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Original Article

Phase Tailoring of Dense Tantalum Films for Improving Hardness of Titanium Implants Using Negative Substrate Bias During DC Sputtering at Low Temperature

Dang Minh Duc[1], Dao Hong Bach[1], Nguyen Duc Trung Kien[2], Truong Quoc Phong[1], Mai Xuan Dung[3], Truong Nguyen Tuan Minh[4], Pham Thi Mai Phuong[1], Le Thai Hung[1], Pham Hung Vuong[1,5,*]

[1]*Hanoi University of Science and Technology (HUST), 1 Dai Co Viet, Hanoi, Vietnam*
[2]*Phenikaa University, Yen Nghia, Ha Dong, Hanoi, Vietnam*
[3]*Hanoi Pedagogical University 2, Vinh Phuc, Vietnam*
[4]*Tampere University, Hervanta Campus, Korkeakoulunkatu 7 Kampusareena, 33720 Tampere, Finland*
[5]*Laboratory of Biomedical Materials, Hanoi University of Science and Technology (HUST), 1 Dai Co Viet, Hanoi, Vietnam*

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Abstract: This work reports the deposition of a dense α-Ta and β-Ta films to enhance the surface hardness and biocompatibility of Ti by applying a different negative substrate bias during direct current (DC) sputtering. When a Ta film was deposited with a negative substrate bias voltage of 70 V, the microstructure of the film exhibited a single β-Ta phase. Whereas, a negative substrate bias of 150 V resulted in the formation of a single α-Ta phase. The deposition of the dense Ta film onto Ti significantly improved the hardness of the Ti film. Specifically, β-Ta films possessed a hardness as large as 21.0 ± 1.5 GPa, substantially higher than that of bare Ti (3.6 ± 0.3 GPa) and α-Ta films (8.3 ± 0.3 GPa). Additionally, the obtained results also showed that bydepositing the dense Ta film, one can get the biocompatible surface.

Keywords: Biocompatibility, Ta coating, hardness, substrate bias, hardness.

* Corresponding author.
E-mail address: vuong.phamhung@hust.edu.vn

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1. Introduction

While titanium (Ti) is generally acknowledged for its biocompatibility [1, 2], its utilization in implants can occasionally lead to complications. This is attributed to the naturally occurring thin layer of titanium oxide on its surface, which tends to possess high defect density. Consequently, this can result in the release of metal ions into the surrounding tissue [3, 4], potentially compromising the intended functionality and longevity of the implant. The presence of significant quantities of Ti has been observed to potentially impede the recovery process by exacerbating local inflammation [5]. Despite this concern, there is a considerable industrial interest in developing coatings aimed at enhancing the surface characteristics of Ti implants. Such thin films technology is aimed to enhance the augment properties of the coatings such as hardness and biocompatibility, thereby potentially mitigating adverse effects and improving overall performance in clinical applications.

Tantalum (Ta) emerges as a highly sought-after refractory metal due to its impressive attributes, including a notably high melting point, low electrical resistivity, exceptional chemical inertness, magnetic resonance, and biocompatibility. Its versatile nature renders it appealing across various domains, ranging from serving as a protective coating for corrosion and wear resistance to finding applications in electrical and medical fields [6, 7].

Huang et al., [8] demonstrated the formation and development of α-Ta and β-Ta phases in thin films using hybrid high-power pulsed and DC magnetron co-sputtering, along with their impact on hardness, elastic modulus, and wear resistance. The results revealed significant differences between the properties of the two phases, providing valuable information for industrial and biomedical applications. Motemani et al., [9] investigated Ti–Ta films engineered to exhibit a characteristic nanostructure and analyzed the impact of Ta composition on the structure and properties of the films. The study showed that the films exhibited high hardness, uniform nanostructure, and significant potential for applications in fields requiring superior mechanical and biological properties. Wang et al., [10] demonstrated that variations in sputtering power significantly affect the crystalline structure, grain size, and Ta doping concentration in the films. The results indicate that adjusting sputtering power can optimize the hardness and wear resistance of the films, thereby enhancing the performance of Ta-doped TiN films for applications demanding high durability.

Recent *in vitro* investigations have highlighted the enhanced bioactivity of Ta coatings compared to both Ti substrates and Ti-deposited glass [11, 12]. Ta exhibits dual phases: an α-phase, characterized by a body-centered cubic structure, known for its softness, ductility, and chemical resistance, and a β-phase, possessing a tetragonal structure, distinguished by its hardness and brittleness [13, 14]. Depending on the specific application requirements, the precise control over either α-Ta or β-Ta phase becomes particularly significant. Previous research has documented the formation of β-Ta film on Cu substrates [15], while α-Ta film was observed on Al substrates [16]. Furthermore, certain investigations have underscored the formation of α-Ta films under high-temperature conditions [17]. These findings collectively contribute to a deeper understanding of the nuanced behavior and applications of tantalum in diverse contexts.

This research introduces an innovative approach aimed at manipulating the phase of Ta to enhance the hardness of Ti by applying a coating of either dense α-Ta or β-Ta film onto Ti surface. This manipulation is achieved through the application of a negative substrate bias during direct current (DC) sputtering [18]. The microstructure and crystalline structure of the Ta-deposited Ti substrate were meticulously examined using field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) techniques, respectively. Additionally, the hardness and elastic modulus of the coated surfaces were quantified through ultra-low load microhardness tests. Moreover, to evaluate the biocompatibility of the dense α-Ta or β-Ta film on Ti implants, cell attachment studies utilizing MC3T3-E1 cells were conducted by confocal laser scanning microscopy (CLSM) technique. By delving into

these comprehensive analyses, this work endeavors to shed light on the potential of tailored Ta coatings to not only enhance the mechanical properties of Ti but also ensure its compatibility with biological systems, thereby advancing the realm of biomaterials and implant technologies.

2. Experimental Procedure

Tantalum films were deposited onto Ti substrates using direct current (DC) sputtering with a variation of a negative substrate bias, to control the phase of Ta films. Ti substrates with dimensions of 10 mm x 10 mm x 1 mm (Kahee Metal, Korea) that were polished with a diamond suspension down to 1 µm, were subjected to ion bombardment in argon flow discharge with a negative bias voltage of 600 V for 30 min using a DC magnetron sputter (Ultech, Daegu, Korea) to remove any residual surface contamination. Ta films were deposited using a Ta target (diameter 75 mm, thickness 5 mm, purity 99.99%, Kojundo, Japan) at a deposited power of 60 W for 90 minutes in high purity argon (99.998% pure). The deposition of Ta films was carried out by varying the application of a negative substrate bias (V_b) up to 150 V to the Ti substrates. For all the films studied herein, the working pressure of 0.6 Pa was employed during reactive sputtering, while the substrate temperature of 100 ^oC was maintained using a halogen heater with a programmable temperature controller.

The crystalline structures of the Ta films were characterized by an X-ray diffractometer (M18XHF-SRA, Mac Science Co, Yokohama, Japan). The microstructure and thickness of the deposited films were determined by FE-SEM (SUPRA 55 VP, CARL ZEISS, Germany). Microhardness tests were performed to evaluate the mechanical properties, such as hardness and elastic modulus, of the Ta-deposited Ti substrates and compared to those of the bare Ti substrate. Ultra-low load microindentation (Fischerscope H100, Germany) was performed under a Vicker's diamond indenter at a load of 10 mN. The load-indentation depth profiles were recorded automatically during the indentations. The microhardness (H) and elastic modulus (E) were evaluated from the load/upload curves using a computer-controlled microhardness tester. Ten indentations were tested to obtain an average and standard deviation.

In this work, we used the contact angle measurement method to assess the surface properties of the samples after modification. This method determines the level of hydrophilicity or hydrophobicity, clarifying structural changes after treatment and supporting optimization for specific applications.

Before cell attachment on the tested samples, bare Ti, α-Ta, or β-Ta films were sterilized by autoclaving at 121 °C for 60 minutes. Preosteoblast cells, MC3T3-E1, were cultured in DMEM at 37 °C in a humidified atmosphere with 5% CO_2. Cell suspensions with a density of 1×10^4 cells/mL were used for attachment onto the bare Ti, α-Ta, or β-Ta films. After culturing for 48 hours, the cells on the samples were fixed in 4% paraformaldehyde for 10 minutes, washed with PBS, permeabilized with 0.1% Triton X-100 for 7 minutes, washed again with PBS, and stained with phalloidin 555 for 60 minutes. The nuclei of the cells were labeled with DAPI for 10 minutes. The stained cells on the samples were mounted on glass slides and observed using a confocal laser scanning microscope (Olympus; FV3000RS, Japan).

3. Results and Discussion

Fig. 1 (A) and (B) display typical XRD patterns of the Ta films deposited on Ti substrates with V_b of 70 V and 150 V during reactive DC sputtering, respectively. On the one hand, the Ta film deposited with V_b of 70 V exhibited a relatively strong peak at $2\theta \sim 33.6^o$, corresponding to the (002) plane of the crystalline β-Ta structure (JCPDS 25-1280), along with an additional peak at $2\theta \sim 70.7^o$, corresponding to (513) plane (pattern "A" in Fig. 1). On the other hand, when a negative substrate bias voltage of 150

V was applied, the Ta film showed a prominent peak at 2θ ~ 69.5°, corresponding to (211) plane of the crystalline α-Ta structure (JCPDS 04-0788), as well as peaks at 2θ ~38.2° and 55.5°, associated with (110) and (200) planes, respectively (pattern "B" in Fig. 1). These results demonstrated that the Ta films deposited with V_b of 70 V and 150 V predominantly exhibited the single β-Ta and the α-Ta crystalline phases, respectively.

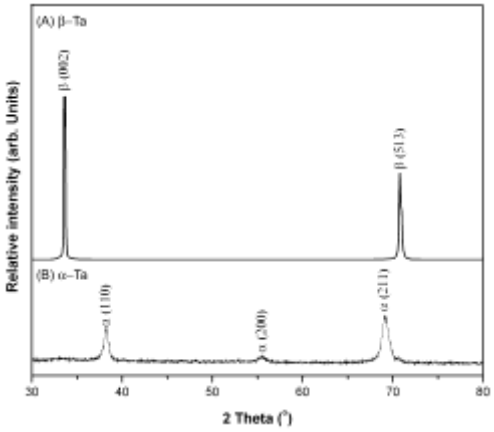

Figure 1. XRD patterns of the β-Ta film deposited at V_b of 70 V (A) and α-Ta film deposited at V_b of 150 V (B).

The microstructures of the Ta films deposited with V_b of 70 V and 150 V are illustrated in Figs. 2 (A)-(D). With a negative substrate bias of 70 V, the Ta film showed a dense and smooth columnar microstructure (Fig. 2A) with a smooth surface of β-Ta (Fig. 2C), whereas a negative substrate bias of 150 V resulted in a relatively rough columnar microstructure (Fig. 2B) with a rough surface of α-Ta. The overall thicknesses of the Ta films deposited with V_b of 70 V and 150 V were approximately 2.5 μm and 1.2 μm, respectively.

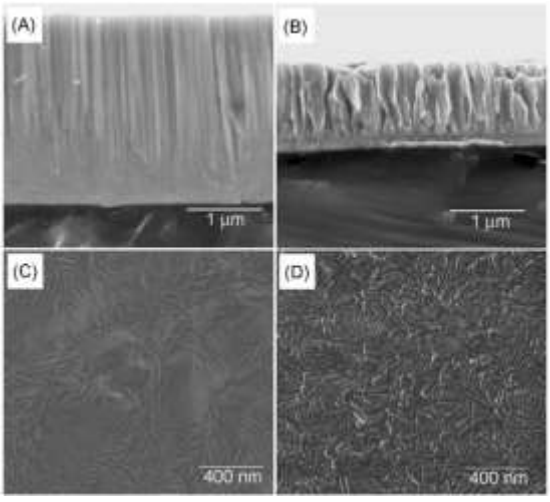

Figure 2. Microstructures of the β-Ta films deposited with V_b of 70V ((A),(C)) and α-Ta films deposited with V_b of 150 V ((B),(D)), ((A)-(B)) : cross-sectional view, (C)-(D) : surface morphology)

The surface hardness and elastic modulus of the Ta-deposited Ti substrates were assessed using an ultra-low load microhardness test, which is an appropriate method to evaluate the mechanical property

of thin film [19, 20]. The typical loading-indentation depth curves of the substrates (bare Ti and Ta-deposited substrates with V_b of 70 V and 150 V) are presented in Fig. 3. Compared to the bare Ti, the Ta-deposited substrates exhibited smaller indentation depths under the same load, indicating effective surface hardening due to the deposition of the Ta films via DC sputtering.

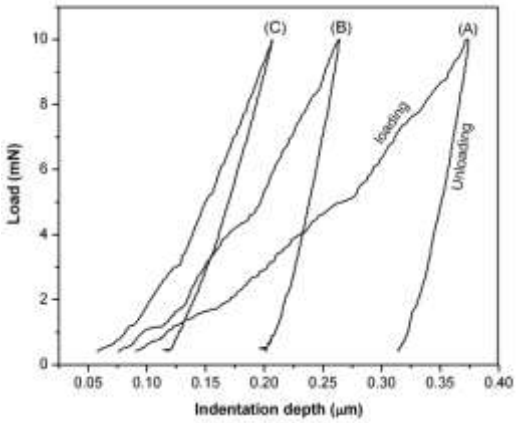

Figure 3. Load-indentation depth curves of (A) the bare Ti, (B) the α-Ta-deposited Ti substrate with V_b of 150 V, and (C) the β-Ta-deposited Ti substrate with a V_b of 70 V.

The hardness and elastic modulus derived from the loading-indentation depth curves are summarized in Table 1. The deposition of the Ta films on the Ti substrate resulted in a significant increase in both hardness and elastic modulus. Notably, the hardness of the β-Ta film deposited with a negative substrate bias of 70 V was much higher than that of the α-Ta film deposited with a negative substrate bias of 150 V by approximately a factor of 2.5. While the hardness of α-Ta film in this study is lower than that of α-Ta film reported in [18], the hardness of β-Ta film is higher than that of β-Ta film reported in [21]. The higher hardness of β-Ta was primarily attributed to its complicated four-layer stacking arrangement of atoms, impeding dislocation motion [22].

Table 1. Hardness (H) and elastic modulus (E) of the bare Ti, Ta-deposited Ti substrates with V_b of 70 V (β-Ta) and with V_b of 150 V (α-Ta)

	Bare Ti	Ta-Deposited Ti Substrates	
		α- Ta	β-Ta
H [GPa]	3.6 ± 0.3	8.3 ± 0.3	21.0 ± 1.5
E [GPa]	117.2 ± 7.1	186.6 ± 8.9	171.0 ± 9.3

Fig. 4 illustrates the wettability images of three samples: bare Ti, α-Ta, and β-Ta. The contact angles of these samples are 65°, 18°, and 21°, respectively, highlighting significant differences in the surface properties of these materials. The bare Ti sample has the largest contact angle at 65°, indicating that this surface is more hydrophobic compared to the samples coated with α-Ta and β-Ta. This suggests that water is less likely to spread on the bare Ti surface, implying it has lower surface energy compared to the coated samples.

The α-Ta sample has a contact angle of 18°, significantly lower than that of bare Ti. This reduction in contact angle indicates that the α-Ta coating makes the surface more hydrophilic, possibly due to changes in surface structure after coating α-Ta on the Ti substrate. The β-Ta sample, with a contact angle of 21°, is also more hydrophilic than bare Ti, though slightly less than α-Ta. This indicates that the β-

Ta surface still has enhanced water interaction compared to bare Ti, but to a lesser extent than α-Ta. Comparing these results, it is evident that coating α-Ta and β-Ta on the Ti substrate increases the surface's hydrophilicity, with the α-Ta coating exhibiting the highest wettability.

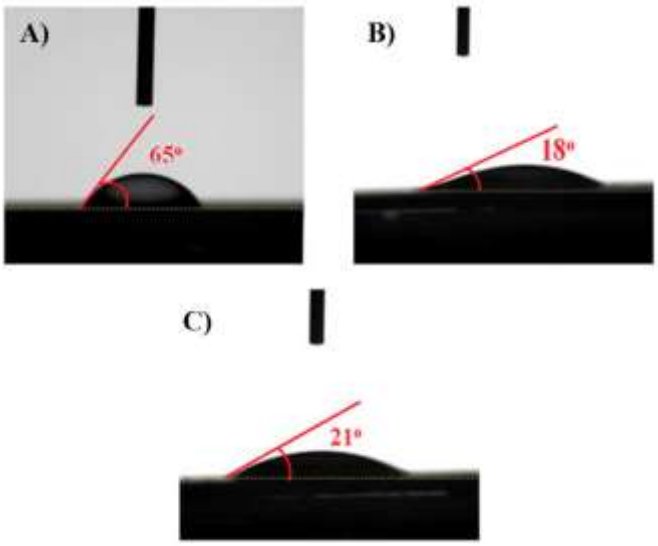

Figure 4. Wettability images of (A) bare Ti; (B) α- Ta and (C) β-Ta-deposited Ti.

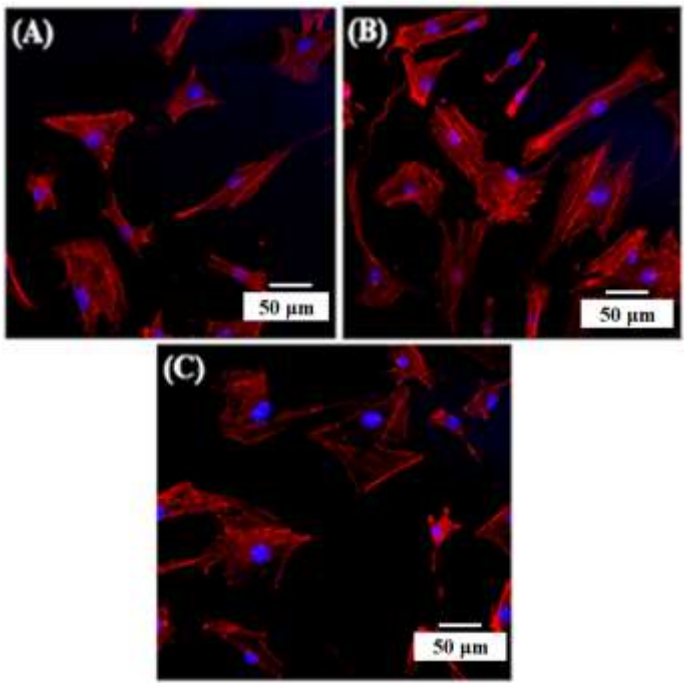

Figure 5. MC3T3-E1 attachment after culturing for 48 h on (A) bare Ti, (B) β-Ta-deposited Ti and (C) the α-Ta-deposited Ti.

Fig. 5 illustrates the cell attachment on the bare Ti, β-Ta, and α-Ta films, with hardness and elastic modulus showed in Table 1. The MC3T3-E1 cells exhibited robust growth on Ti substrate, β-Ta film, and α-Ta films. Noticeably, MC3T3-E1 displayed superior cell spreading on the α-Ta films among different surfaces, characterized by expanded cell shapes and prominent actin stress fibers. The enhanced cell attachment on the α-Ta films could be attributed to nanostructure of the films. Overall, these cell culture test indicates that β-Ta and α-Ta coatings on Ti implants is biocompatibility and non-toxic to the cells. In terms of biocompatibility, the β-Ta and α-Ta films in this study also demonstrate better biocompatibility compared to bare titanium. This highlights the role of Ta on titanium substrates and is consistent with the synthesis of Ta on titanium using other methods [8, 9] or Ti–Ta alloys produced by melting methods [23, 24].

4. Conclusion

In summary, we herein demonstrated that Ti substrates coated with metallic Ta films exhibited significantly enhanced hardness. Specifically, the phase of the Ta films was controlled by applying different negative substrate biases during DC sputtering. At a negative substrate bias of 70 V, the Ta film exhibited a dense, smooth single β-Ta phase, whereas when at a bias of 150 V, a dense and relatively rough single α-Ta phase was achieved. The hardness of the β-Ta- deposited Ti with a negative substrate bias of 70 V reached a value of 21.0 ± 1.5 GPa, considerably exceeding that of bare Ti (3.6 ± 0.3 GPa) and even α-Ta-deposited Ti with a negative substrate bias of 150 V (8.3 ± 0.3 GPa). Both β-Ta and α-Ta coatings demonstrated positive effects in improving hardness and wettability compared to bare titanium. β-Ta and α-Ta-deposited Ti coatings exhibited also biocompatible surfaces, making them potential candidates for biomedical implants.

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