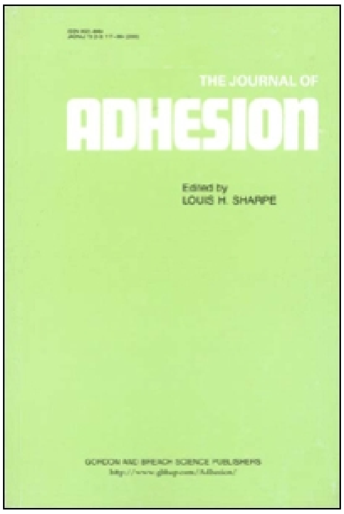
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Stretchable Gold Tracks on Flat Polydimethylsiloxane (PDMS) Rubber Substrate

S. Béfahy[a][b]; S. Yunus[a]; V. Burguet[a]; J. -S. Heine[a]; M. Troosters[b]; P. Bertrand[a]
[a] Université catholique de Louvain, Louvain-la-Neuve, Belgium [b] Neurotech SA, Louvain-la-Neuve, Belgium

To cite this Article Béfahy, S. , Yunus, S. , Burguet, V. , Heine, J. -S. , Troosters, M. and Bertrand, P.(2008) 'Stretchable Gold Tracks on Flat Polydimethylsiloxane (PDMS) Rubber Substrate', The Journal of Adhesion, 84: 3, 231 — 239

To link to this Article: DOI: 10.1080/00218460801954292

URL: http://dx.doi.org/10.1080/00218460801954292

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 84:231–239, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460801954292

Stretchable Gold Tracks on Flat Polydimethylsiloxane (PDMS) Rubber Substrate

S. Béfahy[1,2], S. Yunus[1], V. Burguet[1], J.-S. Heine[1], M. Troosters[2], and P. Bertrand[1]
[1]Université catholique de Louvain, Louvain-la-Neuve, Belgium
[2]Neurotech SA, Louvain-la-Neuve, Belgium

A process to fabricate stretchable gold tracks on silicone rubber substrates is studied by XPS, static water contact angle measurement, AFM, and SEM. The process involves several steps: removing uncured oligomers by hexane Soxhlet extraction; pre-stretching the substrate; activating the strained silicone surface by an oxygen plasma treatment; coating the strained substrate with 5 nm titanium and 80 nm gold layers; and finally releasing the sample. The plasma treatment creates a thin brittle silica-like layer that temporarily increases the substrate's surface energy. Indeed, the plasma treatment is followed by a hydrophobic recovery. As a consequence, the delay between plasma treatment and metal deposition has to be reduced as much as possible. The silica-like layer can be nicely observed after release. The entire process allows us to obtain stretchable metallized samples that remain conductive even after an excessive deformation leading to electrical failure.

Keywords: Buckling; Hydrophobic recovery; Metallization; Plasmatreatment; Polydimethylsiloxane (PDMS); Silica-like layer; Stretchable conductor

INTRODUCTION

Nowadays, implantable electrodes for neurostimulation are mostly fabricated with polydimethylsiloxane (PDMS) rubber as a substrate and platinum as conductive circuitry. Presently, the fabrication of such devices is still complex and usually consists in a mechanical assembly of preformed platinum elements on the PDMS substrate. Our work aims at developing a reliable metallization process that

---

Received 22 August 2007; in final forth 18 December 2007.

One of a Collection of papers honoring John Watts, the recipient in February 2008 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

Address correspondence to Stéphane Béfahy, Neurote SA, Chemin du Cyclotron 6, B-1348 Louvain-la-Neuve, Belgium. E-mail: behafy@neunotech.be

allows the deposition of noble metals, like platinum or gold, to be performed and that avoids mechanical assembly of preformed parts. This process should guarantee strong adhesion between metal and PDMS and good electrical behavior during mechanical deformation. However, before reaching this goal, three key challenges have to be tackled. Firstly, after its preparation, PDMS rubber always contains unreacted oligomers that easily diffuse [1] and dominate the surface properties, preventing an efficient coating process [2]. Secondly, apart from the oligomer diffusion, PDMS rubber has a very low surface energy and, consequently, the PDMS surface has to be activated in order to increase the adhesion of metallic coating [3]. Thirdly, a strategy allowing the metal coating to be compliant and stretchable has to be used [4–6].

In this article we report on our process and analytical measurements of stretchable gold conductors. With the aim to understand and optimize the physico–chemical properties responsible for metal adhesion on silicone rubber, the effects of plasma treatment on the elemental surface composition, on the wettability, and on the surface morphology are studied and discussed. Finally, the adhesion and the surface morphology of a metallized sample is described, as well as its electrical behavior during stretching.

EXPERIMENTS

Dow Corning Sylgard 184 (Midland, MI, USA) samples were processed by mixing silicone polymer and curing agent in a 10:1 weight ratio. After degassing this blend under reduced pressure, the mixture was injected into a tensile test specimen mould of 1 mm thickness and cured for 8 h at 80°C. Once disentangled from the mould, the PDMS samples were cleaned during 24 h in a Soxhlet extractor containing n-hexane as solvent. The tensile test specimens were stretched up to 15% of elastic elongation in the longitudinal direction. The samples, maintained in this position, were then exposed to an oxygen radio frequency cold plasma operating at 60 W and 350 m Torr during 2 minutes. After oxidation, a 5 nm titanium adhesion layer and a 80 nm gold layer were deposited at a rate of ~ 1Å/s by e-beam evaporation in a BOC Edwards AUTO 306 evaporator (Crawley, United Kingdom). A 50 µm thick stainless steel shadow mask was used to define 2 mm wide and 15 mm long metallic tracks. Finally, samples were unloaded.

After plasma exposure and metallization, sample morphology and topography were characterized by SEM using a Leo 982 GEMINI Field Emission (Zeiss, Oberkochen, Germany) and by AFM using a

Nanoscope III (Veeco Instruments, Inc., Woodbury, NY, USA). AFM was performed in air and in contact mode. The spring constant and curvature radius of the MSCT-AUHW cantilevers from Veeco Instruments, Inc., are 0.01 N/m and around 20 nm, respectively. For all microscopies, samples were observed without applying any deformation. The elemental surface composition was determined by XPS on a SSX 100/206 (Surface Science Instruments, Mountain View, CA, USA) equipped with monochromatized Al K_α x-ray radiation (1486.6 eV). The angle between the surface normal and the axis of the analyser lens is 55° and the pass energy is 50 eV. The binding energies were determined by reference to the C1s, peak corresponding to carbon bound to hydrogen and silicon, set at 284.2 eV. Wettability after plasma exposure was determined by static water contact angle measurement. Wettability experiments were performed with 0.3 μl droplets of MilliQ water. Each measurement was performed five times on two samples. For both XPS and static water contact angle measurement, samples were not strained during plasma treatment. After metallization, the adhesion of the metallic coating was qualitatively determined by a peel test using Scotch® tape (3 M, Saint-Paul, MN, USA). The electrical conduction under stretching was measured by means of a homemade device. The electrical contacts were ensured by copper wires attached to the metallic tracks using a conductive silver lacquer. The distance between contacts was around 10 mm. The variation of the electrical resistance upon extension was measured up to electrical failure. The extension was conducted by step, of 7μm every 5 seconds. The resistance value was recorded every second.

DISCUSSION

First, the effects of the plasma treatment will be analysed, *i.e.* the elemental surface composition, the wettability, and the surface morphology The second part of the discussion deals with metallized, samples, the metal coating adhesion, the surface morphology, and the description of the electrical behavior during stretching.

The efficiency of hexane extraction to remove uncured oligomers from a silicone rubber surface, which had already been prove elsewhere [2], was not further developed.

Effects of Plasma Treatment

The elemental surface composition of plasma treated PDMS was followed by XPS analysis Table 1. Without plasma treatment, the measured composition was close to the stochiometric composition.

TABLE 1 XPS Elemental Atomic Composition of Untreated and Plasma Treated Samples

	O	C	Si
Untreated	28.8	47.9	23.3
Plasma treated	56.5	21.6	21.9

After plasma treatment, the carbon content decreases to 21.6% the oxygen rises up to 56.5%, while silicon remains constant. Figure 1 is a high-resolution spectrum of the Si 2p peak before and after plasma treatment in which the intensity scale is normalized on the maxima of the peaks for comparison purpose. The Si 2p peak of untreated sample is centered at 101.75 eV with a full width at half maximum (FWHM) of 1.35 eV. After plasma treatment, the Si 2p peak enlarges and moves to higher binding energies. The FWHM of the Si 2p peak for plasma treated samples grows up to 1.81 eV. This large peak can be resolved into two components, SiO (a silicon linked to two oxygen atoms) and SiO_2(a silicon linked to four oxygen atoms), or into three components by adding $SiO_{1.5}$(a silicon linked to three oxygen atoms). But the key point is that a layer of oxidized silicon, or "silica-like" layer, appears on the PDMS surface after the plasma treatment. These results agree with previous works of Owen and Smith [7] who studied the elemental composition after different types of plasma treatments. They found the same tendency of surface composition evolution after oxygen plasma treatment.

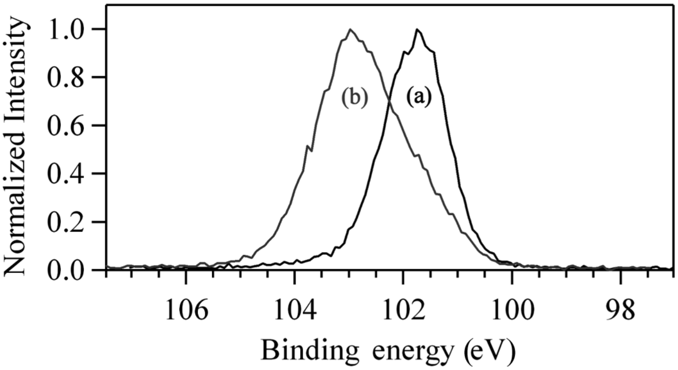


FIGURE 1 High-resolution XPS Si 2p spectra of (a) untreated and (b) plasma treated PDMS.

The wettability evolution of samples after plasma treatment is followed by static water contact angle measurements (Fig. 2). Untreated PDMS rubber is hydrophobic with a contact angle of 109.5°. Five minutes after plasma treatment, the wettability is complete (angle $<5°$). However, as illustrated in Fig. 2 and in agreement with the work of Morra *et al.* [8] and Hillborg *et al.* [9], a hydrophobic recovery occurs and the surface activation vanishes. Indeed, 1 h after the plasma treatment, the contact angle already reaches values around 20°. One week later and for the three following months, the angle values oscillate around 100°. According to Hillborg *et al.* this hydrophobic recovery is due to low molecular mass PDMS oligomers diffusing to the surface. The low molecular mass species can be uncured oligomers or species formed during plasma treatment by Si–O bond breaking. In our case, we suggest that accounting for the Soxhlet extraction, oligomers responsible of hydrophobic recovery are mainly formed during plasma treatment and can prevent an adherent metal coating. Consequently, in a view to metallize silicon rubber the delay between the plasma treatment and the metal deposition has to be reduced as much as possible, or better, the two treatments should be applied in the same apparatus (*i.e.* metallization by plasma sputtering).

The morphology of released samples after plasma treatment was studied by SEM and AFM. In Fig. 3, a 3-D AFM view and a SEM micrograph show that the surface is deformed in a thin wavy layer

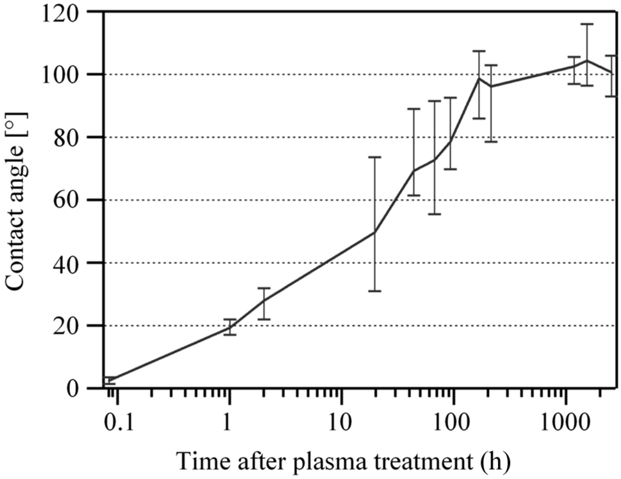


FIGURE 2 Static water contact angle evolution in degrees of an unstrained PDMS sample after plasma treatment.

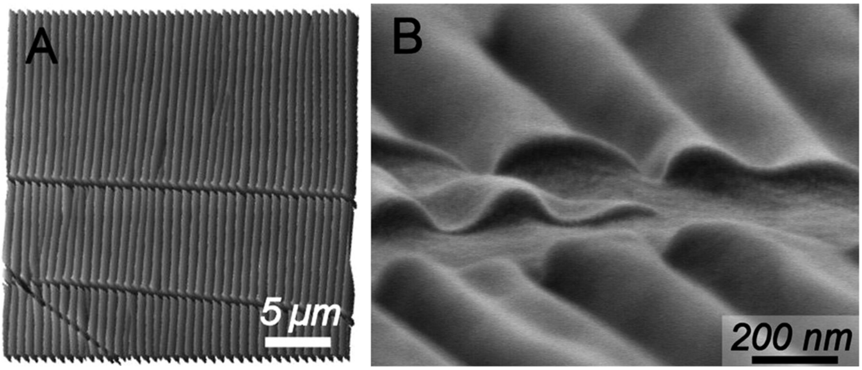


FIGURE 3 AFM and SEM micrographs of a released sample after plasma exposure under strain: (A) 3D AFM view (height scale 200 nm); (B) SEM micrograph of a V-shaped crack.

with wavelets perpendicular to the direction of prestretching. The period and the amplitude of this wavelet morphology range around 500 and 120 nm, respectively. At some locations, large cracks, mostly perpendicular to the wavelet, are present. At the intersection of two cracks, V-shaped portions allow us to evaluate the thickness of this thin, newly created, layer to be between 20 and 50 nm.

This morphology appearing upon release can be understood as a buckling due to a thin surface layer having a larger stiffness than the bulk. This wavelet morphology, also observed by Katzenberg [10], is consistent with the formation of a silica-like layer induced by the plasma treatment. Upon unloading, due to the higher stiffness of the surface layer, surface wrinkling develops in the brittle silica-like layer to accommodate a part of its compression. For the same reason, the expansion in the perpendicular directions leads to large tensile stresses in these directions. The glassy and brittle layer relaxes the stress by initiating and opening cracks in the perpendicular directions. Buckling obtained on plasma treated samples under strain allows us to observe this thin silica-like layer and its cracks (Fig. 3).

Effect of Plasma and Subsequent Metallization Under Strain

After plasma treatment and metallization, peel tests using Scotch tape performed on released samples show a good adherence of the metal coating; there is practically no delamination.

Figure 4A shows a picture of a metallized tensile test specimen. As illustrated by Fig. 4B, an optical micrograph of the metallized track

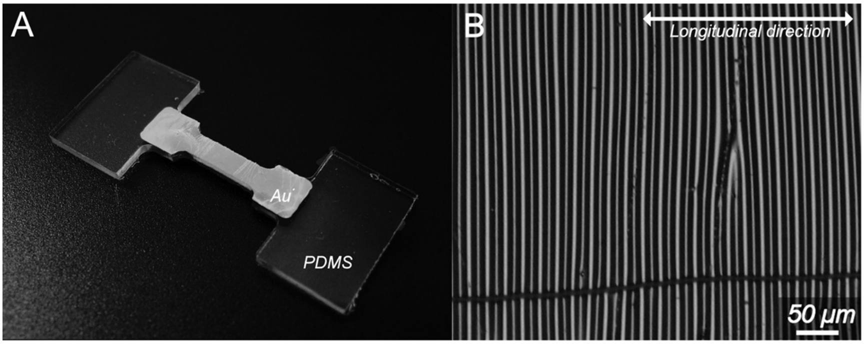


FIGURE 4 Released metallized sample: (A) picture of the sample; (B) optical micrograph of the metallized track.

shows that the surface morphology is comparable with that observed previously in Fig. 3 in the case of plasma treatment alone. The metallic coating forms a periodic morphology with wavelets perpendicular to the tensile axis and with cracks parallel to this direction. However, the wavelength of about 20 μm is larger than the one observed after the plasma treatment. These results agree with previous work of Jones *et al.* [6] who metallized PDMS samples under strain. The increase in wavelength is due to the modification of the stiffness and the thickness of the modified surface layer [11].

Concerning the resilience of these tracks for applications, Figure 5 illustrates a typical evolution of the electrical resistance as a function of longitudinal engineering strain in the tensile bench. The three curves represent the resistance evolution during the loading part, up to the electrical failure, of three successive cycles.

The initial resistance of the released sample is 7Ω which corresponds to a resistivity of $10^{-5}\,\Omega\cdot$cm, only five times as large as the bulk resistivity of gold (2.2 $10^{-6}\,\Omega\cdot$cm at 25°C). Resistivity is calculated using $\rho = R\frac{L}{el}$, where R is the measured resistance, L the length between the contacts (10 mm), e the gold thickness (80 nm), and l the track width (2 mm). During loading, this resistance is constant up to 18% of extension and then gradually increases up to 31% where the electrical failure happens. For our application, this resilience is largely sufficient and, consequently, samples are able to overcome the third key challenge. For the two following loadings, the electrical resistance of 7 Ω at the released position is recovered. The loadings are similar and with electrical failures happening always near 32%.

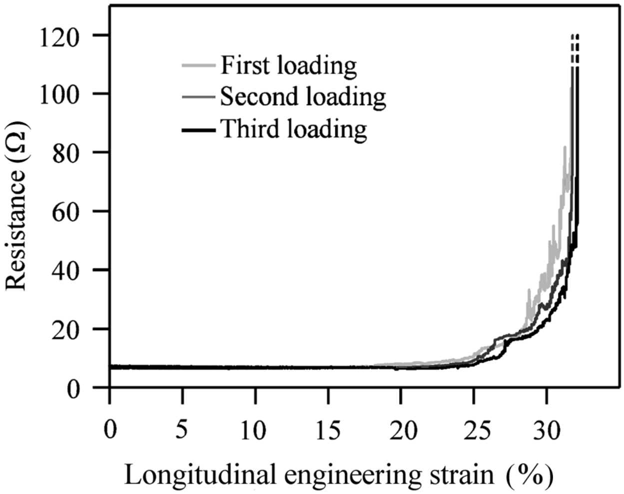


FIGURE 5 Evolution of the electrical resistance of a metallized sample up to electrical failure during the loading part of three successive loading/unloading cycles.

CONCLUSION

This work describes a fabrication process allowing us to overcome different challenges raised by our application. The plasma treatment temporarily increases the surface energy and guarantees good adhesion to the subsequently deposited metal coating. This plasma treatment under strain also allows us to catch a glimpse of the thin silica-like layer. The thickness of this thin brittle layer can then be evaluated to be in a range of 20 to 50 nm. The hydrophobic recovery observed after plasma treatment makes it mandatory to reduce the delay between plasma treatment and metal deposition as much as possible. Finally, the present work not only shows that this fabrication process produces samples with stretchable tracks but also that a device using these tracks should still be operational even after an excessive deformation having led to electrical failure. Further studies will focus on analyzing the influence of the thin silica-like layer on the track stretchability and also on establishing plasma parameters allowing the delay of hydrophobic recovery and reducing the thickness of the silica-like layer as much as possible while keeping adhesion.

ACKNOWLEDGMENTS

This research is supported by the ADVENS program of the Belgium's Walloon region. We acknowledge P. Rouxhet and Y. Dufrêne (CIFA-UCL) for access to the XPS and AFM instruments.

REFERENCES

[1] Graham, D. J., Price, D. D., and Ratner, B. D., *Langmuir* **18**, 1518–1527 (2002).

[2] Delcorte, A., Béfahy, S., Poleunis, C., Troosters, M., and Bertrand, P., *Proc. of Adhesion Aspects of Thin Films '03 Orlando*, (2005), pp. 155–167.

[3] Schmid, H., Wolf, H., Allenspach, R., Riel, H., Karg, S., Michel, B., and Delamarche, E., *Adv. Funct. Mater.* **13**, 145–153 (2003).

[4] Béfahy, S., Yunus, S., Troosters, M., Pardoen, T., and Bertrand, P., *Appl. Phys. Let.* **91**, 141911 (2007).

[5] Gray, D. S., Tien, J., and Chen, C. S., *Adv. Mater.* **16**, 393–397 (2004).

[6] Jones, J., Lacour, S. P., Wagner, S. and Suo, Z., *J. Vac Sci. Technol. A* **22**, 1723–1725 (2004).

[7] Owen, M. J. and Smith, P. J., *J. Adhesion Sci. Technol*. **8**, 1063–1075 (1994).

[8] Morra, M., Occhiello, E., Marola, R., Garbassi, F., Humphrey, P., and Johnson, D., *J. Colloid Inter. Sci.* **137**, 11–24 (1990).

[9] Hillborg, H., Ankner, J. F., Gedde, U. W., Smith, G. D., Yasuda, H. R., and Wikström, K., *Polymer* **41**, 6851–6863 (2000).

[10] Katzenberg, F., *Macromol. Mater. Eng*. **286**, 26–29 (2001).

[11] Huck, W. T. S., Bowden, N., Onck, P., Pardoen, T., Hutchinson, J. W., and Whitesides, G. M., *Langmuir* **16**, 3497–3501 (2000).