

PDMS-Parylene Adhesion Improvement via Ceramic Interlayers to Strengthen the Encapsulation of Active Neural Implants

Bakhshaee Babaroud, Nasim; Dekker, Ronald; Serdijn, Wouter; Giagka, Vasiliki

DOI

[10.1109/EMBC44109.2020.9175646](https://doi.org/10.1109/EMBC44109.2020.9175646)

Publication date

2020

Document Version

Accepted author manuscript

Published in

42nd Annual International Conferences of the IEEE Engineering in Medicine and Biology Society

Citation (APA)

Bakhshaee Babaroud, N., Dekker, R., Serdijn, W., & Giagka, V. (2020). PDMS-Parylene Adhesion Improvement via Ceramic Interlayers to Strengthen the Encapsulation of Active Neural Implants. In *42nd Annual International Conferences of the IEEE Engineering in Medicine and Biology Society: Enabling Innovative Technologies for Global Healthcare, EMBC 2020* (pp. 3399-3402). Article 9175646 (Proceedings of the Annual International Conference of the IEEE Engineering in Medicine and Biology Society, EMBS; Vol. 2020-July). IEEE. <https://doi.org/10.1109/EMBC44109.2020.9175646>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

PDMS-Parylene Adhesion Improvement via Ceramic Interlayers to Strengthen the Encapsulation of Active Neural Implants

Nasim Bakhshae Babaroud, Ronald Dekker, Wouter Serdijn, and Vasiliki Giagka

Abstract—Parylene-C has been used as a substrate and encapsulation material for many implantable medical devices. However, to ensure the flexibility required in some applications, minimize tissue reaction, and protect parylene from degradation *in vivo* an additional outmost layer of polydimethylsiloxane (PDMS) is desired. In such a scenario, the adhesion of PDMS to parylene is of critical importance to prevent early failure caused by delamination in the harsh environment of the human body. Towards this goal, we propose a method based on creating chemical covalent bonds using intermediate ceramic layers as adhesion promoters between PDMS and parylene.

To evaluate our concept, we prepared three different sets of samples with PDMS on parylene without and with oxygen plasma treatment (the most commonly employed method to increase adhesion), and samples with our proposed ceramic intermediate layers of silicon carbide (SiC) and silicon dioxide (SiO₂). The samples were soaked in phosphate-buffered saline (PBS) solution at room temperature and were inspected under an optical microscope. To investigate the adhesion property, cross-cut tape tests and peel tests were performed. The results showed a significant improvement of the adhesion and in-soak long-term performance of our proposed encapsulation stack compared with PDMS on parylene and PDMS on plasma-treated parylene. We aim to use the proposed solution to package bare silicon chips on active implants.

I. INTRODUCTION

Neural interfaces, in general, are used to interact with the nervous system, to record, stimulate or block electrical activity. For this purpose, they are implanted close to the targeted region. To reduce the foreign body response, prevent water permeation into the implanted electronics, and avoid diffusion of corrosion products to the tissue, it is necessary to encapsulate the implantable device [1]. Polymers are commonly used as an encapsulation material due to their mechanical properties. In particular, parylene has the advantage of easy deposition and etching processes, high biocompatibility, and a good ionic barrier property, which makes it a very promising material both for the substrate as well as the encapsulation layer of the implant. However, its high Young's modulus makes it still relatively stiff compared to the tissue [2]. This stiffness might be tolerated in some applications, but might be completely unsuitable in others,

N. Bakhshae, R. Dekker, W. A. Serdijn and V. Giagka are with the Department of Microelectronics, Faculty of Electrical Engineering, Mathematics and Computer Science, Delft University of Technology, Delft, The Netherlands. (N.bakhshae@tudelft.nl, V.Giagka@tudelft.nl).

V. Giagka is also with the Fraunhofer Institute for Reliability and Micro-integration IZM, Berlin, Germany.

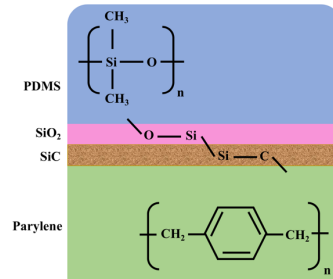


Figure 1. A smooth transition of chemical bonds between parylene and PDMS to improve the adhesion.

where softer elastomers such as PDMS are necessary to avoid tissue damage [3]. In addition, [4] suggests that strong tissue reaction can be developed around parylene-C-based implants after 8-month *in vivo* tests, while tissue reaction to PDMS is minimal. [5] also shows oxidation and chlorine abstraction of parylene after 3.25 years of implantation. As a consequence, an additional outmost encapsulation layer with a similar mechanical property to the tissue is desired.

PDMS has been selected for this purpose due to its low Young's modulus [2]. In such a scenario, the adhesion between the parylene and PDMS layers will be critical for the longevity of the neural interface [6]. Due to the different polymeric backbones of parylene and PDMS, and their hydrophobicity [7], adhesion between them is often based on physical bonds, which are relatively weak, rendering the layers prone to delamination, especially when water is present at the interface [8]. A chemical bond on the other hand is stronger by nature, hence is expected to lead to longer encapsulation lifetimes. To create such chemical bonds a number of different plasma treatments has been proposed to enhance the bonding of PDMS to parylene for microfluidic applications [7]. In another approach, thin ceramic intermediate layers were used to make a chemical bond between PDMS and polyimide [8].

Inspired by the above approach, we have investigated the use of intermediate thin films, namely SiC and SiO₂, to create transient covalent bonds between our parylene and PDMS, as illustrated in Fig. 1. Here, we assume that a carbon-carbon chemical bond can be created between SiC and parylene. A silicon-silicon covalent bond can be created between SiO₂ and SiC [8]. PDMS is expected to have a strong adhesion to SiO₂ due to the presence of hydroxyl groups at the interface.

In the rest of this paper: Section II describes the experiments, results are presented in Section III and discussed in Section IV. Finally, Section V concludes the paper.

II. METHODS

A. Sample Fabrication

1) Si-based samples

To evaluate the proposed concept, relevant test structures were fabricated, as illustrated in Fig. 2.

A 400nm SiO₂ layer was deposited at 400 °C on a Si wafer as an isolation layer by using a plasma-enhanced chemical vapor deposition (PECVD) process. A 5μm parylene layer was deposited using a SCS PDS 2010 parylene coater that employs a chemical vapor deposition (CVD) technique at room temperature, followed by applying a A-174 adhesion promoter. To create flavor 2(a), PDMS (Dow Corning Sylgard 184) was mixed with a curing agent at a 10:1 ratio, spin-coated at 1250 rpm directly on parylene, and cured at 75°C for 3 hours. This resulted in a 50 μm thick layer. For the samples of Fig. 2(b), an oxygen plasma treatment (50 sccm of oxygen flow, 60 W, 0.25 mTorr, Diener electronic GmbH Germany) was applied on the parylene surface for 1 min before PDMS coating to increase the surface activation energy in order to improve the adhesion. The proposed SiC-SiO₂ stack of Fig. 2(c) was created as follows: 25 nm SiC is PECVD deposited on parylene at 180°C temperature. Then 25 nm SiO₂ is deposited in the same chamber. Finally, the PDMS layer is spin-coated on top. For the SiC deposition, three different recipes (*R1*, *R2*, and *R3*) have been developed, as in Table I. Based on [9], a silane starving mode (*R3*) and a non-silane starving mode (*R1* and *R2*) were chosen. The silane starving and non-silane starving modes refer to the precursor ratio (SiH₄/(CH₄+SiH₄)) of 0.17 and 0.29, respectively. Hydrogen is also used as dilution gas. Based on this work, low silane and high hydrogen flow result in higher Si-C bond density.

2) Free standing membrane

This set of test structures was developed for the needs of the peel test described in Section II B.2. For these, the Si/SiO₂ substrates were removed to create free standing parylene-PDMS stacks with all the flavors of Fig. 2. To see the differences between the result for adhesion test for samples with and without ceramic layers, these layers were deposited only on half of the wafer (using some metal masks to cover the other half during deposition) as in Fig.2(d).

B. Characterization

1) Tape Test

To investigate the adhesion between SiC and parylene, a tape test was performed based on ASTM 3359 [10]. To do this, several samples with SiC only (deposited using the three recipes of Table I) on parylene were created. Next, a tape test was performed at a 180-degree on the grid pattern created previously on the film. The grid pattern was optically evaluated before and after test.

2) Peel Test

To do the peel test, one of the layers is clamped and remains fixed in position while the other layer (which is attached onto a moving arm of the testing tool, here a Zwick 1455 tensile testing machine, Fig. 3(b)) is pulled on at a constant speed and at an 180-degree angle. For this test, samples with the same encapsulation stacks as in Section III A.1 were prepared. A Kapton tape was applied on the sample

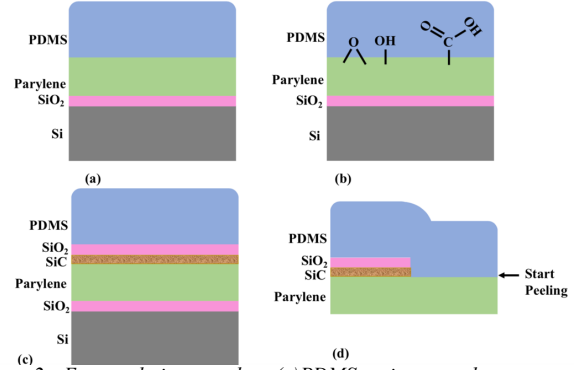


Figure 2. Encapsulation stacks: (a)PDMS spin coated on untreated parylene, (b)PDMS spin coated on plasma-treated parylene, (c)PDMS spin coated on parylene with ceramic interlayers, (d) free standing membrane.

Table I. Three different recipes used for SiC PECVD deposition at 180°C.

Recipe	Deposition parameters				
	SiH ₄ (sccm)	CH ₄ (sccm)	H ₂ (sccm)	P (W)	P (mbar)
<i>R1</i>	20	45	0	4	0.7
<i>R2</i>	1.6	3.7	200	6	2.6
<i>R3</i>	2	10	90	30	2

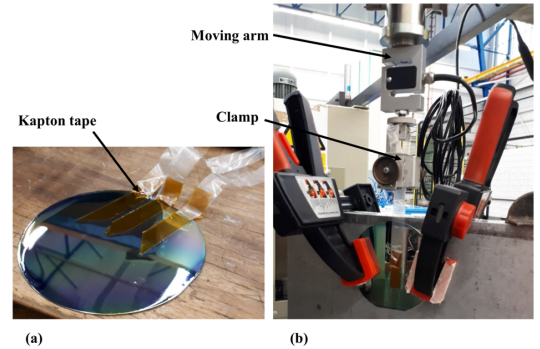


Figure 3. Sample (a) before and (b) after installation in the peel test machine.

before PDMS coating to create a clamping point for the tool and initiate the peeling (see Fig. 3(a)). The peel test was performed by pulling on the PDMS layer at 500μm/s and a load of 10 N via the attached Kapton tape. The above test structures allow for the evaluation of the adhesion of PDMS to the layer underneath. Hence, for the samples in Fig. 2(c) only the adhesion of PDMS to SiO₂ can be evaluated. To evaluate the adhesion among the remaining layers in Fig. 2(c) the free standing membranes of Section II A.2 were created to allow peeling from both the parylene and the PDMS sides.

3) PBS Soak Test

To evaluate the performance of our encapsulation stack in a wet environment like the human body, samples (with grid pattern created on them) were soaked in a PBS solution at room temperature for 60 days. All samples were monitored optically and a tape test was performed after 12 and 60 days.

4) Comparison of the three SiC recipes

In addition to adhesion improvement, ceramic layers also act as a barrier layer against moisture. A layer with smaller

number of pinholes is expected to be a better moisture barrier. To evaluate the number of pinholes of different recipes for SiC, samples including only three different SiC recipes on 400 nm PECVD SiO₂ were placed inside Buffered HydroFluoric acid (BHF) 1:7 for 10 minutes. BHF can penetrate through the pinholes in SiC to reach SiO₂ and etch it, which can be detected optically.

Fourier Transform Infrared spectroscopy (FTIR) and stress were measured for each recipe compared to a bare Si wafer. A comparative study of the FTIR diagrams for the three recipes could indicate the ones with the higher Si-C bond density. Layers with a higher Si-C bond density are expected to have less pinholes, but a higher amount of stress.

III. RESULTS

A. Tape Test

As shown in Fig. 4(a,b), some parts of the layer peeled off from the substrate after the tape test. Detailed inspection revealed that the delamination happened between parylene and its SiO₂ substrate (Fig. 4(b)), leaving the parylene-SiC layers still firmly attached to each other. This result shows that the adhesion of SiC to parylene is better than the adhesion of parylene to SiO₂ (which was confirmed by a separate test).

B. Peel Test

The samples of Section II A.1 that had PDMS on parylene with and without oxygen plasma were easily peeled. On the other hand, no peeling was observed on samples that included the whole stack. The adhesion was so strong that the peel test caused the Si wafer to break and the PDMS layer to tear apart before peeling started. Efforts to strengthen the PDMS layer by making it thicker (80 μ m) lead to the same result.

For the flexible test structures of Section II A.2, peeling was performed by hand. As shown in Fig. 5, peeling of the PDMS layer was very easy on the areas without ceramic layers. But when the peeling reached to the region with ceramic layer, it was not possible anymore and PDMS was torn at the edge of this region, as can be seen from Fig. 5(b).

C. PBS Soak Test

As it was expected, for those samples that had PDMS on parylene with and without oxygen plasma, delamination of PDMS happened after creating the grid patterns on the film and even before a tape test. For those samples that included the whole stack of encapsulation, tape tests performed after 12 and 60 days revealed no delamination.

D. Comparison of the three SiC recipes

As illustrated by the optical image in Fig. 6, there are more pinholes in the *R1* (without hydrogen dilution gas) compared to *R2* and *R3*. The presence of the pinholes depends on the chemistry used for deposition and the cleanliness of the surface. The characterizations for three different SiC layers show less pinholes in the recipes with higher amount of hydrogen dilution gas (*R2* and *R3*), as it can compensate the effect of low deposition temperature (180 °C, due to the low glass transition temperature of parylene) and lead to higher Si-C bond density [9]. As expected, more pinholes and less stress are observed in the recipe without any hydrogen gas (*R1*).

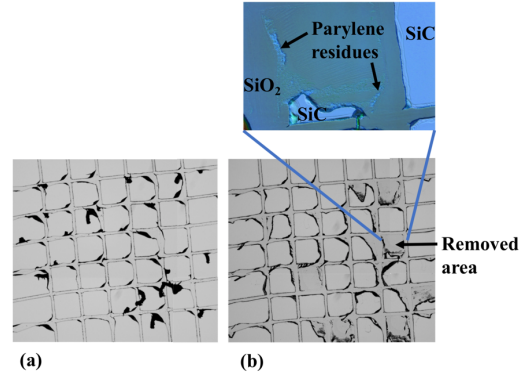


Figure 4. Optical image of a sample with SiC on parylene, (a) before the tape test, (b) after the tape test with zoomed-in picture of the removed area.

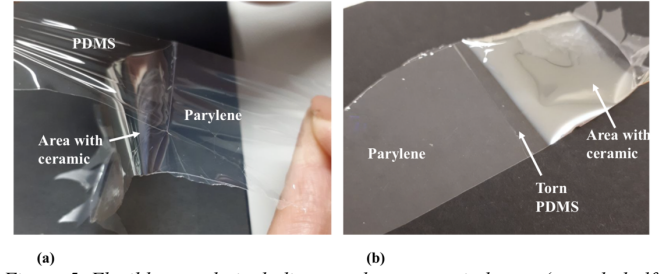


Figure 5. Flexible sample including parylene, ceramic layers (on only half of the sample) and PDMS (a) during peeling, (b) torn PDMS after peeling.

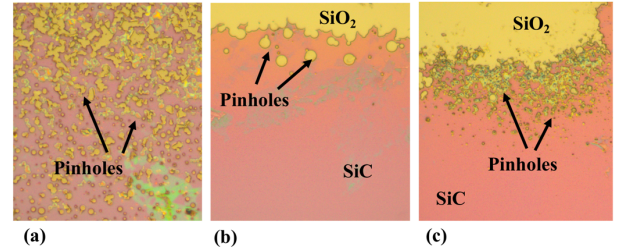


Figure 6. Optical image of pinholes in SiC using recipe (a) *R1*, (b) *R2*, (c) *R3*.

To gain an insight regarding the Si-C bond density of each of the developed recipes, we look at their FTIR diagram in Fig. 7 (here all waveforms are normalized to the maximum peak). In the FTIR spectrum for a SiC layer, based on [9] we expect the following: a peak at a wavenumber (1) between 720 to 780 cm⁻¹ corresponding to Si-C stretching bonds, (2) around 2000 cm⁻¹ related to Si-H_n bonds, and (3) between 2800 to 3000 cm⁻¹ for C-H_n bonds. From these results we observe that *R3* indeed has a high Si-C peak, as expected. However, it also exhibits a higher C-H_n peak, which could explain its relatively higher number of pinholes compared to *R2* (Fig. 6).

R1, *R2* and *R3*, resulted in 205, 585 and 530 MPa compressive stress, respectively. Stress could negatively affect the adhesion and lead to delamination. To investigate this, especially in the humid environment in the long term, samples with different recipes for SiC were placed in soak and investigated after 12 and 60 days. The result showed that the adhesion was so strong that there was no delamination even for those recipes with high amount of compressive stress (*R2* and *R3*).

IV. DISCUSSION

To improve the adhesion of PDMS to parylene, SiC and SiO₂ are used as intermediate adhesion layers. The adhesion of SiC to parylene was initially evaluated with a tape test. The result of this test revealed strong adhesion between the two layers under test, however, it must be noted that such a test is not ideal for investigating thin ceramic layers, as peeling them at 180-degree angle may induce damage in the thin layer. In addition, the tape test can only give a qualitative evaluation of the adhesion strength. The peel test can give a more quantitative evaluation, as the force at which each layer is peeled from its substrate can be recorded. Here, such a test showed that the adhesion for the stack that includes ceramic layers was much stronger than the other two variations. However, peeling of PDMS was not possible for the sample with ceramic layers since the PDMS layer was torn before peeling. Therefore, no quantitative result was reported. The peel test also revealed no difference in the adhesion between plasma treated and non-treated samples. For a better and more complete comparison between these samples, the effect of different power, pressure, and oxygen flow parameters during the plasma treatment process should also be investigated.

As mentioned before, it is expected that ceramic layers can also act as a barrier layer against moisture, which is important especially when the adhesion is not achieved. Our so far soak tests revealed no difference in the performance of the three different recipes of SiC, despite their different characteristics in terms of pinhole density and stress, as adhesion was never compromised throughout the soaking period. To better understand the resulting barrier properties, water vapor transmission rate tests could be employed for a more thorough investigation.

V. CONCLUSION

In conclusion, in this paper we investigate the effect of using thin ceramic layers to improve the adhesion of PDMS to parylene for the encapsulation of implantable devices. Results show that the adhesion of PDMS to parylene after using intermediate SiO₂ and SiC is so strong that no delamination was seen after 60 days soak test at room temperature. In comparison, PDMS-on-parylene and PDMS-on-plasma treated parylene delaminated easily by hand during the same test. This improvement was also confirmed by tape and peel tests on dedicated test structures.

The proposed ceramic layers have a dual function, acting at the same time as a barrier layers against water permeation. In this paper three different SiC recipes were evaluated with respect to the number of pinholes present in each layer. The result shows that the non-silane starving mode with high amount of hydrogen leads to less pinholes in the layer.

Future work will be focusing on further investigations of the adhesion under the effect of applying bias voltage at elevated temperatures, as we expect that such experiments may reveal failure mechanisms which cannot be observed in passive tests, as in [11]. Eventually it is our intension to use the proposed process for the packaging of bare silicon chips

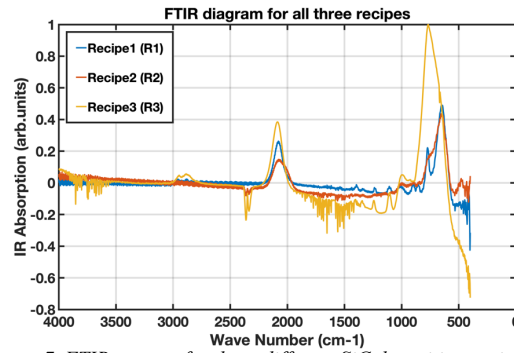


Figure 7. FTIR spectra for three different SiC deposition recipes.

on active implants [12].

ACKNOWLEDGMENT

This research was supported by POSITION-II project funded by the ECSEL JU under grant number Ecsel-783132-Position-II-2017-IA.

REFERENCES

- [1] V. Giagka and W. A. Serdijn, "Realizing flexible bioelectronic medicines for accessing the peripheral nerves – technology considerations," *Bioelectron. Med.*, vol. 4, no. 8, pp. 1–10, 2018.
- [2] C. Hassler, T. Boretius, and T. Stieglitz, "Polymers for neural implants," *J. Polymer Sci.-Part B: Polymer Phys.*, 49, pp. 18–33, 2011.
- [3] I. R. Mineev et al. "Electronic dura mater for long-term multimodal neural interfaces," *Science* 347, no. 6218, pp. 159–163, 2015.
- [4] N. de la Oliva, M. Mueller, T. Stieglitz, X. Navarro, and J. del Valle, "On the use of Parylene C polymer as substrate for peripheral nerve electrodes," *Scientific reports* 8, no. 1:5965, 2018.
- [5] R. Caldwell, M. G. Street, R. Sharma, P. Takmakov, B. Baker, and L. Rieth, "Characterization of Parylene-C degradation mechanisms: In vitro reactive accelerated aging model compared to multiyear in vivo implantation," *Biomaterials*, 119731, 2019.
- [6] A. Vanhoestenbergh, N. Donaldson, "Corrosion of silicon integrated circuits and lifetime predictions in implantable electronic devices," *J. Neural Eng.* 10(3), 031002, 2013.
- [7] P. Rezai, P. R. Selvaganapathy, G. R. Wohl. "Plasma enhanced bonding of polydimethylsiloxane with parylene and its optimization," *J. Micromechanics and Microengineering* 21(6), 065024, 2011.
- [8] J. Ordóñez, S. C. Boehler, M. Schuetzler, and T. Stieglitz. "Silicone rubber and thin-film polyimide for hybrid neural interfaces—A MEMS-based adhesion promotion technique," In *2013 6th International IEEE/EMBS Conference on Neural Engineering (NER)*, pp. 872–875. IEEE, 2013.
- [9] J. M. Hsu, P. Tathireddy, L. Reith, A. R. Normann, F. Solzbacher, "Characterization of a-SiC_x: H thin films as an encapsulation silicon based neural interface devices," *Thin solid films* 516, no. 1, pp. 34–41, 2007.
- [10] ASTM, D. 3359, Standard Test Methods for Measuring Adhesion by Tape Test, (Method B—Cross-Cut Tape Test), Vol. 06.01, 2002. *American Society for Testing Materials, West Conshohocken, PA*, 19428.
- [11] K. Nanbakhsh, M. Kluba, B. Pahl, F. Bourgeois, R. Dekker, W. Serdijn, and V. Giagka, "Effect of Signals on the Encapsulation Performance of Parylene Coated Platinum Tracks for Active Medical Implants," in *Proc. 41st Int. Conf. of the IEEE Engineering in Medicine and Biology (EMBC) 2019*, Berlin, Germany, pp. 3840–3844, IEEE, Jul. 2019.
- [12] V. Giagka, A. Demosthenous, and N. Donaldson, "Flexible active electrode arrays with ASICs that fit inside the rat's spinal canal," *Biomed. Microdev.*, vol. 17, no. 6, pp. 106 – 118, Dec. 2015.