V. Radun*, R. P. von Metzen, T. Stieglitz, V. Bucher, and A. Stett

Evaluation of adhesion promoters for Parylene C on gold metallization

Abstract: Delamination of thin film polymeric coatings from metallization layers is a common cause of failure in biomedical implants. To address the problem, different adhesion promotion techniques can be applied which include surface pre-treatment with oxygen and argon plasma and the use of different adhesion promoters. In this paper the applicability of titanium (Ti), silicon oxide (SiO_x), diamond-like carbon (DLC), tetramethylsilane (TMS) and aluminium oxide (AlO_x) as adhesion promoters is evaluated. A cross cut, peel and scratch test are used to qualify and quantify the adhesion before and after storage in phosphate buffered saline (PBS) for 48 hours at a temperature of 37 °C. Promising results could be achieved by a combination of Ti and DLC as well as by AlO_x.

Keywords: Adhesion; Parylene C; Micro-implants; Adhesion measurement; Cross cut test; Peel test; Scratch test

1 Introduction

Active biomedical micro-implants usually employ flexible electrode arrays for recording or stimulation purposes. The basic structure of those arrays consists of a metallization and an encapsulating polymer as top and bottom layer. Due to the restrictive requirements on materials in biomedical applications, such as biocompatibility, mechanical and electrical properties, there are only few applicable polymers. Popular choices are polyimide and Parylene C [1, 2]. However, a critical aspect of these thin-film coatings is insufficient adhesion to inorganic surfaces. Especially in physiological environment poor adhesion constitutes one of the major challenges. On the one hand, layer delamination and resulting water intrusion changes the electrical functionality through to system failure. On the other hand, without intact adhesion mechanical loads can easily break the delicate metallization structures, also resulting in system failure [3]. As a consequence, adhesion can be identified as limiting factor for long-term reliability. Despite technological advances a lifetime functionality of neural electrodes has not yet been accomplished.

In order to improve durability and reliability efforts have been made to quantify and improve adhesion. Different adhesion promotion techniques were investigated in the past and moderate improvements could be achieved by the application of surface pre-treatments. The use of argon plasma has two effects: It removes contaminations from the surface and simultaneously roughens it for better mechanical interlocking of two distinct layers [4]. Applying oxygen plasma afterwards has proved to successfully increase adhesion due to further surface roughening as well as surface activation [4]. By increasing the amount of carbonyl groups higher surface reactivity is achieved [4]. Additionally, adhesion promoters can be used to form chemical bonds to both, metallization and polymeric surface. In this paper samples of a multi-layer system with the polymer on top of the metallization layer were fabricated according to standard fabrication processes for neural electrodes. Both surface pre-treatments were applied and the influence of different adhesion promoters was tested and compared.

In order to understand and further improve adhesion a reliable measurement setup is necessary. However, until now the quantitative assessment of adhesion of thin film layer systems is problematic. To address that problem, test methods from different fields of applications were transferred to biomedical layer systems: First, a cross cut test serves as rough estimation of the adhesion properties [5]. Second, the peel test is used for first quantifications. However, one has to keep in mind undesired side effects during testing such as non-linear viscoplastic deformation of the materials [2, 6]. As third test method, the scratch test was applied to secure the previous results. To obtain realistic results, all samples were immersed in PBS at body temperature to simulate the influence of the wet and ionic body fluids.

*Corresponding Author: V. Radun: Natural and Medical Sciences Institute (NMI) Tübingen, Markwiesenstraße 55, 72770 Reutlingen, Germany and Hochschule Furtwangen, Jakob-Kienzle-Straße 17, 78054 Villingen-Schwenningen, Germany, E-mail: Victoria.Radun@nmi.de; rav@hs-furtwangen.de
R. P. von Metzen, A. Stett: Natural and Medical Sciences Institute (NMI) Tübingen, Markwiesenstraße 55, 72770 Reutlingen, Germany, E-mail: Rene.vonMetzen@nmi.de, Alfred.Stett@nmi.de
T. Stieglitz: Institut für Mikrosystemtechnik – IMTEK, Georges-Köhler-Allee 102, 79110 Freiburg, Germany, E-mail: stieglitz@imtek.de
V. Bucher: Hochschule Furtwangen, Jakob-Kienzle-Straße 17, 78054 Villingen-Schwenningen, Germany, E-mail: buv@hs-furtwangen.de

2 Methods

The multilayer systems under test were fabricated by means of various thin film technologies. Each sample consisted of a gold metallization, the coating polymer Parylene C and a specific adhesion promoter in between.

Generally speaking, adhesion refers to the attractive force between two materials that has to be overcome in order to separate them. Adhesion mechanisms can be differentiated into three types: The physical bonds (Van der Waals and polar attractions), chemical bonds (ionic, covalent bonds) and mechanical interlocking caused by surface roughness [7]. Due to many influencing factors no universally applicable method of adhesion measurement exists until now. For this reason, the results of three different adhesion tests were evaluated and compared.

2.1 Sample fabrication

The sample fabrication of the upper layer system consisted of three different steps. First, an approx. 300 nm gold metallization was sputter deposited on a 4.9 x 4.9 cm^2 glass substrate (Z550 sputter system). After an intermediate cleaning step, the inorganic adhesion promoters and their combinations were either again sputter deposited (Ti, AlO$_x$) or deposited using plasma-enhanced chemical vapour deposition (DLC, TMS, SiO$_x$) with different layer thicknesses in the range of 100 nm. Finally, a 10 µm coating of Parylene C was polymerized on top of the adhesion promoting layer using the Gorham process [2].

The exact deposition parameters are summarized in Table 1. For each material combination three samples were fabricated. A system without any adhesion promoter served as reference.

2.2 Cross cut test

To obtain a basic overview of the adhesion achieved with different adhesion promoters, the cross cut test was performed after storage of the samples. Based on the guideline of ISO 2409:2007, a grid with six vertical and six horizontal cuts in a distance of 2 mm was lasered (LPKF Protolaser U) through the polymer surface. The Intertape® 4118 with an adhesion force of 2.8 N/cm (specified by manufacturer) was applied over the lattice pattern and afterwards manually removed at an angle of approximately 60°. According to the extent of delamination, the adhesion is classified into six categories ranging from 0% (key figure = 0) to more than 65% (key figure = 5) delaminated struc-

tures [5]. Three tests were performed per multi-layer system.

2.3 Peel test

An adhesion test method with a higher degree of validity and significance is the peel test. The test was employed after immersion in PBS since beforehand adhesion succeeded cohesion which resulted in torn samples. For the test, peel strips with dimensions of 1 x 4.9 cm^2 were prepared using laser structuring. One end of those strips was attached to the load cell of the testing machine (Zwick/Roell Z020). At the same time the substrate was fixed to the table. During the test the peel gripper moved upwards with a constant velocity of 10 mm/min while the substrate's horizontal position was adjusted as to keep the peel angle at 90°. The recorded peel force divided by the width of the peel strip equals the adhesion force P$_{90}$ [2]. For each combination three tests were performed.

2.4 Scratch test

Apart from the cross cut and peel test the so-called scratch test is a well-established method to qualify and compare the adhesion of different coatings. With the NanoScratch Tester by csm instruments a scratch in the surface is applied using a sphero-conical diamond stylus with a radius of 2 µm. It is drawn across the surface at a constant speed of 1 mm/min. Simultaneously, the employed normal force increases from 0.01 N to 0.2 N resulting in increasing stresses at the layer interface. At a certain point, adhesion failure occurs and the coating delaminates. The critical load L$_c$ is a measure for the adhesion strength and is identified by optical means [8]. During the test procedure, normal force, frictional force, penetration depth and displacement are recorded and one test is performed per multi-layer system.

3 Results

3.1 Cross cut test

Prior to storage in PBS all samples except those applying DLC, Ti-SiO$_x$ and TMS as adhesion promoter showed excellent adhesion with a key figure of 0 in the cross cut test.

This implies that the weakest interface is that between the applied tape and Parylene C with a specified adhesion

Table 1: Deposition parameters for metallization, different adhesion promoters and polymer encapsulation.

Material	Process parameters		
	Plasma	Time / Power	Layer thickness
Au		360 s / 1000 W	~300 nm
Silane A174	Ar, O_2	300s	
DLC (TMS / C_2H_2)	Ar	230 s / 400 V	100 nm
TMS	Ar	230 s / 400 V	105 nm
Ti		360 s / 1000 W	~30 nm
Ti – SiO_x	Ar	420 s / 150 W	100 nm
(O_2 / HMDSO)			
Ti – Silane A174	Same as separate processes for Ti and Silane A174		
Ti – DLC – Silane A174	Same as separate processes for Ti, DLC and Silane A174		
AlO_x –	Ar, O_2 Pulsed DC sputtering	T = 1.5 µs,	510 nm
Silane A174		F = 200 kHz,	
		7200 s / 5000 W	
Parylene C	Ar, O_2	Pressure = 10 Pa	~10 µm

Table 2: Summary of cross cut test results.

Adhesion promoter	Key figure before storage	Key figure after storage
None	0	1
Ti	0	1
DLC	1	2
Ti-SiO_x	1	3
TMS	2	4
Ti – Silane A174	0	0
Ti – DLC – Silane A174	0	0
AlO_x – Silane A174	0	0
Silane A174	0	2

strength of 2.8 N/cm. 48 hours of storage in PBS resulted in a decreased adhesion strength as denoted in Table 2.

3.2 Peel test

All samples that were tested prior to immersion in PBS were torn due to better adhesion of the layers than cohesion of the Parylene C. Cohesion failed at a peel force of approximately 4.90 ±0.26 N. Only after storage of 48 hours, the polymer coating could be peeled off the samples listed in Table 3. The other samples could not be evaluated. However, the coarse ranking of the results corresponds to that of the cross cut test.

3.3 Scratch test

In Figure 1 the results of the scratch test on different samples are arranged corresponding to increasing adhesion strength. The critical normal force L_c at which first delamination occurred is denoted by the dashed lines.

In numbers, the normal force ranges from 0.11 N (Ti), 0.12 N (SiO_x), 0.13 N (DLC), 0.14 N (TMS) to 0.15 N (no adhesion promoter). Note that the first delamination cracks show smooth edges which indicates low adhesion strength.

4 Discussion

By applying different adhesion test methods, the performance of various adhesion promoters was investigated and evaluated. Table 4 summarizes the results. Marked in blue is the consistency of the test results while orange shading indicates contradictory results. With the exception of the results for Ti as adhesion promoter, cross cut and peel test yield qualitatively corresponding results. A critical aspect of the peel test is the validity of the results if the sample is not clamped perfectly unbowed. Furthermore, the measuring range of the test is limited to approximately 4.9 N/cm since above that the tear strength of a

Table 3: Summary of peel test results.

Adhesion promoter	$P_{90°}$ in mN/cm (after storage) Mean value + standard deviation
Ti	355, other two samples were torn
DLC	63 ±33
Ti – SiO$_x$	51 ± 6
TMS	Not measurable - delaminated
Silane A174	1575 ± 489

Table 4: Summary of all test results.

Adhesion promoter	Key figure	P_{90} in mN/cm	L_c in N	Evaluation adhesion
None	1	torn	0.15	Good
Ti	1	355, 2 torn	0.11	Ok
DLC	2	63 ± 33	0.13	Bad
Ti – SiO$_x$	3	51 ± 6	0.12	Bad
TMS	4	delaminated	0.14	Bad
Ti – Silane A174	0	torn	–	Above test limit
Ti – DLC – Silane A174	0	torn	–	Above test limit
AlO$_x$ – Silane 174	0	torn	–	Above test limit
Silane A174	0	1575 ± 489	–	Ok
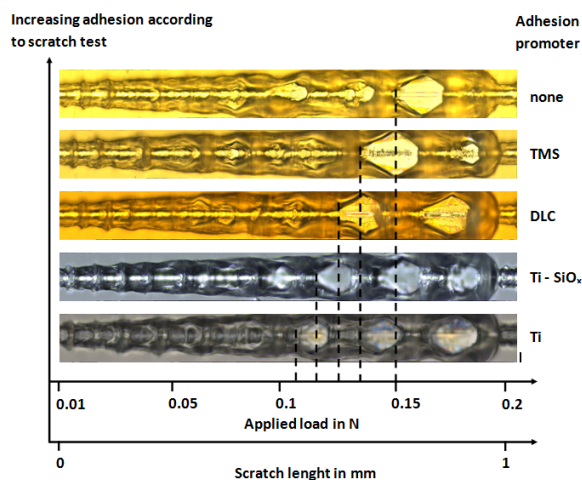
Figure 1: Summary of scratch test results.

10 μm thick Parylene C test strip is exceeded and the material's cohesion fails. Even though, a test result exists for the peel test with Ti as adhesion promoter, two of the samples were torn due to the above-mentioned limitation. Drying effects after immersion almost immediately increased the adhesion strength again above the limit such that only one sample could be measured. In [6] similar measurements were performed. A comparison is possible for the adhesion performance if no adhesion promoter or silane A174 is ap-

plied. Generally, silane A174 decreases adhesion strength between gold and Parylene C. However, the numerical values do not correspond, possibly due to different test substrates. While [6] uses smooth silicon wafers, the surface roughness of glass substrates used in this work may be higher, thus increasing mechanical interlocking.

The scratch test proved to be more challenging to interpret correctly due to the ductility of the polymeric surface. It can be seen in figure 1 that plastic deformation took place since piles of the coating are repeatedly accumulated at the length of the scratch. Furthermore, there are process-related inhomogeneities in the thickness of the Parylene C coating which can further falsify the result since the critical force depends on the surface thickness. This is also a possible explanation for deviations between the scratch test results and the previous tests results.

In summary, it can be said that the combination of Ti and DLC as well as AlO$_x$ showed promising potential as adhesion promoters and will be subject of further studies. In the future, not only the adhesion of Parylene C to metallization layers but also that of polyimide will be tested. Furthermore, samples of the second layer system (polymer, adhesion promoter, metallization) will be fabricated and investigated. Accelerated aging tests for a longer time period will give some indication of the achievable long-term adhesion.

Author's Statement

Conflict of interest: Authors state no conflict of interest. Material and Methods: Informed consent: Informed consent has been obtained from all individuals included in this study. Ethical approval: The research related to human use has been complied with all the relevant national regulations, institutional policies and in accordance the tenets of the Helsinki Declaration, and has been approved by the authors' institutional review board or equivalent committee.

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