Improved chip & component encapsulation by dedicated diffusion barriers to reduce corrosion sensitivity in biological and humid environments.

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Abstract

In order to develop an advanced polymer based package technology to obtain small and flexible medical implants, diffusion barriers are essential to protect electronic chips and components for corrosion caused by leaching of body fluids. These barriers need also to stop diffusion of harmful products such as Cu from the device into the body. Furthermore, the barrier layers need to be biocompatible, biostable, compatible with all process steps of the package fabrication and sterilization. Parylene is under investigation as candidate barrier material. WVTR tests are performed to characterize diffusion of water through the Parylene layer. Adhesion tests of Parylene-C on various substrates are performed and if needed adhesion promotion treatments are optimized, since good adhesion is crucial for corrosion prevention. Dedicated corrosion tests have shown that 5um Parylene-C is protecting Cu lines for corrosion at 70°C for at least 170 hours, more testing needs to be performed. Cell culture test have shown that Cu diffusion is not sufficiently stopped by 5um Parylene-C or -N, a thicker Parylene layer or a combination with other barriers might be essential. Also dedicated cell culture protocols with non-adherent cell types will have to be developed to perform reliable tests on these hydrophobic and cytophobic barrier layers.

Key words: diffusion barriers, corrosion prevention, hermetic packaging, biomedical application

Introduction

Implantable electronic devices such as pacemakers are typically packaged in a rigid Titanium (Ti) box to ensure hermetic and biocompatible packaging of the microelectronic device. Such a Ti-box is a well-known and safe package for implants, but this box is often large compared to the conventionally packaged electronics inside, hence during implantation a larger insertion wound is needed resulting in a more pronounced Foreign Body Reaction (FBR) and a higher infection risk upon implantation. Also irritation and limited user comfort are more likely due to the strong mismatch between the soft body tissue and the rigid Ti-box [Ref. 1, 2]. Finally, for some applications, a flexible and/or stretchable device might be needed or local optical transparency is essential, obviously the traditional Ti-box based package can't provide such properties.

We are currently developing a 'biocompatible packaging for electronics' in order to address these issues. We are extending the miniaturization trends in packaging of microelectronics towards packaging of implanted electronic devices, and we complement this miniaturization by adding hermetic barriers in order to provide a bi-directional diffusion barrier insulating the implanted electronics from the body. Since the body should not suffer from adverse effect upon implantation, the selected packaging materials have to be biocompatible and biostable. The principle of our approach is shown in Fig. 1. Device design, chip/component selection (COTS and/or dedicated chip fabrication) take place first with packaging aspects and final device goal in mind, followed by

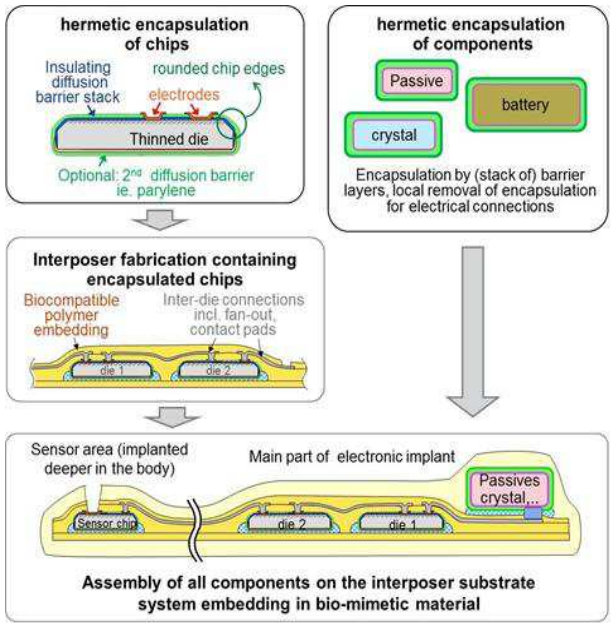

Fig. 1: polymer based packaging concept for implantable electronic devices.

biocompatible hermetic packaging of chips and other components of the final device. A biocompatible alternative of our Ultra-Thin Chip Packaging (UTCP) process (see ref.), will be developed, resulting in an ultrathin (multiple-) chip package. To ensure device functionality and device biocompatibility, the components/device will be equipped with biocompatible bi-directional diffusion barriers. Next, all components are assembled with biocompatibility in mind. By selecting the proper polymer materials for the total device encapsulation, the final package can be made soft, stretchable and biomimetic, resulting in a comfortable implantable device and reducing the risk on pronounced FBR and adverse effects.

The development of such an advanced, thin, flexible package for electronic implants is a complex task with various issues to be solved. The evaluation of biocompatible and biostable bi-directional diffusion barriers is an important subtask, since the body should be protected from harmful components in the electronic device, while the device needs to be protected from the body fluids, to prevent corrosion and device malfunctioning.

Barriers for wafer-level chip encapsulation

Our previous barrier investigations comprised of the evaluation of various typical CMOS materials (both conductive and insulating) as diffusion barrier for wafer-level based chip encapsulation. Using typical CMOS materials has the advantage that their processing can be performed as post-processing in a CMOS clean room, resulting in a lower cost due to parallel processing of many chips. This evaluation has been successfully finished, we decided to encapsulate the chips by a stack of SiO2/SiN/SiC; for the conductive bondpads, a conductive capping of Ta/TaN is used, followed by a protection of Ti/Pt for enhanced biostability. Various tests proved this encapsulation is protecting well against corrosion even while immersing the encapsulated chips in aggressive biofluids. More information can be found in Ref. 3-8.

Essential properties of diffusion barriers

Currently we are focusing our research towards the encapsulation of non-Si-based components (passives, sensors, a battery,..) and of Si chips which we can't buy as full wafer (hence no wafer-based clean room post-processing is possible anymore). Candidate barrier materials for this application are materials which can be deposited on high aspect ratio components with good step coverage. Furthermore, not only the diffusion stopping power (for moisture, oxygen, copper,..) is important, but also various other indispensable properties have to be taken into account, such as biocompatibility, biostability, adhesion promotion treatments on various materials, integration aspects (such as compatibility with temperature steps during further package fabrication, or patterning possibilities to remove the barrier layer on sensor areas) and suitability for standard sterilization techniques. Furthermore, certain implants will gain from additional properties such as flexibility or stretchability, optical transparency,.. hence barrier materials have to be evaluated with their suitability to these additional device features in mind.

Parylene as biocompatible barrier polymer

Parylene is a popular name for a variety of chemical vapor deposited poly(p-xylylene) polymers used frequently as barriers for moisture and gases and as dielectric barriers. Parylenes have a variety of important advantages: the coating process takes place at ambient temperature (hence no different volume expansion between coating and substrate) and high aspect ratio topography is coated with excellent step coverage. Parylene-C, N and HT are reported to be biocompatible and biostable parylenes. Each type has advantages and drawbacks: Parylene-C and -N are not stable when exposed to oxygen at temperatures above ~70°C, Parylene-HT can stand temperatures up to 350°C and higher. Parylene-C can be annealed at higher temperatures in vacuum, resulting in a more dense layer (better barrier) but becoming more brittle. More info about Parylene can be found in Ref. 9.

Although Parylenes are known for their excellent diffusion barrier properties [Ref 10], we have observed on some occasions remaining corrosion problems with Parylene-C. Also other researchers have reported remaining problems [Ref 11], related to moisture diffusion combined with interface contamination (hence no perfect adhesion). Hence we decided to study Parylene barrier and adhesion properties in more detail.

Biocompatibility of Parylenes: cytotoxicity tests

Biocompatibility is an essential requirement for materials in direct contact with body tissue. A first very important step in biocompatibility evaluation consists of cytotoxicity tests, in a later research phase other tests can be performed (sensitization, irritation, etc.). Our tests are always carried out according to the ISO 10993-5 standard regarding biocompatibility, we used direct-contact cell culture tests (See Fig. 2). Traditionally, cell lines are used for these type of tests.

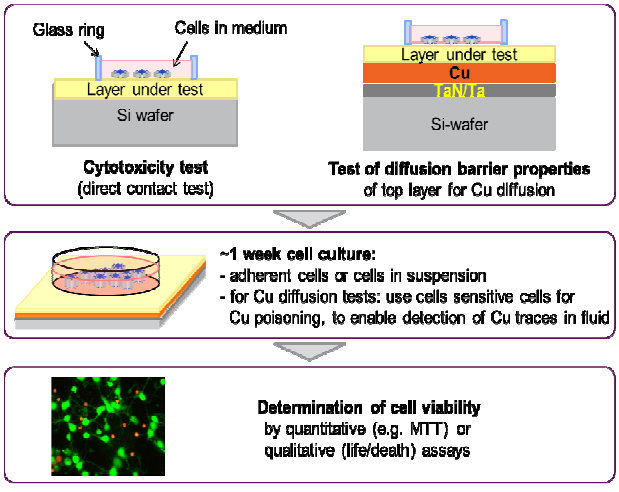

Fig. 2: cell culture protocol for cytotoxicity and Cu diffusion tests, all in accordance with the ISO 10993-5 standard.

Since cell lines are in general rather robust, a cell culture might indicate that a material is not cytotoxic, while later upon test implantations, cytotoxicity problems are observed. Note also that cell culture tests are typically only 1-4 weeks long, while implantation of electronic devices can be for much longer periods, up to tens of years. Hence the use of a sensitive cell type is important to test materials for long term implantation. We selected primary human foreskin fibroblasts (HFF) for the tests reported in this publication.

An issue we encountered during cell culture work on these moisture barriers, is that these barriers are typical hydrophobic and hence cytophobic: cells don't want to adhere on the barrier layers. Fibroblasts are very popular cells for cell culture work, but for these cells it is essential to adhere on a substrate in order to grow well. So fibroblast direct-contact tests on barrier materials need a special surface treatment to promote cell adhesion, and even with this treatment good adhesion is not guaranteed. So the Parylene test samples are pre-treated with fetal bovine serum (FBS) in an attempt to improve cell adhesion. Subsequently, cells are seeded on the Parylene layers. After one week, the cell viability is determined (cell viability: amount of viable attached cells relative to the control (tissue culture polystyrene (TCPS)). All tests are done in triplicate to enhance accuracy. As negative control, a cytotoxic Cu-layer is chosen as substrate, while a TCPS dish is used as positive control. The results are shown in Fig. 3. The viability for the positive and negative controls are as expected: almost 100% for TCPS and below 10% for Cu. For Parylene-C and -N, the viabilities are between 50 and 60%, which is rather low and might indicate some cytotoxicity, although in this experiment this is mostly likely related with the fact that Parylene is hydrophobic, and the HFF cells are an adherent cell type, hence only growing well in case they have a good support. In order to improve cell adhesion, the Parylene layers have been coated with FBS, but due to the hydrophobic nature of the layers, this coating is not always very successful,. To overcome this issue, a dedicated cell culture protocol will be developed for these cytophobic barrier materials, using suspension cell culture types.

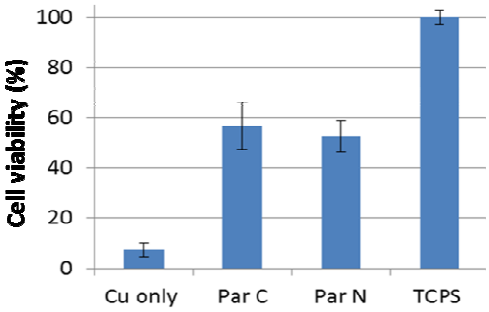

Fig. 3: Cell viability (%) on Parylene-C and -N, compared to the positive and negative control (TCPS and Cu only). Error bars correspond to the 'standard error of the mean' (SEM).

Water diffusion characterization by water vapor transmission (WVT) tests

Water vapor transmission is tested using a MOCON Aquatran system, allowing for a very small detection limit which is ideal for barrier tests. A 25um thick polyimide film (Upilex-S) is first tested since it is used as support for the WVT tests of barrier materials. Later, the polyimide film is covered with a 5um thick Parylene-C layer and the WVT is tested again. To enhance the measurement accuracy, always 2 similar samples are tested. The results are plotted in Fig. 4. Polyimide is known to be a material which still allows some water vapor penetration, hence it will not have sufficient barrier properties to protect electronics encapsulated in polyimide. This is also visible in Fig. 4: the WVT is around 1200-1300 mg/m2.day. When a 5um thick Parylene-C layer is coated on top of the polyimide layer, the WVT is decreasing clearly, but the decrease is limited. This result indicate that thicker Parylene-layers or stacks of Parylene combined with other barriers are essential to prevent moisture diffusion through the package.

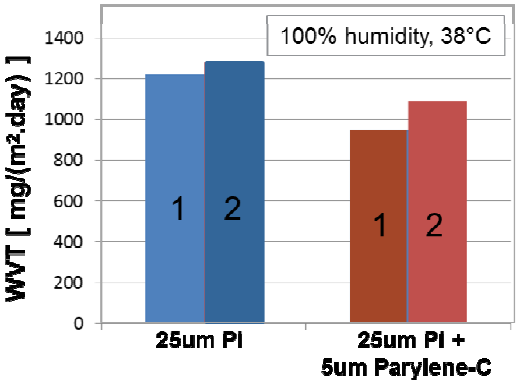

Fig. 4: WVT of a polyimide supporting film and of polyimide coated with 5um Parylene-C. Measurements are performed at 38°C in 100% humidity.

Adhesion of Parylene on various substrates

Barrier layers need to limit or ideally stop diffusion of moisture and ions to protect underlying materials. Secondly, the adhesion of a barrier layer to its carrier substrate is extremely important too. When adhesion is limited, moisture will slowly diffuse to locations of bad adhesion, and locally corrosion will start. Hence attention has to be paid to adhesion properties of barrier layers to relevant materials expected to be present in an electronic devices. Parylenes typically adhere worse on polymers and metals (especially noble metals). For 'difficult' substrates, adhesion promotion treatments are investigated (such as extreme cleaning prior to Parylene deposition, and applying A174-adhesion promoter (silane) and/or plasma treatments). We tested adhesion on plated and sputtered Cu, on Pt and Au, on Si and oxide, and on various types of polyimide, we use the standard ASTM D-3359 tape test. Depending on the technique used to deposit Cu, good adhesion or problems have been observed, but

the use of A174 prior to Parylene deposition was sufficient to solve adhesion problems. Also on Pt, Au and Si, a pre-treatment with A174 solved the adhesion problems. For polyimide, adhesion problems are more persistent and the severity depends on the type of polyimide. On some polyimide types, a treatment with A174 was sufficient to obtain good adhesion, others need the combination of a plasma treatment and a A174 coating.

Cu corrosion tests

We are using a dedicated corrosion test sample, consisting of copper meanders of various linewidths, which are covered with the barrier layer under test. By gluing a glass ring over the Cu meanders, a cavity is created which can be filled with water or a biofluid. These tests can be performed at 37°C for real life testing, but also at higher temperatures in order to accelerate the test procedure (typically 70°C, below 95°C to avoid boiling of fluid). For passive corrosion tests, 4 point measurements at regularly time intervals will inform us about a possible increase in resistance of the Cu meanders, due to corrosion effects.

Some initial test results are shown in Fig. 5. Cu meanders of various widths and 1 um thickness are exposed to Dulbecco's Phosphate-Buffered Saline (DPBS) at 70°C. Fig. 5 shows the resistance measurements of unprotected Cu lines, during DPBS exposure to DPBS up to 200 hours. For the smallest linewidth, corrosion caused interrupted Cu lines after ~40 hours. For larger linewidths, the resistance is increasing with DPBS exposure time, although this increase is slowing down after 55-60 hours. This is caused by a patina layer formed on top of the Cu lines (see green patina layer in Fig. 6B). This patina layer is a mixture of $Cu(OH)_2$ and $CuCO_3$ as a result of the corrosion reaction, and it slows down the corrosion since oxygen has to diffuse through the layer to reach the non-corroded Cu. After 200hours exposure to DPBS, all Cu lines have an infinite high resistance. We removed the patina layer by a 10sec etch in 5% HCl, to enable to see the Cu interconnects, which are severely corroded (See Fig. 6C).

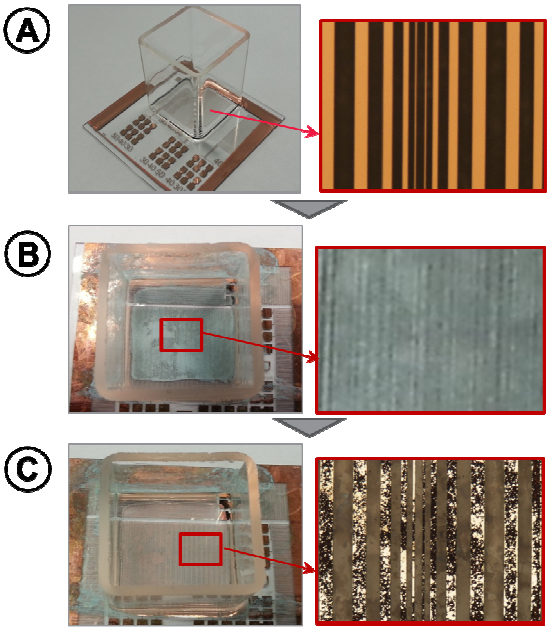

Fig. 6: Cu meanders for corrosion tests, (A) test sample prior to exposure to DPBS, (B) meanders covered with a patina after more than 60 hours DPBS exposure, and (C) Cu meanders after 200 hours DPBS exposure and removal of the patina. Corrosion is clearly visible.

In order to test the Parylene as diffusion barrier, Cu meanders were treated with A174 adhesion promoter and subsequently covered with a 5um thick Parylene-C layer. Again exposure to DPBS is performed at 70°C, meanwhile the resistance of the various Cu lines is monitored, as plotted in Fig. 7. Currently the PBS exposure time is 170 hours, and no resistance change is observed. Also visually, the Cu lines look nice, no green patina layer is seen. Hence the 5um thick Parylene layer is a good barrier for up to 170hours at 70°C, but longer testing will be performed, as well as testing at other temperatures, in order to characterize the Parylene corrosion prevention in sufficient detail.

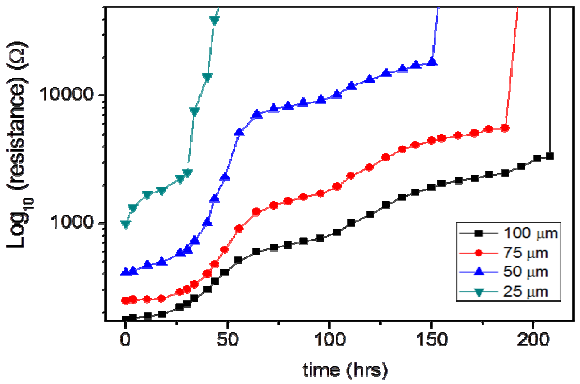

Fig. 5: Evaluation of the resistance change of Cu meanders of 25, 50, 75 and 100um width, exposed to DPBS at 70°C during 200hours. Corrosion causes severe resistance increase and is most pronounced for the smallest linewidths.

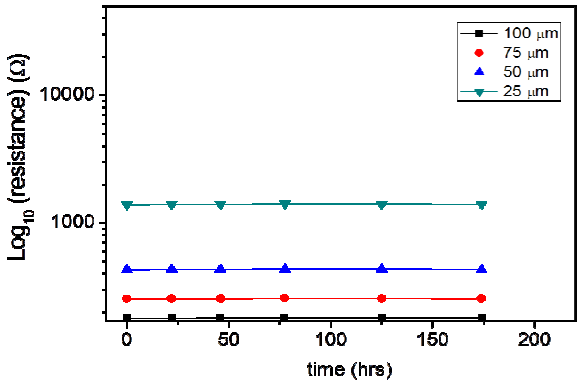

Fig. 7: evaluation of resistance of Cu meanders of 25, 50, 75 and 100um width, protected with a 5um Parylene-C layer and exposed to DPBS at 70°C during ~170hours. Corrosion effects are not observable yet due to efficient Parylene protection, hence testing will be continued.

Cu diffusion evaluation by cell culture tests

Also diffusion from solid materials from the electronic device through the barrier layer into the human body is unacceptable. To test barrier materials for this type of diffusion, we have developed dedicated test methods based on Cu-sensitive cell cultures. We selected to use copper as test vehicle, since Cu is diffusing easy and Cu is cytotoxic. Cu layers are covered with the barrier layer under test, a glass ring is glued on top of this layer, and cell culture tests are carried out using this ring as cell culture dish, see Fig.2. If Cu is diffusing through the barrier layer under test, the fluid on top of the barrier will be loaded with Cu ions which will damage/kill the cells. We selected primary HFF-cells for these tests, 5 um Parylene-C and Parylene-N are deposited on top of a Cu layer, and further sample preparation is performed similar as for the cytotoxicity tests.

The test results are shown in Fig. 8. It is clear that the cell viabilities are higher when the Cu layer is covered with Parylene-C or -N, proving that both Parylene types are severely slowing down the diffusion of Cu into the cell culture medium. Nevertheless, the viabilities are still higher if no Cu layer is present, indicating that some diffusion does still occur through the 5um thick Parylene layers. To stop Cu diffusion, thicker layers or stacks of barrier layers will be needed.

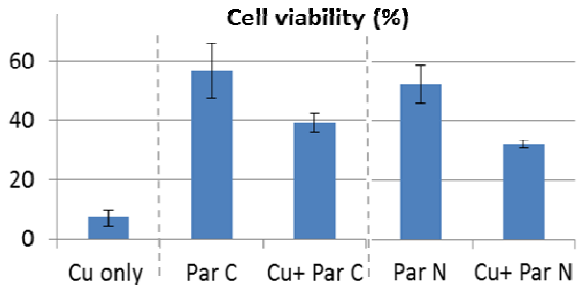

Fig. 8: cell viability (%) for Cu-layers covered with Parylene-C (left) and Parylene-N (right) as diffusion barrier, to be compared to the cell viability of the negative control (Cu only) and positive controls (Par-C and Par-N respectively). Error bars correspond to the 'standard error of the mean' (SEM).

Diffusion evaluation based on direct-contact tests is typically limited to a duration of 7-21 days, since a longer test period will often result in cell death due to overpopulation. This short test period is in contrast with the use of long term implants. Hence protocols for accelerated testing with respect to Cu diffusion through the barrier should be developed. For electronics, accelerated diffusion testing is typically done using elevated temperatures. Note that it is useless to perform cell cultures at elevated temperatures to accelerate diffusion: incubation of cells at temperatures above 45°C results always in cell death.

Stretchability of Parylene-C

A barrier material might be applied on a flexible support, which enables some bending of the final device. In such a case, bending of the device will result in local stress on the barrier layer, and ideally the barrier layer can stretch to releave the stress without losing its function as diffusion barrier. In case a barrier material is used for a stretchable device, than an even larger stretchability of the barrier material is essential. Most barrier materials however have limited stretchability: a small elongation is often resulting in a few (small) cracks which might be invisible by naked eye but the barrier function of the layer will be damaged.

For Parylene-C stretch tests, a 3um, a 16um and a 25um thick Parylene layer is coated on top of 3 stretchable PDMS substrates. Each substrate is stretched cyclic up to 5% elongation, meanwhile the force measured to perform the mechanical displacement is measured. The result for the 3um thick Parylene layer is plotted in Fig. 9: during the 1st stretch cycle, a jump in the curves suggest a crack in the Parylene layer, and some plastic deformation is seen. Further stretch cycles show elastic behavior without 'jumps'. Similar results are observed for 16µm and 25µm thick Parylene-C layers on PDMS. The small cracks upon elongation were not visible by the naked eye, since the thin transparent Parylene layer is hardly visible on the PDMS, but obviously cracks will severely damage locally the barrier function of the Parylene.

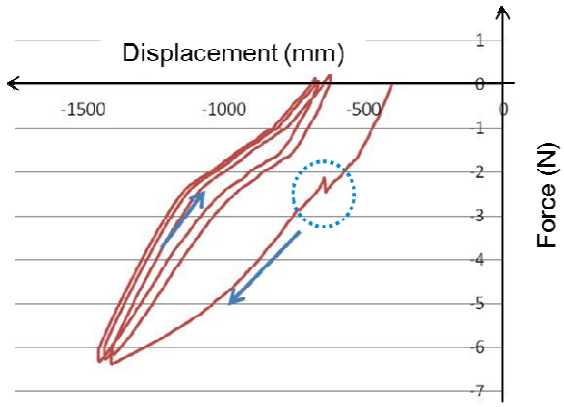

Fig. 9: : Force versus displacement curves for 3 µm parylene-C layers deposited on PDMS, applying 5% maximum stretching. During the 1st stretch cycle, a jump in the curves, indicated by the circle, suggest a crack in the Parylene layer. Further stretch cycles show elastic behavior.

Conclusions and future work

In order to develop an advanced polymer based package technology to obtain small and flexible medical implants, bi-directional diffusion barriers are essential to protect the electronic device and the local tissue against adverse effects from each other.

Parylene is under investigation as candidate barrier material. Adhesion tests of Parylene-C on various substrates are performed and on substrates suffering from bad adhesion, various adhesion promotion treatments are evaluated and optimized, since good adhesion is crucial for corrosion prevention. Dedicated corrosion tests have shown that 5um Parylene-C is protecting Cu lines for corrosion at 70°C for at least 170 hours, more testing needs to be performed in order to fully characterize corrosion prevention by parylene-C. Tests have been limited to passive corrosion tests, but in future active corrosion tests will be performed too: during such a test, a current will flow permanently through the Cu meanders which are exposed to a biofluid. The current flow might create a galvanic reaction, in that case corrosion is more likely to occur.

Cell culture test have shown that Cu diffusion is not sufficiently stopped by 5um Parylene-C or -N, hence a thicker Parylene layer or a combination with other barriers might be essential. Also dedicated cell culture protocols with non-adherent cell types will have to be developed to perform reliable tests on these hydrophobic and cytophobic barrier layers.

Since a 5um thick Parylene-C layer shows only a limited diffusion reduction, the combination of Parylene-C layers with other barrier materials might be a promising option. ALD- Al_2O_3 is such a barrier layer, it is biocompatible (if optimum processing hence no impurities) and low deposition temperatures can be used (<100°C if plasma-ALD is used). Stacks of organic Parylene films and inorganic Al_2O_3 ALD layers might combine interesting barrier properties of both materials [Ref. 12, 13]. Moreover, excellent adhesion between both films eliminates the condensation of moisture around hygroscopic interface contaminants. Hence a stack combining Parylene with ALD-Al_2O_3 might be a very efficient bi-directional diffusion barrier.

Since electronic implants are often designed to stay for many (tens of) years in the body, accelerated tests need further development to predict with high accuracy the prevention of corrosion or adverse tissue effects by the use of bi-directional diffusion barriers.

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