Materials Research Bulletin 47 (2012) 2994–2998

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Synthesis of titanium oxide thin films containing antibacterial silver nanoparticles by a reactive magnetron co-sputtering system for application in biomedical implants

Doo-Hoon Song [a], Soo-Hyuk Uhm [a,b], Si-Eun Kim [a,b], Jae-Sung Kwon [a], Jeon-Geon Han [c], Kyoung-Nam Kim [a,b,*]

[a] Research Center for Orofacial Hard Tissue Regeneration, College of Dentistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-752, Republic of Korea
[b] Department and Research Institute of Dental Biomaterials and Bioengineering, College of Dentistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-752, Republic of Korea
[c] Center for Advanced Plasma Surface Technology, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440-746, Republic of Korea

ARTICLE INFO

Article history:
Available online 25 April 2012

Keywords:
A. Composites
A. Thin films
B. Sputtering
C. Electron microscopy
C. Photoelectron spectroscopy
D. Surface properties

ABSTRACT

Titanium oxide thin films containing silver (Ag) nanoparticles were synthesized on commercially pure titanium (cp-Ti) substrates using a reactive magnetron co-sputtering method. The goal was to maximize bactericidal activity along with sustained biocompatibility. Furthermore, this study examined the correlation between Ag nanoparticle dispersion in the films and the antibacterial efficacy of the Ag ions released from the films. The results showed that there might be two factors affecting the inhibition of bacterial attachment to the surface of the specimens: surface morphology and Ag ion release. MTT assay results demonstrated that there was no cytotoxicity on fibroblast cells in any group. Overall, the magnetron sputtered Ag nanoparticle-containing titanium oxide coatings in this study can be used as an efficient antibacterial layer with sustained biocompatibility.

1. Introduction

Titanium oxide films have been studied for many applications, including electronic devices, anti-corrosion and optical coatings, and biomedical uses [1]. In dentistry, the surfaces of titanium-based dental implants have been modified according to their properties, including biocompatibility, high mechanical strength, and corrosion resistance [2]. Dental implants in particular consistently require antibacterial properties, as bacterial infection after implantation is a significant complication in clinical situations [3,4].

It has been demonstrated that properties of nanomaterials are dependent on shape, size and composition from both theory [5,6] and experiments [7–9]. Silver (Ag) nanoparticles have been known to be potent antibacterial agents in biomedical applications for many years, and they have the advantage that they come in a variety of shapes and sizes [10–12]; therefore, significant considerations have been focused on the synthesis of nanomaterials with controllable structures, sizes and morphologies [13–16]. One of the ways of producing thin compound films is using a reactive magnetron sputtering system, which not only provides flexibility in forming the films with controllable stoichiometry, but also is straightforward to implement in industrial-scale production, as reviewed in previous reports [17,18].

In this study, titanium oxide thin films containing Ag nanoparticles were synthesized on commercially pure titanium (cp-Ti) substrates using a reactive magnetron co-sputtering method. The goal was to maximize bactericidal activity in conjunction with sustained biocompatibility. Also, we focused on the correlation between Ag nanoparticle dispersion in the films as affected by variations in the target power density and bias applied to the substrate, and the antibacterial efficacy of the Ag ions released from the films.

2. Experimental details

2.1. Synthesis of titanium oxide films containing Ag nanoparticles

The experimental details including the compositional gradient titanium oxide interlayer (0.34 Pa of the oxygen partial pressure) were adapted from our previous study [19]. Titanium oxide films containing Ag nanoparticles (200 nm in thickness) were synthesized with variable power input to the Ag target and substrate bias. Table 1 provides the detailed experimental conditions of this final layer for each sample number.

* Corresponding author at: Research Center for Orofacial Hard Tissue Regeneration, College of Dentistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-752, Republic of Korea. Tel.: +82 2 2228 3081; fax: +82 2 364 9961.
E-mail address: kimkn@yuhs.ac (K.-N. Kim).

0025-5408/$ – see front matter
http://dx.doi.org/10.1016/j.materresbull.2012.04.085

Table 1
Variables and detailed experimental conditions for the numbered samples.

Variables	Detailed conditions
Power input to silver target	1.5, 2.0, 2.5 W cm^{-2}
Bias voltage	−100 V DC, no bias
Sample number	**Parameters**
# 1	1.5 W cm^{-2}, −100 V DC
# 2	2.0 W cm^{-2}, −100 V DC
# 3	2.5 W cm^{-2}, −100 V DC
# 4	1.5 W cm^{-2}, no bias
# 5	2.0 W cm^{-2}, no bias
# 6	2.5 W cm^{-2}, no bias

2.2. Characterization of the film morphology and chemical composition (surface and in-depth)

The film morphologies and the surface distribution of the Ag nanoparticles on the films were confirmed by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan). X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo Electron Corporation, England) analysis with an Al Kα X-ray source was conducted. A time-of-flight-secondary ion mass spectrometry (TOF-SIMS 5, ION-TOF, Germany) analysis was performed with the analysis gun (Bi^+ primary ion source) over a 50 μm × 50 μm area. The analysis used a dual beam mode with 1.0 keV of Cs and O_2 sputtering beam; more details are provided in [20].

2.3. Silver ion release test

Ag ion release tests were performed by immersing the specimens in two different kinds of solutions: standard artificial saliva [19] and phosphate buffered saline (PBS) solution. These solutions mimicked the oral and biological environment, respectively. The release of Ag ions at the designated time was measured using a silver ionic selective electrode (Silver ISE, Orion 96-16, Thermo Electron Corporation, England) over a 24-h period.

2.4. Antibacterial activity tests

Antibacterial activity tests were performed against *Staphylococcus aureus* (*S. aureus*, *SA*, *ATCC 6538*) [21]. Each specimen was

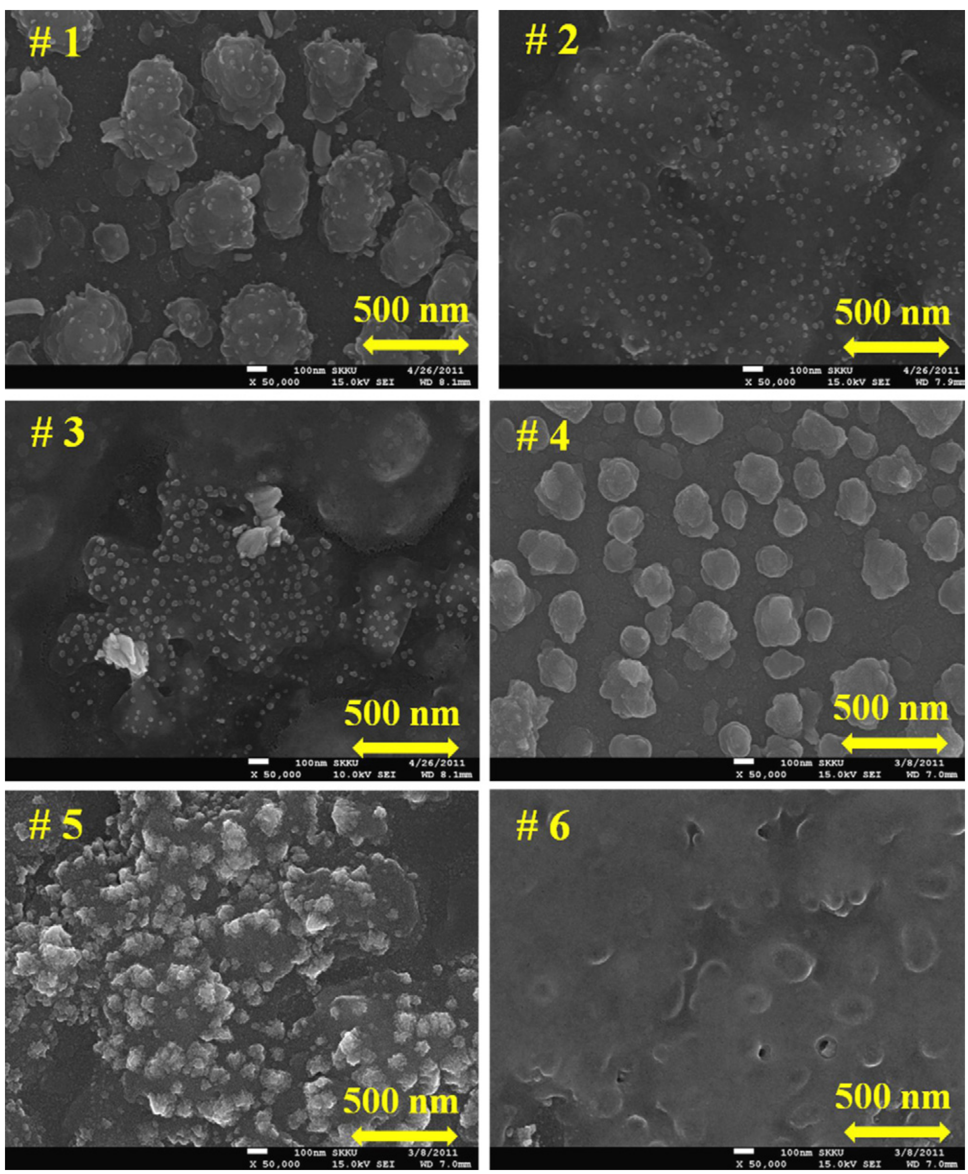

Fig. 1. FE-SEM images of the surface morphology of titanium oxide thin films containing Ag nanoparticles.