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## Low temperature ALD of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> multilayer structures constructed on self-standing films of cellulose nanofibrils

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Keywords: Low temperature ALD, SiO<sub>2</sub>, hybrid multilayers, cellulose nanofibrils, water sensitivity, diffusion barrier

### Summary

In this paper, we have optimised a low temperature Atomic Layer Deposition (ALD) of SiO<sub>2</sub> using AP-LTO® 330 and ozone (O<sub>3</sub>) as precursors, and demonstrated its suitability to surface modify temperature sensitive bio-based films of cellulose nanofibrils (CNF). The lowest temperature for thermal ALD process was 80 °C when the silicon precursor residence time was increased by the stop-flow mode. The SiO<sub>2</sub> film deposition rate was dependent on the temperature varying within 1.5-2.2 Å(cycle)<sup>-1</sup> at the temperature range of 80-350 °C, respectively. Obtained low temperature SiO<sub>2</sub> process was combined with the conventional trimethylaluminium (TMA) + H<sub>2</sub>O process in order to prepare thin multilayer nanolaminates on self-standing CNF films. 1-6 stacks of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> were deposited on the CNF films with the individual layer thickness of 3.7 nm and 2.6 nm, respectively, combined with the 5 nm protective SiO<sub>2</sub> layer as a top layer. The performance of the multilayer hybrid nanolaminate structures were evaluated with respect to the oxygen and water vapour transmission rates. Six stacks of SiO<sub>2</sub>/Al<sub>2</sub>O with the total thickness of ~35 nm efficiently prevented the oxygen and water molecules from interacting with the CNF film. The oxygen transmission rates analysed at RH% 80 decreased from the value of plain CNF film of 130 ml m<sup>-2</sup> day<sup>-1</sup> to 0.15 ml m<sup>-2</sup> day<sup>-1</sup> whereas the water transmission rates lowered from  $630 \pm 50$  g m<sup>-2</sup> day<sup>-1</sup> down to  $90 \pm 40$  g m<sup>-2</sup> day<sup>-1</sup>.

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## Introduction

Potential of plant derived nanoscale cellulosic materials such as cellulose nanofibrils (CNF) have been successfully demonstrated in diverse applications including responsive membranes [1], biobased nanocomposites [2] and diagnostics [3]. The exploitation of these biomaterial based building blocks has gained high interest not only because of their status as green, lightweight, and renewable materials – although these are undoubtedly positive assets – but also due to the fact that nanocellulosic materials possess several inherent features. These include, for example, piezoelectric properties, low thermal conductivity, high thermal stability, and low density coupled with relatively high strength as well as the ability to form flexible films that can act as a gas barrier material. [4-7]

Hybrid structures combining organic with inorganic materials are commonplace and many of the applications, like solar cells, are based on thin film technology. [8] The use of biopolymers, however, has remained a largely unexplored area with thin film hybrids, particularly concerning plant-based polysaccharides like cellulose. Recently such structures in which the inorganic layers are constructed via Atomic Layer Deposition (ALD) have shown to be able to suppress thermal conductivity of ZnO when hybridizing it with nanocellulose. [9] ALD thin layers of Al<sub>2</sub>O<sub>3</sub> have been successfully exploited to enhance the moisture and gas barrier performance of various biobased films and coatings such as CNF, pectin and galactoglucomannan coated board. [10] Improved barrier properties have been obtained by different multilayer structures, such as Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> [11], Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> [12], Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub> [13], Al<sub>2</sub>O<sub>3</sub>/alucone [14] and ZrO<sub>2</sub>/zircone [15]. Multilayer structures and nanolaminates are utilised in order to protect the vulnerable Al<sub>2</sub>O<sub>3</sub> layer and to increase a tortuous diffusion path of the molecules.[16] In addition to the moisture sensitivity control, the nanolaminate structures based on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> may bring multifunctionality to be utilised e.g. as antireflective and optical materials [17]. Moreover, SiO<sub>2</sub> surfaces are well known to be prone to various further chemical reactions. [18] When the peculiar features of CNF films are coupled with the numerous functionalisation opportunities achieved via ALD thin film technology, completely new application areas can be anticipated for cellulosic materials. These may include for example nanoelectronics and solutions for energy harvesting.

ALD itself is a gas-phase thin-film technique that has become the method of choice in e.g. semiconductor industry for fabricating homogeneous pinhole-free oxide and sulphide thin films on large-area and/or nanostructured substrates in a highly reproducible and conformal manner. A unique common feature of ALD is the perfect conformability of the resultant thin-film coating over a variety of imaginative nanostructures.[19] Traditionally ALD coatings have been produced with batch processes, but recently there has been interest towards continuous and roll-to-roll processing when high throughput applications are emerging. [20] However, high temperature levels often required during the depositions is a clear limiting factor when considering the efficient functionalisations of plant-based materials via ALD. In addition, the need for the low temperature processing sets up new challenges in process chemistry as well.[24] For example the low reactivity of ozone hinders the thermal processes below 300 °C in cross-flow ALD tools.

Here, the overall goal is to i) develop the thermal ALD process for  $SiO_2$  deposition to be carried out on sensitive biomaterial substrates and ii) construct inorganic multilayer nanoarchitectures of alternating thin films  $SiO_2$  and  $Al_2O_3$  in order to fabricate hybrid self-standing nanocellulose films with controlled moisture sensitivity and decreased oxygen transmission performance. The thermal ALD process development was carried out by coating silicon substrates in order to optimise the reaction conditions. The formed inorganic multilayer structures were characterised with ellipsometry and X-Ray reflectivity measurements (thickness) as well as with Time-of-Flight Elastic Recoil Detection Analysis (TOF-ERDA) (elemental composition). The optimised ALD conditions were exploited to coat the CNF films and the constructed hybrid structures were characterised by high resolution microscopical methods (SEM and AFM). Finally their oxygen and water vapour permeation rates were benchmarked against an existing similar type of the CNF film structure.

# Materials and Method Cellulose nanofibrils (CNF) and CNF films

Cellulose nanofibrils were produced using a native once dried bleached birch kraft pulp (BHKP) followed by mechanical disintegration with a Microfluidizer. The pulp was first soaked at 1.7% consistency and dispersed using a high shear Diaf dissolver for 10 minutes at 700 rpm. The suspension was pre-refined in a grinder (Supermasscolloider MKZA10-15J, Masuko Sangyo Co., Japan) at 1500 rpm. The pre-refined fibre suspension was fed into a fluidizer (Microfluidics M-7115-30 Microfluidicis Corp.). First the fibre suspension was passed through the chambers having diameters of 500  $\mu$ m and 200  $\mu$ m followed by six passes through a chamber pair with the diameters of 500  $\mu$ m and 100  $\mu$ m at a pressure of 1800 bar. The final material appearance was a viscous and translucent gel (light transmittance of 41.5% at 800 nm by UV-Vis spectroscopy) with a final solid content of 1.6%, pH 6.4, conductivity of 17  $\mu$ S/cm. Basic rheological characteristics of the fibrillated material were analysed with Brookfield rheometer RVDV-III and the spindle type V73 at 0.8% consistency giving the yield stress of approximately 7 Pa and apparent viscosity values of ~54 000 mPas and 4000 mPas at 0.5 rpm and 10 rpm, respectively.

Self-standing CNF films were produced by solvent casting method of cellulose nanofibrils which is based on precise control of adhesion, spreading, drying and delaminating of the material on a plastic substrate with a patented method. [21, 7] Films were manufactured in semi-pilot scale using machinery manufactured by Coatema Coating Machinery GmbH. The CNF dispersion (1.6% solid content) including sorbitol (30wt. % solids in dry film from Sigma) was first carefully pre-homogenized by mixing with Diaf dissolver for 30 min (300 rpm). Then a deareated CNF suspension was coated on a plasma pretreated plastic support substrate (cast polypropylene). Support substrate retreatment was carried out using Vetaphone Corona-Plus (Type TF-415, CP1C MKII 2.0 kW) equipped with Ar/N<sub>2</sub> plasma to adjust surface energy to ensure even CNF spreading and adhesion during drying. After evaporation of the excess of solvent by controlled drying in ambient conditions overnight, the remaining CNF film with the thickness of 25µm was carefully separated from the plastic substrate and cut into A4-sized sheets.

### ALD depositions

 $Al_2O_3$  and  $SiO_2$  depositions were carried out at 100 °C using commercial TMA (CH<sub>3</sub>Al, Strem Chemicals) and AP-LTO® 330 (Air Products & Chemicals Inc.) as aluminium and silicon precursors, respectively.  $N_2$  (>99.999%) from LNG (liquid nitrogen gas) station was used as a carrier gas,  $O_3$  (IN USA, Inc.) as an oxygen source in the SiO<sub>2</sub> processing and  $H_2O$  as oxygen source in  $Al_2O_3$  process. Picosun Sunale R200 ALD tool was used in a single wafer showerhead mode accommodating maximum 200 mm diameter of substrates or in batch mode equipped for 15 pcs of 150mm diameter substrates with optional stop-flow set-up. Initial process development was carried out onto Si(100) substrates. The optimised deposition conditions with respect to temperature and purge times were applied on self-standing CNF films according to the Table 1.

Sample name	ALD layer structure
CNF film	-
CNF film + Al <sub>2</sub> O <sub>3</sub>	20 nm Al <sub>2</sub> O <sub>3</sub>
CNF film + SiO <sub>2</sub>	20 nm SiO <sub>2</sub>
CNF film + Al <sub>2</sub> O <sub>3</sub> +SiO <sub>2</sub>	$20 \text{ nm Al}_2\text{O}_3 + 5 \text{ nm SiO}_2$
$CNF \ film + SiO_2/Al_2O_3 + SiO_2$	$n \times ({\sim}4nm~SiO_2 + {\sim}3nm~Al_2O_3$ ) (n=1-6) + 5 nm SiO_2

Table 1. Various ALD thin film depositions carried out on CNF films.

#### Elemental composition and thickness of ALD layers deposited on Si-substrates

The elemental composition of the inorganic thin films deposited onto silicon substrates was determined by means of Time-Of-Flight-Elastic Recoil Detection Analysis (TOF-ERDA). [22] In this method, a heavy 12.8 MeV 63Cu<sup>7+</sup> ion beam is directed to the sample and the time of flight (velocity) and energy of recoiled sample atoms are measured with a detector telescope at 41° to the beam direction. Independent measurement of the velocity and energy of recoil atoms allows them to be differentiated according to their mass. The elemental depth profiles were determined by means of known geometry, elastic scattering cross-sections and stopping forces. [23]

Thicknesses of the deposited films were measured by ex-situ ellipsometry (SE400adv, Sentech Instruments GmbH). The measurements were performed at an angle of incidence of  $70^{\circ}$  and the data was fitted to Cauchy model, using the thickness value calculated from ALD deposition rates as a starting point.

X-ray reflectivity (XRR) measurements of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks were performed with x-ray diffractometer (Philips X'Pert Pro) utilizing parallel beam conditions and Cu-K<sub> $\alpha$ </sub> x-ray wavelength. Acceleration voltage and anode current were 40 kV and 40 mA, respectively. Measured reflectivity curves were simulated using Parratt's formalism applying in-house developed software to determine the thickness of the nanolaminate layers. [25] The density and roughness values of individual layers could not be trustworthy estimated because the both of the thin Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> layers effect to the critical angle of the total external reflection and the overall intensity level of the reflectance curve.

### Surface morphology of the hybrid films by AFM and SEM

A nanoscope multimode scanning probe microscope (V6.13 R1, Digital Instruments Inc., Santa Barbara, CA, USA) was used to determine the morphology of CNF substrates after ALD Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> depositions. Silicon cantilevers with aluminium coating (HQ:NSC15/Al BS,  $\mu$ Masch, Tallinn, Estonia) and with nominal resonance frequencies of 265-410 kHz were used for imaging in tapping mode under ambient conditions. At least three 5  $\mu$ m × 5 $\mu$ m areas of each sample were scanned. Images were not processed by any other means except flattening.

The scanning electron microscope (SEM, JEOL JSM-6360LV) was used to detect the microstructures of the cross sections of the CNF substrates after the single layer ALD depositions of  $Al_2O_3$  and  $SiO_2$ . The samples were fractured in liquid nitrogen. The images were taken by using secondary electron image (SE) of the fracture surfaces. The used accelerating voltage was 20 kV for the CNF film + 20 nm  $Al_2O_3$  or 10 kV for CNF film + 20 nm  $SiO_2$  and magnification was 2000× in both cases.

### Oxygen/water vapour transmission rates of the hybrid films

Oxygen transmission rates through the CNF+ALD structures were determined according to standard ASTM D3985 using Ox-Tran 2/21 Oxygen Transmission Rate System (Mocon, Modern Controls Inc., USA). The test area of the sample was 50 cm<sup>2</sup>. The tests were carried out at 23°C, 80% RH using 100% oxygen as a test gas. Water vapour transmission rates of the CNF+ALD structures were determined gravimetrically using a modified ASTME-96B (wet cup) procedure. Samples with a test area of 30 cm<sup>2</sup> were mounted on a circular aluminium dish (68-3000 Vapometer EZ-Cups), which contained water. Dishes were stored in test conditions of 23°C and 50% relative humidity and weighed periodically until a constant rate of weight reduction was attained.

## **Results and Discussion**

### Development of low temperature ALD deposition process for SiO<sub>2</sub>

Previously we have reported a thermal ALD process based on AP-LTO® 330 precursor with ozone (O<sub>3</sub>) in a cross-flow ALD reactors in order to deposit silicon oxide (SiO<sub>2</sub>). [24] As shown by Putkonen et al (2014) [24] and in Fig. 1, the highest deposition rate of 0.9-1.2 Å/cycle was obtained at high temperatures of 250–350 °C using a single wafer R&D tool (ALD tool for smaller substrate size) whereas in pilot-scale large batch ALD tool (tool for several substrates with larger size) the deposition rate decreased down to 0.4-0.65 Å(cycle)<sup>-1</sup> probably due to higher volume chamber leading to the lower O<sub>3</sub> concentration.



**Figure 1.** SiO<sub>2</sub> deposition rate as a function of growth temperature and the effect of the stop flow (filled symbols). Open symbols refer to the results of Putkonen et al. (2014) for the comparison purposes [24].

In our previous experiments we obtained lower deposition rates on R&D tool based on the different type of flow geometry. Deposition rates were only 0.3-0.6 Å(cycle)<sup>-1</sup> at 200-350 °C (see Fig. 1) probably due to higher volume showerhead type deposition chamber compared to narrow slot type R&D chambers. In the aforementioned publication it was also shown that the temperature levels lower than 100 °C for successful SiO<sub>2</sub> depositions was achieved only by using plasma enhanced  $O_2$  as reactant in the AP-LTO® 330 process (PEALD). However, the use of the PEALD process for large area substrates or demanding aspect ratio structures affects film uniformity and conformality. The main challenge lies in the recombination loss probability of radicals during plasma collision to the surfaces. [26] On the other hand, biobased materials may suffer from the strong oxidation power of O<sub>3</sub> especially at elevated temperatures and therefore, we concentrated on developing low temperature thermal ALD process using AP-LTO® 330 precursor with O<sub>3</sub> as reactant with the gas flow configuration presented in Fig. 2. Here, the precursor recidence time was increased by reducing the pumping speed and carrier gas flow after the precursor pulse introduction by closing the main pump line allowing pressure to increase during the stop-flow action. Depending on the processing parameters, maximum pressure during the stop-flow dwell was around 10-20 mbar. After stop-flow action deposition, the chamber was purged by increasing pumping speed. During the first 4s of the purging sequence higher carrier gas flow rate were applied in order to remove remaining precursor residues.

As shown by the Fig. 3 the deposition rate was significantly increased by increasing the precursor residence time by applying a stop-flow mode. Typically 10s of stop-flow time was used after precursor pulses leading to a deposition rate of  $1.67\text{Å}(\text{cycle})^{-1}$  at 100 °C. Reasonable SiO<sub>2</sub> deposition rates of  $1.5\text{Å}(\text{cycle})^{-1}$  were achieved at 80 °C whereas without the stop-flow action, practically no silica deposition was taking place at temperatures lower than 200 °C. Thus, it can be concluded that the stop-flow action enabled the exploitation of thermal ALD with low temperature deposition with AP-LTO® 330 and O<sub>3</sub>.



Figure 2. Pressure changes in ALD reactor during a deposition cycle in a stop-flow mode.

In addition, the precursor purge times were increased during the stop-flow operation due to the higher pressure to be evacuated. Typically >5 s purge was needed after silicon precursor dwell and >8s purge after  $O_3$  cycle while depositing SiO<sub>2</sub> layers on silicon reference substrates.



**Figure 3.** SiO<sub>2</sub> deposition rate measured from the leading edge of the substrate as a function of stop flow as well as  $O_3$  and silica precursor purge times. Deposition temperature of 100 °C.

According to TOF-ERDA measurements, the SiO<sub>2</sub> layers deposited at 100 °C were slightly oxygen rich with the Si:O ratio being 1:2.2. H, C and N were the main impurities although the contents were relatively low being  $3.9\pm0.3$  at-% for hydrogen and  $0.4\pm0.1$  at-% for carbon and  $0.03\pm0.02$  at-% for nitrogen. The carbon contamination was approximately at the same level when compared to the previously reported SiO<sub>2</sub> layers deposited at 100 °C using PEALD process whereas the hydrogen content was significantly lower. [24] PEALD SiO<sub>2</sub> films had a deposition rate ~1.8 Å(cycle)<sup>-1</sup> containing around 10-12 at-% of hydrogen when deposited from AP-LTO® 330 + O<sub>2</sub> plasma.

#### Constructuction of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> multilayers on Si-substrate

Although ALD Al<sub>2</sub>O<sub>3</sub> itself has been demonstrated as a versatile low-temperature diffusion barrier material in many applications, its deterioration over high humidities limits usefulness without protective layers, such as other ALD oxides, namely SiO<sub>2</sub> [27] or TiO<sub>2</sub> [28]. Both binary reference films of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as well as multilayer films with different amount of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks (n=1-6) were deposited at 100 °C followed by the deposition of the protective top layer of 5 nm SiO<sub>2</sub>. A multilayer stack was generated by 20 deposition cycles of SiO<sub>2</sub> from AP-330+O<sub>3</sub> and 20 cycles of Al<sub>2</sub>O<sub>3</sub> from TMA+H<sub>2</sub>O at 100 °C. Thicknesses of individual layers in multilayer structures deposited onto reference silicon substrates were derived from XRR measurements. Total thickness of the different stacks was analysed using ellipsometry and XRR, see Fig. 4. Binary film thicknesses resulted in deposition rates of 1.2 Å(cycle)<sup>-1</sup> for Al<sub>2</sub>O<sub>3</sub> and 1.67 for SiO<sub>2</sub> Å(cycle)<sup>-1</sup> which were used to estimate the thin film thickness in stack.



**Figure 4.** Film stack thickness as a number of  $SiO_2/Al_2O_3$  multilayers deposited on Si-substrate measured by ellipsometer and XRR. 5 nm of SiO<sub>2</sub> top layer was always deposited as a last layer. Calculated stack thickness is obtained from binary film deposition rates.

Total stack thicknesses corresponded relatively well with the calculated thickness based on the binary film deposition rates. This indicates only minor effects in the growth mechanisms when  $Al_2O_3$  is deposited on SiO<sub>2</sub> or SiO<sub>2</sub> on  $Al_2O_3$  as expected when combining two rather similar oxide processes together. According to the XRR individual SiO<sub>2</sub> and  $Al_2O_3$  layers had averaged thickness of 3.7 nm and 2.6 nm, respectively. It should be noted that the fitting of the higher layer number nanolaminates XRR measurements proved to be challenging and their technical fitting quality is thus lower than the few-layer nanolaminates. For example, the standard deviations between the XRR analysed individual layer thicknesses of SiO<sub>2</sub> and  $Al_2O_3$  ranged from 0.2 to 1.3 nm. Therefore, the normal accuracy error of  $\pm$  0.2 – 0.5 nm for single and bilayer thin film structures can be assumed to be more significant on our nanolaminates. [29] Due to this inaccuracy, only averaged thickness values are reported.

#### Constructuction of hybrid SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> multilayers on CNF film substrate

SiO<sub>2</sub> thin films were deposited using a low temperature AP-LTO®  $330 + O_3$  process at 100 °C with stop-flow action onto flexible CNF films fabricated using bleached birch kraft pulp derived nanofibrils. Al<sub>2</sub>O<sub>3</sub> thin films were deposited using trimethylaluminium (TMA) + H<sub>2</sub>O at 100 °C. Various ALD nanolaminate constructions on CNF films are collected in Table 1. Fig. 5 shows the AFM topography images of plain CNF film surface as well as the CNF surfaces subsequent to different ALD thin film depositions.



**Figure 5.** 5  $\mu$ m × 5  $\mu$ m AFM topography images of plain CNF film and CNF film after ALD depositions of a single layer of Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> (top row) as well as a CNF film with a single layer of Al<sub>2</sub>O<sub>3</sub> with a protective layer of SiO<sub>2</sub> and CNF film with a multilayer of five SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks with a protective layer of SiO<sub>2</sub> (bottom row) with height scans. The representative height scans are indicated with a white line in each image.

Although the thickness of the inorganic multilayer can be as high as 30-35 nm (see Fig. 4) the typical fibrillar network structure of the CNF film is still visible indicating good ALD film conformality. Simultaneously the surface roughness

remains unaltered and more or less similar fine structure is retained when compared to untreated CNF film. Although both binary materials have been deposited in amorphous state, some granular features can be seen in the AFM images. This phenomena can be linked in a larger extent to the ALD depositions on biomaterial or polymeric substrates since similar cluster and grain growth has been observed with ALD of ZnO on PMMA [30] and Al<sub>2</sub>O<sub>3</sub> on PEN [31]. While the implicit explanation for such behaviour is lacking, one probable reason might originate from the variations in surface chemistry and/or hygroscopic nature of the (bio)polymeric materials resulting in non-ideal ALD growth. Granular growth of SiO<sub>2</sub> during the AP-LTO® 330 + O<sub>3</sub> process may lead to the formation of larger particles on the CNF film surface, see Fig. 6. Since the purging times were optimised for solid substrates, one single reason might be higher porosity of CNF films when compared to the smooth silica substrate. CVD type growth might occur due to long precursor residence time while using stop-flow processing. Therefore relatively long purge times (>25s) were essential while using stop-flow function at low deposition temperatures for CNF substrates in order to eliminate the particle formation. It was noticed that the particle formation did not deteriorate barrier performance of the CNF films which is probably due to the uniform coverage of the SiO<sub>2</sub> layer despite of the larger particles occasionally detected on the topmost surface of hybrid structure.



**Figure 6.** Cross sectional SEM images of Al<sub>2</sub>O<sub>3</sub> (left) and SiO<sub>2</sub> (right) layers deposited on CNF film using the ALD process parameters optimised for silicon substrates.

It is well-known that highly hydrophilic CNF films displays significantly retarded oxygen permeability values also at relatively high humid conditions (RH% 50-75).[6] The oxygen barrier performance of CNF films is completely lost only above the relative humidity level of 80%. This is a remarkable feature of CNF materials when compared to many other films and structures from wood- and agro-derived sources [32, 33]. At high humid conditions, highly polar water molecules interact with OH-groups of cellulose, and these strong interactions loosen the CNF matrix allowing the water penetration inside the structure leading to increased transmission rates of water and oxygen.

Here, the oxygen transmission rate (OTR) measurements carried out at low humidity conditions (RH% 0-50) resulted in very low transmission values. In dry conditions the rates lower than 0.01 ml m<sup>-2</sup> day<sup>-1</sup> were achieved for the inorganic multilayer structures deposited on the CNF film, and the highest value of ~1.7 ml m<sup>-2</sup> day<sup>-1</sup> was recorded for the plain CNF films at RH% 50. Thus, relatively demanding conditions (23 °C and RH% 80) were required in order to see the true differences in oxygen transmission rates. Similarly, the water vapour transmission rates (WVTR) were analysed using wet cup method with rather severe conditions (100/50% RH) especially when considering such highly water sensitive biomaterial structures.

Fig. 7 collects the OTR and WVTR values of both plain CNF film and different hybrid structures constructed on CNF films, and the results were benchmarked against the published values by Hirvikorpi et al. (2011) [10]. Note that the measurement conditions in this study are more demanding with respect to the applied humidity levels.





As shown in Fig. 7, even single ALD layers of Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> with a thickness of approximately 20 nm efficiently decreased both OTR and WVTR values. In addition, the exploitation of the multilayer strategy further retarded the permeation of oxygen and water vapour through the hybrid film structure. All constructed stacks of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with the thickness variation of 10-35 nm (see Fig. 4) significantly lowered the oxygen transmission rates giving the lowest values

of  $0.15 \pm 0.07$  ml m<sup>-2</sup> day<sup>-1</sup> for the structure with 6 stacks of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> plus the protective layer of 5nm SiO<sub>2</sub> deposited on the CNF film. The same layer structure possess the ability to hinder the penetration of the water molecules into the film structure. The water transmission rates lowered substantially from the value of plain CNF film of  $630 \pm 50$  g m<sup>-2</sup> day<sup>-1</sup> down to  $90 \pm 40$  g m<sup>-2</sup> day<sup>-1</sup>.

## Conclusions

Thermal ALD processes based on AP-LTO® 330 and ozone was successfully demonstrated at low temperatures. Previously low reactivity of ozone hindered thermal processes below 300 °C in cross-flow ALD tools, but here we showed that the stop-flow configuration with increased precursor residence time enabled SiO<sub>2</sub> deposition even at 80 °C with a deposition rate of 1.5 Å(cycle)<sup>-1</sup>. We demonstrated the feasibility of AP-LTO® 330 and ozone ALD process for deposition of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> multilayers on sensitive substrates of cellulose nanofibrils. The CNF substrates were coated with the ALD SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> multilayers and both oxygen and water vapour transmission rates were significantly decreased. These findings pave the way towards novel application areas for these intriguing biobased nanoscaled building blocks to be utilised e.g. as moisture sensor elements and components in electronic devices.

## Additional Information

#### **Authors' Contributions**

MP performed the ALD process development part and ellipsometry measurements and contributed to the planning of the experiments and to the writing of the manuscript. PS (Aalto) performed the XRR measurements and analysis and mainly wrote the XRR related manuscript text and provided comments on the manuscript. LS contributed to ALD processing and SiO<sub>2</sub> analysis. TS performed the SiO<sub>2</sub> TOF-ERD analysis. JV performed the OTR and WVTR measurements. IB contributed to setting up the SiO<sub>2</sub> process. UF contributed to the experimental planning and critically reviewed the results and conclusions. PS (VTT) contributed to the ALD process development. TT contributed to the experimental planning, supervised the AFM analysis, critically reviewed the results and conclusions, and mainly drafted and finalised the manuscript. All authors read and approved the manuscript.

#### **Competing Interests**

The author(s) declare that they have no competing interests.

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Tables

	Sample name ALD layer structur	e
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CNF film	-
CNF film + Al <sub>2</sub> O <sub>3</sub>	20 nm Al <sub>2</sub> O <sub>3</sub>
CNF film + SiO <sub>2</sub>	20 nm SiO <sub>2</sub>
CNF film + Al <sub>2</sub> O <sub>3</sub> +SiO <sub>2</sub>	20 nm Al <sub>2</sub> O <sub>3</sub> + 5 nm SiO <sub>2</sub>
$CNF \ film + SiO_2/Al_2O_3 + SiO_2$	$n \times ({\sim}4nm~SiO_2 + {\sim}3nm~Al_2O_3$ ) (n=1-6) + 5 nm SiO_2

#### Figure and table captions

Table 1. Various ALD thin film depositions carried out on CNF films.

Figure 1.  $SiO_2$  deposition rate as a function of growth temperature and the effect of the stop flow (filled symbols). Open symbols refer to the results of Putkonen et al. (2014) for the comparison purposes [24].

Figure 2. Pressure changes in ALD reactor during a deposition cycle in a stop-flow mode.

Figure 3. SiO<sub>2</sub> deposition rate measured from the leading edge of the substrate as a function of stop flow as well as  $O_3$  and silica precursor purge times. Deposition temperature of 100 °C.

Figure 4. Film stack thickness as a number of  $SiO_2/Al_2O_3$  multilayers from 1-6 measured by ellipsometer and XRR. 5 nm of  $SiO_2$  top layer was always deposited as a last layer. Calculated stack thickness is obtained from binary film deposition rates.

Figure 5. 5  $\mu$ m × 5  $\mu$ m AFM topography images of plain CNF film and CNF film after ALD depositions of a single layer of Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> (top row) as well as a CNF film with a single layer of Al<sub>2</sub>O<sub>3</sub> with a protective layer of SiO<sub>2</sub> and CNF film with a multilayer of five SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks with a protective layer of SiO<sub>2</sub> (bottom row) with height scans. The representative height scans are indicated with a white line in each image.

Figure 6. Cross sectional SEM images of Al<sub>2</sub>O<sub>3</sub> (left) and SiO<sub>2</sub> (right) layers deposited on CNF film using the ALD process parameters optimised for silicon substrates.

Figure 7. Oxygen and water vapour transmission rates determined for various inorganic nanoarchitectures constructed on CNF films (filled symbols). The open symbols refer to the results by Hirvikorpi et al. (2011) for the comparison purposes [10]. <sup>a</sup>OTR 50RH%, WVTR 75/0% RH. <sup>b</sup>OTR 80RH%, WVTR 100/50% RH, CNF film contains 30 wt-% of sorbitol.