

Ultrathin, high capacitance capping layers for silicon electronics with conductive interconnects in flexible, long-lived bioimplants

*Jinghua Li, Rui Li, Chia-Han Chiang, Yishan Zhong, Haixu Shen, Enming Song, Mackenna Hill, Sang Min Won, Ki Jun Yu, Janice Mihyun Baek, Yujin Lee, Jonathan Viventi, Yonggang Huang, John A. Rogers**

Dr. Jinghua Li
Department of Materials Science and Engineering
Northwestern University
Evanston, IL 60208, USA
Department of Materials Science and Engineering
Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL, 61801, USA
Department of Materials Science and Engineering
Center for Chronic Brain Injury
The Ohio State University
Columbus, OH 43210, USA

Prof. Rui 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

Chia-Han Chiang, Mackenna Hill, Prof. Jonathan Viventi
Department of Biomedical Engineering
Duke University
Durham, NC 27708, USA

Yishan Zhong
Department of Materials Science and Engineering
Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL, 61801, USA

Haixu Shen
Department of Materials Science and Engineering
Northwestern University
Evanston, IL 60208, USA

Dr. Enming Song, Dr. Sang Min Won
Department of Materials Science and Engineering
Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL, 61801, USA
Center for Bio-Integrated Electronics
Northwestern University
Evanston, IL 60208, USA

Prof. Ki Jun Yu
School of Electrical and Electronic Engineering
Yonsei University
Seoul, 03722, Republic of Korea

Janice Mihyun Baek, Yujin Lee
Department of Chemistry
University of Illinois at Urbana-Champaign
Urbana, IL, 61801, USA

Prof. Yonggang Huang
Department of Civil and Environmental Engineering
Mechanical Engineering
Materials Science and Engineering
Center of Bio-integrated electronics
Northwestern University
Evanston, IL 60208, USA

Prof. John A. Rogers
Department of Materials Science and Engineering
Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL, 61801, USA
Center for Bio-Integrated Electronics,
Simpson Querrey Institute for BioNanotechnology,
Department of Materials Science and Engineering, Biomedical Engineering, Chemistry,
Mechanical Engineering, Electrical Engineering and Computer Science, and Neurological
Surgery
McCormick School of Engineering and Feinberg School of Medicine Northwestern University,
Evanston, IL 60208, USA
Corresponding Author. E-mail: jrogers@northwestern.edu

Keywords: neural interfaces, bio-integrated electronics, biofluid barrier, high- κ dielectrics

Abstract: Bioimplants that incorporate active electronic components at the tissue interface rely critically on materials that are biocompatible, impermeable to biofluids and capable of intimate electrical coupling for high-quality, chronically stable operation *in vivo*. This study reports a materials strategy that combines silicon nanomembranes (Si NMs), thermally grown layers of SiO₂ and ultrathin capping structures in materials with high dielectric constants as the basis for flexible and implantable electronics with high performance capabilities in electrophysiological mapping. Accelerated soak tests at elevated temperatures and results of theoretical modeling indicate that appropriately designed capping layers can effectively limit biofluid penetration and dramatically extend the lifetimes of the underlying electronic materials when immersed in simulated biofluids. Demonstration of these approaches with actively multiplexed, amplified systems that incorporate more than one hundred transistors in thin, flexible platforms highlight the key capabilities and the favorable scaling properties. These results offer an effective encapsulation approach for long-lived bioelectronic systems with broad potential for applications in biomedical research and clinical practice.

1. Introduction

A critical challenge in the development of flexible bioimplants is in the materials science and device engineering of chronically stable bioelectronic interfaces.^[1-3] In some cases, the required timescales correspond to the lifespan of the patient, multiplied by some factor to provide an engineering margin of safety, thus reaching timescales that can reach hundreds of years. The most sophisticated types of bioimplants for neuroscience research and for envisioned classes of biomedical devices for human use involve active semiconductor functionality at the bio-interface for multiplexing, local signal amplification, light emission/detection, and other functions with high spatiotemporal resolution across large areas.^[4-9] This mode of operation involves electrical biases

and continuous power supplied across the entire platform, immediately adjacent to sensitive biological tissues. Here, a biocompatible measurement/stimulation interface serves also as a barrier against both biofluid penetration and current leakage, to avoid damage to the tissue and to the electronics.

An ideal engineered interface for this purpose should offer: 1) efficient coupling between the electronics and the body for high-fidelity sensing/actuation, 2) low reactivity in biofluids and 3) perfect barrier properties for electrical and materials isolation from surrounding biofluids. Conventional encapsulation strategies that exploit deposited thin film coatings of organic and/or inorganic materials are effective for systems that consist of passive electrode arrays,^[10-19] but typically fail to provide barrier function at a level required for powered electronics in advanced applications. Deficiencies arise from some combination of extrinsic (e.g. pinholes, grain boundaries, etc) and intrinsic (e.g. permeability to water/ions, slow reactivity with biofluids, etc) properties of the films.^[20-23] The use of bulk materials in engineered containment enclosures can yield long lifetimes, but without the mechanical flexibility necessary to establish long-lived, intimate electronic interfaces to soft and fragile biotissues.^[24-26] Recent studies demonstrate that ultrathin layers of SiO₂ derived from growth on the surfaces of pristine, device-grade Si wafers through oxidation at high temperatures (1150 °C; thermal SiO₂ or t-SiO₂) can simultaneously serve as perfect barriers to biofluids and as capacitively coupled sensing interfaces, in high performance, flexible bioelectronics platforms with active semiconductor device functionality.^[5-6] The relatively low dielectric constant (κ) of the t-SiO₂ and its small, but finite, rates of hydrolysis under aqueous conditions, however, set fundamental limitations in the scaling of the system. Specifically, to achieve sufficient capacitance coupling for sensing across the device platform, designs favor either large lateral dimension for the measurement sites or reduced thickness for the t-SiO₂ layer.

The former prevents high spatial resolution, while the latter limits the lifetimes set by hydrolysis. As a solution, recent reports describe the use of heavily doped, patterned structures of p-type Si (p^{++} -Si) bonded intimately with layers of t-SiO₂, in structures that we denote as p^{++} -Si//t-SiO₂, for conductive vertical interconnect access (VIAs) that serve as arrays of electrically connections between the electronics and the surrounding bio-tissues.^[27] Although this solution eliminates the constraints set by capacitive coupling, the hydrolysis rate of p^{++} -Si (0.5-100 nm/day at 37 °C)^[27-28] is higher than that of t-SiO₂ (0.04-1.26 nm/day at 37 °C)^[5-6, 29], thereby limiting the lifetimes typically to several years, as determined by accelerated testing. Replacing the p^{++} -Si with TiSi₂ by reaction with Ti yields an insoluble alternative^[30], but additional studies of the properties of this silicide and its suitability as a chronic bio-interface material are necessary. These circumstances motivate the continued development of alternative strategies.

Here we present materials designs and integration schemes for an approach that exploits a layer of HfO₂ formed by atomic layer deposition (ALD), a coating of Au deposited by thermal evaporation, and a structure of p^{++} -Si//t-SiO₂ to serve as a high capacitance sensing interface and chronically stable biofluid barrier for active, flexible electronic bioimplants. Experimental investigations and theoretical modeling results at elevated temperatures indicate that this materials system, at a total thicknesses of only ~1 μm, can reach lifetimes of many decades, with favorable scaling properties to support high resolution mapping. The findings reported here provide insights into the interface science and reactive diffusion mechanisms of silicon and metal oxide multilayer assemblies, and suggest a realistic pathway for high-resolution and long-lived neural interfaces for chronic electrophysiology, with relevance to a wide range of applications in neuroscience and neuroengineering.

2. Results and Discussion

The fabrication focuses on formation of test platforms that include high-quality metal oxide field-effect transistors (MOSFETs) and multilayer capping structures using adapted versions of otherwise standard semiconductor manufacturing techniques. Figure 1 presents a schematic illustration of the sequence. Briefly, the process begins with a silicon-on-insulator (SOI) substrate with a 200 nm-thick layer of device Si (p-type, concentration: 10^{17} cm^{-3}) and a 1 μm -thick layer of buried oxide (BOX), t-SiO₂. Photolithographic patterning followed by wet/dry etching and thermal diffusion doping yields isolated NMIs of n⁺⁺-Si (concentration: 10^{19} cm^{-3}) and p⁺⁺-Si (concentration: 10^{20} cm^{-3}) as the semiconductor material for the MOSFETs and the conductive material for vias to the bio-interface, respectively (Figure 1A). Subsequent steps include deposition, patterning and etching to form n-type MOSFETs with gate electrodes electrically connected to the patterned p⁺⁺-Si NMIs, followed by casting of a uniform overcoat of polyimide (PI) (Figure 1B). A bonding process joins this PI to another thin sheet of PI on a temporary glass handle wafer using an adhesive layer and a coating of Al₂O₃ deposited by ALD. Reactive ion etching (RIE) then removes the Si wafer to expose the t-SiO₂ as the biofluid barrier (Figure 1C). Etching forms openings through the t-SiO₂ aligned to the p⁺⁺-Si NMIs (Figure 1D). Thermal evaporation yields a thin layer of a noble metal (e.g. Au, Pt) on top of this p⁺⁺-Si//t-SiO₂ structure to define the sensing/stimulation sites and to reduce the rate of diffusion of water to the p⁺⁺-Si NMIs. Treatment with O₂ plasma followed by conformal deposition of HfO₂ using ALD forms an ultrathin, high- κ dielectric layer as the basis of an insoluble capacitive bio-interface that further reduces the rate of diffusion of water to the p⁺⁺-Si NMIs. Peeling the device from the temporary glass substrate completes the fabrication. A layer of t-SiO₂ can be integrated onto the back side of the PI substrate to prevent biofluid penetration from this direction.^[6]

Although many published reports describe the deposition of high- κ dielectrics (e.g. Al_2O_3 , HfO_2) by ALD on noble metal surfaces (e.g. Au, Pt) for applications in energy storage, nano-/micro-electronics and other areas,^[31-40] the underlying mechanisms are of interest due to the lack of naturally occurring hydroxyl groups on the surfaces of such metals. Formation of the initial growth interface during the ALD process can significantly affect the quality of the resulting films, of particular importance in demanding applications such as those in biofluid barrier coatings. Measurements show that exposure to O_2 plasma enhances the hydrophilicity of the Au surface, and thus promotes the formation of the initial interface during the first several cycles of ALD. Figure 2A and 2B show the water contact angle of thermally evaporated thin films of Au as a function of the O_2 plasma treatment time (0-120 s, power: 150 W) and corresponding photographs. Before the treatment, the Au surface is hydrophobic with a contact angle of $\sim 90^\circ$. The value drops to $< 10^\circ$ after treatment for 1 min. X-ray photoelectron spectroscopy reveals the surface conditions after O_2 plasma treatment for 5 min. The results plotted in Figure 2C and D show the relative peak intensities in the O 1s region. The untreated sample shows only a peak associated with adsorbed O (Figure 2C) while the treated one exhibits an additional peak from chemically bonded O (e.g. a stoichiometry of $\text{AuO}_{1.5}$ or Au_2O_3) (Figure 2D).^[41] Previous reports describe the presence of hydroxyl groups as surface termination on transition metal oxides^[42] and on Au via reactions between water and oxygen adatoms.^[43] Proton transfer from water to this surface oxygen can yield surface-bound hydroxyl species that enhance the reactivity at the interface for the chemisorption of ALD precursors.^[44-45] Evaporation of a layer of Ti or Cr,^[46] or surface functionalization with self-assembled monolayer (e.g. by the use of OH-terminated alkanethiolate to form Au-S anchor on one end, and -OH groups on the other end for ALD growth)^[47-49] can further improve the adhesion between the Au and HfO_2 and thus enhance the performance as a barrier material.

Systematic studies yield information on the biofluid barrier properties. For these experiments, a thin film of magnesium (Mg) deposited by electron-beam evaporation serves as a sensor for water penetration. Upon exposure to water, Mg quickly reacts to produce $Mg(OH)_2$ and H_2 , and an associated dramatic change in optical properties, easily detectable by optical microscopy or visual inspection. Figure 3A shows an exploded view schematic illustration of such a Mg-based test device that includes a p^{++} -Si//t-SiO₂ structure with capping layers. The fabrication sequence follows steps outlined in Figure 1 but with photolithographically patterned islands of Mg in place of the MOSFETs. Reflectometry measurements reveal the dissolution behavior of films of p^{++} -Si and HfO₂ in aqueous solutions (20 mL) with chemical compositions relevant to biofluids (Figure 3B). At physiological temperatures (37 °C), the p^{++} -Si (sample size: 0.5 × 0.5 cm²) decreases in thickness uniformly at a rate of ~0.52 nm/day in phosphate buffered saline (PBS) and 0.56 nm/day in bovine serum (BS) through the reaction $Si + 4H_2O \rightarrow Si(OH)_4 + 2H_2$. By comparison, the thickness of the HfO₂ remains almost unchanged under similar conditions (Figure 3B) and even at elevated temperatures (96 °C) (Figure S1). The results demonstrate that HfO₂ deposited by ALD is effectively insoluble in aqueous solutions with ions and/or proteins. Figure 3C shows a sequence of optical images of Mg pads beneath p^{++} -Si//t-SiO₂ structures without and with different capping layers. The areas in the images correspond to openings through the t-SiO₂ (1 μm) aligned to regions of p^{++} -Si (170 nm). Experiments at 96 °C on test structures without capping layers reveal average lifetimes of 2.65 days. After, the Mg dissolves in a spatially uniform manner due to the complete hydrolysis of p^{++} -Si. Similar tests at different temperatures reveal average lifetimes of 10.7 and 20.2 days at 80 and 70 °C, respectively. These results are consistent with Arrhenius scaling where the lifetime depends exponentially on 1/T (Figure S2).^[6] The addition of capping layers limits the diffusion of water to the p^{++} -Si and thereby reduces the rate

of hydrolysis of this material. Specifically, a 300 nm-thick capping layer of Au yields average lifetimes of 5.7, 20.4 and 50.1 days at 96, 80 and 70 °C. Figure S3 shows an optical image collected from the Au side before and after 5 days of immersion in PBS at 96 °C. The results indicate a stable interface between the Au and the Si with the formation of pinhole defects but no observable delamination. The coating of HfO₂ formed by ALD further extends the average lifetimes to 17.5, 63.4 and 154.2 days at 96, 80 and 70 °C, respectively. A summary of lifetimes for various capping layers are in Figure S4. In all cases, the p⁺⁺-Si//t-SiO₂ structures serve as perfect, pinhole-free biofluid barriers while the capping layers reduce the rates of hydrolysis of the p⁺⁺-Si, as the main process that limits the lifetime. Devices with insoluble capping layers (Au and HfO₂) demonstrate a failure mode characteristic of water penetration through pinholes or other isolated defects, as forms of extrinsic factors reported in previous studies which is associated with the cleanroom environment available in academic research laboratory. Water that penetrates through such defects moves laterally over time due to diffusion along the interface, eventually dissolving the entire Mg pad. Figure S5 shows an example that highlights this behavior.

Accelerated soak tests in PBS using platforms that incorporate n-type MOSFETs provide additional information on this multilayer encapsulation strategy. Here the thermal oxidation and doping steps partially consume the 200 nm-thick Si NM on the SOI substrate to reduce its thickness to ~60 nm. Figure 3D (inset) provides an optical image of a MOSFET with an effective channel length and width of 16 and 400 μm, respectively. The output characteristics in Figure S6 indicate expected performance, with Ohmic contacts. Figure 3D shows the statistics of the peak effective electron mobility and the threshold voltage of ten n-type MOSFETs prepared in this manner. Figure 3E presents the transfer characteristics of a representative transistor with a peak mobility of ~300 cm² · V⁻¹ · s⁻¹ and a threshold voltage of ~0.2 V. The inset shows a side-view schematic

illustration of the MOSFET stack with capping layers (300 nm Au and 50 nm HfO₂). A representative device exhibits stable operation for ~7 days at 96 °C in PBS (pH = 7.4), followed by a sudden increase in leakage current (Figure 3F). The findings are consistent with results obtained using Mg-based passive devices (with 170 nm p⁺⁺-Si) as described in the previous section. By comparison to previously reported lifetimes of Si bio-interfaces,^[27-28, 30] the results presented here represent an improvement by a factor of ~5-6.

Figure 4 illustrates a theoretical model of reactive diffusion for dissolution of the p⁺⁺-Si NM without and with capping layers of Au or HfO₂/Au. For the ultrathin multilayers under consideration, the initial thicknesses are sufficiently small compared to the in-plane dimensions such that one-dimensional models can capture the diffusion and dissolution behaviors.^[50] The water diffusivity in p⁺⁺-Si, D_{Si} , and the reaction rate constant between water and p⁺⁺-Si, k_{Si} , are key parameters for reactive diffusion modeling, for which a single layer model of p⁺⁺-Si with an initial thickness h_{Si} immersed in PBS is established in Figure 4A. Here, the z axis lies along the thickness direction, with the origin O located at the bottom. The governing equation is $D_{\text{Si}} \partial^2 w / \partial z^2 - k_{\text{Si}} w = \partial w / \partial t$ ($0 \leq z \leq h_{\text{Si}}$),^[51] where w is the water concentration, which depends on both location z and time t . With a constant water concentration, w_0 , of 1 g cm⁻³ at the top and zero water flux at the bottom surface of the p⁺⁺-Si layer, the boundary conditions are $w|_{z=h_{\text{Si}}} = w_0$ and $\partial w / \partial z|_{z=0} = 0$. The initial condition of zero water concentration throughout the thickness requires $w|_{t=0} = 0$ ($0 \leq z < h_{\text{Si}}$). The variable separation method yields an analytic solution for w , by which the thickness of the dissolved p⁺⁺-Si, $h_{\text{dissolved}}$, follows from integration of $h_{\text{Si}} M_{\text{Si}} k_{\text{Si}} w / (4 \rho_{\text{Si}} M_{\text{H}_2\text{O}})$ over both z and t according to $\text{Si} + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 2\text{H}_2$,^[27] giving $h_{\text{dissolved}} \approx [M_{\text{Si}} w_0 \sqrt{k_{\text{Si}} D_{\text{Si}}} \tanh \sqrt{k_{\text{Si}} h_{\text{Si}}^2 / D_{\text{Si}}} / (4 \rho_{\text{Si}} M_{\text{H}_2\text{O}})] t$ after omitting an infinite series

summation that is negligible in this study (details appear in the Appendix, Supporting Information). Here, ρ_{Si} is the mass density of p⁺⁺-Si ($= 2.33 \text{ g cm}^{-3}$), M_{Si} ($= 28 \text{ g mol}^{-1}$) and $M_{\text{H}_2\text{O}}$ ($= 18 \text{ g mol}^{-1}$) are the molar masses of p⁺⁺-Si and water, respectively. Equating $h_{\text{dissolved}}$ with h_{Si} , the total time to reach full dissolution, i.e., the lifetime of the p⁺⁺-Si layer, t_{life} , can be written as

$$t_{\text{life}} \approx \frac{6h_{\text{Si}}}{\sqrt{k_{\text{Si}}D_{\text{Si}}} \tanh \sqrt{\frac{k_{\text{Si}}h_{\text{Si}}^2}{D_{\text{Si}}}}}. \quad (1)$$

With experimentally measured lifetimes for a 100-nm-thick layer of p⁺⁺-Si at 65 and 96 °C (21 and 2 days, respectively), D_{Si} and k_{Si} at different temperatures can be determined by applying the above model as $D_{\text{Si}} = 10^{-4.86-4121/T} \text{ cm}^2 \text{ s}^{-1}$ and $k_{\text{Si}} = 2.03 \times 10^8 \times e^{-9515/T} \text{ s}^{-1}$ (T is the absolute temperature), which follow Arrhenius scaling with an activation energy of 0.82 eV.^[27] Figure 4B plots the lifetimes of a single layer of p⁺⁺-Si at three different temperatures (65, 70, and 96 °C) *versus* the initial thickness. The results from theoretical modeling (lines) agree well with experimental results (dots).

A bilayer model can describe the dissolution of p⁺⁺-Si with Au or HfO₂/Au capping layers (Figure 4C). For p⁺⁺-Si, the governing equation of the single layer model as well as the boundary condition $\partial w / \partial z|_{z=0} = 0$ and initial condition $w|_{t=0} = 0$ remain valid. Since both Au and HfO₂ do not react with water, as revealed by invariant thicknesses of thin films of these materials during soak tests, the behavior of water in Au or HfO₂/Au can be described by diffusion via extrinsic effects, without reaction, i.e., $D_{\text{encap}} \partial^2 w / \partial z^2 = \partial w / \partial t$ ($h_{\text{Si}} \leq z \leq h_{\text{Si}} + h_{\text{encap}}$), with the boundary condition $w|_{z=h_{\text{Si}}+h_{\text{encap}}} = w_0$ and initial condition $w|_{t=0} = 0$ ($h_{\text{Si}} \leq z \leq h_{\text{Si}} + h_{\text{encap}}$), where h_{encap} is the

encapsulation thickness, and D_{encap} the effective water diffusivity in the capping layers, i.e. D_{Au} for Au or D_{equiv} for an equivalent layer of HfO_2/Au . The continuity of interfacial water concentration and flux requires $w|_{z=h_{\text{Si}}-0} = w|_{z=h_{\text{Si}}+0}$ and $D_{\text{Si}} \partial w / \partial z|_{z=h_{\text{Si}}-0} = D_{\text{encap}} \partial w / \partial z|_{z=h_{\text{Si}}+0}$. The variable separation method yields an analytic solution for the water concentration in the bilayer. Following the logic for the single layer model, the total time for full dissolution of the $\text{p}^{++}\text{-Si}$, i.e., the lifetime of the bilayer, t'_{life} , is

$$t'_{\text{life}} \approx \left(1 + \frac{h_{\text{encap}} \sqrt{k_{\text{Si}} D_{\text{Si}}}}{D_{\text{encap}}} \tanh \sqrt{\frac{k_{\text{Si}} h_{\text{Si}}^2}{D_{\text{Si}}}} \right) t_{\text{life}}. \quad (2)$$

The modeling details appear in the Appendix (Supporting Information). With D_{Si} and k_{Si} obtained from the single layer model and the experimentally measured lifetimes for the 300/170-nm-thick $\text{Au}/\text{p}^{++}\text{-Si}$ bilayer at 70 and 96 °C (50.1 and 5.7 days, respectively), D_{Au} at different temperatures can be determined by the bilayer model as $D_{\text{Au}} = 10^{0.65-5344/T} \text{ cm}^2 \text{ s}^{-1}$ based on the Arrhenius scaling. Similarly, soak tests for a 50/300/170-nm-thick $\text{HfO}_2/\text{Au}/\text{p}^{++}\text{-Si}$ structure give lifetimes of 154.2 and 17.5 days at 70 and 96 °C, respectively, which determine the equivalent water diffusivity in the 350-nm-thick capping layer (HfO_2/Au) as $D_{\text{equiv}} = 10^{-1.51-4803/T} \text{ cm}^2 \text{ s}^{-1}$.

Figure 4D plots the predictions of the lifetimes for three structures ($\text{p}^{++}\text{-Si}$, $\text{Au}/\text{p}^{++}\text{-Si}$, and $\text{HfO}_2/\text{Au}/\text{p}^{++}\text{-Si}$) at 96 °C *versus* the initial thickness of the $\text{p}^{++}\text{-Si}$, where the thicknesses of HfO_2 and Au are 50 and 300 nm, respectively. The lifetimes show an approximately linear dependence on h_{Si} . The distribution of saturated water concentration in a representative 50/300/170-nm-thick $\text{HfO}_2/\text{Au}/\text{p}^{++}\text{-Si}$ structure at 96 °C is shown in Figure 4E following the steady-state limit that is expressed in normalized form by

$$\frac{w_{\text{saturation}}}{w_0} = \begin{cases} \frac{\cosh\left(\sqrt{\frac{k_{\text{Si}}}{D_{\text{Si}}}}z\right)}{\cosh\sqrt{\frac{k_{\text{Si}}h_{\text{Si}}^2}{D_{\text{Si}}}} + \frac{h_{\text{encap}}\sqrt{k_{\text{Si}}D_{\text{Si}}}}{D_{\text{equiv}}}\sinh\sqrt{\frac{k_{\text{Si}}h_{\text{Si}}^2}{D_{\text{Si}}}}}, & 0 \leq z \leq h_{\text{Si}} \\ 1 - \frac{h_{\text{Si}} + h_{\text{encap}} - z}{h_{\text{encap}} + \frac{D_{\text{equiv}}}{\sqrt{k_{\text{Si}}D_{\text{Si}}}}\coth\sqrt{\frac{k_{\text{Si}}h_{\text{Si}}^2}{D_{\text{Si}}}}}, & h_{\text{Si}} \leq z \leq h_{\text{Si}} + h_{\text{encap}} \end{cases} \quad (3)$$

The modeling details appear in the Appendix (Supporting Information). The results suggest that the water concentration is significantly reduced by the presence of the HfO₂/Au, reaching only 0.2 g cm⁻³ at the interface between these capping layers and the p⁺⁺-Si even after saturation. A dramatic decrease of water concentration to zero immediately under the top of p⁺⁺-Si indicates a surface-reaction-dominated kinetics for dissolution of p⁺⁺-Si in water. The theoretical temperature-dependent lifetimes of the three structures are in Figure 4F, where the 50/300-nm-thick HfO₂/Au structure provides an increase in lifetime by an order of magnitude for the case of a 170-nm-thick layer of p⁺⁺-Si. This lifetime is two times longer than that of an otherwise similar system but with a capping layer of only a 300-nm-thick film of Au. The theoretical results (lines) are in good agreement with the experimental measurements conducted at high temperatures (dots), and are especially useful for low-temperature (e.g., body-temperature) lifetime predictions for chronic implantable devices that may live for decades,^[30] where experimental studies are impractical. The extrapolated lifetimes at 37 °C of the three cases studies here are 451 (170 nm p⁺⁺-Si), 1811 (300 nm Au/ 170 nm p⁺⁺-Si) and 4574 (50 nm HfO₂/300 nm Au/ 170 nm p⁺⁺-Si) days.

These findings motivate the use of capping layers with the p⁺⁺-Si//SiO₂ structure as a biofluid barrier and sensing/stimulation bio-interface for actively multiplexed, flexible Si electronics. Figure 5A compares the designs of arrays of Si MOSFETs for electrophysiology with

different coupling strategies to bio-tissues. In the most basic design, a uniform layer of t-SiO₂ serves simultaneously as a barrier that prevents water penetration and a dielectric that capacitively couples the underlying semiconducting channels of the electronics to the surrounding biology.^[5-6] As highlighted in the introduction, the relatively low dielectric constant of t-SiO₂ and its slow reaction with water results in a tradeoff between lifetime, resolution and interface coupling strength.^[5] Conductive vias of p⁺⁺-Si through the t-SiO₂ address the limitation in electrical coupling by replacing the capacitive interface with a conductive one, but with increased rates of reaction with water. In the scheme introduced here, a metal pad and ultrathin layer of HfO₂ on top of the p⁺⁺-Si serves to slow the rates of water penetration and to form a direct, high capacitance contact to bio-tissues on one side, through the p⁺⁺-Si features, and conductive connection to the associated electronics on the other side. Figure 5B shows an exploded view schematic illustration of this design. Each unit cell contains two Si MOSFETs: one to support multiplexed addressing and the other to buffer and amplify the signals. Photographs of a representative device with an interconnected array of 64 such unit cells before and after (inset) coating with a thermally evaporated layer of Au appear in Figure 5C. Figure 5D presents corresponding optical images of a unit cell with the via opening size of 30 × 30 μm² (channel length: 16 μm, channel width: 80 μm, p⁺⁺-Si: 270 × 190 μm², unit area: 360 × 360 μm²). Additional optical images at key steps of the fabrication sequence appear in Figure S7. Figure S8 presents the transfer characteristics of a test transistor with a similar layout, showing an on/off ratio of ~10⁶, a peak mobility of ~400 cm² · V⁻¹ · s⁻¹ and a threshold voltage of ~0.1 V.

In vitro assessments highlight the advantages of this design over capacitively coupled systems with a similar structure but without the conductive vias. The evaluations involve immersing the device into electrically biased PBS and collecting data with a back-end data

acquisition system described elsewhere [5-6, 27]. Figure 5E shows the average gain (defined as the ratio of output voltage to input voltage) of the 64 unit cells in a representative device as a function of the input frequency (0.1-100 Hz, input voltage: 2 mV). The performance is stable over a wide dynamic range with the average gain value of ~0.99 (close to the design point of 1). Systematic studies reveal the effects of key parameters on the scalability of conductively coupled Si electronics for high resolution bio-potential recording. Figure 5F displays the average gain and mean noise levels of a system as a function of via opening size in devices with a p⁺⁺-Si fill factor (defined as the ratio of p⁺⁺-Si region to the whole area of the unit) of 39%. The via dimensions range from 200 × 130 to 90 × 60, 30 × 30 and 15 × 15 μm^2 , as displayed in Figure 5D and Figure S9. In all cases, the devices with direct electrical coupling between PBS and the gate electrode of the transistors show stable performances with average gain and mean per-channel noise above 0.97 and below 85 μV , respectively. The ultimate dimension of the via opening is only limited by the features size than can be achieved by lithographic patterning and etching. Minimizing the size of the p⁺⁺-Si enables further scaling. Figure 5G shows the theoretical gain value as a function of the fill factor with capacitive coupling through the t-SiO₂ (1 μm). The capacitance can be calculated using the following equation:

$$C = \epsilon_r \epsilon_0 A / t \quad (4)$$

where ϵ_r is the relative permittivity, ϵ_0 is the vacuum permittivity, A is the area of the capacitor, and t is the thickness of the dielectric. For the capacitance of top-gate dielectrics (C_{TG}), A = 16 × 80 μm^2 , ϵ_r (t-SiO₂) = 3.9, t (t-SiO₂) = 50 nm, ϵ_r (Al₂O₃) = 11, t (Al₂O₃) = 13 nm. As an example, for the capacitance of the sensing interface (C_{CAP}) in a device with a fill factor of 5%, A = 360 × 360 μm^2 × 5%, t (t-SiO₂) = 1 μm . Accordingly, C_{CAP} = ~0.3 C_{TG}. The total capacitance (C_T) driving

the channel of the transistor in the buffer/amplifier can be calculated by combining C_{CAP} and C_{TG} in series:

$$1/C_{\text{T}} = 1/C_{\text{CAP}} + 1/C_{\text{TG}} \quad (5)$$

which yields $C_{\text{T}} = \sim 0.2 C_{\text{TG}}$. As a result, the theoretical value of the gain is ~ 0.2 , as the sensing interface and the top gate dielectrics in series form a voltage divider structure. Similarly, a fill factor of $\sim 90\%$ corresponds to a gain value of ~ 0.83 . The actual value might be slightly higher resulting from the effect of active shielding circuits in the acquisition electronics. Figure 5G (inset) highlights the theoretical gain as a function of the thickness of $t\text{-SiO}_2$ ($p^{++}\text{-Si}$ fill factor: 5%), suggesting that the reduction of the thickness of the interface to 200 nm can yield a gain of ~ 0.58 . Therefore, there is a design trade-off between signal quality and device lifetime.

Capping layers of metal and high- κ dielectrics on top of the conductively coupled system forms an interface with much higher capacitance than that afforded by $t\text{-SiO}_2$ at thicknesses needed for chronic stability. The equivalent circuit diagram of a unit cell appears in Figure S10. For HfO_2 , $\epsilon_r = 25$. With the high fill factor of Au of $\sim 100\%$ ($360 \times 360 \mu\text{m}^2$), the capacitance of 50 nm HfO_2 sensing interface $C_{\text{CAP}} = \sim 700 C_{\text{TG}}$. As a result, C_{T} is almost the same as C_{TG} according to equation (5). More importantly, for the design that requires higher resolution with a smaller unit size and a minimized area of $p^{++}\text{-Si}$ region, this design shows advantage over counterparts with $t\text{-SiO}_2$ interface.^[27] For example, with a whole unit area as small as $80 \times 80 \mu\text{m}^2$, this design can provide a gain of 0.97.

Figure 6A shows the output characteristics of an amplifier in one sensing node in a device of this type with an alternating current (AC) signal of 20 mV (10 Hz, sine wave input). Figure 6B displays the histograms of gain values from 36 units in a typical system. The results indicate an average gain of 0.96. The mean per-channel noise is $\sim 25 \mu\text{V}$ (Figure 6C), suggesting no

degradation in electrical performance compared to devices without an HfO₂ capping layer, as described in Figure 5 due to the high capacitance of the interface. As a comparison, the optimized mean noise level of previously reported devices with capacitive coupling through t-SiO₂ falls into the range of 50-80 μ V.^[5-6] Figure 6D displays the statistics of signal-to-noise ratio (SNR) with an average value of \sim 48 dB.

3. Conclusion

In summary, the results presented here provide a materials and integration strategy that establishes multilayer stacks of HfO₂, Au and a structure of p⁺⁺-Si//SiO₂ as a long-lived biofluid barrier and high quality capacitive sensing interface for flexible, active electronic bioimplants. Experimental and theoretical studies reveal that these capping multilayers on p⁺⁺-Si/t-SiO₂ dramatically reduce the rates of diffusion of water to the p⁺⁺-Si, thereby extending by an order of magnitude the lifetime of the bioimplants. Comparative evaluations highlight the advantages in scaling to high-density, high-resolution arrays with an extended lifetime of about one order of magnitude at physiological temperature compared to the case without coating layers. These findings suggest a promising pathway toward high-resolution neural interfaces with levels of flexibility, recording fidelity and longevity that can address a wide range of applications in biomedical research and clinical practice.

4. Experimental Section

Fabrication of transistor arrays

The fabrication of the transistors began with cleaning of the SOI substrates (200 nm device-grade Si, 1 μ m t-SiO₂ and 200 μ m Si handle wafer). Photolithographic patterning, deposition and etching formed boron (p-type) and phosphorus (n-type) doped Si NMs as the conductive sensing

pathways and NMOS backplane, respectively. Thermal oxidation and ALD formed ~50 nm-thick layers of t-SiO₂ and ~13 nm-thick layers of Al₂O₃ as the gate stack. Photolithographic patterning and immersion in buffered oxide etchant (BOE) opened contact areas to the Si, followed by deposition and patterning of bilayers of Cr (10 nm) and Au (300 nm) as the metal interconnects and source, drain and gate electrodes. An additional metal contact established electrical interconnects between the p⁺⁺-Si regions and the channels of the transistors. Spin coating layer of PI (1.5 μ m) followed by curing in a vacuum oven formed uniform overcoat. Deposition of a 20 nm-thick film of Al₂O₃ on the PI by ALD yielded an adhesion layer for bonding. Separately, a glass slide served as a temporary substrate support for a spin-cast layer of polydimethylsiloxane (PDMS), a Kapton film (12 μ m) and a thin film of ALD-Al₂O₃ (20 nm). A commercial adhesive (Kwik-Sil, World Precision Instruments) facilitated bonding between the surface of the device and material stack on the handling substrate (pressure: 50 kPa). Inductively coupled plasma (ICP) RIE with SF₆ and O₂ removed the Si handle wafer and exposed the buried t-SiO₂. Photolithographic patterning followed by combined dry (CF₄/O₂) and wet (BOE) etching opened selective regions aligned to the p⁺⁺-Si as the conductive via. Thermal evaporation of 10 nm Cr/300 nm Au, photolithography and metal etching yielded metal pads on the top to define the sensing areas. Additional steps using ALD formed a conformal coating of ~50 nm HfO₂ (100-120 °C) as the final top layer. Tetrakis(dimethylamido)hafnium(IV) (TDMAH) and H₂O served as the precursors. Covering the electrical contact area with Kapton tape before ALD minimized the growth of HfO₂ on the terminal pads for subsequent removal steps. Carefully peeling off the tape followed by photolithography, dry (ICP-RIE with SF₆ and O₂) and wet etching (BOE) opened contact areas for electrical measurement. Cutting the device with a razor blade and peeling the device off completed the fabrication steps. A probe station measured the electrical properties of the MOSFETs. In vitro

assessments of multiplexed Si transistor arrays used a customized data acquisition system reported elsewhere.^[5-6]

Soak tests for passive and active devices

A well structure formed in PDMS confined PBS over the target area of the device. Ultraviolet ozone treatment enhanced the adhesion between PDMS and the surface of the sample. For active devices, metal traces formed by electron-beam evaporation connected the active area to contact pads outside of the well for measurement and evaluation.

Supporting Information

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

Acknowledgements

J.L., R.L. and C.-H. C. contributed equally to this work. This work was supported by the Center for Bio-Integrated Electronics at Northwestern University. We acknowledge the use of facilities in the Micro and Nanotechnology Laboratory and the Frederick Seitz Materials Research Laboratory for Advanced Science and Technology at the University of Illinois at Urbana-Champaign, and the Northwestern University's Atomic and Nanoscale Characterization Experimental Center (NUANCE). J. L. Acknowledges the support from the start up funds of The Ohio State University. R.L. acknowledges the support from the National Natural Science Foundation of China (11972103), LiaoNing Revitalization Talents Program (XLYC1807126), and Fundamental Research Funds for the Central Universities of China (DUT18GF101). C.-H. C and J.V. acknowledge support from the National Institutes of Health (U01-NS099697). K.J.Y. acknowledges the support from the National Research Foundation of Korea (NRF-2019R1A2C2086085 and NRF-2018M3A7B4071109).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] B. Litt, R. Esteller, J. Echauz, M. D'Alessandro, R. Shor, T. Henry, P. Pennell, C. Epstein, R. Bakay, M. Dichter, G. Vachtsevanos, *Neuron* **2001**, *30*, 51.
- [2] A. Canales, X. T. 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.
- [3] 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.
- [4] J. Viventi, D. H. Kim, L. Vigeland, E. S. Frechette, J. A. Blanco, Y. S. Kim, A. E. Avrin, V. R. Tiruvadi, S. W. Hwang, A. C. Vanleer, D. F. Wulsin, K. Davis, C. E. Gelber, L. Palmer, J. Van der Spiegel, J. Wu, J. L. Xiao, Y. G. Huang, D. Contreras, J. A. Rogers, B. Litt, *Nat. Neurosci.* **2011**, *14*, 1599.
- [5] H. Fang, K. J. Yu, C. Gloschat, Z. J. Yang, E. M. Song, C. H. Chiang, J. N. Zhao, S. M. Won, S. Y. Xu, M. Trumpis, Y. D. Zhong, S. W. Han, Y. G. Xue, D. Xu, S. W. Choi, G. Cauwenberghs, M. Kay, Y. G. Huang, J. Viventi, I. R. Efimov, J. A. Rogers, *Nat. Biomed. Eng.* **2017**, *1*, 0038.
- [6] H. Fang, J. N. Zhao, K. J. Yu, E. M. Song, A. B. Farimani, C. H. Chiang, X. Jin, Y. G. Xue, D. Xu, W. B. Du, K. J. Seo, Y. D. Zhong, Z. J. Yang, S. M. Won, G. H. Fang, S. W. Choi, S. Chaudhuri, Y. G. Huang, M. A. Alam, J. Viventi, N. R. Aluru, J. A. Rogers, *P. Natl. Acad. Sci. USA* **2016**, *113*, 11682.
- [7] J. Viventi, D. H. Kim, J. D. Moss, Y. S. Kim, J. A. Blanco, N. Annetta, A. Hicks, J. L. Xiao, Y. G. Huang, D. J. Callans, J. A. Rogers, B. Litt, *Sci. Transl. Med.* **2010**, *2*, 24ra22.
- [8] M. A. Escabi, H. L. Read, J. Viventi, D. H. Kim, N. C. Higgins, D. A. Storace, A. S. K. Liu, A. M. Gifford, J. F. Burke, M. Campisi, Y. S. Kim, A. E. Avrin, J. Van der Spiegel, Y. G. Huang, M. Li, J. Wu, J. A. Rogers, B. Litt, Y. E. Cohen, *J. Neurophysiol.* **2014**, *112*, 1566.
- [9] T. Someya, Y. Kato, T. Sekitani, S. Iba, Y. Noguchi, Y. Murase, H. Kawaguchi, T. Sakurai, *P. Natl. Acad. Sci. USA* **2005**, *102*, 12321.

- [10] G. T. Hwang, D. Im, S. E. Lee, J. Lee, M. Koo, S. Y. Park, S. Kim, K. Yang, S. J. Kim, K. Lee, K. J. Lee, *ACS Nano* **2013**, *7*, 4545.
- [11] M. H. Park, J. Y. Kim, T. H. Han, T. S. Kim, H. Kim, T. W. Lee, *Adv. Mater.* **2015**, *27*, 4308.
- [12] N. T. Kalyani, S. J. Dhoble, *Renew. Sust. Energ. Rev.* **2015**, *44*, 319.
- [13] X. Z. Xie, L. Rieth, S. Merugu, P. Tathireddy, F. Solzbacher, *Appl. Phys. Lett.* **2012**, *101*, 09370.
- [14] J. Ahmad, K. Bazaka, L. J. Anderson, R. D. White, M. V. Jacob, *Renew. Sust. Energ. Rev.* **2013**, *27*, 104.
- [15] M. C. Choi, Y. Kim, C. S. Ha, *Prog. Polym. Sci.* **2008**, *33*, 581.
- [16] T. N. Chen, D. S. Wuu, C. C. Wu, C. C. Chiang, Y. P. Chen, R. H. Horng, *Plasma Process Polym.* **2007**, *4*, 180.
- [17] M. D. Groner, S. M. George, R. S. McLean, P. F. Garcia, *Appl. Phys. Lett.* **2006**, *88*, 051907.
- [18] D. Yu, Y. Q. Yang, Z. Chen, Y. Tao, Y. F. Liu, *Opt. Commun.* **2016**, *362*, 43.
- [19] J. Jeong, F. Laiwalla, J. Lee, R. Ritasalo, M. Pudas, L. Larson, V. Leung, A. Nurmikko, *Adv. Funct. Mater.* **2019**, *29*, 1806440.
- [20] P. J. Rousche, R. A. Normann, *J. Neurosci. Meth.* **1998**, *82*, 1.
- [21] R. R. Harrison, P. T. Watkins, R. J. Kier, R. O. Lovejoy, D. J. Black, B. Greger, F. Solzbacher, *IEEE J. Solid-St. Circ.* **2007**, *42*, 123.
- [22] A. C. Hoogerwerf, K. D. Wise, *IEEE T. Bio-Med. Eng.* **1994**, *41*, 1136.
- [23] K. D. Wise, D. J. Anderson, J. F. Hetke, D. R. Kipke, K. Najafi, *P. IEEE* **2004**, *92*, 76.
- [24] R. S. Sanders, M. T. Lee, *P. IEEE* **1996**, *84*, 480.
- [25] 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.
- [26] L. Bowman, J. D. Meindl, *IEEE T. Bio-Med. Eng.* **1986**, *33*, 248.
- [27] J. H. Li, E. M. Song, C. H. Chiang, K. J. Yu, J. Koo, H. N. Du, Y. S. Zhong, M. Hill, C. Wang, J. Z. Zhang, Y. S. Chen, L. M. Tian, Y. D. Zhong, G. H. Fang, J. Viventi, J. A. Rogers, *P. Natl. Acad. Sci. USA* **2018**, *115*, E9542.
- [28] Y. K. Lee, K. J. Yu, E. M. Song, A. B. Farimani, F. Vitale, Z. Q. Xie, Y. Yoon, Y. Kim, A. Richardson, H. W. Luan, Y. X. Wu, X. Xie, T. H. Lucas, K. Crawford, Y. F. Mei, X. Feng, Y. G. Huang, B. Litt, N. R. Aluru, L. Yin, J. A. Rogers, *ACS Nano* **2017**, *11*, 12562.

- [29] Y. K. Lee, K. J. Yu, Y. Kim, Y. Yoon, Z. Q. Xie, E. M. Song, H. W. Luan, X. Feng, Y. G. Huang, J. A. Rogers, *ACS Appl. Mater. Inter.* **2017**, *9*, 42633.
- [30] J. H. Li, R. Li, H. N. Du, Y. S. Zhong, Y. S. Chen, K. W. Nan, S. M. Won, J. Z. Zhang, Y. G. Huang, J. A. Rogers, *ACS Nano* **2019**, *13*, 660.
- [31] X. Feng, S. R. Dong, H. Wong, D. Q. Yu, K. L. Pey, K. Shubhakar, W. S. Lau, *Microelectron. Reliab.* **2016**, *61*, 78.
- [32] Y. W. Lu, J. Shieh, F. Y. Tsai, *Acta Mater.* **2016**, *115*, 68.
- [33] F. J. Ramos, T. Maindron, S. Bechu, A. Rebai, M. Fregnaux, M. Bouttemy, J. Rousset, P. Schulz, N. Schneider, *Sustain. Energ. Fuels* **2018**, *2*, 2468.
- [34] J. Rhie, D. Lee, Y. M. Bahk, J. Jeong, G. Choi, Y. Lee, S. Kim, S. Hong, D. S. Kim, *J Micro-Nanolith. Mem.* **2018**, *17*, 023504.
- [35] R. Yang, H. T. Li, K. K. H. Smithe, T. R. Kim, K. Okabe, E. Pop, J. A. Fan, H. S. P. Wong, *Nat. Electron.* **2019**, *2*, 108.
- [36] L. Wu, H. X. Liu, J. B. Li, S. L. Wang, X. Wang, *Nanoscale Res. Lett.* **2019**, *14*, 177.
- [37] A. S. Sokolov, Y. R. Jeon, S. Kim, B. Ku, D. Lim, H. Han, M. G. Chae, J. Lee, B. G. Ha, C. Choi, *Appl. Surf. Sci.* **2018**, *434*, 822.
- [38] Y. L. Chueh, C. N. Boswell, C. W. Yuan, S. J. Shin, K. Takei, J. C. Ho, H. Ko, Z. Y. Fan, E. E. Haller, D. C. Chrzan, A. Javey, *Nano Lett.* **2010**, *10*, 393.
- [39] M. M. Xiao, C. G. Qiu, Z. Y. Zhang, L. M. Peng, *ACS Appl. Mater. Inter.* **2017**, *9*, 34050.
- [40] M. Thammasack, G. De Micheli, P. E. Gaillardon, *J. Electroceram.* **2017**, *39*, 137.
- [41] D. E. King, *J Vac. Sci. Technol. A* **1995**, *13*, 1247.
- [42] P. Ganesh, P. R. C. Kent, G. M. Veith, *J. Phys. Chem. Lett.* **2011**, *2*, 2918.
- [43] Z. Wu, Z. Jiang, Y. Jin, F. Xiong, W. Huang, *J. Phys. Chem. C* **2014**, *118*, 26258.
- [44] F. Xu, I. Fampiou, C. R. O'Connor, S. Karakalos, F. Hiebel, E. Kaxiras, R. J. Madix, C. M. Friend, *Phys. Chem. Chem. Phys.* **2018**, *20*, 2196.
- [45] M. S. Ide, R. J. Davis, *Acc. Chem. Res.* **2014**, *47*, 825.
- [46] J. Yota, *ECS Trans.* **2013**, *53*, 281.
- [47] E. K. Seo, J. W. Lee, H. M. Sung-Suh, M. M. Sung, *Chem. Mater.* **2004**, *16*, 1878.
- [48] H. Moshe, G. Levi, D. Sharon, Y. Mastai, *Surf. Sci.* **2014**, *629*, 88.
- [49] L. Newton, T. Slater, N. Clark, A. Vijayaraghavan, *J. Mater. Chem. C* **2013**, *1*, 376.

- [50] R. Li, H. T. Cheng, Y. W. Su, S. W. Hwang, L. Yin, H. Tao, M. A. Brenckle, D. H. Kim, F. G. Omenetto, J. A. Rogers, Y. G. Huang, *Adv. Funct. Mater.* **2013**, *23*, 3106.
- [51] P. V. Danckwerts, *T. Faraday Soc.* **1950**, *46*, 300.

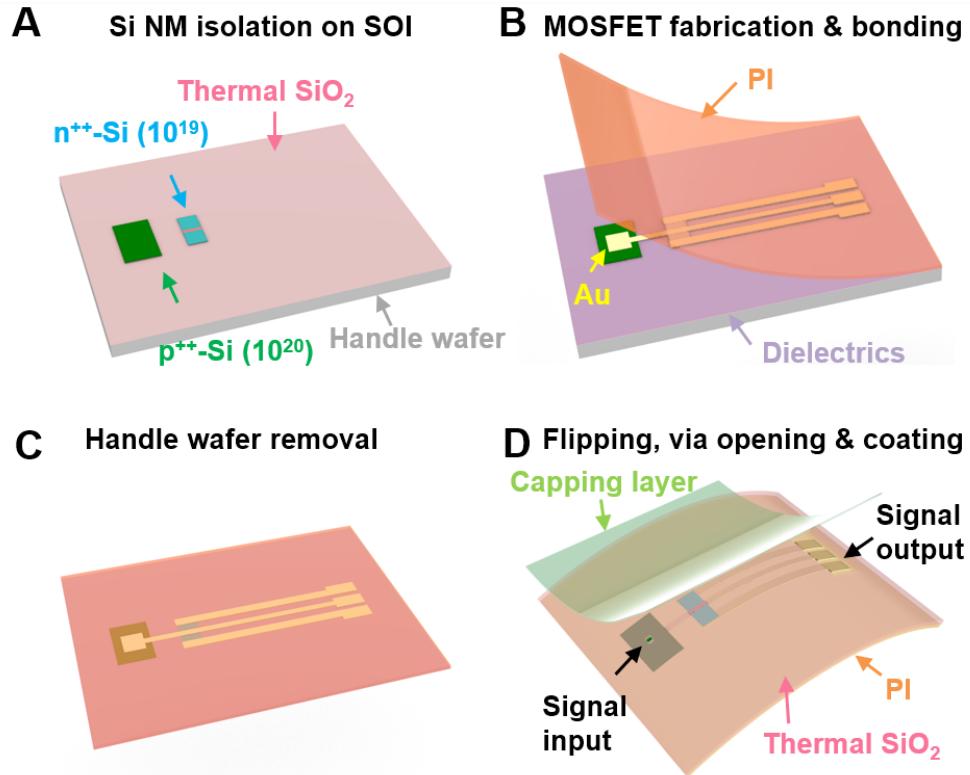


Figure 1. Schematic illustrations of integration strategies for use of a monolithic assembly of p⁺⁺-Si NM, t-SiO₂ and capping layers as sensing interfaces and biofluid barriers in flexible and long-lived bio-integrated electronic systems. (A) Doping and patterning of the device layer of a SOI substrate formed isolated p⁺⁺-Si and n⁺⁺-Si NMs on the buried oxide layer, t-SiO₂. (B) Fabricating MOSFETs with gate electrodes electrically connected to p⁺⁺-Si NMs and encapsulating the device with PI on the top. (C) Removing the Si handle wafer by dry etching to expose the bottom surface of the t-SiO₂. (D) Flipping the device, opening small windows through the t-SiO₂ to locally expose the p⁺⁺-Si NMs as the electrical interconnects and then depositing capping layers to limit the penetration of biofluids and to form the bio-interface.

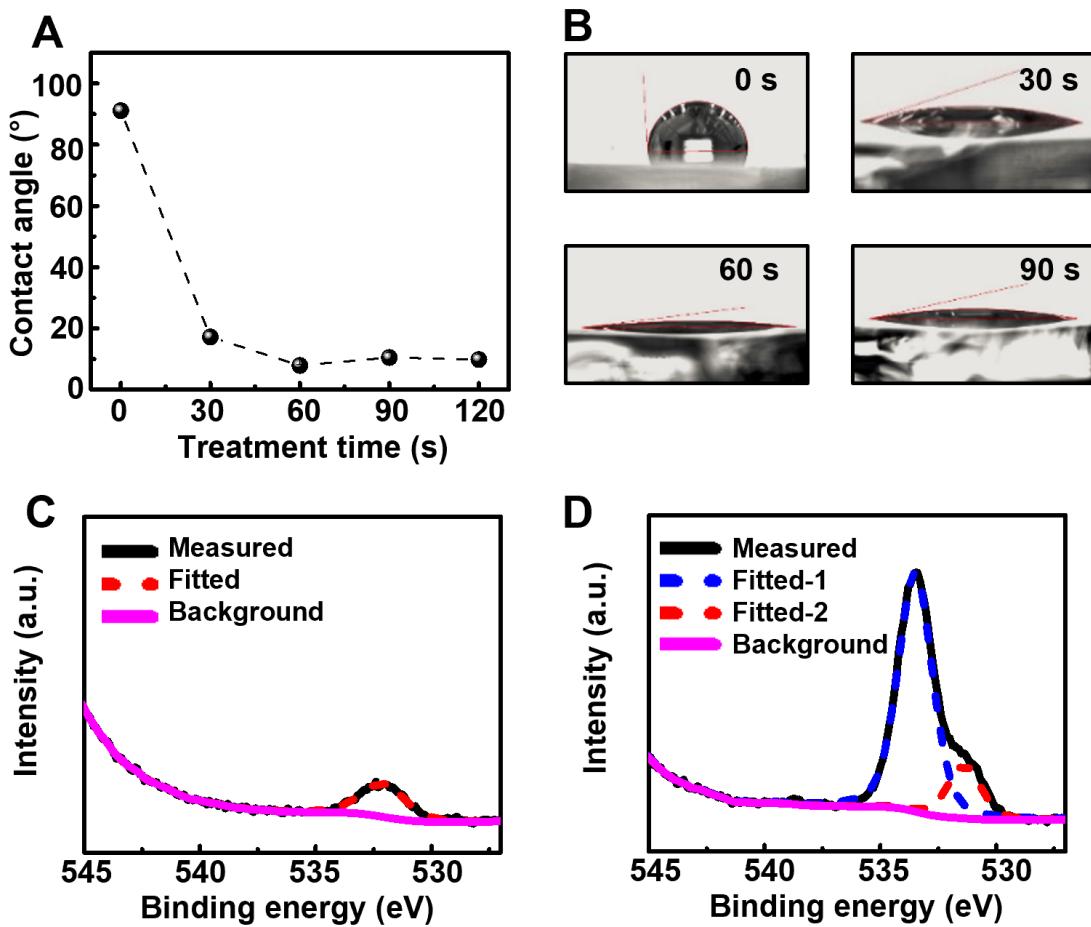


Figure 2. Surface characterization of Au before/after treatment with O₂ plasma. (A) Water contact angle of the Au surface as a function of the O₂ plasma treatment time (0-120 s, pressure: 200 mTorr, power: 150 W). The Au film was exposed to air for 3 days after evaporation. The measurements occur immediately after treatment with O₂ plasma. (B) Contact angle images of water droplets on Au surfaces with different treatment times. (C-D) XPS spectra of Au surfaces before (C) and after (D) treatment with O₂ plasma (power = 150 W, pressure = 200 mtorr, treatment time = 5 min). The dash lines represent fitted peaks of chemically bonded O and/or adsorbed O.

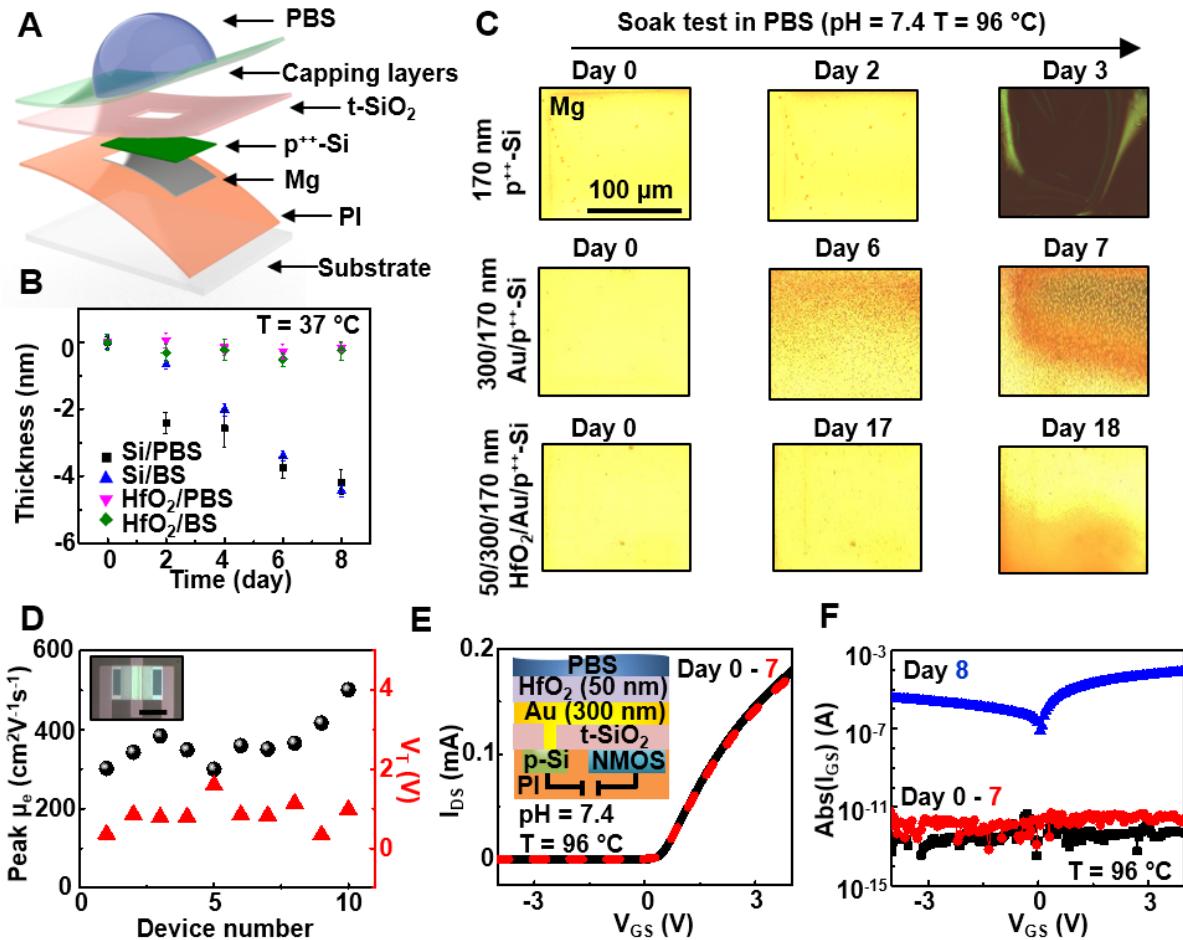


Figure 3. Effect of the types of capping layers on the lifetimes of passive and active devices. (A) Exploded view schematic illustration of a Mg-based passive device used in soak tests. (B) Measured changes in thickness as a function of time for layers of p⁺⁺-Si and HfO₂ immersed in PBS and bovine serum at 37 °C. (C) Sequences of optical micrographs of Mg-based passive devices encapsulated by p⁺⁺-Si (170 nm)//t-SiO₂ (1 μm) without and with different capping layers (300 nm Au and 50 nm HfO₂) during immersion tests in PBS (pH = 7.4) at 96°C. (D) Statistics of threshold voltage and mobility of ten transistors produced in the manner described in Figure 1. Inset: optical image of a transistor with channel length and width of 16 and 400 μm, respectively (scale bar: 200 μm). (E) Transfer characteristics of a transistor with p⁺⁺-Si (60 nm)//SiO₂ (1 μm), Au (300 nm) and HfO₂ (50 nm) during a soak test at 96 °C in PBS (pH = 7.4). The device shows stable operation for 7 days. Inset: cross-sectional view of the NMOS transistor used for the soak test, highlighting key functional layers. (F) Leakage characteristics of the test transistor in frame (E) during immersion in PBS (pH = 7.4) at 96 °C. The results indicate catastrophic failure of the transistor at day 8.

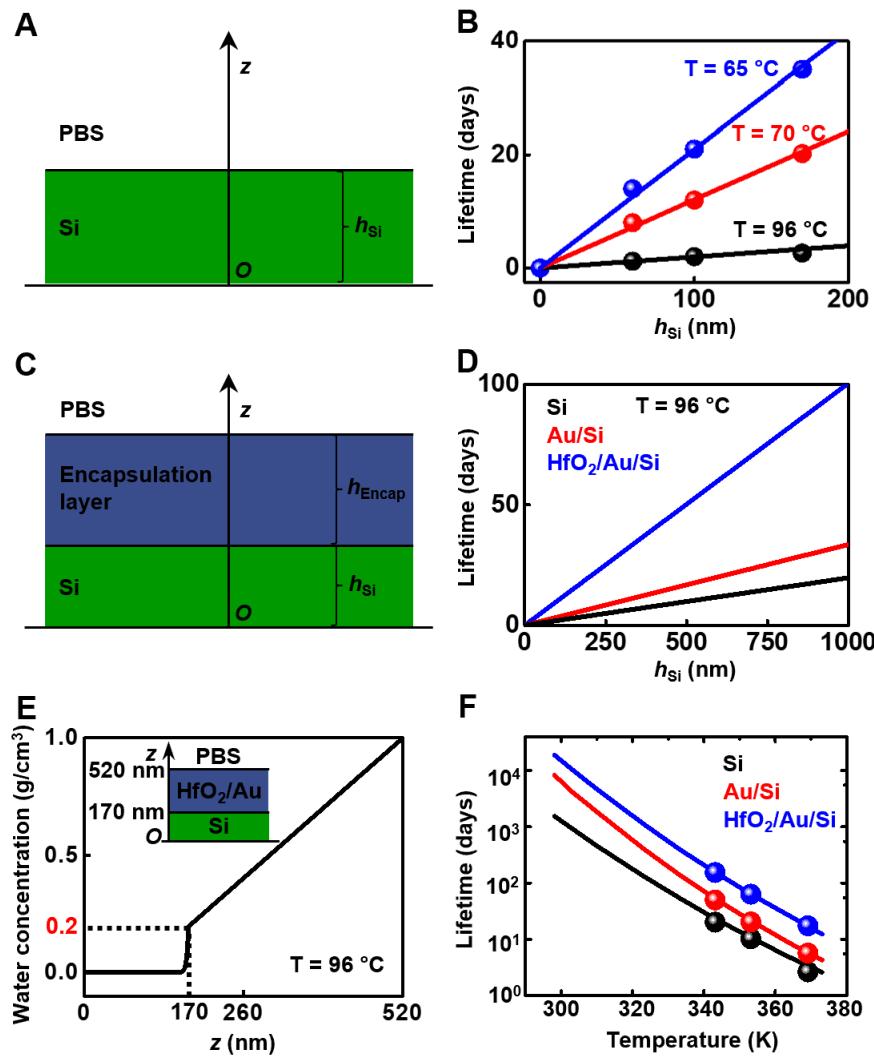


Figure 4. Theoretical modeling of reactive diffusion of $\text{p}^{++}\text{-Si}$ with Au or Au/HfO₂ capping layers. (A) Schematic illustration of the single layer model. (B) Theoretical (lines) and measured (dots) lifetimes of $\text{p}^{++}\text{-Si}$ as a function of initial thickness immersed in water at 65, 70, and 96 °C. (C) Schematic illustration of the bilayer model. (D) lifetimes of $\text{p}^{++}\text{-Si}$ without and with capping layer(s) as a function of initial $\text{p}^{++}\text{-Si}$ thickness immersed in water at 96 °C (HfO₂: 50 nm, Au: 300 nm). (E) Distribution of saturated water concentration in a 50/300/170-nm-thick HfO₂/Au/ $\text{p}^{++}\text{-Si}$ structure immersed in water at 96 °C. (F) Theoretical (lines) and measured (dots) temperature-dependent lifetimes of the $\text{p}^{++}\text{-Si}$, Au/ $\text{p}^{++}\text{-Si}$, and HfO₂/Au/ $\text{p}^{++}\text{-Si}$ structures immersed in water at 96 °C, with the thicknesses of HfO₂, Au, and $\text{p}^{++}\text{-Si}$ equal to 50, 300, and 170 nm.

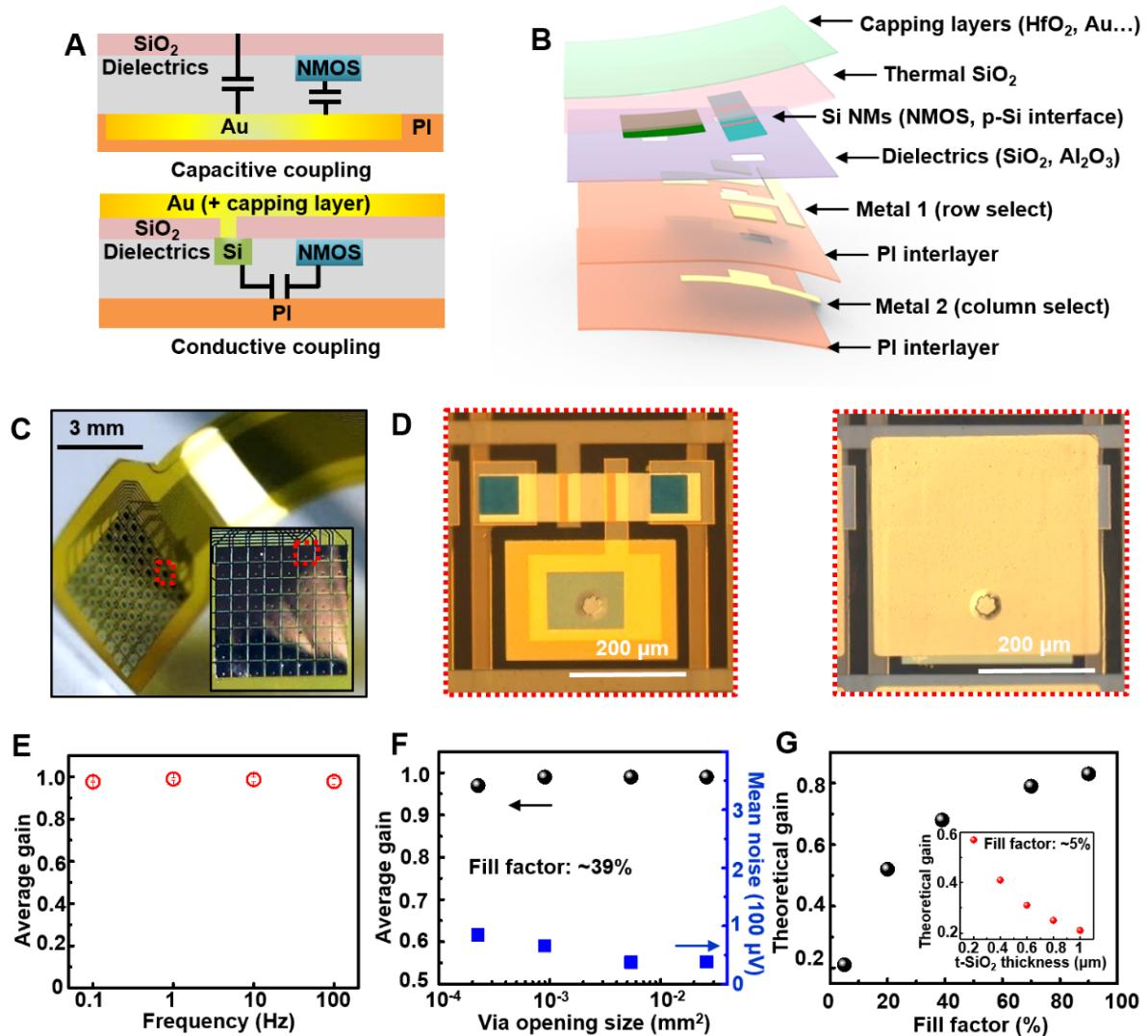


Figure 5. Comparisons between actively multiplexed Si electronics with capacitively and conductively coupled interface designs. (A) Side-view schematic illustrations of electronics with $t\text{-SiO}_2$ (top) and capping layers/ $p^{++}\text{-Si}/t\text{-SiO}_2$ (bottom) as the interface between the devices and the surrounding biology. (B) Exploded view schematic illustration of the layer configuration for a system with capping layer(s)/ $p^{++}\text{-Si}/t\text{-SiO}_2$. The labels highlight key functional layers. (C) Photograph of a flexible sensing system with 128 transistors and an $p^{++}\text{-Si}/\text{SiO}_2$ interface in a slightly bent configuration. Inset: the device with capping layer (Au) on the top to define the sensing area and enhance the lifetime. (D) Optical images of a sensing node before (left) and after (right) the deposition of metal on $p^{++}\text{-Si}/\text{SiO}_2$. (E) Average gain of a representative device with 64 conductively coupled unit cells as a function of the input frequency (from 0.1 to 100 Hz). (F) Average gain and mean noise as a function of via opening size for active electronics with $t\text{-SiO}_2$ thickness of $\sim 5 \mu\text{m}$. (G) Theoretical gain as a function of fill factor (%). The theoretical gain increases with fill factor, reaching a plateau around 80-100%. An inset shows the fill factor for a $t\text{-SiO}_2$ thickness of $\sim 5 \mu\text{m}$ as a function of $t\text{-SiO}_2$ thickness (μm).

conductively coupled designs (p^{++} -Si region: $270 \times 190 \mu\text{m}^2$, fill factor of p^{++} -Si: $\sim 39\%$, via opening size (from left to right): 15×15 , 30×30 , 60×90 and $200 \times 130 \mu\text{m}^2$). (G) Theoretical gain values as a function of p^{++} -Si fill factor ($1 \mu\text{m}$ t-SiO₂) and the thickness of t-SiO₂ (inset, p^{++} -Si fill factor: 5%) for capacitive coupling through t-SiO₂ interface.

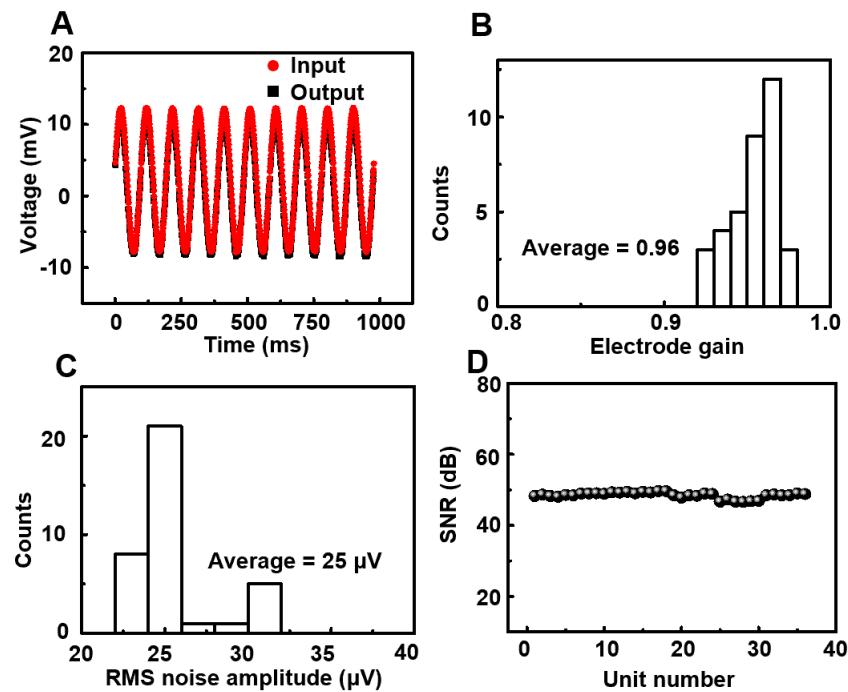


Figure 6. In vitro characterization of the electrical performance of a conductively coupled sensing system with Au (300 nm) and HfO₂ (50 nm) capping layers. (A) Output characteristics of a sensing node with an AC input sine wave signal (20 mV, 10 Hz). (B-D) Histograms of gain and noise, and statistics of signal-to-noise ratio associated with 36 sensing units in a typical device of this type.