



## Controls in wettability of TiOx films for biomedical applications

Zeng Lin<sup>a,b</sup>, Gun-Hwan Lee<sup>c</sup>, Chun-Ming Liu<sup>b</sup>, In-Seop Lee<sup>d,\*</sup>

<sup>a</sup> School of Mechanical Engineering & Automation, Northeastern University, Shenyang 110004, China

<sup>b</sup> School of Materials & Metallurgy, Northeastern University, Shenyang 110004, China

<sup>c</sup> Korea Institute of Materials Science, Gyeongnam 641-831, Korea

<sup>d</sup> Atomic-scale Surface Science Research Center, Yonsei University, Seoul 120-749, Korea

### ARTICLE INFO

Available online 24 August 2010

#### Keywords:

Titanium oxide  
E-beam evaporation  
Wettability  
Surface chemistry  
Irradiation  
Topography

### ABSTRACT

The interaction between metal surface and cell/tissue is important for the biocompatibility of metallic implants, and surface modification has been studied extensively to alter its surface characteristics, and improve biocompatibility. Titanium oxide (TiOx) films were deposited by electron-beam evaporation system using TiO<sub>2</sub> as a source material. The films deposited by various thickness and growth rate were investigated by X-ray diffraction patterns, field emission scanning electron microscopy, X-ray photoelectron spectra and atomic force microscopy. TiOx films were etched subsequently by different plasma to obtain different surface morphology. The structure of TiOx film was uninfluenced after being etched, but the composition of films was changed from nonstoichiometric to stoichiometric due to etching process, and the surface roughness of TiOx films was decreased. TiOx films became highly hydrophilic by ultraviolet (UV) irradiation and returned to its original hydrophobic state by visible-light (VIS) irradiation. The wettability of the TiOx surface was enabled to convert between hydrophilic and hydrophobic reversibly by alternative UV and VIS irradiation. TiOx films were further modified by self-assembled monolayer (SAM) of silanes.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

The possibility to modify and control the surface wettability of different materials has attracted significant scientific and technological interest. Particularly for biological systems the nature of hydrophobic and hydration forces plays a key role on the mediation of solute (e.g. protein) adsorption and cell adhesion [1–3]. Titanium oxide film is a widely used biocompatible material; therefore alterations of surface topography and wetting behavior are of great importance for its biomedical application [4,5]. Several approaches using UV light or organic monolayer have been reported to control the surface wettability of TiO<sub>2</sub> structures in our previous study [6].

In general, TiO<sub>2</sub> films in biocompatible applications were prepared preferentially by the dry processes such as electron-beam evaporation [7–9], ion-beam assisted deposition (IBAD) [10,11], magnetron sputtering [12,13] and metal-organic chemical vapor deposition (MOCVD) [14]. Among them, electron-beam evaporation is a powerful technique to prepare well-crystallized oxide films with higher deposition rate and controlled stoichiometry by adjusting the conditions such as substrate temperature, oxygen gas pressure and evaporation rate [15].

In another paper of our group, we examined thin titanium oxide film formed by e-beam evaporation for biomedical applications [16]. These works revealed that the oxygen supply and the post-deposition heat treatment would influence the composition and crystallinity of the films and the deposited titanium oxide film demonstrated high cell adhesion and little platelet adhesion. In this paper, we would like to describe our investigation on the surface and wetting properties of E-beam evaporation TiOx film that is further modified by plasma treatment, light irradiation and self-assembled monolayer (SAM). To our knowledge, there have been only limited studies on modifying E-beam evaporated TiOx films. The morphology and chemical composition of these oxide films influences the wettability as well as the subsequent adhesion properties of proteins.

The aim of the present study is to investigate the effect of the surface properties (chemical composition, surface topography as well as microstructure) on wettability of TiOx film. The aim is to develop a correlation between the wetting properties and the parameters of the film deposition and further modification process. This will be useful for investigations of the potential correlation of the surface properties and the biological reactions (such as protein adsorption) in the near future.

### 2. Experimental procedure

#### 2.1. Film preparation and characterization

The TiOx films under study were prepared in the electron-beam evaporation system. The distance between the rotating substrate

\* Corresponding author. 134 Shinchon-dong Seodaemoon-gu, Institute of Physics & Applied Physics, and Atomic-scale Surface Science Research Center, Yonsei University, Seoul 120-749, Korea. Tel.: +82 02 2123 4806; fax: +82 02 313 3537.

E-mail address: [inseop@yonsei.ac.kr](mailto:inseop@yonsei.ac.kr) (I.-S. Lee).

holder and the electron-beam evaporation source was 380 mm. The chamber was evacuated by a mechanical pump and a turbo molecular pump. The films were deposited in oxygen atmosphere using  $\text{TiO}_2$  as a source material. The base pressure is  $2.0 \times 10^{-6}$  Torr, and the working pressure is increased to  $0.5\text{--}2.0 \times 10^{-4}$  Torr when pure oxygen gas with various flow rates is supplied to the chamber at a constant pumping speed. The substrates used are polished Si wafers, which were sputter-etched with argon ions ( $\text{Ar}^+$ ) for 20 min prior to the deposition to remove any residual pollutants on the surface. The substrate temperature was maintained at 200 °C. The film thickness is about 0.2–1.2  $\mu\text{m}$  measured by  $\alpha$ -step measurement system.

The surface morphology was evaluated by P-12 surface profiler, field emission scanning electron microscopy (JSM-6500F, JEOL, Tokyo, Japan) and a Dimension 3100 AFM (Digital Instruments, Veeco, CA) in tapping mode at ambient temperature. Composition and valence state analyses of various species present in the films were carried out by XPS (PHI-5700, PHI, Minnesota, USA) with Mg-K $\alpha$  radiation. All spectra were calibrated with the C1s peak at 284.6 eV. The background pressure of the system was less than  $10^{-8}$  Torr. The spectra were curve-fitted using a computer-assisted Lorentzian-Gaussian peak model. The film crystallinity was investigated by GAXRD (XRD; D/max-RINT 2700, Rigaku, Japan) operated under the conditions of 40 kV and 100 mA, equipped with a thin-film attachment on which the glancing angle was fixed at 2°.

Surface wettabilities were evaluated by the water contact angle. The sessile drop method was used for contact angle measurements with a commercial contact angle meter (CA-X, Kyowa Interface Science, Saitama, Japan). The amount of water droplets used for the measurement was 0.5  $\mu\text{L}$ . The contact angles were measured at five different points on the surface of thin films. Contact angle measurements were performed under room temperature in air.

## 2.2. Wettability control

The  $\text{TiO}_x$  film surface was etched by Ar or  $\text{O}_2$  plasma to obtain different surface morphology. Different etching degree of films surface can be controlled by changing etching process, such as etching time, etching voltage, pressure etc.

For light irradiation, ultraviolet (UV) illumination was carried out using a 20-W black light bulb (PHILIPS TL20W, Netherlands) with a light intensity of 0.1  $\text{mW}/\text{cm}^2$  incident upon the sample. Visible-light (VIS) irradiation was carried out using a 150-W xenon lamp (64478 IM, Osram Halolux Ceran, Germany). The wavelength of VIS irradiation was ranged above 430 nm. Both UV and VIS irradiation were performed in ambient air, i.e. the temperature was 298 K, and relative humidity (RH) was 60%.

For chemical modification, procedures given in literature [1,17–19] were used. The samples were placed in the beaker with 10 mL of an octadecylsilane ( $\text{C}_{18}\text{H}_{37}\text{SiH}_3$ ) solution. The solutions contained 50  $\mu\text{M}$  of the organic modifier (97%, Aldrich, America) in 1 L of toluene (99.5%, Duksan, Korea). Upon addition of the solution, the beakers were left at room temperature in the dark. After a given time (48–40 h), the samples were taken out, subsequently washed with acetone and ultra pure water, then dried under nitrogen gas flow and then dried in the oven at 70 °C overnight.

## 3. Results and discussion

### 3.1. Effect of growth rate and thickness

$\text{TiO}_x$  films were prepared with various evaporation rates (0.12 nm/s, 0.22 nm/s and 1.06 nm/s) and film thicknesses (200 nm, 700 nm and 1200 nm). For the samples prepared at fixed 0.22 nm/s, when the thickness increased from 200 nm to 1200 nm, the roughness increased from 1.47 nm to 3.30 nm. In the groups with different fixed evaporation rates, a similar effect of film thickness on

film surface roughness in each group was observed: with increasing film thickness surface roughness increased. On the other hand, other groups are compared to study the influence of the evaporation rate on surface roughness when the film thickness is fixed. For the samples with thickness at fixed 700 nm, when the evaporation rate increased from 0.12 nm/s to 1.06 nm/s, the roughness increased from 1.77 nm to 2.78 nm. It showed an increased surface roughness when the evaporation rate was increased in each group. This result reflected that the grain size variations caused the surface roughness change on  $\text{TiO}_x$  films prepared with different parameters (film thickness and evaporation rate). In thicker films, there are some wider voids between the columns expected [20]. Our result, as shown in Fig. 1 clearly demonstrated the void formation as a function of film thickness.

From the XRD spectrum (not shown), it indicated that the structure of the  $\text{TiO}_x$  film was uninfluenced by thickness and growth rate. It is well known that XPS is capable of providing both qualitative and quantitative information about the presence of different elements at the surface. Fig. 2 shows the comparison of high-resolution XPS-spectra of titanium oxide film with a 700-nm thickness prepared at 1.06 nm/s: (a) Ti 2P; (b) O 1 s; and (c) C 1 s and the film with a 200-nm thickness prepared at 0.12 nm/s: (d) Ti 2P; (e) O 1 s; and (f) C 1 s. The original high-resolution XPS-spectrum of the Ti 2p peak (Fig. 2a) shows three peaks. After peak-fitting treatment, the dominant doublet peaks in the spectrum were attributed to  $\text{TiO}_2$ , corresponding with Ti 2p $_{3/2}$  at a binding energy (BE) of 458.0 eV and Ti 2p $_{1/2}$  at BE of 463.6 eV, being a typical value for  $\text{TiO}_2$  [20–22]. The binding energy difference of 5.6 eV between these two peaks for  $\text{TiO}_2$  correlated well with previous studies (DBE from 5.5 eV to 5.8 eV) [22,23]. In addition,  $\text{Ti}^{2+}$  (Ti 2p $_{3/2}$  at BE of 456.3 eV) from substoichiometric oxide,  $\text{TiO}$ , was present, as also reported in previous XPS studies [23]. The O 1-s peak (Fig. 2b) shows three components: the first, at 531.0 eV, was attributed to the titanium oxide; the second peak at 532.3 eV was fitted and assigned to hydroxide and hydroxyl species; the third oxygen peak at BE of 533.2 eV was associated with surface contamination, usually water and carbonates [21–23]. XPS survey spectrum demonstrates the carbon contamination on the surface, which is typical for adventitious, unavoidable hydrocarbon contamination, adsorbing spontaneously from ambient air onto the surface [24]. From the high-resolution spectrum of C 1 s (Fig. 2c), three peaks were fitted and assigned as follows: the main carbon peak at 284.8 eV was assigned to hydrocarbon species (C–H); the other two fitted peaks attributed to C–O (i.e. alcohol) species at 286.1 eV and C=O (i.e. carbonates) species at

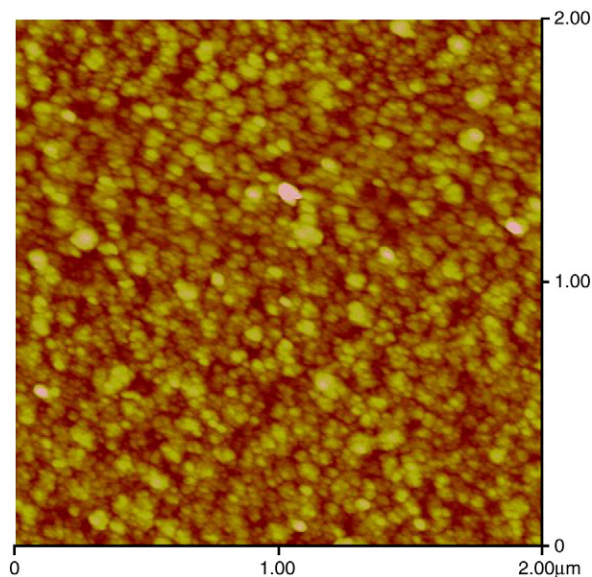


Fig. 1. AFM image of  $\text{TiO}_x$  film deposited at 1.06 nm/s.

Download English Version:

<https://daneshyari.com/en/article/1659704>

Download Persian Version:

<https://daneshyari.com/article/1659704>

[Daneshyari.com](https://daneshyari.com)