

ULTRA-THIN ATOMIC LAYER DEPOSITION FILMS FOR CORROSION RESISTANCE

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ABSTRACT

We evaluated the chemical and electrochemical corrosion resistance of ultra-thin films deposited via atomic layer deposition (ALD) for potential wafer-scale passivation of biomedical microdevices. A variety of ALD coatings can be deposited conformally on metal or silicon surfaces at low temperature. We were able to protect aluminum electrodes against corrosion in ionic media with a voltage stress of 1V for 200 hours using a double ALD film stack of 5nm Al₂O₃ and 5nm HfO₂.

KEYWORDS

Passivation, corrosion, MEMS, thin film, ALD, atomic layer deposition, packaging, biocompatible.

INTRODUCTION

Microelectromechanical systems (MEMS) have been widely used in research and clinical biomedical and biological applications. However, passivation and packaging are crucial for devices where silicon or metal are exposed to ionic media to prevent chemical or electrochemical corrosion and also provide biocompatibility [1, 2]. Typical passivation coatings can be deposited by low-pressure chemical vapor deposition (LPCVD) or sputtering. Organic LPCVD coating (i.e. parylene) can routinely be deposited at room temperature, while inorganic film can be sputtered near room temperature (TiO₂) or deposited from 300 °C to 800 °C via LPCVD (SiO₂, Si₃N₄). Although parylene [3] is more compliant than inorganic coating alternatives (silicon nitride, silicon oxide) and can be deposited at lower temperatures, water diffuses relatively quickly and thick coatings (e.g. 5-10 μm) must be used for multi-day electrical stability [4]. Unfortunately, such thick films can deleteriously affect the mechanical properties of MEMS, especially nanoscale devices [5]. Atomic Layer Deposition is a technique that uses self-limiting chemical reactions to controllably deposit ultra-thin metal or dielectric films. Unlike films deposited by sputtering or LPCVD, ALD [6] can be used to coat extremely high aspect ratio devices and to deposit thin oxide films with excellent quality and uniformity. ALD passivation films have been shown to prevent corrosion in biosensors [7]. However the long-term performance of ultra-thin ALD coatings has not yet been demonstrated.

In this work we focused on three different ALD oxide films for MEMS passivation: aluminum oxide (Al₂O₃), hafnium oxide (HfO₂) and zirconium oxide (ZrO₂). 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) [8]. Zirconium oxide is also expected to be chemically stable, and has been deposited on CMOS biosensors via sputtering [9]. 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 5-20 nm in order to ensure viability for coating nanomechanical devices.

METHOD

Fabrication

To test ALD film stacks, we designed and fabricated simple test structures using a single mask process (Figure 1). The device consists of a resistor loop and capacitor electrode of four different sizes (1, 2, 4, 8mm). We started the fabrication with single crystal silicon (100) wafers and grew 1000 Å silicon oxide at 1000 °C. Then, we sputtered 250 nm Aluminum and spun 1.6μm SPR3612 photoresist. Using a transparency mask we patterned the resist and wet etched the aluminum in AL-11 (72% H₃PO₄:3% C₂H₄O₂:3% HNO₃:12% H₂O) at 40 °C. Next, we stripped the resist in PRX-127 and cleaned the wafer in PRS-1000. The wafers were manually cleaved, and individual dies were coated with the desired ALD films (5-20 nm) at 200 °C in a Cambridge Nanotechnology Savannah reactor. The films of HfO₂, Al₂O₃, and ZrO₂ coatings were deposited using alternating pulses of water and tetrakis(dimethylamido)hafnium, trimethylaluminum or tetrakis(ethylmethylamido)zirconium, respectively.

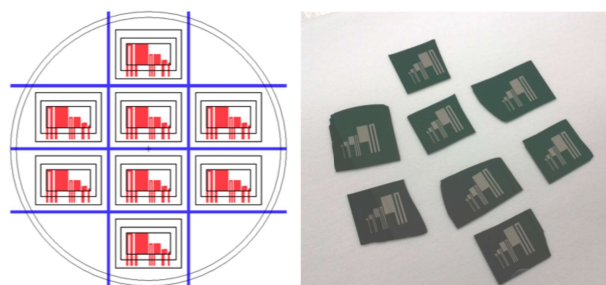


Figure 1: Left: Photolithography mask in "data dark" for metal etching. The edges of the PDMS gasket are shown in black and the cleave lines are shown in blue. Right: Dies after processing and cleaving.

Each die was glued on a glass slide and wire bonded to a surfboard to allow for electrical connection to a

circuit board via custom cables. Contacts openings in the ALD film were not required; the thermosonic wire bonder has enough force to breakthrough the ultra-thin ALD film and bond to the aluminum pads. We fabricated polydimethylsiloxane (PDMS) gaskets to contain the liquid on top of the electrodes and protect the wirebonds from short circuits.

The capacitor electrode was used to measure the interface impedance of the film, while the resistor loop structure was intended to detect aluminum corrosion.

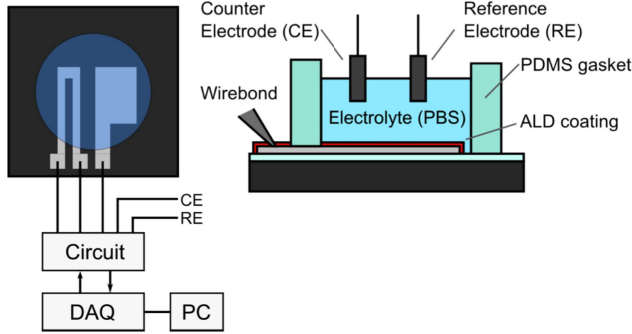


Figure 2: Experimental setup. Left: Top view of a test die with the aluminum traces in gray and the liquid in blue contained in a PDMS gasket. The die is wire-bonded to a surfboard and connected to our measurement circuit. Right: Side view of the experimental setup showing the PDMS gasket containing the ionic solution with two electrodes and the coated aluminum traces.

Experimental setup

To characterize the corrosion resistance of the passivation film, we measured the real impedance of the resistors by applying a small DC bias (< 100 mV) while the capacitor complex impedance was extracted using a large DC voltage (1-10 V) combined with a small AC voltage (50 mV at 20 Hz). All experiments were performed at room temperature with pH 7.4 phosphate-buffered solution (PBS) containing approximately 200 mM NaCl. A potentiostat circuit (Figure 2) controls the relative bias between the solution and aluminum traces.

The circuit (Figure 3) consists of three electrodes: the working electrode (the test structure), a counter electrode

(Pt wire) and a reference electrode (Ag/AgCl reference). The three-wire potentiostat circuit ensures that the applied potential is only across the ALD-double layer interface rather than at the counter electrode interface. The second stage of the circuit uses a transimpedance amplifier (AD820) to sense the potentiostat current. We defined failure as when either the resistor or capacitor showed a sudden change in impedance. Similarly, we used another transimpedance amplifier (AD820) to amplify the small current from the resistor loop structure. The experiment was controlled using Matlab and an NI USB-6212 data acquisition board and data were locally stored on a computer to be later analyzed.

Corrosion testing

The electrical breakdown field was measured by sweeping the DC bias voltage from 0 V to 10 V. The breakdown was identified as a sudden interface resistance drop due to current leaking through the ALD coating. In contrast, a smaller bias voltage was applied across the film to test the corrosion resistance. Typically a voltage corresponding ≤ 0.5 the breakdown field was used. Indeed, when the bias voltage across the film was too close to its breakdown voltage, the film would fail within seconds. Note that the DC + AC bias was applied during the entire experiment. Also for short experiments (< 1 hour) we continuously recorded data, however for long experiments we only gathered 10 seconds of data every 10 to 30 minutes to limit the amount of memory used since we were sampling at 200 sample/s to keep information about complex impedance. To quantify the quality of the films we identify the time to failure for each film at different bias voltages. The film was considered failing when either resistor or capacitor impedance started to drift or when a sharp change in impedance was recorded. Finally, we optically inspected devices and look for signs of corrosion in the aluminum electrodes.

RESULTS

Interestingly, the capacitor structure turned out to be more sensitive for measuring corrosion due to its high initial impedance. We expected to see a resistance drop in the

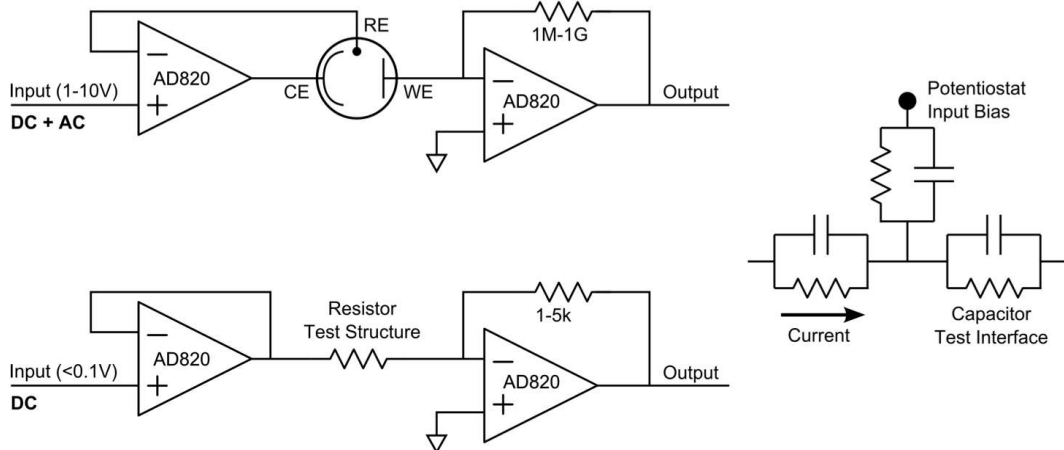


Figure 3: Measurement circuit. Top: Three electrodes are used in a potentiostat configuration to control the applied potential at the liquid-ALD coating interface. Right: Equivalent circuit for the potentiostat. Bottom: test resistor circuit that applies a small current through the resistor and amplifies the current to measure the resistance change.

resistor loop structure when aluminum was corroding due to the decrease of cross-section area, however a resistance increase was instead observed. This effect can be explained by current injection from the resistor to the liquid and is still an indication of film failure.

The electrical breakdown test (Figure 4) finds Al_2O_3 has the highest breakdown field (3.5 MV/cm) and interface impedance (100 G Ω). Both HfO_2 and ZrO_2 exhibit lower initial interface impedance, which relates to a higher leakage current. Similarly, ZrO_2 shows low interface impedance and poorer electrical stability. Furthermore, the impedance drop at breakdown is not as sharp as the Al_2O_3 case. Although, we cannot explain this phenomenon, we believe it is an indication of lower film uniformity or higher defect density. We should also note that previous research (unpublished data) studied the electrical breakdown of these exact films with a standard “dry” capacitor. We noticed that the electrical breakdown voltages measured in this work are constantly about three times lower.

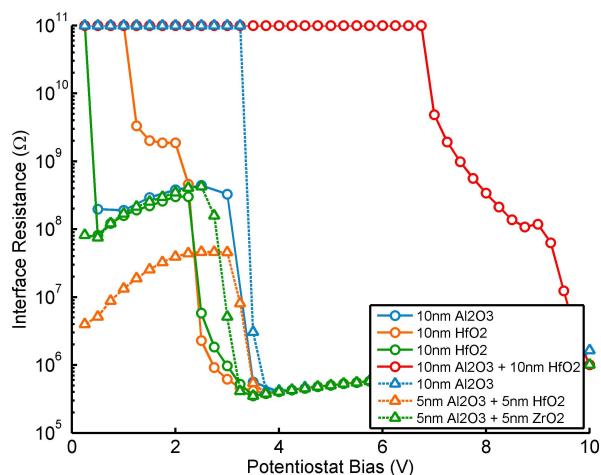


Figure 4: Interface resistance versus potentiostat bias voltage. The sharp resistance drop is due to film breakdown. Overall Al_2O_3 has better breakdown characteristics (3.5 MV/cm) with very high interface resistance at low voltage (100 G Ω).

In contrast, a bilayer film of Al_2O_3 and HfO_2 exhibits better long-term stability than pure Al_2O_3 (Figure 5). Although Al_2O_3 has superior electrical properties, HfO_2 provides better corrosion resistance; therefore they perform better in combination than individually. Operation of over 200 hours was possible for 1 mm structures biased at 1 V and 4.5 hours biased at 2.5 V which is roughly half the breakdown voltage.

Figure 6 shows several 1 mm test structures after experiments of varying duration and electrical bias. Displayed on figure 6a, is a typical die with the capacitor electrode on the left and the resistor loop on the right. The passivation film on figure 6b has obviously failed; the metal electrodes have visible holes due to corrosion. We can also observe more damage in the resistor loop electrode than the capacitor electrode, which is due to current flowing through the resistor and helping electrochemical corrosion of aluminum. Lastly, the film

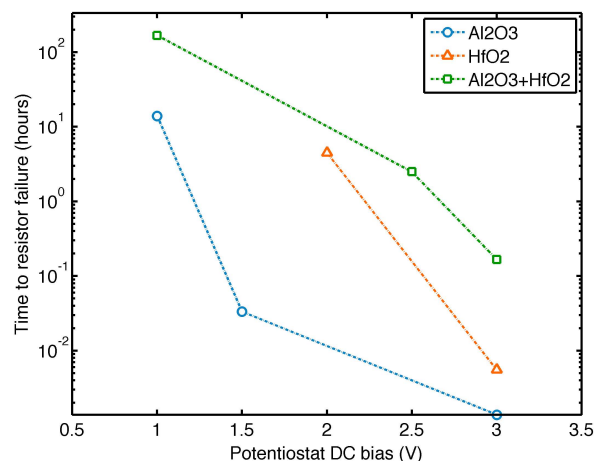


Figure 5: Time to failure versus potentiostat bias of three 10nm thick ALD coatings. Long term investigation shows 5nm Al_2O_3 / 5nm HfO_2 can sustain 1V bias for 200 hours and 2.5V for 2.5 hours which is better than pure Al_2O_3 or HfO_2 .

on figure 6c shows obvious damage after 200 hours and will probably fail soon, but the aluminum underneath shows no sign of corrosion and data from this sample exhibit no obvious interface impedance change.

Based on our initial bilayer results, we tried coating Al_2O_3 with ZrO_2 (Figure 7), unfortunately it shows poor electrical stability and the film quickly fails even at sub-breakdown field. These results suggest $\text{Al}_2\text{O}_3/\text{HfO}_2$ ALD stacks can provide protection equal to or better than traditional methods with unprecedented film thickness.

CONCLUSION

We have designed and developed simple test structure to characterize the corrosion resistance of ultra-thin ALD coatings in ionic media. We tested a variety of metal oxide films, Al_2O_3 , HfO_2 , ZrO_2 and some bilayers of

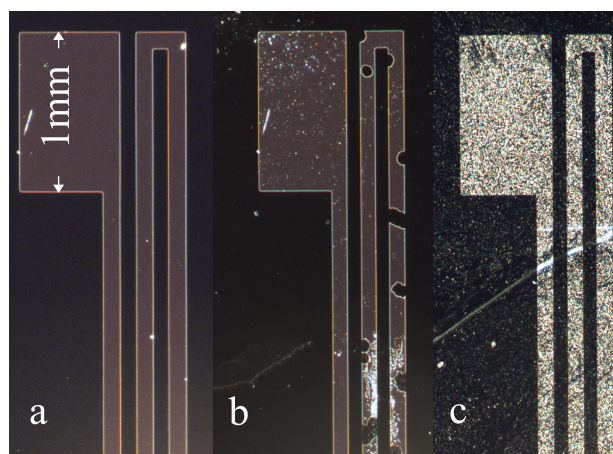


Figure 6: Test structure with 5 nm Al_2O_3 / 5 nm HfO_2 coating a) before test b) after 24 hours in PBS at 2.5 V showing obvious corrosion of the aluminum c) after 200 hours in PBS biased at 1V.

$\text{Al}_2\text{O}_3/\text{HfO}_2$ and $\text{Al}_2\text{O}_3/\text{ZrO}_2$. We measured their electrical breakdown characteristic when immersed in PBS. As expected aluminum oxide was the most electrical stable film of this study with a breakdown electrical field of 3.5 MV/cm.

We then compared the same film in terms of interface resistance for longterm stability. As predicted, HfO_2 was more stable than Al_2O_3 . We can clearly see the interface impedance of the Al_2O_3 slowly drifting down in Figure 7. Furthermore a bilayer of Al_2O_3 and $\text{HfO}_3\text{-HfO}_2$ performed the best and was able to sustain a 1 V bias for 200 hours. However, ZrO_2 did not show good stability even when combined with Al_2O_3 .

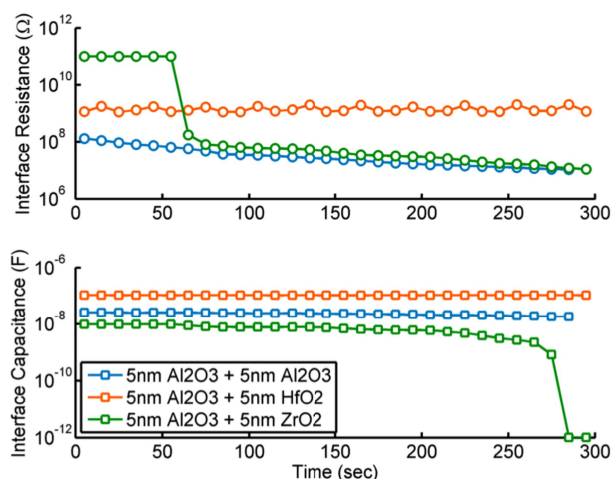


Figure 7: Interface resistance (top) and interface capacitance (bottom) versus time for various films biased at 2.25V.

Future work will include coating and testing functional nanomechanical devices to test the effect of mechanical stress. Based on the good results from a bilayer film, we want to engineer nanolaminate films of Al_2O_3 and HfO_2 . We think we can better take profit of the good electrical properties of alumina and the good electrochemical stability of hafnia.

We are also looking into ways to artificially increase the corrosion rate in our experiment. Indeed, long-term experiments take a long time (up to 200 hours in this study) and other phenomenon might induce instability or drift in our impedance measurements (e.g. the Ag/AgCl electrode might degrade). Thermal aging may be an option, and thermal effect on corrosion should be studied, because self-heating in MEMS devices is often happening. Another way to induce aging is to introduce wet/dry cycles. However, both aging methods have to be characterized and the effect quantify before it can be used in the experiment.

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