Transferred, Ultrathin Oxide Bilayers as Biofluid Barriers for Flexible Electronic Implants

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The work presented here introduces a materials strategy that involves physically transferred, ultrathin layers of silicon dioxide (SiO$_2$) thermally grown on silicon wafers and then coated with hafnium oxide (HfO$_2$) by atomic layer deposition, as barriers that satisfy requirements for even the most challenging flexible electronic devices. Materials and physics aspects of hydrolysis and ionic transport associated with such bilayers define their performance and reliability characteristics. Systematic experimental studies and reactive diffusion modeling suggest that the HfO$_2$ film, even with some density of pinholes, slows dissolution of the underlying SiO$_2$ by orders of magnitude, independent of the concentration of ions in the surrounding biofluids. Accelerated tests that involve immersion in phosphate-buffered saline solution at a pH of 7.4 and under a constant electrical bias demonstrate that this bilayer barrier can also obstruct the transport of ions that would otherwise cause drifts in the operation of the electronics. Theoretical drift–diffusion modeling defines the coupling of dissolution and ion diffusion, including their effects on device lifetime. Demonstrations of such barriers with passive and active components in thin, flexible electronic test structures highlight the potential advantages for wide applications in chronic biointegrated devices.

1. Introduction

Emerging classes of flexible hybrid electronics/optoelectronic devices offer attractive capabilities as active interfaces to biological systems of relevance to both clinical practice and biomedical research. Associated embodiments range from flexible filaments for optoelectronic stimulation of targeted neural circuits in the brain,[1–4] to conformal sheets for high-resolution multiplexed electrophysiological mapping on the epicardial surfaces.[5–9] Such platforms are of great interest because they can form minimally invasive interfaces to dynamic, soft biological systems, while providing performance characteristics that can approach those of conventional, wafer-based semiconductor devices.[10–20] A critical challenge in this field is in the development of materials that, in flexible, thin film form, can simultaneously serve as perfect barriers...
to biofluids and as high-quality interfaces to the surrounding biology with multidecade lifetimes.

An ideal material for this purpose must be biocompatible, with both exceptionally low flexural rigidity and water/ion permeability. Conventional encapsulation strategies, ranging from bulk metal/ceramic enclosures in standard implantable devices to organic/inorganic multilayer stacks in organic light emitting diode displays, fail, typically by orders of magnitude, to simultaneously meet both of these latter two critical requirements.[21–27] Even for materials that have minimal permeability, challenges in forming perfect, pinhole-free coatings over large areas can be difficult or impossible to overcome, particularly in academic laboratory conditions. A recently reported solution involves a physically transferred layer of SiO₂ thermally grown on a pristine silicon wafer. Results indicate extraordinary water barrier properties at thicknesses that allow both compliant mechanics and a high capacitance electrical measurement interface.[28] Due to its extremely low water permeability and pinhole-free nature, this type of barrier offers key advantages over conventional coatings, as extrapolated from temperature-dependent studies of immersion in phosphate-buffered saline (PBS) solution. Additionally, the nature of the growth process and the transfer procedures eliminate the need for particulate-free fabrication environments. System demonstrators exploit 1-μm-thick layers of transferred thermal SiO₂ as water barriers and capacitive measurement interfaces in which backplanes of flexible silicon electronics provide amplification and multiplexed addressing for in vivo electrophysiological mapping on the brain and heart.[29]

An intrinsic limitation of this strategy is that the rates for hydrolysis of thermal SiO₂ (0.04 nm d⁻¹ at 37 °C, ≈ 90 nm d⁻¹ at 96 °C) limit the ability to exploit ultrathin film geometries (e.g., 100 nm thick) for enhanced capacitive coupling. Also, ions commonly present in biofluids, particularly sodium, can diffuse through thermal SiO₂ where they can shift and/or degrade the switching properties of the underlying transistors. The addition of silicon nitride can mitigate the diffusion issue, but its rate of hydrolysis exceeds that of SiO₂,[30] thereby requiring its use as an underlayer, away from the biofluid interface.

Here, we present materials, designs, and integration strategies for an ultrathin, transferred barrier that combines thermally grown SiO₂ with a coating of HfO₂ formed by atomic layer deposition (ALD). By comparison to previous work on single-layer systems of thermal SiO₂, systematic experimental studies and reactive diffusion modeling suggest that this bilayer barrier can offer significantly enhanced longevity for underlying flexible electronics, at ultrathin geometries. Accelerated immersion tests demonstrate that the HfO₂ slows the dissolution of the underlying SiO₂ in simulated biofluids by orders of magnitude, even when present with some density of pinholes. Additional results establish aspects of ionic transport through such materials via measurements of electrostatically induced shifts in the electrical properties of the underlying transistors. A combination of soak tests and temperature-dependent simulations provides foundational understanding of the role of two competing failure mechanisms—dissolution and ion diffusion—on device lifetime. The findings indicate that this bilayer barrier offers excellent capabilities of relevance to a diverse range of biointegrated flexible electronic devices.

2. Results and Discussion

Standard semiconductor processing strategies in growth and transfer printing enable the fabrication of high-quality electronics directly on oxide layers as barriers to biofluids (Figure 1a). The scheme used here combines some aspects of conventional strategies in which deposition of encapsulation material occurs as a last step, with more recently reported alternatives in which device processing occurs in a layer-by-layer fashion on a preformed barrier layer. Figure 1a outlines the four main steps. Briefly, electronic devices formed on an ultrathin layer of thermal SiO₂ on a silicon wafer, with the SiO₂ onto a flexible plastic substrate. Subsequently, deposition of HfO₂ by ALD forms a capping layer on the top, exposed surface of the SiO₂. For the studies reported here, the electronics consist of an array of transistors formed on a silicon-on-insulator (SOI) wafer (~100-nm-thick device Si and 300-nm-thick buried thermal SiO₂) with the device Si (silicon nanomembranes, Si NM) as the active channel material. The transfer process bonds the front side of the wafer to a thin polyimide film laminated on a glass plate as a temporary support. Inductively coupled plasma reactive ion etching removes the silicon wafer and simultaneously reduces the buried thermal SiO₂ thickness to 100 nm, as shown in the Appendix and Figure S1 (Supporting Information). Peeling the device from the glass after depositing HfO₂ (100 nm thick, by a rate of 1.07 Å cycle⁻¹ in 200 °C) by ALD on the SiO₂ yields a piece of flexible electronics encapsulated by an ultrathin bilayer barrier of HfO₂/SiO₂. Details appear in the Experimental Section. Such devices, by virtue of their small combined thicknesses, exhibit excellent mechanic flexibility in cyclic bending tests (see details in the Appendix and Figure S2, Supporting Information). Recent work demonstrates that SiO₂ formed and processed in similar fashion can serve as front and back side encapsulation for flexible, actively multiplexed electrophysiological mapping systems.[28] The two upper insets of Figure 1b are optical images of flexible electronics with a set of NMOS transistors (channel length L = 20 μm, width W = 200 μm). The bilayer barrier consists of a 100-mm-thick capping layer of ALD HfO₂ (biofluids side) and 100-mm-thick underlying layer of thermal SiO₂ (device side), as illustrated in the lower inset.

Results of accelerated soak tests of NMOS transistors while immersed in PBS solution with a pH of 7.4 at a temperature of...
96 °C are in Figure 1b, in the form of transfer characteristics of a representative transistor at a supply voltage $V_{DS} = 0.1$ V. Here, the accelerated tests refer to those performed at elevated temperatures to increase the rate of the hydrolysis reaction. At Day 0, Figure 1c demonstrates the transfer characteristics in both linear and semilog scales. The on/off current ratio is $\approx 10^8$ and the peak effective electron mobility is $\approx 400$ cm$^2$ V$^{-1}$ s$^{-1}$ (see Supporting Information). All transistors exhibit stable performance for 10 d (Figure 1b) until a sudden failure at Day 11 (inset of Figure 1c). Previous research indicates that although the water permeability through thermal SiO$_2$ is extremely small, a slow hydrolysis process (SiO$_2$ + 2H$_2$O $\rightarrow$ Si(OH)$_4$, corresponding to a dissolution rate of $\approx 90$ nm d$^{-1}$ in 96 °C PBS solution at a pH of 7.4) consumes the material, thereby leading to eventual failure. By comparison, a 100/100-nm-thick bilayer of HfO$_2$/SiO$_2$ barrier has a lifetime $\approx 10$ times longer than that of an isolated 100-nm-thick layer of thermal SiO$_2$ barrier ($\approx 1$ d in the same condition, consistent with the dissolution rate of $\approx 90$ nm d$^{-1}$ in previous report), as displayed in the Appendix and Figure S3a (Supporting Information). A single layer of HfO$_2$ (100 nm thick) fails quickly due to a small, but finite density of pinholes, as in the Appendix and Figure S3b (Supporting Information). As a result, the HfO$_2$/SiO$_2$ bilayer, in which the HfO$_2$ slows the dissolution of the SiO$_2$ and the SiO$_2$ forms a defect-free barrier, can provide an attractive solution to the challenge of chronic encapsulation of thin, flexible electronics. A corresponding schematic illustration of the multilayer configuration is shown in Figure 1d, as an exploded view.

Soak tests using setups that incorporate thin films of magnesium (Mg), as in Figure 2, instead of transistors can facilitate rapid evaluation of various water barriers. The strong reactivity of Mg with water (Mg + 2H$_2$O $\rightarrow$ Mg(OH)$_2$ + H$_2$) leads, upon exposure, to defects that are immediately and easily visible by optical microscopy. Here, a 200 $\times$ 400 µm$^2$ pad of 300-nm-thick layer of Mg deposited by electron-beam evaporation serves, in this manner, as a water-penetration sensor to test the barrier properties of different layers deposited or transferred on top. Figure 2a shows a schematic illustration of a test setup (Figure 2b), for which accelerated testing involves continuous immersion in PBS solution at 96 °C. For present purposes, the barrier lifetime corresponds to the period between immersion and the appearance of the first defect observable on the Mg pad by optical microscopy. This criteria has practical value because the lifetimes (days) for systems of interest here are much longer.
than the time (minutes to hours) for an initial defect in the Mg pad to propagate laterally across its entire spatial extent. As a result, uncertainties in the time to identify the first observable defect are much smaller than the lifetime itself.

As shown in the single-layer row in Figure 2c, the device encapsulated by a 100-nm-thick layer of thermal SiO$_2$ survives for 30 h, after which time the entire Mg layer dissolves at once, in a “bulk” mode, by consequence of the spatially uniform dissolution of SiO$_2$, at a consistent rate of $\approx 90$ nm d$^{-1}$ at 96 °C (0.04 nm d$^{-1}$ at 37 °C)$_{[28]}$ and its pinhole free nature. The addition of a layer of HfO$_2$, which itself is insoluble in water (inset of the Appendix and Figure S4, Supporting Information) and simultaneously is nontoxic and biocompatible$_{[31,32]}$, can dramatically increase the time for failure of the SiO$_2$ layer by hydrolysis. The main limitation of using HfO$_2$ alone is the nearly unavoidable formation of pinholes or other defects across the area of interest during deposition in the type of cleanroom environments available to academic labs. Under our experimental conditions, degradation of Mg with a single layer of HfO$_2$ as a barrier occurs in a very short time in Figure 2c (see also Figure S4, Supporting Information) due to these defects. Nevertheless, diffusion of water through the HfO$_2$ can be significantly impeded, with consequent reductions on the rate of dissolution of the underlying SiO$_2$.

These observations motivate the use of a bilayer barrier that combines thermal SiO$_2$ (device side) and HfO$_2$ (contact with PBS). The SiO$_2$ serves as a water-impermeable barrier without defects, and HfO$_2$ serves as an insoluble, capping layer that

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**Figure 2.** Effects of the capping layer thickness and materials type on the rate of dissolution of SiO$_2$. a) Illustration of the layer configuration for tests that use thin films of Mg as indicators of water penetration. b) Top-view optical image of a Mg pad encapsulated by a barrier layer. c) Results of accelerated immersion tests that involve immersion in PBS solution at 96 °C. The single-layer row displays findings for 100-nm-thick layers of SiO$_2$ and HfO$_2$ as barriers, respectively. The double-layer rows show sequential images of Mg encapsulated by various capping layers on SiO$_2$, including HfO$_2$, Parylene C, Ti/Pt, and LPCVD SiN$_x$. 

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slows the dissolution of the SiO2. The HfO2/SiO2 (100/100 nm thick) bilayer, as shown in the second row of Figure 2c, leads to isolated defects in the Mg pad after 10 d, which then expand to consume the entire layer of Mg in a few hours (consistent with active-transistor results in Figure 1b). Here, isolated visible defects in the Mg appear at a density of 3–4 per pad (200 × 400 μm²). As a result, the HfO2/SiO2 bilayer eventually fails due to dissolution through these pinholes (see details in the Figure S5, Supporting Information). Experiments performed in the same manner but with various other capping materials provide points of comparison. Other metal-oxide layers, for example, Al2O3 or TiO2, show inferior barrier properties compared HfO2 (Appendix and Figure S6, Supporting Information) due to correspondingly higher densities of pinholes. Polymers, for example, lead to Mg degradation in a ‘bulk’ mode, associated with water permeation across the entire area (see the Appendix and Table S1, Supporting Information). Others, such as platinum/titanium, display more severe pinhole issues and much shorter lifetimes compared to the bilayer barrier of HfO2/SiO2. Another possibility is SiN, but its dissolution rate in PBS solution surpasses that of thermal SiO2 by orders of magnitude.[38] As shown in Figure 2c, the performance of HfO2/SiO2 bilayer barrier is superior to all other combinations explored, due to a combination of low water diffusivities, small pinhole densities, and low effective dissolution rates for HfO2.

Figure 3 shows results of theoretical modeling of reactive diffusion in thermal SiO2 and HfO2/SiO2 in PBS solution. A 1D single-layer model captures dissolution of thermal SiO2, without any capping layer, since the initial thickness h0 is much smaller than the lateral dimensions.[39] Figure 3a presents a schematic illustration of the model, where y denotes the thickness direction, with y = 0 at the bottom of the layer. The governing equation is[34]

\[
\frac{\partial^2 w}{\partial y^2} - k_{SiO2} \frac{\partial w}{\partial t} = 0 \quad 0 \leq y \leq h_0
\]

where \( D_{SiO2} \) and \( k_{SiO2} \) are the diffusivity of water and the reaction constant between the SiO2 and water, respectively, \( w \) is the water concentration, which depends on position \( y \) and time \( t \). The boundary conditions can be written as \( w|_{y=0} = w_0 \) and \( \partial w/\partial y |_{y=0} = 0 \), corresponding to a water concentration that is constant \( w_0 (= 1 \text{ g cm}^{-3}) \) at the water/SiO2 interface and a water flux at the bottom surface of the thermal SiO2 layer that is zero. The initial condition is zero water concentration in the thermal SiO2, that is, \( w|_{t=0} = 0 \) (0 ≤ y ≤ h0). The water concentration can be analytically solved by applying the method of separation of variables, which gives the thickness \( h_{SiO2} \) of the thermal SiO2 layer as a function of time (details appear in the Appendix, Supporting Information). For the present study

\[
\frac{h_{SiO2}}{h_0} \approx 1 - \frac{t}{t_{critical}}
\]

or

\[
\frac{h_{SiO2}}{h_0} \approx \frac{1 - \frac{t}{t_{critical}}}{1 - \frac{h_{SiO2}}{h_0}},
\]

where

\[
\alpha = \frac{h_{SiO2}}{h_0} \frac{D_{SiO2}}{D_{HfO2}} \frac{k_{SiO2}}{k_{HfO2}} \frac{M_{SiO2}}{M_{HfO2}} \frac{\rho_{SiO2}}{\rho_{HfO2}}
\]

and

\[
\alpha = \frac{h_{SiO2}}{h_0} \frac{D_{SiO2}}{D_{HfO2}} \frac{k_{SiO2}}{k_{HfO2}} \frac{M_{SiO2}}{M_{HfO2}} \frac{\rho_{SiO2}}{\rho_{HfO2}}
\]

is the critical time for full dissolution of the thermal SiO2. Here, \( q (= 2) \) is the number of water molecules that react with each atom of SiO2, \( \rho_{SiO2} \) is the mass density of thermal SiO2 (2.33 g cm⁻³), \( M_{SiO2} \) (60 g mol⁻¹) and \( M_{HfO2} \) (18 g mol⁻¹) are the molar masses of SiO2 and water, respectively.

From soak tests of thermal SiO2 in PBS solution, the diffusivity \( D_{SiO2} \) and reaction constant \( k_{SiO2} \) can be extracted using this model as \( D_{SiO2} \approx 1.5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \) and \( k_{SiO2} \approx 2 \times 10^{-4} \text{ s}^{-1} \) at 96 °C. These values fall within the range of those inferred from previous studies for PECVD SiO2 (\( k = 5.3 \times 10^{-5} \) to 8.1 \( \times 10^{-3} \) s⁻¹)[33] and silica glass (\( D = 2.1 \times 10^{-18} \) to 1.3 \( \times 10^{-14} \) cm² s⁻²)[35,36] The two constants at the other temperatures can be inferred from those at 96 °C by experimentally measured dissolution rates and the Arrhenius equation, with an apparent activation energy \( E_A = 1.32 \text{ eV} \) (details appear in the Appendix, Supporting Information).[38] Figure 3b shows the change in the thickness of the thermal SiO2 with time in PBS solution at 96 °C. The simulated results (lines) agree well with those measured (symbols; Mprobe Station, SemiconSoft, USA) for all three initial thicknesses, that is, 30, 50, and 75 nm. For a layer of ALD HfO2 submerged in PBS solution, experiments show that the thickness does not change with time (inset of Figure S4, Supporting Information), indicating that the reaction constant between HfO2 and water is zero.

A bilayer model for the case of HfO2/SiO2 is in Figure 3c. For the thermal SiO2, the reactive diffusion Equation (1), as well as the boundary condition \( \partial w/\partial y |_{y=0} = 0 \) and initial condition \( w|_{t=0} = 0 \), still apply. For the HfO2 layer, the diffusion equation is

\[
D_{HfO2} \frac{\partial^2 w}{\partial y^2} = \frac{\partial w}{\partial t} (h_0 \leq y \leq h_0 + h_{HfO2})
\]

with the boundary condition \( w|_{y=h_0+h_{HfO2}} = w_0 \) and initial condition \( w|_{y=0} = 0 \) \( (h_0 \leq y \leq h_0 + h_{HfO2}) \), where \( D_{HfO2} \) is the diffusivity of water in HfO2. The continuity of concentration and flux of water at the HfO2/SiO2 interface requires \( w|_{y=h_0+h_{HfO2}} = w|_{y=h_0+h_{HfO2}} \) and \( \partial w/\partial y |_{y=h_0+h_{HfO2}} = \partial w/\partial y |_{y=h_0+h_{HfO2}} \). By applying the method of separation of variables, an analytical solution for the water concentration for this bilayer model can be obtained, which gives the thickness of the thermal SiO2 layer (details appear in the Appendix, Supporting Information). For the present study

\[
\frac{h_{SiO2}}{h_0} \approx \frac{1 - \frac{t}{t_{critical}}}{1 - \frac{h_{SiO2}}{h_0}}
\]

where

\[
t_{critical} = \frac{h_{SiO2}}{h_0} \frac{D_{SiO2}}{D_{HfO2}} \frac{k_{SiO2}}{k_{HfO2}} \frac{M_{SiO2}}{M_{HfO2}} \frac{\rho_{SiO2}}{\rho_{HfO2}}
\]

represents the time when the thermal SiO2 layer completely disappears \( (h_{SiO2} = 0) \), that is, the lifetime of the HfO2/SiO2 bilayer barrier. Here

\[
\alpha = 1 + \sqrt{D_{SiO2}k_{SiO2}h_{SiO2}h_0^2 D_{HfO2} k_{HfO2} M_{SiO2} \rho_{SiO2} \rho_{HfO2}}
\]

From soak tests, the diffusivity \( D_{SiO2} \) is determined from the bilayer model as \( D_{SiO2} = 2.5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \) at 96 °C. For
different polymer capping materials on thermal SiO₂, the soak tests in Table S1 (Supporting Information) yield the polymer diffusivities, for example, $D_{SU-8} = 7 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, $D_{PI} = 5.5 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. The detailed simulated results of polymer/SiO₂ barriers appear in the Appendix and Figure S7 (Supporting Information). The findings clearly indicate that the low water diffusivity of HfO₂ makes it superior to all examined polymers. Figure 3d predicts the bilayer barrier lifetime as a function of the initial thermal SiO₂ thickness, for the case of a 100-nm-thick HfO₂ layer. The simulated results (line) agree well with those measured (symbols). Figure 3e shows the water concentration as a function of time at the interface ($y = 100 \text{ nm}$) of a 100/100 nm bilayer of HfO₂/SiO₂. The water concentration gradually reaches saturation at $\approx 0.13 \text{ g cm}^{-3}$ at the HfO₂/SiO₂ interface after $\approx 3 \text{ h}$, revealing a fast equilibrium between reaction and diffusion. Here, HfO₂ serves as a passive layer to effectively mitigate the dissolution of the underlying SiO₂.

Figure 3f shows the changes in thickness of the SiO₂ in a bilayer barrier of HfO₂/SiO₂ with a 100-nm-thick layer of SiO₂ and HfO₂ with initial thicknesses of 0, 10, 50, and 100 nm. The inset presents the simulated (line) and measured (symbols) lifetime of a HfO₂/SiO₂ bilayer barrier with a 100-nm-thick layer of SiO₂ and different thicknesses of HfO₂ (0, 10, 50, and 100 nm).

Figure 3. Theoretical modeling of reactive diffusion for the hydrolysis of thermal SiO₂ and HfO₂/SiO₂ barriers. a) Schematic illustration of the single-layer model. b) Simulated (lines) and measured (symbols) changes in thickness of a single layer of thermal SiO₂ with initial thicknesses of 30, 50, and 75 nm in PBS solution at 96 °C. c) Schematic illustration of the bilayer model. d) Simulated (line) and measured (symbols) lifetime of a HfO₂/SiO₂ bilayer barrier with a 100-nm-thick layer of HfO₂ and different thicknesses of thermal SiO₂. e) Distribution of water concentration at the interface of a 100-nm/100-nm-thick bilayer of HfO₂/SiO₂ barrier. f) Changes in thickness of thermal SiO₂ in a HfO₂/SiO₂ bilayer barrier with a 100-nm-thick layer of SiO₂ and HfO₂ with initial thicknesses of 0, 10, 50, and 100 nm. The inset presents the simulated (line) and measured (symbols) lifetime of a HfO₂/SiO₂ bilayer barrier with a 100-nm-thick layer of SiO₂ and different thicknesses of HfO₂ (0, 10, 50, and 100 nm).
with those measured (symbols). The temperature-dependent lifetimes are also investigated. With $D_{\text{diff}}$ at 96 °C, the diffusivities at different temperatures can be determined according to the Arrhenius scaling, thus giving the lifetime as a function of temperature (Appendix and Figure S8, Supporting Information) by Equation (6). Specifically, a bilayer barrier of HfO$_2$/SiO$_2$ (100/100 nm thick) offers a projected lifetime of over 40 years at 37 °C PBS (pH of 7.4).

The enhanced lifetime indicates that the HfO$_2$ capping layer effectively delays the permeation of biofluid to the underlying SiO$_2$. Since biofluids contain not only water molecules but alkali metal ions that are known to accelerate the SiO$_2$ dissolution, parametric studies of different ionic concentrations provide additional insights into the underlying chemistry. Figure 4 describes the ion effect on the dissolution of SiO$_2$ and its lifetime with/without HfO$_2$ capping layer. The solutions use $10 \times 10^{-3}$ M Tris to adjust the pH to a physiological condition, pH 7.4. Figure 4a summarizes changes in the reflectance of a 320-nm-thick single layer of thermal SiO$_2$ on a silicon wafer after soaking in different solutions with different concentrations of sodium chloride (NaCl), indicative of various [Na$^+$], for 14 h at 96 °C. The uniform color distributions are consistent with macroscopically uniform rates of dissolution for all values of [Na$^+$]. The peaks of the reflectance curves in Figure 4a shift toward shorter wavelengths as the thicknesses decreases. The rates for these shifts increase with concentration, thereby demonstrating the catalyzing effect of Na$^+$ on dissolution. Previous studies show that alkali and alkaline metal ions accelerate the dissolution of quartz and other amorphous silica polymorphs in near-neutral pH solutions.$^{[37–42]}$ As an example for the systems studied here, Figure 4b shows similar soaking results in solutions containing Ca$^{2+}$. Here, 0.047 and 0.333 M calcium chloride (CaCl$_2$) concentrations yield ionic strengths similar to those of the 0.14 and 1 M NaCl solutions in Figure 4a. The dissolution behavior depends more strongly on [Ca$^{2+}$] than [Na$^+$] at the same ionic strength. Figure 4c summarizes the dissolution rates of thermal SiO$_2$ in solutions with various values of [Na$^+$] and [Ca$^{2+}$], quantitatively determined from the reflectance data in Figure 4a,b. The results indicate that the presence of Ca$^{2+}$ could determine the lifetime of the SiO$_2$ layer even when its concentration is lower than that of Na$^+$. According to studies in the literature, cations facilitate deprotonation of –OH groups on the surface of SiO$_2$ by shielding negative charges, as supported by empirical rate laws that indicate an increase in dissolution rates with surface charge.$^{[40,41,43]}$ Other experimental and computational evidence suggest that cations can modify the interfacial water structure to promote hydrolysis of Si–O–Si bonds.$^{[39,42]}$

Figure 4d shows results of experiments on the lifetimes of a 100-nm-thick layer of thermal SiO$_2$ with/without an HfO$_2$ capping layer, all in the presence of ions. The two dotted curves correspond to lifetimes in Na$^+$ (black) and Ca$^{2+}$ (red) containing...
solutions. The results are consistent with the dissolution rates of SiO$_2$ (Figure 4c). The solid lines show prolonged lifetimes with the addition of the 100-nm-thick capping layer of HfO$_2$. As with the single layer of SiO$_2$ barrier, the results for HfO$_2$/SiO$_2$ barrier show longer lifetimes in Na$^+$ solutions than in Ca$^{2+}$ solutions at the same ionic strength. Compared to 100-nm-thick layer of thermal SiO$_2$, the bilayer barrier of HfO$_2$/SiO$_2$ (100/100 nm thick) enhances the lifetime by a factor of ten. Figure 4e calculates the lifetime ratios between the bilayer of HfO$_2$/SiO$_2$ barrier (100/100 nm thick) and single layer of thermal SiO$_2$ barrier (100 nm thick) at each ionic strength. This ratio increases up to a certain level as the ionic strength increases. In the same context, the HfO$_2$/SiO$_2$ more strongly mitigates the diffusion of Ca$^{2+}$ rather than Na$^+$, possibly due to a larger hydrated ionic radius and higher positive charge of Ca$^{2+}$ compared to Na$^+$.\[44]\n
In addition to their effects on dissolution, ions in biofluids (mostly positive species such as Na$^+$) that diffuse through the barriers can adversely affect the performance of underlying transistors, mainly by electrostatically shifting their threshold voltages ($V_T$).\[45]\n
Specifically, ion diffusion in PBS can accumulate a layer of positive ions (most Na$^+$) at the transistor channel, as schematically illustrated in Figure 5a, thus leading to an additional electric field that acts in concert with the gate voltage ($V_G$) at the transistor front gate. These positive ions give rise to a positive enhancement to $V_G$. As a result, the transistor switches on with a more negative $V_G$ at the front gate, corresponding to a negative shift in $V_T$ for an NMOS device. Ion drift-diffusion tests on encapsulated NMOS transistors (layer configuration shown in Figure 1d) allow comparisons of HfO$_2$/SiO$_2$ and SiO$_2$ as ion barriers. Results of accelerated soak tests of NMOS transistors during application of an external bias while immersed in PBS solution at 96°C and pH of 7.4 are shown in Figure 5b,c. The bias ($V_{app}$, 3 V) exists between a platinum probe in the PBS solution and the transistor electrodes (source, drain, and gate), as illustrated in the insets. For present purposes, device failure is defined as the point when the shift in the threshold voltage $\Delta V_T$ reaches 1 V. The positive $V_{app}$ serves as a driving force to impel positive ion transport through barriers, the result of which shifts $V_T$ of transistors under a 200-nm-thick layer of SiO$_2$ barrier by electrostatic interactions with the Si channel, as shown in Figure 5b. As shown in Figure 5c, the key performance characteristics of transistors with bilayer barriers of HfO$_2$/SiO$_2$ (100/100 nm thick) remain constant in accelerated soak tests (in 96 °C PBS solution) over the full duration of the experiments. The results demonstrate that the bilayer of HfO$_2$/SiO$_2$ barriers can effectively retard ion diffusion process compared to the single layer of SiO$_2$ barriers. Results of modeling of Na$^+$ transport processes appear in Figure 5d,e. Here, Figure 5d shows the shift in $V_T$ extracted from Figure 5b for a 200-nm-thick layer of SiO$_2$ within 1 d with
$V_{app} = 3 \text{ V at } T = 96 \degree \text{C}$. The drift diffusion is closely related to the layer of surface charge density $Q_s$ of Na⁺ located at the thermal SiO₂/substrate Si interface (Appendix and Figure S9, Supporting Information). To find the relationship between $Q_s$ and $\Delta V_T$, we numerically simulate a 2D NMOS transistor with commercial software (Sentaurus Technology Computer Aided Design) using experimentally determined device parameters. The numerical result predicted by this model (red solid lines) fits well with experimental data (red solid dots), as displayed in Figure 5d. Corresponding calculation details appear in the Appendix (Supporting Information). The inset of Figure 5e presents values of $\Delta V_T$ extracted from data in Figure 5c with a 100/100-nm-thick bilayer of HfO₂/SiO₂ barrier. Here, the shifts in $V_T$ are extraordinarily small (less than ~0.05 V) in all cases, which further support the outstanding properties of HfO₂/SiO₂ as bilayer ion barriers.

Modeling can also capture the competition between dissolution and ion diffusion in SiO₂ and HfO₂/SiO₂. Figure 5e presents such competition for a 200-nm-thick layer of thermal SiO₂ and a 100/100-nm-thick bilayer of HfO₂/SiO₂, respectively, both of which form on transistors. The inset of Figure 5e shows the configuration without $V_{app}$. We consider an acceleration factor (AF) for the failure time as a function of temperature, considering both dissolution and ion diffusion failures together. In all cases, device failure corresponds to the point when the SiO₂ disappears due to hydrolysis or when the shift in the threshold voltage $\Delta V_T$ reaches 1 V. The AF is defined as $t_{\text{failure}}(T)/t_{\text{failure}}(369 \text{ K})$, normalized at 369 K. The temperature-dependent Na⁺ diffusion coefficient follows an Arrhenius relationship: $D = D_0 e^{-E_A/kT}$, where $k$ is the Boltzmann constant and $T$ is temperature. $D_0$ is the pre-exponential factor and $E_A$ is the activation energy. We extracted $D_0$ and $E_A$ from the data of Figure 5d. For the single layer of SiO₂ barrier, ion penetration dominates the failure time, because the corresponding dissolution failure time is much longer than that of the ion-diffusion process. On the other hand, the bilayer of HfO₂/SiO₂ barrier offers improved ion-barrier properties. Here, dissolution plays an important role. The AF of HfO₂/SiO₂ (100/100 nm thick) uses the dissolution failure time from Figure 3d (369 K) and corresponding simulations for other temperatures in the Appendix and Figure S5 (Supporting Information). A bilayer of HfO₂/SiO₂ barrier offers a projected lifetime of over 40 years at 37 °C PBS (pH of 7.4), leading to a much higher AF (three orders of magnitude) than that of SiO₂, due to the enhanced ion-barrier properties.

4. Experimental Section

Details of fabrication steps, test structures, immersion studies at various ion concentrations and temperatures, theoretical analysis including reactive diffusion models and sodium-ion transport appear in the Appendix (Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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