



Sektion Medizinische Werkstoffkunde und Tech- nologie

Die Sektion „Medizinische
Werkstoffkunde und Technologie“
(MWT) fokussiert auf
medizintechnische, Biomaterial-
orientierte Forschung und
Entwicklung (F&E).



Sektion Medizinische Werkstoffkunde &
Technologie
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Sektionsleitung (komm.)



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AG Rupp:

„Biomaterialien und Implantate am biologischen
Interface“

AG Krajewski:

„Biokompatibilität und
Oberflächenfunktionalisierung“

AG Spintzyk:

„Dentaltechnologie“



Biomaterial Surface and Interface Phenomena:

1. Wettability, roughness induced wetting, surface energy (Frank Rupp)
2. Biological responses at the implant interface (Antonia Link)





Biomaterial/Interface Phenomena:

Wettability, roughness induced wetting, surface energy

Prof. Frank Rupp



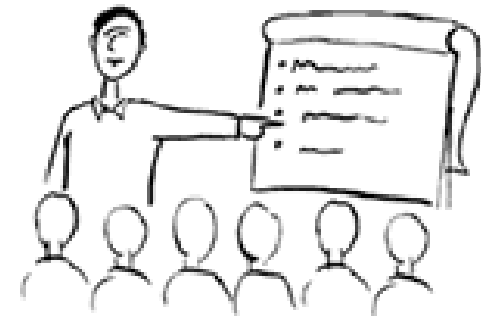
Sektion
Medizinische Werkstoffkunde
und Technologie



Biomaterial / Interface phenomena

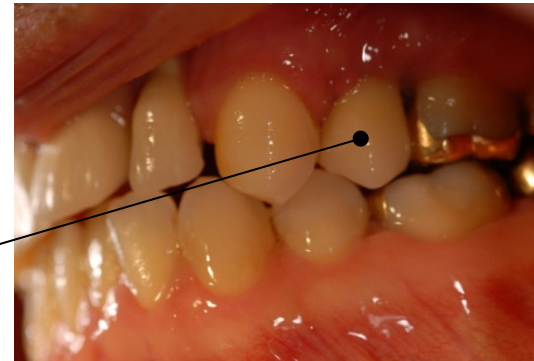
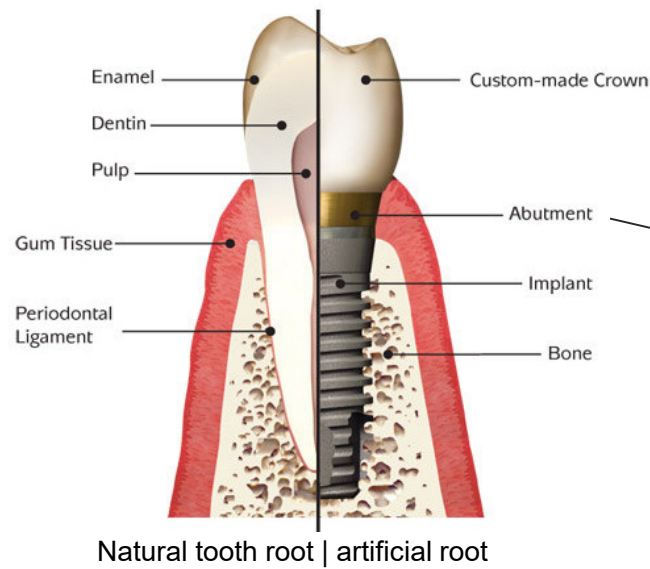
We will talk about...

- dental implants
- role of roughness for osseointegration
- hydrophobicity – a possible drawback of certain implant types
- methods for gaining hydrophilic surfaces
- roughness induced wetting
- surface free energy
- clinical impact of hydrophilic implants



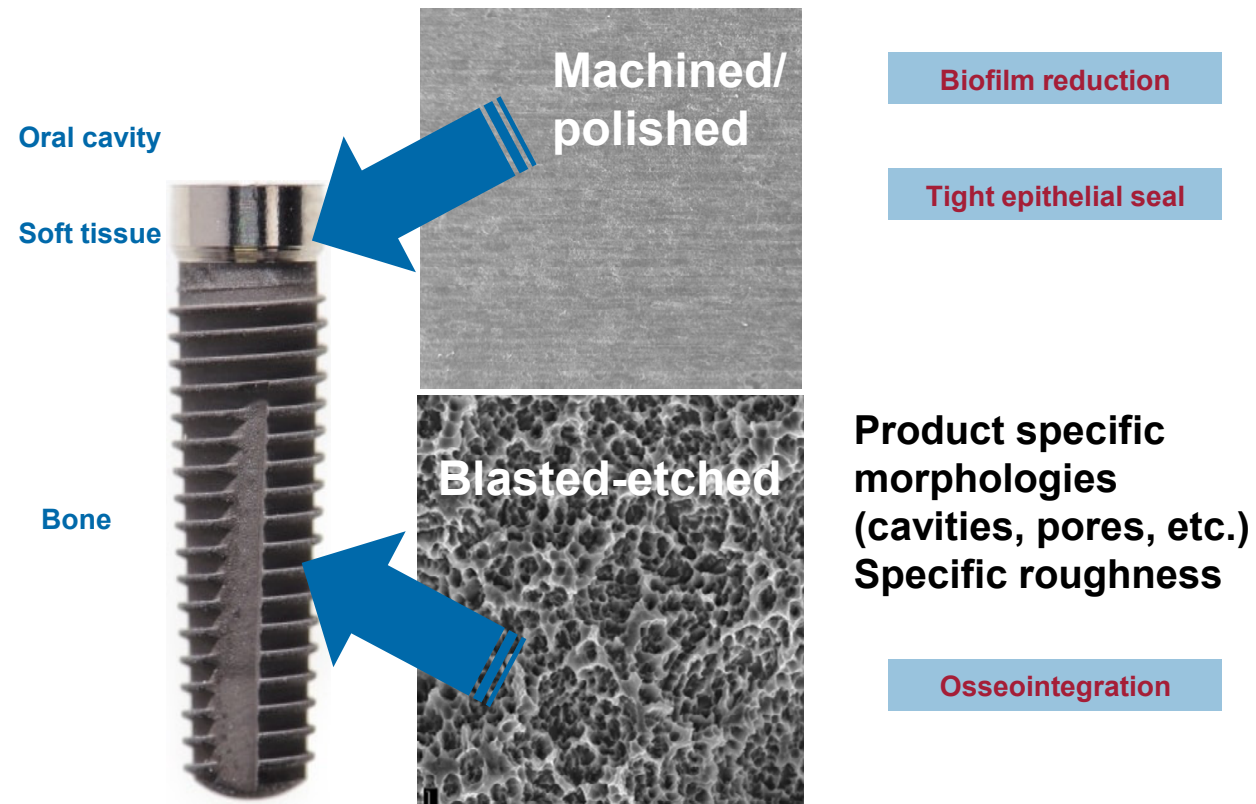


Dental implant: An artificial tooth root



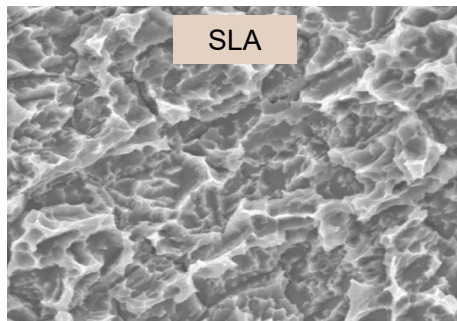
© The dental centre london

Dental implant: A hybrid implant



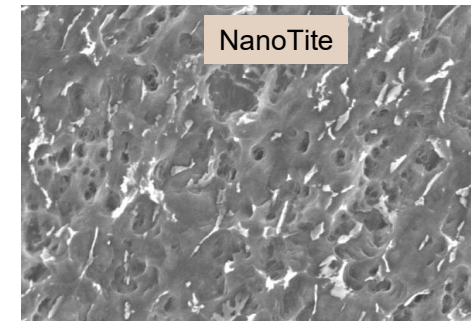


Topography of implant surfaces: Roughness by additive and subtractive methods



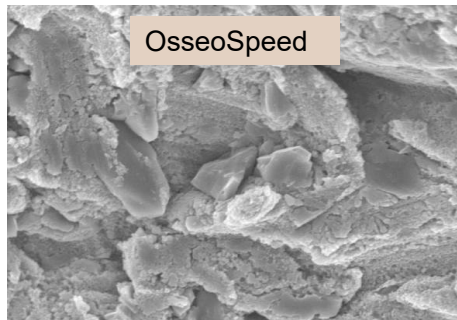
SLA

Blasting / acid etching



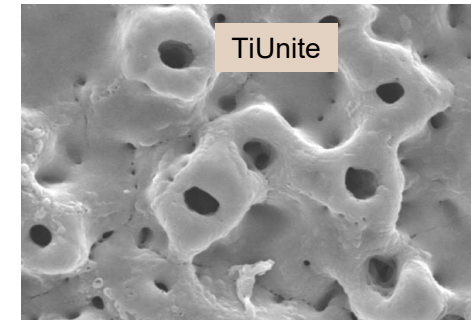
NanoTite

Acid etching /
Ca-P deposition



OsseoSpeed

Blasting/ Fluoridization



TiUnite

Anodic oxidation



Clinical relevance: Roughness influences the biological response

...The biological benefit is best for S_a roughness between 1 and 1.5 μm ...

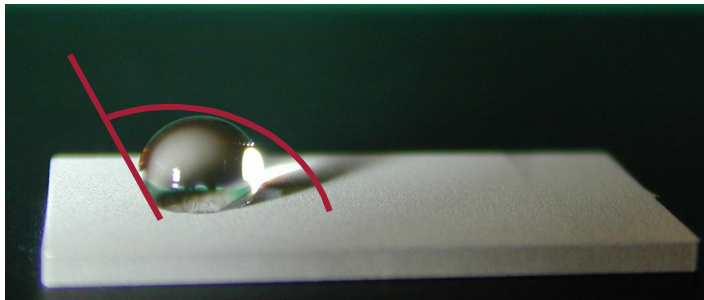
Ellingsen JE. Surface configurations of dental implants.
Periodontology 2000 **1998**;17: 36-46.

...Moderately rough surfaces (S_a 1-2 μm) showed stronger bone responses than smoother or rougher surfaces...

Wennerberg A , Albrektsson T. Effects of titanium surface topography on bone integration: a systematic review.
Clin Oral Impl Res 20, 172-184, **2009**



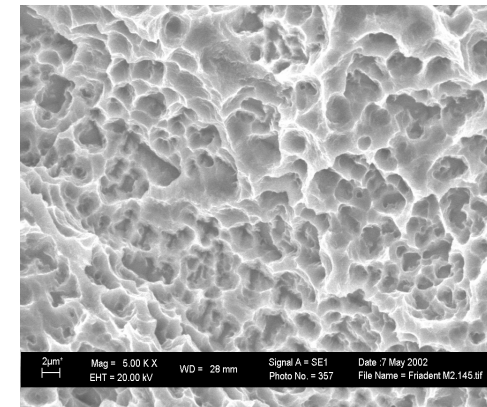
Phenomenon of hydrophobic microstructured surfaces



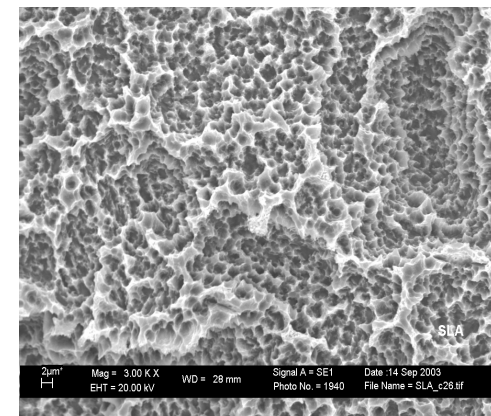
Water contact angles $\sim 140^\circ$

Rupp F et al. *Biomaterials* 25, 1429-1438, 2004

Friadent plus



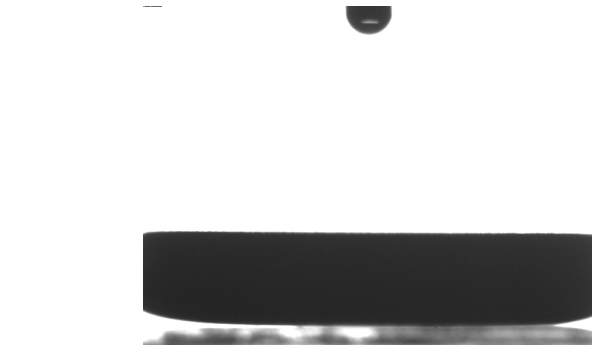
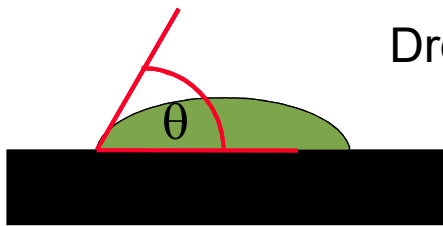
Straumann
SLA



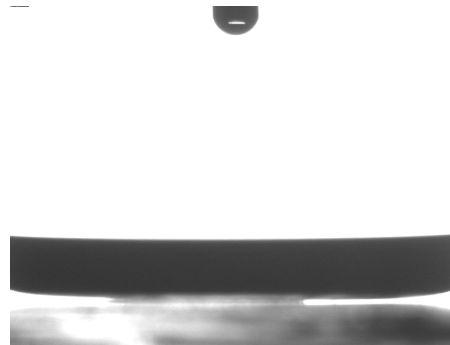


Contact angle analysis

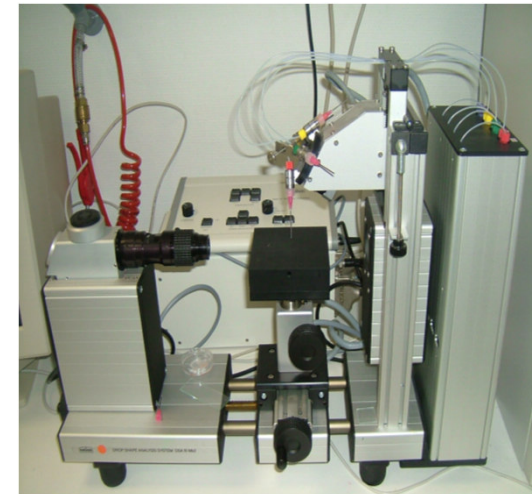
Drop shape analysis (sessile drop technique)



Blasted-etched (SLA)

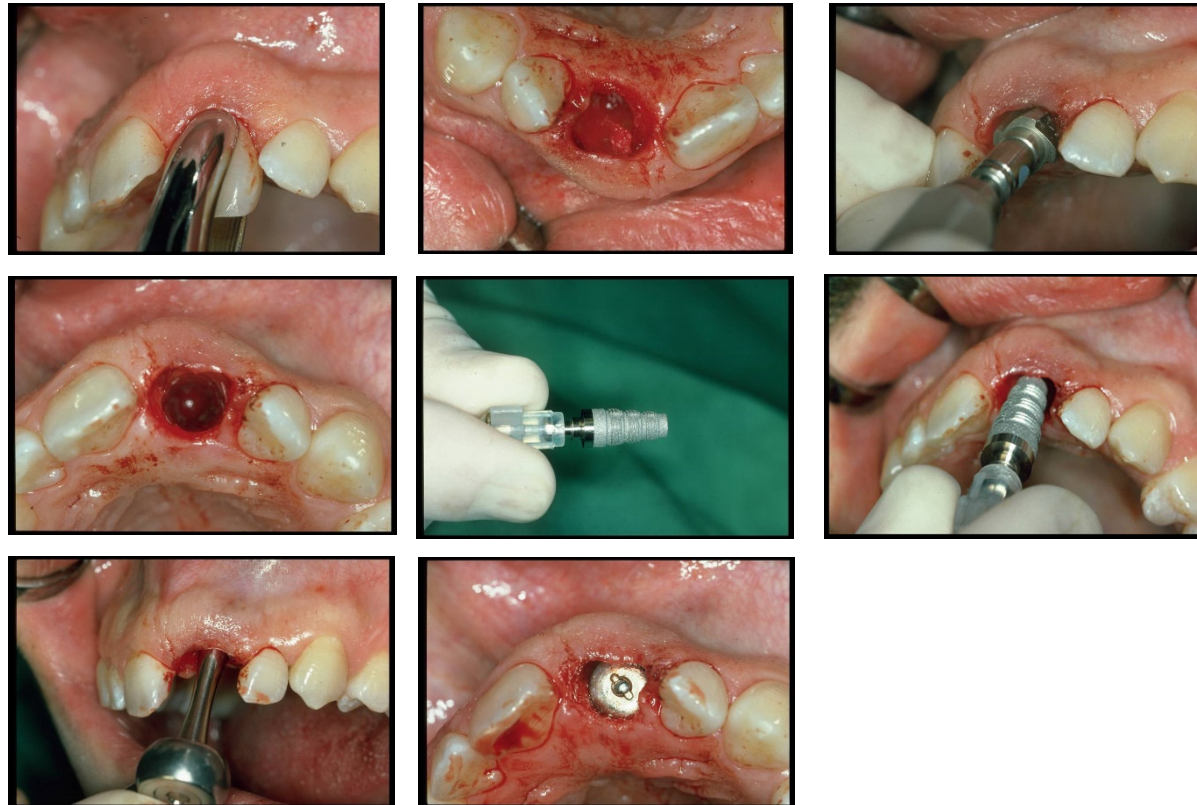


Machined/smooth





Dental implant: Clinical insertion





Implant Surfaces: Impact of wetting

Hydrophilicity, *i.e.*, a high degree of water wettability, is a desirable property to achieve...

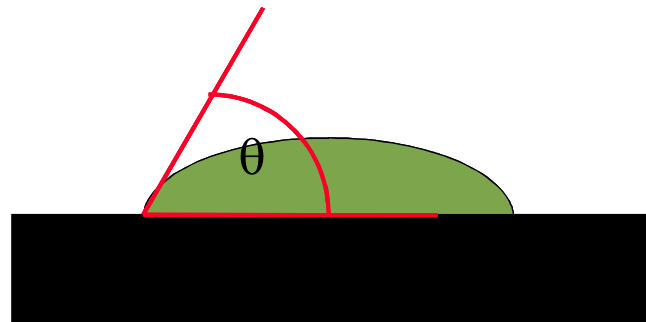
...fast wetting with aqueous bioliquids (blood) directly after implant insertion

...fast conditioning with macromolecules (e.g. proteins)

→→→ accelerated osseointegration



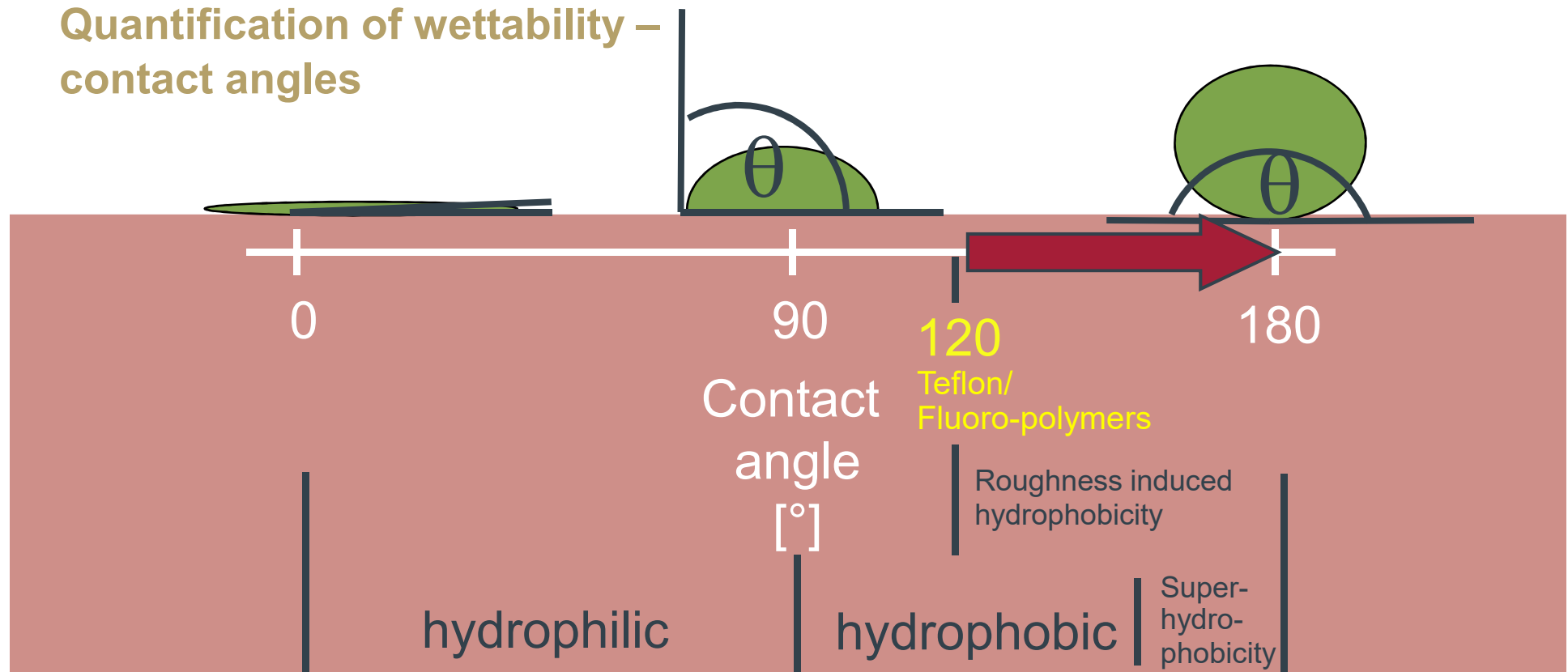
Hydrophilicity



Can be quantified by contact angles



Quantification of wettability – contact angles





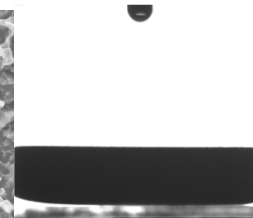
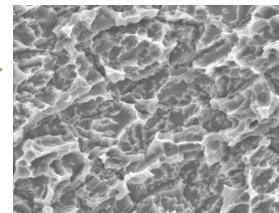
Approaches for getting hydrophilicity: SLActive

Neutralization and final storage
under ambient atmosphere

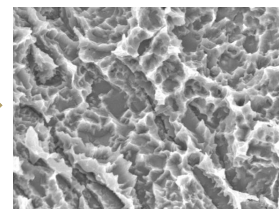
Blasting → Acid
etching

Neutralization and final storage in
saline under protective nitrogene
(N₂) gas conditions

SLA



Hydrophobic



Hydrophilic

SLActive

(Launched 2005)

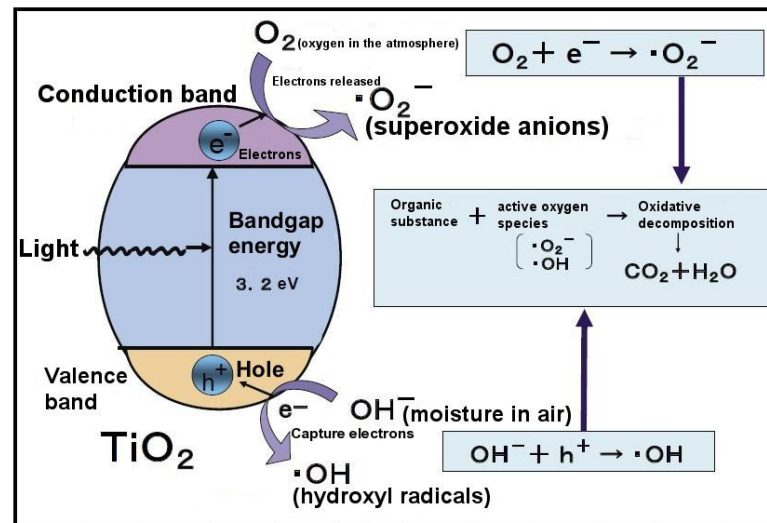
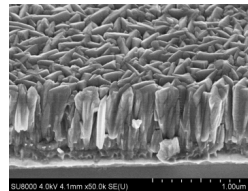


Approaches for getting hydrophilicity: Photofunctionalization

Light induced surface modulation of a biomaterial to promote a desired biological response



Anatase

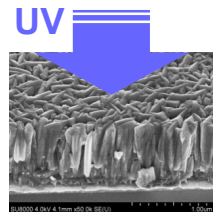


Photocatalysis

Source: http://sangakukan.jp/journal/journal_contents/2010/06/articles/1006-03-2/1006-03-2_earticle.html



Approaches for getting hydrophilicity: Photofunctionalization



Photocatalytic effects

Lab-work!

Radicalic/anionic species
(O_2^- ; $\cdot OH$)

Surface restructuring
(hydroxylation)

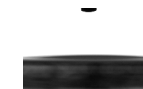


Decomposition of
organic substance

($CO_2 + H_2O$)

Fujishima A, and Honda K.
Nature 1972;238(5358):37–8

Superhydrophilicity



Wang R et al. *Nature*
1997;388(6641):431–2

Hashimoto K, et al. *Jpn J Appl Phys* 2005;44(12):8269–85.

Anatase on dental implants Possible applications

Oral cavity

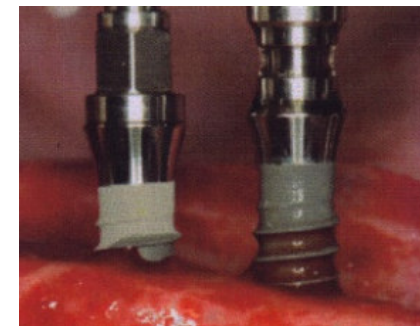
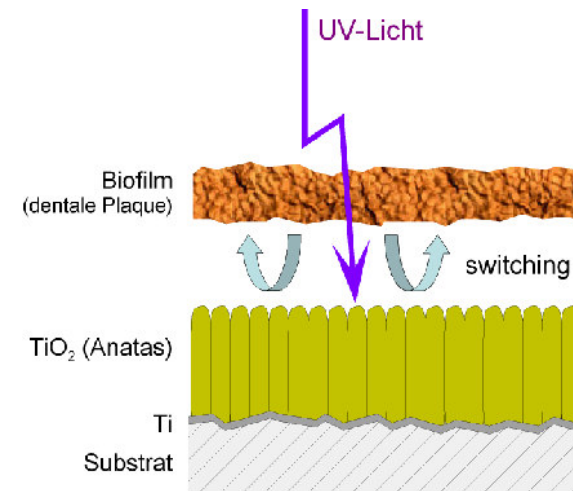
Soft tissue

Bone



Therapeutic photocatalytic
biofilm attack at the
material/biofilm interface

Chair-side
(Super) Hydrophilization



Bornstein MM et al. Clin Oral Impl Res 19;233-241, 2008

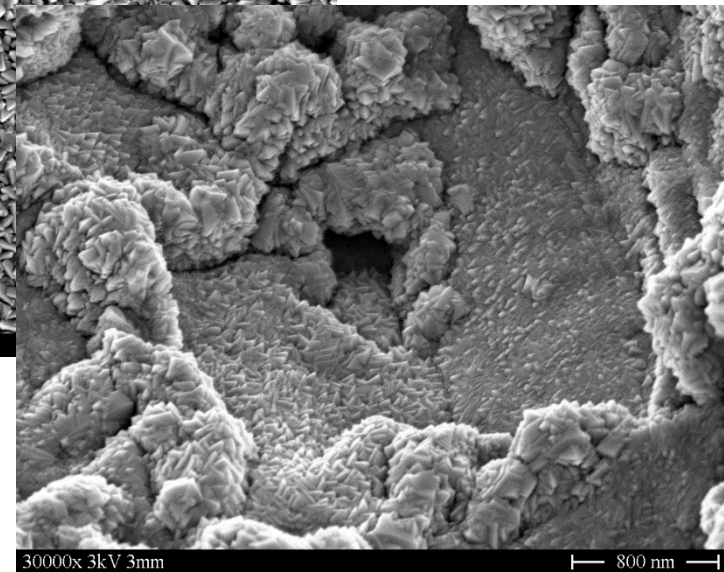
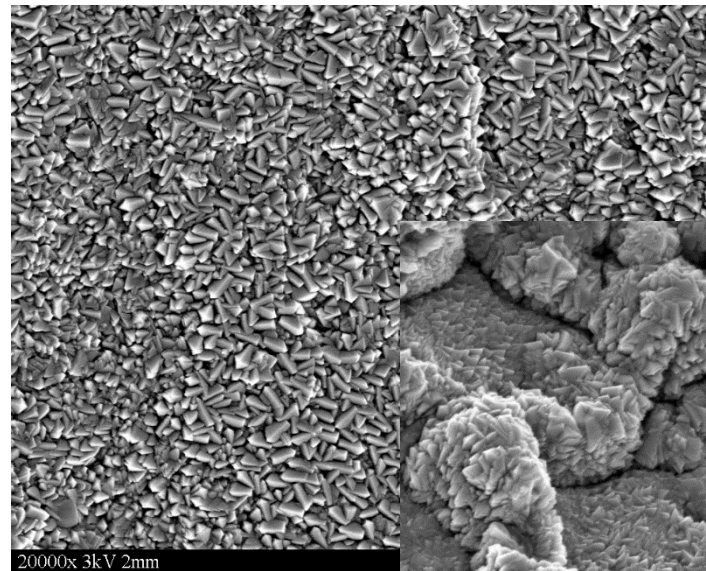
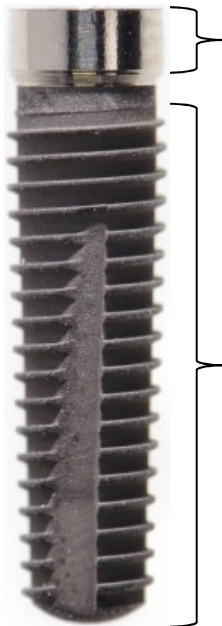


Anatase on dental implants

Possible applications

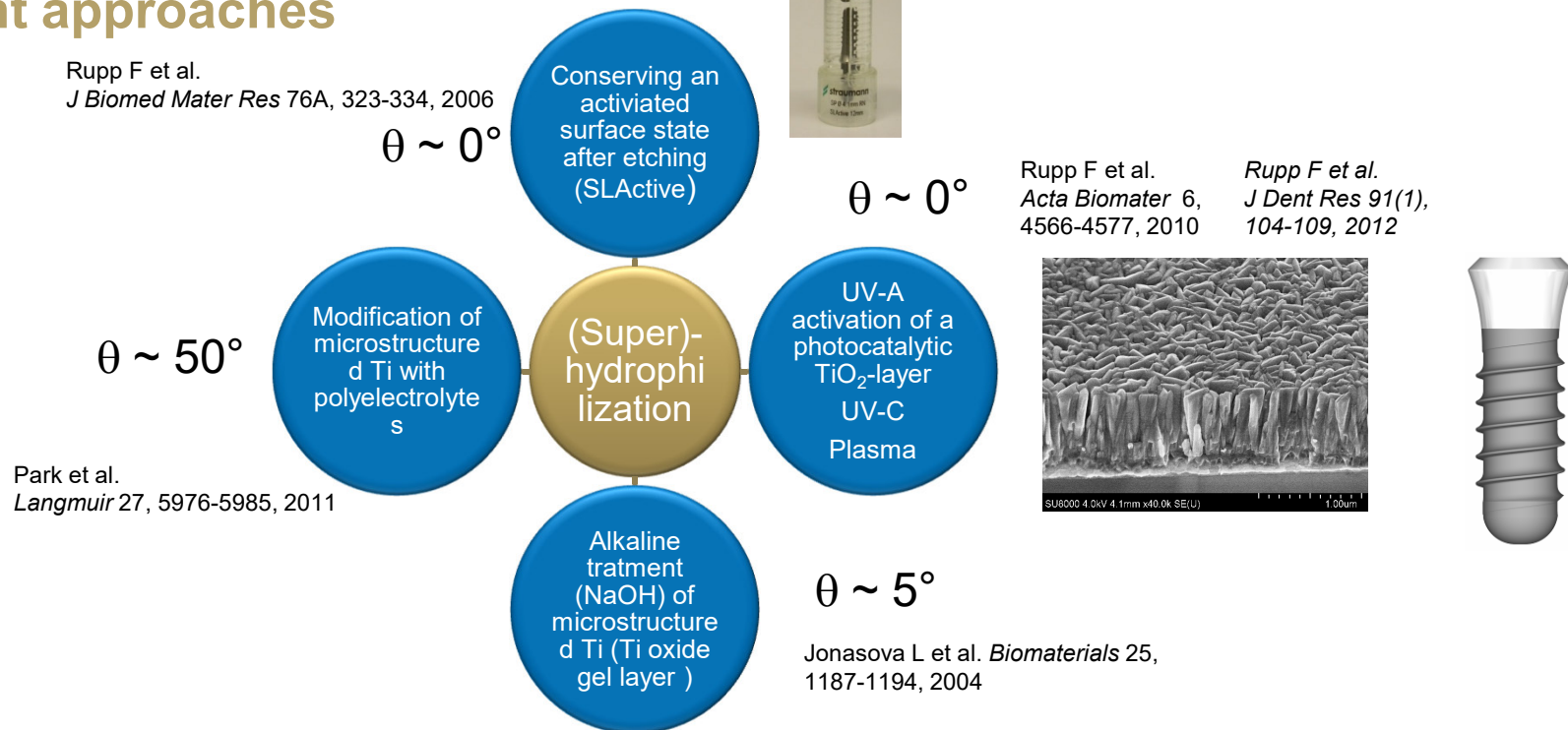
Oral cavity
Soft tissue

Bone





Hydrophilization of Titanium-surfaces: Different approaches





Wettability Study

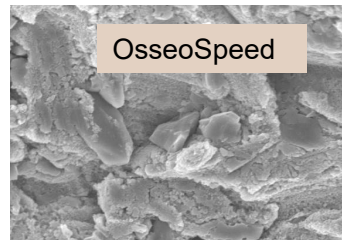
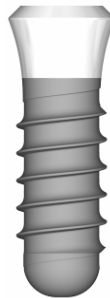
Dynamic CA-Analysis of Dental Implantat Systems

Astra Tech	Camlog	Dentsply Friadent	Heraeus Kulzer	Institut Straumann	Nobel Biocare	Osstem Implant	Biomet 3i
							
OsseoSpeed	Screw Implant	XiVE S plus	IQ:NECT	Standard Plus Implant	MkIII TiU RP	GS II	Certain Implant
OsseoSpeed	Promote	Plus	Ti:Active	SLA SLActive	TiUnite	RBM	NanoTite

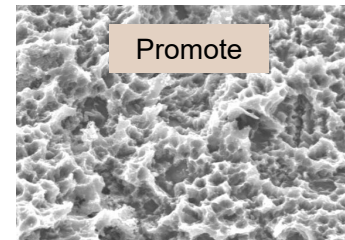
Rupp F et al. *Int J Oral Maxillofac Impl* 26;1256-1266, 2011



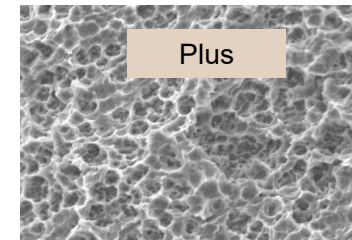
Wettability: Dynamic Analysis



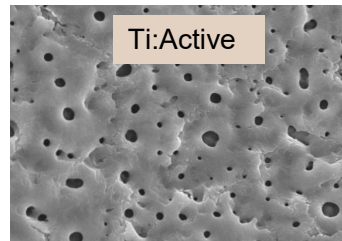
OsseoSpeed



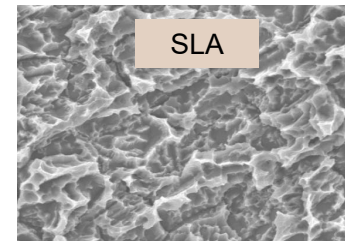
Promote



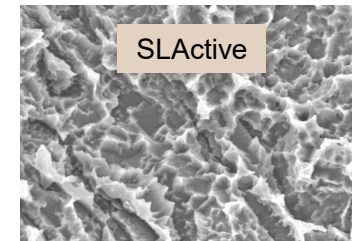
Plus



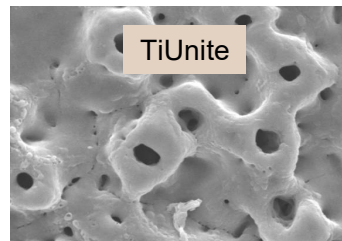
Ti:Active



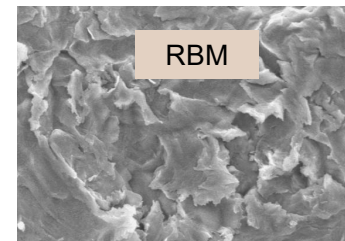
SLA



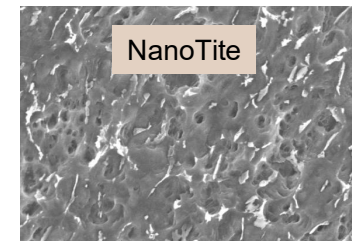
SLActive



TiUnite



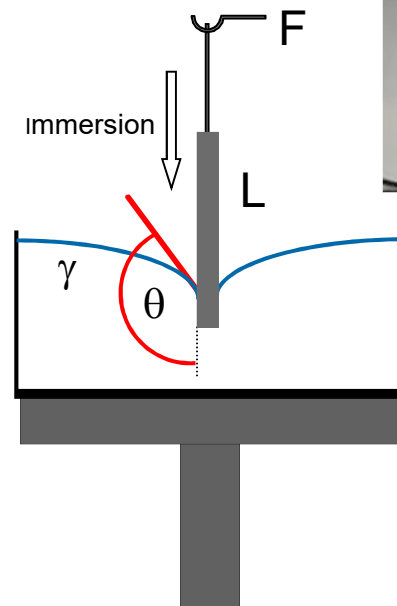
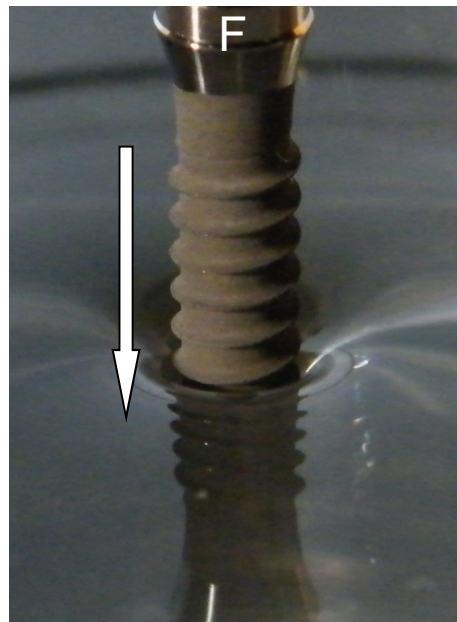
RBM



NanoTite

Wettability: Dynamic Analysis

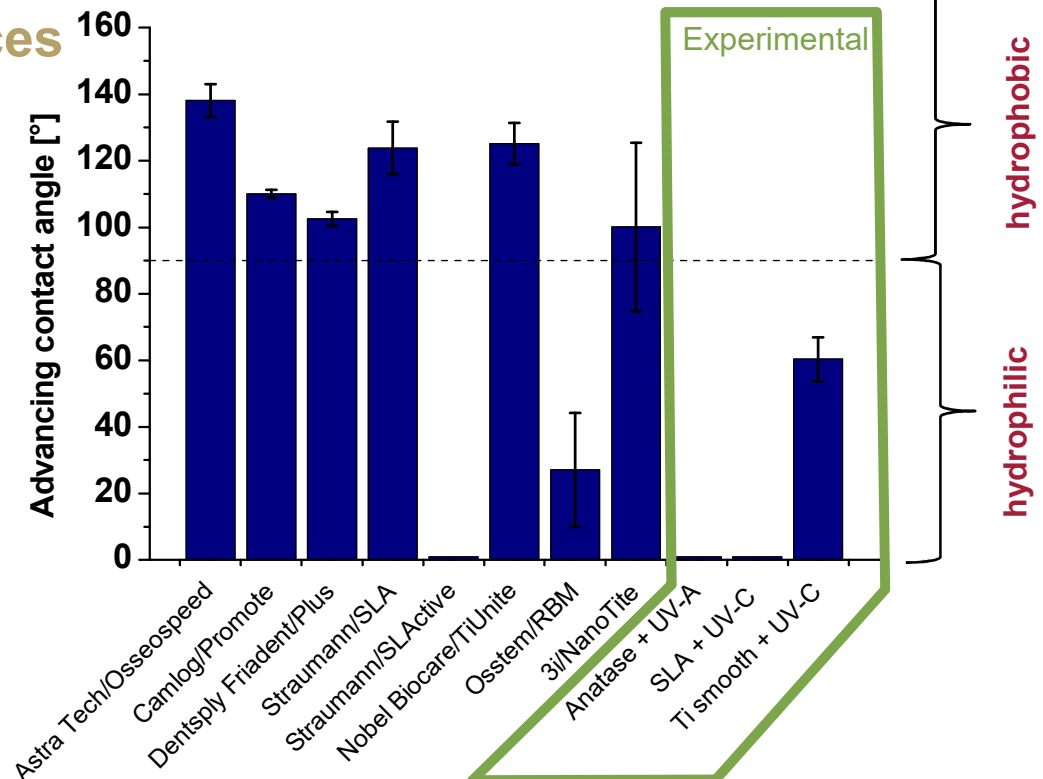
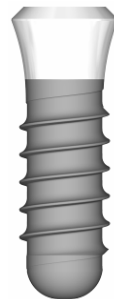
Tensiometry



$$\gamma \cdot \cos\theta = \frac{F}{L}$$



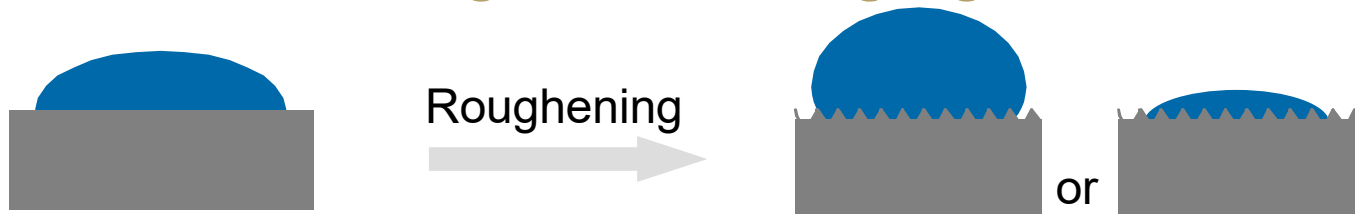
Wettability of marketed and experimental implant surfaces



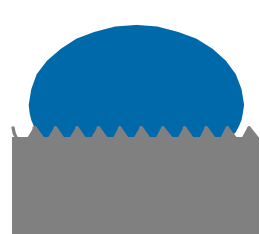
Rupp F et al.
Acta Biomater 6,
4566-4577, 2010

Rupp F et al.
JOMI 26,
1256-1266, 2011

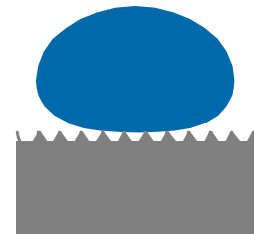
Wetting: Models of roughness-induced wetting Homogeneous and heterogeneous wetting regimes



$\text{contact angle}_{\text{smooth}} \neq \text{contact angle}_{\text{rough}}$



Homogeneous wetting
(*Wenzel 1936*)



Heterogeneous wetting
(*Cassie-Baxter 1944*)



Wetting: Models of roughness-induced wetting Homogeneous and heterogeneous wetting regimes

Homogeneous wetting
(*Wenzel 1936*)



$$\cos\theta^* = r \cos\theta$$

θ^* : Apparent (measured) contact angle

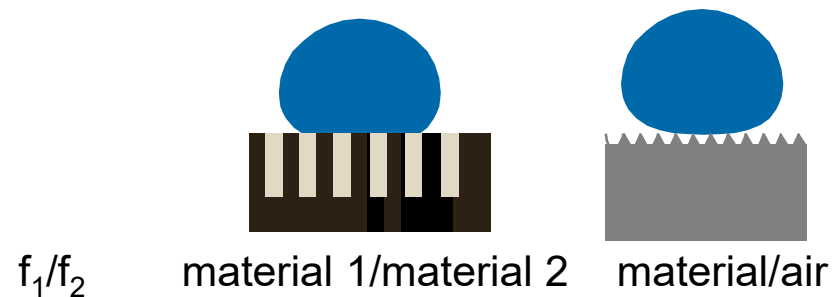
θ : Young contact angle (thermodynamically stable)

r : Roughness factor: real surface area/geometric surface area (r is always > 1)



Wetting: Models of roughness-induced wetting Homogeneous and heterogeneous wetting regimes

Heterogeneous wetting
(*Cassie-Baxter 1944*)



$$\cos\theta^* = f_1\cos\theta_1 + f_2\cos\theta_2$$

θ^* : Apparent (measured) contact angle

θ : Young contact angle (thermodynamically stable)

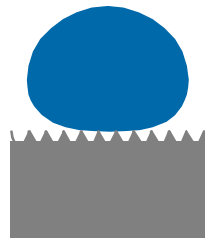
f_1, f_2 : Surface fractions (material, air)

$$\cos\theta^* = f_1\cos\theta_1 + f_1 - 1$$



Wetting: Models of roughness-induced wetting Superhydrophobicity

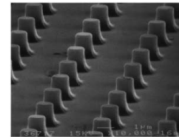
Superhydrophobicity by roughening hydrophobic surfaces (according to Wenzel equation)



Superhydrophobicity by specific topographies even on hydrophilic surfaces (against Wenzel prediction)

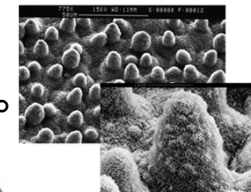
Roughness induced wetting: (Super)hydrophobicity

Bico et al.
Europhys Lett 55, 214-20, 2001



Technical
surface

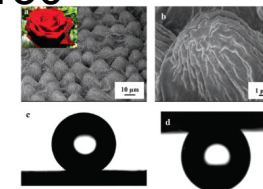
$\theta \sim 175^\circ$



Courtesy of W. Barthlott

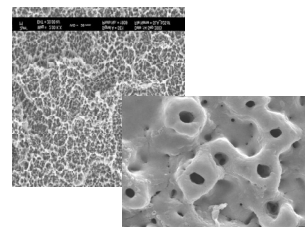
Barthlott & Neinhuis
Planta 202, 1-8, 1997

$\theta \sim 150^\circ$

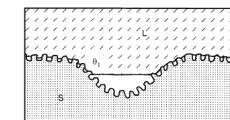


Feng et al.
Langmuir 24, 4114-19, 2008

Liu et al.
JOP: Condensed Matter 19, 356002, 2007



Closed-
pore
surface



Herminghaus.
Europhys Lett 52,
165-70, 2000

Self-
affine
surface

Super-
Hydrophobicity



Dental Implantats/Biomaterials

Effects of roughening



What is expected if surfaces are roughend?

- Increased surface area available for biolog. interactions
 - Protein adsorption
 - Cell /Bacteria adhesion
- Modulated wetting properties
 - Increase in hydrophilicity oder hydrophobicity
 - Superhydrophobicity (Lotus-, Petal-, closed-pore effects...)
- Modulated biological responses:
 - Protein conformation, conditioning film formation
 - Cell adhesion, -proliferation...
 - Bacterial adhesion, biofilm formation

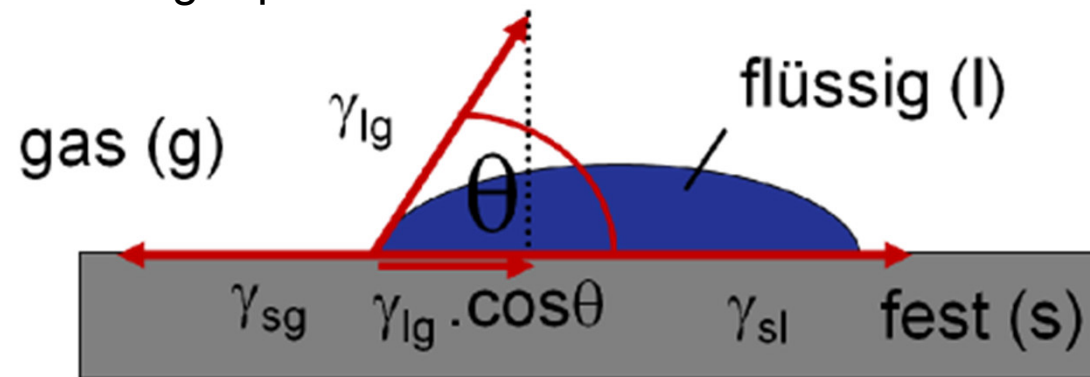


Wetting: Wetting of ideal surfaces

On ideal surfaces drops are in thermodynamic equilibrium

Ideal: chemically homogeneous, smooth, rigid

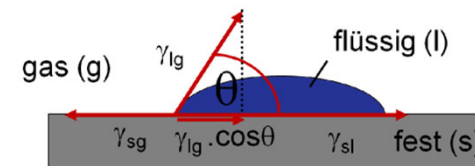
Here applies the Young-equation :



$$\cos \theta_{\text{Young}} \gamma_{lg} = \gamma_{sg} - \gamma_{sl}$$

Wetting: Meaning of the Young-Equation

$$\cos\theta_{\text{Young}} \gamma_{lg} = \gamma_{sg} - \gamma_{sl}$$



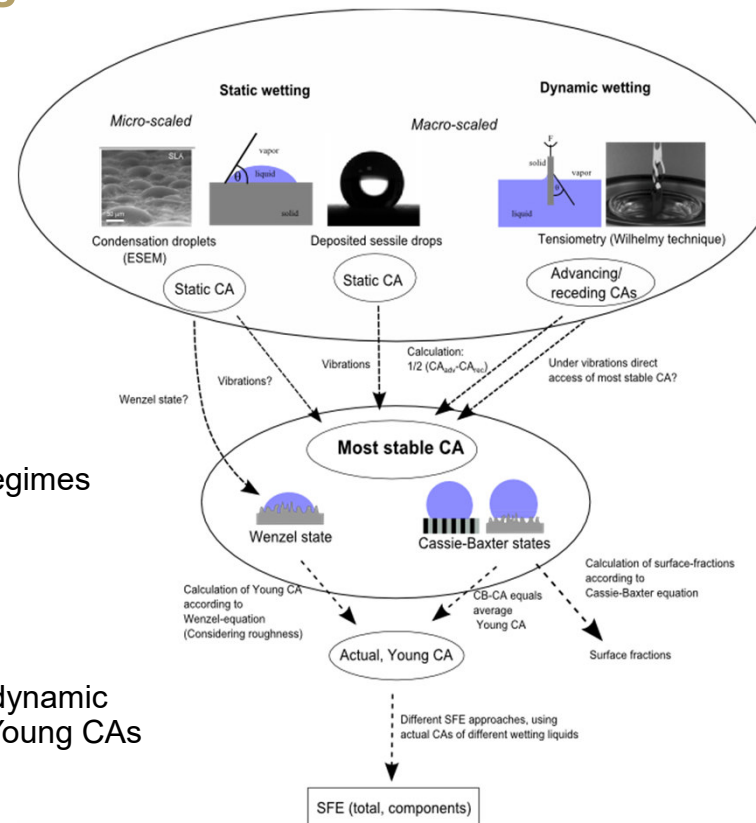
1. Surface free energy (SFE) of a solid material cannot be directly measured
2. The wetting tension is what is directly accessible
3. Based on the Young-equation, the SFE of a solid material can be estimated by different mathematical approaches - CA measurements of different liquids with different surface tensions are required.
4. Problem: Young CAs are not directly accessible on rough or chemically inhomogeneous surfaces.

Dental Implantats/Biomaterials From contact angle to surface free energy (SFE)

Experiment

Considering wetting-regimes

Calculation of thermodynamic
parameters applying Young CAs

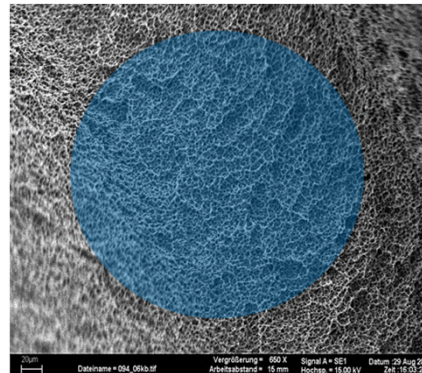


Rupp F et al. A Review on the Wettability of Implant Surfaces I: Theoretical and Experimental Aspects. Acta Biomaterialia 10; 2894–2906, 2014.

Dental Implantats/Biomaterials

From contact angle to surface free energy (SFE)

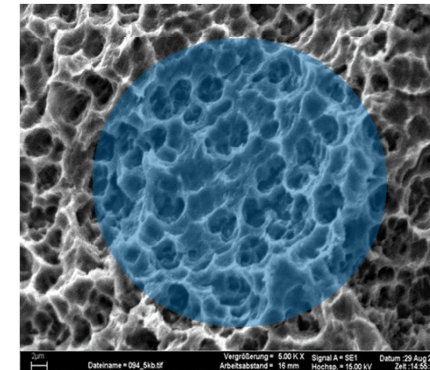
**Role of drop size
for contact angles
on hierarchically
structured surfaces**



SLA 650x magnification

Drop diameter ~200 μm

Drop „sees“ blasting
grooves on SLA



SLA 5.000x magnification

Drop diameter ~20 μm

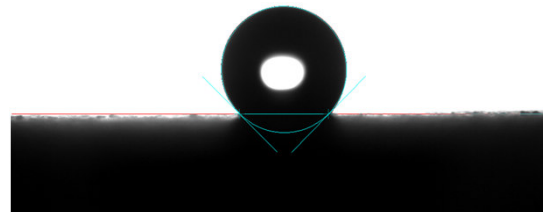
Drop „sees“ etched
pores



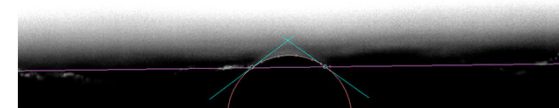
Dental Implantats/Biomaterials

From contact angle to surface free energy (SFE)

**Role of drop size
for contact angles
on hierarchically
structured surfaces**



1,4 µL drop, CA 135°



140 pL drop, CA 36°

Contact angle on SLA depends on the drop size



Dental implant: Surface factors that influence osseointegration

Implant finish

Albrektsson T et al. *Acta Orthop Scand* 52, 155-170, **1981**

Surface energy

Schwartz Z, Boyan BD. *J Cell Biochem* 56, 340-347, **1994**

Roughness Sa 1-2 μm

Wennerberg A, Albrektsson T. *Clin Oral Impl Res* 20, 172-184, **2009**

Hydrophilicity (SLActive)

Buser D et al. *J Dent Res* 83, 529-33, **2004**
Schwarz et al *J Biomed Mater Res* 88B: 544-57, **2009**

Micro-roughness / Nano-roughness / Wettability

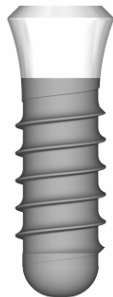
Wennerberg A et al. *Clin Oral Impl Res* 25, 1041-50, **2014**

Rupp F et al. *Acta Biomaterialia* 10, 2894-2906, **2014**

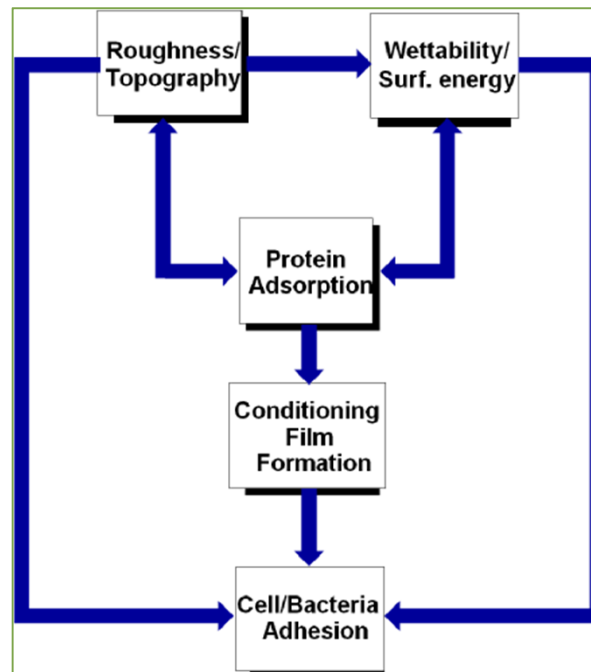
Gittens RA et al. *Acta Biomaterialia* 10, 2907-18, **2014**



Dental Implants: Factors influencing the biological response



Rupp F et al.
Biomaterials 25,
1429-1438, 2004

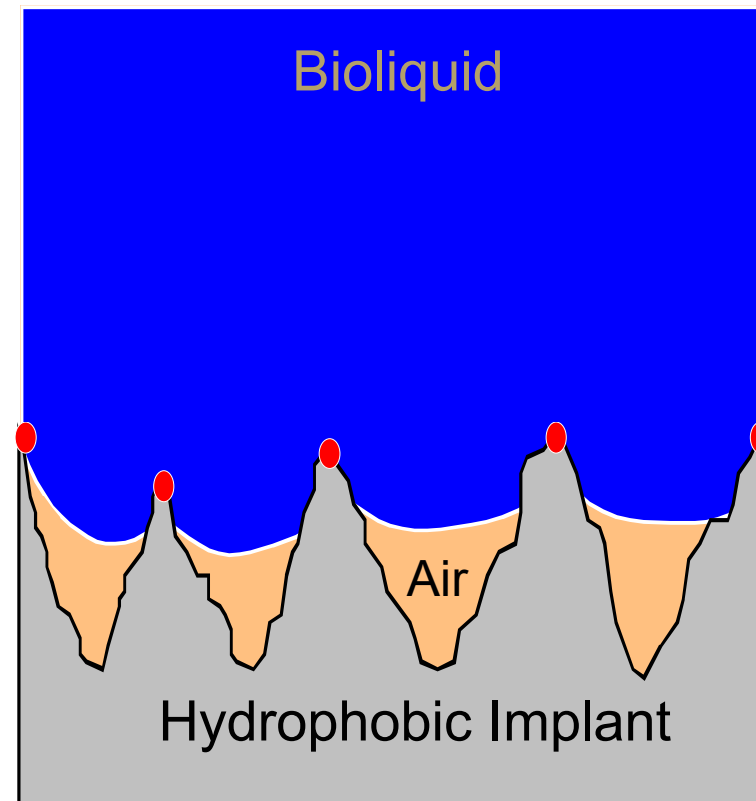


Dental implant: Biological impact of hydrophilicity

Initial state:

- Microstructured
- Hydrophobic
- **Low protein conditioning**

● Proteins

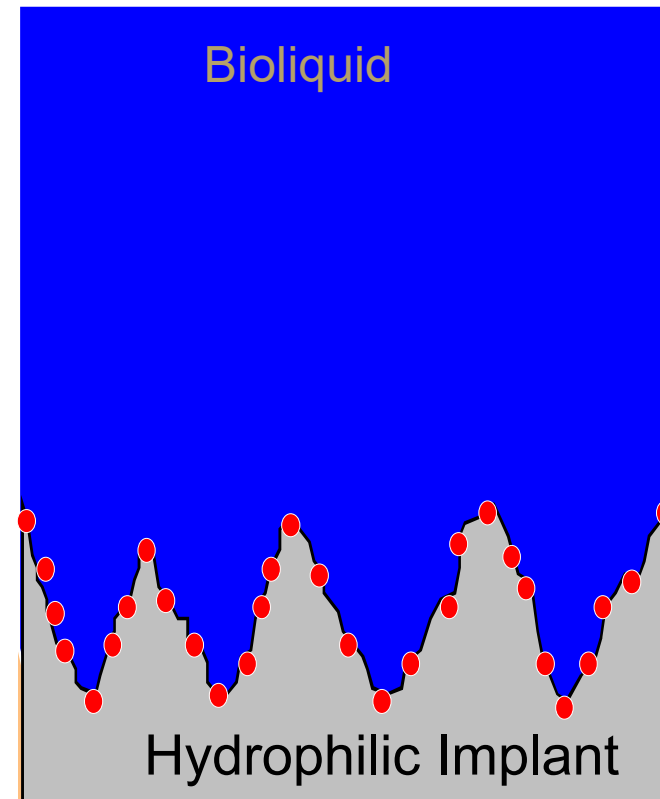


Dental implant: Biological impact of hydrophilicity

Modified state:

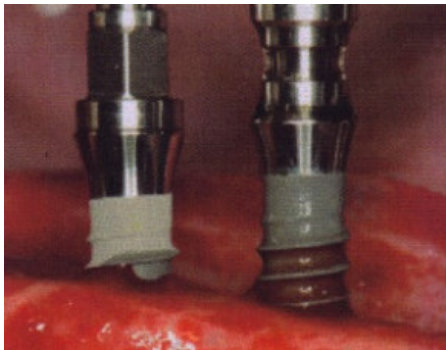
- microstructured
- superhydrophilic
- **Increased biologically available surface area**
- **Faster, complete conditioning**

● Proteins





Clinical impact of hydrophilicity: Blood clot formation



Initial stages of acute inflammation and wound healing

1. Blood contact
2. Adsorption of proteins / immune responses
3. Formation of a blood clot (coagulum)
4. Bone apposition by osteoblasts
5. Bone remodelling

Animal-Study SLA vs SLActive

1. During the first days after implantation the **blood clot is more closely adhered to the hydrophilic surface**
2. This blood clot promotes the ingrowth of new blood vessels from the adjacent alveolar bone → formation of a collagen-rich connective tissue matrix
3. **Blood vessel formation (angiogenesis) and new bone formation seem to be directly correlated**

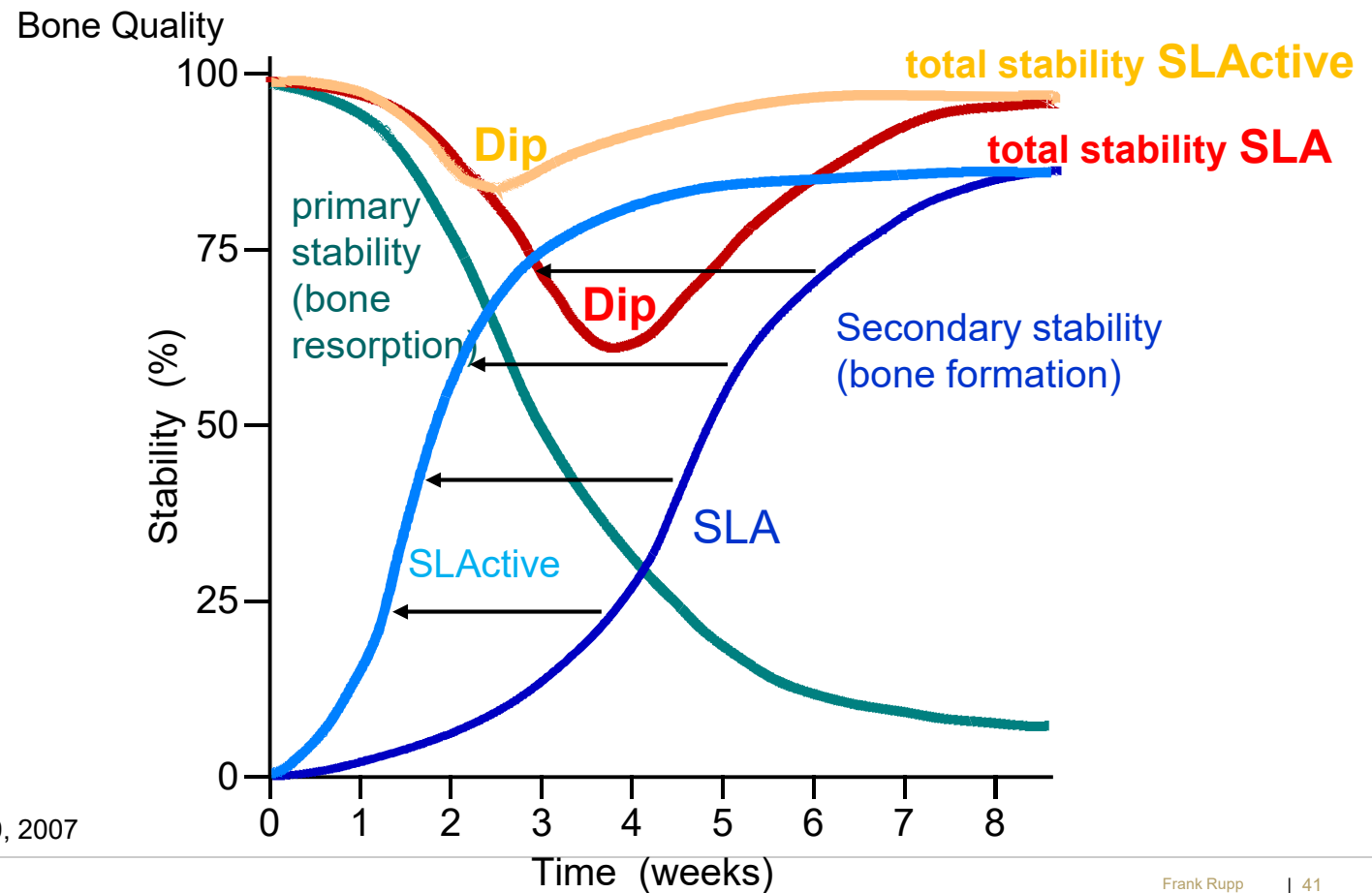
Bornstein MM et al. Clin Oral Impl Res 19;233-241, 2008

Schwarz F et al. Clin Oral Impl Res 18;481-488, 2006



reduced healing time ← Shift of the stability dip

Clinical impact of hydrophilicity



Oates TW et al.
Int J Oral Maxillofac Impl 22;755-760, 2007



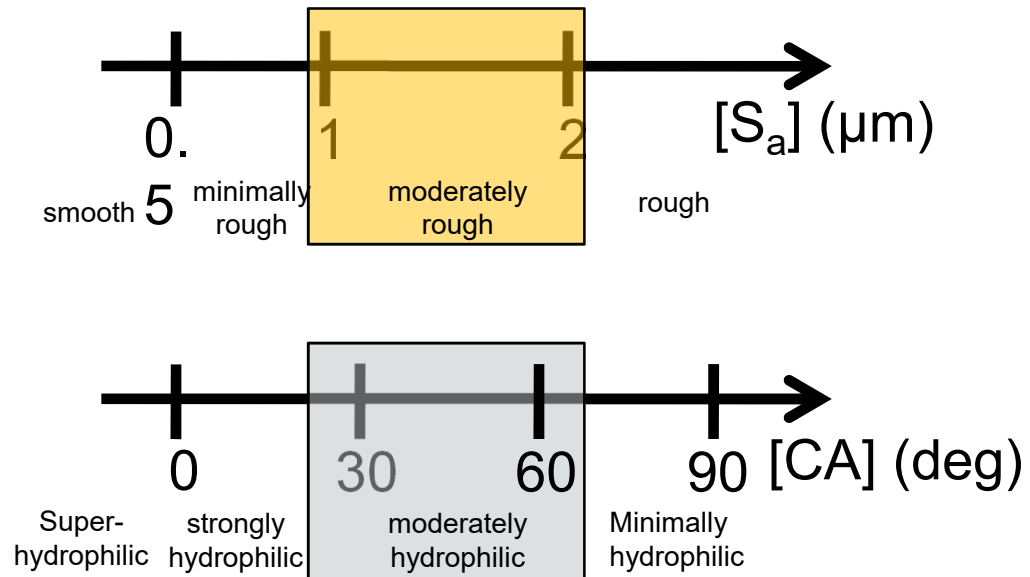
Dental implant: Clinical impact of hydrophilicity

- To our current knowledge, hydrophilicity most likely has an impact on the biological response, at least on the early interfacial reactions cascade (blood protein adsorption, clot formation, migration of pre-osteoblasts to the implant surface, cell response).
- Obviously, hydrophilic implants induce shorter healing times.
- More studies investigating the biological and clinical effects of hydrophilic implant surfaces have to be done in future to clarify the role of hydrophilicity in osseointegration and possible synergistic effects of nanostructures and hydrophilicity



Dental implants

Where does the journey go?

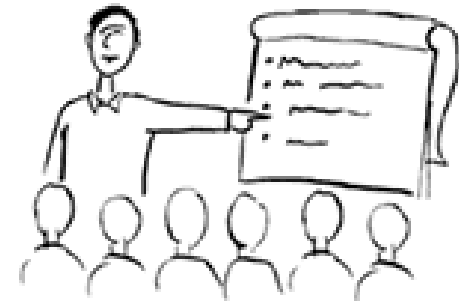




Take home message

We highlighted...

- ✓ hydrophilicity as a desired property of implant surfaces
- ✓ roughness influencing the wetting behavior of implants
- ✓ hydrophilic surface modifications
- ✓ a change of paradigm, that is from focusing on pure microroughness to study now micro-/nanoroughness and related wetting characteristics





Thank you very much
for your attention