Improved Stability of Porous Silicon in Aqueous Media via Atomic Layer Deposition of Oxides

Jonathan Rasson[®] and Laurent A. Francis^{*}

Institute of Information and Communication Technologies, Electronics and Applied Mathematics, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium



ABSTRACT: In this work, porous silicon (PSi) samples were conformally coated with ultrathin films of aluminum oxide (Al_2O_3) and hafnium oxide (HfO_2) using atomic layer deposition (ALD) to passivate their internal surface and improve their overall stability in aqueous media. Their porosity and optical properties were characterized before and after ALD treatment. The stability over time in aqueous media of the ALD passivated porous layers was then evaluated and compared to PSi layers oxidized at 800 °C (PSiO₂), which is a treatment widely used in the literature for biosensing applications. The ALD oxide-covered samples performed equally to the oxidized PSi samples, but exhibited a higher mean refractive index, which results in a better contrast. These improved optical properties resulted in a signal exhibiting a significantly decreased noise. This in turn leads to a theoretical limit of detection improved by a factor 13 and 16 for PSi/Al₂O₃ and PSi/HfO₂, respectively, compared to the standard PSiO₂. This could thus result in an improved sensitivity for biosensing applications.

INTRODUCTION

In recent years, porous silicon (PSi) has been widely used as a platform for various optical sensing applications $(gas/vapor,^{1-4} biomolecules,^{5-10} bacteria,^{11-13} etc.)$ due to its optical properties and large reactive surface area.¹⁴ Most particularly, a specific interest has been brought to the use of PSi for biosensing applications, which require the porous layer to be in contact with aqueous media. Unfortunately, PSi is oxidized and/or dissolved in such media, which results in unwanted variations of the optical properties of the probed PSi layer.^{15,16} The main challenge is thus to develop stabilization methods to prevent these reactions from occuring. To this end, various methods have been studied to stabilize the optical properties of PSi over time. Among those, the most used technique nowadays to protect against aqueous dissolution is the thermal oxidation of the porous layer, which converts the highly reactive SiH_x species into Si–O bonds.^{6-8,15,17-24} Another scheme used to oxidize PSi is to perform an ozone oxidation at room temperature; this produces a more hydrated oxide, which slightly stabilizes the porous layers but results in a quicker dissolution in aqueous media than its thermally oxidized counterpart.^{15,16,19,25}

Additionally, several chemical modification methods have been developed to create stable Si-C bonds to stabilize PSi. Various chemical derivatization methods, involving, for instance, Grignard and aryllithium reagents, were investigated^{26,27} as well as electrochemical routes using alkynes and alkyl species.^{28–30} Nevertheless, the most used method, vastly studied by the Buriak group and others, is the hydrosilylation using alkenes or alkynes, which can be Lewis acid mediated, light promoted, or thermal.^{29,31–39}

Finally, thermal carbonization routes were explored. On one hand, the Salonen group studied the thermal hydrocarbonization of PSi by using the thermal dissociation of acetylene,^{40–45} while, on the other hand, the Sailor group worked on the carbonization of poly(furfuryl alcohol) to obtain a stable thin layer of glassy carbon coating the pores.^{46,47}

This work focuses on the use of atomic layer deposition (ALD) to passivate the internal surface of PSi layers. ALD is a method of choice due to its properties: it offers a highly conformal coating, which is ideal for PSi with its high-aspect ratio nanostructures, a precise thickness control down to the Ångström via its self-limiting mechanism, and it allows a vast array of materials.⁴⁸ It has been used in many applications such

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as photonics,^{49–51} solar cells,^{52–54} semiconductor devices,^{55–57} fuel cells and batteries,^{58–60} and surface passivation for biosensors^{61–64} among many others. The first use of ALD in PSi was recorded in 1996⁶⁵ and was since expanded for various applications thanks to the large internal surface and tunability of PSi. Applications of ALD in PSi for gas sensors,⁶⁶ capacitors,^{67,68} and the growth of nanotubes⁶⁹ were recorded among others.

In this work, we demonstrate the stabilization of PSi and its optical properties in aqueous media using ALD to conformally coat the internal surface of PSi with oxides. The resulting ALD oxide-coated PSi samples exhibit a stability comparable to the one obtained with PSi thermally oxidized at 800 $^{\circ}$ C for an hour, with decreased noise level, which can lead to an improved limit of detection, and thus sensitivity in the case of biosensing applications.

EXPERIMENTAL SECTION

Materials. Silicon wafers (0.8–1.2 m Ω ·cm resistivity, (100) orientation, single side polished, boron-doped) were purchased from Sil'tronix Silicon Technologies (France). Aqueous hydrofluoric acid (HF, 49%) was obtained from Chem-Lab nv (Belgium), and absolute ethanol was acquired from VWR Chemicals (France). The precursors for the atomic layer deposition, trimethylaluminum (TMA) and tetrakis-(dimethylamido)hafnium (TDMAHf) for Al₂O₃ and HfO₂, respectively, were purchased from SAFC Hitech (UK). Phosphate buffered saline (PBS, 0.01 M phosphate, pH 7.4) was purchased from Sigma-Aldrich (USA).

Porous Silicon Samples Fabrication. The PSi samples were prepared by electrochemically etching heavily doped ptype silicon using a custom-made Teflon etch-cell, a platinum coil as the counter-electrode, and a potentiostat as the current source as previously described.⁴ The electrolyte used for the porosification is a 3:1 (v/v) solution of 49% HF and absolute ethanol. The first step consists in cleaning the samples by electrochemically etching a sacrificial layer of PSi at a current density of 200 mA/cm² for 30 s in the HF electrolyte. This layer is then removed using a 2 M solution of KOH until no more reaction is observed, the sample is then rinsed in deionized (DI) water and finally in 2-propanol before being dried under a stream of nitrogen. This step helps to obtain an improved pore size and to get rid of the transitional layer.^{25,70,71} The desired PSi layer is then obtained by adding the HF electrolyte to the etch cell and then applying a current density of 200 mA/cm² for 50 s. The sample is then rinsed with 2propanol and dried under nitrogen. Following this, part of the samples were thermally oxidized, while the rest underwent oxide coating by ALD.

Thermal Oxidation. The samples to be thermally oxidized were slowly introduced, to avoid thermal shock, in a tubular furnace heated beforehand to 800 $^{\circ}$ C. They were oxidized for 1 h with a 1.8 L/min flow of oxygen and were then slowly removed from the furnace.

Atomic Layer Deposition. The rest of the samples were coated with Al_2O_3 or HfO_2 by ALD in thermal mode at 200 °C. The oxide growths were performed in a Fiji F200 ALD reactor (Veeco/CNT, MA, USA) in exposure mode, meaning that the chamber was isolated from the pump during the precursor pulses to allow the precursors to penetrate deeply into the nanostructure to ensure a homogeneous coating throughout the whole depth of the porous matrix with a high aspect ratio. The first precursors are TMA and TDMAHf for Al_2O_3 and

HfO₂, respectively, while the second precursor is water vapor in both cases. Each half-cycle starts with the closing of the automatic pressure control (APC) valve followed by a pulse of precursor with a duration of 0.1 s for TMA and H₂O and 0.5 s for TDMAHf. After a 1 min delay to allow the precursor to react, the APC valve is fully opened for 5 min before starting the next half-cycle to ensure the removal of both the unreacted precursor molecules and the reaction byproducts. Each fullcycle, starting with the TMA or TDMAHf half-cycle and followed by the water precursor half-cycle, is repeated a given number of times depending on the growth rate and desired thickness. The full-cycles were repeated 100 and 85 times for Al₂O₃ and HfO₂, respectively.

Ellipsometry. The thickness of the Al_2O_3 and HfO_2 films deposited by ALD was measured at room temperature in situ in the reactor chamber on a flat silicon surface using a UVISEL ellipsometer (HORIBA Jobin Yvon) with the help of the DeltaPsi2 software. The obtained thickness corresponds to the oxide deposited on top of the samples and acts as an indicator of the total thickness deposited inside the porous matrix.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The thickness and pore diameter of the PSi layers were measured using a Carl Zeiss Ultra 55 SEM. The SEM was also coupled with an EDX detector and used with the Esprit software to analyze in cross-sectional view the deposition of Al_2O_3 and HfO_2 inside the porous layer to ensure an oxide deposition down to the bottom of the layer.

Optical Determination of Thickness and Porosity. The thickness and open porosity of the PSi samples were measured before and after treatment using the spectroscopic liquid infiltration method (SLIM).⁷² In short, the reflectivity spectrum of a sample is recorded both in air and in ethanol. The effective optical thickness (EOT) of the sample is then obtained by performing a Fourier transform on the reflectivity spectrum, which returns a peak whose position corresponds to the EOT. By fitting the data on a two-component Bruggeman effective medium approximation and knowing the refractive indices of silicon, air, and ethanol, the open porosity and the layer thickness were obtained.⁷² The reflectivity spectra are recorded perpendicularly to the sample surface using a halogen light source, a bifurcated optic fiber, and a JAZ spectrometer (Ocean Optics) in combination with the software OceanView.

Optical Stability Measurements. For the stability measurements, the sample is placed inside a polycarbonate fluidic cell (Figure 1) with a continuous flow of PBS (pH 7.4) at a flow rate of 0.5 mL/min for 120 min. PBS was chosen as a model buffer since biological interactions mostly take place in aqueous media at physiological pH. The cell is secured to



Figure 1. Schematic of the polycarbonate fluidic cell used for stability measurements. PSi surface exposed to PBS is 1.2 cm^2 .

prevent any movement that would disturb the measurements. The method used is the reflective interferometric Fourier transform spectroscopy (RIFTS),⁷ of which the working principle is very similar to that of SLIM. The reflectivity spectra are acquired over time (one spectrum every 30 s, with an integration time of 200 ms and an average of three scans to minimize the noise), and the Fabry–Pérot fringes are then processed using a Fourier transform to obtain the effective optical thickness, EOT = 2nL, with *n* being the average refractive index of the porous layer in PBS and *L* being its thickness. The evolution over time of the EOT is then computed as a percentage change such that

$$\frac{\text{EOT}}{\text{EOT}_0} = \frac{\text{EOT}_t}{\text{EOT}_{\text{PSi}}} \times 100 \, [\%]$$

where EOT_{PSi} is the initial 2nL of the studied sample (either thermally oxidized or ALD coated with Al_2O_3 or HfO_2) and EOT_t is 2nL of the same sample after a time *t* expressed in minutes.

Noise and Limit of Detection Determination. In parallel to the stability measurements, the optical data were analyzed to evaluate the noise level inherent to the measurements following the RIFTS data processing. To do so, a fit using a least-squares error approximation was performed on the EOT/EOT_0 versus time data, and the difference between the actual data and the fit was computed. Having these difference values allows the computation of the mean and standard deviation for each type of sample analyzed and thus determine the noise level of the measurement as the average of the standard deviation for each sample of a given type. Additionally, the noise level leads to the determination of the theoretical limit of detection (LoD) defined as follows:

 $LoD = 3\sigma_N$

with $\sigma_{\rm N}$ being the standard deviation of the noise as described above. 71

RESULTS AND DISCUSSION

PSi Layer Characterization. Porosity, Thickness, and Pore Morphology. The PSi samples are prepared by electrochemical etching of heavily doped silicon in an HF-based electrolyte. Their surface is then passivated, either by thermal oxidation at 800 °C or by atomic layer deposition of Al_2O_3 or HfO₂ as described above. The freshly etched and passivated samples were characterized by SEM and SLIM to determine their thickness and porosity before and after the treatments (Table 1).

The porosity and thickness of PSi and $PSiO_2$ are computed via the Bruggeman effective medium approximation using an average of the refractive index of Si and SiO_2 over the considered wavelength range for the value of the refractive

Table 1. Porosity and Thickness of Freshly Etched PSi and Passivated PSi Samples

		SLIM		
	SEM thickness [nm]	thickness [nm]	open porosity [%]	n _{skeleton}
PSi	4581 ± 38	4585 ± 18	85.7 ± 0.9	N/A
PSiO ₂	4826 ± 22	5069 ± 47	87.2 ± 1.0	N/A
PSi/Al_2O_3	4558 ± 19	N/A	58.6 ± 1.2	2.28 ± 0.06
PSi/HfO_2	4544 ± 30	N/A	43.8 ± 1.2	2.43 ± 0.07

index of the porous skeleton (n_{skeleton}) .⁷³ Concerning PSi/Al₂O₃ and PSi/HfO₂ samples, the quantity of oxide deposited inside the porous layer is unknown, which prevents us from knowing the refractive index of the porous skeleton beforehand. Additionally, no significant changes in the porous layer thickness before and after ALD were observed using SEM (Table 1). The thickness measured by SLIM for each PSi sample before ALD is then used to compute the resulting porosity and n_{skeleton} of the samples that underwent ALD of oxide using the Bruggeman effective medium approximation.

We observe in Table 1 concordant values for the thickness obtained by SEM and SLIM for freshly etched PSi, while a small difference is observed for $PSiO_2$ as it is often the case for oxidized samples.^{7,72} Overall, we observe an increase in thickness of the porous layer after thermal oxidation, due to the increase in volume by replacing Si with SiO2.74,75 SLIM results also show a 1.5% increase in porosity after the thermal oxidation, while a decrease could be expected. This change, while being somewhat reduced by taking into account the standard deviation, could be attributed to measurement imprecision due to noise. Indeed, for PSiO₂ samples, a weak contrast is observed due to the low refractive index of PSiO₂ compared to the bulk Si underneath. This leads to low intensity Fabry-Perot fringes and results in an imperfect fit due to noise in the measurement. This is confirmed while using the twocomponent Bruggeman approximation with small changes in $n_{\rm skeleton}$ leading to large changes in the resulting porosity and thickness. Finally, this small increase could also be due to an improved infiltration of the ethanol inside the porous layer as the surface becomes hydrophilic, which improves the interactions with the hydroxyl group of ethanol.

Additionally, when comparing the porosity of the samples before and after ALD of oxides, a large decrease of porosity is observed. As mentioned, with SLIM we measure the open porosity of a sample; this drop can thus be explained by the closing of the top part of smaller pores during the oxide deposition and thus the creation of closed porosity, which is not accessible to ethanol.^{25,72} This hypothesis is supported by the low value of n_{skeleton} obtained, which is significantly lower than the refractive index of Si (n = Si3.96 for a wavelength range 500–800 nm⁷³) and thus indicates the presence of inaccessible voids.

The surface characterization of the porous layers using SEM also corroborates the observations made using SLIM. Figure 2 shows the pores on the surface of the porous layer for each type of sample (freshly etched PSi, PSiO₂, and ALD oxide-passivated PSi). Additionally, SEM images were analyzed using MATLAB (MathWorks) to extract data regarding the pore density as well as their average diameter. We observe in Figure 2a,b that there are no significant changes in the pore morphology after the thermal oxidation of the porous layer with average pore diameters of 43.8 \pm 19.4 and 43.2 \pm 19.8 nm and a pore density of 269 and 263 pores/ μ m² for PSi and PSiO₂, respectively. Figure 2c,d shows an increase in the pore wall thickness due to the ALD oxide growth; this leads to a decrease in the pore size and the closing of smaller pores. The pore density is thus decreased as characterized by image analysis for resulting densities of 169 and 150 pores/ μ m² for PSi/Al₂O₃ and PSi/HfO₂, respectively, while the average pore diameters are, respectively, 36 ± 16.7 and 35.8 ± 20.6 nm.

Porous Layer Passivation. An important criterion in the passivation of PSi samples is the ALD oxide coverage inside the pores to ensure that no silicon is in contact with the aqueous

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Figure 2. SEM images of the surface of porous silicon layers: (a) freshly etched PSi, (b) $PSiO_{2'}$ (c) PSi/Al_2O_3 , and (d) PSi/HfO_2 .

medium to prevent the silicon oxidation/dissolution. To evaluate the oxide coating, PSi/Al₂O₃ and PSi/HfO₂ samples were observed in cross section by SEM, and the chemical composition of the porous layers was characterized by EDX. We see in Figure 3a a SEM picture of a PSi sample coated with Al_2O_3 in cross section with the zones analyzed by EDX and the corresponding EDX spectra (Figure 3b). As expected, we distinguish three peaks corresponding to the K α bands of oxygen, aluminum, and silicon at 0.525, 1.486, and 1.740 keV, respectively. However, a difference in the intensity of the peaks can be observed depending on the depth characterized inside the porous layer. Indeed, on the top part of the layer the signal for aluminum is stronger than the bottom of the layer, while the opposite is observed for silicon. This could be explained by a thicker layer of Al_2O_3 on the top part than at the bottom, and thus, the layer thickness resulting from the ALD would be a gradient depending on the probed depth. Results for PSi/HfO₂ are shown in Figure 4 where we observe a similar difference in the peak intensity depending on the depth for peaks corresponding to oxygen, hafnium, and silicon, with hafnium being represented by two peaks in the probed energy region located at 1.646 (M α) and 1.7 keV (M β), which is close to the energy of the silicon K α band (1.740 keV), thus causing the two peaks to not be independently defined from one another. As it is the case for Al_2O_3 , a decrease in the intensity of the HfO₂ peak is observed when going deeper into the porous layer, while the intensity of the Si peak increases, which allows the two peaks to be more defined. Again, this change in peak intensity is explained by a gradient in the thickness of oxide deposited inside the porous layer while still having the presence of the passivating oxide layer down to the bottom of the pores.

Additionally, the thickness of the oxide deposited by ALD was measured on top of the samples by ellipsometry to gauge the quantity of oxide deposited on and inside the porous layers. Thicknesses of 13.3 \pm 1 and 9 \pm 0.2 nm were measured, corresponding to growth rates of 1.33 and 1.06 Å/cycle for Al₂O₃ and HfO₂, respectively. These results are in agreement







Figure 3. (a) Cross section SEM image of a PSi/Al_2O_3 layer with EDX analysis area and (b) corresponding EDX spectra for the top and bottom of the porous layer.

with previous studies performed in exposure mode as well as a study showing an increase in growth rate for increased exposure times. $^{76-78}$

Stability in Aqueous Media. The optical readout stability of the porous layers in a flow of PBS is assessed over a period of 120 min, which corresponds to a maximum assay time goal for PSi biosensing.¹² The stability is characterized as a ratio of EOT/EOT_0 between the effective optical thickness of the layer at the beginning of the experiment and after a given time. Figure 5 illustrates the observed behavior for the changes in the relative EOT as a function of time for PSi, PSiO₂, PSi/Al₂O₃, and PSi/HfO₂ samples. As expected, nonpassivated PSi samples exhibit a significant instability in aqueous media due to the oxidation/dissolution taking place. Passivated samples exhibit an improved stability with PSiO₂ and PSi/Al₂O₃ showing a downward slope, while PSi/HfO₂ is characterized by a slightly upward slope, corresponding to a red shift in the position of the EOT peak. Values of EOT shift after 120 min averaged for several samples are given in Table 2. As expected, some variability in the final shift in EOT is observed, with PSiO₂ and

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Figure 4. (a) Cross section SEM image of a PSi/HfO_2 layer with EDX analysis area and (b) corresponding EDX spectra for the top and bottom of the porous layer.

 PSi/Al_2O_3 exhibiting blueshift of the same order of magnitude as well as a similar distribution, while PSi/HfO_2 samples show a very small red shift and low variability, making the measurement more reliable.

However, when comparing $PSiO_2$ and PSi/Al_2O_3 data we observe significantly reduced noise for samples coated with Al_2O_3 , which lead to a greater confidence regarding the accuracy of the measured shifts. Indeed, using the theoretical LoD metric allows us to determine the significance of an observed shift, whether it is observed over a long period of time, as is the case for stability measurements, or if it is a faster phenomenon, for instance, a response to analytes in the case of biosensing applications. The improvement of theoretical LoD for ALD oxide-covered samples, by a factor 13 and 16 for PSi/ Al_2O_3 and PSi/HfO₂, respectively, compared to thermally oxidized PSiO₂ sample is thus of a great importance to detect small and rapid changes in sensing applications.

Additionally, the same stability measurements were performed on PSi/Al_2O_3 and PSi/HfO_2 samples for 24 h in order to evaluate the behavior of such samples for applications



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Figure 5. Relative EOT optical response of PSi (dark blue), $PSiO_2$ (green), PSi/Al_2O_3 (red), and PSi/HfO_2 (blue), as a function of time while exposed to a continuous PBS flow at a rate of 0.5 mL/min.

Table 2. Average Optical Shift of EOT Observed for Samples Immersed in PBS during 120 min, Corresponding Noise of the Signal, and Theoretical Limit of Detection (LoD)

	PSiO ₂	PSi/Al ₂ O ₃	PSi/HfO ₂
EOT ₁₂₀ / EOT ₀ [%]	-0.171 ± 0.262	-0.280 ± 0.265	0.044 ± 0.095
mean noise level [%]	0.086	0.0067	0.0054
theoretical LoD [%]	0.258	0.0201	0.0162

requiring longer exposition time to aqueous media than rapid biosensing. In Figure 6 we observe a behavior and noise levels



Figure 6. Relative EOT optical response of PSi/Al_2O_3 (red) and PSi/HfO_2 (blue), as a function of time for a 24 h long exposition to PBS.

similar to those observed in Figure 5. Shifts after 24 h (EOT_{24h}/ EOT₀) of -0.803% and 0.028% are observed for PSi/Al₂O₃ and PSi/HfO₂, respectively. This results in a lower average rate of change than the 2 h stability measurements, which is explained by the fact that most of the EOT change occurs in the first few hours as observed in Figure 6. The stabilization of PSi using Al₂O₃ and HfO₂ deposited by ALD is thus also suitable for applications requiring long exposition of PSi to aqueous media.

CONCLUSION

In this article, we demonstrated the use of oxides grown by atomic layer deposition to efficiently passivate porous silicon samples for their use in aqueous media toward optical biosensing applications. The homogeneity of the ALD coating of Al_2O_3 and HfO_2 was characterized throughout the depth of the porous layer as well as the effects on the morphology and the optical properties of the resulting porous samples. ALD oxide-coated PSi layers were compared to standard thermally oxidized PSi and exhibited similar results in terms of optical stability while demonstrating a significantly reduced noise level regarding optical measurements, thus leading to an improvement of the theoretical limit of detection by a factor 13 and 16 for PSi coated with Al_2O_3 and HfO_2 , respectively.

AUTHOR INFORMATION

Corresponding Author

*E-mail: laurent.francis@uclouvain.be.

ORCID ©

Jonathan Rasson: 0000-0002-8330-7248

Notes

The authors declare no competing financial interest.

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