Materials Science and Engineering C 74 (2017) 508–514

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Vacuum arc plasma deposition of thin titanium dioxide films on silicone elastomer as a functional coating for medical applications

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ARTICLE INFO

Article history:
Received 26 October 2016
Received in revised form 30 November 2016
Accepted 11 December 2016
Available online 12 December 2016

Keywords:
Silicone elastomer
Titanium dioxide
Coating
Vacuum arc plasma
Cytocompatibility
Cytotoxicity

ABSTRACT

Silicone elastomer is a promising material for medical applications and is widely used for implants with blood and tissue contact. However, its strong hydrophobicity limits adhesion of tissue cells to silicone surfaces, which can impair the healing process. To improve the biological properties of silicone, a triggerless pulsed vacuum cathodic arc plasma deposition technique was applied to deposit titanium dioxide (TiO_2) films onto the surface. Scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and contact angle measurements were used for coating characterization. Deposited films were about 150 nm thick and exhibited good adhesion to the underlying silicone substrate. Surface wettability and roughness both increased after deposition of the TiO_2 layer. In addition, cell-biological investigations demonstrated that the *in-vitro* cytocompatibility of TiO_2-coated samples was greatly improved without impacting silicone's nontoxicity. For validation of use in medical devices, further investigations were conducted and demonstrated stability of surface properties in an aqueous environment for a period of 68 days and the coating's resistance to several sterilization methods.

1. Introduction

Silicone elastomers have been widely used for decades as materials for long-term implantation in devices such as cardiac pacemakers, mammary implants, maxillofacial implants, voice prostheses, finger-joint prostheses, drainage tubes, and catheters. The silicone elastomers most commonly used for medical applications are crosslinked polydimethylsiloxanes (PDMS), which are composed of an alternating Si-O-Si backbone with organic methyl side groups. In this work, silicone elastomers are also referred to as silicones or PDMSs. The bulk properties of PDMSs make them particularly attractive for medical applications: they are chemically and physiologically inert, resistant to sterilization and disinfection, transparent, and high flexible [1]. The inertness enables stable mechanical properties and long-term use of PDMS in biological environments without degradation of the polymer [2]. Moreover, medical-grade silicone is reported to be nonimmunogenic and nontoxic [2,3,4].

Compared to other polymeric materials, PDMS exhibit a strongly hydrophobic surface due to the presence of nonpolar methyl groups there [1]. The strong hydrophobicity causes pronounced nonspecific protein adsorption and surface-mediated conformation changes of proteins [5,6], which can initiate adverse reactions, chronic inflammatory response and fibrous encapsulation (so-called foreign-body reaction) [7]. Excessive foreign-body reaction with thick fibrosis capsule can become clinically symptomatic [8]. Moreover, the pocket around the implant can provide bacteria with an environment in which to develop and may engender infections [9].

Hydrophilic modifications of silicone elastomer intended to improve bio- and cytocompatibility is a current research topic in biomedical engineering. Various strategies have been pursued including physical modification techniques [10,11], bulk modifications with hydrophilic blends and copolymers [12], as well as covalent surface modifications and chemical grafting [3,13,14]. However, they still suffer from important limitations, especially concerning potential use in biomedical devices. Modifications should not affect the mechanical properties of PDMS, nor contain any potentially toxic substance. Enduring stability of surface modifications is often limited by so-called hydrophobic recovery. The rotational flexibility of the Si-O-Si backbone causes grafted species to rearrange inside the PDMS bulk and get replaced on the surface by new nonpolar methyl groups within a few hours [3,10,14,15]. The main challenges confronting thin coatings are overcoming the strong inertness of the bare PDMS surface to ensure good coating adhesion, and ensuring that the coatings do not delaminate if the flexible silicone substrate is mechanically deformed or during prolonged contact with

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http://dx.doi.org/10.1016/j.msec.2016.12.045
0928-4931/

biological fluids [16,17]. Moreover, to be usable in medical devices, modifications should be resistant to sterilization, easy to process, reproducible, persistently stable, and cost effective.

On the other hand, titanium is a well-established material for biomedical applications, especially in dental and orthopedic implants, because of its excellent biocompatibility. This is due to the spontaneous formation of a passive oxide layer (titanium dioxide), which undergoes hydroxylation in aqueous environments and gives the surface its hydrophilic properties [18]. This is assumed to lead to favorable protein adsorption [19] and improved *in-vitro* cytocompatibility [20,21] of titanium dioxide. Improvements of the bioadhesion of titanium dioxide coatings have been reported *in vivo* with nonelastomeric substrates such as polyethylene and PTFE [21,22].

The objective of this work was to combine the excellent bulk properties of silicone elastomer with the biocompatibility of titanium dioxide. Thin titanium dioxide coatings were produced through triggerless pulsed vacuum cathodic arc plasma deposition. This coating technique can be used to deposit very stable, reproducible thin coatings with strong adhesion to the substrate [23]. The advantage of this technique is that coating composition can be very accurately controlled, which is crucial for biomedical applications. Another major advantage of this technique compared to other physical vapor deposition techniques is the presence of ions with high kinetic energy. Those ions are subplanted when they hit the substrate surface, which assures a good coating substrate bond, whereas a punctually high-energy impact can quickly dissipate without damaging the overall substrate structure [24]. This technique can be used to produce a big variety of coatings [25]. In particular, it was used, *e.g.*, to metalize silicone for manufacturing flexible electrodes [26]. Besides improving bioadhesion thanks to TiO_2, coated material should comply with requirements imposed on biomedical devices, such as enduring stability, non-cytotoxicity, and resistance to sterilization.

2. Materials and methods

2.1. Sample preparation

2.1.1. PDMS substrate preparation

Wacker Chemie AG, Germany, provided the medical-grade HTV (high temperature vulcanizing) silicone elastomer (Silpuran® UR 9030/60). It was mixed in the ratio 1:100 with a platinum catalyst (Silpuran® Curing Agent M, Wacker Chemie AG, Germany) and vulcanized in a heating press for 10 min at 200 °C and 50 bar as 2 mm thick plate. Post-curing was carried out for 4 h at 200 °C. PDMS samples were cleaned in 70% isopropanol for 20 min in an ultrasonic bath and vacuum dried before coating.

2.1.2. TiO_2 coating

The silicone plates prepared as described in the previous paragraph were used as a substrate for the deposition of TiO_2 coating using a triggerless pulsed vacuum cathodic arc plasma deposition technique. Fig. 1 shows the schematic setup of the deposition system. Here, titanium plasma was produced by cathodic arc discharge operated in pulsed mode. The cathode consisted of a titanium rod with a diameter of 15 mm. A copper tube surrounding the cathode served as an anode. To insulate the cathode from the anode, a matching size Al_2O_3 ceramic tube was placed between them. A Pulse Forming Network (PFN) provided high current, high voltage pulses for the discharge. The insulator surface was coated with a thin conductive layer to ignite the arc in the so-called triggerless mode [27]. After ignition, the strong discharge current caused evaporation and ionization of titanium from the cathode surface. An additional supply of pure oxygen into the vacuum chamber near the substrate was used to form TiO_2. The working pressure was set to $2.5 \cdot 10^{-1}$ mbar. Thus an optimal oxygen rate was provided for titanium dioxide formation at maximum deposition rate. The substrate was insulated from the chamber walls to avoid accidental discharge on its surface. The discharge operated at 1 Hz to ensure deposition while substrate temperature did not considerably exceed room temperature. The deposition process' parameters are summarized in Table 1.

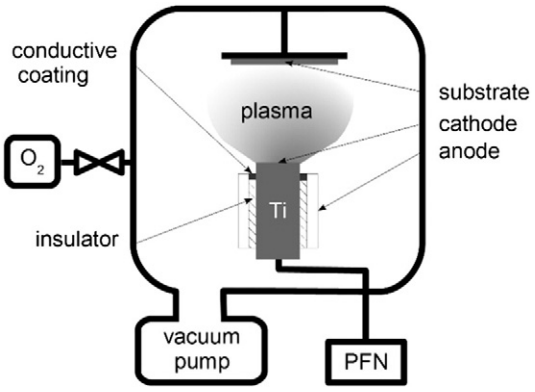

Fig. 1. Schematic representation of the vacuum arc system for depositing TiO_2.

Additional silicone samples were prepared to visualize the coating's effect on cell adhesion. For this, the substrate was partially covered by an additional thin foil to create coated and uncoated areas for direct comparison of cell adhesion on coated and uncoated surfaces.

Silicone-substrate surface roughness and structure depend heavily on the plate structure used for manufacturing. This makes it particularly difficult to investigate coating thickness and growth structure. To be able to conduct this investigation independently of substrate properties, Si wafers with surface roughness in the subnanometer range were also coated using the original process parameters. A suitable tool for coating growth structure and thickness analysis could thus be provided.

2.2. Coating analysis

2.2.1. Microscopic analysis

Scanning electron microscopy (SEM) was used to analyze the morphology of the coated silicone surface. Here, TM3030 Tabletop SEM (Hitachi Ltd., Japan) was used. Since the atomic weight difference between Ti and Si atoms is significant, a backscattered electron (BSE) detector could also be used to visualize the distribution of different atomic species.

Moreover, reaction of the samples to tensile load could be investigated. For this purpose, a special probe mounting was used, which allowed the silicone substrate to be stretched to 200% of its initial length. In this manner, a mounted sample was further investigated using SEM.

To determine the coating thickness and to visualize the cross section of the coating, field emission SEM JSM 7500F (JEOL Ltd., Japan) was used due to its higher resolution capability. TiO_2-coated silicon wafers were fractured along their preferential crystal orientation to visualize the cross section.

2.2.2. Composition of the coating

X-ray photoelectron spectroscopy (XPS) was used to investigate the coating composition. A ESCA + (Scienta Omicron GmbH, Germany) system with an Argus CU analyzer was used here. XPS was operated with a magnesium K-α source at an excitation energy of 1253.6 eV. In contrast

Table 1
Coating conditions for TiO_2 layer.

Specimen temperature	Room temperature [293 K]
Basic vacuum	10^{-4} mbar
Working pressure	$2.5 \cdot 10^{-1}$ mbar
Pulse duration	400 μs
Peak discharge current level	~500 A
Number of pulses	1000
Substrate	Silupran® UR 9030/60