Structure and Properties of Titanium Oxide Layers prepared by Metal Plasma Immersion Ion Implantation and Deposition

I. Tsyganov, M. F. Maitz[1], E. Wieser[1], F. Prokert[1], E. Richter[1] and A. Rogozin[1]

Lipetsk State Technical University, Moscowskaya 30, 398055 Lipetsk, Russia

[1]Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf e.V., P.O.Box 510119, 01314 Dresden, Germany

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. Coatings based on titanium oxide are a very promising approach in this direction.

Objectives

Synthesis of bioinert and blood compatible coatings based on titanium oxide 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), surface roughness and electrical properties of titanium oxide layers on the deposition parameters

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

Summary

- MePIIID provides a useful technique to control composition and structure of titanium oxide films. In dependence on the deposition parameters amorphous and nanocrystalline structures, crystalline layers composed of anatase and brookite as well as layers dominated by the rutile phase 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 clearly reduces the clot forming property of the surface
- Microstructure of the Ti oxides showed a opposite effects on platelet adherence and activation of the clotting cascade. However, P^+- doped rutile shows an improved behaviour in both cases
- Roughness of the surface below 50 nm seems to be no important parameter

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)

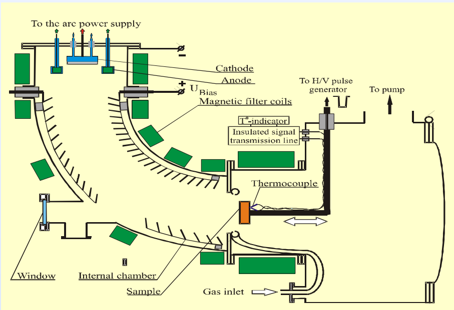
Implantation: 10^{15} P^+/cm^2 (30 keV); 5×10^{17} Cr^+/cm^2 (30 keV)

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

- oxygen concentration is nearly independent of oxygen flow rate F (see **Fig. 1**), 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 (see **Fig.1**)
- influence of the implantation voltage on the deposition rate is only weak

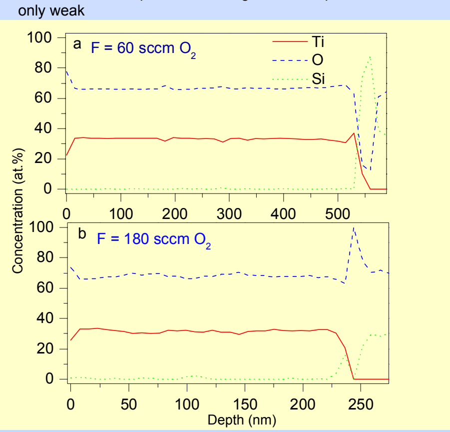


Fig.1.
AES depth profiles of Ti oxide layers deposited with U = 2.5 kV at Tmax = 120 °C for different oxygen flow rates F

Phase composition of the oxide layer

Dependence of the Ti oxide structure on the deposition parameters

structure	T, °C	F, sccm	U, kV
rutile	~ 450	180	- 2.5
anatase + brookite	~ 350	60	- 2.5
amorphous TiO_2- layer	~ 80	180	0
nanocrystalline anatase + brookite	~ 60	60	0

Electrical properties and roughness of the different Ti oxide layers

structure	sheet resistance	roughness S_z, nm
rutile	>200 kOhm	high – 34.2
rutile + P^+ implantation (II)	~90 kOhm	high – 30.1
rutile + P^+-II + annealing	~60 kOhm	high – 39.8
anatase + brookite	~25 Ohm	high – 42.7
amorphous TiO_2- layer	>200 kOhm	low – 4.15
amorphous TiO_2- layer + Cr^+-II	~100 Ohm	high – 31.9
nanocrystalline anatase + brookite	~100 Ohm	low – 5.35

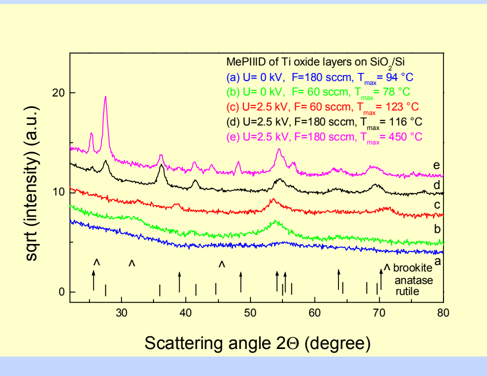


Fig.2.
XRD pattern of Ti oxide layers deposited with different parameters

Blood compatibility

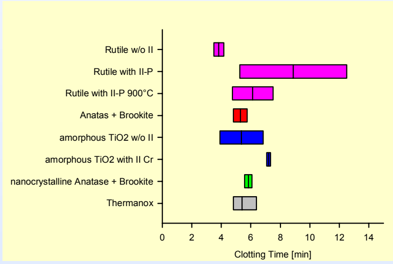


Fig.3. Clotting time:
Median and quartils of the blood clotting time on the test surfaces

- both P^+ and Cr^+ ion implantation (II-P and II-Cr) increase the clotting time, i.e. reduce the activation of the clotting cascade by this surface
- well crystallized samples dominated by the rutile structure show the lowest clotting time
- the behaviour of the amorphous and nanocrystalline samples is in between

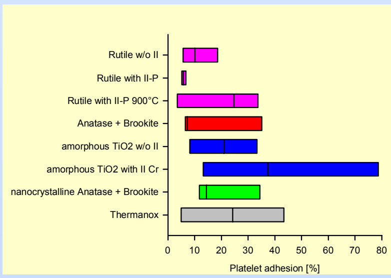


Fig.4. Platelet adhesion:
Bars indicate median and quartils of the percent adherent platelets from a sample platelet rich plasma on the test surfaces

- P^+ ion implantation (II-P) 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)

contact:
Dr. Igor Tsyganov
Tel.: +7 (0742) 722668
e-mail: zyganov@stu.lipetsk.su

Dr. Manfred Maitz
Tel.: +49 (351) 2602014
e-mail: m.maitz@fz-rossendorf.de