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Protection of active implant electronics with organosilicon open air plasma coating for plastic overmolding

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Abstract: To overcome challenges for manufacturing of modern smart medical plastic parts by injection molding, e.g. for active implants, the optimization of the interface between electronics and the polymer component concerning adhesion and diffusion behavior is crucial. Our results indicate that a nano-sized $SiO_xC_yH_z$ layer formed by plasma-enhanced chemical vapour deposition (PE-CVD) via open air atmospheric pressure plasma jet (APPJ) and by use of a hexamthyldisiloxane (HMDSO) precursor can form a non-corrosive, anti-permeable and biocompatible coating. Due to the open air character of the APPJ process an inline coating before overmolding could be an easy applicable method and a promising advancement.

Keywords: active implants; APPJ; HMDSO; injection molding; PE-CVD.

1 Introduction

An important requirement in manufacturing of modern smart medical plastic parts will be the ability for direct, assembly free integration of various electronic elements, like sensors or components for information storage, part identification/ traceability or plagiarism protection. In this context injection molding as an established and economically proven process to manufacture plastic parts must be considered. However diverse challenges occur from the assembly free integration of electronic parts by injection molding and the intended use as an active implant: Electronic insert parts have to face high mechanical, thermal and thermo-mechanical stresses [1] as well as chemical or other application related loads (see Figure 1).

An additional challenge is the optimization of the interface between electronics and polymer component concerning form-fitting connection, adhesion and diffusion behavior.

Especially for implants with integrated electronics, which are so far protected to the human body with metal or glass packaging a coating is suggested as an alternative [2–4]. In the present study nano-sized $SiO_xC_yH_z$ layers, formed by PE-CVD via APPJ and by use of a HMDSO precursor, are evaluated as an appropriate barrier between sensitive, potentially non-biocompatible electronic materials and a part forming overmolded polymer casting.

Different authors already reported advanced surface properties after plasma coating [5–10]. For example Pihan et al. state better adhesion properties with $SiO_xC_yH_z$ coating [7]. Other groups achieve sufficient protection against corrosion [8–10].

Especially an inline $SiO_xC_yH_z$ thin film coating combined with polymer overmolding is a promising approach to form a non-corrosive, anti-permeable, biocompatible packaging for active implants.

2 Material and methods

2.1 Test specimen and plasma parameters

In this study different test specimen are coated by PE-CVD with use of a hexamethyldisiloxane (Sigma-Aldrich Chemie GmbH, Germany, $\geq 98\%$) precursor. Different materials, comprising stainless steel, aluminum, and a FR-4 based printed circuit board (PCB, $6 \times 10 \times 1.5$ mm) with and without a digital temperature/humidity SHT21 sensor (Sensirion AG, Switzerland), have been coated.

The $10 \times 10 \times 1$ mm stainless steel (316L) and aluminum specimens first have been cleaned in an ultrasonic cleaning bath filled with acetone (VWR, USA)

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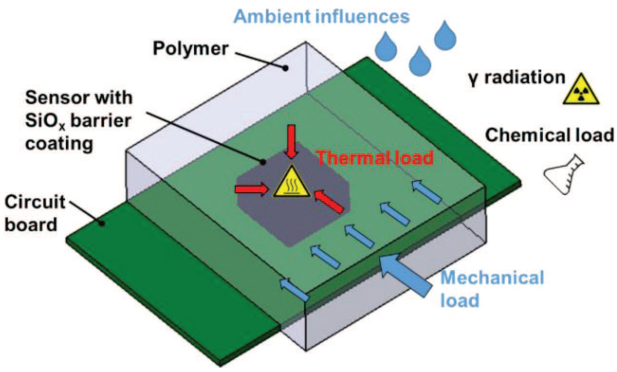

Figure 1: Challenges for direct, assembly free integration of electronic components by injection molding and for use as a smart medical device.

and following with ethanol (Sigma-Aldrich, 30%). Subsequently the samples have been etched for 10 min with nitric acid and cleaned again. The PCB specimen have been cleaned only with compressed air.

The PlasmaPlus® jet (Plasmatreat GmbH, Germany) was operated at 23 kHz plasma power (280 V, 14.3 A) and a plasma cycle time of 100% with clean dry industrial air as ionization gas at a flow of 2000 l/h. The precursor was mixed with nitrogen gas (carrier gas, 300 l/h) in an evaporator at 100°C and added to the plasma flame.

In a distance of 20 mm to the nozzle the test substrates first have been pre-treated/activated two times by moving through the precursor-free plasma torch with a speed of 10 m/min (see Figure 2). After adding the precursor with a flow rate of 40 g/h the materials have been coated by two or respectively eight coating passes.

2.2 Experimental setup

Film deposition and properties have been studied by SEM surface analysis (JSM-5400, Jeol GmbH, Germany) and contact angle (CA) measurement (OCA20, Data Physics Instruments GmbH, Germany). The character of the film regarding thickness and roughness has been exemplarily measured by ellipsometry (SE 800, SENTECH Instruments GmbH, Germany) on silicon wafers.

Additionally a cytotoxicity analysis according to DIN EN ISO 10993-5 (elution test, 72 h eluting time) using Hs27 fibroblasts and a CCK-8 cell counting kit (Dojindo Laboratories, Japan) has been performed to study the bioprotective effect of the $SiO_xC_yH_z$ thin film coating. As a substrate for the coating exemplarily stainless steel specimens were used which in advance have been etched according to ASTM D2651 to gain cytotoxic properties.

To analyse corrosion effects all coated specimens have been visually checked after immersion in 5% NaCl solution for 48 h at 37°C by use of a VHX-5000 digital microscope (Keyence Corporation, Germany).

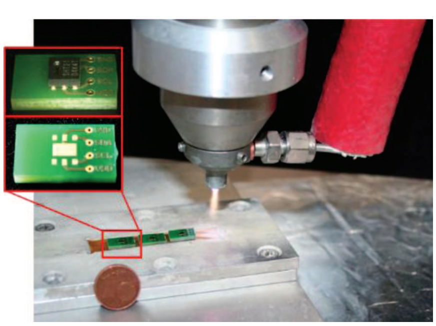

Figure 2: APPJ with evaporator and electronic test specimen (FR-4 based printed circuit board with/without sensor).

3 Results and discussion

3.1 Film deposition and properties

Film deposition could be shown by static measurement of the contact angle before and after coating (see Figure 3). Measurements of CA on stainless steel and on FR-4 PCB substrates showed approximately hydrophilic properties (54–59°) before coating and a shift to hydrophobic surfaces after two (84–86°) as well as after eight coating passes (88–101°).

In SEM analysis after two passes a coating was not visible, but CA measurement indicate a polymer-like $SiO_xC_yH_z$ film. After eight coating passes a homogenous particle distribution on the surfaces could be seen (see Figure 4).

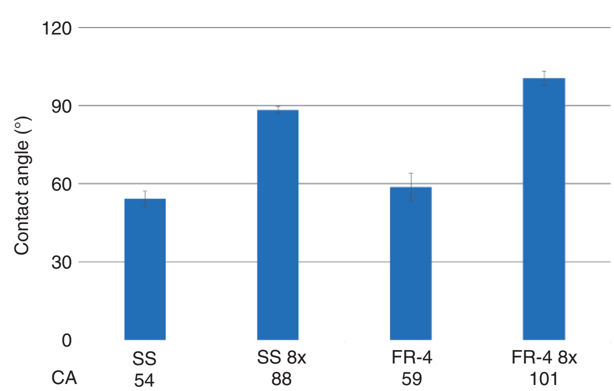

Figure 3: CA measurement of uncoated and 8x coated stainless steel (SS, n = 7) and FR-4 (n = 4) samples.

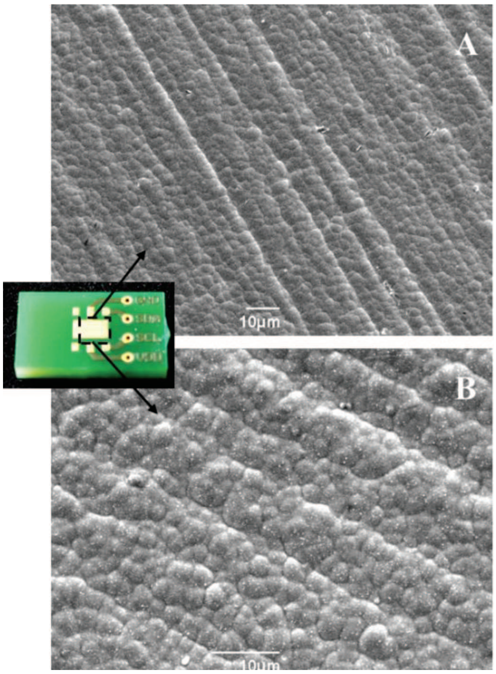

Figure 4: SEM images of PCB surface, uncoated (A) and after 8 coating passes with polymer-like $SiO_xC_yH_z$ film and homogeneous particle distribution (B).

Ellipsometry after eight passes showed a film thickness of up to 200 nm and a surface roughness of 10–20 nm.

3.2 Cytotoxicity

The ASTM D2651 etching procedure with no post treatment ensured a guaranteed cytotoxic surface on the stainless steel specimen as can be seen in Figure 5 (stainless steel).

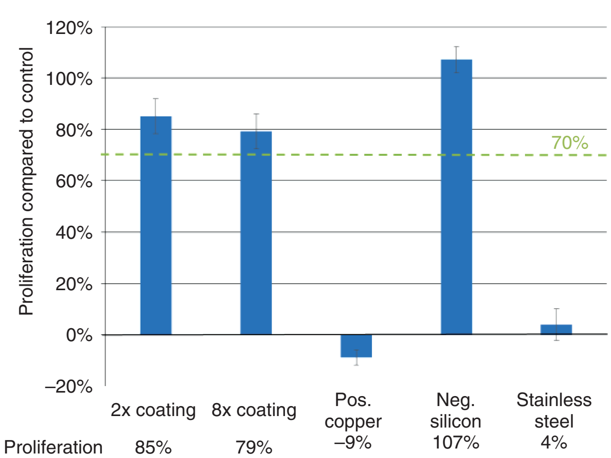

Figure 5: Proliferation of Hs27 fibroblast cells compared to control (n = 3).

Table 1: Sensor functional test without and after 2x coating (Sensor precision: temperature ±0.3°C humidity ±2% RH).

Parameter	Sensor uncoated	Sensor coated
Temperature [°C]	22.94	23.17
Humidity [%RH]	39.39	39.10

As additional positive control a copper substrate and as negative control biocompatible silicon has been used.

According to DIN EN ISO 10993-5 for a classification of non-cytotoxicity a minimum proliferation rate of 70% has to be reached. No cytotoxic effect could be measured on the steel substrate after two (85% proliferation) and eight (79% proliferation) coating passes.

This shows that the coating, at least for the cytotoxic stainless steel specimens, very effectively protects against the cytotoxic properties of the substrate.

3.3 Sensor function after coating

Function studies showed that $SiO_xC_yH_z$ film coating did not affect the function of the sensors (see Table 1).

This was not expected because a temperature of up to 181°C was measured on the specimen surface during treatment. This is an interesting observation since also in overmolding high temperature loads occur.

3.4 Corrosion protection

Immersion in 5% NaCl leads to a definite pitting corrosion of uncoated aluminum specimens. This could clearly be reduced already by two coating passes (see Figure 6).

4 Outlook and conclusion

Our studies showed that the APPJ process is an easy applicable method to deposit $SiO_xC_yH_z$ films on different

Figure 6: Aluminium samples without (left) and with 2 plasma coating passes (right) after 48 h immersion in 5% NaCl solution.

substrates and sensitive electronic components. It works as an effective protection against cytotoxic properties of the substrate and corrosive attacks, which supports observations of other groups [3, 5–10].

In further experiments we showed that the surface of the $SiO_xC_yH_z$ film coating could be hydrophilized by additional plasma activation (without precursor). This would lead to optimized surface adhesion properties for a subsequent polymer casting [11] of the insert by overmolding, which is currently under investigation in our group.

In summary the $SiO_xC_yH_z$ film coating applied by APPJ is a very promising and inline applicable technology to prepare electronic parts for assembly free integration in plastic components to realize smart medical devices.

Author's Statement

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References

[1] Heinle M, Drummer D. Measuring mechanical stresses on inserts during injection molding. Adv. Mech. Eng. 2015;7:1–6.
[2] Hogg A, Uhl S, Feuvrier F, Girardet Y, Graf B, Aellen T, et al. Protective multilayer packaging for long-term implantable medical devices. Surf Coat Technol. 2014;255: 124–9.
[3] Hsiao CR, Lin C-W, Chou C-M, Chung C-J, He J-L. Surface modification of blood-contacting biomaterials by plasma-polymerized superhydrophobic films using hexamethyldisiloxane and tetrafluoromethane as precursors. Appl Surf Sci. 2015;346:50–6.
[4] Morales JMH, Souriau J-C, Ratel D, Berger F, Simon G. Biophysicochemical Evaluation of Passivation Layers for the Packaging of Silicon Microsystems in Medical Devices. At: IEEE Electronic Components & Technology Conference 2014.
[5] Merche D, Vandencasteele N, Reniers F. Atmospheric plasmas for thin film deposition: a critical review. Thin Solid Films. 2012;520:4219–36.
[6] Pulpytel J, Kumar V, Peng P, Micheli V, Laidani N, Arefi-Khonsari F. Deposition of organosilicon coatings by a non-equilibrium atmospheric pressure plasma jet: design, analysis and macroscopic scaling law of the process. Plasma Process Polym. 2011;8:664–75.
[7] Pihan SA, Tsukruk T, Förch R. Plasma polymerized hexamethyldisiloxane in adhesion surface. Surface & Coatings Technol. 2009;203:1856–62.
[8] Lommatzsch U, Ihde J. Plasma polymerization of HMDSO with an atmospheric pressure plasmajet for corrosion protection of aluminium an low-adhesion surfaces. Plasma Process Polym. 2009;6:642–8.
[9] Bonova L, Zahoranová A, Kováèik D, Èernák M. Deposition of polymer films on aluminium surface using atmospheric-pressure plasma. Chem. Listy. 2012;106:1431–4.
[10] Regula C, Ihde J, Lommatzsch U, Wilken R. Corrosion protection of copper surfaces by an atmospheric pressure plasma treatment. Surface & Coatings Technol. 2011;205:355–8.
[11] Awaja F, Gilbert M, Kelly G, Fox B, Pigram PJ. Adhesion of polymers. Prog Polym Sci. 2009;34:948–68.