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Long-term Encapsulation of Platinum Metallization Using a HfO_2 ALD - PDMS Bilayer for Non-hermetic Active Implants

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***Abstract*—In this work, we investigate the insulating performance of an atomic layer deposited (ALD) HfO_2 - polymer bilayer for platinum (Pt) metallization. As test vehicles, Pt interdigitated comb structures (IDC) were designed and fabricated on SiO_2/Si substrates. The IDCs were first coated with a 100 nm thin HfO_2 ALD layer. A group of samples was further encapsulated with a low-viscosity biocompatible polydimethylsiloxane (PDMS) which resulted in an HFO_2-PDMS bilayer. All samples were soaked in phosphate buffered saline for 450 days at room temperature. Evaluation of the coatings included monthly optical inspection and electrochemical impedance spectrometry. For ALD-only coated IDC structures, impedance results right after submersion in saline indicated the presence of defects in the layer. Long-term impedance recordings showed a slight drop, indicating water ingress through the defects, further exposing the metal to saline. For the HfO_2-PDMS encapsulated samples, on the other hand, stable impedance results were recorded over the duration of the soak study. This suggests the excellent properties of low-viscosity PDMS both in filling the defects of the ALD layer and in maintaining a long-term underwater adhesion to HfO_2. The results from this investigation, therefore, propose a new encapsulation method based on HfO_2-PDMS bilayer for long-term packaging of active implants incorporating Pt metallization.**

***Keywords*—non-hermetic implants, ALD, PDMS, platinum, bioelectronic medicine, lifetime reliability, packaging, leakage**

I. Introduction

For years, active implantable medical devices have relied on hermetic cans for protecting the implantable electronics against the body and vice versa. For hermeticity, metal, ceramic or glass is typically used as the can material and lifetime hermeticity prediction is implemented based on the helium leak test method according to the Mil-Std-883 standard [1]. Recently, with the advances offered by microfabrication, new devices can be fabricated with significantly reduced dimensions and weight, while incorporating more functionality [2], [3]. Such devices have opened up new avenues of research in neuroprosthetics and bioelectronic medicine [2], [4]. For maintaining the low weight and footprint, however, new packing solutions are needed since the conventional hermetic housing can no longer satisfy the necessary physical requirements [4].

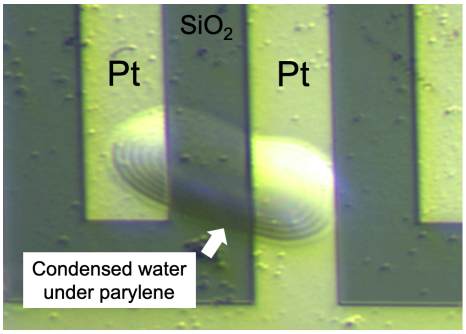


Figure 1: Water condensation under parylene coating causing shunt leakage paths between Pt metal tracks.

Non-hermetic packaging using organic polymers such as epoxies has long been used in the microelectronics industry. Polymers are known to be permeable to moisture [5]. It has been shown, however, that the lifetime reliability of polymer encapsulated devices relies on the good adhesion of the polymer to the underneath materials and failure of adhesion will lead to water condensation and eventual failure [6], [7]. This, therefore, can create challenges for packaging more complex circuits and systems. In such cases, it is important that the encapsulant maintains good adhesion to all of the underlying materials, as any adhesion failure could be a starting point for total device failure. As an example, Fig. 1 depicts parylene coated platinum (Pt) tracks after 120 days of soaking in saline [7]. As it can be seen, the weak adhesion of parylene to Pt has resulted in water condensation, first starting on the metal and later spreading to adjacent regions resulting in a shunt leakage path. Moreover, water build up under the parylene can create additional stress in the layer, leading to cracks and exposure of the metal.

Adopted from the semiconductor industry, various inorganic thin-film coatings have been reported recently with high barrier properties against oxygen and water [8]. These thin coatings can be deposited in various ways with their insulation properties being greatly dependent on the deposition parameters. Among these deposition techniques, atomic layer deposition (ALD) can create an ultra-thin conformal coating with almost no defects or pinholes. More importantly, the deposition temperature for ALD can be kept below 200 °C, making it suitable for devices incorporating sensitive metallization or polymers. The lifetime reliability of such coatings, however, does not rely only on the conformality and adhesion of the layer, but also on the stability of the layer in ionic media. For example, Al_2O_3 has been reported to have one of the highest barrier properties of all inorganic ALD layers, yet its low underwater stability can result in dissolution [8], [9]. Given the ultra-low thicknesses of these coatings, any degradation or dissolution can significantly affect their insulating properties.

Stacking organic and inorganic ALD layers can bring together the advantages of both, with the inorganic layer acting as an intermittent adhesion layer with high barrier properties, and the top organic polymer protecting the ALD layer from any chemical or mechanical degradation. In [9], an ALD-parylene bilayer was shown to have longer lifetime reliability compared to a standalone parylene layer. Also, in [10], ALD stacks were used in between polyimide layers resulting in an increased packaging life-time.

Polydimethylsiloxane (PDMS) is known to be one of the most biocompatible polymers causing minimal tissue reaction while having a long reported biostability [1], [5]. Nevertheless, its high permeability to moisture has reduced its favorability when used as an encapsulant for protecting noble metals such as Pt. Previous investigations, however, have shown that PDMS can maintain excellent long-term adhesion to inorganic ceramic substrates, resulting in devices which have lasted for years within the body [5], [11].

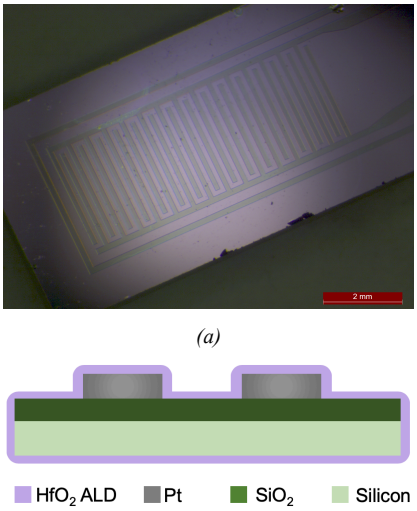
For this reason, in this work, for the first time we use HfO_2 ALD as an intermittent adhesion layer between Pt and PDMS and investigate the long-term insulation performance of the bilayer using a 450-day soak study. Section II briefly presents the sample design and encapsulation process. The experimental set-up is also given in this section. Section III presents the study results together with a discussion and future work. Finally, conclusions are drawn in section IV.

II. Materials and Methods

A. Sample Preperation

1) IDC using Pt Metallization

Interdigitated capacitors (IDC) are useful test vehicles for evaluating encapsulation performance and coatings [11]. In this work, IDCs were fabricated by sputtering 600 nm of Pt on top of a 1 µm thick plasma enhanced chemical vapor deposition (PECVD) SiO_2 layer with a 10 nm titanium adhesion layer in between. More details on the fabrication of the IDC can be found in [7].



(a)

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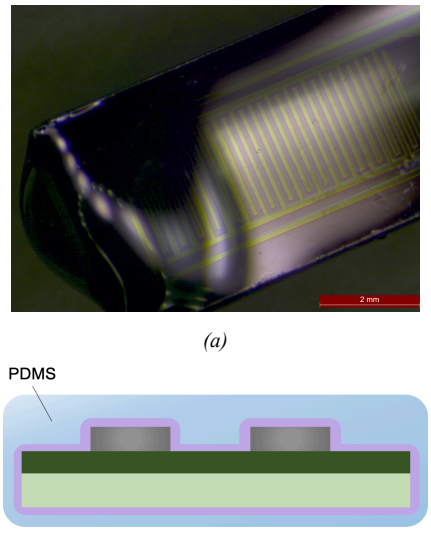
Figure 2: HfO_2 ALD coating on IDC, (a) optical image and (b) schematic cross-section illustration of materials stack.



(a)

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Figure 3: HfO_2 - PDMS coated IDC, (a) optical image and (b) schematic cross-section illustration of materials stacks.

2) ALD Coating

ALD coating was done in collaboration with Picosun Oy using the Picosun® R-200 Advanced ALD reactor and under reduced pressure (N_2 atmosphere) of about 1 mbar. The PicoHot source system (PH-300) and PicoSolution (both Picosun Oy, Finland) precursors were vaporized from stainless-steel precursor bottles at increased and room temperature, respectively. Thermal ALD-processes at 200 °C were applied with a layer-by-layer deposition method where the two different precursor materials (separated by N_2 purge) were used to build up the HfO_2 coating. For the ALD deposition, four samples were placed on a mesh plate which allows a 3D coating on each sample. To further ensure conformal ALD coating, the process was tested at wafer level and optimized before deposition on actual samples.

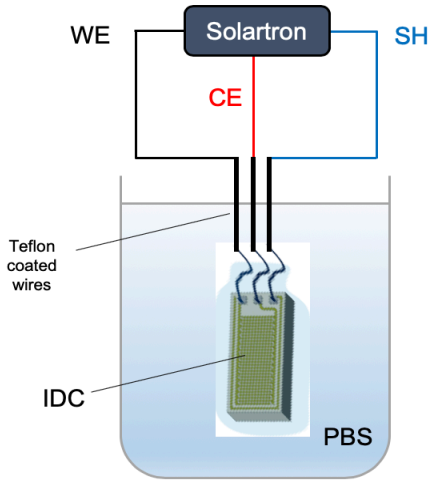


Figure 4: Experimental set-up with IDCs submerged in PBS.

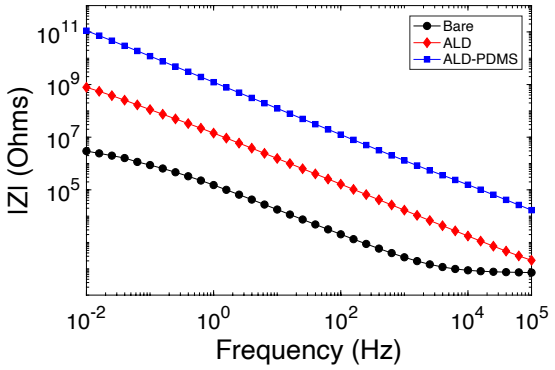
3) *PDMS encapsulation*

Two samples out of four were further encapsulated with a biocompatible PDMS layer (MED2-6215, NuSil Carpinteria, USA). A dip coating process was used for the encapsulation. The low viscosity would allow the PDMS to easily flow over the sample. Fig. 2 and 3 give a microscopic image of the samples with a schematic illustration of the layers. The thickness of the PDMS could not be easily determined for these samples but based on our prior experience we assume it to be within 50 - 100 µm.

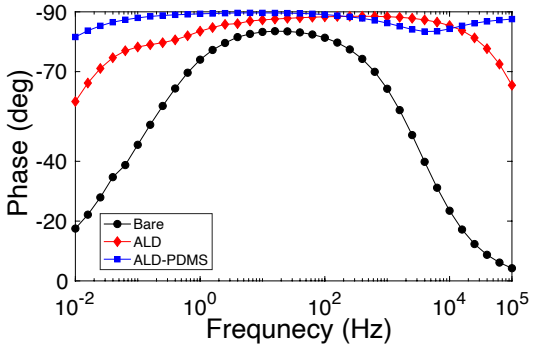
B. *Experimental Set-up*

For electrical connection, the IDCs were soldered to Teflon coated stainless steel wires. Extra PDMS was applied on the solder area for proper insulation. Long-term soaking was done by using 50 ml vials filled with 1X phosphate buffered saline (PBS). Soaking was conducted in room temperature (23 °C) with proper sealing to avoid any evaporation and deterioration of the PBS. More details on the set-up specifications and preparation can be found in [12]. In this work, electrochemical impedance spectrometry (EIS) was carried out to evaluate the insulating performance of the ALD and ALD-PDMS bilayer over time. Measurements were carried out using a Solartron Analytical Modulab XM® system. All measurements were done in a two-cell electrode configuration between the combs of the IDC structure. A shield (SH) metal line surrounds the IDC structure to protect and shield the measurements from any extraneous interferences. A femtoammeter module was also added to the system to be able to measure pA current levels.

The open circuit potential (OCP) between the working electrode (WE) and counter electrode (CE) was set to 0 V given that both the WE and CE are made from similar metal (Pt). Fig. 4 illustrates the set-up used for EIS measurement with the two combs of the IDC connected to the WE and CE terminals of the measurement device. All measurements were done in a dedicated Faraday cage with proper shielding.



(a)



(b)

Figure 5: EIS Bode plot results at T=0 as (a) impedance magnitude and (b) phase angle for three samples, namely a bare, a HfO_2-coated and a HfO_2-PDMS-coated IDC.

III. Results, Discussion & Future Work

A. *Measurement Results*

As an informative measurement technique, impedance spectrometry was used to evaluate and track the changes in the insulation properties of the investigated layers. After sample preparation and submersion in saline, first measurements were done at T=0. Fig. 5 shows the EIS results for three samples: a bare IDC with exposed Pt metal, an IDC coated with HfO_2 ALD and an IDC coated with an ALD-PDMS bilayer. Bode plots are presented as impedance magnitude (Fig. 5a) and phase angle (Fig. 5b) results. For the bare IDC, in the middle frequency band (1 Hz – 1 kHz) a constant phase element (CPE) behavior is seen with the phase being around -80° while in the lower frequencies the polarization resistance is dominant (R_F) resulting in a phase around -20°. The impedance at higher frequencies is dominated by the spreading resistance (R_{saline}), representing the resistance seen from one comb of the IDC to the other through saline. Comparing to the bare IDC, the ALD coated sample shows higher impedance values with a more capacitive behavior seen across the spectrum. This capacitance is represented by the Pt metal on one side and the electrolyte on the other with the ALD layer as the dielectric in between. A fully conformal coating on the metal would show a purely capacitive spectrum in the EIS results, yet any defects in the film would result in a deviation from that. The ALD-PDMS bilayer, on the other hand, shows an

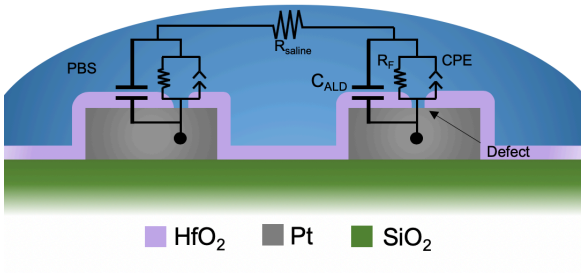


Figure 6: Equivalent circuit model for ALD coated samples with defects when submerged in saline.

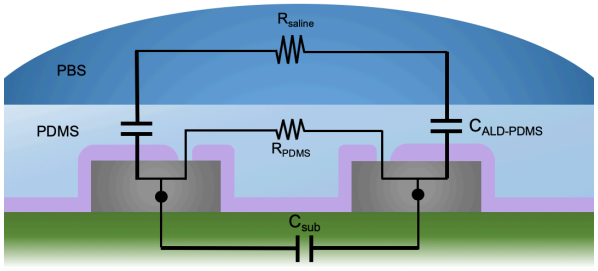


Figure 7: Equivalent circuit model for ALD-PDMS coated samples submerged in saline.

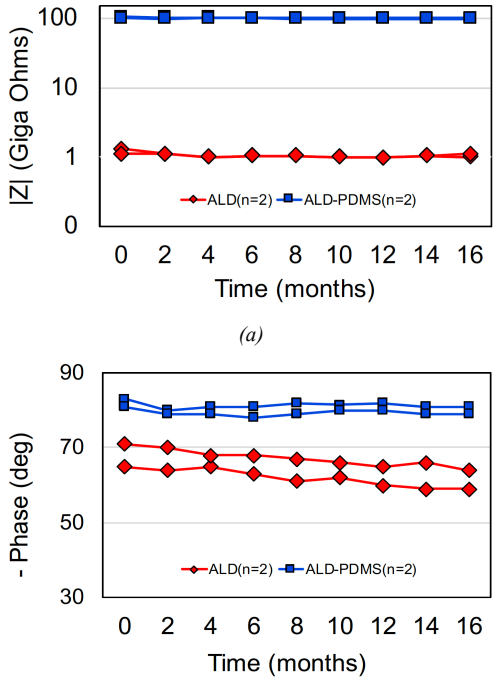


Figure 8: EIS results @ 0.01Hz over time presented as (a). impedance magnitude and (b). phase angle for ALD (n=2) and ALD-PDMS (n=2) samples.

almost pure capacitive behavior across the entire spectrum with phase angle result close to -90°. To interpret the EIS data, Fig. 6 and Fig. 7 give a lumped element circuit model for the ALD and ALD-PDMS samples, respectively. In Fig. 6, the capacitance of the ALD interface is presented by C_{ALD}. A defect in the layer would expose the metal to saline, creating a parallel path to the C_{ALD}. This would result in a deviation from a pure capacitive behavior and is more significantly captured in the lower frequency (< 100 mHz) phase angle results. Any further delamination or cracking of the ALD would expose more metal, consequently lowering the impedance and absolute value of the phase. In Fig. 5, a comparison between the ALD and ALD-PDMS bilayer shows a two orders of magnitude higher impedance value for the bilayer and a more capacitive behavior seen across its entire spectrum. This is due the fact that the bilayer capacitance is a series combination of the ALD plus the 50-100 µm PDMS stack, resulting in a lower interface capacitance ($C_{ALD-PDMS}$). As a result of the lower bilayer capacitance, the overall measured value will be the parallel combination of the bilayer and the substrate capacitance ($C_{ALD-PDMS} \parallel C_{sub}$). Furthermore, the exposed metals through the ALD defects are encapsulated with a PDMS layer, having a sheet resistance of approximately 10^{15} Ω.cm [5]. Due to the highly resistive PDMS path (R_{PDMS}), the parallel capacitive part of the system would dominate, resulting in a phase angle close to -90°. Any delamination of the PDMS from ALD would, however, allow water condensation in between the ALD and PDMS interface, causing an impedance drop with a phase angle moving more towards resistive behaviors.

To track changes in the encapsulation performance, monthly EIS measurements were done on all four samples. As an indicator for change over time, impedance and phase angle values at 0.01 Hz were selected for all four samples. Fig. 8 gives the results over the 450 days of the soak study. For the ALD only samples, a drop in the phase angle was measured after the first months of soaking, suggesting that possibly water made more contact with the metals through the defects in the layer. Over the duration of the study, however, stable results were observed. This indicates two outcomes: first, the high stability of the HfO_2 in ionic media and second, the long-term adhesion of HfO_2 to Pt. Any dissolution of HfO_2, for example, would result in a higher C_{ALD}, creating a drop in impedance magnitude and any delamination of the ALD from Pt would result in a more resistive behavior which could have been captured in the phase angle results. Optical inspections of the ALD-coated samples further supported the EIS data since no signs of layer discoloration or degradation were found. For the ALD-PDMS samples, stable results were recorded over the period of the study, indicating excellent underwater adhesion between the two layers.

B. Discussion

In the field of neuroprosthetics, Pt has widely been used as the interface electrode between tissue and electronics mainly due to its high biocompatibility and biostability [2]. For microfabricated implants, Pt can also serve as the main metallization for connecting components, which would therefore, further simplify the fabrication process. One main challenge, however, is the weak adhesion of various known encapsulants such as PDMS, parylene and epoxy to Pt. Adding

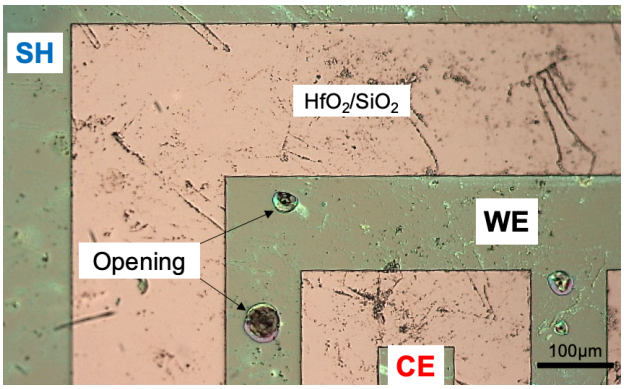
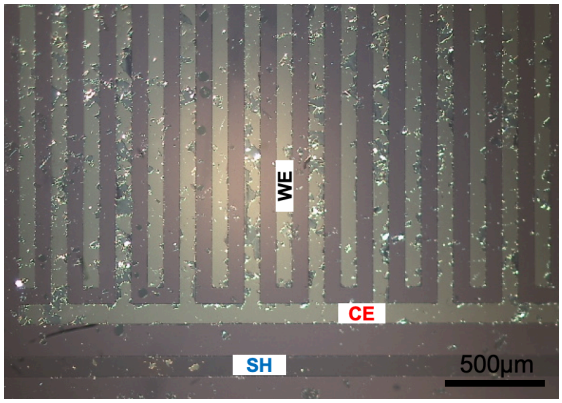


Figure 9: Optical inspection of an ALD-coated sample where WE and CE are applied to 5V DC stress for one hour. Enlargement of the defects are seen as openings.

an inorganic layer in between could mitigate this problem, only if the inorganic film could maintain long-term underwater adhesion to both the metal and top organic polymer. In this work, we used a HfO_2 ALD layer as an intermediate adhesion layer between Pt and PDMS. Our results on ALD coated IDCs indicated that HfO_2 ALD could maintain a stable adhesion to Pt over the duration of the 450 day soak study. Nevertheless, the impedance data suggested the presence of defects in the film, albeit not being detectable with optical microscopy. We believe these defects could either be due to particle impurities or contamination on the IDC surface prior to coating, or due to mechanical damages induced during sample preparation and handling. Nevertheless, to confirm the presence of defects, one ALD-coated IDC was applied to a 5 V DC voltage for 24 hours. Techniques such as DC leakage measurement and linear sweep voltammetry have been reported as methods for evaluating ALD layers, however, their use could result in further degradation and opening of the defects [9], [13]. In this work, our purpose was merely to be able to confirm the presence of defects in the layer. Fig. 9 shows a microscopic image of the sample after one hour of exposure to DC voltage where openings are seen on the voltage stressed metals (WE and CE) while the floating shield metal (SH) remains intact. We suspect these openings were initially small defects in the ALD layer which could not be detected using our optical microscope. After exposure to the DC voltage, electrolysis and gas evolution further opened and enlarged the defective area, making them more visible. Fig. 10a shows the same sample after 24 hours of continuous exposure to the 5V signal. It can be seen that the ALD on the metal tracks applied to the DC voltage has been completely removed, fully exposing the metal to saline. The SH metal, on the other hand, still remains coated. Fig. 10b gives a more magnified image of the exposed Pt with some remaining HfO_2 residues on the WE and CE metals. It is worth mentioning that despite the severe electrolysis and generated mechanical pressure during bubbling, the HfO_2 still maintained adhesion to the SiO_2 substrate (between metals).

As previously explained, adding a polymer on top of ALD layers has been reported to improve the overall insulating properties of the coating. Nevertheless, in [14] it was reported that water permeation through parylene defects resulted in the dissolution of Al_2O_3 ALD and compromised the insulating



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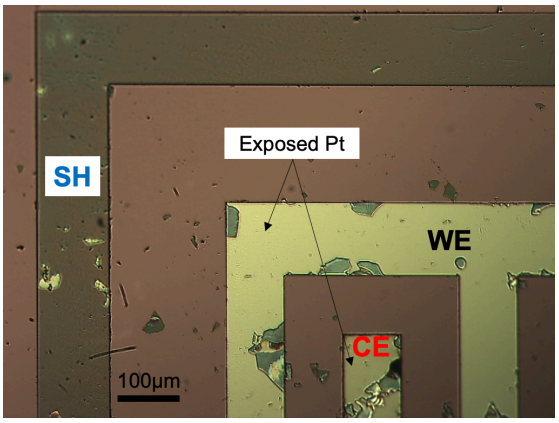

(b)

Figure 10: Cracking and delamination of ALD coating localized to Pt tracks connected to DC voltage (WE and CE) after 24 hours (a) overview of the IDC structure and (b) magnified section showing the cracked and delaminated ALD layer from Pt.

properties of the bilayer. We would like to add to this the possibility of underwater adhesion failure between parylene and ALD which would result in water condensation on the Al_2O_3 and dissolution of the layer.

In terms of insulating properties, the bilayer proposed in this work has the following main advantages: firstly, the HfO_2 ALD has shown significantly higher stability in ionic media, thereby, providing longer protection in case of any delamination or water permeation through the polymer. Secondly, we hypothesize that the low viscosity PDMS could flow in-between defects and crevices while creating a better and long-lasting adhesion with the ALD layer. Finally, for chronic in vivo applications, PDMS is the most suitable polymer with the highest compatibility with tissue.

C. *Future work*

Future work will be needed to evaluate the ALD-PDMS layer in accelerated soak studies with larger samples sizes. Furthermore, in previous investigations we have demonstrated that different failure mechanisms for polymer encapsulated structures can be triggered based on the different applied

voltages [7]. Therefore, to investigate all scenarios of failure, various stress signals will also be applied during the accelerated soak studies.

In addition, to fully characterize the use of the proposed bilayer for packaging active implants, its encapsulation performance on implantable CMOS chips would also have to be investigated. To this end, we have previously reported a CMOS sensor array for monitoring moisture/ion ingress [15], which we intend to utilize to gain further insight on the encapsulation properties of the proposed bilayer.

IV. Conclusion

In conclusion, in this work we investigated for the first time the long-term encapsulation performance of an HfO_2 ALD–PDMS bilayer for insulating Pt metal tracks. Soak investigations showed stable impedance results over the 450-days of the study, indicating good adhesion of the PDMS to the HfO_2 ALD. Results also showed the high stability of the HfO_2 ALD in ionic media with reasonable adhesion to Pt. The proposed bilayer, therefore, could be used as a long-term encapsulation method for non-hermetic implants.

Acknowledgment

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