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MODIFICATION OF TITANIUM SURFACE BY GOLD ION BEAM

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Abstract

Various surface treatments have been developed to increase the clinical performance of titanium-based implants (TiO_2). Our idea is to apply gold ions from electron cyclotron resonance ion source (ECRIS) and thermal evaporation of gold atoms to modify the surface in order to enhance bone-cell-growth properties. This paper focuses on how the Ti surface is modified by Au ion beam and Au nanoparticles (NPs) in order to improve bioinert properties.

I. Introduction

Titanium has been widely used in several different areas such as aerospace industry, machinery, medicine including dental implants. TiO_2 has various good properties e.g. corrosion resistance and also bioinertness which makes this material beneficial in medical applications. In order to define the quality of the surface treatment, bone

cell should be grown onto the surface. To reach bone cells to grow to the surface, appropriate osseointegration is necessary [1]. Osseointegration is an essential biological process in the field of modern dental implants which is a biological process where bioinert materials (e.g. Ti, Ti covered by TiO_2 or other materials) establish a special bond to bone [2]. Therefore distinct surface treatment techniques for dental subgingival Ti implants should be developed. This paper focuses on near-surface modification of titanium dental implants which is a relatively modern and highly promising methodology to create better properties of implants [3]. To reach the best properties of the TiO_2 to grow bone cells we need to modify the material itself, i.e. physical investigations should precede the biomedical ones.

The biocompatibility [4] and the properties of the surface can be modified uniquely by gold ions produced by electron cyclotron resonance ion source (ECRIS), so we were working on the possibility to combine thermal deposition with ECR-served ion implantation to modify the Ti surface by Au nanoparticles.

II. Experimental methods

The novelty of this work was the modification of the Ti surface by gold ion beam produced by ECRIS. The surface modification was created by a 14.5 GHz ECRIS locating in MTA Atomki [5, 6]. This stand-alone device is able to produce variously low-energy ion beams. So far we produced H, He, N, O, Si, Ar, Kr, Xe ions (from gases) and C, C_{60}, Ca, Zn and Au ions (from solids) to form plasmas and ion beams

[7, 8]. We produced the beam to this measurement by sputtering [9]. The titanium surface modification experiments were performed using from 1 to 10-times ionized Au beams. The kinetic energy of the beam particles is developed by the ion source voltage which was 2 kV. In the experiments Au^{q+} (where q=1-10) ions were directed to the titanium target with beam current (~15μA). The dose of the irradiation was $1,5*10^{16}$ ion/cm^2.

Near-surface modification was justifiable in order to reach the ideal conditions to obtain resistant bond between bone and implant. Thus the surface was irradiated by gold ions. Due to this process Gaussion-like depth density distribution of the gold was obtained, measured by secundary neutral mass spectroscopy (SNMS). The maximum of this distribution was around 10 nm deep. The irradiation conditions were modeled by the well-known simulation code, SRIM [10]. Good agreement between the experimental data (provided by SNMS) and the simulated density distribution of the gold atoms was found.

Before the Au irradiation the 10x10mm^2 titanium plates (99.6 at%, grade 2, Spemet Co., Taipei, Taiwan) were cleaned. These were selected as substrate material. Before the ion implantation, all of the substrate surfaces were mechanically polished to #2000 grit level, followed by 1μm Al_2O_3 powder to produce a mirror-like surface. All the substrates were immersed in fresh 30% HNO_3 for 30 min at room temperature. Then all plates were further sonicated in ethanol for 30 min, rinsing with distilled water for further 30 min, and then were air-dried.

All these samples were half-covered with a mask made of aluminum during the irradiation resulting two different areas of the surface. Afterwards gold thin layer was covered (15 nm thickness) on the samples by thermal evaporation which physical vapor deposition

(PVD) is a highly productive technique to establish thin layers. During this treatment the samples were half-covered again but perpendicularly rotated then before. Thus we had the surface partitioned for four separated areas: untreated titanium (Ti), ion beam modified surface (IBMS), thermal evaporated surface (TES) and also ion beam modified and thermal evaporated surface (IBM-TES) as well (Fig. 1.). Figure 1 also shows how each segments particularly separated from each other.

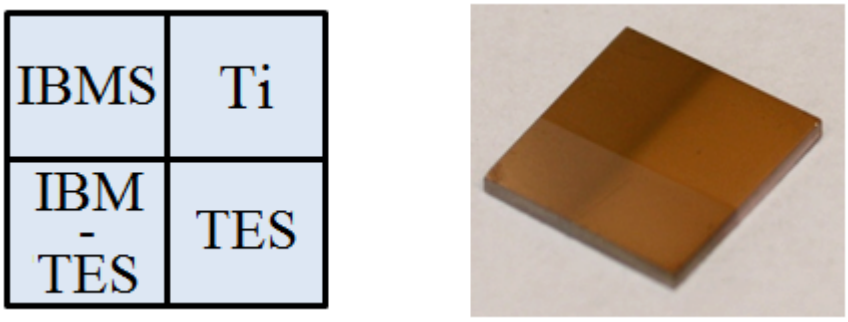

Fig. 1. Schematic (left) and real picture (right) of the sample is shown.

After the PVD we inserted all the samples into an oven for 6 hours at 550°C. Thus gold nanoparticles (GNPs) were created.

Before all these treatments (ECR irradiation, PVD, heat treatment), the samples were undergone physical analysis including atomic force microscope (AFM), SNMS, scanning electron microscope (SEM) and even energy dispersive spectroscopy (EDS). Afterwards the samples were undergone physical investigation again to compare the modifications of the titanium surface.

III. Results

The untreated quarter of the surface of the titanium shows that the roughness of the surface has increased from 4-5 nm up to 12-13 nm due to the heat treatment (Fig. 2.).

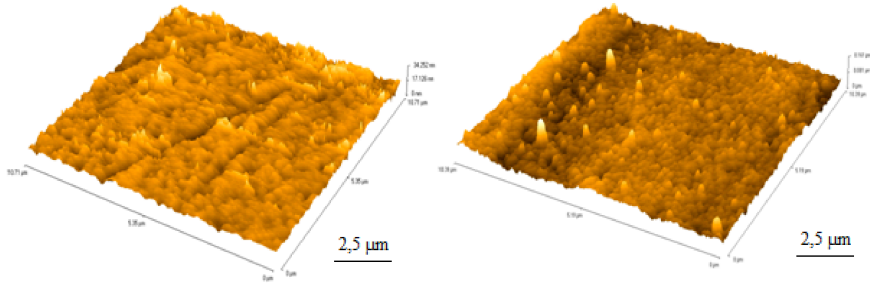

Fig. 2. AFM image topography of the untreated titanium sample is shown before (left) the heat treatment and after it (right).

On the IBMS we experienced that the Au ion beam produced by ECRIS assisted to smoothing [11] the titanium surface from 4-5 nm to 3-4 nm although then the roughness has increased up to 8-9 nm due to the heat treatment (Fig. 3.). A remarkable phenomena was observed, namely GNPs were formed on the IBMS which was captured by SEM+EDS. The IBMS has also investigated by SNMS to obtain beneficial information about the Au depth distribution of the irradiated Au ion beam.

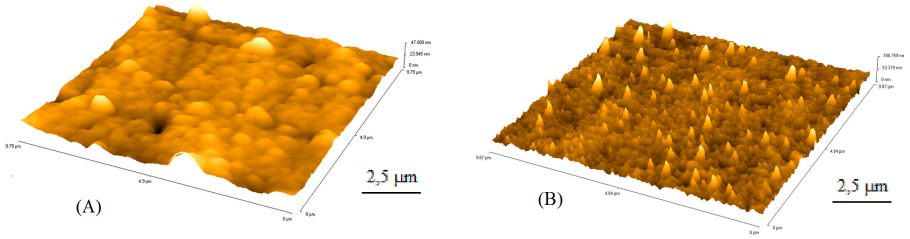

Fig. 3. AFM images of the IBMS (A) and the IBMS after heat treatment (B).

On the TES a 15 nm thick Au layer was covered which decreased the roughness of the surface from 4-5 nm to 3-4 nm. GNPs have appeared on the surface after heating on this partition as well. This phenomena is shown by the Fig. 4.

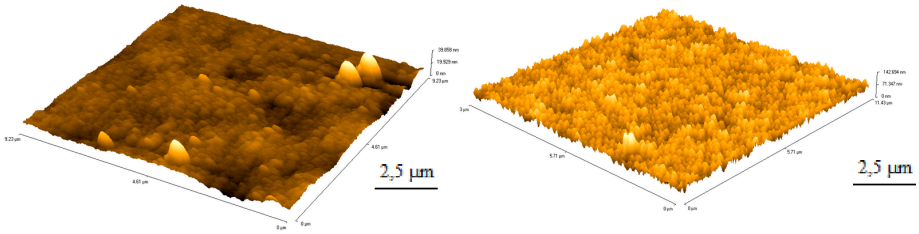

Fig. 4. AFM image topography of the Au covered titanium (TES) is shown before (left) the heat treatment and after it (right).

The IBM-TES was smoothed by the reason of ECR irradiation even as the IBMS. Then Au layer was established onto the surface which didn't change the roughness significantly. However, after the heating the roughness of the surface was increased. Namely GNPs were forming. The explanation is that heating cause the roughness.

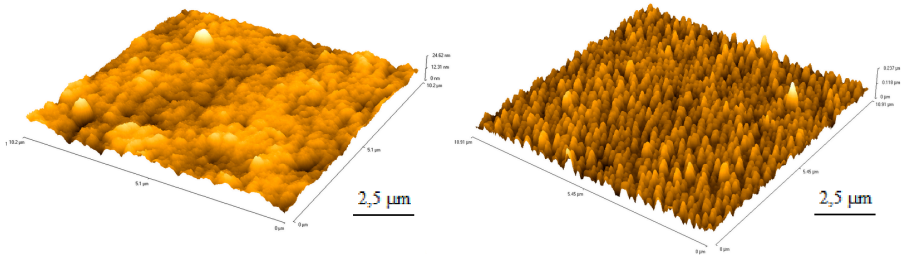

Fig. 5. AFM image topography of the IBM-TES is shown before (left) the heat treatment and after it (right).

From medical point of view it's important to establish an intimate bond between bone and bioinert implant. To improve the resistance of bonding we applied nanoparticles on the surface. As the size of the nanoparticles is a cardinal factor we need to know some details of them. So to get numerical information about the parameters of the GNPs, SEM analysis was applied.

From the SEM images on the Figure 6(A) GNPs were observed due to the ECR irradiation and the heating. The size of these nanoparticles is ~60 nm with a 0.3% duty factor.

On the untreated Ti surface (B) there are also nanoparticles. Nevertheless these aren't GNPs but Si, C by reason of contamination. The distribution of these nanoparticles is random.

GNPs were formed on the TES (D) as well. The average size of the GNPs is 90 nm with 12% duty factor on this area. The dispersion of size of the GNPs on this area is quite little which shows that the size of GNPs is fairly similar.

Evolution of the GNPs is observed on IBM-TES (C) as well. The size of the GNPs on this segment is changed due to the ECR irradiation (one and half times larger than the size of GNPs on the TES).

The average quantity of these nanoparticles is twice greater than on TES but the duty factor is remains unchanged (12%).

During the physical investigation we also observed that the time of heat treatment and the thickness of the Au layer can easily modify the physical parameters of the GNPs to reach the best conditions to bone-cell-growth. From the SEM images the size differences of the GNPs are clearly visible on Figure 6.

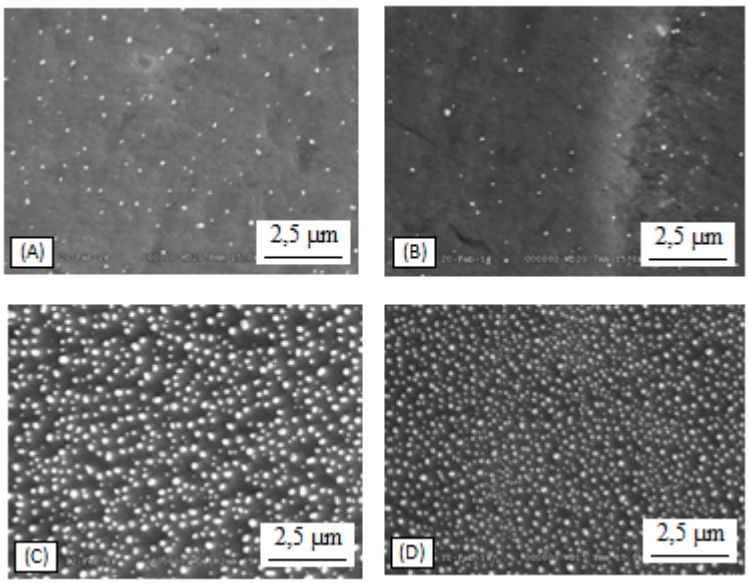

Fig. 6. SEM images of the IBMS after heat treatment (A), untreated Ti (B), IBM-TES (C) and TES (D).

IV. Summary

We produced GNPs on the titanium surface with two different techniques. On the one hand we created GNPs by gold ion beam and on the other hand with thermal evaporation. With both methods (completed with heat treatment) GNPs were forming successfully. Various sized gold nanoparticles were created on the IBMS, TES, IBM-TES. We observed that the size of the GNPs depends on the thickness of the previously evaporated Au cover and the time of the heat treatment. Also a remarkable result is obtained, namely the size of the GNPs can be easily modified by the ECR ion source. Moreover the Au ion beam (produced by ECRIS) assisted to smoothing the titanium surface which results higher and faster surface diffusion on the surface of the titanium. Therefore the contiguous field became noncontiguous with higher roughness on the treated areas (IBMS, TES and even IBM-TES) due to the heating which results GNPs.

To gain more information about the bioinert properties of the titanium, further physical investigations (adhesion test, cross sectional analysis) and biomedical measurements are required and planned.

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