Fabrication and Physical Properties of Titanium Nitride/ Hydroxyapatite Composites on Polyether Ether Ketone by RF Magnetron Sputtering Technique

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Abstract. Titanium nitride coatings have been used very successfully in a variety of applications because of their excellent properties, such as the high hardness meaning good wear resistance and also used for covering medical implants. Hydroxyapatite is a bioactive ceramic that contributes to the restoration of bone tissue, which together with titanium nitride may contribute to obtaining a superior composite in terms of mechanical and bone tissue interaction matters. This paper aim to optimize deposition conditions for films synthesis on PEEK by varying sputtering parameters such as nitrogen flow rate and direction, deposition time, d-s (target-to-substrate distance) and 13.56 MHz RF power. The plasma conditions used to deposit films were monitored by the optical emission spectroscopy (OES). Titanium nitride/Hydroxyapatite composite films were performed by gas mixture with nitrogen and argon ratio of 1:3 and target-to-substrate distance at 8 cm. The gold colour, as-deposited film was found on PEEK with high hardness and higher surface energy than uncoated PEEK. X-ray diffraction characterization study was carried to study the crystal structural properties of these composites.

1. Introduction

In recent years, many studies were carried on the development of composite coatings, of metallic biocompatible materials (strength, hardness) [1] and bioactive ceramic materials based on biodegradable calcium phosphates [2].Titanium nitride (TiN) is a biocompatible ceramic material which possesses high values for hardness and good wear and corrosion resistance properties [3]. Hydroxyapatite is a calcium phosphate ceramic material used successfully in orthopaedics and dentistry due to the bioactive properties and its structure nearly the same chemical composition as human bone, and can be used to guide bone regeneration [4]. PEEK (poly-ether-ether-ketone) is well known as a high-performance thermoplastic polymer able to replace metallic components

This research aims to study and develop the procedure to find optimize deposition conditions for fabricate TiN/HA films on PEEK. TiN/HA films prepared by RF pulse reactive magnetron sputtering using various sputtering parameters such as nitrogen flow rate, d-s (target-to-substrate distance) and RF power. The physical properties of coatings such as contact angle, surface energy and microhardness were measured. The crystallographic structure of the deposited films was investigated by X-ray diffractometer (XRD).

2. Experiment

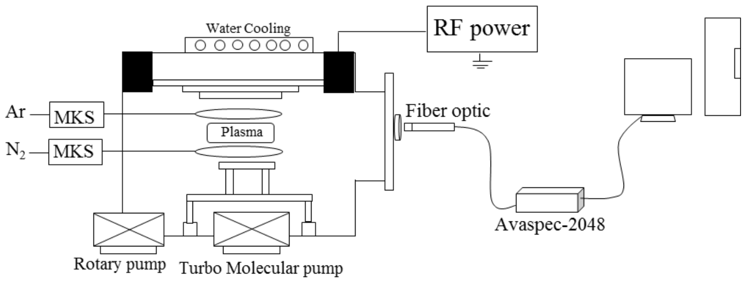

Figure 1. Experimental set up with optical emission spectroscopy

The sputtering chamber made of a stainless-steel, rectangular-shaped with 37 x 37 x 37 cm^3 in dimension. The cathodic target was a 99.999% pure Ti with a diameter of 100 mm half covered with 7.5 cm HA as co-axis configuration. The target-to-substrate distance was adjusted from 3.5 to 8 cm. The system was evacuated by using a turbomolecular pump backed by rotary pump giving a base pressure less than 9 x10^{-6} Torr. In this experiment, nitrogen gas was separated and fed through a distribution ring positioned below the argon gas feeding about 50 mm. The flow rates of each gas were controlled by using a MKS mass-flow controller. Argon (99.9995%) gas flow rate was fixed at 3 sccm. Nitrogen gas (99.9995%) flow rate was varied from 1, 3 and 6 sccm. The sputtering pressure was varied from 5 x10^{-3} to 5 x 10^{-2} Torr. The sputtering RF power was varied from 100 to 200 watt. Each experiment continues for 120 min. After that, measure surface energy and hardness of TiN/HA films by contact angle and Vickers microhardness test respectively. The frequencies of power source is the radiofrequency (RF) with a most common value of 13.56 MHz.

The plasma emission spectra from of deposited plasma were recorded through the UV quartz window on the side of the deposition chamber as shown in Figure 1.The optical emission spectra were recorded in the wavelength range 200 to 800 nm.

3. Results and Discussion

3.1 OES measurements of deposited plasma

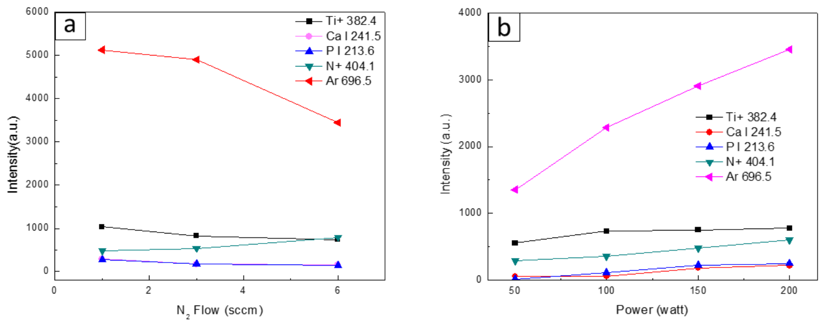

Figure 2. Spectrum of the deposited plasma

Figure 2 (a) show the emission intensity of deposited plasma species at different N_2 and Figure 2 (b) show the emission intensity of deposited plasma components at different RF power. In the spectrum of the deposited plasma with Titanium and HA target Figure 2 (a,b) spectral lines and bands of Ti^+, Ar, Ar^+ ,Ca, P and N^+ were identified. The emission intensities of the analyzed atomic lines and molecular bands were investigate versus the RF power and nitrogen flow Figure 2 (a), respectively. It can be seen from Figure 1, the intense peak of N^+ (404.1) increase with increasing N_2 content, whereas it resulted in the fall in the emission intensities of Ar and others. The species of N^+, Ti^+, Ca, P and Ar are an important role in the growth of deposited films. From Figure 2 (b), when the RF power increased, the emission intensity of all deposited plasma slightly increased except of the Ar. Due to the higher RF power is the raise of energetic particles to excite the other components in the plasma system.

3.2 Contact angles and Surface energy

Table 1. Contact angle on coatings

TiN/HA films		
Power (watt)	Contact angle θ	work of adhesion W_a (dynes/cm)
Uncoated PEEK	118.26	38.34
100	78.65	87.13
150	73.32	93.69
200	72	95.29

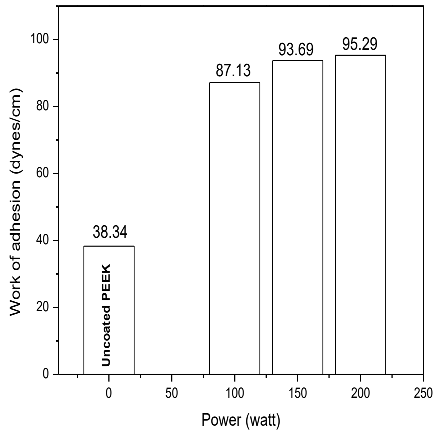

Figure 3. Surface energy of the coatings at different RF power

According to Young's equation, there is a relationship between the surface free energy γ_{SV} of the solid, the contact angle θ, the surface tension of the liquid γ_{SL} and the interfacial tension γ_{LV} between liquid and solid [5]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta_c \quad (1)$$

So the work of adhesion is:

$$W_a = \gamma_{LV}(1+\cos\theta_c) \quad (2)$$

Where the energy of adhesion (W_a) is directly related to the surface free energy of the contact between two phases. The work of adhesion of contact angle at 118.26, 78.65, 73.32 and 72 deg. is 38.34, 87.13, 93.69, 95.29 dynes/cm respectively, so the highest work of adhesion of TiN/HA as-deposited film is 95.29 dynes/cm.

3.3 Hardness

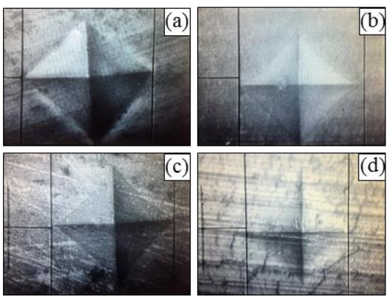

Figure 4. Vickers indentation of 100 W, 150W and 200W coatings on PEEK

Figure 4 (a) presents the hardness profile of the uncoated PEEK. It had a hardness value of 20.66 HV. These results are consistent with those reported in the literature [6]. Figure 4 (b) presents indentation of the 100 W coating on PEEK. It had hardness value of 22.18 HV. The pyramid is well identifiable in the substrate, and has small area than uncoated PEEK. Figure 4 (c) shows the hardness profile of the 150 W coating on PEEK harder than the 100W coating with the hardness value of 23.48 Hv. Figure 4 (d) presents the indent that were carried out on the coating. The hardness value of the 200W coating on PEEK was 33.15 Hv. The pyramid indent in the PEEK is well defined. A well-defined pyramid indents indicate resistance to fracturing of material.

3.4 Crystal Structure

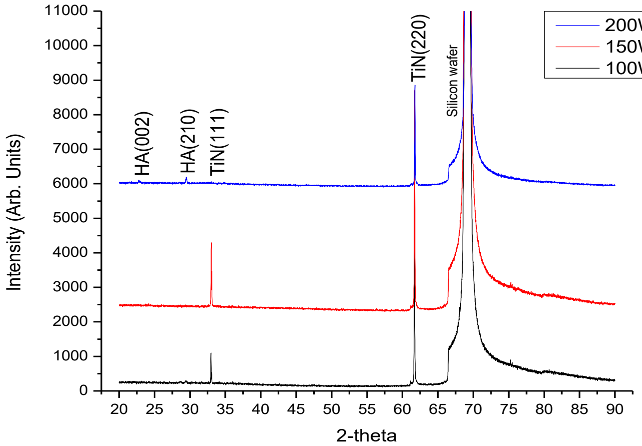

Figure 5. XRD pattern of films prepared by RF power at100W, 150W and 200 W

Figure 5 show the X-ray diffraction pattern of the as-deposited titanium nitride and hydroxyapatite composites on silicon wafer obtained by reactive RF magnetron sputtering by varying RF power in the rage 100-200W. The intensity of the TiN (220) peak is higher than that of the TiN (111) peak at 100W, 150W and 200W respectively. The TiN (220) peak and TiN (111) peak change with decrease in RF power but the HA (002) and HA (210) appear only at RF power of 200W.

Conclusion

From the results, condition for sputtering was examined by OES. The emission intensity increase with RF power and nitrogen flow. The intensity of all components in plasma raise maximum at 1 sccm of N_2 content. Furthermore, the physical properties of the TiN/HA film as-deposited was found on PEEK with high hardness and higher surface energy than uncoated PEEK. The higher RF power enhanced orientation of TiN/HA film deposited at 200 watt.

Reference

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