Institute for Ion Beam Physics and Materials Research

Forschungszentrum Rossendorf

Titanium Oxide Layers prepared by Metal Plasma Immersion Ion Implantation and Deposition (MePIIID) as Hemocompatible Surfaces

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Motivation

Titanium oxide is known for a good bio- and hemocompatibility, but this has not yet been correlated with crystal structure or electronic properties of this semiconductor. These physical features may be interesting because surface charges interact with charges of the protein and induce conformational changes of the protein with a change of function.

Chemical oxidation of proteins on the surface is under discussion for blood clotting activation. Surfaces which prevent electron acceptance should have improved blood compatibility.

Objectives

- Synthesis of TiO_2 layers with various crystal structure by MePIIID
- Modification of chemical and electronic properties by ion beam implantation.
- Investigation of the blood compatibility of the surfaces.

Film Deposition

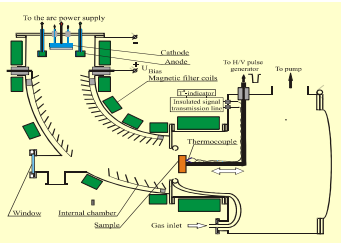
Deposition of TiO_2 films with different parameters

Titanium metal plasma by cathodic arc evaporation
- arc current: 110A
- Basic vacuum 0.5 – 1 x 10^{-3} Pa
- Working Pressure 0.5 – 1 x 10^{-1} Pa

Deposition on oxidized Si substrates
- deposition rate 0.2-1.1µm/min
- resulting substrate temperature 25-500°C

Implantation during deposition
- pulsed negative substrate bias 0, -2.5kV

Supply of oxygen near the substrate
- 60-180 sccm



Post Deposition Ion Beam Implantation

Phosphorous into rutile (30keV, 5 x 10^{15} cm^{-2}), annealing at 900°C.
- → P is n doping element and prevents electron acceptance by the surface
  low dose implantation for semiconductor effects

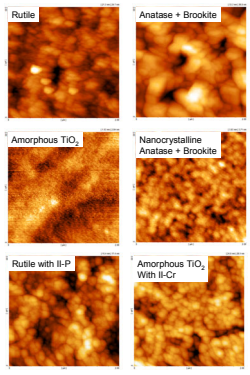
Chromium into amorphous TiO_2 (30keV, 5 x 10^{17} cm^{-2})
- → Cr has low redox potential and by this prevents electron acceptance
  high dose implantation for chemical effects

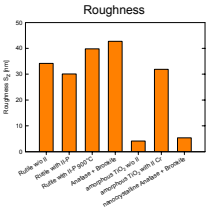
Physical Properties

XRD reveals the following film structures

F_O [sccm]	U [kV]	T [°C]	Structure
180	-2.5	~ 450	Rutile + Anatase
60	-2.5	~ 450	Anatase + Brookite
180	0	~ 80	Amorphous TiO_2
60	0	~ 60	Nanocrystalline Anatase + Brookite

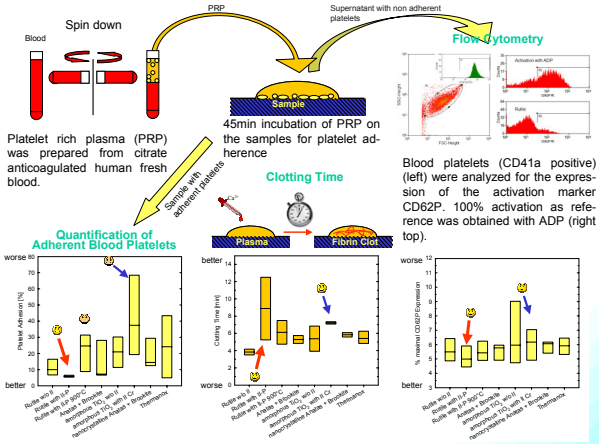
Depending from oxygen flow and bias voltage TiO_2 layers can be obtained with different crystal structure





Surface roughness measured by atomic force microscopy. All samples were smooth below 50 nm, the roughness of the amorphous and nano-crystalline layers was about $^1/_{10}$ of the others.

Biological Properties



Platelet rich plasma (PRP) was prepared from citrate anticoagulated human fresh blood.

45min incubation of PRP on the samples for platelet adherence

Blood platelets (CD41a positive) (left) were analyzed for the expression of the activation marker CD62P. 100% activation as reference was obtained with ADP (right top).

Blood platelet adhesion (median and quartiles) as indicator for increased blood clot formation.

Clotting Time as indicator for the activation of the clotting cascade. Note the effect of Cr implantation.

CD62P expression as marker of activation in non-adherent platelets. Trends are the same as for platelet adherence.

Summary and Conclusions

- ✓ MePIIID is a useful technique to produce Ti based coatings with defined crystal structure.
- ✓ The effect of crystal structure of TiO_{2-x} surfaces on blood compatibility is only small and could not be proven here.
- ✓ Ion implantation of both antioxidant elements, Cr and P, prevented activation of the clotting cascade.
- ✓ P implantation reduces both clotting activation and blood platelet activation and adherence, however the mechanism is unclear, as the effect disappears after annealing, what makes the electronic effect of n doping more unlikely.

Literature:

Tsyganov I., Maitz M.F., Wieser E., Prokert F., Richter E., Rogozin A. **Structure and properties of titanium oxide layers prepared by metal plasma immersion ion implantation and deposition.** Surf Coat Techn **174-175C**: 591-596 (2003).

Maitz M.F., Tsyganov I., Pham M.-T., Wieser E. **Blood compatibility of titanium oxides with various crystal structure and element doping.** J Biomater Appl **17**(4): 303-320 (2003).

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