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PARYLENE-C THIN FILM FOR BIOCOMPATIBLE ENCAPSULATIONS WITH VERY STRONG ADHESION AND SUPERIOR BARRIER PROPERTIES

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Abstract: Adhesion of Parylene-C to metal (platinum) was investigated. A plasma polymerization process combined with a Parylene deposition process through a customized system seems to improve the adhesion and barrier properties of the film. Adhesion level of 2.1 N/cm and impedance of 10^8 Ω/cm^2 at 100 Hz were measured by means of adhesion test and the Electrochemical Impedance Microscopy (EIS) respectively.

Keywords: Parylene-C; platinum; plasma polymer; wet adhesion; electrical properties

Introduction

As biocompatible material, platinum is used in different medical sectors [1-6]. Intercortical sensors and nerve stimulators are some of the most recent applications for this material [2-4]. In this field a miniaturized electrode array, usually from platinum, is used for stimulation, for recording or both. Today the trend is to realize such arrays on a flexible substrate in order to minimize the damage on the tissues surrounding it [7, 8].

The used material is not only a substrate but also plays the role of a passivation layer for the supporting electronics so it should fulfill many requirements: corrosion protection, biocompatibility and electrical properties being the most critical factors.

Those challenges are usually addressed using polymer coatings [9, 10]. Among them, Parylene is one of the most promising polymers because of its native biocompatibility and the conformal nature of the deposited film.

Although they display numerous free radicals at their surface as well as buried in the bulk, Parylene films usually poorly adhere to metallic surfaces due to the strong dissimilarity between their surface energy and that of the substrate [11].

A glow discharge process is a surface and interface engineering technique that allows tailoring a material surface by creating the proper free radicals and/or manipulating its surface energy [12].

In this work a specially designed deposition system uses such a glow discharge as a pre-processing step prior to Parylene coating. The result is a remarkable improvement in Parylene-C adhesion in comparison to the use of the traditional silane-based adhesion promoter named A-174.

Experimental

Substrate description

The substrate consists of 200 nm of platinum evaporated on top of 300 µm thick soda-lime glass or Pyrex. An additional 20 nm titanium seed layer assures a good adhesion between the platinum layer and the underlying glass or Pyrex. The substrate was diced in pieces of 11.8 mm by 11.8 mm.

Process technology

The two main processes, the plasma pre-processing and the Parylene deposition process, are carried out in a custom designed cluster system. Each process is run in a different chamber; both being connected to a common load lock unit. The samples are loaded into the system and carried into the respective processing chamber by a robotic arm.

After transferring the samples to the plasma pre-processing chamber under high vacuum, a two step AF (audio frequency 15 kHz) magnetron-enhanced plasma process is conducted [13, 14]. The first step is a surface treatment consisting of oxygen or argon glow discharge; the second is a plasma polymerization process using TMS (Trimethylsilane) as gaseous precursor, which generates a polymeric nano-film on the surface of the substrate.

Using the robotic arm and under high vacuum, the samples are moved to the Parylene deposition chamber through the load lock where a standard Parylene deposition process (Gorham's process) [15] is performed to deposit a Parylene film with a thickness of approximately 1.5 to 1.8 µm. Table 1 summarizes the performed processes.

Table 1: Multilayer coatings, Ar: Argon, O_2: Oxygen, TMS: Trimethylsilane

Recipe	Multilayer combinations
1	Platinum on glass substrate → O_2 → TMS → Parylene
2	Platinum on glass substrate → Ar → TMS → Parylene

Film characterization

To investigate the performance of the generated multi-layer film two tests were performed: a wet adhesion test and Electrical Impedance Spectroscopy (EIS)

Wet adhesion test

Three groups of three samples each were tested. The first one is coated through process 1 in Table 1, the second is coated through process 2 and the third group is a control one where the samples are treated only by oxygen followed by Parylene deposition without TMS deposition. Two of the coated samples from each group were boiled in saline solution for one hour; the solution was prepared by adding 900 mg NaCl to 100 ml of deionized water and mixed using a magnetic stirring bar. A hot plate was used to boil the solution, and the samples were placed into the boiled solution. After boiling, the samples were examined under a microscope in order to detect any trace of delamination. The last sample from each group underwent a 90 ^{o} adhesion tape test to estimate the adhesion strength using a Dage-series-4000PXY (Dage Semiconductor GmbH, Germany) bond tester with the cartridge (WP 10KG) and a tape with a brand name 'Nopi'. The adhesion strength was estimated using a formula described in [16].

Electrical properties

To estimate the electrical performance of the coating which in turn gives an idea about its barrier properties an Electrochemical Impedance Spectroscopy (EIS) test was performed where the sample was used as the working electrode and a platinum wire was used as counter electrode; both were immersed in saline solution (900 mg NaCl in 100 ml deionized water).

Using a Solartron 1260A an alternative voltage of 100 mV was swept over a frequency range (100 Hz to 10^5 Hz), and the Bode plot was extracted using the Z-VIEW software.

Every day for a period of 20 days, the samples were tested; after each test the samples were washed by deionized water and stored in dry conditions until the next test.

Results and Discussion

Wet adhesion

After 10 minutes of boiling, water pockets appeared under the coatings of the control samples (O_2 then Parylene). In contrast, the samples processed by recipe 1 and 2 did not show any delamination after 10 min of boiling. At the end of the test (60 min) the control samples lost their coating while the other samples displayed only a very small indication of film delamination at the edges of the substrate. Figure 1 shows microscopic pictures the samples after the test.

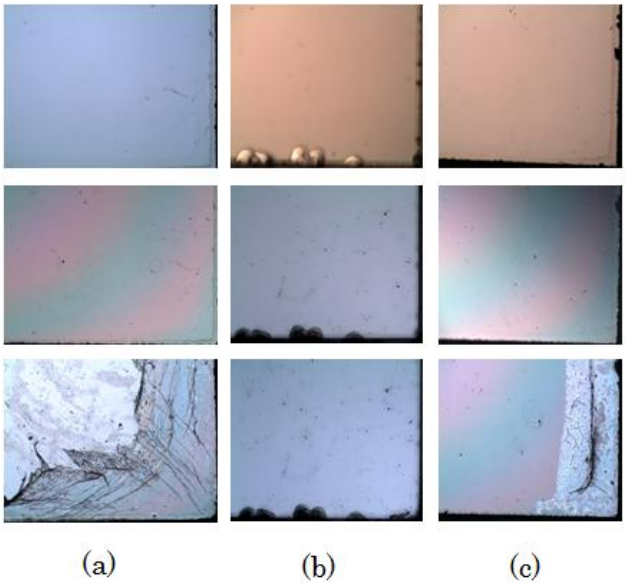


Fig. 1 The wet adhesion behaviour of multilayer combination a) the control sample, b) the sample processed by recipe 1, and c) the sample processed by recipe 2. The top photos were taken before coating, the middle ones are of the same area after coating, and the bottom photos are of the same area after the test

The tape adhesion test was done on one sample from each group. The test was repeated five times on the same face of the sample and it shows no or very little film removal at the corners while the coating of the control sample peeled off completely after the first time.

An adhesion strength of 0.7 N/cm for the control sample and 2.1 N/cm for the samples produced using recipe 1 and recipe 2 were recorded.

The results of both tests confirm that a plasma nano-film as adhesion promoter applied before Parylene deposition leads to a tremendous improvement of the Parylene adhesion to substrate in comparison to the control sample or to the silane based adhesion promoter [7].

The improvement in adhesion comes from the fact that a plasma polymer contains a high amount of dangling bonds [12] which in turn stimulate a radical interaction between the plasma polymer and the Parylene film, and raise the adhesion strength. In addition, the similarity in surface energy between both the used plasma polymer and the Parylene film encourages the Parylene adhesion [11].

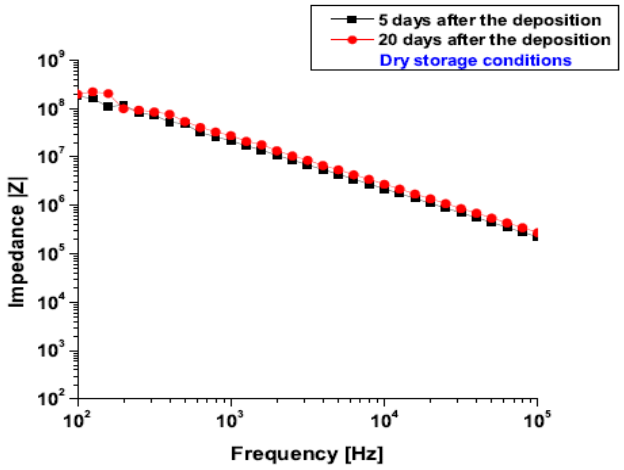
Electrical properties

At a frequency of 100 Hz an impedance level of 10^8 Ω/cm^2 was measured and a phase of approximately 90^o was recorded over the whole sweep range (100 Hz to 10^5 Hz). Figure 2 depicts the impedance and the phase response of the coating over the monitoring period.

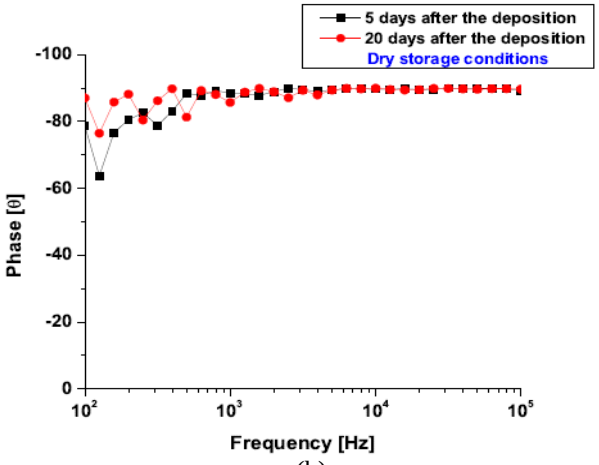
Using a plasma polymer as adhesion promoter leads to several effects on the whole performance of the generated

coating. Two effects are of interest: firstly, the excellent adhesion between the Parylene film and the substrate which lowers the effect of the intruded water at the Parylene/substrate interface. Secondly, the hydrophobic nature of the used plasma polymer (TMS) reduces the amount of intrusive water at the Parylene/substrate interface [11, 17].

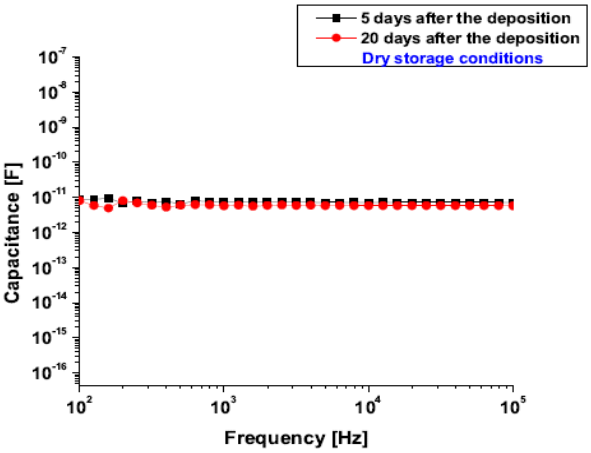
Both effects lead to a better electrical behavior which is reflected in an improvement of the barrier properties against water intrusion. The improvement can be clearly seen when comparing the electrical performance of the coating generated by recipe 2 (10^8 Ω/cm^2 at 100 Hz) to the performance of the coating using the silane-based adhesion promoter (10^5 Ω at 100 Hz) [7].



(a)



(b)



(C)

Fig. 2 The electrical behavior of the coating obtained with recipe 2, five and 20 days after the deposition: a) impedance, b) phase, and c) capacitance

Conclusion

The use of a plasma nano-film in combination with a Parylene deposition process seems to give extraordinary results in terms of both adhesion to the substrate and barrier properties of the produced films. An adhesion level of 2.1 N/cm and an impedance of 10^8 Ω/cm^2 at 100 Hz were achieved.

This originates from the principle that plasma polymers modify the surface energy of the substrate to make it more suitable for Parylene deposition [11]. In addition, the generated plasma polymer contains a high amount of dangling bonds [12] on its surface and buried in its bulk, thus offering anchoring sites for the subsequently deposited Parylene film.

The excellent adhesion of the Parylene film to a substrate and the hydrophobic nature of the used plasma polymer (TMS) lead to a tremendous reduction of the effect of water and/or water vapor at the interface between Parylene film and substrate. As a result, this leads to an improvement in the barrier properties of coatings and prolong the service life of the generated Parylene film especially in harsh and aggressive environment.

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