

Supporting Information

Atmospheric Plasma-Enhanced Spatial Chemical Vapor Deposition of SiO₂ using Trivinylmethoxysilane and Oxygen Plasma

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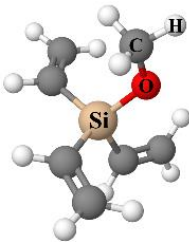
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1. ALD reactivity of TVMS precursor

To our best knowledge, trivinylmethoxysilane (TVMS, see table S1 for details on the precursor) has never been used for the deposition of Si or SiO₂ by CVD or ALD. Some physical properties of TVMS, as well as bond dissociation enthalpies at 298 K of reactive bonds in TVMS are shown in Table S1. As the bond SiO – CH₃ has lower bonding energy as compared to the bond Si – C₂H₃, if TVMS would react with OH^{*} surface groups, the obtained sample should exhibit a hydrophobic behavior, due to the aliphatic termination of the adsorbed monolayer formed. Therefore, we have exposed TVMS vapor to different substrates such as micro-glass slides, silicon wafers and oxygen plasma-treated silicon wafers in order to check if TVMS shows any ALD reactivity, i.e. surface adsorption on the substrate surfaces. However, no change in contact angle between a water droplet and TVMS-exposed surfaces was observed, while FTIR measurement did not show any C–H, Si–C or Si–O absorption peaks as a ‘fingerprint’ or TVMS layer absorbed on the surface, as shown in Figure S1. This leads to the conclusion that TVMS does not show any ALD activity on the tested substrates, at atmospheric pressure and in a temperature range of [RT, 260 °C].

Table S1: Some properties of trivinylmethoxysilane (TVMS)

Chemical structure	Boiling point	Density	Vapor pressure @ 25 °C
	131 °C	0.818 g/cm ³	30.7 ±0.2 mmHg
Bond Dissociation Enthalpies at 298 K: Si – C ₂ H ₃ (527 kJ/mol), ¹ SiO – CH ₃ (358 kJ/mol) ²			

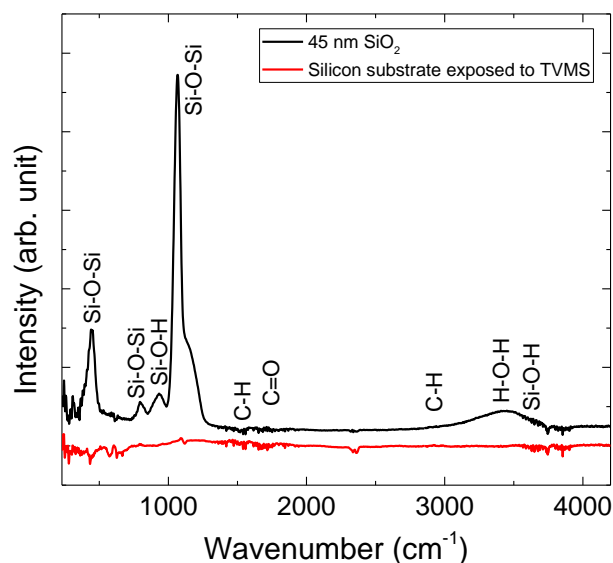


Figure S1: FTIR spectra of 45 nm of SiO₂ thin film deposited on Silicon substrate at 75 °C by APE-SCVD using TVMS and oxygen plasma (black curve) and a silicon substrate exposed to TVMS for 15 min at 100 °C (red curve)

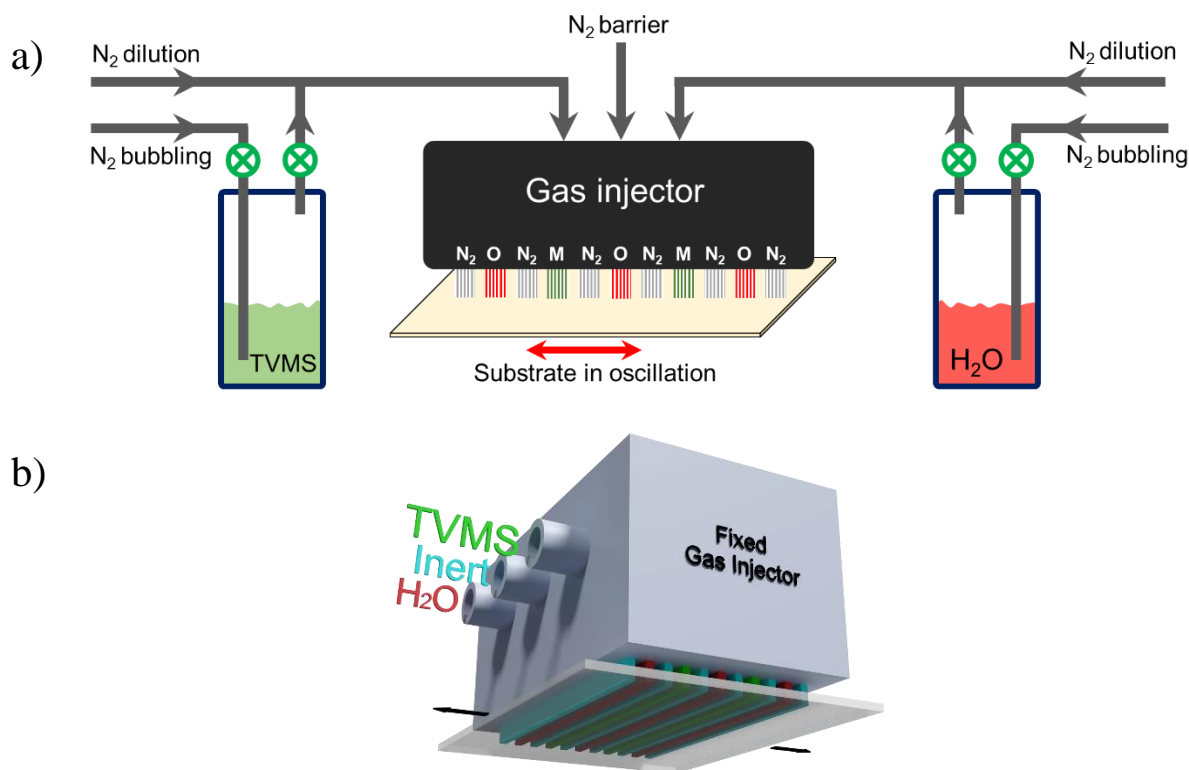


Figure S2: Schematic representation of: a) a close-proximity SALD deposition system (*M* refers to TVMS, *O* refers to oxidizing agent, i.e. H₂O in this figure), b) SALD head used for testing the surface adsorption activity of TVMS over different surfaces. The Silicon precursor outlets were kept away from the oxidizing agent outlets, and in between these reactive gas channels, nitrogen flows were used to prevent the former from mixing. By adjusting the gap between the head and the substrate, CVD mode can be obtained.³

As expected from our reactivity tests, when our standard SALD injection head was used, no deposition was observed. The schematic representations of the SALD system and SALD injection head used in these experiments are shown in Figure S2. In this case, the TVMS outlets are spatially

separated from the oxidizing agent outlets. Additionally, inert gas barriers are alternatively located in between these reactive gas flows to prevent them from mixing in the gas phase. The nitrogen flows bubbled through TVMS and H_2O (or H_2O_2) were 100 sccm and 150 sccm, respectively. These were then diluted with an extra nitrogen flow (100 sccm for TVMS and 150 sccm for the oxidizing agent) before being sent to the injection head. Finally, the nitrogen barrier flow was adjusted to obtain a flow of 100 sccm per outlet. When ozone was used as oxidizing agent, 300 sccm of pure oxygen were delivered to the plasma generator to produce ozone. This flow was then sent to the injection head. The gap between the substrate and the head was kept at a standard value, i.e. 150 μm . These tests were performed in a wide range of temperatures, from RT to 260 $^\circ\text{C}$. The absence of film deposition in all cases again confirms the non-adsorption of TVMS over the substrate surface. Tests performed in SCVD mode also failed to produce a thin film, thus indicating that TVMS does not react with H_2O , H_2O_2 or O_3 in the conditions tested.

2. Effect of plasma power

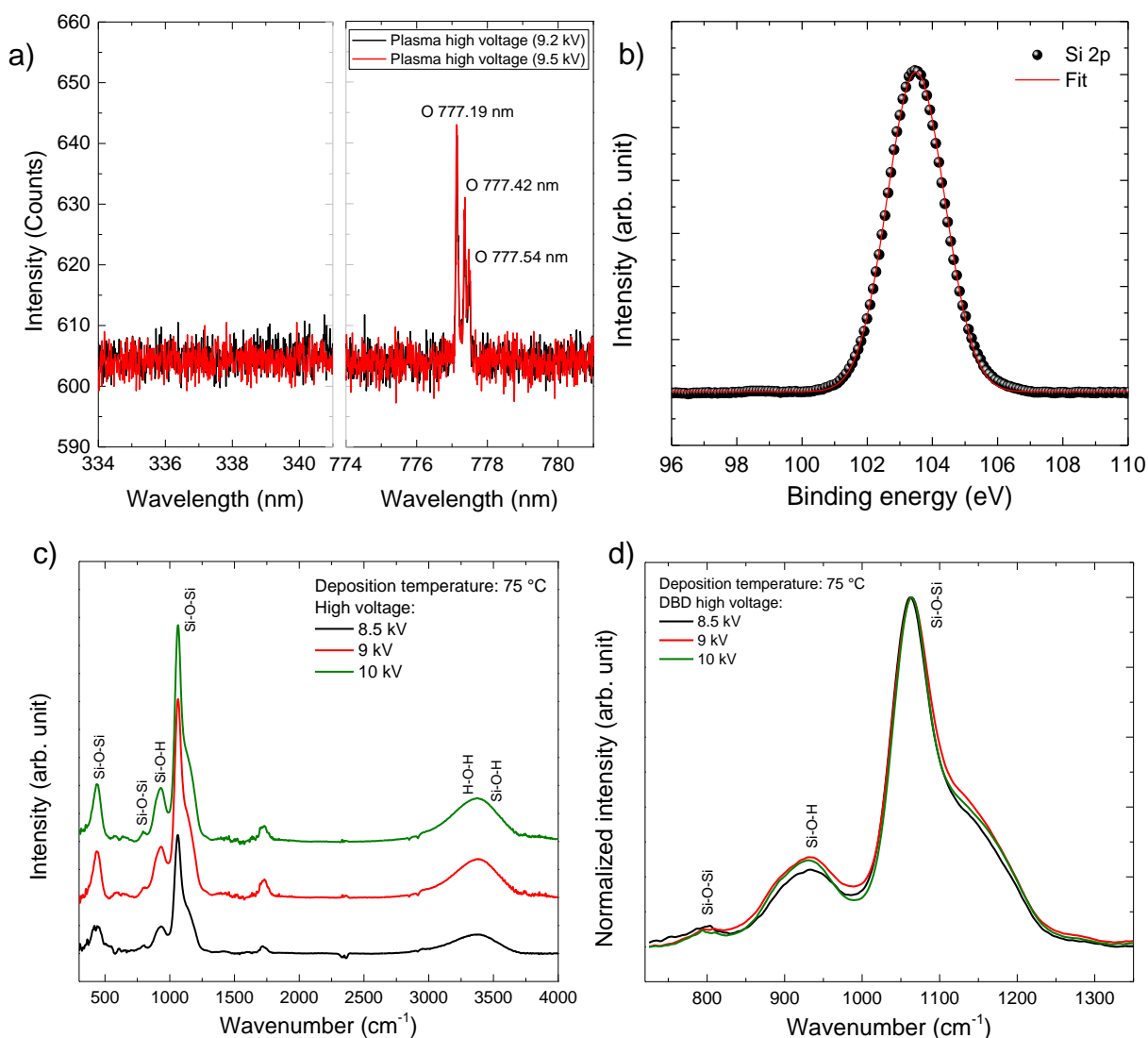


Figure S3: a) emission spectrum of oxygen plasma in the open-air condition. DBD high voltages: 9.2 and 9.5 kV, frequency: 8 kHz, oxygen flow through the DBD: 200 sccm; b) Si 2p core level XPS spectra of APE-SCVD SiO_2 films; c) FTIR spectra over a wavenumber range [250 cm^{-1} , 4000 cm^{-1}] of SiO_2 samples prepared with different DBD high voltages; d) a zoom into the Si-O-Si FTIR peaks, the peak intensity is normalized. These samples shown here were grown at 75 $^\circ\text{C}$.

Figure S3a shows the emission spectrum of oxygen plasma in open-air conditions. The spectrum was recorded in the dark using two values of DBD high voltages (9.2 kV and 9.5 kV) and the plasma frequency was maintained at 8 kHz. The pure oxygen flow was fixed at 200 sccm when delivering to the DBD. As can be seen, the characteristic peaks of oxygen plasma, which are located at 777.19 nm, 777.42 nm and 777.54 nm, can be clearly observed, while the strong emissions from nitrogen second positive system (N_2 SPS) at nearby 337 nm did not appear, which confirms that the reactive species generated from the plasma are only atomic oxygen but not nitrogen radicals even if the plasma was generated in the open air. The XPS measurement (Figure S3b) shows a clear Si 2p peak without contamination of Si-N or Si-C peaks even though the deposition was carried out at low temperature (75 °C) and in the open air condition. FTIR spectra (Figure S3c) over a wavenumber range [250 cm^{-1} , 4000 cm^{-1}] of SiO_2 samples prepared with different DBD high voltages, from 8.5 kV to 10 kV, only show Si-O-Si peaks but not Si-N or Si-C peaks. A close-up of normalized FTIR spectra (Figure S3d) in the range of [720 cm^{-1} , 1350 cm^{-1}] indicates that different high voltage applied to the DBD would not lead to a significant change in FTIR spectra of samples, but only the intensity.

3. Effect of quick annealing in open-air

As discussed above, the as-deposited SiO_2 sample has C=O, Si-OH, and H-O-H peaks in its FTIR spectrum, which can be attributed to byproduct residual in the film or water absorption during the deposition. Figure S4a shows the normalized FTIR spectra of as-deposited and annealed SiO_2 samples deposited on silicon substrate by APE-SCVD at 75 °C. The annealing process was performed in air atmosphere at 300 °C and 400 °C for 5 minutes. The C=O peak disappears after 5 mins of annealing at 300 °C, while the intensities of Si-OH and H-O-H peaks decrease significantly. Then, these peaks were observed to be completely removed after an annealing at 400 °C for 5 minutes. Additionally, a close-up of normalized FTIR spectra (Figure S4b) in the range of [700 cm^{-1} , 1400 cm^{-1}] shows the intensity variation of the main Si-O-Si FTIR peaks AS1 and AS2, which indicates a better quality (denser and better stoichiometry) of the annealed samples compared to the as-deposited one.

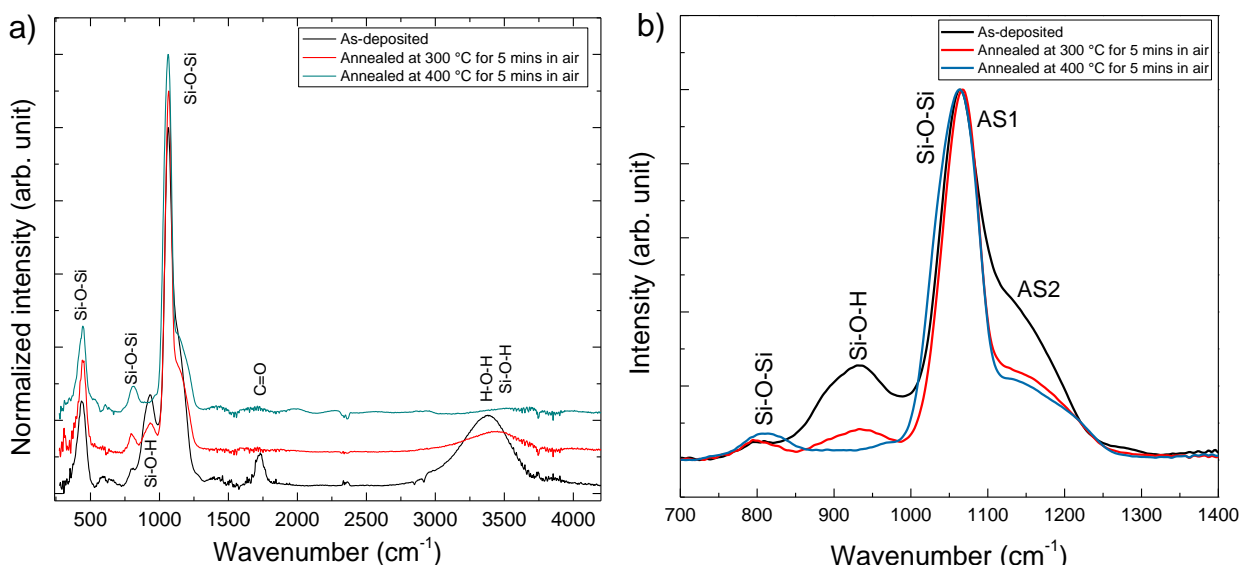


Figure S4: a) FTIR spectra of as-deposited SiO_2 sample deposited by APE-SCVD, and of the same sample annealed at 300 °C and 400 °C in the open-air condition; b) a zoom of the normalized FTIR spectra of these samples into the main peak regions, showing a better quality of SiO_2 sample after annealing. The sample was initially prepared at 75 °C on silicon substrate.

To evaluate the variation of film density versus annealing conditions, we conducted an XRR measurement for these films. The XRR result is shown in Table S2. Interestingly, the film thickness decreases when performing the annealing and increasing the temperature from 300 °C to 400 °C, while the film density is improved from 1.84 g/cm³ to 2.0 g/cm³. However, annealing at 400 °C seems to make the film rougher. It should be noted that the current values of the film density are still not optimized when compared to amorphous SiO₂ film density grown in a dry atmosphere, which usually results a value of about 2.2 g/cm³.^{4,5}

Table S2: Summary of fitting result from XRR patterns of as-deposited and annealed SiO₂ sample prepared by APE-SALD at 75 °C on silicon substrate

Samples	Thickness (nm)	Roughness (nm)	Density (g/cm ³)
As-deposited	52.3 ± 0.5	0.6 ± 0.2	1.84 ± 0.02
Annealed at 300 °C in air	45.1 ± 0.5	0.5 ± 0.2	1.98 ± 0.02
Annealed at 400 °C in air	41.0 ± 0.5	0.98 ± 0.2	2.0 ± 0.02

4. Comsol simulation

A combination of three modules from Comsol Multiphysics was used for performing 2D simulations: heat transfer in fluids, laminar flow and transport of diluted species. In reality, there are several types of gas existing in the deposition system including nitrogen, oxygen, oxygen atom, TVMS, by-product gas... It is also very difficult to access the physical properties of the mixture. For the sake of simplicity, it has been assumed that the physical properties of the gas in the whole system (viscosity, density, specific head, thermal conductivity) are identical to the case of nitrogen, which is the carrier gas and thus the most abundant species. The simulation shown in the main manuscript was obtained using this approximation. A schematic representation of the APE-SCVD head used for the simulation is shown in Figure S5 below. The parameters used for the simulation are listed in Table S3.

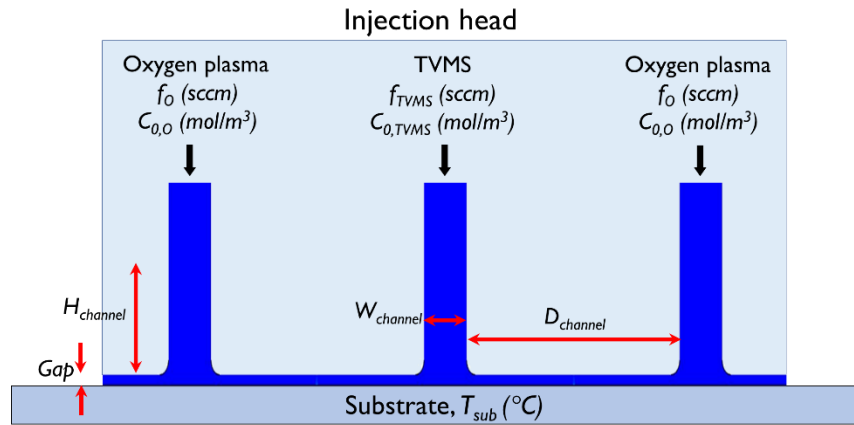


Figure S5: schematic representation of the APE-SCVD head used in this work. The 2D Comsol Multiphysics simulation takes place in the blue area, which corresponds to the gas flows.

Table S3: parameters used for the 2D Comsol Multiphysics simulation

Parameter	Description	Value [unit]
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gap	Distance between the injection head and the substrate	150 [μm], 500 [μm]
W_{channel}	Width of the TVMS and O atom outlets	1 [mm]
H_{channel}	Height of the TVMS and O atom channel	5 [mm]
D_{channel}	Distance between channels	5 [mm]
T_{sub}	Substrate temperature	100 [$^{\circ}\text{C}$]
D_{TVMS}	Diffusion coefficient of TVMS	2.18×10^{-6} [m^2/s]
D_{O}	Diffusion coefficient of oxygen atomic	2.18×10^{-6} [m^2/s] ⁶
f_{TVMS}	Flow rate of TVMS containing gas at its outlet	100 [sccm]
f_{O}	Flow rate of oxygen atom containing gas at its outlet	100 [sccm]
$C_{\text{O,TVMS}}$	Molar concentration of TVMS at the input of the TVMS channel	0.3 [mol/m^3]
$C_{\text{O,O}}$	Molar concentration of oxygen atoms at the input of the oxygen atom channel	0.3 [mol/m^3]

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