

Blood Compatibility 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 **ion implantation (P and Cr)** and annealing

Study of the dependence of crystal structure (**crystalline rutile, anatase and brookite**, nanocrystalline, amorphous TiO_2 , $\text{TiN}_{1-x}\text{O}_x$, **TiN**) of **titanium** based layers on the deposition parameters

Investigation of the relation between physical properties of the **titanium** based layers and **blood compatibility**

Summary

- MePIIID provides a useful technique to control composition and structure of **titanium** based films. In dependence on the deposition parameters amorphous and nanocrystalline structures, **crystalline** layers composed of anatase and brookite, layers dominated by the **rutile** phase as well as different **titanium oxynitrides** have been produced
- Crystal structure and crystallite size of **titanium oxide** films seem to have only minimal influence on the activation of the plasmatic clotting system. As a trend, **amorphous**, nanocrystalline and fine-grained layers induce less **clotting of blood plasma** than well **crystallized rutile** films
- **P** and **Cr** ion implantation into **titanium oxides** clearly reduces the **clot forming property** of the surface
- Clotting time of **TiN** and **TiN_{1-x}O_x** (low x) is higher compared to **Ti oxide**
- **Ti oxides** and **oxynitrides** show an opposite dependence of **platelet adhesion** and **activation** of the clotting cascade. However, **P⁺**-doped **rutile** shows an improved behaviour in both cases

Experimental

Deposition parameters:

Specimen temperature (T_{max}): 25 – 500 °C
 Oxygen flow rate (F): 60 – 180 sccm
 Bias voltage (ion energy): 0 – 2.5 kV
 TiO_2 deposition rate (R_{dep}): 0.2 – 1.1 $\mu\text{m}/\text{min}$
 Current of the cathodic arc discharge (I): 110 A
 Basic vacuum: $0.5 - 1 \times 10^{-3}$ Pa
 Working pressure: $0.5 - 1 \times 10^{-1}$ Pa
 Substrate: SiO_2 on Si (100)

Implantation: 10^{15} P⁺/cm² (30 keV);
 5×10^{17} Cr⁺/cm² (30 keV)

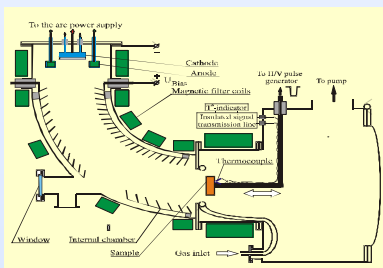
Post-implantation annealing:

900 °C for 1 h (vacuum)
 depth distribution of the elements
 phase formation and identification
 thickness of the deposited films
 AFM: roughness of the deposited films
 Four point probe technique: sheet resistance

Blood compatibility:

blood clotting time
 platelet adhesion and activation

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



Schematic diagram of the MePIIID device

Layer properties

Oxygen concentration and deposition rate of the oxide layers

- oxygen concentration is nearly independent of oxygen flow rate F substrate temperature and implantation voltage; TiO_2 is formed
- deposition rate increases strongly with substrate temperature
 450 °C - $1.1 \mu\text{m}/60$ s and 116°C - $0.23 \mu\text{m}/60$ s
 for U=2.5 kV and F=180 sccm
- increasing F reduces the deposition rate strongly
 60 sccm - $540 \text{ nm}/60$ s, 120 sccm - $350 \text{ nm}/60$ s,
 180 sccm - $240 \text{ nm}/60$ s
 for U=2.5 kV and T_{max} =120°C
- influence of the implantation voltage on the deposition rate is only weak

Phase composition of the oxynitride layers

Dependence on the relation of the O_2/N_2 partial pressures

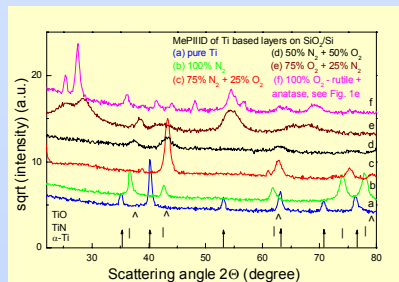


Fig. 2. XRD pattern of Ti oxynitride layers

Phase composition of the oxide layers

Dependence of the Ti oxide structure on the deposition parameters (see Fig. 1)

structure	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

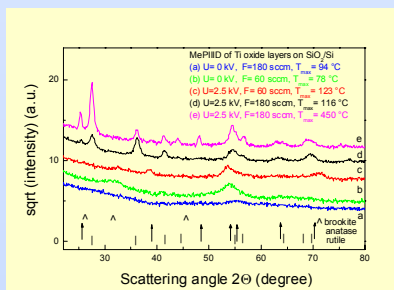


Fig. 1. XRD pattern of Ti oxide layers deposited with different parameters

structure	O ₂	N ₂
rutile + anatase	100%	0%
$\text{TiO}_{2-x}\text{N}_x$ (rutile + anatase) + TiO	75%	25%
TiO + TiN	50%	50%
$\text{TiN}_{1-x}\text{O}_x$	25%	75%
TiN	0%	100%

Blood compatibility

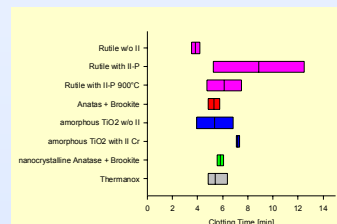


Fig. 3. Clotting time on the Ti oxide layers: Median and quartils of the blood clotting time on the test surfaces

- both P⁺ and Cr⁺ ion implantation (II-P and II-Cr) into **Ti oxides** increase the clotting time, i.e. reduce the activation of the clotting cascade by this surface
- well **crystallized Ti oxides** dominated by the **rutile** structure show the lowest clotting time
- the behaviour of the amorphous and nanocrystalline **Ti oxides** is in between
- the clotting time of **TiN** and **TiN_{1-x}O_x** (low x) is higher compared to **Ti oxide**

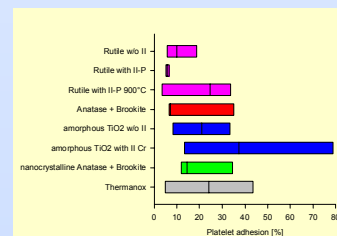


Fig. 4. Platelet adhesion on the Ti oxide layers: Bars indicate median and quartils of the percent adherent platelets from a sample platelet rich plasma on the test surfaces

- P⁺ ion implantation (II-P) into **Ti oxides** reduces the platelet adherence to the surface, whereas Cr⁺ ion implantation (II-Cr) greatly increases it
- As a vague trend lower platelet adherence on **crystalline** coatings than on **amorphous** ones is found (contrary to the behaviour of the clotting time)
- **TiN** and **oxynitrides** show higher platelet adherence as **Ti oxide**

