this process through the versatility of ALD may of interest to avoid multifunctional coatings.

[0067] The evident interest of this porous SiO_2 layer has been applied to a 3D material. Various thickness of SiO_2 has been deposited on an anodic aluminium oxide (AAO) membrane and results are shown in figure 18. It clearly appears that the porosity obtained on planar substrates is transposed on 3D surfaces. This let suggest many applications that need hydrophilicity or low contaminants layer with a high precision on thickness deposited.

Revendications

1. Procédé de dépôt de couches atomiques pour le revêtement d'oxyde de silicium sur un substrat, notamment sur un matériau inorganique, effectué à la température ambiante, impliquant au moins trois précurseurs, lesdits au moins trois précurseurs étant du tétrachlorure de silicium, de l'eau et un agent de type base de Lewis, ledit agent de type base de Lewis étant de préférence de l'ammoniac, comprenant les étapes:
   a. d'exposition sur ledit substrat pendant un temps d'exposition dudit agent de type base de Lewis,
   b. d'exposition sur ledit substrat pendant un temps d'exposition dudit tétrachlorure de silicium, et
   c. d'exposition sur ledit substrat pendant un temps d'exposition d'eau,

   caractérisé en ce qu'au moins une étape de purge avec de l'azote gazeux est effectué après chacune des étapes (a), (b) et (c) pendant un temps de purge.

2. Procédé selon la revendication 1, caractérisé en ce que ladite au moins une étape de purge avec de l'azote gazeux présente un rapport flux d'azote gazeux/pression totale qui est inférieur à 5 Torr, 4 Torr, 3 Torr, 2 Torr ou 1 Torr, préférentiellement inférieure à 2 Torr.

3. Procédé selon l'une quelconque des revendications 1-2, caractérisé en ce que ledit temps d'exposition des précurseurs est compris entre 50 millisecondes et 200 secondes.

4. Procédé selon l'une quelconque des revendications 1-3, caractérisé en ce que
   a. le temps d'exposition du tétrachlorure de silicium est compris entre 50 millisecondes et 200 millisecondes, préférentiellement compris entre 80 millisecondes et 120 millisecondes, plus préférentiellement de 100 millisecondes; et
   b. le temps d'exposition de l'agent de type base de Lewis et de l'eau est compris entre 1 seconde et 3 secondes, préférentiellement compris entre 1,8 seconde et 2,2 secondes, plus préférentiellement de 2,0 secondes.

5. Procédé selon l'une quelconque des revendications 1-3, caractérisé en ce que ledit temps d'exposition des précurseurs est compris entre 50 secondes et 200 secondes, préférentiellement compris entre 70 secondes et 99 secondes, plus préférentiellement de 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97 ou 98 secondes, encore plus préférentiellement de 90 secondes.

6. Procédé selon l'une quelconque des revendications 1-4, caractérisé en ce que ledit temps de purge avec de l'azote gazeux est compris entre 1 seconde et 20 secondes, préférentiellement compris entre 5 secondes et 15 secondes, plus préférentiellement de 10 secondes.

7. Procédé selon l'une quelconque des revendications 1-3 ou 5, caractérisé en ce que
   a. le temps de purge avec de l'azote gazeux après l'étape (a) est compris entre 100 secondes et 240 secondes, préférentiellement compris entre 160 secondes et 200 secondes, plus préférentiellement de 180 secondes;

b. le temps de purge avec de l'azote gazeux après l'étape (b) est compris entre 10 secondes et 100 secondes, préférentiellement compris entre 40 secondes et 80 secondes, plus préférentiellement de 60 secondes; et
c. le temps de purge avec de l'azote gazeux après l'étape (c) est compris entre 200 secondes et 360 secondes, préférentiellement compris entre 280 secondes et 320 secondes, plus préférentiellement de 300 secondes.

8. Procédé selon l'une quelconque des revendications 1-7, caractérisé en ce que lesdites étapes (a), (b) et (c) avec des étapes de purge concomitantes sont répétées entre 50 et 5000 fois, préférentiellement entre 500 et 2500 fois.

9. Procédé selon l'une quelconque des revendications 1-8, caractérisé en ce que ledit matériau inorganique est constitué de silicium, d'oxyde de silicium, de titane, d'oxyde de titane, d'aluminium, d'oxyde d'aluminium, de zinc, d'oxyde de zinc ou de toutes combinaisons de ceux-ci, ou de tout autre, préférentiellement du silicium.

10. Procédé selon la revendication 9, caractérisé en ce que lesdits matériaux de silicium sont nettoyés selon la procédure RCA avant les étapes d'exposition.

11. Procédé selon l'une quelconque des revendications 1-10, caractérisé en ce que ledit procédé est mis en œuvre dans un réacteur qui est équipé d'un analyseur de gaz résiduel adapté pour déterminer ledit temps d'exposition et ledit temps de purge.

12. Procédé selon la revendication 11, caractérisé en ce que ledit réacteur est en outre équipé d'une microbalance à cristal de quartz adaptée pour le contrôle gravimétrique de la croissance du film et/ou d'un spectromètre de masse adapté pour contrôler la composition du gaz.

13. Film d'oxyde de silicium obtenu par le procédé selon l'une quelconque des revendications 1-12, caractérisé en ce que ledit film d'oxyde de silicium comprend un niveau de contaminant de chlore qui est inférieure à 5%, 4%, 3%, 2% ou 1% de la masse totale dudit film d'oxyde de silicium, préférablement inférieure à 3% de la masse totale dudit film d'oxyde de silicium.

14. Film d'oxyde de silicium selon la revendication 13, caractérisé en ce que ledit film d'oxyde de silicium comprend des pores, lesdits pores étant préférentiellement des micropores, des mésopores ou des nanopores.

15. Film d'oxyde de silicium selon l'une quelconque des revendications 13-14, caractérisé en ce que ledit film d'oxyde de silicium comprend des propriétés superhydrophiles, des propriétés anti-réfléchissantes et/ou des propriétés isolantes.

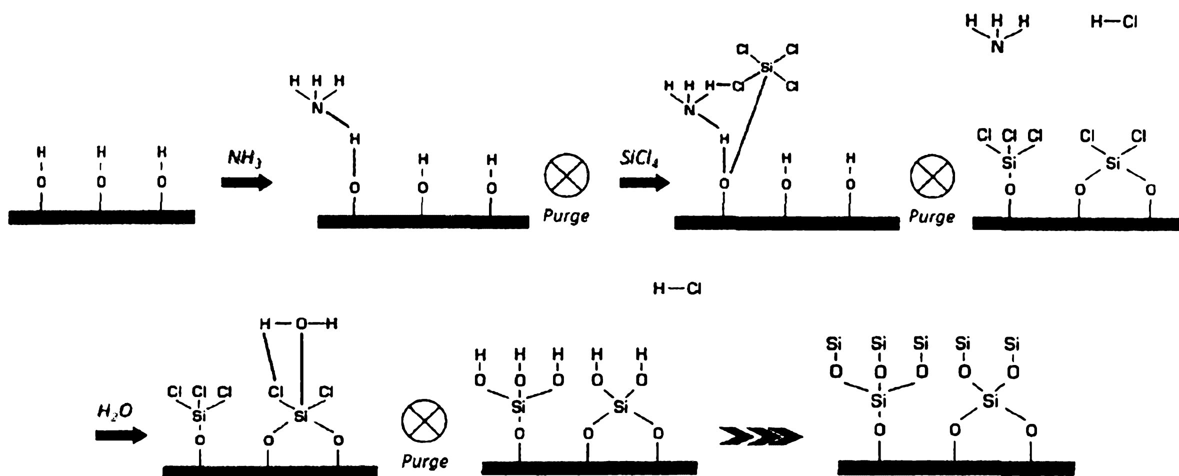


Fig. 1

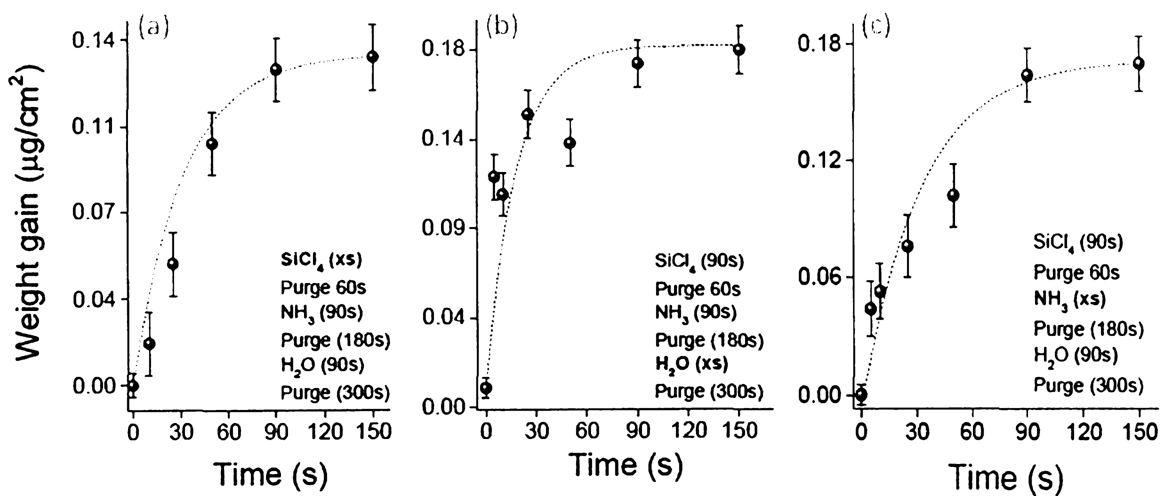


Fig. 2

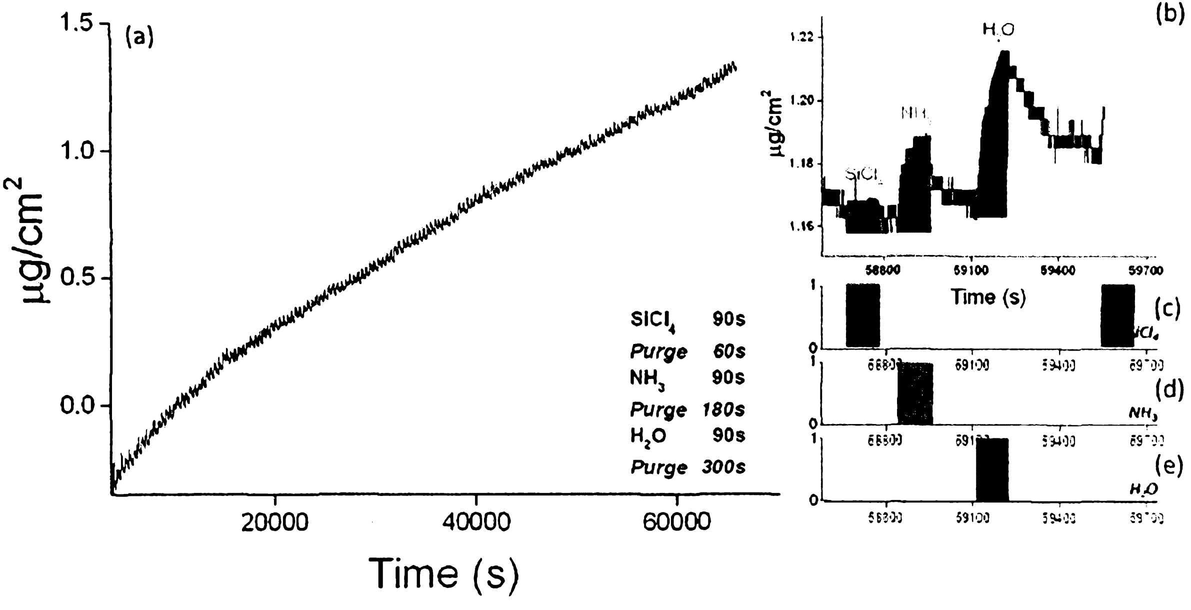


Fig. 3

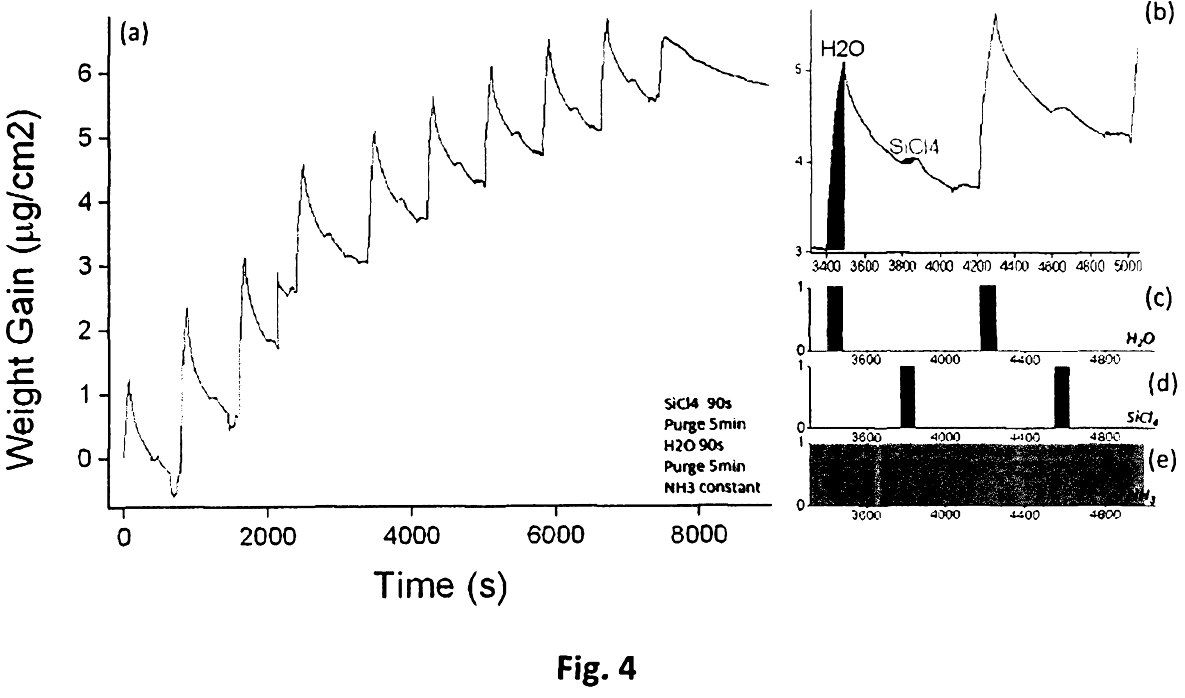


Fig. 4

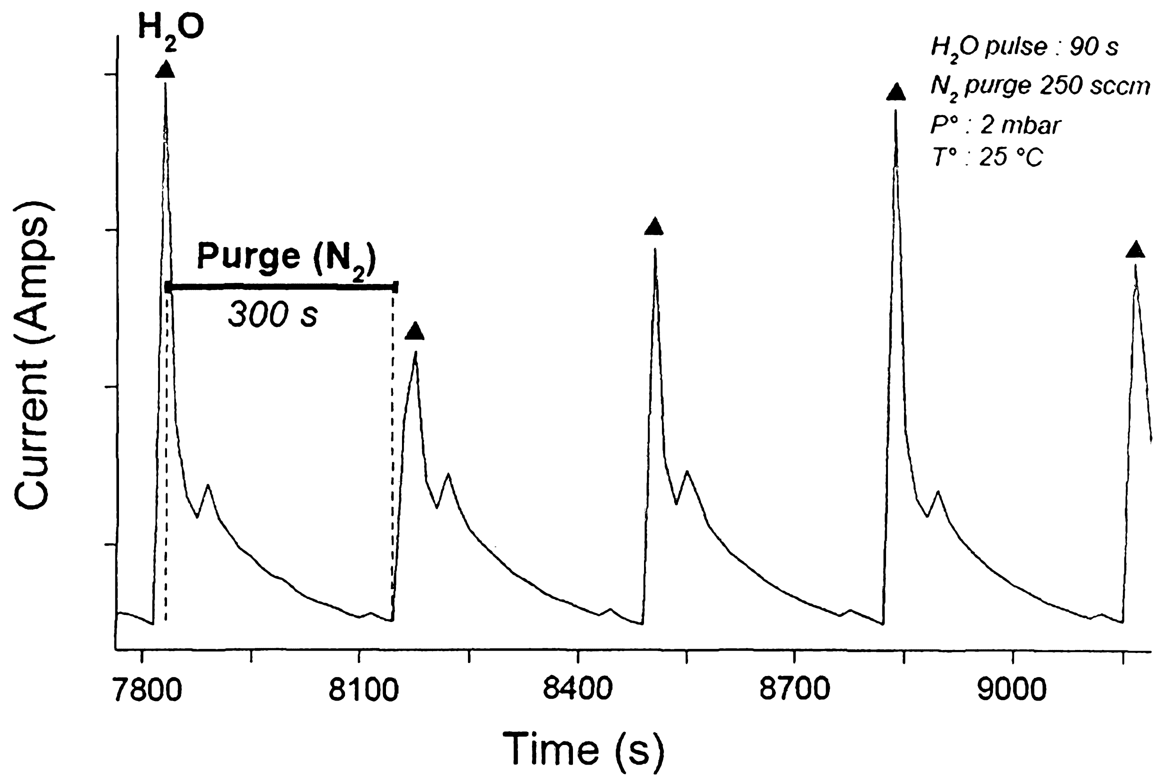


Fig. 5

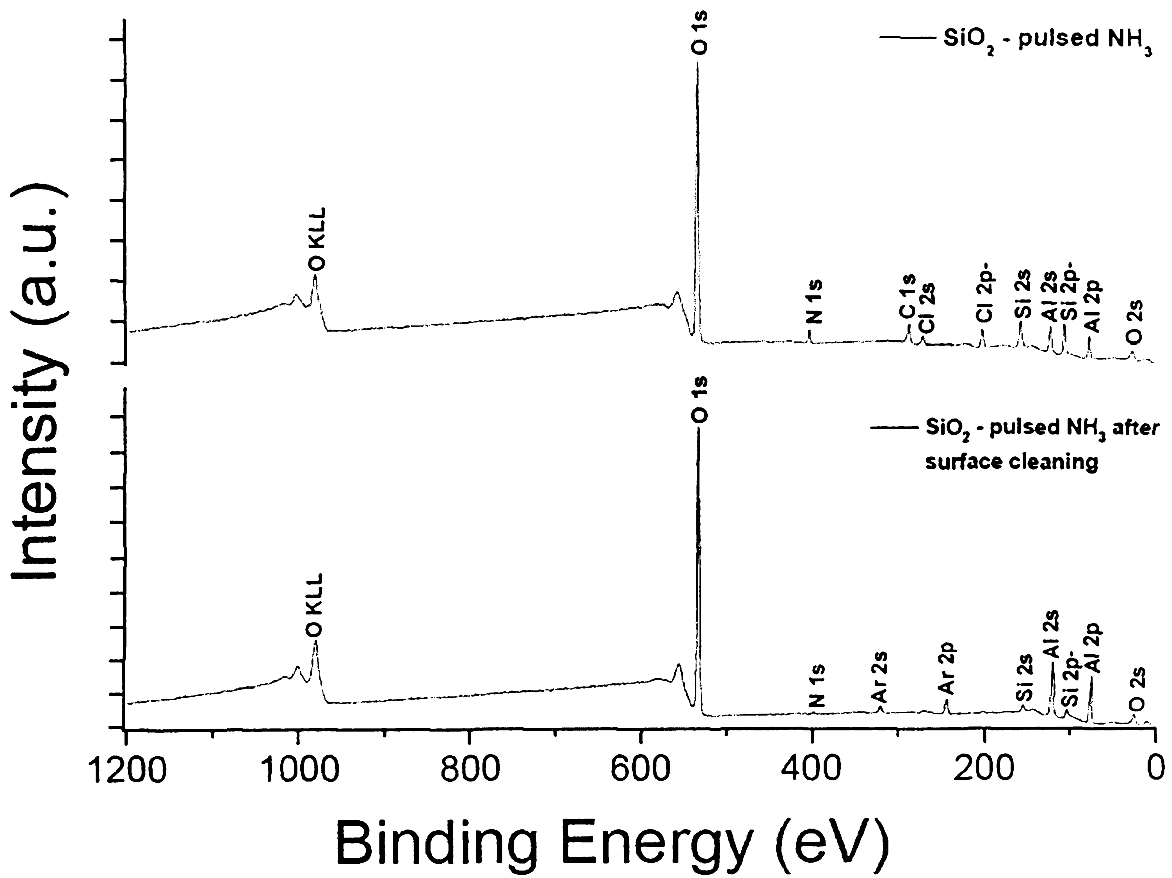


Fig. 6

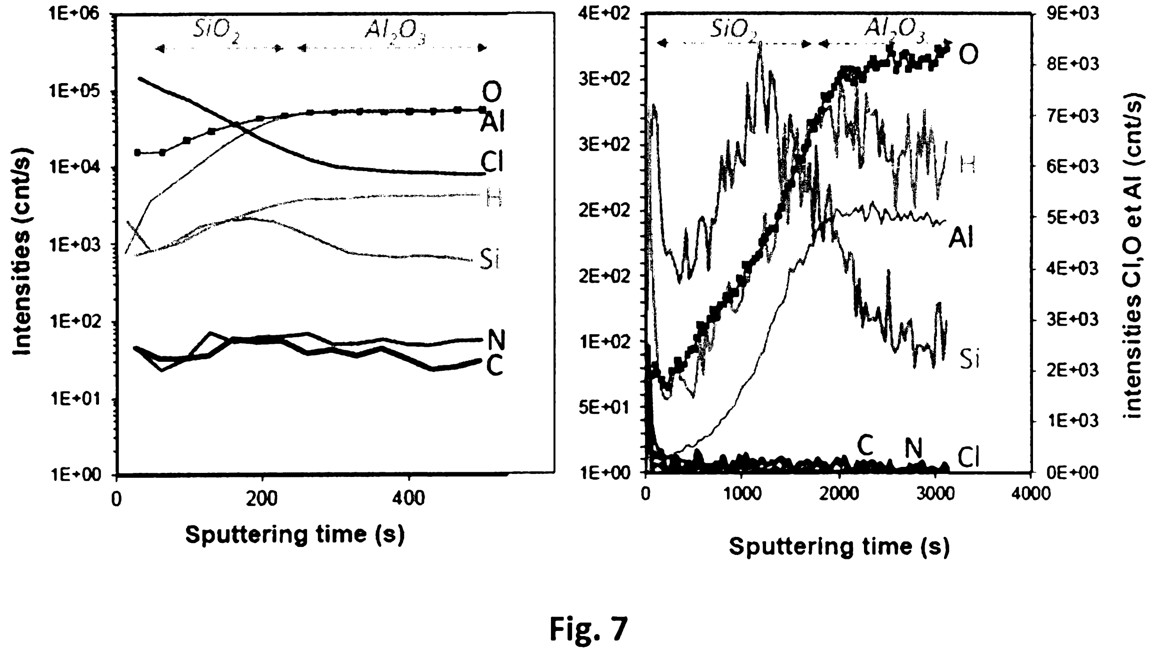


Fig. 7

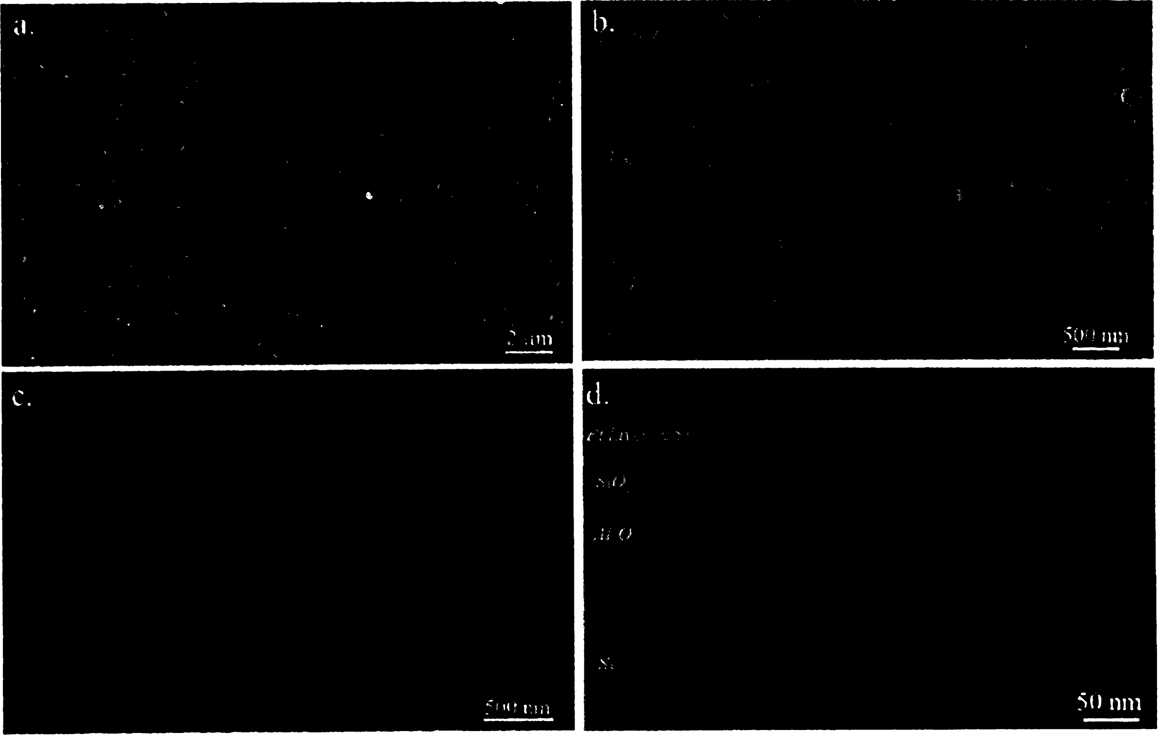


Fig. 8

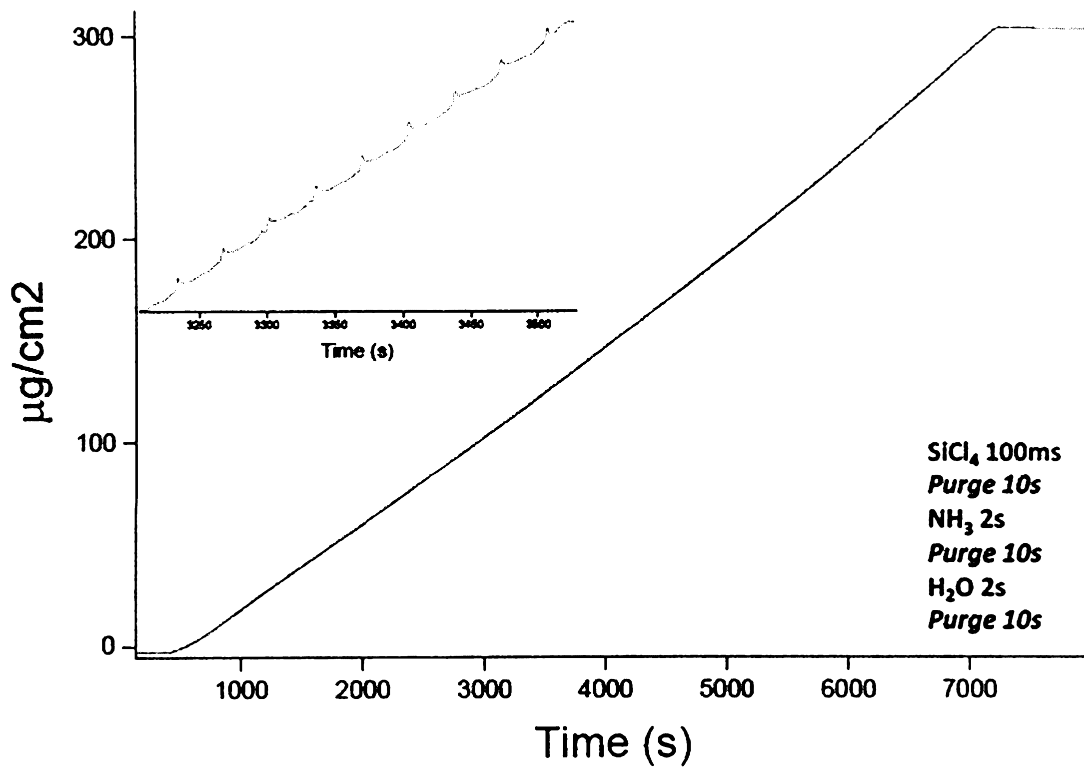


Fig. 9

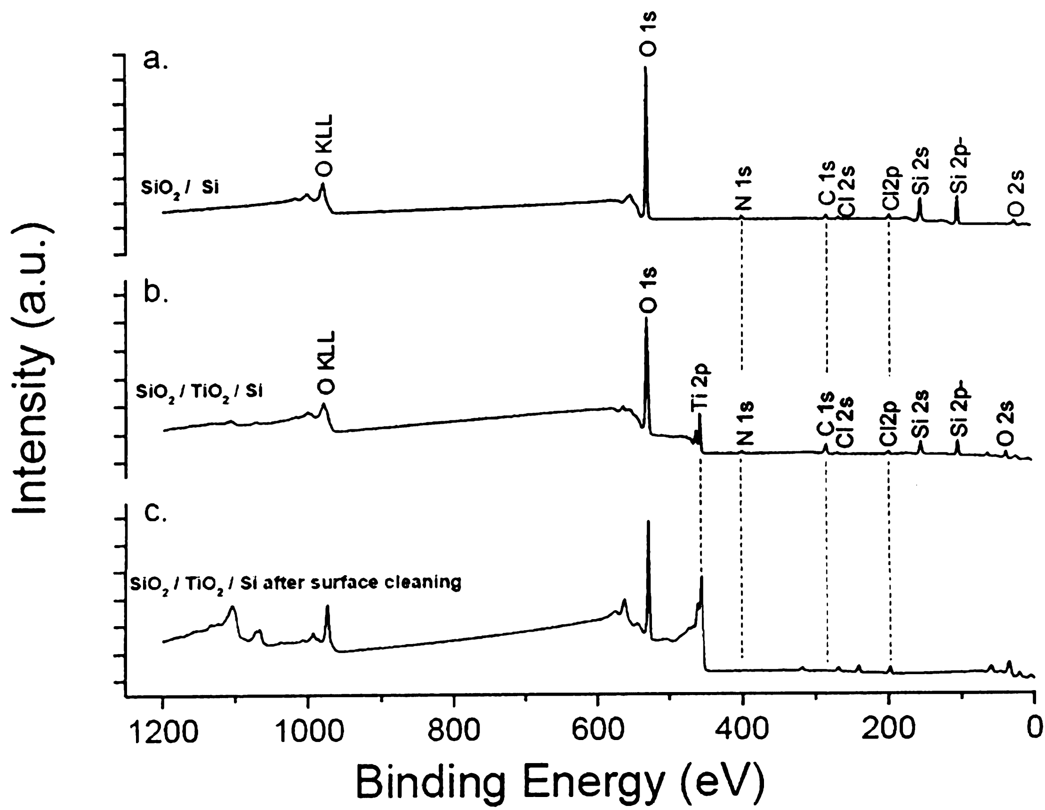


Fig. 10

Name	At %	At % depth profiling
SiO_2 / TiO_2 / Si		
Si 2p	16.39	-
O 1s	58.76	63.41
N 1s	1.4	-
Cl 2p	1.13	3.79
C 1s	14.66	-
Ti	7.66	32.8
SiO_2 / Si		
Si 2p	25.61	34.38
O 1s	60.45	62.86
N 1s	1.55	2.27
Cl 2p	1.03	0.48
C 1s	10.95	<1

Fig. 11

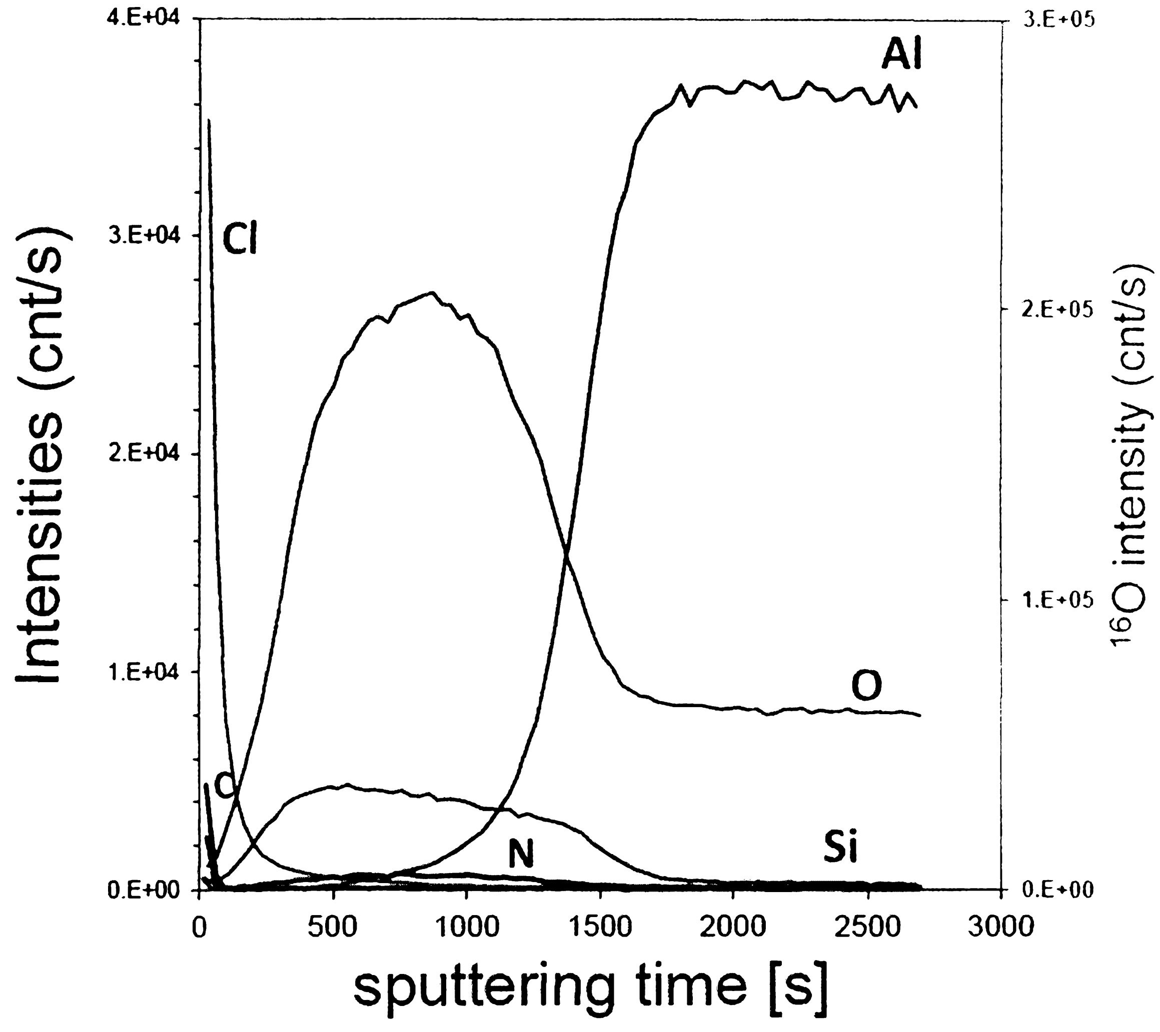


Fig. 12

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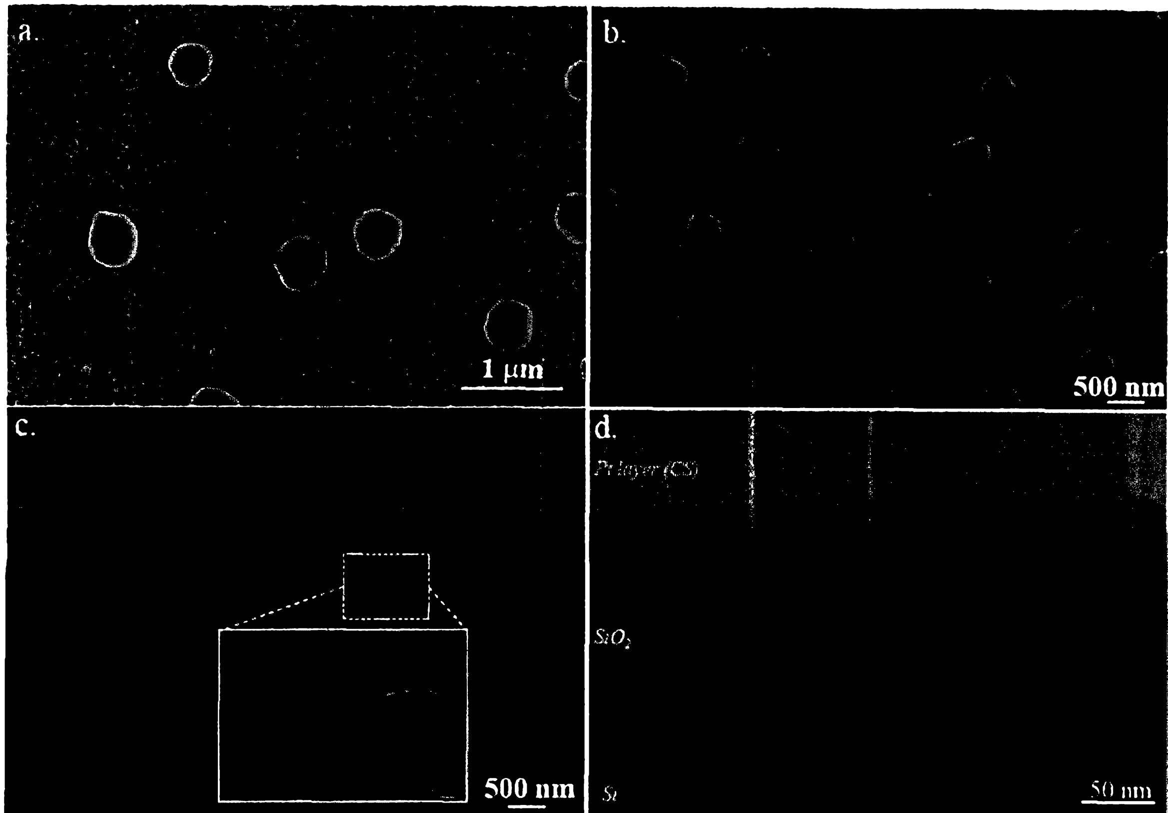

Fig. 13

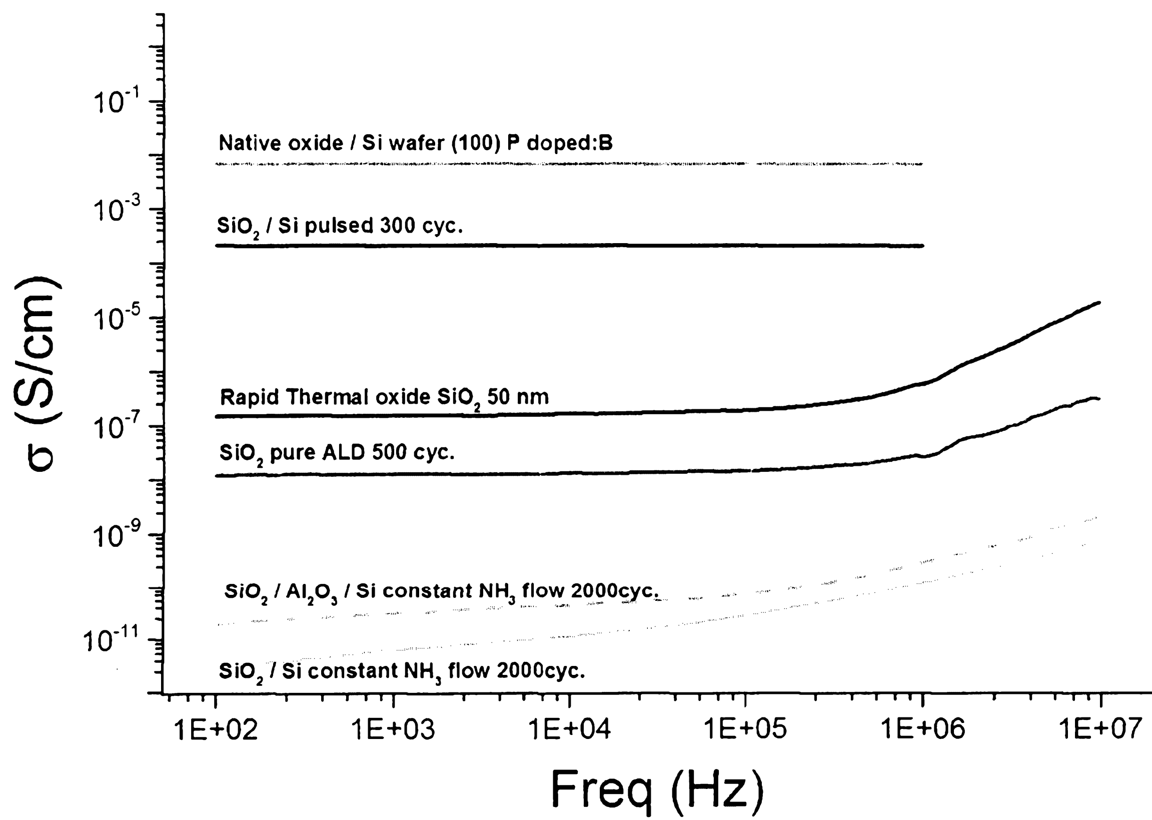

Fig. 14

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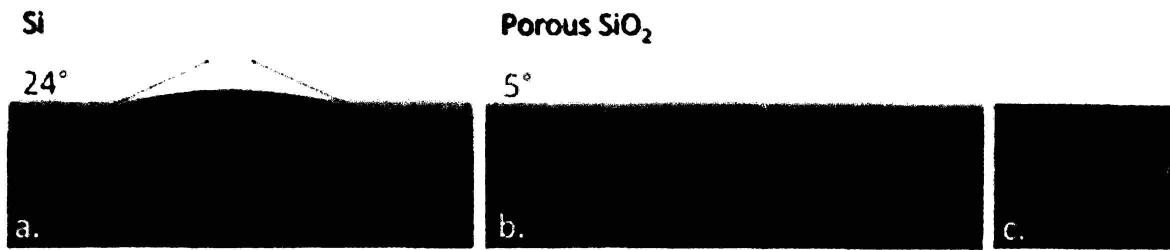

Fig. 15

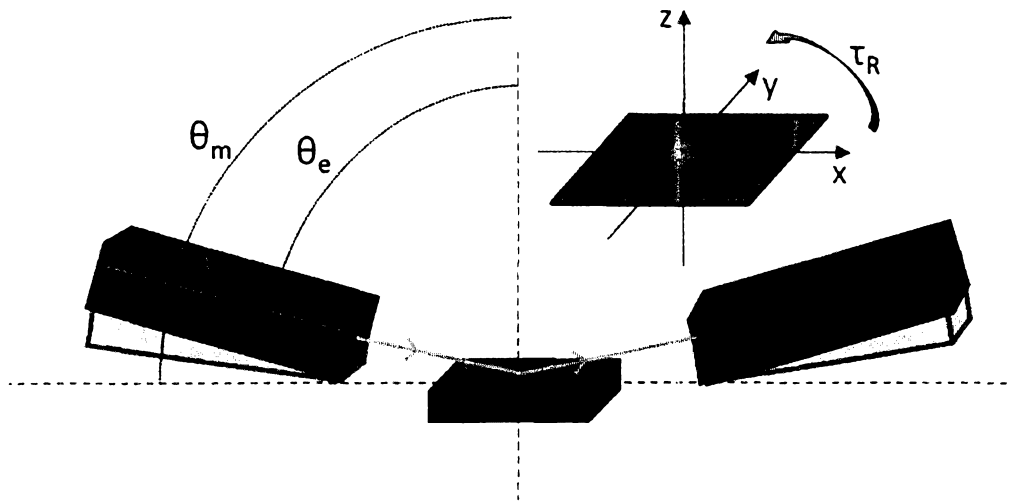

Fig. 16

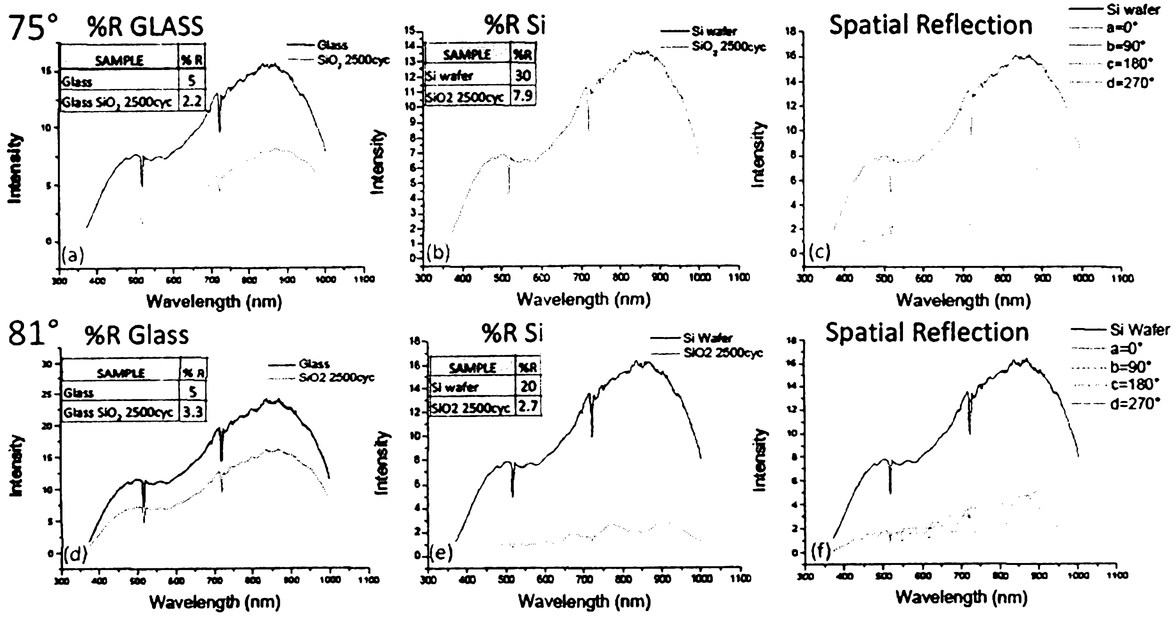

Fig. 17

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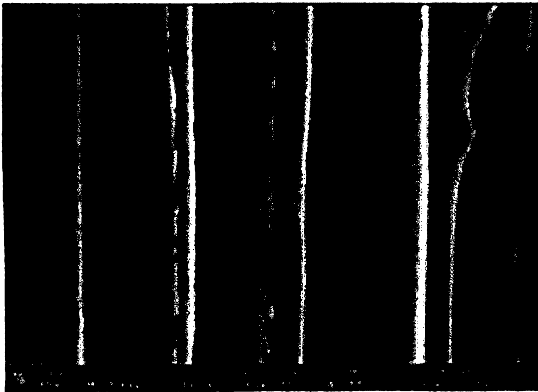
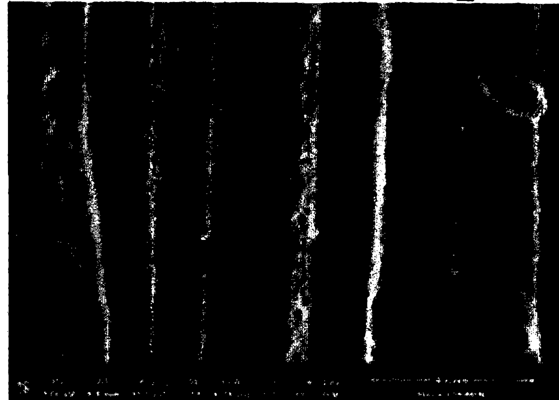
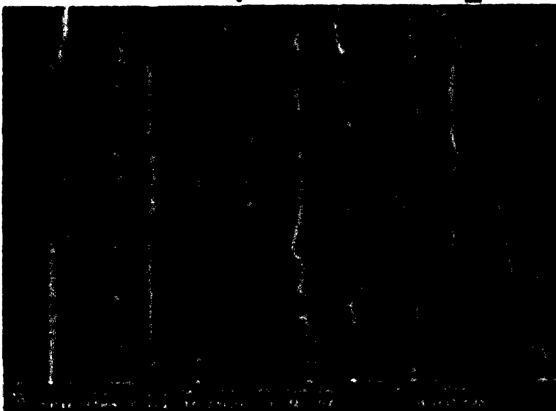
AAO



100 cycles SiO_2



200 cycles SiO_2



300 cycles SiO_2

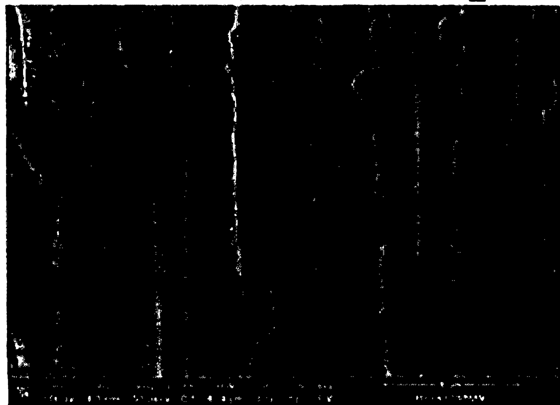


Fig. 18

Abstract

The invention is directed to a process of atomic layer deposition for the deposition of silicon oxide on a substrate, performed at room temperature, involving at least three precursors, being silicon tetrachloride, water and one Lewis base agent, being preferentially ammonia. Said process comprises the steps of exposing on said substrate during an exposure time (a) said one Lewis base agent, (b) said silicon tetrachloride, and (c) said water. Said process is remarkable in that at least one step of purge with nitrogen gas is performed after each of the steps (a), (b) and (c) during a purge time. The invention is further directed to a film of silicon oxide which is remarkable in that it comprises a low level of chlorine contaminant and a significant degree of porosity with pores, said pores being preferentially micropores, mesopores or nanopores.

(Fig. 1)

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Ministère de l'Économie
et du Commerce extérieur

SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

National Application Number

LO 1167
LU 92795

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	EP 1 925 691 A1 (APPLIED MATERIALS INC [US]) 28 May 2008 (2008-05-28) * figure 3 * -----	13-15 1	INV. C23C16/455 C23C16/40
X	US 4 239 811 A (KEMLAGE BERNARD M [US]) 16 December 1980 (1980-12-16) * column 3, line 58 * * column 4, line 60 - line 66 * -----	13-15	
A,D	DU ET AL: "SiO2 film growth at low temperatures by catalyzed atomic layer deposition in a viscous flow reactor", THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 491, no. 1-2, 22 November 2005 (2005-11-22), pages 43-53, XP005082942, ISSN: 0040-6090, DOI: 10.1016/J.TSF.2005.05.051 * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (IPC)
A	US 2006/134331 A1 (THOMPSON JEFFERY S [US]) 22 June 2006 (2006-06-22) * page 1, right-hand column, paragraph 11 * -----	1	C23C

The present search report has been drawn up for all claims

	Date of completion of the search	Examiner
	15 April 2016	Schuhmacher, Jörg

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

ANNEX TO THE SEARCH REPORT ON LUXEMBOURG PATENT APPLICATION NO.

LO 1167
LU 92795

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-04-2016

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		US 2006134331 A1	22-06-2006
		WO 2006033731 A2	30-03-2006

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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Ministère de l'Économie
et du Commerce extérieur

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
LO1167	10.08.2015		LU92795

International Patent Classification (IPC)
INV. C23C16/455 C23C16/40

Applicant
Luxembourg Institute of Science and Technology

This report contains indications relating to the following items:

- ☒ Box No. I — Basis of the opinion
- ☐ Box No. II — Priority
- ☐ Box No. III — Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV — Lack of unity of invention
- ☒ Box No. V — Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI — Certain documents cited
- ☒ Box No. VII — Certain defects in the application
- ☐ Box No. VIII — Certain observations on the application

Form LU237A (Cover Sheet) (January 2007)	Examiner Schuhmacher, Jörg

WRITTEN OPINION

Box No. I Basis of the opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-12
	No:	Claims	13-15
Inventive step	Yes:	Claims	1-12
	No:	Claims	13-15
Industrial applicability	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

   see separate sheet

WRITTEN OPINION

Box No. VII Certain defects in the application

The following defects in the form or contents of the application have been noted:

see separate sheet

1 **Re Item V**

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1.1 Reference is made to the following documents:

D1 EP 1 925 691 A1 (APPLIED MATERIALS INC [US]) 28 May 2008 (2008-05-28)

D2 US 4 239 811 A (KEMLAGE BERNARD M [US]) 16 December 1980 (1980-12-16)

1.2 The present application does not meet the criteria of patentability, because the subject-matter of claims 13-15 is not new, for the following reasons.

Independent claim 13 partly defines a product in terms of the process by which the product is made. The claim as a whole is directed to a film of silicon oxide. This claim is not permissible for the following reason: It lacks novelty over prior art D2. Even if made by an undisclosed process, it appears to be inherently the same as, or indistinguishable from, SiO2 films known from D2.

D2 already discloses porous silicon dioxide films with chlorine content inferior to 3 % (D2, column 3, line 58 in combination with whole teaching of D2 to lower chlorine content) and which comprises pores as evidenced by the values of refractive index (D2, column 4, lines 60-67).

1.3 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and D1 discloses (D1, Figure 3, column 6, par 34-36) a process of atomic layer deposition according to the preamble of claim 1 and parts of the characterizing part of claim 1. D1 discloses a purge with nitrogen (D1, par 35 in combination with par 31) after steps (b) and (c) as indicated in current claim 1. The temperature in D1 includes room temperature (D1, par 29) and the silicon precursor can be SiCl4 (D1, par 24).

The subject-matter of claim 1 therefore differs from this known process in the purge with nitrogen after step (a) and is therefore new.

The technical problem to be solved by the present invention may be regarded to avoid inclusions of chlorides of the Lewis acid into the film (compare description page 4, first paragraph).

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step. No prior art was retrieved that would motivate the skilled person to purge the Lewis base catalyst before the silicon precursor is introduced.

2 **Re Item VII**

Certain defects in the application

2.1 Although claim 1 is drafted in the two-part form, the feature a purge with nitrogen after steps (b) and (c) as indicated in current claim 1. is incorrectly placed in the characterising portion, as it is disclosed in D1 in combination with the features placed in the preamble.

2.2 The relevant background art disclosed in D1 is not mentioned in the description, nor is this document identified therein.