A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 60 2015 Issue 2
DOI: 10.1515/amm-2015-0122

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RF MAGNETRON SPUTTERING COATING OF HYDROXYAPATITE ON ALKALI SOLUTION TREATED TITANATE NANORODS

MAGNETRONOWO NAPYLANE POWŁOKI HYDROKSYAPATYTU NA NANOPRĘTY TLENKU TYTANU WYTWORZONE W ROZTWORZE ALKALICZNYM

Hydroxyapatite (HA) is a material with outstanding biocompatibility. It is chemically similar to natural bone tissue, and has therefore been favored for use as a coating material for dental and orthopedic implants. In this study, RF magnetron sputtering was applied for HA coating. And Alkali treatment was performed in a 5 M NaOH solution at 60°C. The coated HA thin film was heat-treated at a range of temperatures from 300 to 600°C. The morphological characterization and crystal structures of the coated specimens were then obtained via FE-SEM, XRD, and FT-IR. The amorphous thin film obtained on hydrothermally treated nanorods transformed into a crystalline thin film after the heat treatment. The change in the phase transformation, with an enhanced crystallinity, showed a reduced wettability. The hydrothermally treated nanorods with an amorphous thin film, on the other hand, showed an outstanding wettability. The HA thin film perpendicularly coated the nanorods in the upper and inner parts via RF magnetron sputtering, and the FT-IR results confirmed that the molecular bonding of the coated film had an HA structure.

Keywords: HA (Hydroxyapatite), RF Magnetron sputtering, Nanorod, Alkali solution

1. Introduction

Titanium has high strength, is resistant to both corrosion and fatigue, and is highly biocompatibility, and for these reasons has found wide use in implants [1-3]. A passive TiO2 thin film formed on a titanium surface can support the biocompatibility of the material. However, even in this case, Ti requires quite a long time for osseointegration. In order to improve osseoconduction and adhesion between the bone and the implant, an HA coating can be applied. The methods that allow dry coating of HA include plasma spraying, pulsed laser deposition, matrix-assisted pulsed laser evaporation, ion-beam-assisted deposition, and radio-frequency (RF) magnetron sputtering [4,5].

Plasma spraying an HA coating is highly favored due to its low cost and high reproducibility. However, the rapid coating and cooling can occur simultaneously during plasma spraying, resulting in pores, cracks, and unmelted particles. Therefore, RF magnetron sputtering can be a suitable alternative that can prevent such conditions. HA-coating via RF magnetron sputtering leads to uniformity in the chemical composition and density of the film. The preferred orientation and the amorphous properties of the thin films can be determined by adjusting the processing conditions during RF magnetron sputtering [6,7]. For example, the amorphous HA films can be transformed to crystalline thin films by heating, further increasing the spread of human osteoblast cells.

In this study, the phase transformation of the thin film was observed by coating an HA film on Si wafer with an RF power of 150-250 W, followed by heat treatment. An alkali treatment for hydrothermal synthesis on pure titanium was performed to further examine the presence of super-hydrophilic nanorod structures. The HA film on the nanorod structures was heated to 400°C, and the changes in surface morphology, molecular bonding, and wettability were studied.

2. Experimental

2.1. Titanium specimen preparation

A titanium specimen with a purity of 99.9% cp-Ti (ASTM Grade II, Kobe Steel Co., Japan) was prepared with a diameter of 15 mm and a thickness of 3 mm. Mechanical polishing was performed to even out the surface, and the specimen was cleaned ultrasonically in ethanol, in acetone, and was distilled in water each for 5 minutes.

2.2. Alkaline hydrothermal synthesis process

The prepared specimen was immersed in 5 M NaOH and was heated at 60°C for 12 hours to form the nanochannel structure. The specimen was then cleaned with distilled water, and after cleaning, it was immersed in distilled water for 4 hours and was heated at 60°C to form the nanorod structures.

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2.3. HA thin film coating

The HA thin film was coated using an RF magnetron sputtering system (A-Tech system co., Korea). The distance between the specimen and the target was of 80 mm, and a 4 in sputtering diameter was used. The pressure in the chamber was initially set to less than 4×10^{-4} Pa. A mass flow controller was used to generate a 50-sccm Ar gas flow into the chamber. The processing pressure of the Ar gas atmosphere was kept at 2.6 Pa, and 200 W of RF power were applied, which led to the formation of plasma. Prior to deposition, pre-sputtering took place for 5 minutes with Ar gas, with a shield protecting the sample. The HA thin film was coated at an RF power of 100-250 W, while the rotational speed was maintained at 10 rpm. The deposition speed of the HA thin film was of 0.2-0.3 μm/hr, and the deposited HA thin film was heat-treated at 400°C for an hour in an atmospheric environment.

2.4. Characterization

The nanorod structure was produced through an alkaline hydrothermal synthesis and was observed via Field Emission-Scanning Electron Microscopy (FE-SEM, Hitachi S-4700. Japan). The composition of the HA thin film was analyzed using Energy Dispersive X-ray spectroscopy (EDX, EMAX Energy EX-200, Horiba, Japan), and an X-ray Diffractometer (XRD, X'Pert PRO Multi Purpose, PANalytical, Netherlands) was used to observe the crystallinity of the HA thin film. Furthermore, the characteristics of the molecular bonding were observed via FT-IR (Shimadzu IRPrestige-21, Japan) with a range of 4000-400 cm^{-1} at room temperature. The wettability measurements were undertaken with the Image J software program, with Drop analysis as a JAVA plugin [8].

3. Results and discussion

Figure 1 shows the structure of the nanorods after being treated in distilled water at 60°C, where the structure was obtained by immersing titanium in the 5 M NaOH at 60°C. The sodium hydrogen titanate nanorods were formed after alkaline hydrothermal processing, and the titanate phase was confirmed via XRD [9]. The nanorods were observed to face upwards uniformly over the entire surface of the specimen, with a length of approximately 400 nm. The structure of nanorods will be an advantage for RF magnetron sputtering since the inner part of nanostructure will be coated as well.

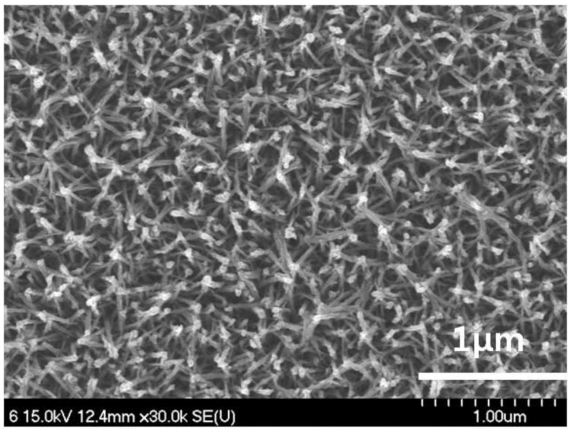

Fig. 1. FE-SEM morphology of the nanorod structures after immersing titanium in 5 M NaOH at 60°C and treating in distilled water at 60°C

In Figure 2, the XRD diffraction patterns were observed in order to analyze the change in the phase transformation of the HA film, which was deposited on the Si wafer with RF power of 100 W, under different heating conditions. The XRD diffraction patterns of the as-sputtered samples, and samples heat-treated at 400°C, 500°C, and 600°C are shown in Figure 2 (a-d). The amorphous structure of HA film transformed into crystalline one after the heat treatment of 500°C. The relative intensity of peaks at 500°C and 600°C were maintained, even when a higher temperature was applied. The main peaks of the HA thin films at 500°C included the plane indices of (211), (112), and (300). Moreover, the high relative intensity of plane (002) indicated that the heated HA thin film had the preferred orientation.

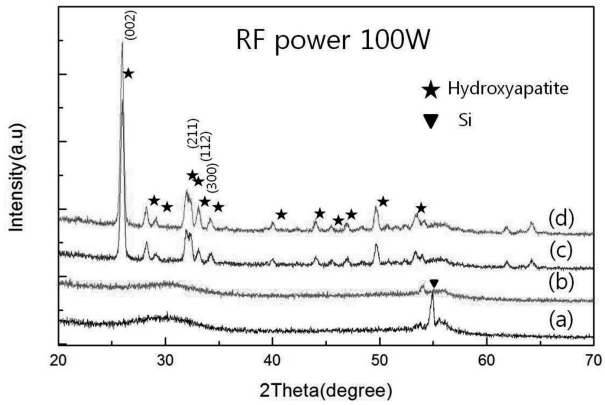

Fig. 2. XRD patterns of the HA thin films coated on an Si substrate after heat treatment: (a) as-sputtered, (b) 400°C, (c) 500°C, and (d) 600°C

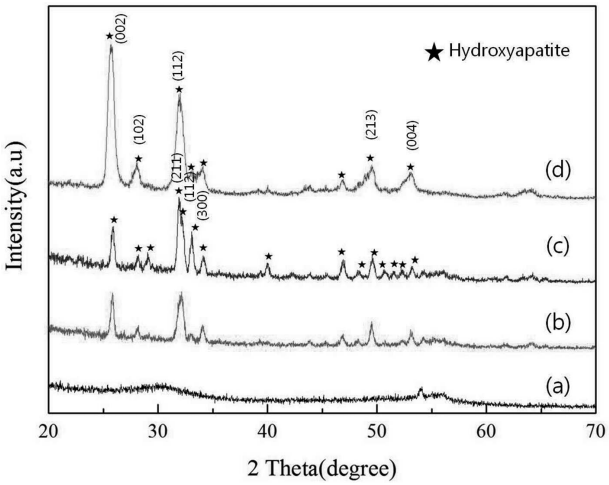

Fig. 3. XRD patterns of the HA thin film as a function of the RF power conditions: (a) 100 W, (b) 150 W, (c) 200 W, and (d) 250 W

Figure 3 shows the XRD diffraction pattern according to the different RF power conditions for HA thin film deposited on the Si wafer through RF magnetron sputtering and heated at 400°C for an hour. The different RF power conditions shown in Figure 3 (a-d) were of 100 W, 150 W, 200 W, and 250 W. The thin film deposited with an RF power of 100 W resulted in an identical XRD pattern to that of the as-sputtered HA thin film

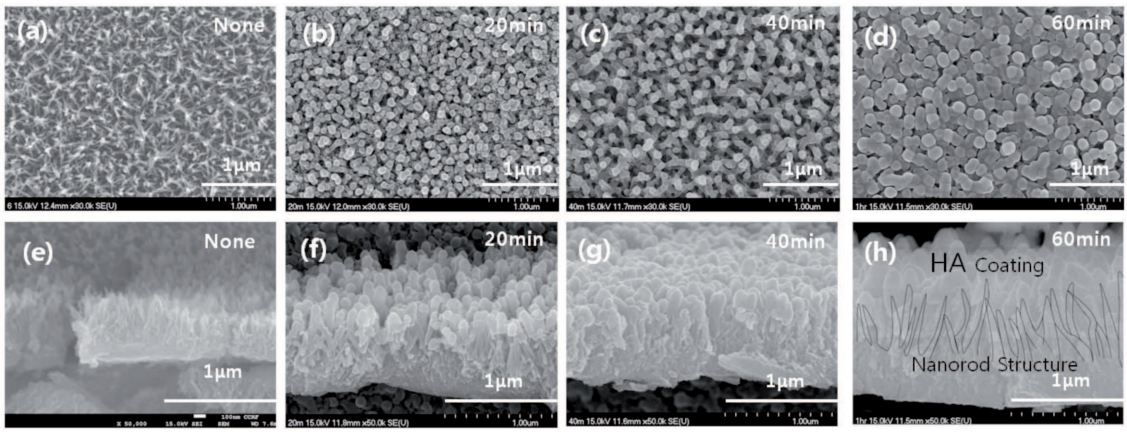

Fig. 4. FE-SEM morphologies of the HA-coated titanate nanostructures treated in NaOH at different sputtering times: top view images of (a) none, (b) 20 min, (c) 40 min, (d) 60 min, and cross section images of (e) none, (f) 20 min, (g) 40 min, and (h) 60 min

with an amorphous phase. The amorphous phase of the HA thin film was a result of the disordered atomic arrangement, and the amorphous HA thin film gradually transformed into a crystalline structure as the RF power increased.

TABLE 1
Variation of relative intensities of the X-ray peaks for the HA film on Si wafer as a function of RF power

RF power	Diffracted Planes			
	(211)	(112)	(300)	(002)
250W	-	24.6	-	100
200W	100	56.8	53.3	54.2
150W	70	100	12.5	87.5
100W	-	-	-	-
JCPDS(#9-0432)	100	60	60	40

Table 1 shows the relative intensities of the X-ray peaks shown in Figure 3. The deposited HA thin film with an RF power of 200 W showed relative intensities identical to those of the reference (JCPDS, #9-0432). The high relative intensity of the plane (002) was analyzed for an RF power of 250 W, which showed a preferred orientation of the HA film. An RF power of 150 W resulted in an HA thin film that including both characteristics from the RF powers of 200 W and 250 W. This clearly indicated that the relative intensities of the XRD pattern depend on the processing conditions, which explains why a preferred orientation could result from a specific RF power. Wolke showed that a film coated at an RF power of 700 W had characteristics of the (002) preferred orientation when a sample rotation was applied [6]. In our study, the HA coating processed with sample rotation resulted in a preferred orientation when an RF power of 250 W was applied, and the coating process therefore led to an HA thin film with a characteristic in the preferred orientation, which was highly affected by the sample rotation and RF power.

Figure 4 shows the SEM morphologies of the HA thin film coated on the nanorods. The specimens were coated at an RF power of 200 W and were then heated to 400°C. Figure 4(a-d) shows the top view, while (e-h) shows the cross-sectional images. The HA thin film shown in Figure 4(b) was deposited on top of the nanorods with a round shape. The increase in the coating time led to an increase in the size, which thoroughly filled the inner space and formed into columnar structures.

The analysis of the EDX line profile from Figure 4 (h) is shown in Figure 5. The Ca and P elements were concurrently found in the upper and inner parts of the HA thin film, while both elements decreased in the direction of the titanium substrate. Oxygen was evenly distributed in both parts of the HA thin film, while titanium increased towards the substrate. As shown in the EDX lines for Ca and P, the upper and inner parts of the HA film were favorably coated with nanorods in the perpendicular orientation.

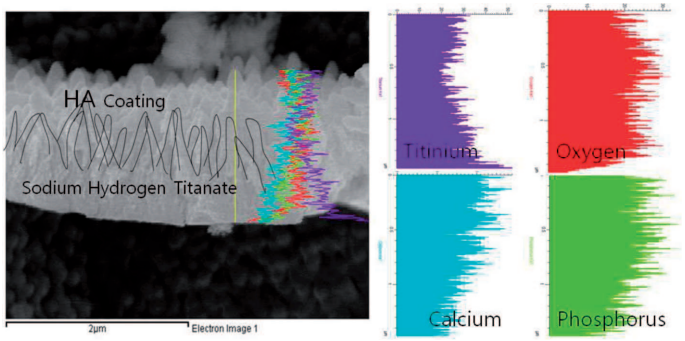

Fig. 5. Cross sectional FE-SEM morphology and EDX line profiles of HA films for a sputtering time of 60 min with heat treatment at 400°C

Figure 6 refers to the FT-IR analysis of the HA thin film coated on the nanorods at an RF power of 200 W and then heat-treated at 400°C. According to Saber-Samandari [10], the HA peaks via FT-IR analysis showed PO_4^{3-} asymmetric stretching at 1029 cm^{-1} and 1092 cm^{-1}, PO_4^{3-} symmetric stretching at 961 and 471 cm^{-1}, P group bonding at 602 and 563 cm^{-1}, and OH^- at 3570 and 630 cm^{-1}. The resulting peaks of the asymmetric stretching at 1012 cm^{-1}, symmetric stretching at 963 cm^{-1}, phosphate group bonding at 600 and 564 cm^{-1}, and OH^- at 3570 cm^{-1} indicate that the HA thin film was coated.

The wettability is related to many bioactive factors, such as protein adsorption, platelet adhesion/ activation, blood coagulation, and cell adhesion [11]. Figure 7 shows the wettability of surfaces, which was measured by contact angles using distilled water, for (a) polished pure Ti, (b) NaOH

treated nanorods, (c) HA coated nanorods, and (d) HA coated nanorods after heat treatment. The HA surface in Figure (c) was coated on the nanorod for 30 min, and the heat-treated HA film in Figure (d) was processed at 400°C. Figure 7 (b) shows how the NaOH hydrothermal synthesis led to super-hydrophilic nanorods with a 3° contact angle. The 5° contact angle seen in Figure 7(c) was higher than that of 7(b) as a result of the different surface morphologies. The increased contact angle of the HA thin film after heat treatment showed that the crystalline thin film had low wettability relative to the amorphous thin film. However, the crystalline thin film had a lower contact angle of 24° than the polished pure Ti with an angle of 54°. The HA coating on the TiO2 nanotubes had contact angles of 66° for the Ti alloy and 22° for the HA film [12]. As a result of the nanorods, the hydrothermal treated specimen increased its wettability.

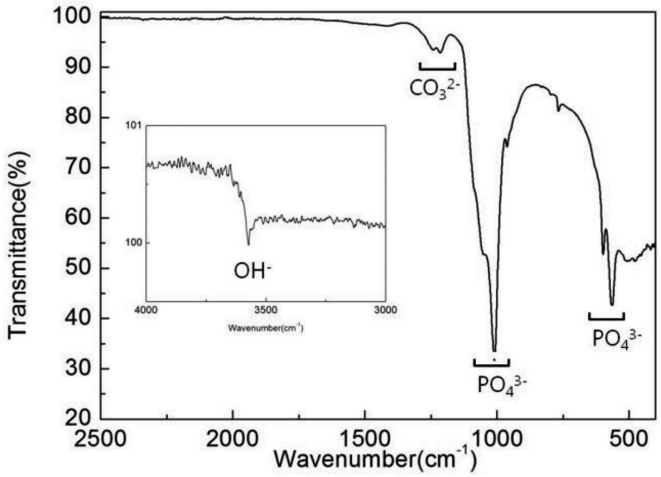

Fig. 6. FT-IR spectrum of HA thin films on nanorod being heat-treated at 400°C

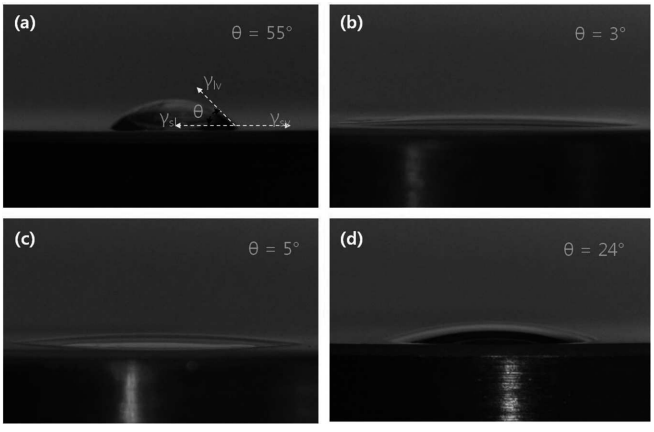

Fig. 7. Contact angle measurement of (a) pure Ti, (b) NaOH treated specimen, (c) HA coated nanorods, and (d) HA coated nanorods after heat treatment

Received: 20 November 2014.

4. Conclusions

The analysis of the XRD patterns confirmed that coating the HA on a Si wafer using RF magnetron sputtering resulted in a preferred orientation, depending on the RF power. The HA thin films formed perpendicularly along the nanorods and were favorably coated in the upper and inner parts via RF magnetron sputtering. The FT-IR results confirmed that the molecular bonding of coated films corresponded to the HA structure. The hydrothermal treated nanorods and the amorphous thin films showed exceptional wettability. The heat-treated amorphous HA thin films transformed into a crystalline thin film, whereas the wettability of HA surface was reduced.

Acknowledgements

This work was supported by the Human Resource Training Program for Regional Innovation through the Ministry of Education and National Research Foundation of Korea (NRF-2012H1B8A2026256).

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