Atmospheric Pressure Spatial Atomic Layer Deposition of Silicon Oxide Using DIPAS and Ozone

Poojitha Durgamahanti,[a,b] Soumyadeep Saha,[c] Louis-Vincent Delumeau,[c] Tristan Grovu,[c] Craig A. Wheaton,[d] Kerim Samedov,[d] Kevin P. Musselman [a,b,*]

[a] Department of Mechanical and Mechatronics Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

[b] Waterloo Institute for Nanotechnology, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada.

[c] Nfinite Nanotechnology Inc., 265 Frobisher Drive, Unit 1, Waterloo, Ontario N2V 2G4, Canada.

[d] GreenCentre Canada, 945 Princess St, Suite 105, Kingston, Ontario K7L 0E9, Canada

KEYWORDS. Atmospheric-pressure spatial atomic layer deposition, Silicon oxide, Ozone, DIPAS, Thin films.

ABSTRACT. Silicon oxide (SiO_x) is a highly versatile material used in different applications. However, its conventional growth and deposition methods often require very high temperature or the use of plasma. In this work, we present a plasma-free, low-temperature process for depositing high-quality SiO_x thin films using atmospheric-pressure spatial atomic layer deposition (AP-SALD). An aminodisilane precursor, diisopropylaminosilane ($SiH_3N(C_3H_7)_2$, DIPAS), was synthesized and tested with different oxidants such as ozone and 30% hydrogen peroxide aqueous solution. Initial attempts with hydrogen peroxide solution resulted in precursor condensation and the formation of nano crystallite SiO_x contaminated with organic molecules, indicating that the deposition process is oxidant limited. In contrast, using ozone as the oxidant facilitated the deposition of high-quality amorphous SiO_x films. The microstructure was highly dependent on the deposition temperature, transitioning from nano crystallites at lower temperatures to amorphous films at temperatures of 70°C to 100°C. X-ray photoelectron spectroscopy (XPS) confirmed the deposition of SiO_x films at 70°C or above using ozone, and the growth per cycle was ~1 Å/cycle, consistent with ALD of SiO_x. This work shows that high-quality SiO_x films can be produced by AP-SALD using DIPAS and ozone, without the aid of plasma or any surface functionalization, at low growth temperatures (T >= 70°C).

1. INTRODUCTION

Thin-film silicon oxide (SiO_x) is a highly versatile material that finds use in many different areas of nanotechnology, including dielectric materials in microelectronic devices,[1] electrode materials for supercapacitors,[2] nanocoating films for barrier applications and many more.[3] Various techniques have been developed to deposit SiO_x films, such as thermal chemical vapor deposition (CVD),[4] plasma-enhanced CVD,[5] and plasma-enhanced atomic layer deposition (PE-ALD)[6] to name a few. However, these processes involve elevated temperatures or the use of plasma, limiting their applicability to certain substrates and applications. Therefore, the ability to deposit high-quality SiO_x thin films using a scalable method at a relatively low temperature is highly desired.

One such scalable method is atmospheric-pressure spatial atomic layer deposition (AP-SALD). Compared to conventional ALD where the precursors are temporally separated, in AP-SALD, the precursors are separated spatially using inert gas curtains, thereby accelerating the deposition process. Also, operating in an open atmosphere facilitates scaling of the substrate size (e.g., roll-to-roll)[7] and allows for a high saturation dose, which further speeds up the process.[8]

Some AP-SALD studies have been carried out to deposit SiO_x using organic precursors. Mione et. al reported the use of plasma-enhanced AP-SALD to deposit SiO_x within the temperature range of 100-250°C. They reported a growth per cycle (GPC) ranging from 1 to 1.2 Å/cycle using bisdiethylaminosilane (BDEAS, $SiH_2[NEt_2]_2$) as the Si precursor and oxygen plasma as the oxidant.[9] In another study, Nguyen et al. successfully deposited SiO_x using trivinylmethoxysilane (TVMS) by modifying the reactor head to incorporate oxygen plasma. They increased the spacing between the reactor head and the substrate, allowing for precursor crosstalk and thus operated in CVD mode.[10] They reported that the use of the modified reactor head and oxygen plasma led to the formation of SiO_2 films at low temperatures ranging from room temperature to 80°C.[10]

While these studies emphasize the significance of AP-SALD, all the reported techniques use plasma as an oxidant source. This damage-inducing process may limit the application of AP-SALD to sensitive substrates such as polymers. Moreover, a plasma-based oxidation process is expensive and might not be appropriate for high-throughput applications.

Given the versatility of SiO_x, various silicon-based precursors have been investigated. Some of the important conventional precursors which have been widely studied using CVD and conventional ALD include heterosilanes like SiH_4[11] and halide-based precursors like $SiCl_4$,[12] SiH_2Cl_2,[13] and Si_2Cl_6.[14] While these precursors produce high-quality films, they pose risks of film contamination due to adsorption of by-products when deposited at low temperatures. The by-products released are also hazardous and thus should be avoided for open-air, high-throughput processes such as AP-SALD.

A preliminary screening was carried out to assess possible silicon precursors for use specifically in AP-SALD. The organosilane class of Si precursors, such as tetraethoxyorthosilicate (TEOS),[15] bis(diisopropylamino)disilane (BDIPADS),[16] bis(dimethylaminosilane) (BDMAS),[17] and trivinylmethoxysilane (TVMS)[8] emerged as promising candidates. Diisopropylamino silane (DIPAS) (Figure 1), one of these amino silane organic precursors, has a high vapor pressure of ~23 torr at room temperature, is non-pyrophoric, and is not expected to produce any harmful reactive byproducts, making it well-suited for AP-SALD.[18] Therefore, DIPAS was synthesized in this work for the development of a plasma-free AP-SALD process.

Various conventional ALD studies have been conducted using DIPAS. For instance, the study by Nam et al. and another similar study[19,20] reported the deposition of SiO_x films using DIPAS and ozone. However, films could not be deposited below 100°C.[19,20] Plasma was required to reduce

the deposition temperature; for instance, Lee et. al. deposited SiO_x films using DIPAS and oxygen plasma at 60°C using conventional ALD.[21]

To address these challenges, in this study, we use a custom-built AP-SALD system to test the plasma-free deposition of SiO_x films using DIPAS as the Si precursor and either ozone or 30% hydrogen peroxide aqueous solution (30% w/w in water, peroxide-30)) as the oxidant. We conduct a systematic study of this plasma-free process to understand the effect of various parameters, such as temperature, precursor flow rate, and oxidant flow rates on the composition and morphology of the deposited materials. We find that for peroxide-30, a reaction with DIPAS only occurs below 50°C, resulting in the deposition of nano crystallites rather than a continuous film due to precursor condensation. In contrast, ozone, a stronger oxidant, reacts with DIPAS to give the desired amorphous SiO_x films at deposition temperatures of 70°C and above. At temperatures below 70°C, by-product desorption and precursor condensation become challenging. To the best of our knowledge, this is the first time that AP-SALD of SiO_x films has been demonstrated without plasma.

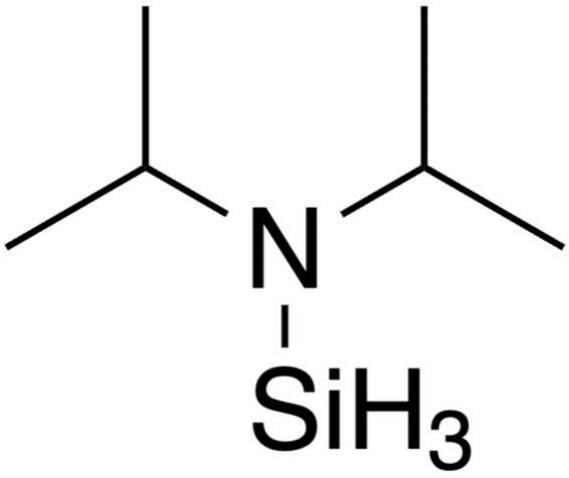


Figure 1. Diisopropylamino silane (DIPAS) molecular structure.

2. EXPERIMENTS AND PROCEDURE

DIPAS synthesis: DIPAS was synthesized in a two-step process – $SiCl_4$ and diisopropylamine reacted to form 1,1,1-trichloro-N, N-diisopropylsilanamine ($C_6H_{14}Cl_3NSi$) which was then reduced to DIPAS ($C_6H_{17}NSi$) in a second step (Figure S1 a).

An oven-dried, 3-neck, 3-L round-bottom flask was filled with 1.2 L of anhydrous pentane followed by the addition of 100 g of $SiCl_4$. 250 ml of diisopropylamine was added to the silicon chloride solution, resulting in vigorous evolution of HCl along with salt formation ($C_6H_{14}Cl_3NSi$) after continuous overnight stirring. The excess pentane was distilled off. This salt mixture was dissolved in ~500 mL of dry tetrahydrofuran (THF).

Later, 18.5 grams of $LiAlH_4$ (Pellet form, Aldrich product 323403) was dissolved separately in 500 mL of THF to form a suspension. This suspension was added slowly to the $C_6H_{14}Cl_3NSi$ salt mixture at -1°C with the temperature rising to 13°C later. The reaction mixture was a grey slurry. This mixture was stirred overnight at room temperature. The volatiles were distilled from this solution. Later, excess THF was removed by distillation, leaving behind 46.2 grams of colorless liquid, DIPAS. The ^1H NMR spectrum confirmed the formation of DIPAS with a small amount of THF (~7%) (Figure S1 b).

Silicon oxide deposition: A custom-built AP-SALD system was used (Figure 2). In this system, a reactor head with dimensions of 145 mm × 31 mm × 64 mm was kept fixed and the substrate was oscillated beneath it on a stage that was heated from room temperature up to 100°C. DIPAS was used as the Si precursor and was bubbled using high-purity nitrogen (5.0 rated) at flow rates ranging from 80 to 550 sccm. The bubbled DIPAS was combined with a nitrogen dilution carrier line for a total flow of 800 sccm from one outlet channel on the underside of the reactor, unless specified otherwise. Hydrogen peroxide or ozone was used as the oxidant, delivered to two outlet

channels, with only one oxidant used at a time, selected via the oxidant selector shown as “switch” in Figure 2. The hydrogen peroxide (30% w/w in water, peroxide-30) was bubbled with 100 sccm of nitrogen and combined with a 300 sccm carrier flow. For experiments conducted with ozone, an ATLAS -30 UHC ozone generator was utilized to produce ozone from 92.5% oxygen gas (balance nitrogen). The generator is expected to produce ozone at a rate of 22.48 g/h when operating at maximum voltage (100V) and 20 psig gas pressure. The ozone generator’s potentiometer was adjusted between 10 to 80 V to control the ozone generation percentage, and the oxygen/ozone flowmeter was set to 300 sccm. As shown in Figure 2, inert nitrogen curtains and exhaust channels were used to separate the DIPAS and oxidants. The nitrogen curtain gas-flow rate was kept constant at 3000 sccm, which was divided between 2 outlet channels. All gas outlet channels were 1 mm wide and 130 mm long. 1.5 mm-wide exhaust channels were used to help remove excess precursor. The substrate oscillation speed was set to 30 mm/sec and the path length depended on the size of the substrate, which was roughly 60 mm in length, implying it required 4 seconds to complete one AP-SALD oscillation, which is equivalent to two temporal ALD cycles.

Characterization: Film thicknesses were measure by ellipsometry (Filmsense FS-1) on silicon wafers (76.2mm Si, N-type wafer, P doped <100>, 1-10ohms-cm, SSP prime). The microstructure and roughness of the films were studied using atomic force microscopy (Bruker, Dimension FastScan in ScanAsyst mode) on the same silicon substrates. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Nexsa G2 Surface Analysis System from Thermo Scientific. The X-ray source used was monochromatic Al K-alpha (400 um). The results were analyzed using CasaXPS software and the energy scale was calibrated using C1s as the reference. For the XPS measurements, we used ITO/glass substrates from Delta Technologies Limited

(polished float glass, 16 x 16 x 1.1 mm, SiO_2 passivated/indium tin oxide coated on polished surface). Scanning electron microscopy (SEM) was performed with a Merlin SEM (Zeiss) at 2kV on the same Si substrates. Energy-dispersive x-ray spectra (EDS) were obtained with an EDAX Octane detector.

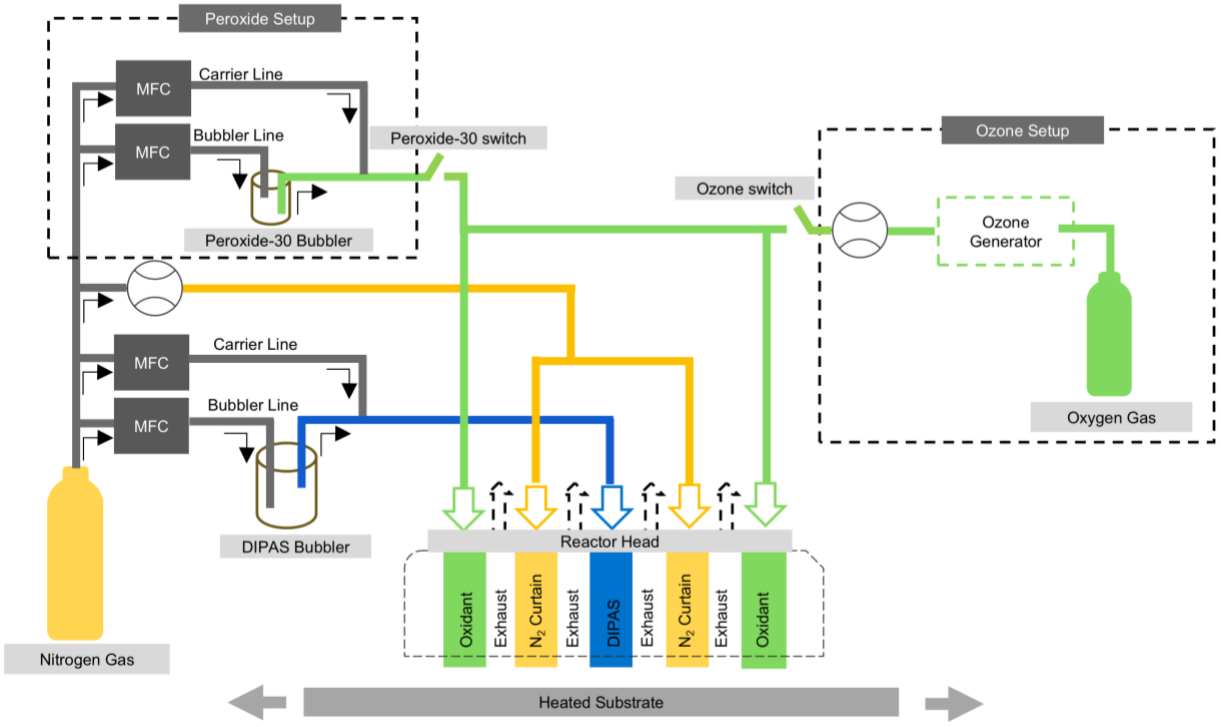


Figure 2. Schematic of AP-SALD system.

3. RESULTS AND DISCUSSION

3.1 Peroxide-30 as the oxidant

As an initial step, we examined the interaction of DIPAS with peroxide-30, a mild oxidant. We found that DIPAS showed minimal reactivity with peroxide-30 at temperatures below 50°C. At room temperature, AFM analysis revealed that nano crystallites were deposited on a silicon substrate (Figure 3a). At this temperature, the deposition process is expected to be in the precursor-condensation regime. The precursor molecules were primarily physically adsorbed onto the substrate surface, which facilitated a degree of reactivity, leading to the formation of the nano

crystallite phase. However, the lack of thermal energy is expected to lead to accumulation of contaminants, such as unreacted ligands from the precursor.

XPS was conducted to assess the composition of the nano crystallites deposited at room temperature. Figure 3b presents the XPS survey. The Si signals were weaker than those from Si films grown using ozone, as discussed later (section 3.2), implying a smaller amount of Si was present in the nano crystallites. The broad Si 2p spectrum (Fig 3c) was deconvoluted into multiple peaks. The peak at 103.3 eV was attributed to SiO_2, while the peak at 102.1 eV might correspond to aminosilane on SiO_2.[22] The peak at 105.48 eV is not well defined; however, literature suggested the presence of a Si-O bond.[23] A previous report suggested that this peak can be attributed to silicates (SiO_4), which are suspected to react with other elements, such as C and N, to form a more stable compound.[24] In Figure 3d, the deconvoluted peaks of the O 1s spectrum at 530.43 eV and 531.28 eV are related to the ITO/glass substrate,[25] and the peak at 532.88 eV was related to the strong Si-O bond in SiO_2.[26] The XPS survey also showed the presence of a high carbon content as compared to the amorphous film formed using ozone that will be discussed in Figure 6a. Similarly, we observed a very small peak at ~400 eV (inset of Figure 3b), which indicated the presence of nitrogen. It will be shown that this peak was not present in the films deposited using ozone as the oxidant (Figure 6a). The excess carbon and nitrogen are consistent with condensation of the DIPAS. It was reported that the desorption energy of the primary by-product, di-isopropylamine (DIPA), is relatively high (~0.40 eV) due to the presence of a lone pair of electrons on the N atom, inhibiting the adsorption of new DIPAS molecules, depending on the configuration.[27] This makes the formation of a dense film difficult, leaving organic contaminants behind. XRD was used to examine the structure of the nano crystallites (Figure S2). The additional diffraction peaks at 2θ angles of 15.9°, 17.9°, 24.9° and 34.3°, as compared to the XRD pattern of an amorphous SiO_x

film deposited using ozone (section 3.2), confirmed the formation of a crystalline phase. The peak at 24.9° was tentatively attributed to ethanolamine silicon oxide (JCPDS 00-051-1423), based on analysis using X'pert Pro software. However, the origin of the other peak remains undetermined. As continuous SiO_x films are ultimately desired, we next investigated depositions at higher temperatures with DIPAS and peroxide-30.

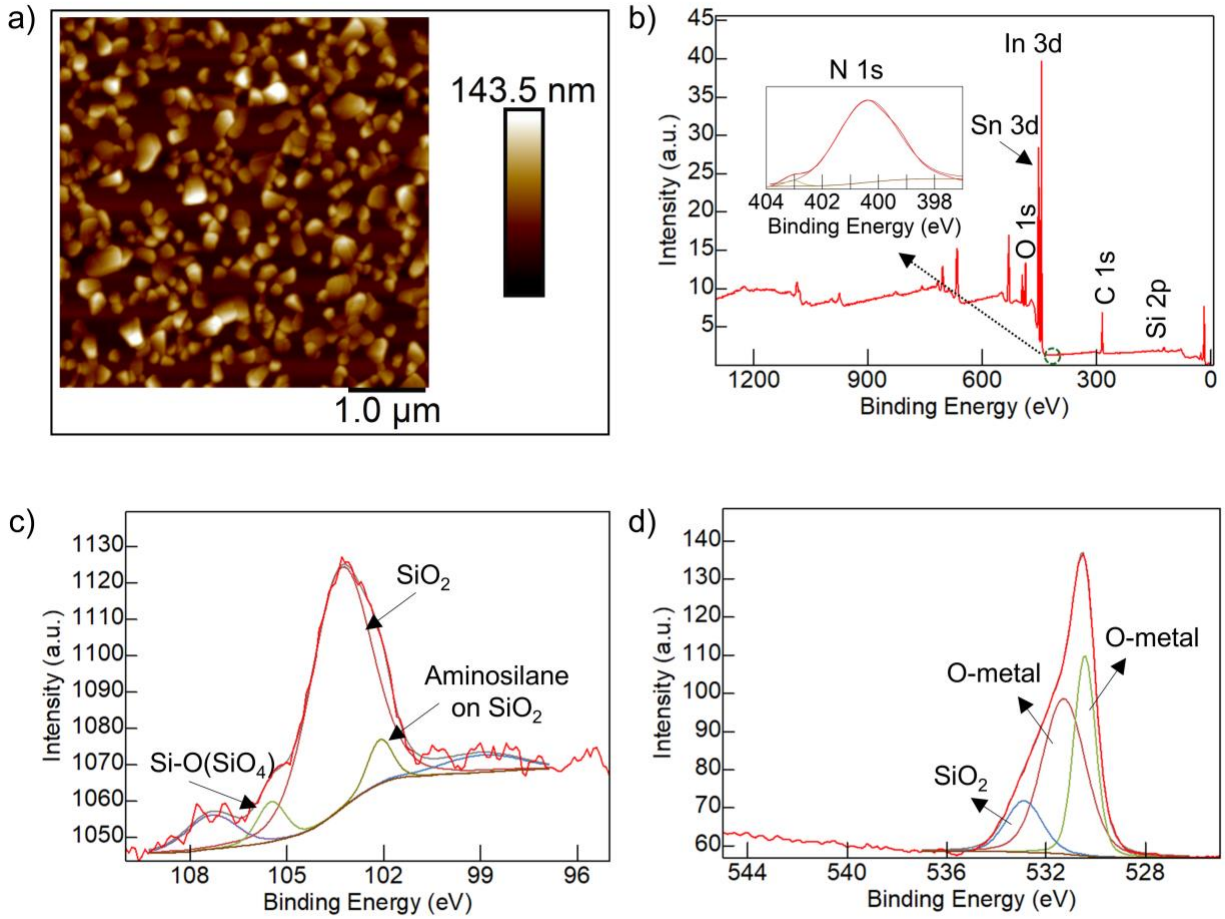


Figure 3. Nano crystallites deposited using DIPAS and peroxide-30 at room temperature. (a) AFM image on silicon substrate. (b) XPS survey, (c) Si 2p spectrum, and (d) O 1s spectrum on an ITO/glass substrate.

As the substrate temperature was increased up to 50°C, no reaction occurred between DIPAS and peroxide-30. A transition from the precursor-condensation regime to the atomic layer deposition (ALD) regime is expected at higher temperatures. In the ALD regime, the precursor molecules are expected to undergo a self-limiting chemical reaction with the substrate, resulting in the formation of a monolayer of silicon oxide. However, this reaction is highly sensitive to the oxidizing power of the oxidant used. The first-principles study by Lee et al stated that the Si-H bond cleavage (by oxidation) of SiH_3 adsorbate has a high activation energy of 1.19 eV and is the rate-determining step in the deposition process.[28] Therefore, we can conclude that hydrogen peroxide and water, due to their relatively weak oxidizing properties, are ineffective to oxidize the DIPAS molecule in the desired low-temperature ALD regime.

3.2 Ozone as the oxidant

Due to the inability to produce a continuous film with the peroxide-30 at the low temperatures of interest, ozone was investigated as a more potent oxidizing agent. The effect of ozone concentration and temperature were studied (Figure 4a) by varying the ozone-generator voltage from 10 V to 80 V and the temperature from room temperature to 100°C. The DIPAS bubbling rate was kept constant at 100 sccm, and depositions were performed for 300 cycles.

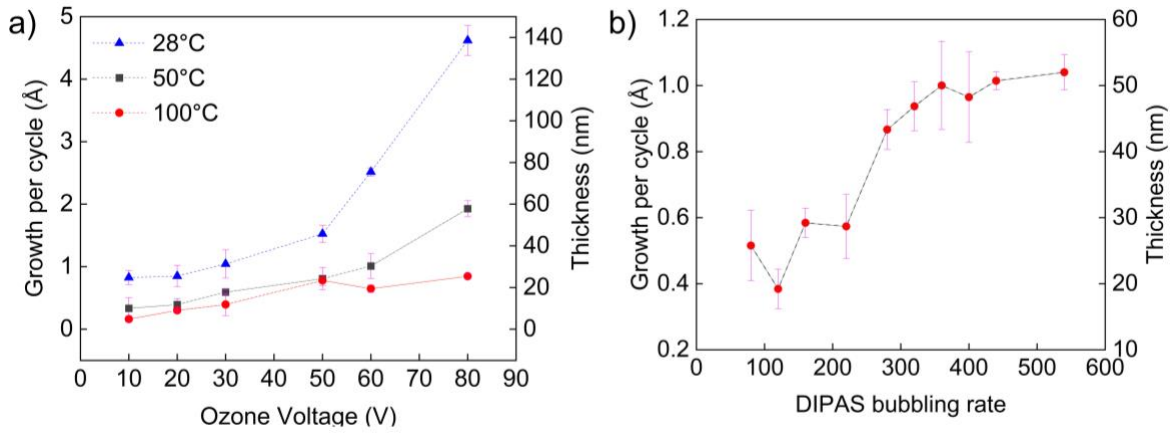


Figure 4. SiO_x depositions using DIPAS and ozone. Thickness and GPC as a function of (a) ozone-generator voltage and deposition temperature, (b) DIPAS bubbling rate.

At lower temperatures (i.e., 28°C and 50°C), a cloudy film texture was observed, similar to that seen with peroxide-30, and the film thickness increased with increasing ozone voltage, as shown in Figure 4a. However, ellipsometry analysis using the standard "silicon dioxide on Si" model showed a high fit error, indicating a complex film structure (Figure S3a). The continuous increase in GPC with ozone voltage at 28°C and 50°C suggested that ALD-type growth is not occurring. Indeed, the measured GPCs at the higher ozone voltages are larger than what is expected for ALD of SiO_x.

At a substrate temperature of 100°C, an improved, more uniform film texture was observed (Figure S3b). The GPC increased slightly as the voltage was increased from 10 V to 50 V. This was expected; as the oxidant concentration is increased, the probability of DIPAS molecules reacting with ozone molecules should increase, leading to a higher GPC. However, beyond 50 V, the GPC stabilized at approximately 0.8 Å/cycle. This is slightly less than the GPC of 1.2 Å/cycle at 150°C that has previously been reported for SiO_x,[29] suggesting that the 100 sccm bubbling rate might not be delivering sufficient precursor to saturate the surface.

Therefore, we fixed the ozone-generator voltage at 30 V and the deposition temperature at 100°C and systematically varied the DIPAS bubbling rate to verify if the deposition process was occurring under ALD conditions (Figure 4b). The number of cycles were kept constant at 500, and the DIPAS carrier-gas flow rate was adjusted accordingly to make sure the total flow from the DIPAS channel was kept constant at 800 sccm. It was observed that as the DIPAS bubbling rate was increased from 80 sccm, the growth per cycle increased, which implies that the surface was not fully saturated. At a DIPAS bubbling rate of 400 sccm, the GPC saturated at ~1 Å/cycle, implying complete saturation of the surface. Notably, this GPC of ~1 Å /cycle achieved for AP-SALD with DIPAS and ozone is similar to what has been reported in the literature for temporal ALD.[29] However, the rate of deposition was ~0.5 Å /sec, based on a 2-second cycle duration, whereas temporal ALD studies employing DIPAS and ozone reported cycle times of 23 to 32 seconds, including purging time.[19,27] This deposition rate could be further optimized in the future and highlights the rapid nature of AP-SALD.

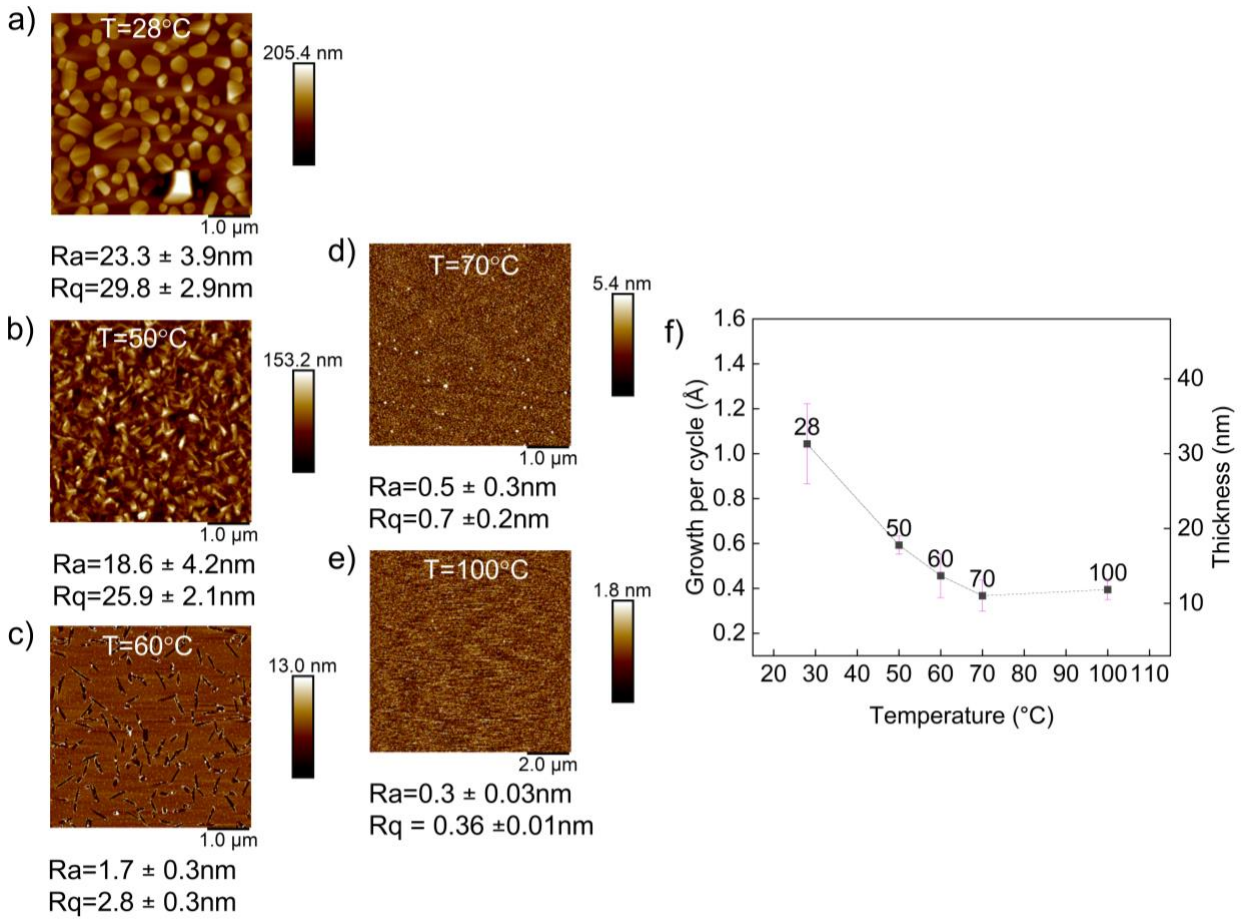


Figure 5. Microstructures produced using DIPAS and ozone at different temperatures.

After achieving ALD-type growth with DIPAS and ozone, we studied the microstructure of these films as a function of the deposition temperature (Figure 5) to better understand the growth window. The DIPAS bubbling rate was set to 80 sccm, the DIPAS carrier flow was set to 800 sccm, the ozone-generator voltage was set to 40V, and the depositions were carried out for 300 cycles. Figure 5e shows that at 100°C, an amorphous, smooth, pinhole-free SiO_x film with an average roughness of 0.3±0.03 nm was obtained. The lowest temperature to get an amorphous SiO_x film was observed to be 70°C (Figure 5d). The GPC was unchanged at 70°C (Figure 5f) and only a slight increase in surface roughness to Ra = 0.5±0.3 nm was observed. This deposition temperature is lower than what has been reported in the literature by Nam et al. Their study showed

that the lowest temperature possible to deposit SiO_x via conventional ALD using DIPAS and ozone was 100°C. The ability to deposit at 70°C increases the range of temperature-sensitive substrates to which amorphous, ALD-quality SiO_x films can be applied.

It is seen in Figures 5a-c that at deposition temperatures below 70°C, the structure became more crystalline, similar to the nano crystallites produced using peroxide-30. We suspect that a similar phenomenon of precursor condensation was occurring, which results in an increase in thickness as the temperature is lowered from 60°C to room temperature (28°C), as shown in Figure 5e. To confirm the composition of the amorphous films and the nano crystallites, XPS and EDX were conducted.

XPS analysis of a film deposited on ITO/glass at 100°C with ozone as the oxidant is shown in Figure 6. The film was deposited in the same manner as those in Figure 5, with a film thickness of ~12 nm. The XPS survey in Figure 6a clearly indicates the presence of silicon oxide, implying that the SiO_x (predominantly SiO_2) film entirely covers the substrate, as expected. It can also be seen that signals from In and Sn are negligible, however low-intensity signals may be attributed to potential pinhole defects or localized variations in film coverage. In Figure 6b the Si 2p peak was deconvoluted. The peaks at 103.06 eV and 103.69 eV indicate the presence of SiO_2 thin film and Si-O bond.[30,31] Similarly, the O 1s peaks at 532.6 eV and 532.9 eV in Figure 6c show the presence of the non-bridging oxygen, Si-O, and SiO_2 bond respectively.[32,33] Analysis of the XPS spectra indicates the oxygen to silicon ratio is approximately 1.92, deviating slightly from the ideal SiO_2 stoichiometry. The carbon peak at ~285 eV has a reduced intensity compared to that observed for the nano crystallites formed with peroxide-30 (Figure 3b), suggesting significant precursor condensation was avoided. For the samples deposited at low temperatures, EDS was used for compositional analysis of the nano crystallites.

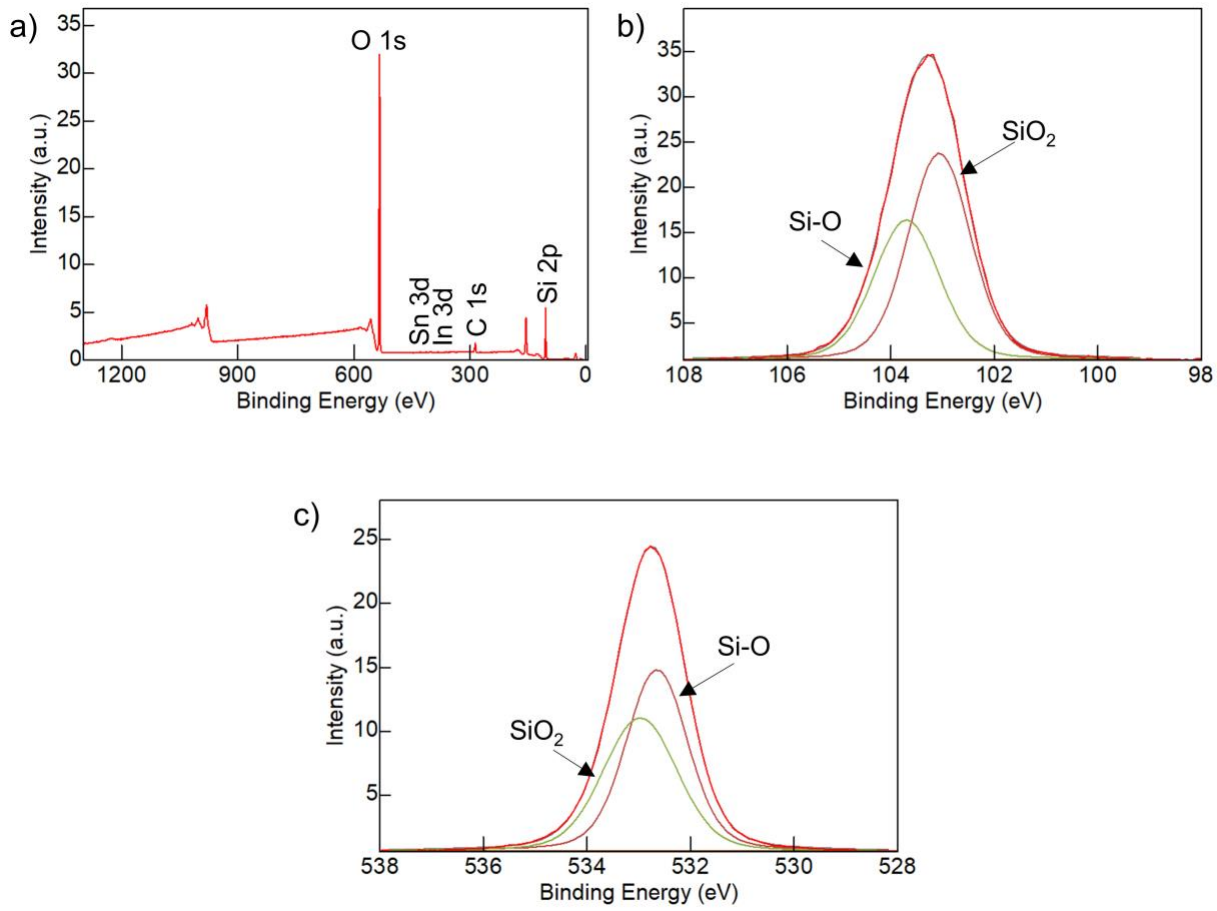
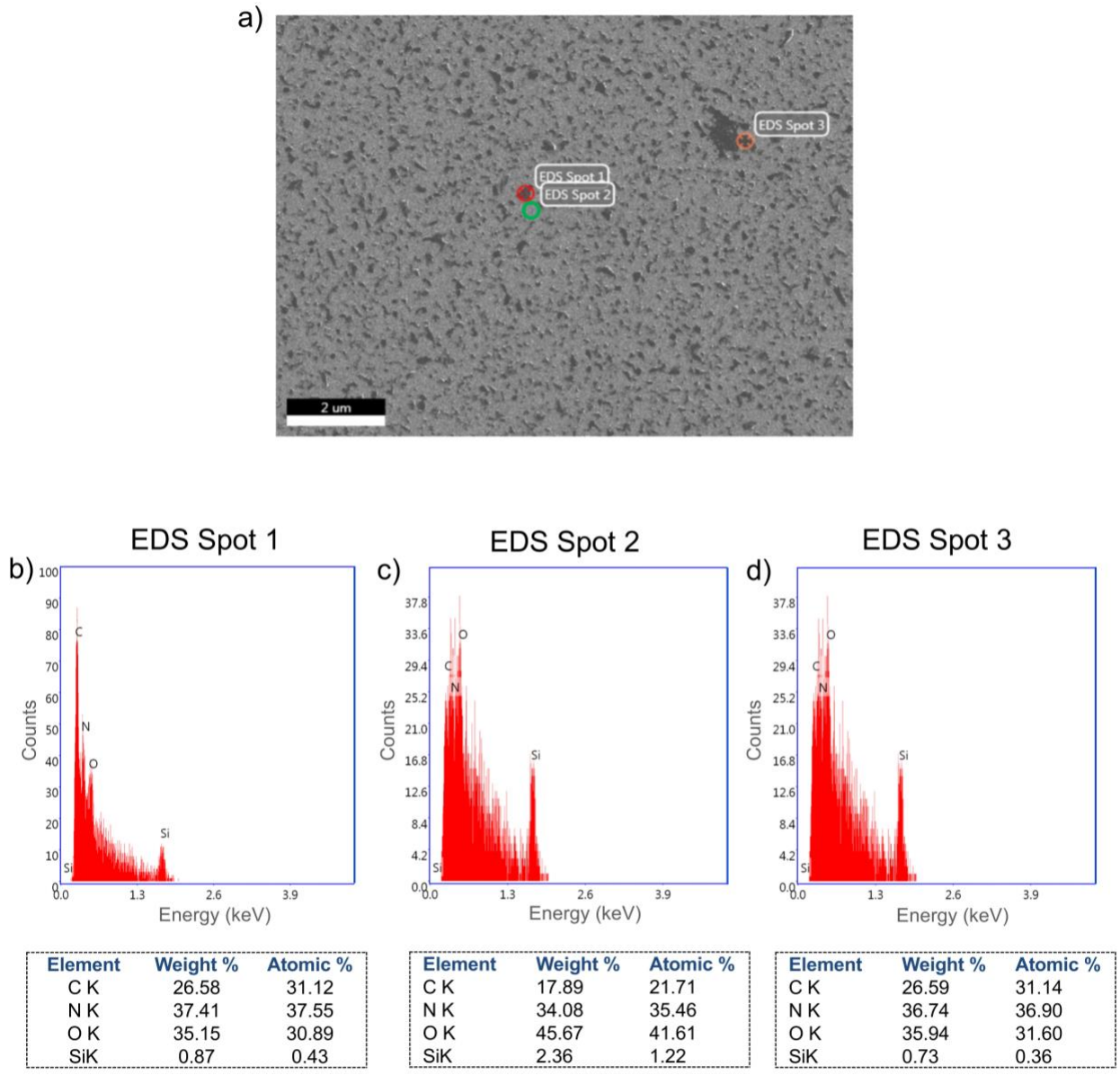


Figure 6. (a) XPS survey, (b) Si 2p spectrum, and (c) O 1s spectrum for a silicon oxide film deposited using DIPAS and ozone at 100°C on an ITO/glass substrate.

Figure 7a shows a back-scattered SEM image of the nano crystallite phase formed at room temperature on a Si substrate using DIPAS and ozone. A 2 keV electron beam was used to reduce the depth of penetration and probe the sample and not the substrate. Spot 1 and spot 3 include areas covered by the nano crystallite phase, whereas spot 2 is focused on the area not covered by this phase. Spot 1 and spot 3 show a high presence of carbon and nitrogen, exhibiting N:Si ratios of 43 and 50.3, respectively, compared to spot 2 which contains less carbon and nitrogen (N:Si ratio of 14.4). Hence, the nano crystallite features at spots 1 and 3 are contaminated with nitrogen-containing compounds, suggesting the presence of unreacted or partially reacted DIPAS. This

suggests that at lower temperatures the by-product desorption is difficult, even with the use of ozone, which eventually leads to formation of a complex Si compound. As previously mentioned, this has been reported in various theoretical studies on DIPAS, which stated that the desorption of by-products and oxidation of the Si-H bond are the most-energy-consuming steps. [20,34]



Element	Weight %	Atomic %
C K	26.58	31.12
N K	37.41	37.55
O K	35.15	30.89
SiK	0.87	0.43

Element	Weight %	Atomic %
C K	17.89	21.71
N K	34.08	35.46
O K	45.67	41.61
SiK	2.36	1.22

Element	Weight %	Atomic %
C K	26.59	31.14
N K	36.74	36.90
O K	35.94	31.60
SiK	0.73	0.36

Figure 7. (a) Backscattered SEM image of nano crystallites deposited on a Si substrate at room temperature using DIPAS and ozone. EDS spectra at (b) spot 1 – nano crystallite phase, (c) spot 2 - substrate, and (d) spot 3 - nano crystallite phase

4. CONCLUSION

We have successfully demonstrated plasma-free AP-SALD of SiO_x films using DIPAS and ozone at temperatures of 70 to 100°C. Initial attempts with peroxide-30 showed limited reactivity between the precursors, which yielded Si-based nano crystallites because of precursor condensation, and it was concluded that the oxidation of the Si-H bond was the limiting factor. As a result, a more potent oxidizing agent, ozone, was selected. We used ozone to create ALD-quality SiO_x films on silicon and ITO/glass substrates at a temperature as low as 70°C and at high growth rates of 0.5 Å/sec. AFM and XPS measurements confirmed that the films were amorphous with the SiO_x film covering the entire substrate. The microstructure was temperature-dependent; changing from an amorphous film to nano crystallites as the deposition temperature was reduced, which was attributed to precursor condensation. We believe that the open-air, plasma-free AP-SALD technique described herein will pave the way for future improvements in SiO_x depositions at lower temperatures, potentially broadening their applications in a variety of areas.

ASSOCIATED CONTENT

Supporting Information. Additional data including NMR, XRD data and ellipsometry measurements.

AUTHOR INFORMATION

Corresponding Author

*Kevin P. Musselman - Department of Mechanical and Mechatronics Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada; Waterloo Institute for Nanotechnology, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada.

Email: kevin.musselman@uwaterloo.ca

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

P.D. and K.P.M acknowledge funding from the NSERC I2I program (#I2IPJ #570986-22).

P.D. acknowledges a Waterloo Institute for Nanotechnology (WIN) Nanofellowship. The University of Waterloo's QNFCF facility was used for this work. This infrastructure would not be possible without the significant contributions of CFREF-TQT, CFI, ISED, the Ontario Ministry of Research & Innovation and Mike & Ophelia Lazaridis. Their support is gratefully acknowledged.

ABBREVIATIONS

AFM, atomic force microscopy; ALD, atomic layer deposition; AP-SALD, atmospheric pressure spatial atomic layer deposition; CVD, chemical vapor deposition; DIPAS, diisopropylaminosilane; EDS, energy dispersive spectroscopy; GPC, growth per cycle; PE-ALD, plasma-enhanced atomic layer deposition; SEM, scanning electron microscopy; XPS, x-ray photoelectron spectroscopy; XRD, x-ray diffraction.

REFERENCES

(1) Kim, D. H.; Lee, H. J.; Jeong, H.; Shong, B.; Kim, W. H.; Park, T. J. Thermal Atomic Layer Deposition of Device-Quality SiO2 Thin Films under 100 °c Using an Aminodisilane Precursor. *Chemistry of Materials* 2019, *31* (15), 5502–5508. https://doi.org/10.1021/acs.chemmater.9b01107.

(2) Sajjad, M. Recent Advances in SiO2 Based Composite Electrodes for Supercapacitor Applications. *J Inorg Organomet Polym Mater* 2021, *31* (8), 3221–3239. https://doi.org/10.1007/s10904-021-01899-1.

(3) Lee, Y.; Seo, S.; Oh, I. K.; Lee, S.; Kim, H. Effects of O2 Plasma Treatment on Moisture Barrier Properties of SiO2 Grown by Plasma-Enhanced Atomic Layer Deposition. *Ceram Int* 2019, *45* (14), 17662–17668. https://doi.org/10.1016/j.ceramint.2019.05.332.

(4) *SiO 2 Chemical Vapor Deposition at Room Temperature Using SiCl 4 and H 2 O with an NH 3 Catalyst*; 2000.

(5) Lee, Y. S.; Lee, S. H.; Kwon, J. D.; Ahn, J. H.; Park, J. S. Silicon Oxide Film Deposited at Room Temperatures Using High-Working-Pressure Plasma-Enhanced Chemical Vapor Deposition: Effect of O2 Flow Rate. *Ceram Int* 2017, *43* (13), 10628–10631. https://doi.org/10.1016/j.ceramint.2017.05.095.

(6) Lee, Y.-S.; Han, J.-H.; Park, J.-S.; Park, J. Low Temperature SiOx Thin Film Deposited by Plasma Enhanced Atomic Layer Deposition for Thin Film Encapsulation Applications. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 2017, *35* (4). https://doi.org/10.1116/1.4985140.

(7) 1. Musselman, K. P.; Uzoma, C. F.; Miller, M. S. Nanomanufacturing: High-Throughput, Cost-Effective Deposition of Atomic Scale Thin Films via Atmospheric Pressure Spatial Atomic Layer Deposition. *Chemistry of Materials* 2016, 8443–8452.

(8) Poodt, P.; Mameli, A.; Schulpen, J.; Kessels, W. M. M. (Erwin); Roozeboom, F. Effect of Reactor Pressure on the Conformal Coating inside Porous Substrates by Atomic Layer Deposition. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 2017, *35* (2). https://doi.org/10.1116/1.4973350.

(9) Mione, M. A.; Vandalon, V.; Mameli, A.; Kessels, W. M. M.; Roozeboom, F. Atmospheric-Pressure Plasma-Enhanced Spatial ALD of SiO2Studied by Gas-Phase Infrared and Optical Emission Spectroscopy. *Journal of Physical Chemistry C* 2021, *125* (45), 24945–24957. https://doi.org/10.1021/acs.jpcc.1c07980.

(10) Nguyen, V. H.; Sekkat, A.; Masse De La Huerta, C. A.; Zoubian, F.; Crivello, C.; Rubio-Zuazo, J.; Rubio-Zuazo, J.; Jaffal, M.; Bonvalot, M.; Vallée, C.; Aubry, O.; Rabat, H.; Hong, D.; Muñoz-Rojas, D. Atmospheric Plasma-Enhanced Spatial Chemical Vapor Deposition of SiO2Using Trivinylmethoxysilane and Oxygen Plasma. *Chemistry of Materials* 2020, *32* (12), 5153–5161. https://doi.org/10.1021/acs.chemmater.0c01148.

(11) Han, S. M.; Aydil, E. S. Study of Surface Reactions during Plasma Enhanced Chemical Vapor Deposition of SiO2 from SiH4, O2, and Ar Plasma. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 1996, *14* (4), 2062–2070. https://doi.org/10.1116/1.580082.

(12) *SiO 2 Chemical Vapor Deposition at Room Temperature Using SiCl 4 and H 2 O with an NH 3 Catalyst*; 2000.

(13) Lee, J. H.; Kim, U. J.; Han, C. H.; Rha, S. K.; Lee, W. J.; Park, C. O. Investigation of Silicon Oxide Thin Films Prepared by Atomic Layer Deposition Using SiH2Cl2 and O3 as the Precursors. *Japanese Journal of Applied Physics, Part 2: Letters* 2004, *43* (3 A). https://doi.org/10.1143/jjap.43.l328.

(14) Lee, S. W.; Park, K.; Han, B.; Son, S. H.; Rha, S. K.; Park, C. O.; Lee, W. J. Atomic Layer Deposition of Silicon Oxide Thin Films by Alternating Exposures to Si2Cl6and O3. *Electrochemical and Solid-State Letters* 2008, *11* (7). https://doi.org/10.1149/1.2908201.

(15) Chaudhary, S.; Head, A. R.; Sánchez-De-Armas, R.; Tissot, H.; Olivieri, G.; Bournel, F.; Montelius, L.; Ye, L.; Rochet, F.; Gallet, J. J.; Brena, B.; Schnadt, J. Real-Time Study of CVD Growth of Silicon Oxide on Rutile TiO2(110) Using Tetraethyl Orthosilicate. *Journal of Physical Chemistry C* 2015, *119* (33), 19149–19161. https://doi.org/10.1021/acs.jpcc.5b04985.

(16) Kim, D. H.; Lee, H. J.; Jeong, H.; Shong, B.; Kim, W. H.; Park, T. J. Thermal Atomic Layer Deposition of Device-Quality SiO2 Thin Films under 100 °c Using an Aminodisilane Precursor. *Chemistry of Materials* 2019, *31* (15), 5502–5508. https://doi.org/10.1021/acs.chemmater.9b01107.

(17) Kamiyama, S.; Miura, T.; Nara, Y. Comparison between SiO2 Films Deposited by Atomic Layer Deposition with SiH2[N(CH3)2]2 and SiH[N(CH3)2]3 Precursors. *Thin Solid Films* 2006, *515* (4), 1517–1521. https://doi.org/10.1016/j.tsf.2006.04.033.

(18) *DIPAS[Di-isopropylaminosilane]*. https://www.upchem.co.kr/m/eng/product/dram.php?ptype=view&prdcode=1706210029&catcode=111211&page=& (accessed 2024-10-21).

(19) Lee, Y. S.; Choi, D. won; Shong, B.; Oh, S.; Park, J. S. Low Temperature Atomic Layer Deposition of SiO2 Thin Films Using Di-Isopropylaminosilane and Ozone. *Ceram Int* 2017, *43* (2), 2095–2099. https://doi.org/10.1016/j.ceramint.2016.10.186.

(20) Nam, T.; Lee, H.; Choi, T.; Seo, S.; Yoon, C. M.; Choi, Y.; Jeong, H.; Lingam, H. K.; Chitturi, V. R.; Korolev, A.; Ahn, J. H.; Kim, H. Low-Temperature, High-Growth-Rate ALD of SiO2 Using Aminodisilane Precursor. *Appl Surf Sci* 2019, *485*, 381–390. https://doi.org/10.1016/j.apsusc.2019.03.227.

(21) Lee, Y.-S.; Han, J.-H.; Park, J.-S.; Park, J. Low Temperature SiOx Thin Film Deposited by Plasma Enhanced Atomic Layer Deposition for Thin Film Encapsulation Applications. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 2017, *35* (4). https://doi.org/10.1116/1.4985140.

(22) Bousiakou, L. G.; Karapetis, S. Determination of Au Film Thiolation and Silane Bonding onto SiO2 Films within the Frame of Biosensor Surface Functionalization - An Analysis of Best Practices and Techniques. *Croatica Chemica Acta*. 2020. https://doi.org/10.5562/CCA3640.

(23) Yamaguchi, H.; Takahashi, H.; Kato, M.; -, al; Lauren MacDonald, C. A.; Turner, K. W.; McDonald, I.; Tang, C.; Cai, C.; Zhang, J. *Chinese Physics* 2001*,* Vol. 10.

(24) Eun Wang, S.; Park, J. S.; Ji Kim, M.; Chan Kang, Y.; Soo Jung, D. One-Pot Spray Pyrolysis for Core–Shell Structured Sn@SiOC Anode Nanocomposites That Yield Stable Cycling in Lithium-Ion Batteries. *Appl Surf Sci* 2022, *589*. https://doi.org/10.1016/j.apsusc.2022.152952.

(25) Yang, S.; Zhong, J.; Sun, B.; Zeng, X.; Luo, W.; Zhao, X.; Shu, Y.; Chen, J.; He, J. Influence of Base Pressure on Property of Sputtering Deposited ITO Film. *Journal of Materials*

Science: Materials in Electronics 2019, *30* (14), 13005–13012. https://doi.org/10.1007/s10854-019-01662-w.

(26) Joo, S. Y.; Loka, C.; Jo, Y. W.; Reddyprakash, M.; Moon, S. W.; Choi, Y. S.; Lee, S. E.; Cho, G. S.; Lee, K. S. ITO/SiO2/ITO Structure on a Sapphire Substrate Using the Oxidation of Ultra-Thin Si Films as an Insulating Layer for One-Glass-Solution Capacitive Touch-Screen Panels. *Coatings* 2020, *10* (2). https://doi.org/10.3390/coatings10020134.

(27) Yang, J. H.; Baek, S. Bin; Kim, Y. C. Initial Surface Reaction of Di-Isopropylaminosilane on a Fully Hydroxyl-Terminated Si (001) Surface. *J Nanosci Nanotechnol* 2014, *14* (10), 7954–7960. https://doi.org/10.1166/jnn.2014.9474.

(28) Lee, K.; Shim, Y. First-Principles Study of the Surface Reactions of Aminosilane Precursors over WO3(001) during Atomic Layer Deposition of SiO2. *RSC Adv* 2020, *10* (28). https://doi.org/10.1039/d0ra01635g.

(29) Lee, Y. S.; Choi, D. won; Shong, B.; Oh, S.; Park, J. S. Low Temperature Atomic Layer Deposition of SiO2 Thin Films Using Di-Isopropylaminosilane and Ozone. *Ceram Int* 2017, *43* (2). https://doi.org/10.1016/j.ceramint.2016.10.186.

(30) Fang, H.; Liu, Q.; Feng, X.; Yan, J.; Wang, L.; He, L.; Zhang, L.; Wang, G. Carbon-Coated Si Nanoparticles Anchored on Three-Dimensional Carbon Nanotube Matrix for High-Energy Stable Lithium-Ion Batteries. *Batteries* 2023, *9* (2). https://doi.org/10.3390/batteries9020118.

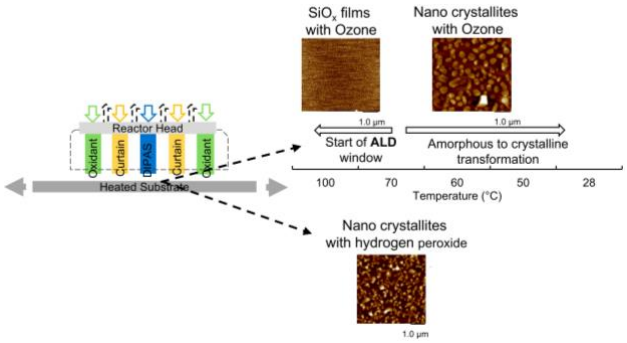
(31) Barr, T. L. An XPS Study of Si as It Occurs in Adsorbents, Catalysts, and Thin Films. *Applications of Surface Science* 1983, *15* (1–4). https://doi.org/10.1016/0378-5963(83)90003-X.

(32) Prabhakaran, K.; Kobayashi, Y.; Ogino, T. Chemically Prepared Oxides on Si(001): An XPS Study. *Surf Sci* 1993, *290* (3). https://doi.org/10.1016/0039-6028(93)90707-Q.

(33) Nyamtara, K. J.; Song, J. K.; Karima, N. C.; Kim, S. H.; Nguyen, M. C.; Duong, T. P. M.; Lee, K. J.; Ahn, W. Two Step Pyrolysis Synthesis Method of Graphite-Enhanced Nano-Si/Pitch Composite as Long Cycle Life Anode for Lithium-Ion Batteries. *J Alloys Compd* 2024, *976*. https://doi.org/10.1016/j.jallcom.2023.173229.

(34) Huang, L.; Han, B.; Fan, M.; Cheng, H. Design of Efficient Mono-Aminosilane Precursors for Atomic Layer Deposition of SiO2 Thin Films. *RSC Adv* 2017, *7* (37), 22672–22678. https://doi.org/10.1039/c7ra02301d.

TOC Graphic


SiOx films with Ozone
Nano crystallites with Ozone
1.0 µm
1.0 µm
Reactor Head
Oxidant
Curtain
DEPAS
Curtain
Oxidant
Start of ALD window
Amorphous to crystalline transformation
Heated Substrate
100
70
60
50
28
Temperature (°C)
Nano crystallites with hydrogen peroxide
1.0 µm