Flexible Electronics

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

Enming Song, Yoon Kyeung Lee, Rui Li, Jinghua Li, Xin Jin, Ki Jun Yu, Zhaoqian Xie, Hui Fang, Yiding Zhong, Haina Du, Jize Zhang, Guanhua Fang, Yerim Kim, Younghee Yoon, Muhammad A. Alam, Yongfeng Mei, Yonggang Huang, and John A. Rogers*

The work presented here introduces a materials strategy that involves physically transferred, ultrathin layers of silicon dioxide (SiO₂) thermally grown on silicon wafers and then coated with hafnium oxide (HfO₂) 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 HfO₂ film, even with some density of pinholes, slows dissolution of the underlying SiO₂ 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

E. Song, Prof. Y. Mei Department of Materials Science Fudan University Shanghai 200433, P. R. China E. Song, Y. K. Lee, Dr. J. Li, Y. Zhong, H. Du, J. Zhang, G. Fang, Y. Kim, Y. Yoon Frederick Seitz Materials Research Laboratory Department of Materials Science and Engineering Department of Chemistry University of Illinois at Urbana-Champaign Urbana, IL 61801, USA Prof R Li State Key Laboratory of Structural Analysis for Industrial Equipment Department of Engineering Mechanics International Research Center for Computational Mechanics Dalian University of Technology Dalian 116024, P. R. China X. Jin, Prof. M. A. Alam School of Electrical and Computer Engineering Purdue University West Lafayette, IN 47907, USA

Dr. K. J. Yu School of Electrical and Electronic Engineering Yonsei University Seoul 03722, Republic of Korea Dr. Z. Xie AML, Department of Engineering Mechanics Center for Mechanics and Materials Tsinghua University Beijing 100084, China Dr. Z. Xie, Prof. Y. Huang Department of Mechanical Engineering Department of Civil and Environmental Engineering and Department of Materials Science and Engineering Northwestern University Evanston, IL 60208, USA Dr. H. Fang Department of Electrical and Computer Engineering Northeastern University Boston, MA 02115, USA

DOI: 10.1002/adfm.201702284



FUNCTIONAL MATERIALS

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 temperaturedependent studies of immersion in phosphate-buffered saline (PBS) solution. Additionally, the nature of the growth process and the transfer procedures eliminate the need for particulatefree 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; \approx 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 singlelayer systems of thermal SiO₂, systematic experimental studies and reactive diffusion modeling suggest that this bilayer barrier

Prof. J. A. Rogers

Department of Materials Science and Engineering
Department of Biomedical Engineering
Department of Neurological Surgery
Department of Chemistry
Department of Mechanical Engineering
Department of Electrical and Computer Science
Center for Bio-Integrated Electronics
Simpson Querrey Institute for Nano/biotechnology
Northwestern University
Evanston, IL 60208, USA
E-mail: jrogers@northwestern.edu
The ORCID identification number(s) for the author(s) o

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201702284.

can offer significantly enhanced longevity for underlying flexible electronics, at ultrathin geometries. Accelerated immersion tests demonstrate that the HfO_2 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 transfer, 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 NMs) 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 $L = 20 \ \mu m$, width $W = 200 \ \mu m$). The bilayer barrier consists of a 100-nm-thick capping layer of ALD HfO2 (biofluids side) and 100-nm-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 SCIENCE NEWS _____ www.advancedsciencenews.com





Figure 1. Transferred, ultrathin bilayer of SiO₂ thermally grown on silicon wafers and HfO₂ formed by ALD serve as excellent barriers to biofluids and ions in flexible electronic implants. a) Scheme for fabricating test structures that include silicon transistors: 1) Fabrication of transistors on an SOI wafer; 2) Pressure bonding the top surface of this wafer, face down, onto to a glass substrate that is laminated with a thin film of polyimide (Kapton, 13 μ m); 3) Removal of the silicon handle wafer by dry etching; 4) Surface cleaning and ALD of HfO₂; release of the flexible device from the substrate. b) Transfer characteristics collected during immersion in PBS solution at pH 7.4 and 96 °C for 10 d, at a supply voltage V_{DS} = 0.1 V. The upper insets show optical images of a sample produced in this manner with a 100/100-nm-thick bilayer of HfO₂/SiO₂ as a barrier on its top surface and a single transistor structure after bonding. The lower inset shows a schematic illustration of the NMOS transistor stack. c) Transfer characteristics at Day 0 plotted in both linear and semilog scales, at a supply voltage V_{DS} = 0.1 V. The inset shows transfer characteristics collected at the time of failure on Day 11. d) Schematic illustration of the material stack at the location of an NMOS transistor.

96 °C are in Figure 1b, in the form of transfer characteristics of a representative transistor at a supply voltage $V_{\text{DS}} = 0.1$ 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 $\approx 400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (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 SiO₂ is extremely small, a slow hydrolysis process $(SiO_2 + 2H_2O \rightarrow Si(OH)_4$, corresponding to a dissolution rate of ≈ 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 HfO₂/SiO₂ barrier has a lifetime ≈10 times longer than that of an isolated 100-nm-thick layer of thermal SiO₂ barrier (≈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 HfO₂ (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 $(Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2)$ leads, upon exposure, to defects that are immediately and easily visible by optical microscopy. Here, a $200 \times 400 \ \mu\text{m}^2$ 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







Figure 2. Effects of the capping layer thickness and materials type on the rate of dissolution of SiO₂. 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 SiO₂ and HfO₂ as barriers, respectively. The double-layer rows show sequential images of Mg encapsulated by various capping layers on SiO₂, including HfO₂, Parylene C, Ti/Pt, and LPCVD SiN_x.

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 SiO₂ 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 SiO₂, at a consistent rate of ≈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 HfO₂, 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 SiO₂ 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 SiO₂.

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

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 $(200 \times 400 \ \mu m^2)$. As a result, the HfO₂/SiO₂ bilayer barrier 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_x, but its dissolution rate in PBS solution surpasses that of thermal SiO2 by orders of magnitude.^[30] As shown in Figure 2c, the performance of HfO_2/SiO_2 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 h_0 is much smaller than the lateral dimensions.^[33] Figure 3a presents a schematic illustration of the model, where γ denotes the thickness direction, with $\gamma = 0$ at the bottom of the layer. The governing equation is^[34]

$$D_{\text{SiO}_2} \frac{\partial^2 w}{\partial \gamma^2} - k_{\text{SiO}_2} w = \frac{\partial w}{\partial t}, \ 0 \le \gamma \le h_0$$
(1)

where D_{SiO_2} and k_{SiO_2} 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 $w|_{y=h_0} = w_0$ and $\partial w/\partial y|_{y=0} = 0$, corresponding to a water concentration that is constant w_0 (= 1 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, $w|_{t=0} = 0$ ($0 \le y < h_0$). The water concentration can be analytically solved by applying the method of separation of variables, which gives the thickness h_{SiO_2} of the thermal SiO₂ layer as a function of time (details appear in the Appendix, Supporting Information). For the present study

$$\frac{h_{\rm SiO_2}}{h_0} \approx 1 - \frac{t}{t_{\rm critical}} \tag{2}$$

where

$$t_{\rm critical} = \frac{h_0 q \rho_{\rm SiO_2} M_{\rm H_2O}}{w_0 M_{\rm SiO_2} \sqrt{k_{\rm SiO_2} D_{\rm SiO_2}} \tanh \sqrt{\frac{k_{\rm SiO_2} h_0^2}{D_{\rm SiO_2}}}}$$
(3)

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, ρ_{SiO_2} is the mass density of thermal SiO₂ (= 2.33 g cm⁻³), $M_{\text{SiO}_2} \ (= 60 \text{ g mol}^{-1})$ and $M_{\text{H}_2\text{O}} \ (= 18 \text{ g mol}^{-1})$ are the molar masses of SiO₂ and water, respectively.

From soak tests of thermal SiO2 in PBS solution, the diffusivity D_{SiO_2} and reaction constant k_{SiO_2} can be extracted using this model as $D_{\rm SiO_2} = 1.5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ and $k_{\rm SiO_2} =$ 2×10^{-4} s⁻¹ at 96 °C. These values fall within the range of those inferred from previous studies for PECVD SiO₂ $(k = 5.3 \times 10^{-5} \text{ to } 8.1 \times 10^{-3} \text{ s}^{-1})^{[33]}$ and silica glass $(D = 2.1 \times 10^{-18} \text{ to } 1.3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1})^{.[35,36]}$ 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).^[28] 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 HfO_2/SiO_2 is in Figure 3c. For the thermal SiO₂, the reactive diffusion Equation (1), as well as the boundary condition $\partial w/\partial \gamma|_{\gamma=0} = 0$ and initial condition $w|_{t=0} = 0$, still apply. For the HfO_2 layer, the diffusion equation is

$$D_{\mathrm{HfO}_{2}} \frac{\partial^{2} w}{\partial y^{2}} = \frac{\partial w}{\partial t} \quad \left(h_{0} \leq y \leq h_{0} + h_{\mathrm{HfO}_{2}}\right) \tag{4}$$

with the boundary condition $w|_{y=h_0+h_{\rm HfO_2}} = w_0$ and initial condition $w|_{t=0} = 0$ ($h_0 \le y \le h_0 + h_{\rm HfO_2}$), where $D_{\rm HfO_2}$ is the diffusivity of water in HfO_2. The continuity of concentration and flux of water at the HfO_2/SiO_2 interface requires $w|_{y=h_0-0} = w|_{y=h_0+0}$ and $D_{\rm SiO_2} \frac{\partial w}{\partial y}|_{y=h_0-0} = D_{\rm HfO_2} \frac{\partial w}{\partial y_{y=h_0+0}}$. 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 SiO_2 layer (details appear in the Appendix, Supporting Information). For the present study

$$\frac{h_{\rm SiO_2}}{h_0} \approx 1 - \frac{t}{t'_{\rm critical}} \tag{5}$$

where

$$t'_{\rm critical} = \alpha t_{\rm critical} \tag{6}$$

represents the time when the thermal SiO₂ layer completely disappears ($h_{SiO_2} = 0$), that is, the lifetime of the HfO₂/SiO₂ bilayer barrier. Here

$$\alpha = 1 + \sqrt{D_{\text{SiO}_2} k_{\text{SiO}_2}} \frac{h_{\text{HfO}_2}}{D_{\text{HfO}_2}} \tanh \sqrt{\frac{k_{\text{SiO}_2} h_0^2}{D_{\text{SiO}_2}}}$$
(7)

From soak tests, the diffusivity D_{HfO_2} is determined from the bilayer model as $D_{HfO_2} = 2.5 \times 10^{-16}$ cm² s⁻¹ at 96 °C. For







Figure 3. Theoretical modeling of reactive diffusion for the hydrolysis of thermal SiO₂ and HfO₂/SiO₂ barriers. a) Schematic illustration of the singlelayer 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).

different polymer capping materials on thermal SiO₂, the soak tests in Table S1 (Supporting Information) yield the polymer diffusivities, for example, $D_{SU-8} = 7 \times 10^{-15}$ cm² s⁻¹, $D_{PI} = 5.5 \times 10^{-15}$ cm² 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 ($\gamma = 100$ nm) of a 100/100 nm bilayer of HfO₂/SiO₂. The water concentration gradually reaches saturation at ~0.13 g cm⁻³ at the HfO₂/SiO₂ interface after ~3 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 SiO_2 in a bilayer barrier of HfO_2/SiO_2 with a 100-nm-thick layer of SiO_2 and HfO_2 with initial thicknesses of 0, 10, 50, and 100 nm. The lifetime as a function of the initial HfO_2 thickness appears in the inset. The simulated results (line) show good agreement





with those measured (symbols). The temperature-dependent lifetimes are also investigated. With D_{HFO_2} 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 HfO₂/SiO₂ (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 HfO₂ capping layer effectively delays the permeation of biofluid to the underlying SiO₂. Since biofluids contain not only water molecules but alkali metal ions that are known to accelerate the SiO2 dissolution, parametric studies of different ionic concentrations provide additional insights into the underlying chemistry. Figure 4 describes the ion effect on the dissolution of SiO₂ and its lifetime with/without HfO₂ capping layer. The solutions use 10×10^{-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 SiO₂ 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 Ca²⁺. Here, 0.047 and 0.333 M calcium chloride (CaCl₂) 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 SiO₂ in solutions with various values of [Na⁺] and [Ca²⁺], quantitatively determined from the reflectance data in Figure 4a,b. The results indicate that the presence of Ca²⁺ could determine the lifetime of the SiO₂ 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 SiO₂ 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 Ca²⁺ (red) containing



Figure 4. Ion effect on SiO₂ dissolution and lifetimes for thermally grown SiO₂ with/without a capping layer of HfO₂. a) Optical properties of a 320-nmthick layer of thermal SiO₂ after soaking in solutions with various [Na⁺]. Optical images (left) and reflectance (right) of the SiO₂. b) Optical properties of the same SiO₂ layer after soaking in solutions with various [Ca²⁺]. c) Dissolution rates for a single layer of SiO₂ in solutions containing Na⁺ and Ca²⁺. d) Lifetime of barrier layer of SiO₂ (100-nm thick) with and without a capping layer of HfO₂ (100-nm thick) in solutions with various [Na⁺] and [Ca²⁺]. e) Relative lifetime of a bilayer of HfO₂/SiO₂ with respect to a single layer of SiO₂ in solutions containing Na⁺ and Ca²⁺. Here, the ratios of the lifetimes between bilayer barriers and single-layer barriers are presented.



solutions. The results are consistent with the dissolution rates of SiO₂ (Figure 4c). The solid lines show prolonged lifetimes with the addition of the 100-nm-thick capping layer of HfO₂. As with the single layer of SiO₂ barrier, the results for HfO₂/SiO₂ barrier show longer lifetimes in Na⁺ solutions than in Ca²⁺ solutions at the same ionic strength. Compared to 100-nm-thick layer of thermal SiO₂, the bilayer barrier of HfO₂/SiO₂ (100/100 nm thick) enhances the lifetime by a factor of ten. Figure 4e calculates the lifetime ratios between the bilayer of HfO2/SiO2 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 HfO₂/SiO₂ more strongly mitigates the diffusion of Ca²⁺ rather than Na⁺, possibly due to a larger hydrated ionic radius and higher positive charge of Ca²⁺ compared to Na⁺.^[44]

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] 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 $V_{\rm G}$. As a result, the transistor switches on with a more negative $V_{\rm G}$ at the front gate, corresponding to a negative shift in $V_{\rm T}$ for an NMOS device. Ion drift-diffusion tests on encapsulated NMOS transistors (layer configuration shown in Figure 1d) allow comparisons of HfO₂/ SiO₂ and SiO₂ 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 $(V_{app}, 3 \text{ V})$ 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 $\Delta V_{\rm T}$ reaches 1 V. The positive $V_{\rm app}$ serves as a driving force to impel positive ion transport through barriers, the result of which shifts $V_{\rm T}$ of transistors under a 200-nm-thick layer of SiO₂ 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 HfO₂/SiO₂ (100/100 nm thick) remain





Figure 5. Experimental and simulation results for the behavior of NMOS transistors encapsulated with SiO₂ and HfO₂/SiO₂ barriers in various tests of immersion in PBS solution at pH 7.4 and 96 °C. a) Cross-sectional illustration of the embedded MOSFET device with sodium in the channel region. Results of tests for b) a 200-nm-thick layer of SiO₂ and c) a 100/100-nm-thick bilayer of HfO₂/SiO₂ in PBS soak tests at 96 °C and with an applied bias, $V_{app} = 3$ V. Schematic illustrations of the samples and bias configurations appear in the upper insets. d) Shift in the threshold voltage as a function of time with $V_{app} = 3$ V bias for a 200-nm-thick layer of SiO₂ at 96 °C. The solid dots are experimental data and the lines are simulations. Inset indicates shifts in threshold voltage for a 100/100 nm bilayer of HfO₂/SiO₂ as a function of time with $V_{app} = 3$ V bias at 96 °C. e) Acceleration factors for both ion diffusion and dissolution as a function of temperature for a 200-nm-thick layer of SiO₂ and a 100/100 nm bilayer of HfO₂/SiO₂, respectively. The inset offers a schematic illustration of the geometry.

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 $V_{\rm T}$ extracted from Figure 5b for a 200-nm-thick layer of SiO₂ within 1 d with



FUNCTIONAL MATERIALS www.afm-iournal.de

 $V_{app} = 3 \text{ V}$ at T = 96 °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 ΔV_T , we numerically simulate a 2D NMOS transistor with commercial software (Sentaurus Technology Computer Aided

and Av_T , we future field with the a 2D for the state of the state

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 displays 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 $\Delta V_{\rm T}$ reaches 1 V. The AF is defined as t_{failure} (T)/ t_{failure} (369 K), normalized at 369 K. The temperaturedependent Na⁺ diffusion coefficient follows an Arrhenius relationship: $D = D_0 \cdot e^{-E_A/kT}$, 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.

3. Conclusion

In summary, the use of coatings of HfO_2 on top of ultrathin layers of SiO_2 thermally grown on device-grade silicon wafers can provide excellent water/ion barrier performance for flexible electronic devices. A comprehensive combination of experiments and simulations highlights the underlying physical and chemical effects associated with this type of bilayer barrier. Implementing these strategies in active flexible electronic and optoelectronic platforms will allow for a wide range of chronic studies in animals and, potentially, for use in advanced bioelectronic implants in humans.

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.

Acknowledgements

E.S., Y.K.L., R.L., and J.L. contributed equally to this work. This work was supported by Defense Advanced Research Projects Agency Contract HR0011-14-C-0102, and the Center for Bio-Integrated Electronics. The authors acknowledge the use of facilities in the Micro and Nanotechnology Laboratory for device fabrication and the Frederick Seitz Materials Research Laboratory for Advanced Science and Technology for device measurement at the University of Illinois at Urbana-Champaign. E.S. acknowledges support from China Scholarship Council. R.L. acknowledges the support from the Young Elite Scientist Sponsorship Program by China Association for Science and Technology (CAST). Z.X. acknowledges the support National Natural Science Foundation of China (Grant No. 11402134). Y.H. acknowledges the support from NSF (Grant Nos. DMR-1121262, CMMI-1400169, and CMMI-1534120) and the NIH (Grant No. R01EB019337). M.A. acknowledges the support from NSF Nano-biosensing Program Grant No. 1403582 and NSF NCNNEEDS Program under Grant No. 1227020-EEC.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

biofluids, hafnium oxide, hermetic packaging, silicon dioxide, water-and-ion barriers

Received: April 28, 2017 Revised: June 1, 2017 Published online:

- J.-W. Jeong, J. G. McCall, G. Shin, Y. Zhang, R. Al-Hasani, M. Kim, S. Li, J. Y. Sim, K. I. Jang, Y. Shi, D. Y. Hong, Y. Liu, G. P. Schmitz, L. Xia, Z. He, P. Gamble, W. Z. Ray, Y. Huang, M. R. Bruchas, J. A. Rogers, *Cell* **2015**, *162*, 662.
- [2] K. L. Montgomery, A. J. Yeh, J. S. Ho, V. Tsao, S. M. Iyer, L. Grosenick, E. A. Ferenczi, Y. Tanabe, K. Deisseroth, S. L. Delp, A. S. Y. Poon, *Nat. Methods* **2015**, *12*, 969.
- [3] T. Kim, J. G. McCall, Y. H. Jung, X. Huang, E. R. Siuda, Y. Li, J. Song, Y. M. Song, H. A. Pao, R.-H. Kim, C. Lu, S. D. Lee, I.-S. Song, G. Shin, R. Al-Hasani, S. Kim, M. P. Tan, Y. Huang, F. G. Omenetto, J. A. Rogers, M. R. Bruchas, *Science* **2013**, *340*, 211.
- [4] A. Canales, X. Jia, U. P. Froriep, R. A. Koppes, C. M. Tringides, J. Selvidge, C. Lu, C. Hou, L. Wei, Y. Fink, P. Anikeeva, *Nat. Biotechnol.* **2015**, *33*, 277.
- [5] J. Viventi, D.-H. Kim, J. D. Moss, Y.-S. Kim, J. A. Blanco, N. Annetta, A. Hicks, J. L. Xiao, Y. Huang, D. J. Callans, J. A. Rogers, B. Litt, *Sci. Transl. Med.* **2010**, *2*, 24ra22.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com



- [6] D.-H. Kim, N. S. Lu, R. Ghaffari, Y.-S. Kim, S. P. Lee, L. Xu, J. Wu, R.-H. Kim, J. Song, Z. Liu, J. Viventi, B. d. Graff, B. Elolampi, M. Mansour, M. J. Slepian, S. Hwang, J. D. Moss, S.-M. Won, Y. Huang, B. Litt, J. A. Rogers, *Nat. Mater.* **2011**, *10*, 316.
- [7] L. Xu, S. R. Gutbrod, A. P. Bonifas, Y. Su, M. S. Sulkin, N. Lu, H.-J. Chung, K.-I. Jang, Z. Liu, M. Ying, C. Lu, R. C. Webb, J.-S. Kim, J. I. Laughner, H. Cheng, Y. Liu, A. Ameen, J.-W. Jeong, G.-T. Kim, Y. Huang, I. R. Efimov, J. A. Rogers, *Nat. Commun.* **2014**, *5*, 3329.
- [8] D.-H. Kim, R. Ghaffari, N. Lu, S. Wang, S. P. Lee, H. Keum, R. D'Angelo, L. Klinker, Y. Su, C. Lu, Y.-S. Kim, A. Ameen, Y. Li, Y. Zhang, B. d. Graff, Y.-Y. Hsu, Z. Liu, J. Ruskin, L. Xu, C. Lu, F. G. Omenetto, Y. Huang, M. Mansour, M. J. Slepian, J. A. Rogers, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 19910.
- [9] X. Dai, W. Zhou, T. Gao, J. Liu, C. M. Lieber, Nat. Nanotechnol. 2016, 11, 776.
- [10] B. Tian, T. Cohen-Karni, Q. Qing, X. J. Duan, P. Xie, C. M. Lieber, *Science* 2010, 329, 830.
- [11] R. Nawrocki, N. Matsuhisa, T. Yokota, T. Someya, Adv. Electron. Mater. 2015, 2, 1.
- [12] D.-H. Kim, N. Lu, R. Ma, Y.-S. Kim, R.-H. Kim, S. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T.-I. Kim, R. Chowdhury, M. Ying, L. Xu, M. Li, H.-J. Chung, H. Keum, M. McCormick, P. Liu, Y.-W. Zhang, F. G. Omenetto, Y. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, *333*, 838.
- [13] D. J. Lipomi, M. Vosgueritchian, B. C. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, Z. Bao, Nat. Nanotechnol. 2011, 6, 788.
- [14] M. C. McAlpine, H. Ahmad, D. Wang, J. R. Heath, Nat. Mater. 2007, 6, 379.
- [15] W. Gao, S. Emaminejad, H. Y. Nyein, S. Challa, K. Chen, A. Peck, H. M. Fahad, H. Ota, H. Shiraki, D. Kiriya, D. H. Lien, G. A. Brooks, R. W. Davis, A. Javey, *Nature* **2016**, *529*, 509.
- [16] W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T. F. Heinz, J. Hone, Z. L. Wang, *Nature* **2014**, *514*, 470.
- [17] S. Xu, Y. Zhang, L. Jia, K. E. Mathewson, K. I. Jang, J. Kim, H. Fu, X. Huang, P. Chava, R. Wang, S. Bhole, L. Wang, Y. J. Na, Y. Guan, M. Flavin, Z. Han, Y. Huang, J. A. Rogers, *Science* **2014**, *344*, 70.
- [18] M. Kaltenbrunner, T. Sekitani, J. Reeder, T. Yokota, K. Kuribara, T. Tokuhara, M. Drack, R. Schwödiauer, I. Graz, S. Bauer-Gogonea, S. Bauer, T. Someya, *Nature* **2013**, *499*, 458.
- [19] C. M. Lochner, Y. Khan, A. Pierre, A. C. Arias, *Nat. Commun.* 2014, 5, 5745.
- [20] D. Son, J. Lee, S. Qiao, R. Ghaffari, J. Kim, J. E. Lee, C. Song, S. J. Kim, D. J. Lee, S. W. Jun, S. Yang, M. Park, J. Shin, K. Do, M. Lee, K. Kang, C. S. Hwang, N. Lu, T. Hyeon, D.-H. Kim, *Nat. Nanotechnol.* **2014**, *9*, 397.
- [21] N. T. Kalyani, S. J. Dhoble, Renewable Sustainable Energy Rev. 2015, 44, 319.

- [22] L. Bowman, J. D. Meindl, *IEEE Trans. Biomed. Eng.* **1986**, *BME-33*, 248.
- [23] J.-S. Park, H. Chae, H. K. Chung, S. I. Lee, Semicond. Sci. Technol. 2011, 26, 034001.
- [24] H. S. Mayberg, A. M. Lozano, V. Voon, H. E. McNeely, D. Seminowicz, C. Hamani, J. M. Schwalb, S. H. Kennedy, *Neuron* 2005, 45, 651.
- [25] B. S. Wilson, C. C. Finley, D. T. Lawson, R. D. Wolford, D. K. Eddington, W. M. Rabinowitz, *Nature* **1991**, *352*, 236.
- [26] R. S. Sanders, M. T. Lee, Proc. IEEE 1996, 84, 480.
- [27] J. Ahmad, K. Bazaka, L. J. Anderson, R. D. White, M. V. Jacob, *Renewable Sustainable Energy Rev.* 2013, 27, 104.
- [28] H. Fang, J. Zhao, K. J. Yu, E. Song, A. B. Farimani, C.-H. Chiange, X. Jin, Y. Xue, D. Xu, W. Dui, K. J. Seo, Y. Zhong, Z. Yang, S. M. Won, G. Fang, S. W. Choi, S. Chaudhuri, Y. Huang, M. A. Alam, J. Viventi, N. R. Aluru, J. A. Rogers, *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 11682.
- [29] H. Fang, K. J. Yu, C. Gloschat, Z. Yang, E. Song, C.-H. Chiang, J. Zhao, S. M. Won, S. Xu, M. Trumpis, Y. Zhong, S. W. Han, Y. Xue, D. Xu, S.W. Choi, G. Cauwenberghs, M. Kay, Y. Huang, J. Viventi, I. R. Efimov, J. A. Rogers, *Nat. Biomed. Eng.* **2017**, *1*, 0038.
- [30] S.-K. Kang, S.-W. Hwang, H. Cheng, S. Yu, B. H. Kim, J.-H. Kim, Y. Huang, J. A. Rogers, Adv. Funct. Mater. 2014, 24, 4427.
- [31] M. Schindler, S. K. Kim, C. S. Hwang, C. Schindler, A. Offenhäusser, S. Ingebrandt, Phys. Status Solidi RRL 2008, 2, 4.
- [32] L. Maggiorella, G. Barouch, C. Devaux, A. Pottier, E. Deutsch, J. Bourhis, E. Borghi, L. Levy, *Future Oncol.* 2012, *8*, 1167.
- [33] R. Li, H. Cheng, Y. Su, S.-W. Hwang, L. Yin, H. Tao, M. A. Brenckle, D.-H. Kim, F. G. Omenetto, J. A. Rogers, Y. Huang, *Adv. Funct. Mater.* **2013**, *23*, 3106.
- [34] P. V. Danckwerts, Trans. Faraday Soc. 1950, 46, 300.
- [35] K. M. Davis, M. Tomozawa, J. Non-Cryst. Solids 1995, 185, 203.
- [36] M. Tomozawa, K. M. Davis, Mater. Sci. Eng. 1999, A272, 114.
- [37] J. D. Rimstidt, Geochim. Cosmochim. Acta 2015, 167, 195.
- [38] P. M. Dove, N. Han, J. J. De Yoreo, Proc. Natl. Acad. Sci. USA 2005, 102, 15357.
- [39] P. M. Dove, D. A. Crerar, Geochim. Cosmochim. Acta 1990, 54, 955.
- [40] P. V. Brady, J. V. Walther, Chem. Geol. 1990, 82, 253.
- [41] M. Karlsson, C. Craven, P. M. Dove, W. H. Casey, Aquat. Geochem. 2001, 7, 13.
- [42] O. Majérus, T. Gérardin, G. Manolescu, P. Barboux, D. Caurant, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol., Part B 2014, 13, 261.
- [43] K. C. Jena, P. A. Covert, D. K. Hore, J. Phys. Chem. Lett. 2011, 2, 1056.
- [44] P. M. Dove, C. J. Nix, Geochim. Cosmochim. Acta 1997, 61, 3329.
- [45] S. M. Sze, Semiconductor Devices: Physics and Technology, 2nd ed., John Wiley & Sons, Hoboken, NJ, 2008.