

Corrosion Resistant ALD Coatings



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1 Introduction

Microelectromechanical systems (MEMS) have been widely utilized for research and clinical biomedical applications in recent years. However, passivation and packaging are crucial when metal or silicon surfaces are exposed to ionic media in order to provide biocompatibility and prevent chemical or electrochemical corrosion [1, 2].

Typical passivation coatings are deposited using either low pressure chemical vapor deposition (LPCVD) or sputtering. Organic LPCVD coatings can typically be deposited near room temperature (e.g. parylene), while inorganic coatings can be deposited near room temperature via sputtering (e.g. TiO_2) or at temperatures from 300-700°C via LPCVD (e.g. SiO_2 , Si_3N_4).

Although parylene is more mechanically compliant than the inorganic coating alternatives and can be deposited at lower temperature, water diffuses relatively quickly through it and thick coatings (e.g. 5-10 μm) must be used for multi-day electrical stability [3]. Although inorganic coatings have lower rates of water diffusivity, films more than a 10-20nm thick can deleteriously affect the mechanical properties of nanoelectromechanical systems. Additionally, both sputtering and LPCVD are not perfectly conformal and can have substantial coating thickness nonuniformity, so devices with high aspect ratios or undercut features may require especially thick passivation coatings.

Atomic Layer Deposition (ALD) [4] is a technique that uses self-limiting chemical reactions to controllably deposit ultra-thin metal or dielectric films. Importantly, ALD can be used to coat extremely high aspect ratio devices and to controllably deposit thin oxide films with excellent uniformity.

Prior research has demonstrated that ALD passivation films can prevent corrosion. Multilayer thermal ALD aluminum oxide and hafnium oxide films have been used to coat CMOS biosensors [5], while plasma enhanced ALD aluminum oxide films have been used to protect steel samples from salt spray corrosion for several hours [6]. We are trying to improve upon these prior ALD passivation coatings and develop a standard process for SNF lab members.

In this work we focused on three different ALD oxide films for MEMS passivation: aluminum oxide (Al_2O_3), hafnium oxide (HfO_2) and zirconium oxide (ZrO_2). Aluminum oxide is widely used in microelectronics for its high relative permittivity, high resistivity and high electrical breakdown field. However, aluminum and its oxide readily corrode in moderately acidic or

basic solutions [1]. Hafnium oxide is more chemically stable, and has an isoelectric point of pH 7, making it particularly well suited for depletion-type microdevices (e.g. ion-sensitive field-effect transistors) [7]. Zirconium oxide is also expected to be chemically stable, and has been deposited on CMOS biosensors via sputtering [8]. We aimed to use multiple films in combination to simultaneously optimize the electrical and corrosion properties of passivation coatings, while limiting the maximum coating thickness to 10-20nm in order to ensure viability for coating nanomechanical devices.

2 Experimental Methods

In order to compare the chemical and electrochemical corrosion resistance of the ALD films, we used the following metrics:

- Electric breakdown field
- Leakage current below breakdown
- Time to failure at sub-breakdown fields

We designed and fabricated simple test structures using a single mask process. The device consist of a resistor loop structure and a capacitor electrode with four different sizes on each die (1mm, 2mm, 4mm and 8mm). We measured the impedance of the resistor by applying a small DC bias (< 100 mV), while the capacitor impedance was measured using a large DC voltage (e.g. 3V) combined with a small AC voltage (e.g. 50 mV @ 20 Hz) in order to simultaneously measure the resistance and capacitance of the ALD coating. All experiments were performed at room temperature with pH 7.4 phosphate-buffered solution (PBS) containing approximately 200 mM NaCl.

2.1 Circuits

We designed electronic circuits to apply and control the potentials on the test die as well as the ionic media. We used a National Instruments data acquisition board (DAQ) connected to a PC in order to interface with the measurement circuit. MATLAB was used to control the DAQ board, perform data fitting and plot the results.

In order to control the relative bias between the solution and aluminum traces we built a potentiostat circuit. The circuit consists of three electrodes:

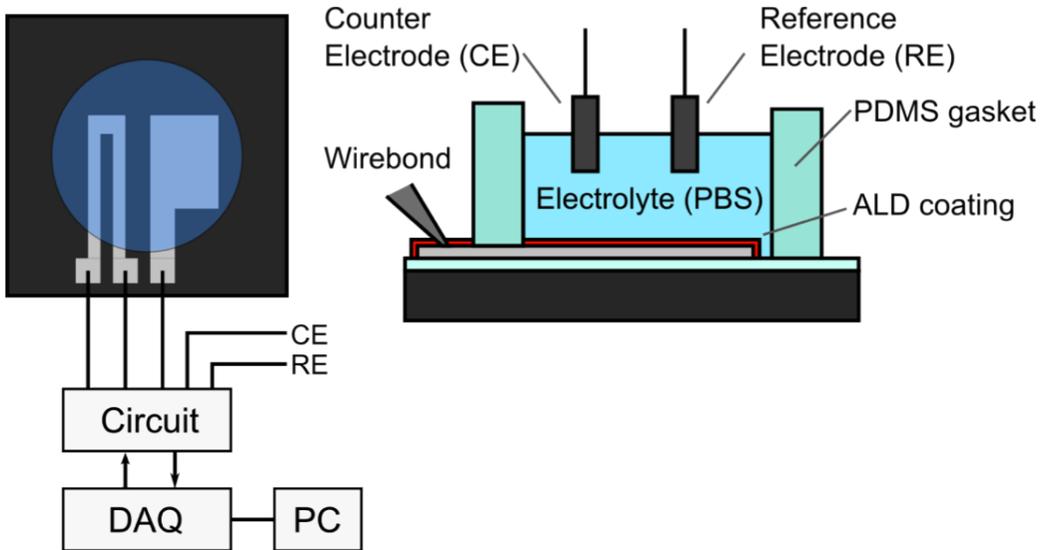


Figure 1: Experimental setup. Left: Top view of a test die with the aluminum traces in gray and the liquid in blue contained in a PDMS gasket. The die is wire-bonded to a surfboard and connected to our measurement circuit. Right: Side view of the experimental setup showing the PDMS gasket containing the ionic solution with two electrodes and the coating aluminum traces.

the working electrode (our test structure), a counter electrode (a Pt wire) and a reference electrode (Ag/AgCl reference). In the circuit, the control signal drives the non-inverting input of an op-amp while its inverting input and output are connected to the reference and counter electrodes, respectively. The op-amp forces current to flow between the counter electrode and working electrode (our test structure) in order to maintain the reference electrode at the control bias level. In order to ensure that current primarily flowed to the working electrode rather than to the reference electrode terminal we used a JFET-input op-amp (AD820) with low-input bias current (25 pA) and high input impedance ($10^{13}\Omega$). The three-wire potentiostat setup ensures that the potential drop we apply is only across the ALD-double layer interface rather than also including an unknown, variable drop at the counter electrode interface. The second stage of the measurement circuit uses a transimpedance amplifier to amplify and allow measurement of the potentiostat current.

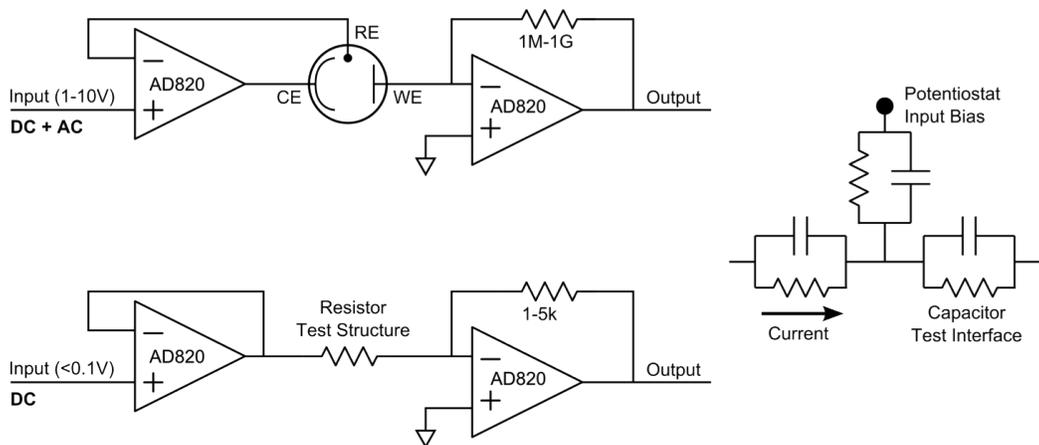


Figure 2: Measurement circuit. Top: Three electrodes are used in a potentiostat configuration to control the applied potential at the liquid-ALD coating interface. Right: Equivalent circuit for the potentiostat. Bottom: test resistor circuit, that applies a small current through the resistor and amplifies the current to measure the resistance change.

2.2 Device Design and Fabrication

We started the fabrication with bare (100) silicon wafers. We grew 1000\AA of SiO_2 and sputtered 250nm of aluminum in Gryphon. We used a transparency mask to pattern photoresist and wet etch the aluminum. We stripped the photoresist in PRX-127, cleaved the test structures from the wafer, cleaned the samples in PRS-1000 and coated them in the Savannah ALD system. Finished devices are shown in Figure 3.

The test die were wirebonded to a surfboard and connected to the circuit with custom cables. We fabricated PDMS gaskets to hold enough liquid on the device to be able to immerse the counter and reference electrodes. To do so, acrylic squares were cut using a laser ablator and epoxied to a petri dish. 10:1 PDMS was poured around the acrylic squares, being careful not to cover them completely. After curing for two hours at 60°C , the PDMS was peeled out and cut into gaskets using a razor blade.

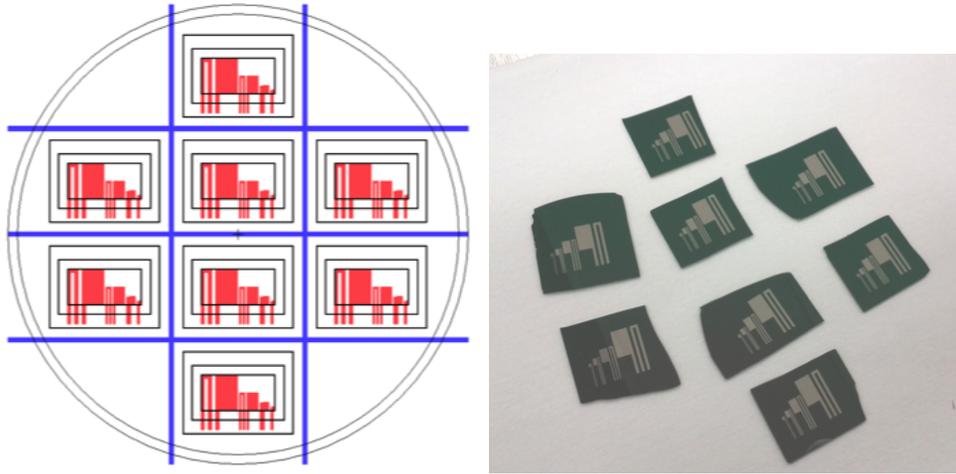


Figure 3: Left: Photolithography mask in "data dark" for metal etching. The edges of the PDMS gasket are shown in black and the cleave lines are shown in blue. Right: Dies after processing and cleaving.

2.3 ALD Coatings

The following films have been deposited and tested to date:

- 10nm Al_2O_3
- 10nm HfO_2
- 10nm Al_2O_3 + 10nm HfO_2
- 5nm Al_2O_3 + 5nm HfO_2
- 5nm Al_2O_3 + 5nm ZrO_2

3 Results

Figure 4 shows the DC impedance of the ALD film as a function of applied bias. The ALD films failed when electric fields greater than 0.25-0.35 V/nm were applied, presumably due to electrical breakdown. The Al_2O_3 films appear to perform slightly better than HfO_2 . For example, 10nm of Al_2O_3 is

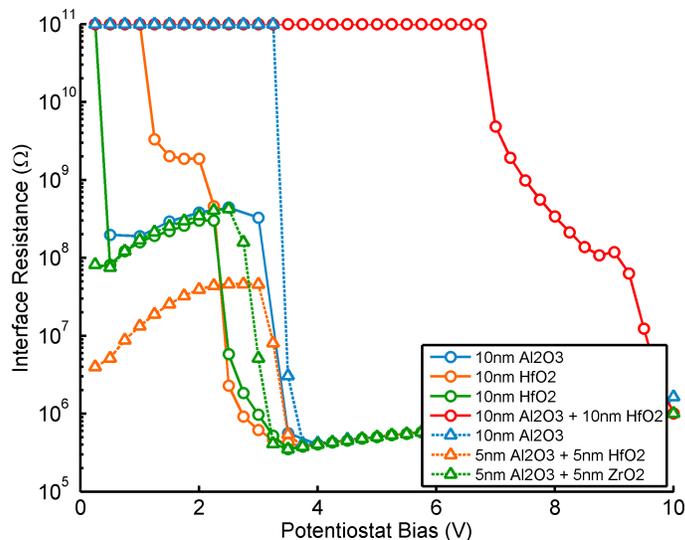


Figure 4: Plot of the interface resistance versus applied voltage more a variety of ALD films in PBS. The steep drop in resistance indicates the film is failing and opens current channels.

stable up to $\approx 3.5\text{V}$ before the impedance sharply drops due the passivation breaking down. HfO_2 generally shows a lower breakdown voltage, as demonstrated in the Fall 2010 EE412 ALD project, but also shows that breakdown occurs gradually. Several measurements started out with a relatively low impedance (e.g. $10^7\Omega$) which increased before a final clear breakdown step; we are still unsure about the process that is leading to this behavior.

Initially we planned to quantify passivation coating failure by measuring the impedance of the resistor test structure. Our initial hypothesis was that the impedance would increase as the metal corroded and reduced the cross-sectional area of the resistor. However, the liquid was biased relative to the grounded terminal of the resistor, so the measured impedance would either increase (metal corrosion) or decrease (current injection from solution) depending on where the resistor began corroding. The capacitor structure proved to be a more sensitive measure of corrosion because of its high initial impedance ($> 10^9\Omega$).

In order to investigate longer term corrosion, we applied a bias of $\approx 50\%$

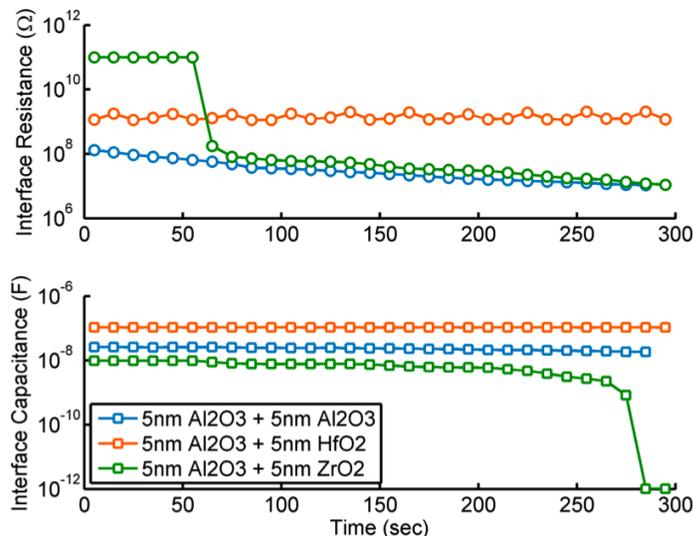


Figure 5: Interface resistance (top) and interface capacitance (bottom) versus time.

of breakdown and maintained it for 10 minutes (Figure 5). We found that a bilayer $\text{Al}_2\text{O}_3 + \text{HfO}_2$ was most stable over time. We also tested films for much longer durations at lower bias voltages but did not observe any corrosion. For example, 10nm of Al_2O_3 was stable after 15 hours at 1V bias.

4 Conclusion

The most stable film tested so far is $\text{Al}_2\text{O}_3 + \text{HfO}_2$. For sufficiently large bias fields (0.25-0.35 V/nm), the ALD films fail almost immediately. Failures appear in local patches, possibly due to local defects or thickness inhomogeneity. The failure fields are ≈ 3 times smaller than those measured for dry, forming gas annealed ALD films between two metal electrodes.

When films are operated at less than half of the breakdown voltage they appear to be quite stable. However, additional long-term testing is required to show performance differences at lower voltages. To date we have only investigated single and double layer films, but nanolaminates might provide another mechanism to combine the corrosion and electrical properties from

multiple films.

5 Acknowledgments

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Appendices

The MATLAB code used to perform the voltametry experiments is included in the four attached files.

rampTests.m Measure the breakdown voltage of a test structure by applying a ramped control voltage to the potentiostat and measure the current flow through the ALD film and test resistor.

deviceTest.m Measure the long term characteristics of the test structure by applying a constant DC bias and small AC while measuring the current flow through the ALD film and test resistor.

analyzeData.m A set of scripts for importing, plotting and analyzing test data.

RCFit.m Fit a parallel RC circuit model to the ALD interface. The best-fit R and C values are calculated by a fitting the model to the measured current data by minimizing the squared sum of the residual errors.