Structural properties of PVD coatings on implants and their influence on stimulation performance in pacing applications

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Abstract

An overview about the opportunities to apply PVD coatings with different morphologies on implants will be given. Using magnetron sputtering technology single and multiple layers of metals, alloys, composites and ceramics can be deposited. These coatings can improve biocompatibility or wear resistance and serve as an electrical insulation or diffusion barrier. This presentation will focus on coatings to enhance cardiac and neurological stimulation. Various metallic and ceramic coatings have been sputtered and the influence of material, thickness and surface morphology on their impedance characteristics has been investigated by electrochemical impedance spectroscopy. An increase in electrochemical capacitance that yields an impedance enhancement is best achieved by morphological changes resulting from process parameters or thickness. Due to the limited charging process velocity at the electrode surface the capacitance experiences a frequency dependent saturation. Knowing the kinetics of these exchange reactions at the electrode-tissue interface and the physical and chemical coating properties permits coatings to be applied with tailored characteristics for electrotherapy.

The PVD coating process

Coatings investigated in this paper have been applied by PVD (Physical Vapor Deposition). Among the different PVD processes available metallic and reactive DC magnetron sputtering techniques were used. The working principle of DC magnetron sputtering is shown in figure 1. A detailed explanation of sputter processes can be found in [1].
For metallic DC magnetron sputtering processes (Ir, Pt, PtIr etc.) Ar was used as a process gas whereas for reactive processes a reactive gas was added to form a chemical compound and deposit it as a layer. Titanium nitride, for example is sputtered off a Ti target in an Ar/N_2 mixture.

PVD coatings on medical implants

PVD coatings can be applied onto substrates like medical implants in different ways. While for semifinished materials

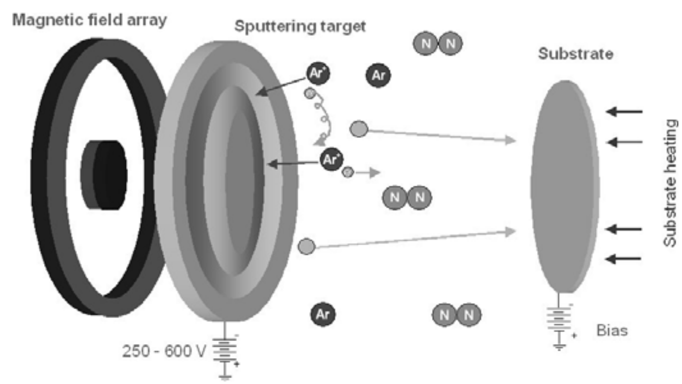

Figure 1: DC magnetron sputtering. The substrate is the medical implant to be coated with the material that the target is made of.

(e.g. wires) an inline-process is favored for cost-reasons, precision parts are typically coated in batch processes. The coatings serve as diffusion barriers, wear resisitance or electrical insulation. To coat only selective portions of a medical implant, masking is required.
An example about coating stents with an iridium oxide film resulting in an improvement of biocompatibility is given in [2].

PVD coatings for pacing applications

<u>Requirements:</u> The requirements on pacemaker electrodes contacting tissue for electrotherapy and the resulting needs on the electrode tissue interface are described in detail in [4], [5], [6], [7] and [8]. Looking from an electrochemical perspective the interface between electrode and tissue represents an electrode-electrolyte interface, which can be approximated by the equivalent circuit known as “Randles cell” (fig. 2). To reduce polarization effects at the electrode surface it is necessary to decrease the impedance of this electrochemical system. This is typically achieved by increasing capacitance C_p (fig. 2), resulting from coating the stimulation electrode with either a reduction-oxidation capable material or a material with a large physical surface area. The investigations

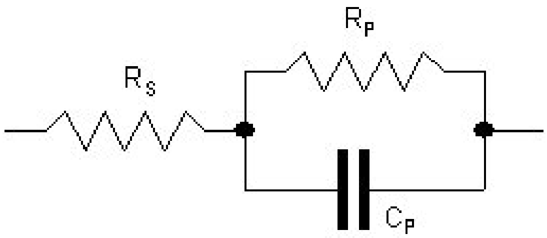

Figure 2: Equivalent circuit Randle´s Cell

carried out in the course of this work focus on the structural properties of high physical surface area coatings. Using those the increase of capacitance is due to the Helmholtz double-layer occuring between the electrode surface and the electrolyte respectively tissue.

<u>Electrochemical measurements:</u> Electrochemical impedance spectroscopy and cyclovoltammetry have been conducted using an EG&G potentiostat Model 273A and a frequency response detector model 1025. As an electrolyte 0.9 % NaCl solution was used at a temperature of 37°C. A standard calomel electrode served as a reference electrode and the counter electrode mesh consisted of Pt.

<u>Structural and electrochemical properties:</u> The influence of film morphology on the electrochemical properties shall be illustrated on Titanium nitride. A simplified model for adjusting film morphology has been proposed by Thornton (fig. 3) [3].
He created a zone diagram on film structure depending on process working pressure and homologous temperature, which is the ratio between deposition temperature and melting

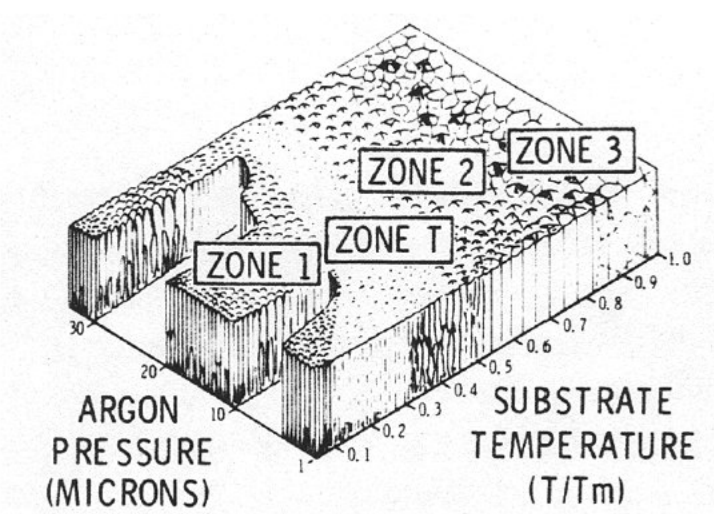

Figure 3: Thornton´s zone model [3]

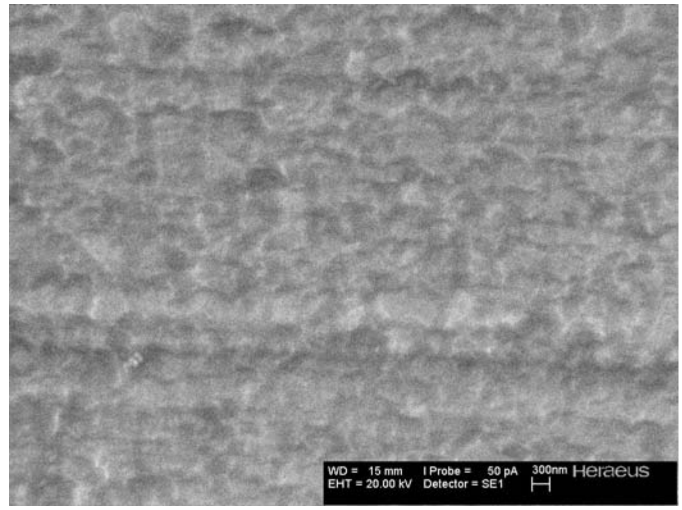

Figure 4: SEM image of titanium nitride film (zone T)

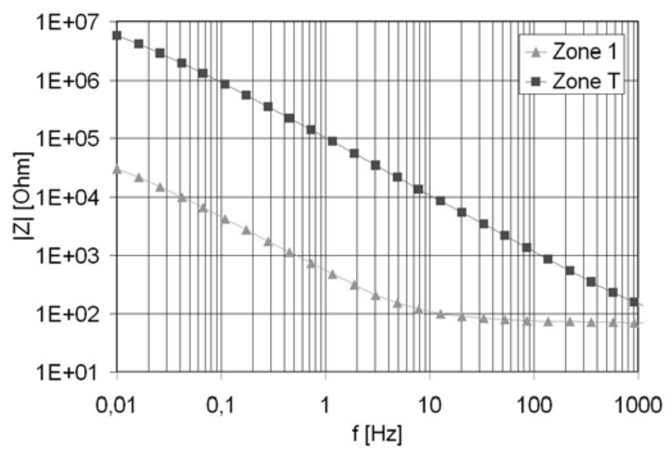

Figure 5: Impedance spectra for 3µm titanium nitride layers deposited under different process conditions.

temperature of the material to be deposited. A columnar grown, polycrystalline film is deposited in zone 1 while a smooth polycrystalline, mostly transparent film can be deposited in zone T. With higher deposition temperature crystal size increases and a dense, smooth crystalline film is grown on the substrate.
To taylor the titanium nitride film morphology for stimulation applications electrodes have been coated using two parameter sets, representing a smooth (zone T) and a columnar grown, porous (zone 1) titanium nitride film.
SEM images of the coatings are shown in fig. 4 (zone T) and fig. 6, sample A (zone 1). Both coatings have a thickness of 3µm. As one can see in fig. 5, an impedance improvement takes place for the zone 1 film only. Its larger physical surface area causes a significant increase in Helmholtz capacitance. Thus, for cardiac and neurological stimulation a columnar grown, porous titanium nitride film, is necessary.

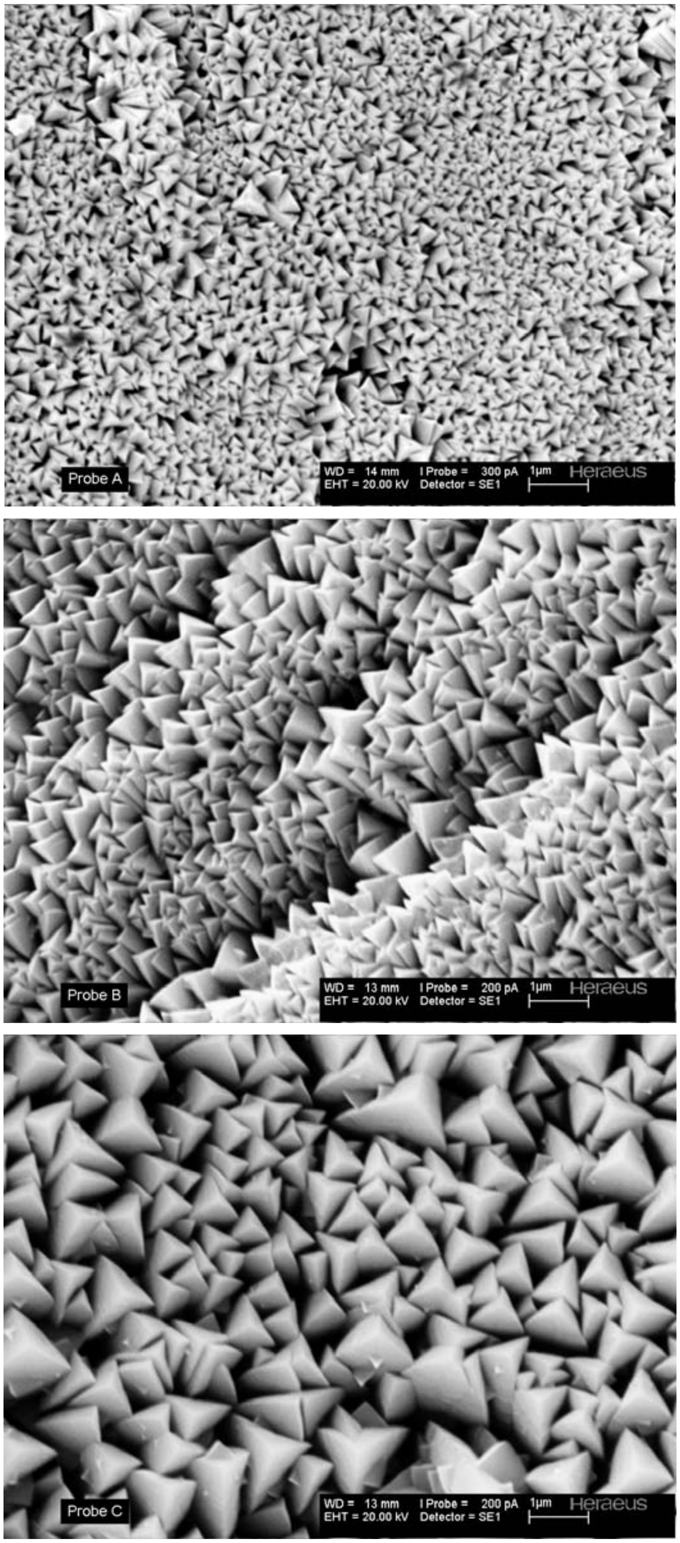

Figure 6: Titanium nitride morphology for different thicknesses (A: 3µm, B: 8µm, C: 20µm)

To visualize the influence of film thickness on the electrochemical properties electrodes were coated with

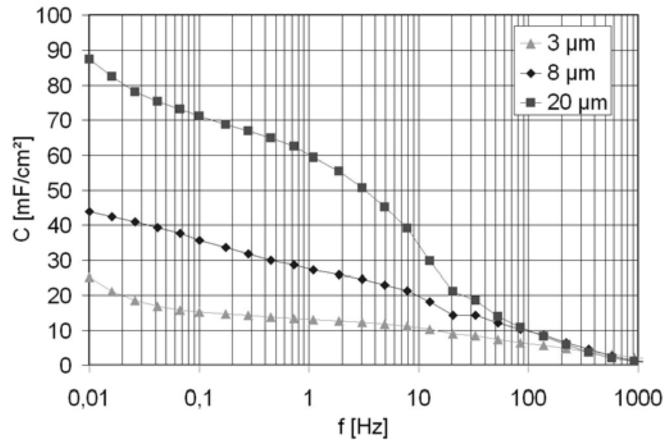

Figure 7: Capacitance spectra for titanium nitride depending on coating thickness

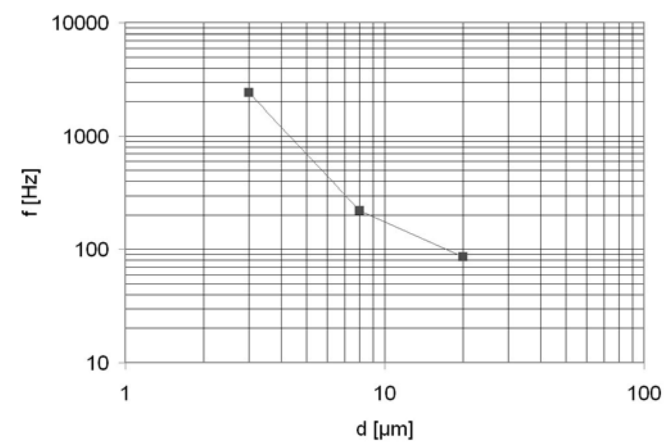

Figure 8: Upper frequency limit for further increasing Helmholtz capacitance

different thicknesses of titanium nitride (Sample A: 3µm, B: 8µm, C: 20µm). The SEM images of these three coatings are shown in fig. 6. The increasing grain size of the columnar grains is due to the "survival of the fastest" effect during a PVD process. Faster growing grains shadow smaller grains and grow not only normal to the substrate surface but also wider. In terms of stimulation performance this yields an increasing capacitance (fig. 7). With increasing thickness the gain in capacitance takes place only at the lower frequency range. Above an upper frequency limit the capacitance can not be increased further by just growing the titanium nitride film thicker. This is most likely due to the limited speed at which charging and discharging processes take place at a porous coating. With increasing thickness the upper frequency limit, above which the capacitance saturates, decreases (fig. 8).
Another parameter to compare coatings regarding their electrode properties is cut-off frequency. It can be determined in an arrhenius plot of impedance vs. frequency [9]. As it can

be seen in table 1, the increasing capacitance yields a shift in cut-off frequency towards lower frequencies.

Table 1: Cut-Off frequency for titanium nitride

Thickness [µm]	Cut-Off frequency [Hz]
3	8
8	3,5
20	1,5

Other coatings: Above results for titanium nitride exemplified the influence of coating process and thickness. Nevertheless, coating materials taylored for stimulation applications are not limited to titanium nitride. Other coatings are being used, among them iridium and platinum. Eventhough other processes than PVD can be used, it is possible to deposit these films using magnetron sputtering techniques as well. Above perceptions regarding morphology dependence on process and thickness are valid for those coatings as well, eventhough they exhibit morphologies entirely different from titanium nitride (fig. 9). As table 2 indicates there is no significant difference in capacitance for the different materials at similar film thickness.

Table 2: A comparison of electrode coatings regarding capacitance

Material	Thickness [µm]	Specific capacitance at f=10mHz [mF/cm²]
Titanium nitride	3,3	25
Iridium	3,7	24
Platinum	2,9	27

Summary

Coatings can be applied on stimulation electrodes with taylored properties for cardiac and neurological stimulation. An extremely flexible deposition method is PVD, especially magnetron sputtering. The thin-flim morphology is typically adjusted by process parameters like pressure and temperature. Tuning the impedance of the electrode tissue interface arises from adjusting coating thickness. Nevertheless, due to restricted charging speeds the increase in capacitance takes place only below an upper frequency limit, that drops with increasing thickness.

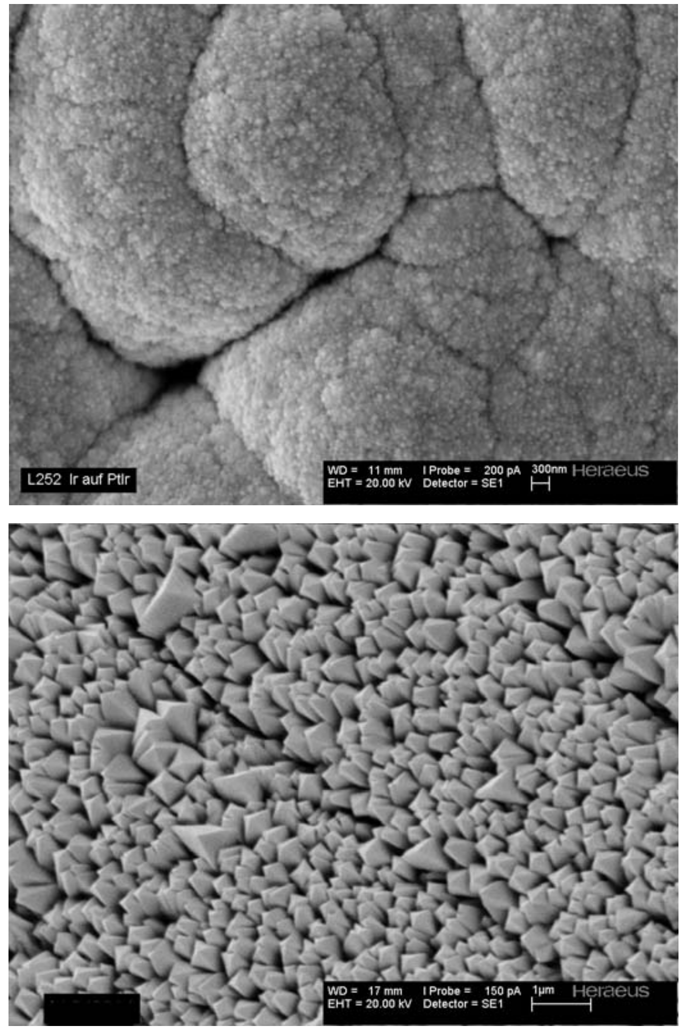

Figure 9: Morphology of dc magnetron sputtered iridium (top) and platinum film (bottom).

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