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, $TiN_{1-x}O_x$, 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** 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 adherence and activation of the clotting cascade. However, **P^+**- doped rutile shows an improved behaviour in both cases

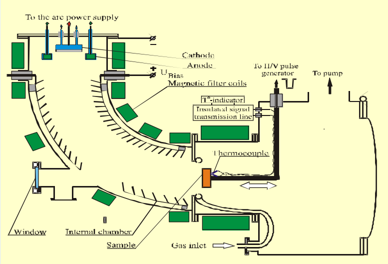
Experimental

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 μm/min
Current of the cathodic arc discharge (I):	110 A
Basic vacuum:	0.5 – 1 x 10^{-3} Pa
Working pressure:	0.5 – 1 x 10^{-1} Pa
Substrate:	SiO_2 on Si (100)
Implantation:	10^{15} **P^+**/cm² (30 keV); 5x10^{17} **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
	RBS:	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 μm/ 60 s and 116 °C - 0.23 μm/ 60 s
  for U=2.5 kV and F=180 sccm
- increasing F reduces the deposition rate strongly
  60 sccm - 540 nm/ 60 s, 120 sccm- 350 nm/ 60 s,
  180 sccm- 240 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

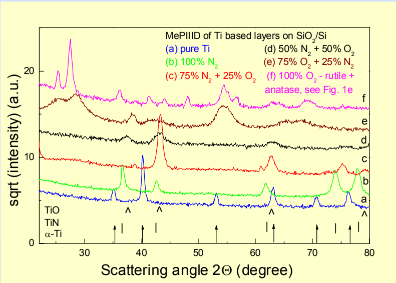


Fig.2. XRD pattern of Ti oxynitride layers

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

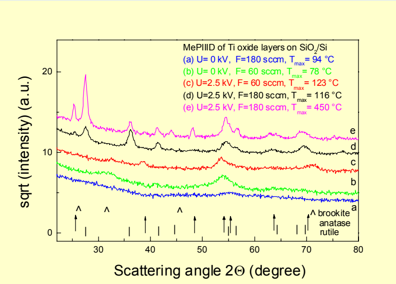


Fig.1.
XRD pattern of Ti oxide layers deposited with different parameters

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structure	**O_2**	**N_2**
rutile + anatase	100%	0%
$TiO_{2-x}N_x$ (rutile + anatase) + TiO	75%	25%
TiO + TiN	50%	50%
$TiN_{1-x}O_x$	25%	75%
TiN	0%	100%

Blood compatibility

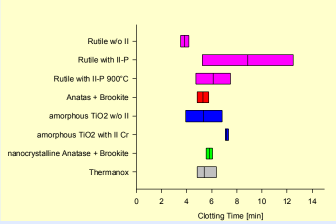

Fig.3. Clotting time on the Ti oxide layers:
Median and quartils of the blood clotting time on the test surfaces

- 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

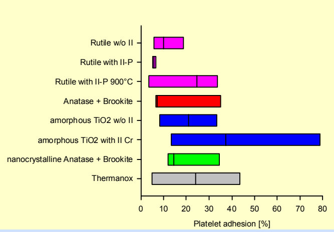

Fig.4. Platelet adhesion on the Ti oxide layers :
Bars indicate median and quartils of the percent adherent platelets from a sample platelet rich plasma on the test surfaces

- **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

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