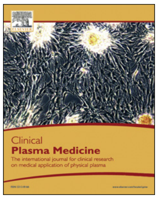
Clinical Plasma Medicine 3 (2015) 3–9

Contents lists available at ScienceDirect

Clinical Plasma Medicine

journal homepage: www.elsevier.com/locate/cpme



Plasma deposited silicon oxide films for controlled permeation of copper as antimicrobial agent

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ARTICLE INFO

Article history:
Received 28 July 2014
Received in revised form
16 January 2015
Accepted 27 January 2015

Keywords:
Antimicrobial deposition
Atmospheric plasma jet
Copper
Dental implant
Peri-implantitis

ABSTRACT

The aim of this study is to test silicon oxide (SiO_x) coatings on copper surfaces as permeation barrier for copper ions affecting the release into the surrounding medium.

SiO_x films have been deposited on copper coated micro-structured titanium samples by means of a plasma jet. Siloxane layers have been formed from hexamethyldisiloxane (HMDSO) and oxygen using different mixing ratios.

FT-IR spectroscopy reveal different SiO_x layer characteristics depending on the HMDSO:O_2 ratio. The permeation and release of copper is mainly determined by structural defects of the SiO_x layer promoting pinhole corrosion and leading to enhanced Cu release compared to uncoated samples.

1. Introduction

In the past decades dental implantology has evolved in particular with respect to biological acceptance and osseo-integration. However, long-term success is still impaired by microbial bio-film formation followed by peri-implant diseases, which are present in two forms – peri-implant mucositis and peri-implantitis. Both of these are characterized by an inflammatory response of tissues surrounding an implant [1]. Peri-implantitis can affect the entire implant surrounding tissues which are in contact with the smooth surface of implant abutment as well as the microstructured intra osseous part [2]. The basic procedure to prevent peri-implantitis or to support the healing process is the removal of microbial biofilms [3] and decontamination applying different methods. In recent studies the decontamination and conditioning of titanium implant surfaces by atmospheric plasma treatment has been suggested as an alternative method [4–8]. Atmospheric pressure jet-like discharges have been shown to be a promising tool for a variety of surface modifications since the gas temperature can be adjusted to room temperature or slightly above. Thus, it is compatible to biological specimen and relevant materials in dentistry. Furthermore, the production of active species in the plasma is very effective due to pulsed microwave excitation. The well controllable interaction region of the plasma on the substrate surface with typical lateral sizes of 1–2 mm allows for highly defined surface modifications like activation, etching, or material deposition.

Until now, all decontamination procedures show no long-lasting effects in therapy due to the lack of long-term antimicrobial effects. A recent challenge is the development of antimicrobial surfaces with a sustaining release of inhibitors against the bio-film formation, like a “controlled drug-delivery system”. SiO_x thin film encapsulation of active agents could provide the basis for this application. Recently, it has been discovered that siloxane films exhibit good biocompatibility [9]. Hence, the implementation of such films is regarded for various promising applications in medicine. Prasad et al. showed a high proliferation rate and viability of rat aortic smooth muscle cells on siloxane films [10]. Hayakawa et al. [11] have demonstrated that the high vapor deposition of HMDSO on titanium benefit the adsorption of fibronectin on titanium at the early stage of formation. This opens up the potential applicability as a dental implant material.

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http://dx.doi.org/10.1016/j.cpme.2015.01.001
2212-8166/

Furthermore, Zhou et al. [9] have described that deposited SiO_x-like films have an excellent corrosion resistance in 0.1 mol/l NaCl solution and thereby it improves the corrosion resistance of Ti alloy (Ti6Al4V). A further approach is the use of SiO_x thin films as a permeation barrier of oxygen using for food packing application [12] and the capability to transfer metal ions like silver through such films [13]. The bactericidal effect of silver-containing coatings deposited by atmospheric pressure plasma chemical vapor deposition and combustion chemical vapor deposition has been shown by Zimmerman et al. [14]. Similar research activities on the effect of alternative metal ions like copper coated by SiO_x thin films are not yet represented in literature. In our study we used copper as a potential anti-microbial agent. The anti-microbial effect of copper was reported by Mulligan et al. The study shows the impact of phosphate based glasses doped with copper on the viability of biofilm of *Streptococcus sanguis* [15].

The aim of the present study is to investigate the release of copper ions through plasma deposited SiO_x layers into a surrounding aqueous medium depending on the SiO_x thin film deposition conditions.

2. Material and methods

2.1. Plasma jet system

Plasma assisted deposition of SiO_x thin films has been performed using an atmospheric pulsed microwave plasma jet at 2.45 GHz, which was developed by Leibniz Institute of Surface Modification (IOM). The plasma jet source and the microwave pulse generator are described in detail by Lehmann et al. [16]. A schematic drawing of the source and the system is shown in Fig. 1(a) and (b), respectively. The plasma jet discharge is generated by a helium gas flow of 700 sccm emerging from the source nozzle, which is ignited and sustained by the high frequency electrical field of the microwave. A shielding gas flow of 700 sccm N_2 surrounds the plasma discharge. For the formation of SiO_x thin films the liquid precursor hexamethyldisiloxane HMDSO ($Si_2O_2C_6H_{18}$) is evaporated in a N_2 bubbler (hereinafter termed as N_2/HMDSO). Both the pure N_2 shielding gas flow and the HMDSO enriched N_2 flow are fed to the peripheral channel of the plasma source (see Fig. 1(a)).

Additionally, O_2 is admixed to the central He gas flow. The gas composition is shown in Table 1. All gas flows are controlled by mass flow controllers (Bronkhorst, Ruurlo, The Netherlands). SiO_x films with uniform thickness have been deposited on the substrate by scanning the surface applying a raster path with working distance of 4 mm, scan velocity of 0.2 mm/s, and line feed distance of 0.1 mm. Thin film deposition has been performed using the following plasma parameters: rectangular microwave pulses with maximum power: 200 W, duty cycle: 2%, mean power: 4 W, pulse repetition frequency: 4 kHz. The plasma jet source is mounted on a 3-axis motion system which allows a computer controlled motion scheme over the entire sample surface.

2.2. Sample preparation

All experiments have been performed on etched and sand blasted titanium discs (Friadent, Mannheim, Germany, 10 mm in diameter, 2 mm in thickness and with a roughness of $R_a = 2.1\ \mu m$). Ti samples have been coated on one face by a copper film of 200 nm thickness and 8 mm in diameter using a magnetron sputtering system Z400 (Leybold Heraeus, Germany). A total mass of approximately 0.087 mg has been deposited on the surface based on a density of copper of 8.69 g cm^{-3}. Subsequently, the copper deposits have been encapsulated by SiO_x films. A schematic sketch of the layer stack is shown in Fig. 2.

In order to investigate the influence of different SiO_x layer compositions and structural properties on the release of copper during corrosion experiments the plasma operation parameters have been varied. Different gas flow rates for O_2 and N_2/HMDSO, respectively, have been chosen as indicated in Table 1. Four sample groups A, B, C, and D have been prepared and investigated. Since deposition rate depends on the precursor flow the effective dwell time has been properly adjusted to obtain the same SiO_x film

Table 1
Process parameter of SiO_x thin film deposition, deposition rates and stoichiometries.

Group	O_2 flow [sccm]	N_2/HMDSO flow [sccm]	Deposition rate [10^{-5} mm^3/s]	Stoichiometry SiO_x
A	2	7	5.1	1.91
B	7	7	6.0	1.94
C	10	7	6.1	1.94
D	7	10	8.0	1.94

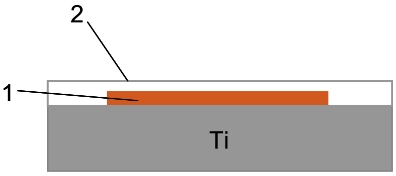

Fig. 2. Schematic sketch of the layer stack (1: 200 nm Cu, 2: 170–180 nm SiO_x thin film).

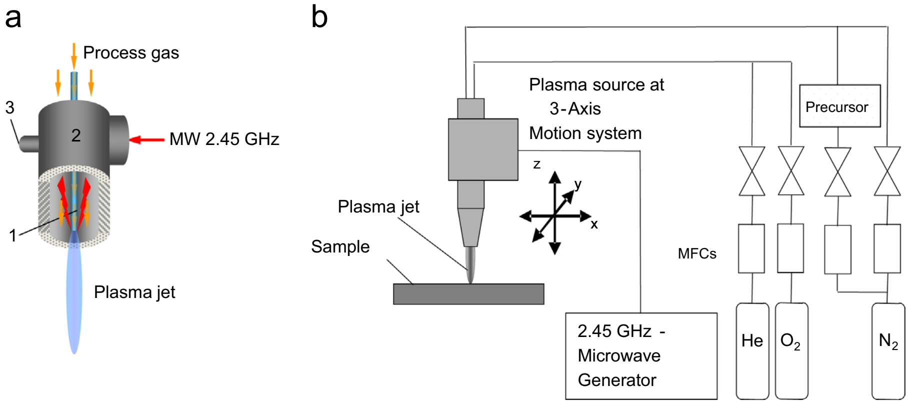

Fig. 1. (a) Sketch of the plasma source with gas and microwave supply. 1-inner tube, 2-source body, 3-peripheral gas channel for HMDSO/N_2 flow. (b) Schematic drawing of plasma jet processing system.