Determination of the Water Vapour Transmission Rate of Polymer-Metal Oxide Layer Composites

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Abstract — **Parylene-C is a multifunctional polymer coating in the coating industry. In medical technology, it is approved for implants due to its biocompatibility. For example, it is used as a coating for electronic components and parts. The problem is that Parylene-C alone is too permeable to body water and the ions that are dissolved in it. Application as a coating material for long-term implants is therefore not possible. The infiltrating water not only corrodes the electronic components, but also reduces the adhesion between the Parylene-C and the coated surface. Therefore, layer systems of metal oxides and polymers are used for encapsulation. The aim of this work is to find out how different layer systems behave in relation to their water vapour transmission. Thicker systems should allow less water vapour to pass through than thinner ones. The task is to find this out using the test method for water vapour transmission barriers and to determine the water vapour transmission rate. It has been proven that in some cases the thicker layers performed worse than the thinner layer systems by a factor of ten. It has been shown that there is a relationship between the base substrate thickness, the thickness of the layer system and their flexibility.**

I. Introduction

Electronic components are used in active implants in medical technology. These implants consist of an energy supply, actuators and sensors which usually are not able to deal with the harsh environment of the human body. The biochemical processes, elevated temperatures and the dissolved ions in the body fluid attack the sensitive electronic components and cause them to corrode. For this reason, the sensitive components are hermetically encapsulated. Rigid housings are chosen as the simplest solution, for example in the case of a pacemaker. However, the disadvantage is that inflexible implants cannot be used in places with limited space, such as the skull. [1, 2]

For flexible implants, the electronic components are embedded in suitable polymers. In contrast to the rigid housing materials like metals or ceramics, these polymers have a high permeability to ions and body fluids [3], which leads to corrosion and ultimately to failure of the implant. One solution is to create a hybrid system with polymer coatings for flexibility and wafer-thin metal oxide coatings for the barrier property. The metal oxide layers are deposited using the atomic layer deposition (ALD), a cyclically coating process which allows the formation of ultra-thin, conformal and defect free layers. [4]

The polymer used in this study is Parylene-C. This polymer is characterized by its biocompatibility (FDA approval) and flexibility [4, 5]. Metal oxide films of alumina (Al_2O_3) and titania (TiO_2) are used. Alumina exhibits a very good barrier effect against water vapor transmission but is not stable in saline. On the other hand, titanium oxide exhibits less water vapor diffusion, but has a high chemical resistance.

Both oxides can be bonded together in a sandwich layer. The aluminium oxide contributes to the barrier effect, while the titanium oxide protects the aluminium oxide. This created synergy helps to achieve the greatest possible barrier effect. [4]

The barrier effect of three different layer systems was determined by the water vapor transmission rate (WVTR) in a self-designed test set-up. Water vapour permeability is the amount of water that transmits through one square metre per 24 hours ($\frac{g}{m^2*d}$) [6].

Before starting with the respective layer system, a layer of 5 nm thick titanium oxide was applied. This layer is primarily applied to encapsulate and protect the aluminium oxide. While aluminium oxide is not chemically stable in vivo and is slowly dissolved under hydrolysis by the body water, titanium oxide is chemically inert [4]. Therefore, the total thickness of the metal oxides of the layer system applied by ALD was varied from 25 nm to 65 nm. The layer sequence and thickness of the respective layer systems remain identical from 20 nm to 60 nm in each experiment, because the TiO_2 layer is applied initial only once. The hypothesis that will be investigated in this paper is that by increasing the thickness of the layer system, the water vapour transmissions rate would decrease.

II. Materials and Methods

A. Sample preparation

The goal is to produce a layer system that can be clamped into the experimental setup as a thin film. In a first test, the hybrid coating (organic/inorganic layer system) were applied directly to a 6" silicon wafer. However, the layer systems could not be detached from the wafer without being damaged. In a second run, a mixture of commercially available rinsing agent (surfactants) and water in a mixing ratio of 1:10 (10 g rinsing agent, 100 g water) was applied to the wafer in a finely sprayed form before coating. The idea was to create a soluble layer on the wafer so that the layer system could be easily detached. Again, in some cases the system could not be removed from the wafer at all. In addition, the coating had bubbles and was irregular.

Finally, an Adwill film with 65 µm thickness was glued onto the wafer. The Adwill film is a PET film with a UV-dissolvable adhesive. This was applied to the 6" silicon wafers with a wallpaper roll without bubbles. Then, the wafer with the film was placed under UV light for 15 minutes. This reduced the adhesive strength of the film, which led to a stress-free removal of the layer system after coating, which was deposited directly onto the adhesive film. Three circular samples with a diameter of 60 mm could be punched out of a wafer with the respective layer system.

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B. Multilayer coating system

The multilayer coating system, consisting of the metal oxides aluminium oxide (Al_2O_3) and titanium oxide (TiO_2), is sandwiched by 7.5 µm thick Parylene-C in each case. It is coated on the 6" silicon with the clued Adwill film on it. After the Adwill film has been applied to the wafer, it is treated with UV-Light and then placed in the Labcoater serie 300 (Plasma Parylene Systems GmbH, Rosenheim/Pang, Germany) to be coated with Parylene-C. Three wafers were coated at the same time. In addition, a separate silicon wafer piece is added for measuring the coating thickness via interferometry using the NanoCalc-XR (Ocean Optics Inc., Seminole Florida, USA) after the coating procedure.

Before the wafers with the applied Adwill film were coated, they were pre-treated with an oxygen plasma for 300 s. After that, the adhesion promoter Silane A-174 was pulsed into the recipient to increase the adhesion between the Adwill film and the Parylene-C. To reach a coating thickness of 7.5 µm, 12 g of Parylene-C powder is used.

Afterwards, the process of atomic layer deposition was carried out using the FlexAL ALD (Oxford Instruments plc, Abingdon, England). Before the metal oxide layers are deposited, the Parylene-C is again pre-treated with oxygen plasma using an inductively coupled plasma source for 180 s. After the pre-treatment, a layer of 5 nm thick titanium oxide was applied, for the protection of the aluminium oxide. Three different layer systems were applied and measured, which are shown in Figure 1.
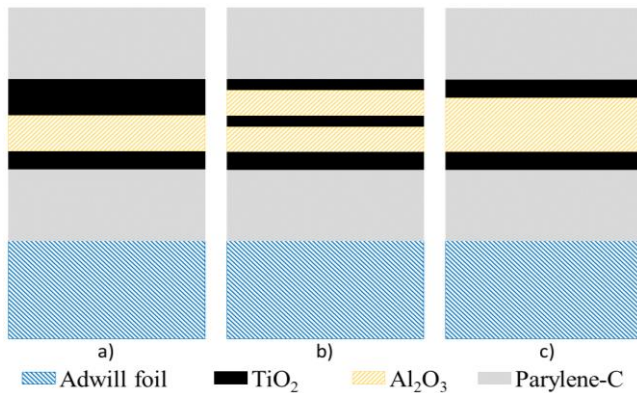

Figure 1: Schematic layout of the three-layer systems
a) system 1: Stack with 10 nm Al_2O_3 and 10 nm TiO_2
b) system 2: Stack with 7 nm Al_2O_3 and 3 nm TiO_2
c) system 3: Stack with 15 nm Al_2O_3 and 5 nm TiO_2

To produce a metal oxide layer with the ALD process, two different precursors were used. For the aluminium oxide trimethylaluminium TMA (C_3H_9Al), and for titania titaniumtetraisopropoxide TTIP ($C_{12}H_{28}O_4Ti$) was used. Also, an oxygen plasma as a coreactant was used. The process temperature was 100 °C. The process runs in several cycles. Table 1 show, how many cycles are required to reach the corresponding thickness. On these numbers, the growth per cycle rate for TMA is approximately 1.54 Å and for TTIP approximately 0.4 Å. All three-layer combinations in each case are 20 nm thick. In total, three thicknesses were measured: 20 nm, 40 nm and 60 nm plus the 5 nm TiO_2 as the initial layer. The thickness of the different systems is described in the following without the initial applied

5 nm TiO_2. The layer thickness combinations were always applied alternately, so that there is one multilayer at 20 nm and three multilayers at 60 nm.

Table 1: ALD coating cycles for different thicknesses of Al_2O_3 and TiO_2

	Thickness (nm)	Cycles
Al_2O_3 (TMA)	15	100
	10	75
	7	50
TiO_2 (TTIP)	10	250
	5	125
	3	75

C. Measurement setup

For clamping the samples, two tubes with a flange are used, which are shown in Figure 2. The tubes are held together by a clamping ring. One tube is open at the end, the other is closed. In the closed tube system a MSR385SM climate sensors (MSR Electronics GmbH, Seuzach, Switzerland) is placed, which record the current temperature and humidity every 60 seconds and send this by radio to the MSR385WD data logger (MSR Electronics GmbH, Seuzach, Switzerland). The data is collected and stored on a PC.

In the first step, the punched-out films are placed between two rubber seals. Then, the samples are placed in a glove box (Sylatech GmbH, Walzbachtal, Germany) with a defined nitrogen gas atmosphere. The content of water inside the box is under 20 ppm. The temperature inside the glove box does not deviate much from the 23 °C in the climate chamber, because a higher deviation of the temperatures leads to an expansion or contraction of the air inside the measuring tube. As a result, the film to be measured acts like a membrane and is mechanically stressed by the pressure difference between the atmosphere and the enclosed air.

The tubes with the flange pieces and the climate sensors are also inserted. The sensors are cast in silicone which absorbs water. That is the reason why the sensors are placed in the box 24 hours before. The residual moisture in the silicone can evaporate.
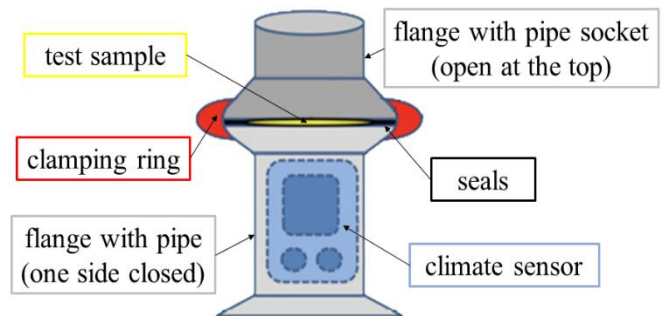

Figure 2: Test setup to measure the water vapour transmission rate

The experimental setup is assembled in the glove box. In the first step, the climate sensor is placed in the sealed tube. After that, the coated film to be tested is placed on the flange between the rubber seals. The coated side of the film faces away from the climate sensor. The counterpart, which is open

at the top, is placed on top and the flanges are closed with the clamping ring.

Nine set-ups can be tested in one measurement run. For every thickness of the layer system (20 nm, 40 nm, 60 nm) three samples of each layer combination can be measured at the same time. Before the test set-ups are loaded from the glove box, it is checked whether the sensors emit a signal. The signal is transmitted to the data logger wireless. If the feedback is positive, the samples are placed into the climate chamber. An MKF 115 E3.1 interchangeable climate chamber (BINDER GmbH, Tuttlingen, Germany) is used for the climatically constant environment. The humidity is set at 85 % and the temperature at 23 °C. They remain there for 10 days. Like in Figure 2, the opening of the tube on one side allows humidity to diffuse through the coated film with the multilayer coating system and the climate sensor records the relative humidity change. This allows to determine the water vapour permeability rate of the respective layer.

The recorded humidity values can be displayed over time in a diagram. After a certain time, a steady state is reached, meaning the transmissions rate of water through the coated film is constant. The slope is calculated from this steady state. Based on this slope, the water vapour transmission rate can be calculated using the following formula.

$$WVTR = \frac{s * 0.01 * P * V}{R * T * (\pi * r^2)}$$

P	Saturation vapour pressure of water, depending on temperature	T	Absolute temperature
	2803 Pa		296 K
R	Specific gas constant of water	r	Radius of the sample
	$461.5 \frac{J}{kg*K}$		0.025 m
V	Volume of the closed tube	s	Slope
	9.81 * 10-5 m³		

III. RESULTS

The measured results are shown in Figure 3. The first number of the layer systems always describes the thickness of aluminium oxide. The second number after the hyphen related to the thickness of titan oxide. Both numbers are given in the unit nm.

In the first test, the Adwill film without coating was measured as a reference. Here the WVTR values showed an average of 2.7882 $\frac{g}{m^2*d}$ with a standard deviation of 0.8338 $\frac{g}{m^2*d}$. Subsequently, the first layer system with 20 nm was measured. Striking here are the systems 2 (2x (7-3)) and 3 (15-5). Both show a high scattering of the measured values with a standard deviation of 0.1488 $\frac{g}{m^2*d}$ and respectively 0.1308 $\frac{g}{m^2*d}$.

The next layer thickness with 40 nm shows lower values for system 1 and 2 compared to the previous ones. The layer system 2 shows an approximate improvement by a factor of 10 from 0.6378 $\frac{g}{m^2*d}$ (20nm) to 0.0772 $\frac{g}{m^2*d}$ (40nm). On the other hand, layer system 3 with 0.8051 $\frac{g}{m^2*d}$ is clearly worse than the previously measured system 3. With standard deviations of 0.0206 $\frac{g}{m^2*d}$ down to 0.0041 $\frac{g}{m^2*d}$, all systems show a lower dispersion compared to the three systems at 20 nm.

The last layer thickness measured was 60 nm. All three systems performed significantly worse than those previously measured. Each system has a higher water vapour transmission rate. In addition, layer system 3 (15-5) has a very high scatter of values with a standard deviation of 0.3296 $\frac{g}{m^2*d}$.

Some measurements were repeated. Firstly, the measurements of 20 nm with the layer systems 2 (2x(7-3)) and 3 (15-5) were measured again. Here, the Adwill film was so difficult to remove from the wafer that visible mechanical damage had already occurred on the test samples. Furthermore, the layer systems 1 (10-10) and 2 (2x(7-3)) were repeated at a layer thickness of 60 nm. Here the result was worse than expected. The initial hypothesis that by increasing the thickness of the layer system, the water vapour transmissions rate would decrease could not be demonstrated, which is why these tests were measured again.

All repeated experiments were coated now on a thicker Adwill film base substrate, with a thickness of 203 µm. This should provide more stability when detaching from the wafer, so that damage and stress to the layers can be kept to a minimum. The barrier effect of the Adwill film is infinitesimal compared to the deposited layers. Therefore, the thicker film can be neglected in the measurement results.

The repeated tests of the layer thickness 20 nm showed a water vapour transmission rate of 0.0231 $\frac{g}{m^2*d}$ in both layer systems. The values for the layer thickness 60 nm were 0.0373 $\frac{g}{m^2*d}$ for system 1 and 0.0244 $\frac{g}{m^2*d}$ for system 2. For both repeated layer thicknesses, the scatter of the values was very low with standard deviations between 0.0013 $\frac{g}{m^2*d}$ and 0.0046 $\frac{g}{m^2*d}$.

IV. DISCUSSION

As described in the chapters before, the water vapour transmission rate of different layer systems was measured. The original hypothesis was that by increasing the thickness of the individual layer systems, the rate measured in $\frac{g}{m^2*d}$ would decrease, speaking for better barrier properties. This hypothesis could not be confirmed by the carried-out measurements.

First, the thicker layer systems perform worse than the thinner ones in some cases by a factor of 10. The measured values show a rather high scatter. The reason for this could be the internal stress, which is bigger in thicker layers than in thinner ones. The thickest layer, 60 nm, has the highest water vapour transmission rate of all layer systems. The thicker layers are not as flexible as the thinner ones. Consequently, they break up more easily when they detached from the wafer. The layer system to be measured is no longer homogeneous.
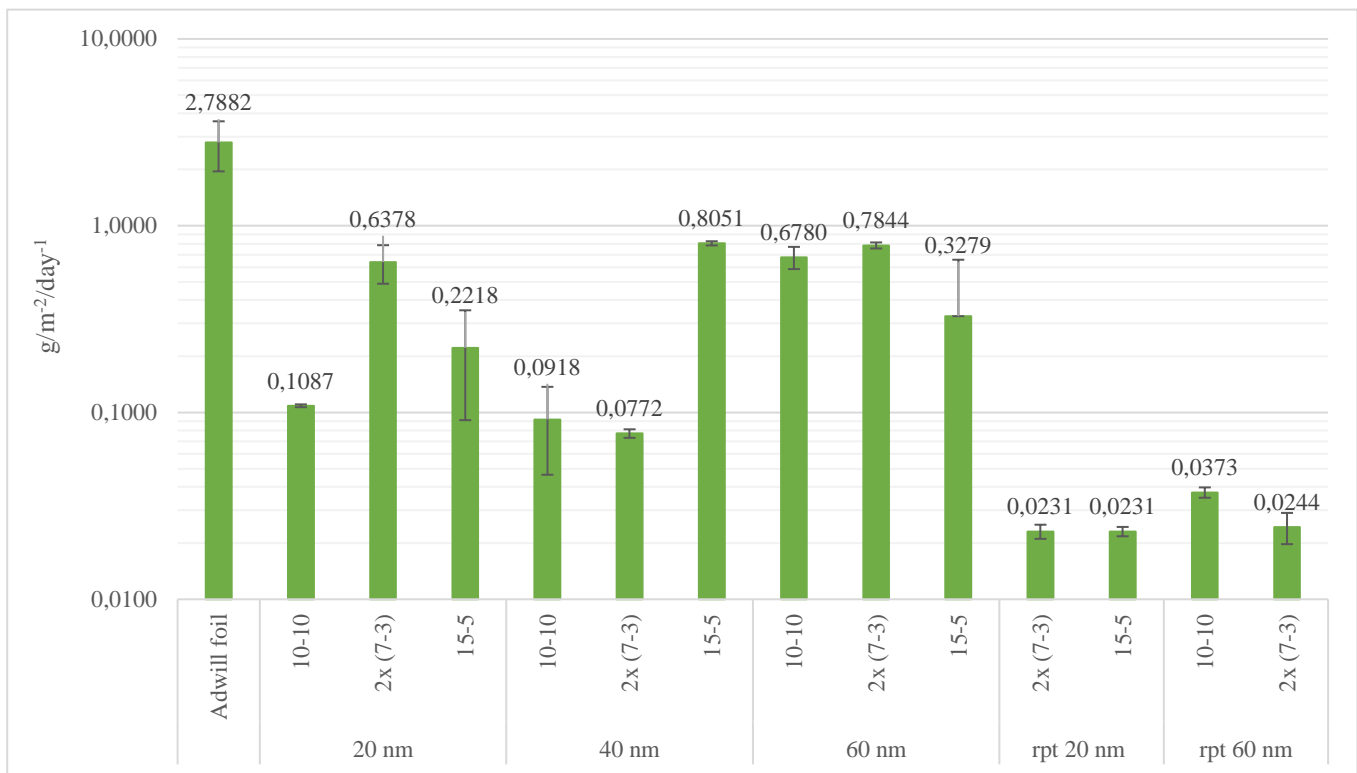
Figure 3: Water vapour transmissions rate of the different multilayer coating systems

Second, the layer system 3 (15-5) with a layer thickness of 40 nm stands out with particularly poor values compared to the previous tests. In all three measurements, similarly bad values were measured. Of the entire layer system, the metal oxide layers contribute the most to the barrier effect. Such a high WVTR must therefore be associated with a defective metal oxide layer.

Last in the repeated tests, a thicker Adwill film was chosen to generate more stability for the layer systems. These tests consistently show a lower WVTR. It can be concluded that there is a relationship between the base substrate thickness, the thickness of the layer system and their flexibility. A thinner base substrate consequently means thinner deposited layer systems, which can follow the flexibility of the substrate. Thicker layer systems require thicker base substrates for more stability.

V. CONCLUSION & OUTLOOK

Parylene-C is ideally suited as a coating material for medical implants because of its flexibility and biocompatibility. Long-term implants can be realised by layering Parylene-C with metal oxides and created so-called multilayer hybrid systems. These systems must be selected in such a way, that a minimum amount of water penetrates through them. The amount of water vapour that has transmitted through the layer systems was measured in this work.

For sample production, the layer system must be deposited on a substrate. Direct deposition and subsequent release onto the wafer are not possible without damaging the layer system. For this reason, the layer systems to be measured were deposited on an Adwill film.

Against the expectations, thicker layer systems showed higher water vapour transmission rates than thinner ones. The trend from the measured values indicates a new hypothesis. The layer thickness generated by ALD must be adapted to the thickness and flexibility of the base substrate. If the ratio is incorrectly chosen, the coating layer could not follow the flexibility of the base substrate and get damaged. Consequently, no statistically reliable measurements can be made. The new hypothesis must be investigated in further experiments.

VI. REFERENCES

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