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**POLYIMIDE-ALD-POLYIMIDE LAYERS AS HERMETIC
ENCAPSULANT FOR IMPLANTS**

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Abstract

Several requirements exist for medical devices for long term implantation. Firstly, the foreign body reaction and/or inflammation occurring upon implantation should remain mild and short in time. Moreover, the device needs to be biocompatible during the total implantation duration, hence not causing reactions which decrease the patient's health. Finally, the device needs to work properly and safe during the total period of implantation, not suffering from corrosion or chemical degradation. To meet these requirements, diffusion of body fluids into the package should be avoided as well as diffusion of toxic device materials into the body, hence a hermetic packaging method is an absolute necessity. Here, a flexible hermetic packaging is presented using alternating polyimide and atomic layer deposited (ALD) metal oxides. Good adhesion between the inorganic ALD layers and the polyimide is required to avoid the creation of lateral diffusion pads. To obtain this, surface modifications of both polyimide and ALD layers are optimized, as presented in this paper. The hermeticity is evaluated in terms of water vapor transmission rate measurements of the film stack.

Keywords: Hermetic Packaging, implants, ALD

1. Introduction

Today, microelectronic devices for long term implantation (> 30 days) are being developed to act as sensors, hearing aids, neural prosthetics,... In general, the device packaging material needs to be biocompatible, result in a minimum of foreign body reaction and act as a hermetic sealing around the device. For most electronic implants,

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the packaging is realized using rigid materials such as steel, titanium alloys or glass. Although these packaging materials are good to protect the inside electronics, the packaging results in a quite large and rigid implant. Replacing these hard materials by soft polymers has two major advantages. First, the mechanical properties of the soft materials match much better with the mechanical properties (flexibility and elasticity) of the surrounding tissues. The resulting reduced friction will cause less scar tissue formation and will give higher user comfort. Second, the size of the implants can be reduced which enables less invasive surgery and will result in a milder foreign body reaction upon implantation (Scholten and Meng, 2015).

The major drawback of polymer materials as encapsulation for implants is that they are weaker barriers against diffusion of gasses, ions and water. An implant is permanent in contact with body fluids at 37°C, hence the packaging material needs to hermetically seal the electronic device. This means that on one hand, corrosion products, metals or other toxic materials from the electronics should not diffuse into the body environment. On the other hand, diffusion of body fluids, salts or other biomolecules into the device will lead to device failure, especially in case of long term implantation. In order to realize the essential improvement of barrier properties of polymers, a stacked layer of polymers and ALD layers is of ultimate interest: the very thin ALD (atomic layer deposition) layers provide a huge improvement in barrier properties of the polymer/ALD film, while maintaining the desired flexibility and low volume.

To convert polymer foils into high diffusion barriers, surface modification with ALD films of metal oxides is an emerging strategy. In general, ALD films are pin-hole free and have a high conformality. Together with the excellent barrier properties against oxygen and water vapor of some metal oxides this results in ideal films to act as barrier layers for devices or objects with complex 3D shapes. More information about the ALD technique, mechanism and film properties can be found in an excellent review of S. George (George, 2010). Although the nucleation and adhesion of the metal oxides deposited on silicon or other metal oxides is good, the deposition on polymers is often less easy. Moreover, thermal ALD process for metal oxide films are preferable performed at higher deposition temperatures (250-300°C) for most metal oxides to avoid extremely low ALD deposition speeds. Hence a thermally stable polymer is preferred.

Several soft and biocompatible polymers have been explored as packaging materials for implantable (electronic) devices such as PDMS, Parylene-C, LCP and polyimide (Scholten and Meng, 2015). In this work, polyimide films are chosen for several reasons, with as most important one the high thermal stability (up to 300°C) of polyimides which is preferred for subsequent deposition of thermal ALD films.

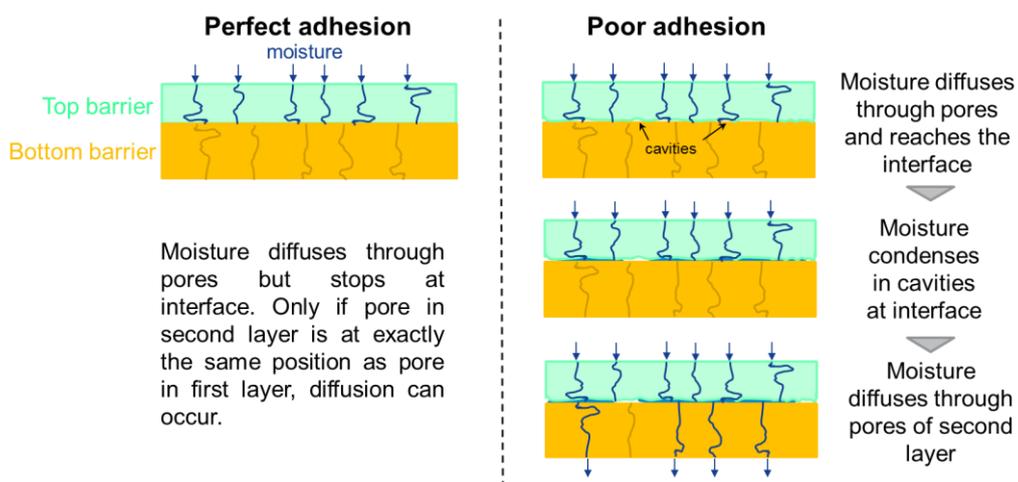


Fig. 1. Schematic illustration of the consequences of poor adhesion between the different material layers (PI and ALD stack) for the barrier properties of the total stack.

Excellent adhesion between ALD layers and polyimide and *vice versa*, is an absolute necessity to create hermetic sealing. In case of perfect adhesion between two barrier layers, the moisture diffuses through defects (pores, pinholes or other) but stops at the interface between both barriers. Only if a pore in the bottom layer is at the same position as in the top layer, diffusion can occur through the total stack, which is unlikely if the deposition of the individual layers is optimized to obtain the lowest possible amount of defects (Figure 1 left). When there is poor adhesion between the barrier layers, cavities are present at the central interface. Moisture diffuses through some cavities present in the top layer and condenses in the cavities at the interface, which allow for a fast lateral displacement of water (See Fig. 1 right). Hence, the moisture can diffuse easily further through the defects of the

bottom layer causing bad overall barrier film properties. Hence good adhesion is crucial for stacked diffusion barriers, which can be obtained by tailored surface modifications of the polyimide and ALD materials.

In this work, the surface modification of polyimide with an oxygen plasma is presented to improve adhesion and nucleation of deposited ALD layers. Next, the surface modification of the hafnia ALD layers with APTES (3-aminopropyltriethoxysilane) is discussed. This APTES modification is performed to improve wettability and adhesion of the polyimide layer coated on top of the ALD layer. The surface modifications are characterized by water contact angle measurements. The adhesion of modified and non-modified surfaces is determined with a standardized tape test. Finally, the barrier properties of an alternating stacked film of polyimide/ALD stack/polyimide is evaluated by water vapor transmission measurements.

2. Experimental

All glass used as processing substrate and for contact angle measurements is cleaned using a standard RBS cleaning method. APTES (3-aminopropyl triethoxysilane, 99%) is purchased from Sigma Aldrich. The APTES surface modification method is obtained from literature (Metwalli et al., 2006).

PI2611 (spin coating solution) and VM652 (adhesion promotor solution) is obtained from HD Microsystems (Germany). PI2611 is spin coated for 30 seconds at 3000 rpm followed by pre curing at 200°C for 10 min on a hotplate. A final curing is performed in a nitrogen purged oven at 350°C for 60 min. VM652 is spin coated for 30 seconds at 1000 rpm followed by a baking step of 10 min at 120 °C on a hot plate.

The oxygen plasma treatment is performed on a O₂ stripper instrument from plasma technologies. The plasma is performed for 2 min at an oxygen pressure of 300 mTorr.

ALD deposition of the HfO₂ (8 nm) / Al₂O₃ (20 nm) / HfO₂ (8 nm) stack is performed in one run using a Savannah instrument from Ultratech. Water and trimethylaluminum are used as precursors for the alumina deposition. For hafnia deposition, water and tetrakis(ethylmethyl)amidohafnium are used as precursors. The deposition temperature was 250°C at a pressure of 0.4 mTorr.

Adhesion is evaluated by scotch tape test (ASTM D3359). In this test a cross-cut is made in the film to the substrate, pressure-sensitive tape is applied over the cut and then removed, and adhesion is assessed qualitatively on the 0 (bad adhesion) to 5 (very good adhesion) scale.

WVTR is determined by the Mocon method using a MOCON instrument (modified ASTM F1249) at 38° and 100% RH. The detection limit for this instrument is 0.5 mg/m² day (Hogg et al., 2013).

3. Results and discussion

In this work, the three ALD layers are always deposited consecutive, resulting in a HfO₂/Al₂O₃/HfO₂ stack (hereinafter referred to as ALD stack) which is located in between two polyimide (PI) layers. Alumina ALD layers are good barriers against water vapours and other gases. However, the alumina start to decompose when in direct contact with water due to hydrolysis (Abdulagatov et al., 2011). Therefore, the alumina layer is capped by two hafnia layers on top and bottom. Capping of alumina with silica has already shown to increase the stability (Dameron et al., 2008). Here, hafnia layers are chosen because they provide excellent chemical stability and barriers against liquid water.

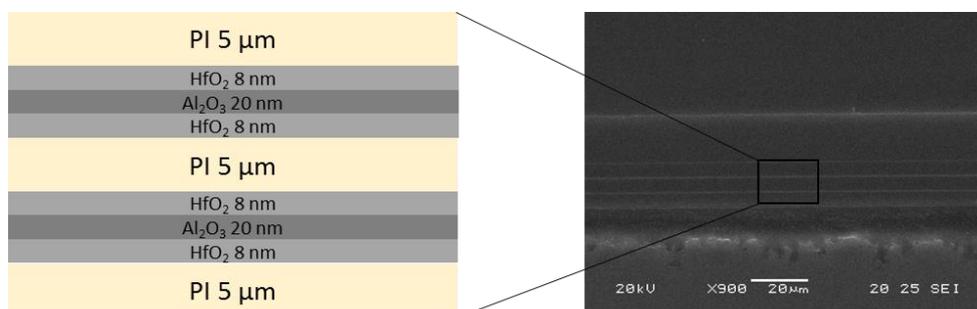


Fig. 2. Left: schematic illustration of a typical hermetic stack. Right: SEM micrograph of a cross section of the stack.

A typical stack consists of alternating layers of ALD deposited HfO₂/Al₂O₃/HfO₂ and spin coated PI2611 (see Figure 1). On the SEM micrograph, the ALD layers are visible as white lines between the spin coated PI layers (gray colour).

3.1. Surface modification of polyimide to improve adhesion towards the ALD stack

The first optimization that will be discussed is the ALD deposition of HfO₂ on the surface of PI. The static water contact angle (SCA) of the PI2611 surface is 72° (table 1). PI2611 is a polyimide generated by double thermal condensation of BPDA (biphenyl-tetracarboxylic acid dianhydride) and PDA (para-phenylene diamine). This means that theoretically the only polar functional groups - originating from this polymer- which can be present on the surface are cyclic diimides (R-CO-N-CO-R). To increase the reactivity and physical interaction of the polyimide surface towards the hafnium precursors, an oxygen plasma modification step is performed directly before the introduction of the samples into the ALD reaction chamber. These functional groups can include hydroxyl, carboxylates, ketones, aldehydes,... After this plasma treatment, the SCA of the PI2611 is smaller than 10° (total spreading). Adhesion measurements on these ultrathin ALD films are difficult to perform at this stage. Hence, other layers are added on top of the ALD layer to enable good adhesion measurements of both interfaces at the bottom and the top of the ALD layer. These results will be discussed in the adhesion evaluation section below.

Table 1. Static water contact angle on (modified) material surfaces (n=5).

Material stack	Surface modification(s)	Contact angle (°) ± STD (°)
Glass	-	< 10
Glass	VM652	54 ± 1
Glass	APTES	33 ± 5
Glass	ALD stack	22 ± 5
Glass + PI2611	-	72 ± 2
Glass + PI2611	O ₂ plasma	< 10
Glass + PI2611	O ₂ plasma + ALD stack	17 ± 4
Glass + PI2611	O ₂ plasma + ALD stack + APTES	28 ± 7

3.2. Adhesion between the Al₂O₃ and HfO₂ ALD layers

The in situ ALD deposition of metal oxide layers on metal oxide layers reveal no problem in nucleation and adhesion due to the natural presence of hydroxyl groups. Moreover, the three ALD layers HfO₂/Al₂O₃/HfO₂ are deposited in the same deposition process which eliminates contamination of the interfaces due to air exposure. So very good adhesion and nucleation of these layers is obtained without extra treatments, but by performing only one combined ALD deposition process.

3.3. Surface modification of the HfO₂ surface to improve the adhesion towards PI2611

The second challenge is the deposition of PI2611 via spin coating and post curing on HfO₂ surface with excellent adhesion at the interface. The HfO₂ surface contains hydroxyl groups which can be used to chemically anchor a silane coupling agent. It is known that adhesion promoters based on APTES (3-aminopropyl triethoxysilane) are used for PI2611. However, commercial adhesion promoters for spin coating like VM652 do not result in sufficient adhesion in this case (table 2). Therefore, an APTES treatment based on an APTES solution followed by rinsing steps and thermal treatment is applied here. Tests are also performed on glass (SiO₂) and result in a contact angle increase from total spreading (SCA < 10°) to 33°. When HfO₂ surfaces are treated, the contact angle increases from 17° to 28° in case of an ALD stack on the polyimide. As a comparison, if APTES is deposited on glass the SCA increases from <10° to 33°. The increase of the contact angle can be attributed to the introduction of chemically bonded (hydrolyzed) APTES molecules on the surface which were not removed during the rinsing steps.

3.4. Adhesion evaluation with tape tests

Determination of adhesive strength of thin films is not straightforward (Mittal, 1995). Peel or pull tests cannot be executed due to the small thicknesses and fragility of the ultrathin ALD layers. The most suitable test in this case is the (scotch) tape test described by the ASTM-D3359 standard, performed after coating a thicker polyimide layer over the ALD stack. In this case the adhesion of all involved interfaces is tested simultaneously. Table 2 shows the results of the tape peel test for treated and untreated surfaces glass and ALD surfaces, both covered with polyimide

From table 2 it is clear that the adhesion is markedly increased in for both modification methods. Spin coated PI2611 on cleaned glass shows very poor adhesion. After APTES modification of the cleaned glass and of the ALD stack, the highest value is obtained. Commercial spin coated VM652 leads to poor adhesion.

Knowing that the adhesion of PI on APTES treated glass is very good, a stack to evaluate the effect of the plasma treatment on the adhesion of ALD on modified PI2611 can be evaluated. The tape test on sample 5 results in total removal of the top PI. The locus of the fracture is difficult to determine. It is certain that the fracture is not cohesive in the PI film. Several possibilities remain:

- Adhesive failure between PI and ALD layers
- Partially cohesive failure in the ALD layer and adhesive failure between PI and ALD layers
- Cohesive failure in ALD stack

Adhesive failure between APTES and PI is excluded due to results obtained for sample 3. Therefore, for stack nr. 5, it can be concluded that the failure is due to the weak interface between non plasma treated PI2611 and the ALD stack. This is confirmed by the good adhesion obtained from sample 6, where plasma treatment is performed prior to ALD deposition

Table 2. Static water contact angle on (modified) material surfaces (n=5).

Stack nr.:	Material stack	Tape test value
1	Glass + PI2611	0
2	Glass + APTES + PI2611	5
3	Glass + VM652 + PI2611	2
4	Glass + ALD stack + APTES + PI2611	5
5	Glass + APTES + PI2611 + ALD Stack + PI2611	0
6	Glass + PI2611 + PI2611 + O2 plasma + ALD Stack + PI2611	5

3.5. WVTR test results

The final tests of the barrier layers is the determination of water vapor transmission rate (WVTR) using a MOCON test.

Table 3. WVTR of 3 different films.* This value is equal to the detection limit.

Film composition	WVTR (mg/m ² .day)
PI2611	4300
PI2611 – Al ₂ O ₃ (20 nm) – PI2611	4
PI2611 - HfO ₂ (8 nm)/Al ₂ O ₃ (20 nm)/HfO ₂ (8 nm) – PI2611	< 0.5*

To the best of our knowledge, there is no standard for the hermeticity of polymer containing packaging for medical electronic device implants. Our ultimate goal is to reach a WVTR value of 10⁻³ mg/m² day, although this is an arbitrary set value. Therefore, in future, additional WVTR tests of multilayers of PI2611 and ALD stacks will be performed.

4. Conclusions

Surface modification of the ALD stack with APTES and PI2611 with oxygen plasma leads to high adhesion between the corresponding materials. This creates new possibilities to produce alternating stacks of PI2611 and HfO₂/Al₂O₃/HfO₂ as packaging materials for flexible implants. WVTR results have shown that capping of the Al₂O₃ ALD layers with HfO₂ layers on both sides increases the WVTR by a factor of 10.

Acknowledgements

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