# Comparative Experimental Investigation of Mechanical Properties and Adhesion of Low Temperature PVD Coated TiO$_2$ Thin Films

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**Abstract.** Titanium dioxide (TiO$_2$) has been widely used as a biomaterial due to its excellent mechanical and wear resistance properties. In this study, we have deposited TiO$_2$ thin films on stainless steel substrate at low temperature (90 °C) by middle frequency (MF) magnetron sputtering and cathodic arc PVD techniques at two different substrate surface roughness. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) techniques have been utilized for the study of surface morphology and stoichiometric elemental chemical composition of the TiO$_2$ thin films. Scratch adhesion and nano indentation experiments were conducted for the assessment of the film adhesion and mechanical properties of the TiO$_2$ thin films respectively. Results proved that the TiO$_2$ thin film deposited on higher substrate surface roughness (0.7 µm) samples by MF magnetron sputtering PVD process have superior adhesion and mechanical properties. Correlation comparative analysis of the TiO$_2$ thin films deposited by the MF magnetron sputtering PVD process gave the optimum results at 1238 nm film thickness and 0.7 µm substrate surface roughness. The maximum of 14 N adhesion strength, 13.8 GPa hardness and 345.6 GPa elastic modulus values have been recorded.

**Keywords:** PVD · Stainless steel · TiO$_2$ · Thin films

## 1 Introduction

Stainless steel has been widely used in the manufacturing of medical devices and implants for in recent years. Due to the inferior corrosion resistance, wear resistance and mechanical properties, the extended utilization of stainless steel as a biomaterial has been limited to only few engineering applications. The use of stainless steel in implants may cause serious problems due to its poor hardness and wear resistance. This problem can be solved by depositing ceramic films on the surface of stainless steel [1, 2].

Titanium dioxide ($TiO_2$) has been proved to be very biocompatible, non-toxic and widely used biomaterial for its excellent mechanical and wear resistance properties [3]. The best way to deposit the $TiO_2$ film by Physical Vapor Deposition (PVD) technique. Among the different PVD techniques; Cathodic Arc and MF magnetron sputtering are the famous used PVD processes to deposit $TiO_2$ films [4]. Most of the researchers have deposited $TiO_2$ films on the stainless steel by keeping the very low substrate surface roughness. However, it has been proven that substrate surface roughness could have the strong influence in deciding the adhesion and mechanical properties of the films [5].

In this research, we have deposited $TiO_2$ thin films on stainless steel substrate at low temperature (90 °C) by using cathodic arc and MF magnetron sputtering PVD techniques. The purpose to keep the substrate deposition temperature low (90 °C) is to avoid the tempering of the stainless-steel substrate; as substrate could lose its mechanical properties on reaching its tempering temperature. Furthermore, we have deposited $TiO_2$ thin films at two different substrate surface roughness levels in order to check its impact on the adhesion and mechanical properties. A comprehensive correlation comparison has been made between substrate surface roughness, film thickness and suitable PVD method in order to evaluate the optimum properties for these $TiO_2$ thin films.

## 2    Materials and Methods

### 2.1    Sample Preparation

In this study, 316 stainless steel (medical grade) was employed as the substrate material. It was cut into the circular discs of 5 mm thickness and 35 mm diameter by the Electric Discharge Machining (EDM) wire cut. Twelve samples were grinded with SiC emery papers (400–3000 grit) for the preparation of the two levels of substrate surface roughness (Ra) i.e., 0.7 µm and 0.3 µm. Multitoyo surface roughness meter was utilized for measuring the substrate surface roughness. Six sets of samples carrying the two specimens of each substrate surface roughness were made. Three sets of samples were deposited by Cathodic Arc and three sets were deposited by MF Magnetron Sputtering Physical Vapor Deposition (PVD) process.

### 2.2    Coating Deposition

Before the deposition, all the specimens were degreased in ultrasonic bath containing ethanol for 15 min. Then these samples were washed with methanol and deionized water respectively. After that, all the samples were dried by blowing highly pure Argon (Ar) gas in order to remove any contaminants from the surface. 99.98% Ti target was employed for the deposition of the $TiO_2$ film. In the cathodic arc PVD process Ti target acts as cathode and steel chamber acts as the anode. The deposition was carried out at discharge current 1.1 A, 90 °C substrate temperature and 100 V bias voltage. The pressure of the chamber was set below $1 \times 10^{-6}$ Pa. High pure (N5.0) Argon (Ar) and Oxygen ($O_2$) gases were utilized as working and reactive gases respectively, and their flow was controlled by mass flow controllers. The flow of the Ar and $O_2$ was 25 sccm

and 140 sccm respectively. Other three sets of samples were deposited by MF Magnetron Sputtering PVD process at 60 kHz frequency. The chamber was vacuumed up to $1 \times 10^{-4}$ Pa and the Ti (99.98%) target was used for deposition. The Ar and $O_2$ flow rate was 60 sccm and 40 sccm respectively. The deposition was carried out at 2A arc current, 100 V bias voltage, 90 °C substrate temperature. $TiO_2$ thin films usually show different color formation due to the interference effect from grey to blue. These colors are used to determine the film thickness and the deposition rate. The color of $TiO_2$ thin film turned to blue at approximately 3 min and 8 min for the MF Magnetron Sputtering and cathodic arc PVD process respectively. Trzcinski et al. [6] had reported 55 nm film thickness at blue color. Thus, the deposition rate for the cathodic arc and MF magnetron sputtering was taken 18.3 nm/min and 6.9 nm/min respectively. However, the film thickness was counter confirmed from the SEM analysis. The cross-sectional image of the MF magnetron sputtering $TiO_2$ film at 180 min deposition time and cross-sectional images of the Cathodic arc deposition $TiO_2$ film at 60 min deposition time are shown in the Fig. 1. The detailed summary of the samples and film thicknesses is given in Table 1.
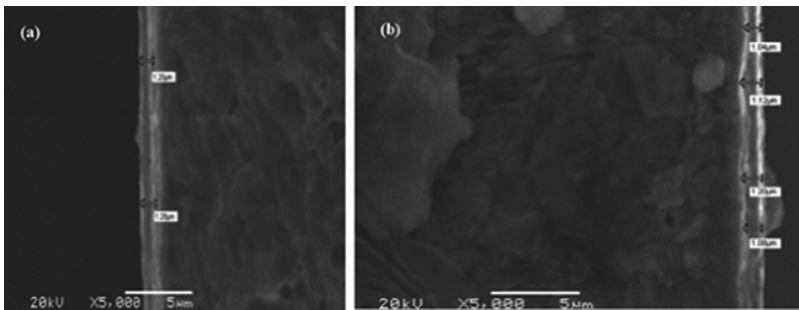


**Fig. 1.** Cross sectional SEM image (a) MF magnetron sputtering (b) Cathodic arc deposition.

## 2.3 Characterization of the $TiO_2$ Thin Film

Scanning Electron Microscope (SEM) was deployed for the examination of the surface morphology and the chemical composition of the $TiO_2$ film was estimated from the Energy Dispersive X-ray (EDX) analysis.

## 2.4 Scratch Adhesion Tests

The adhesion strength of the $TiO_2$ film was measured by the nano scratch tester supplied by CSM instruments Switzerland [7]. It has the Rockwell type diamond indenter of 200 μm diameter. The tests were started with the 0.03 N initial load, the loading rate was set to 9.99 (N/min) and the tests were finished at the maximum load of 25 N. The indenter linear speed was set to 1.2 (mm/min) and the scratch length was 3 mm. Film was delaminated on the critical load at which the substrate becomes visible. After the test, the scratch was observed by the optical microscope.

**Table 1.** Summary of samples for both type of PVD coatings.

| Sample ID | Substrate surface roughness Ra (μm) | PVD coating | Deposition time (min) | Film thickness (nm) |
|---|---|---|---|---|
| Sa-1 | 0.3 | Cathodic arc | 60 | ≈1100 |
| Sa-2 | 0.7 | | | |
| Sb-1 | 0.3 | | 90 | ≈1650 |
| Sb-2 | 0.7 | | | |
| Sc-1 | 0.3 | | 120 | ≈2200 |
| Sc-2 | 0.7 | | | |
| Sd-1 | 0.3 | Middle frequency magnetron sputtering | 60 | ≈412 |
| Sd-2 | 0.7 | | | |
| Se-1 | 0.3 | | 120 | ≈825 |
| Se-2 | 0.7 | | | |
| Sf-1 | 0.3 | | 180 | ≈1238 |
| Sf-2 | 0.7 | | | |

## 2.5   Nano Indentation

Nano indentation tests were utilized for the measurement of the nano mechanical (elastic modulus and hardness) properties of the $TiO_2$ films on the Nano hardness tester supplied by the CSM instruments Switzerland. The equipment contains the Berkovich diamond indenter, and the experiments were conducted on 40.0 mN maximum load. The loading and unloading rate were set to 80.0 mN/min for all the experiments. A little pause of 10 s was set at the end of maximum load to establish the complete penetration of the indenter into the $TiO_2$ film. Three indentations for each sample were made and the average of these values were recorded as the elastic modulus (E) and hardness (H) of each sample. During the indentation test the increase in load and penetration depth were continuously recorded, and then these values were used to make loading and unloading curve (displacement curve). The elastic modulus of the $TiO_2$ film was calculated from the displacement curve by using the Eqs. (1) and (2).

$$E_r = \frac{\sqrt{\pi}}{2} - \frac{S}{A_p} \tag{1}$$

Where Er is the reduced modulus, Ap is the projected area of the contact and S is the slope during unloading. Since the reduced modulus is the combination of sample material ($TiO_2$ film) and diamond indenter elastic modulus so elastic modulus (indentation modulus) of the $TiO_2$ film was calculated from the Eq. (2).

$$E_{IT} = \frac{(1 - v^2)}{\frac{1}{E_r} - \frac{(1 - v_i^2)}{E_i}} \tag{2}$$

Where EIT is the indentation elastic modulus of the sample material (TiO$_2$ film), v is the Poisson's ratio of the specimen material (0.29 for TiO$_2$ film), $v_i$ is the Poisson's ratio of the indenter, and $E_i$ is the elastic modulus of the diamond indenter. Finally, the hardness of the sample material (TiO$_2$ film) was calculated from Eq. (3).

$$H_{IT} = \frac{F_m}{A_p} \tag{3}$$

Where Fm is the applied force and Ap is the projected area of the contact.

# 3   Results and Discussion

## 3.1   TiO$_2$ Thin Film Surface Characterization

Figure 2 shows the surface morphologies of TiO$_2$ film deposited by cathodic arc and MF magnetron sputtering. The SEM surface scan of cathodic arc (Fig. 2a) reveals that there are macro particles present on the surface of the TiO$_2$ film which is the typical characteristic defect of the cathodic arc process. These macro particles are formed on the surface as the result of unreacted metal ions; fast evaporation during the cathodic arc deposition process creates atoms which are not fully ionized prior to arrival at substrate [8].
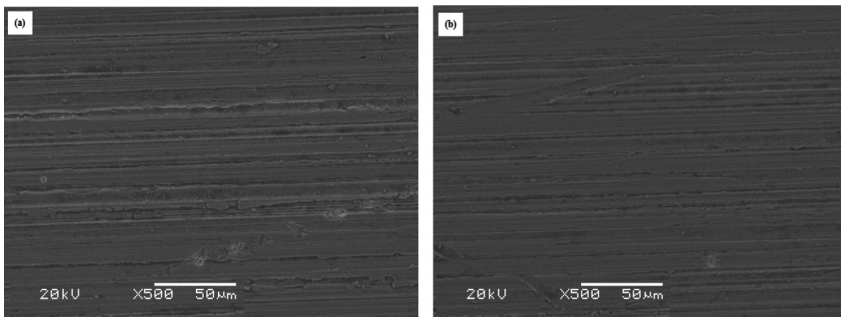


**Fig. 2.** SEM micrographs of TiO$_2$ film (a) Cathodic arc deposition (b) MF magnetron sputtering.

Figure 2b shows the surface morphology of the TiO$_2$ film deposited by MF magnetron sputtering. It can be seen that the surface has no macro particles unlike the cathodic arc TiO$_2$ film. This is because of the fact that in MF magnetron sputtering deposition rate is lower, and thus atoms get enough time to be ionized before reaching to the substrate surface.

Figure 3 represents the EDX spectrum of the TiO$_2$ film for both the cathodic arc and MF magnetron sputtering deposition. The spectrum shows peaks corresponding to the elements present in the film and the substrate. No peaks are observed other than the

elements which are present in the $TiO_2$ film and stainless-steel substrate, and it depicts that the $TiO_2$ films contain no impurity. The atomic ratio of O and Ti is 2.07 for the MF magnetron sputtering (see Fig. 3a) and 1.74 (see Fig. 3b) for the cathodic arc PVD process. It is clearly seen that O and Ti (in MF magnetron sputtering $TiO_2$ film) are present in stoichiometric concentrations while $TiO_2$ film for the cathodic arc process lacks O stoichiometrically [9]. In MF magnetron sputtering as the deposition rate is slow so the Ti and O ions get enough time for bond and thus stoichiometric $TiO_2$ films are formed. While in cathodic arc process as the deposition rate is higher so the some Ti or O ions remain unreacted as the result of that unstoichiometric $TiO_2$ films are produced [10].
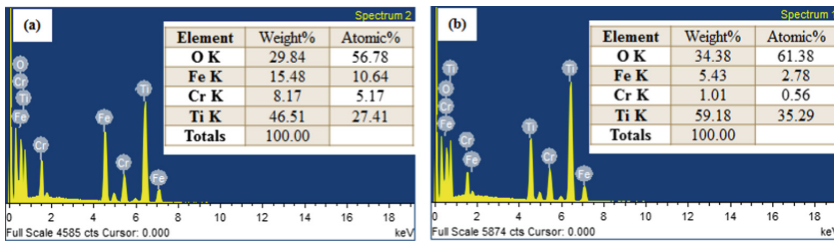


**Fig. 3.** EDX spectrum of $TiO_2$ film (a) MF magnetron sputtering (b) Cathodic arc deposition

## 3.2    Adhesion Strength of the $TiO_2$ Film

Nano scratch tester was used to measure the adhesion of the $TiO_2$ film with the stainless-steel substrate. Conical shaped diamond stylus moves along the surface of the film surface and the progressive load is applied normally. As the stylus moves forward then cracks starts to formed in the film which propagates along with the scratch length. Cracks are built due to the residual stresses which are produced as the result of applied load. When these residual stresses exceed the adhesion of the film with the base material then this point is called the critical load. When the first chipping of the film occurs, it is called first critical load (LC1). Furthermore, the loads at which complete chipping off the film and complete unveiling of the base material occurs are called the critical loads, LC2, LC3, and LC4 [11]. Scratch images of maximum adhesion strength sample (Sf-2) are shown in Fig. 4. The results of the adhesion are given in Table 2.

Figure 5 represents the adhesion of the $TiO_2$ film against film thickness and varying substrate surface roughness for both the cathodic arc and MF magnetron sputtering PVD process. It can be seen that the adhesion of the $TiO_2$ film increases with the increase in film thickness for both the PVD techniques. In addition, it is noteworthy that the adhesion of the $TiO_2$ film for the samples of higher substrate surface roughness is always more than the samples with lower substrate surface roughness at all film thicknesses and for both the PVD process. It is due to the fact that there are cavities or crevices on the surface of the substrate; higher substrate surface roughness samples have more cavities than the samples with less surface roughness. As a result, samples of
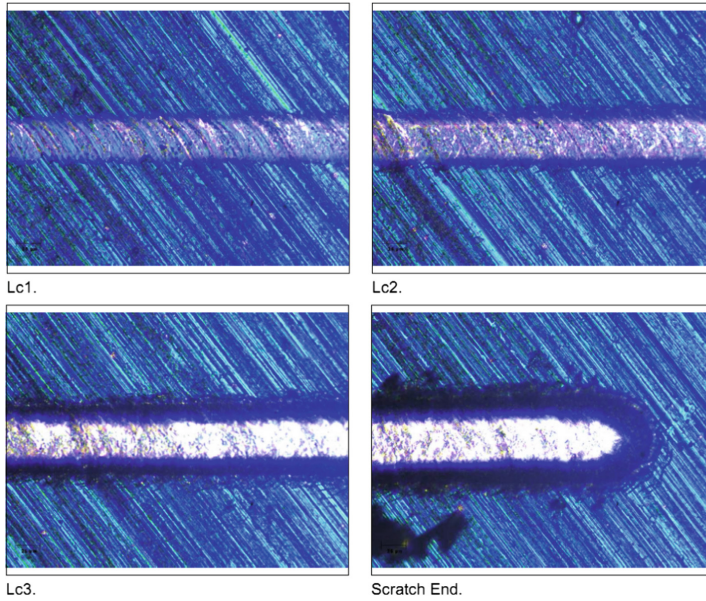
Lc1.   Lc2.   Lc3.   Scratch End.

**Fig. 4.** Scratch image of the maximum adhesion sample.

**Table 2.** Summary of adhesion, hardness (H), elastic modulus (E) and H/E values.

| Sample ID | PVD coating | Film thickness (nm) | Adhesion (N) | H (GPa) | E (GPa) | H/E |
|---|---|---|---|---|---|---|
| Sa-1 | Cathodic | ≈1100 | 4.6 | 6.30 | 241.8 | 0.02605 |
| Sa-2 | arc | | 8.5 | 6.31 | 253.6 | 0.02488 |
| Sb-1 | | ≈1650 | 7.0 | 9.0 | 255.1 | 0.03528 |
| Sb-2 | | | 10 | 10.6 | 222.3 | 0.04768 |
| Sc-1 | | ≈2200 | 12 | 8.23 | 200.6 | 0.04103 |
| Sc-2 | | | 13 | 9.52 | 195.9 | 0.0486 |
| Sd-1 | Middle | ≈412 | 3.62 | 10.1 | 236.8 | 0.04265 |
| Sd-2 | frequency | | 4 | 10.2 | 345.6 | 0.02951 |
| Se-1 | magnetron | ≈825 | 9.5 | 12 | 217.5 | 0.05517 |
| Se-2 | puttering | | 11 | 13.8 | 275.2 | 0.05015 |
| Sf-1 | | ≈1238 | 12 | 11.8 | 216.5 | 0.0545 |
| Sf-2 | | | 14 | 12.4 | 316.7 | 0.03915 |

higher substrate surface roughness have strong mechanical interlocking between the film and substrate that's why they show higher adhesion of the $TiO_2$ film [12]. The dependence of adhesion on the film thickness and base material surface roughness is accordance with the previous studies [13, 14].
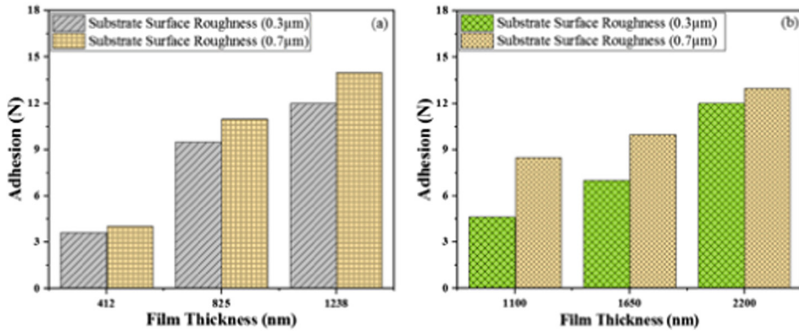
**Fig. 5.** Adhesion of the TiO$_2$ film (a) MF magnetron sputtering (b) cathodic arc deposition.

### 3.3    Nano Mechanical Properties of TiO$_2$ Thin Film

Nano indentation method was employed to evaluate the hardness (H) and elastic modulus (E) of the TiO$_2$ film. Nano hardness tester presents the output in the form of load displacement curves. H and E are calculated using these curves by Oliver and Pharr's method [15]. The detailed results of mechanical properties are given in Table 2.

Figure 6 shows the hardness of the TiO$_2$ film against film thickness and varying substrate surface roughness for both the cathodic arc and MF magnetron sputtering PVD process. It is seen that hardness increases as the film thickness increases up to the 825 nm for MF magnetron sputtering and 1650 nm for cathodic arc process then it starts to decrease for both the PVD processes. This trend can be explained by the fact that as the film thickness increases then the compressive stresses also increases up to the particular critical thickness. After reaching the critical thickness transition of phase shift takes place from compressive to tensile stress which causes to decrease in the hardness [16]. But, the samples with more substrate surface roughness give relatively higher values of the hardness than the samples with the less surface roughness. It is accordance to the fact that hardness of the films strongly depends on the base material surface roughness and thickness of the film [17].
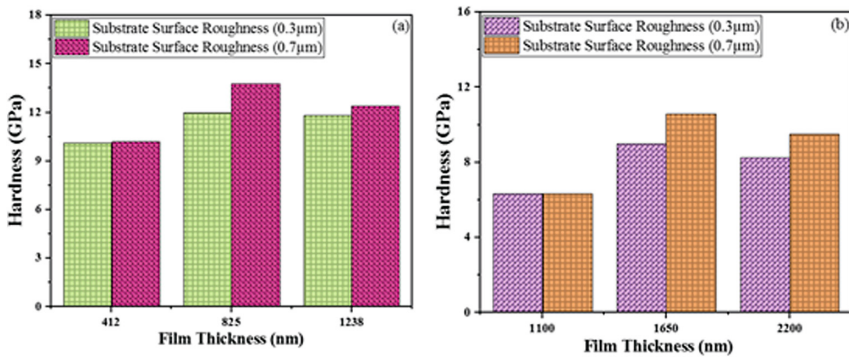


**Fig. 6.** Hardness of the TiO$_2$ film (a) MF magnetron sputtering (b) cathodic arc deposition.

Conventionally, it was considered that only the hardness of the film played an important role for the wear resistance but researches proved that elastic modulus of the films has also contributed in explaining the wear resistance of these films. The ratio of H/E, in several researches, is thought to be a vital parameter in explaining the wear of these films. Films which have higher H/E ratio are more likely to be more wear resistant [18]. The detailed values of H/E ratio are given in the Table 2. It can be seen that the H/E ratio values are relatively greater for the cathodic arc $TiO_2$ film as compared to the MF magnetron sputtering.

## 4  Conclusion

This study presents the successful deposition of $TiO_2$ thin films on stainless steel by cathodic arc and MF magnetron sputtering PVD process. EDX analysis shows that the film deposited by MF magnetron sputtering has stoichiometric concentration of Ti and O. Samples with higher surface roughness give superior hardness and adhesion of the films irrespective of the deposition process. Furthermore, the samples deposited by MF magnetron sputtering demonstrates relatively better adhesion and hardness results as compared to the cathodic arc deposition even at half of the $TiO_2$ film thickness deposited by cathodic arc PVD process.

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