

Structure and Properties of Titanium-Based Coatings prepared by Metal Plasma Immersion Ion Implantation and Deposition



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Motivation

For medical materials in contact with **blood** it is important to minimize the tendency of their surface to adsorb blood proteins and to induce blood clotting, hence, to reduce the danger of thrombosis. **Titanium**-based coatings are a very promising approach in this direction.

Objectives

Synthesis of bioinert and **blood compatible titanium**-based coatings by **Metal Plasma Immersion Ion Implantation and Deposition** (MePIIID), modification of the surface layers by different partial pressures of **O₂** and **N₂** and subsequent **ion implantation (P and Cr)** into **TiO₂**.

Investigation of the relation between physical properties of the **titanium**-based layers and **blood compatibility** (clotting time, thrombocyte adhesion, fibrinogen adsorption) for

- **P**- and **Cr**-implanted **TiO₂** and
- **TiN_xO_y**

Experimental

Deposition parameters:

Specimen temperature (T_{max}): 25 – 500 °C
Gas flow rate (F): 60 – 180 sccm
Bias voltage (ion energy): 0 – 2.5 kV
Coating deposition rate (R_{dep}): 0.35 – 1.1 μm/min
Current of the cathodic arc discharge (I): 110, 140 A
Basic vacuum: 0.5 – 1 × 10⁻³ Pa
Working pressure: 0.5 – 1 × 10⁻¹ Pa
Substrate: SiO₂ on Si (100)

Implantation: 10¹⁵ P⁺/cm² (30 keV);
5 × 10¹⁷ Cr⁺/cm² (30 keV)

Post-implantation annealing: 900 °C for 1 h (vacuum)

Analysis AES: depth distribution of the elements
XRD: phase formation and identification
AFM: roughness of the deposited films
Contact angle: wettability, surface energy

Blood compatibility: blood clotting time
thrombocyte adhesion,
fibrinogen adsorption

MePIIID: metal deposition + plasma immersion ion implantation (PIII)
metal plasma by cathodic arc evaporation
implantation by pulsed negative substrate bias
supply of oxygen near the substrate

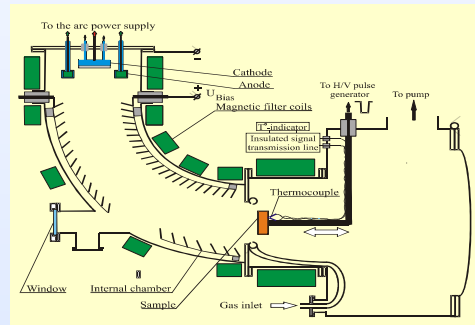


Fig. 1. Schematic diagram of the MePIIID device

Layer properties

Oxide layers

Dependence of the **TiO₂** structure on the deposition parameters

structure (XRD)	T, °C	F, sccm	U, kV
rutile + anatase	~ 450	180	- 2.5
anatase + brookite	~ 350	60	- 2.5
amorphous TiO ₂ - layer	~ 80	180	0
nanocrystalline anatase + brookite	~ 60	60	0

Oxynitride layers

Dependence on the relation of the **O₂/N₂** partial pressures

crystalline phases (XRD)	average atomic composition (AES)	structure	p(O ₂)/p(N ₂)
rutile + anatase	TiO ₂	TiO ₂	only O ₂
rutile + anatase + TiO	TiN _{0.3} O _{1.7}	(rutile + anatase) TiO ₂ N _x (rutile + anatase) + TiO	3/1
TiN + TiO	TiN _{0.4} O _{1.6}	TiN + TiO + TiO ₂ (amorph)	1/1
TiN _{1-x} O _x	TiN _{0.7} O _{1.3}	TiN _{1-x} O _x + TiO ₂ (amorph)	1/3
TiN	TiN	TiN	only N ₂

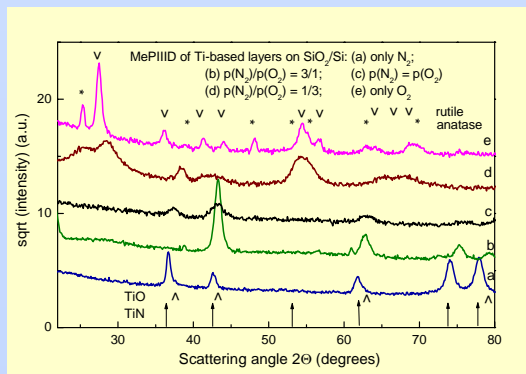


Fig. 2. XRD pattern of Ti-based layers

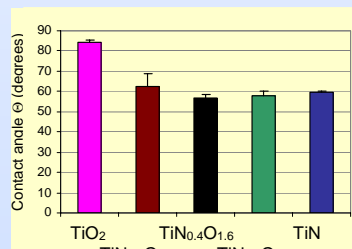


Fig. 3. Contact angle with water for different layer compositions

- Decrease by incorporation of nitrogen

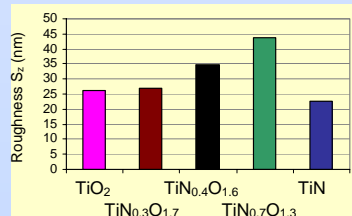


Fig. 4. Roughness of different layer compositions

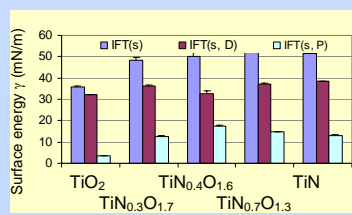


Fig. 5. Dispersive IFT(S,D) and polar IFT(S,P) components of the coatings surface energy IFT(s)

Summary

- MePIIID provides a useful technique to control composition and structure of **titanium**-based films. In dependence on the deposition parameters different **titanium oxynitrides** have been produced
- **TiN** and **TiN_xO_y** have lower blood clotting activation compared to **TiO₂**
- **Thrombocyte adhesion** and **fibrinogen adsorption** are lower for **TiN_xO_y** than for **TiO₂**
- This decrease is related to the decreasing **contact angle** and increasing **surface energy**
- The quantity of nitrogen incorporation and the surface roughness show no significant influence
- **P** and **Cr** implantation into **TiO₂** clearly reduce the **clot forming property** of the surface

Blood compatibility

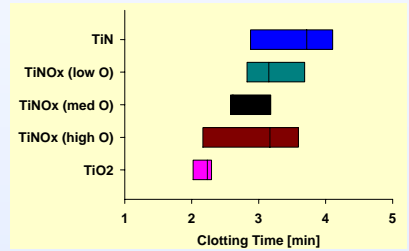


Fig. 6. Clotting time on the titanium oxynitride layers (median and quartils of the blood clotting time on the test surfaces)

- It is longer than the also shown **TiO₂** (rutile) value

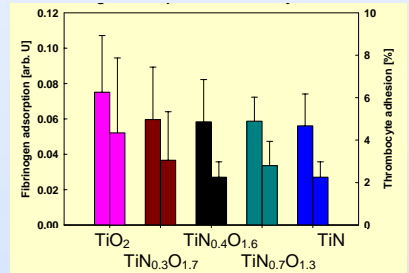


Fig. 7. Thrombocyte adhesion and fibrinogen adsorption on the titanium oxynitride layers

- Both values are reduced by the nitrogen incorporation in comparison to **TiO₂**

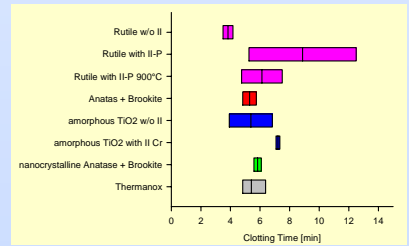


Fig. 8. Clotting time on the TiO₂ layers (median and quartils of the blood clotting time on the test surfaces)

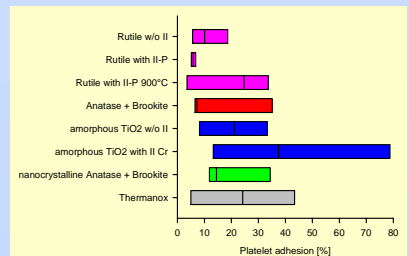


Fig. 9. Platelet adhesion on the TiO₂ layers (bars indicate median and quartils of the percentage platelets from a sample platelet-rich plasma on the test surfaces)

- both **P⁺** and **Cr⁺** ion implantation (II-P and II-Cr) into **TiO₂** increase the clotting time, i.e. reduce the activation of the clotting cascade by this surface, and decrease the thrombocyte adhesion

