Metallic and Ceramic Coatings for Medical Devices Deposited by Vacuum Based Methods

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Meet&Match Surface Technologies for Medical Devices

10. July 2014
Karlsruhe

LiMedIon

Content

Vacuum Based Deposition
PVD, IBAD, MS, CVD, PE-CVD

CrNx-coatings by IBAD
Influence of Ion Beam Parameters on coating properties

TiO_2-coatings by Magnetron Sputtering
Influence of pulse mode on morphology and cristallinity

Zn-based bioabsorbable alloys
Oxide layer densification by annealing in oxygen plasma

Si_3N_4-coatings by PE-CVD
Influence of frequency on internal stress

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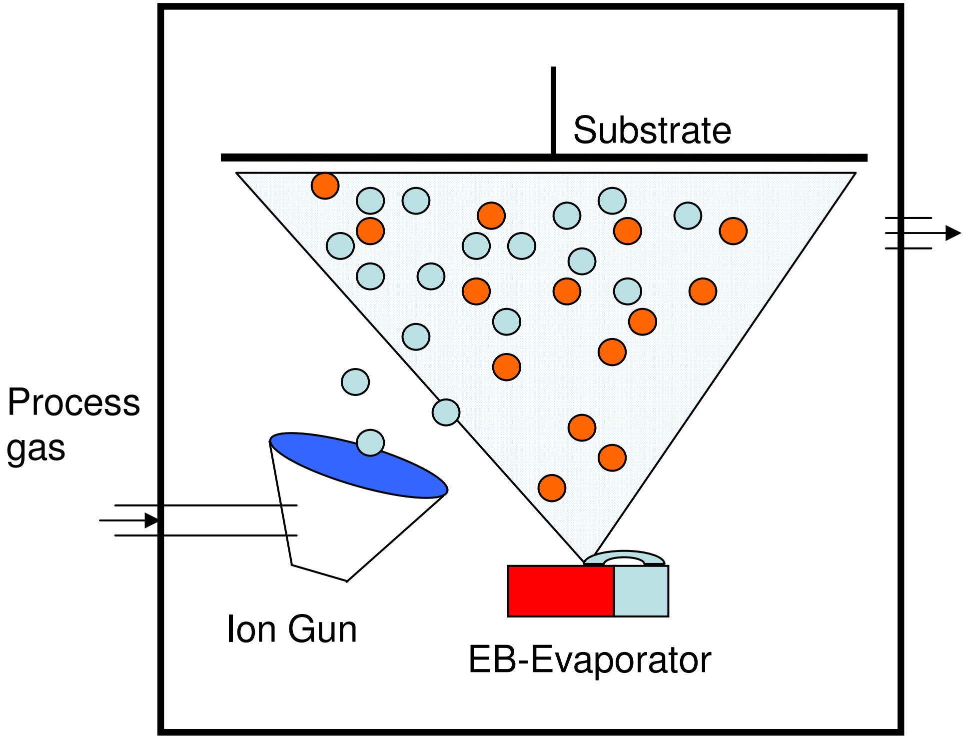
Physical Vapor Deposition (PVD)
Thermal Evaporation
Ion Beam Assisted Deposition (IBAD)



Evaporation

Electron Beam or electrical resistance heating

Ion Beams

Sputter cleaning, Reactive process

Coating densification

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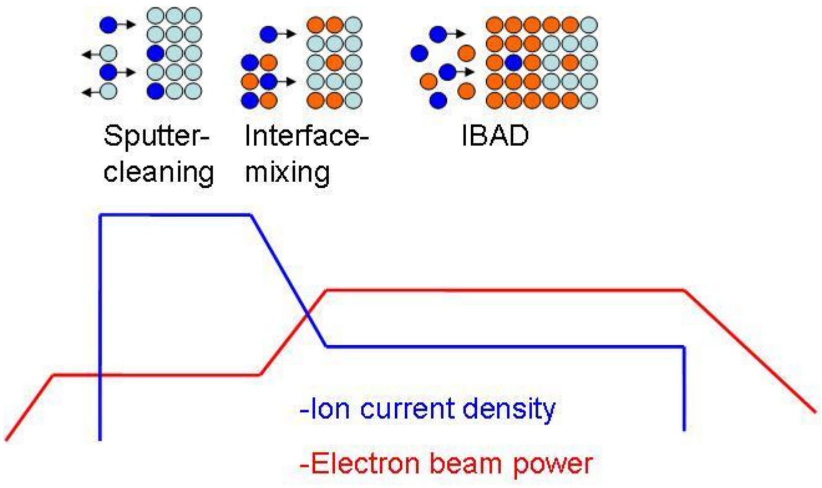
Ion Beam Assisted Deposition (IBAD)

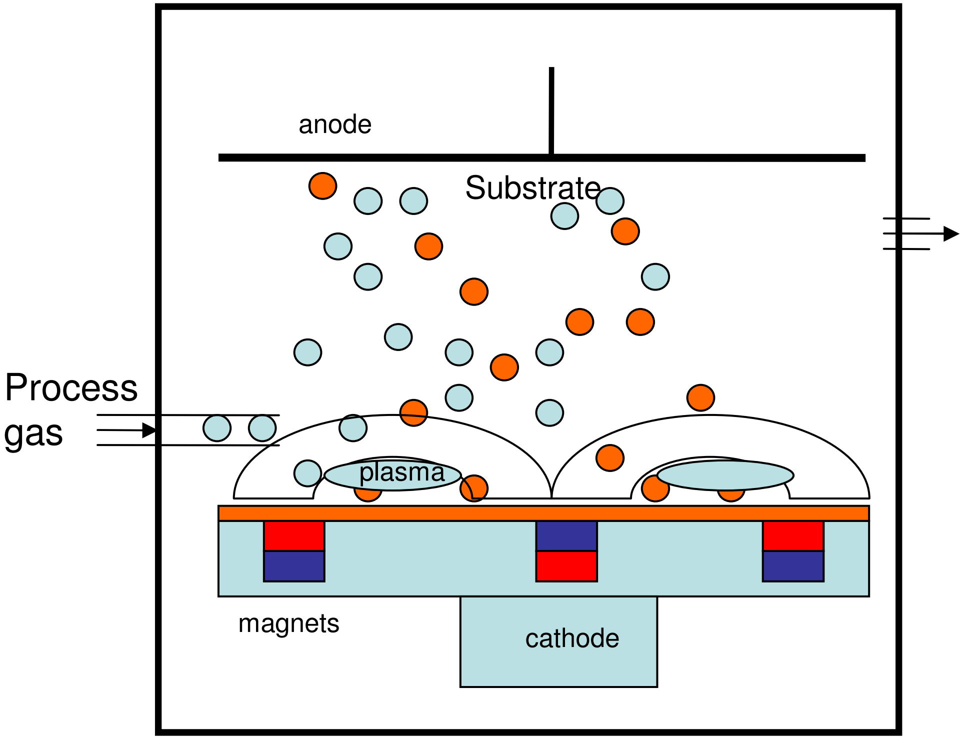


Evaporated material	metals, composites
Ion Beam	inert or reactive
Ion to atom ratio (I/A)	0,001 bis 1
Deposition rate	0,01 to 100 nm/sec
Ion energies	from 50 eV to several keV
Ion incidence angle	0°-90°
Substrate temperature	50°C-1000°C
Coating thickness	few nm to several µm
Pressure	10^{-4}-10^{-6} mbar

Parameter variation influences

Coating composition, Cristallinity/Texture, Morphology, Porosity, Internal stress, hardness, Adhesion, Corrosion resistance, Wear resistance, Friction

PVD
Magnetron Sputtering



DC-Sputtering

Voltage applied between anode (substrate) and cathode (target)

RF-Sputtering

Plasma through high frequency input (13,56/27,12MHz)

Pulsed DC-MS: Unipolar/bipolar

High-power Impulse Magnetron Sputtering (HIPIMS)

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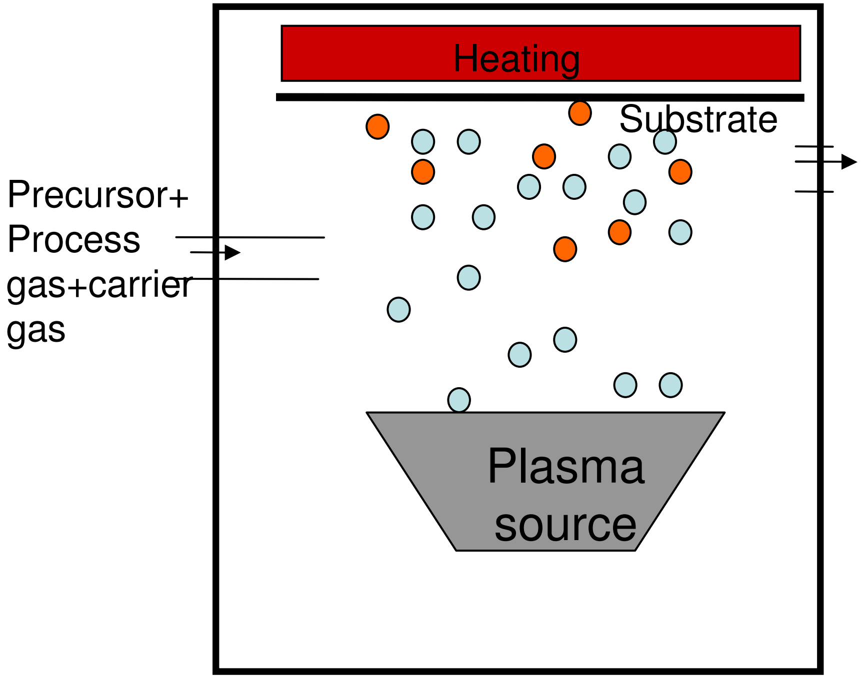
Chemical Vapor Deposition (CVD)



CVD hot substrate (500-1000℃) is exposed to one ore more volatile precursors

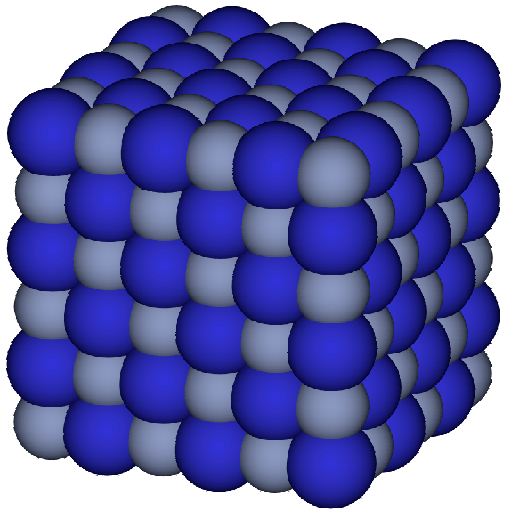
PE-CVD plasma enhancement allows lower substrate temperatures (200-500℃)

Coating	Precursor
Si3N4	SiH_4 + N_2
SiC	Trimethyl silane
SiO2	SiH4 + O2/TMSO + O_2
TiO2	Titanium 2-propoxide
DLC	CH4 /C2H2/H2

Ion Beam Assisted Deposition (IBAD)

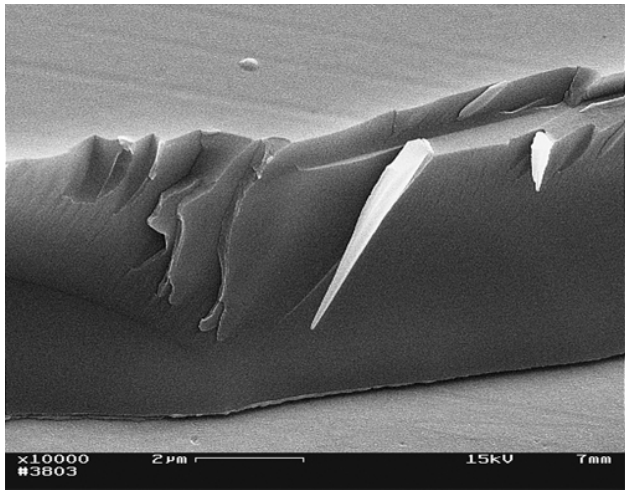
CrN-coatings

- High Hardness
- Improved wear resistance, low friction
- Creates a chemically inert barrier
- Improves corrosion resistance
- Higher temperature resistance than TiN
- Uniform,metallic silver appearance over repeated autoclaving cycles



Applications:

Surgical tools like scissors, saws, drills



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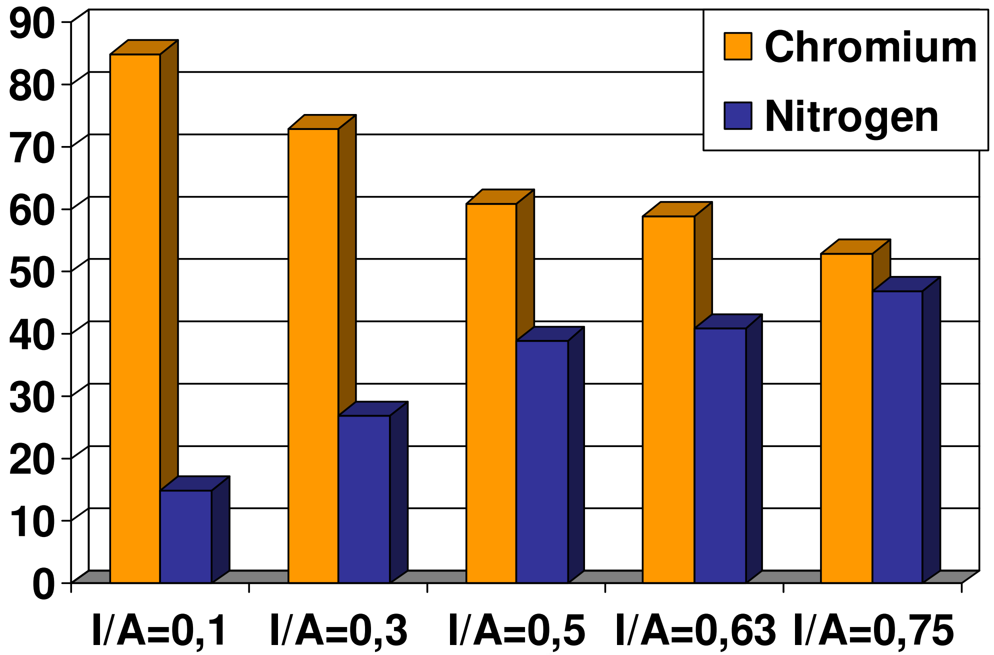
Ion Beam Assisted Deposition (IBAD)

CrNx-coatings,
Influence of I/A to composition

$$\frac{I}{A} = \frac{j}{R} \cdot \frac{M_m}{Ne\rho}$$

j: ion current, R: deposition rate, M_m:molecular mass,

N: Avogadro constant, e: elementary charge, ρ: density



Ion energy: 500eV

Ion incident angle: 20°

No substrate heating

→**gradient layers**

Substrate – Cr- CrN

In case of very different thermal expansion coefficients of substrate and CrN

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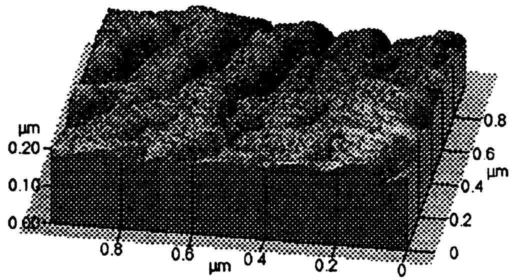
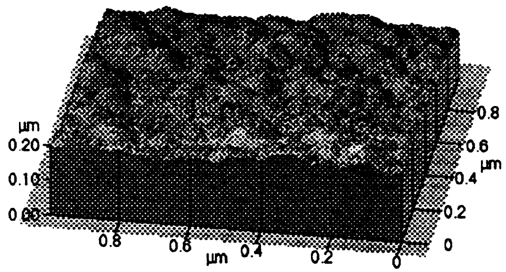
Ion Beam Assisted Deposition (IBAD)

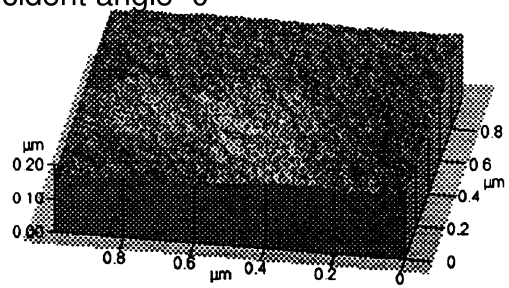
CrNx-coatings,
Influence of ion incidence angle on surface morphology



Ion incident angle 0°



Ion incident angle 30°



Ion incident angle 60°

Ion energy:	500eV
Ion current density:	120µA/cm2
I/A:	0,5
No substrate heating	

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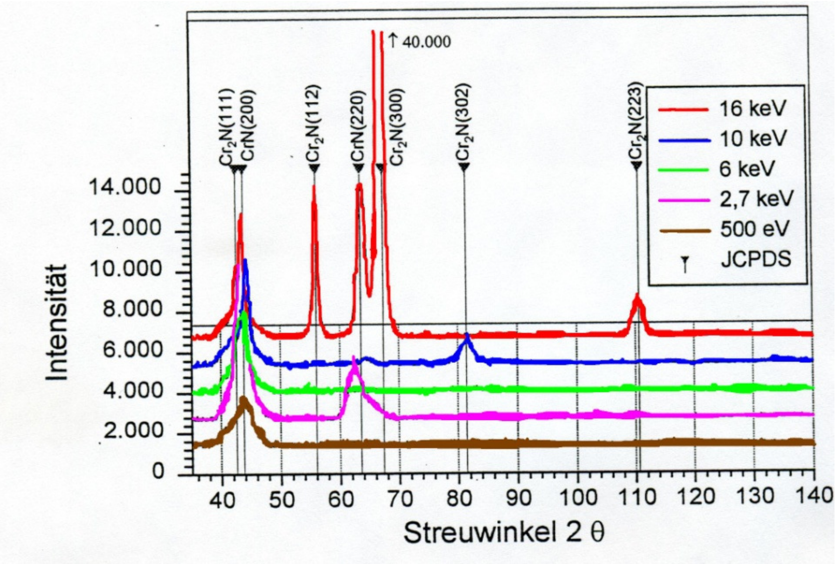
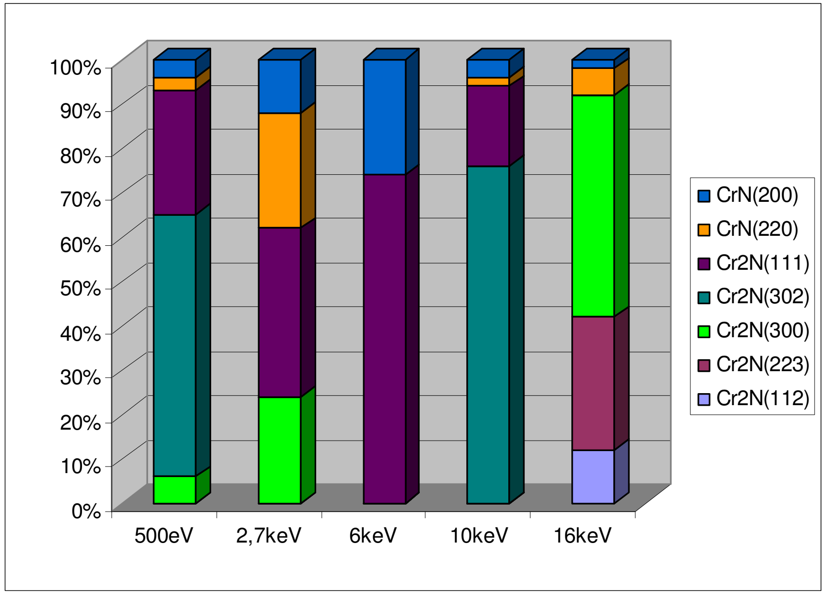
Ion Beam Assisted Deposition (IBAD)

CrNx-coatings,
Influence of ion energy on composition and cristallinity





Ion incidence angle:	0°
I/A:	0,5
No substrate heating	

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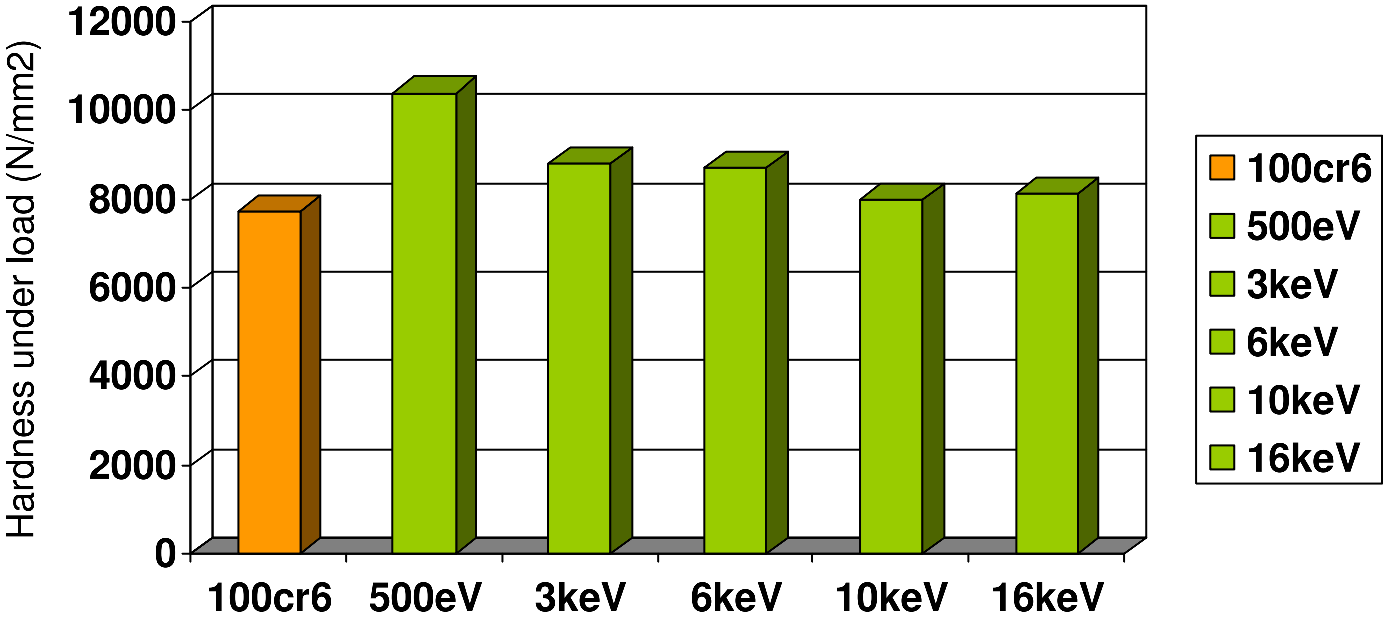
Ionenstrahlunterstützte Abscheidung (IBAD)

CrNx-coatings,
Influence of ion energy to micro hardness



Ion incidence angle :	0°
I/A:	0,5
Coating thickness:	1,4µm
No substrate heating	

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PVD-Magnetron Sputtering

Photocatalytic TiO_2-coatings

Hospital Acquired Infections (HAI)

•are still widespread (estimated annually 400T-900T in Germany)
•cause a high morbidity (10T-30T annually in Germany*) and
•high costs (annually 10 Billion US$ in the USA)
•About half of the nosocomial infections are device related infections (DRI) associated with indwelling devices like short term implants and prosthetic implants

Antimicrobial surfaces help to reduce DRI

Photocatalytic TiO2-surfaces are antimicrobial, biocompatible, easy to realize and cheap.

*P. Gastmeier, Nosokomiale Infektionen in Deutschland and

Deutsche Ges. f. Krankenhaushygiene, Bis zu 30.000 Tote jährlich durch Krankenhausinfektionen

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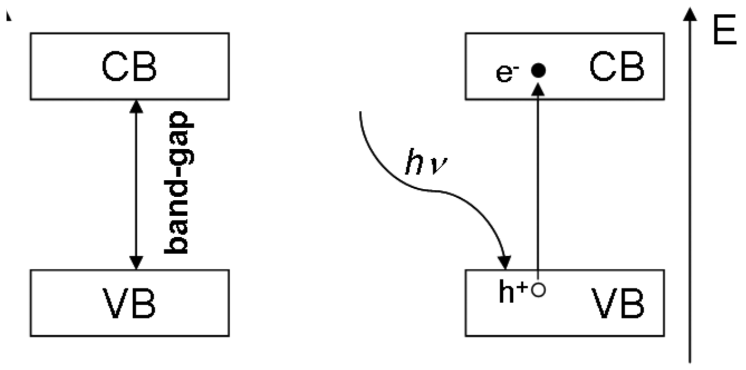
PVD-Magnetron Sputtering

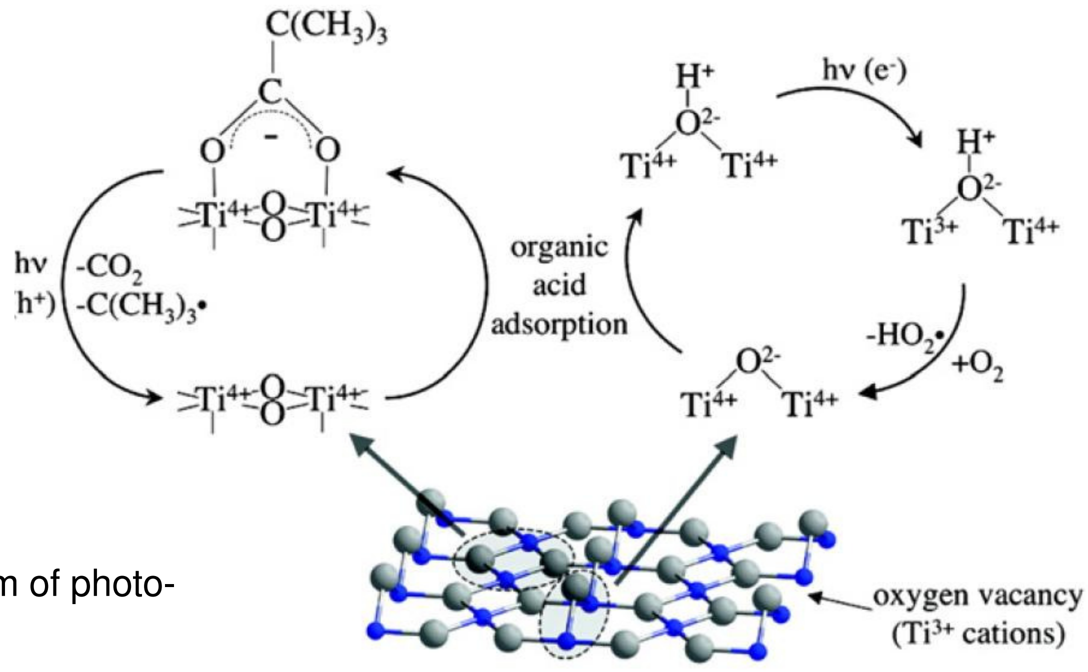
Photocatalytic TiO_2-coatings



(a) (b)

Band energetic structure **(a)** and mechanism of photo-irradiation **(b)** of a TiO2 surface..

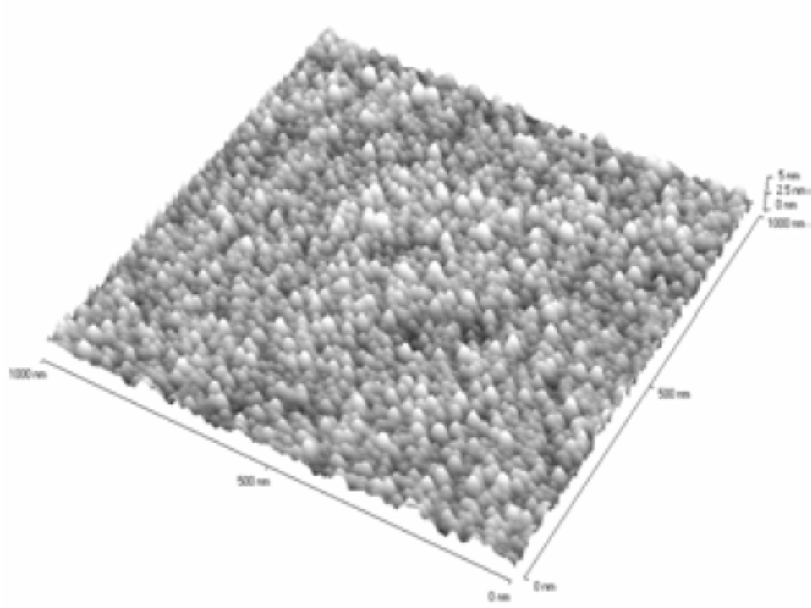
Livia Visai et al



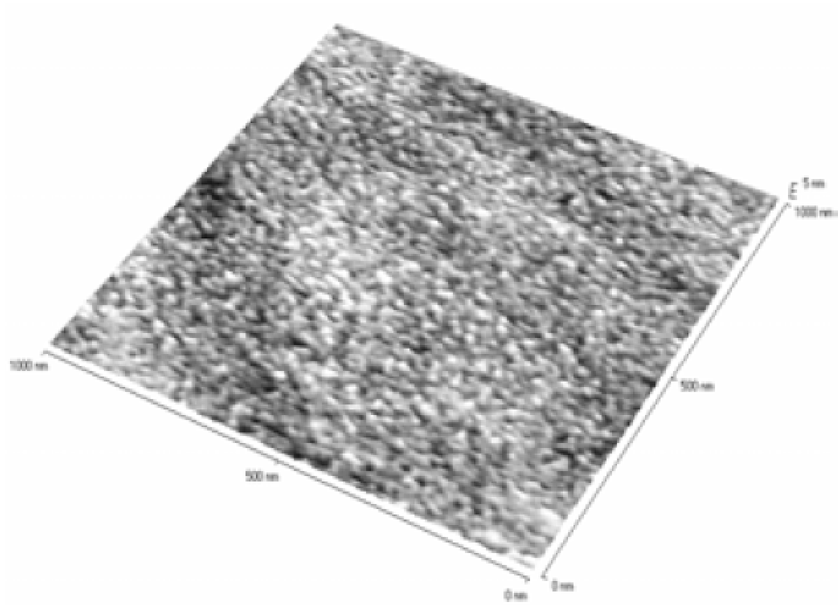
Reaction scheme for both redox processes associated with photodecomposition of trimethyl acetic acid (TMAA) on a TiO2-surface

PVD-Magnetron Sputtering

Photocatalytic TiO_2-coatings



Unipolar mode, 10 kW
Ra=0,48 nm



Bipolar mode, 10 kW
Ra=0,20 nm

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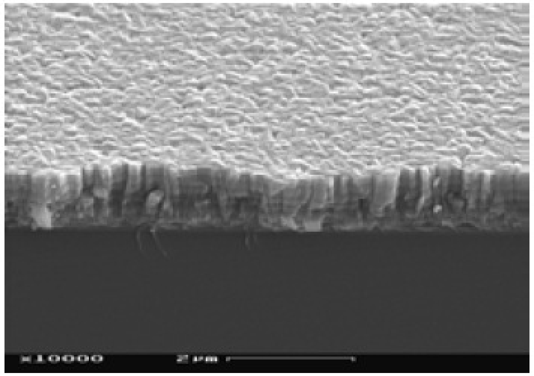
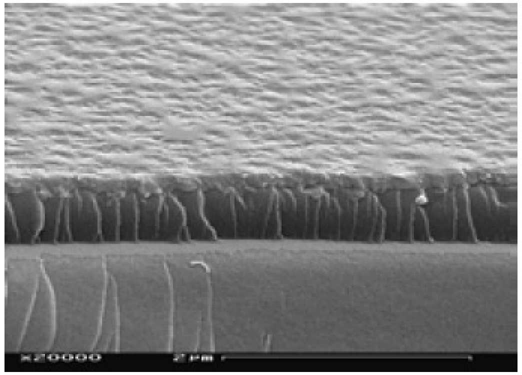
PVD-Magnetron Sputtering

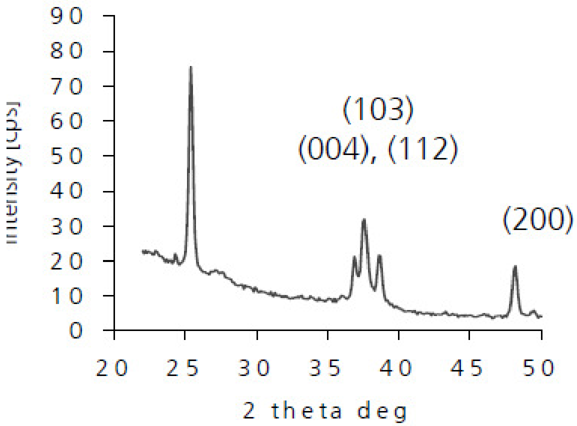
Photocatalytic TiO_2-coatings
Influence of sputtering mode on cristallinity

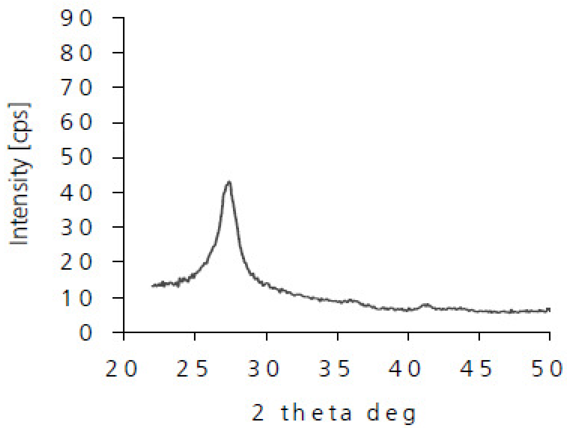


FEP

Dresden







Unipolar mode, 10 kW

Bipolar mode, 10 kW

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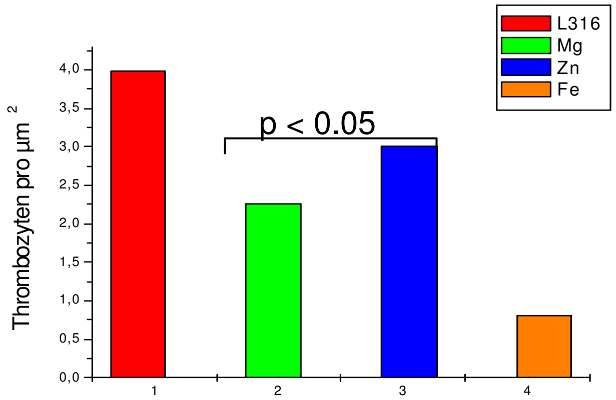
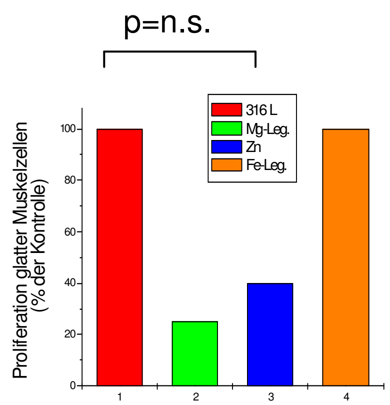
Plasma Modifications

Photocatalytic ZnO-coatings on bioabsorbable zink alloys





Oxide layer treatment of the native oxide layer using O_2-plasmas+annealing

→Prolongued bioabsorption times through densification of the protective oxide layer

→Cristallinization resulting in enhanced photocatalytic activity

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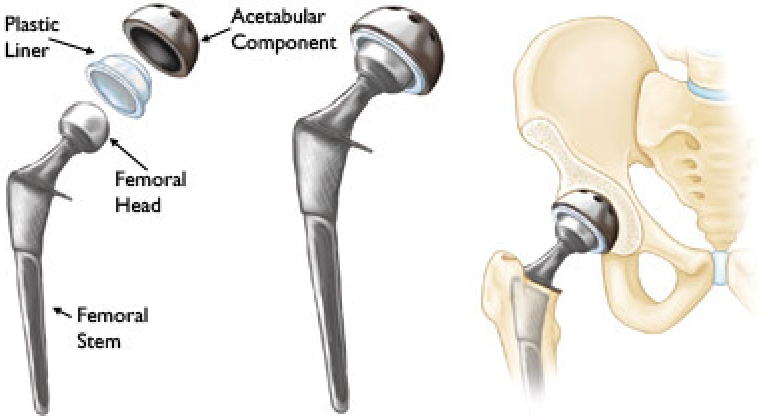
Plasma Enhanced Chemical Vapor Deposition

Si_3N_4-coatings

Si_3N_4 spinal implant for interbody fusion
Potential material for femoral head in total hip joint replacements

excellent biocompatibility,
low wear rates
relatively high fracture toughness and strength



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Plasma Enhanced Chemical Vapor Deposition

Si_3N_4 Silane and Ammonia/N_2

Advantages:

- Coating deposition starting at 250°C
- High quality, pinhole-free coatings can be achieved
- High deposition rates (500nm/min)

Disadvantages:

- H_2 can be integrated into the coatings→ less dense coatings
- incorporated H_2 can diffuse to the interface and deteriorate the substrate

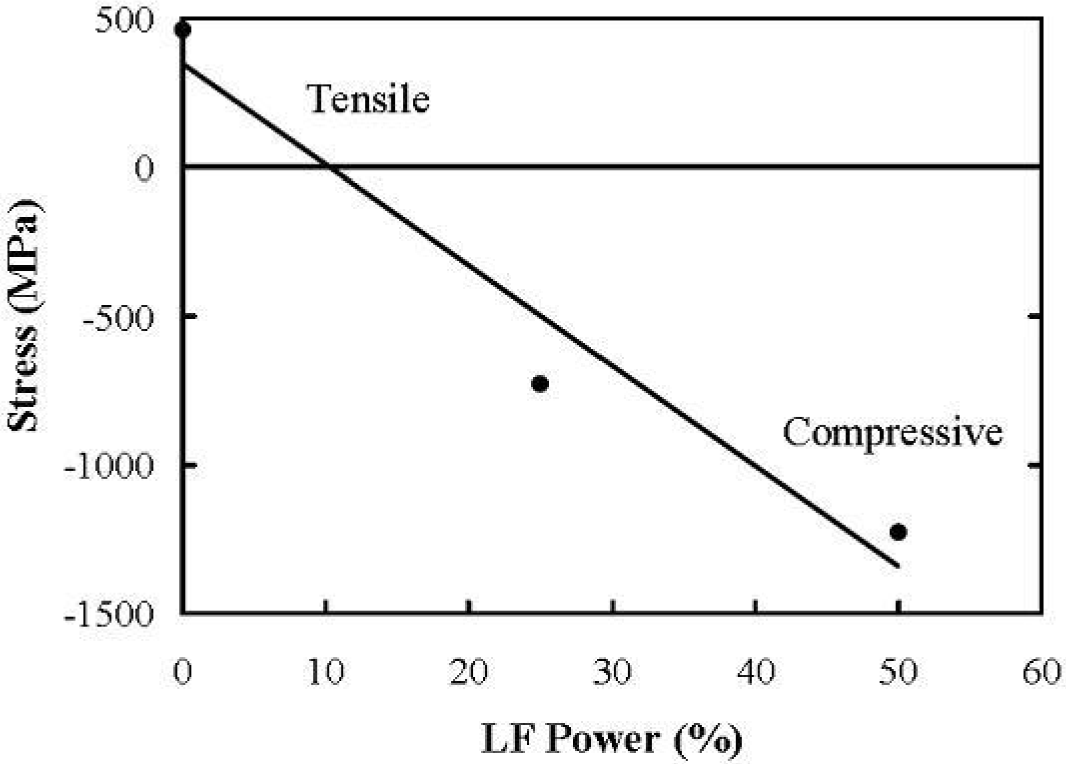
Plasma Enhanced Chemical Vapor Deposition

Parameter variation

•Gas flows, gas supply geometry
•Plasma parameters like power, plasma gas
•Pressure
•Substrate temperature

e.g:
•Plasma power and temperature increase, pressure reduction (Huang et al)
→Increase of hardness + E-Modulus
Or:
•Dual frequency PE-CVD: Overlap of two microwave frequencies (13,6 MHz and 340kHz)
→Control of the intrinsic stress

Plasma Enhanced Chemical Vapor Deposition



Si_3N_4: Influence of an additional frequency to intrinsic stress (Mackenzie et al)

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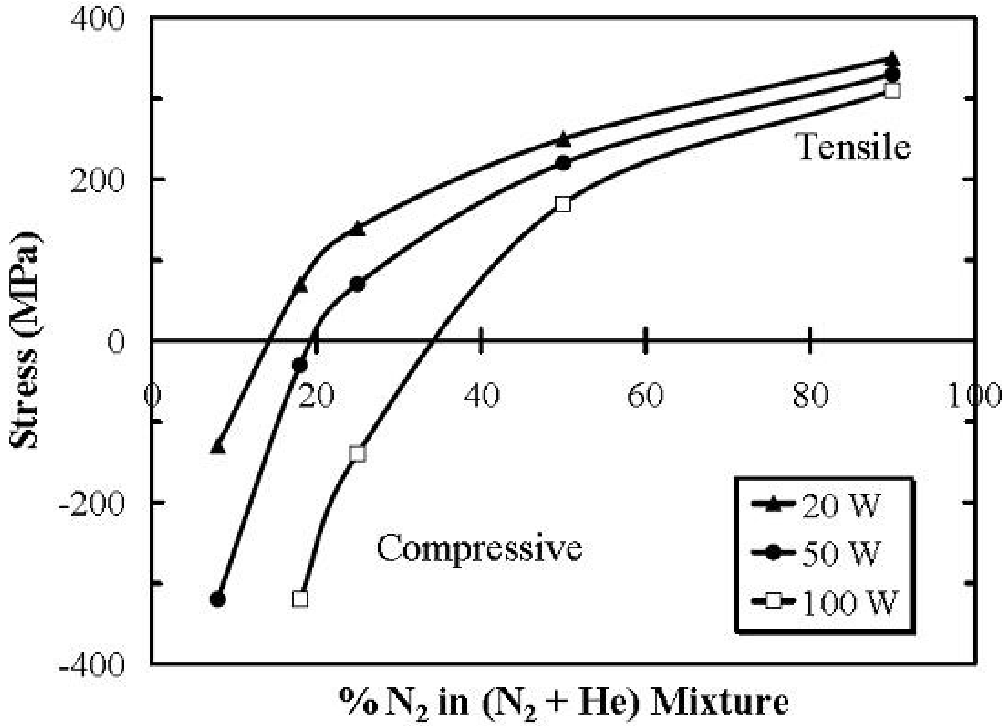
Plasma Enhanced Chemical Vapor Deposition



Si_3N_4: Influence of plasma power and helium addition on intrinsic stress

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Thank you

Danke

Merci