Composites

- Materials consiting of 2 or more chemically distinct constituens at the **macro-size** range.
- One or more discontinous phases are embedded within a continous phase:
  - Discontinous phase: is usually harder and stronger; is called the *reinforcement* or *reinforcing material*.
  - Continous phase: is termed the „*matrix*“ and most often consists of fibrous biomaterials including hydrogels

Courtesy R. Zenz

Composites

- Their properties are described by the properties of their constituent materials, their distribution, and the interaction among them.
- Mostly fabricated to provide mechanical properties such as:
  - Strength, stiffness, fatique resistance,...
- Biocombatibility: being composed of 2 or more materials enhances the probability of causing adverse tissue reactions.

Courtesy R. Zenz

Reinforcing systems

Composites are classified by their strength. Strength is defined by the geometry of the reinforcement. The geometry is defined by the material (fibruos or particulate)

- Carbon fibres:
  - Produced from organic precursors: PAN (polyacrylonitrile), rayon, etc.
  - Can be stiffer and stronger than steel!
  - Used for (problem: poor shear strength):
    - Reinforcement of porous polytetraflourethylen (Teflon) for soft tissue augmentation.
    - Surface coating for the attachment of orthopedic implants.
    - Reinforcement of ultra high molecular weigth (UHMW) polyethylene used as bearing surface in total joint prostheses (problem: osteolysis).
    - Tendon and ligament repair material (no final approval from the FDA, due to permanent wear debris).
    - Reinforcement of fracture fixation devices.
    - Design flexibility, strength, lightweight → make ideal composites for aids able to return even atlethic performances to impaired people.

Courtesy R. Zenz

Reinforcing systems

- Polymer fibres:
  - For the majority of applications polymer fibres are not strong or stiff enough to reinforce other polymers.
  - Possible exceptions:
    - UHMW polyethylen fibres (excellent biocompatibility, but rather inert surface, resticting matrix binding)
      - Invertebral disc prostheses
      - Dentistry (acrylic resin enforcement)
    - Kevlar (aramid fibres; aromatic polyamid fibres):
      - High strength and stiffness
      - Resistance to fatique and stress rupture
      - Potential applications (concerns: biocompatibility and long-term fate):
        - Hip prostheses stems
        - Fracture fixation devices
        - Tendon prostheses
      - Current applications:
        - Dentistry
        - Ligament prostheses

Courtesy R. Zenz

Reinforcing systems

- Resorbable polymer fibres:
  - Used to reinforce resorbable polymers.
  - PLA and PGA polymers
    - Resorbable sutures
    - Scaffolds for implants with living cells
    - Drug release devices
- Ceramics (particulate composites):
  - Most biocompatible ceramics, when loaded in tension or shear, are relatively weak and brittle.
  - Reinforcement:
    - Various calcium phosphates (TCP, HA; = bio-ceramics)
    - Bone mineral

Courtesy R. Zenz

Fracture fixation

- Resorbable devices (absorbable matrix composites) for bone fixation have 2-fold advantage:
  - Reduced stress protection
  - No secondary operation needed to remove hardware

Rigid fixation during healing may cause bone to undergo stress protection atrophy; can result in significant bone mass loss and osteoporosis.

Relative large difference in stiffness/elasticity → disproportionate load sharing; high stress concentration at the bone-implant junction

- Metall and alloys conventionally used have the above mentioned problem and additionally:
  - Corrode to some degree
  - released ions can cause:
    - Adverse effects on bone mineralization
    - immune response
    - Adverse systemic response such as local tumor formation

Courtesy R. Zenz

Resorbable fracture fixation

- PLA (poly-lactic acid), PGA (poly-glycolic acid), Polydioxinone
- PLA:
  - Degrades in the body at a rate that can be controlled by mixing with PGA. Degradation gradually transfers load to the healing bone
  - Degradation products are non-toxic, biocompatible:
    - Lactic acid: metabolized to CO_2 and H_2O
  - However, mechanical properties are relatively low:
    - Only adequate for low-load situations.
    - Except: when reinforced with carbon-based fibers: stronger than steel but far more flexible

Courtesy R. Zenz

Dental Composites

- Tought as an alternative to amalgam
  - Composite material
    - 60-70% glass-and silica crystals
    - 30-40% polymers (non-degradable)
  - Soft mixture – light curing (UV)- shrinking
  - Good aesthetic and optical qualities
  - Inexpensive and easy to handle
  - Endurance like amalgam
  - High wear rates

Courtesy R. Zenz

Courtesy R. Zenz

Surface Modifications

- Use of biomaterial in particular applications often dictated by bulk properties:
    - e.g. Strength & toughness for load bearing applications,
    - wear resistance for articulating surfaces,
    - flexibility & compliance for vascular and soft tissues.

- Cells/tissues interact with material surfaces.
- Biomaterial surface chemistry and structure is directly responsible for cell/tissue responses.
- Aim: retain bulk properties but promote cell/tissue interaction with material.

Courtesy R. Zenz

Surface Modifications

- Biological modifications:
  - Biologically functional molecules (and perhaps cells) are chemically or physically immobilized on substrate.
- Immobilization techniques may either be permanent or temporary:
  - Surfaces express or modified to express reactive groups (e.g. -OH, $-NH_2$, -COOH, -SH, $-CONH_2$).
  - Reactive groups reacted with coupling agent.
  - Coupling agent(s) used to react with groups on biological molecules.

Courtesy R. Zenz

Surface Modifications

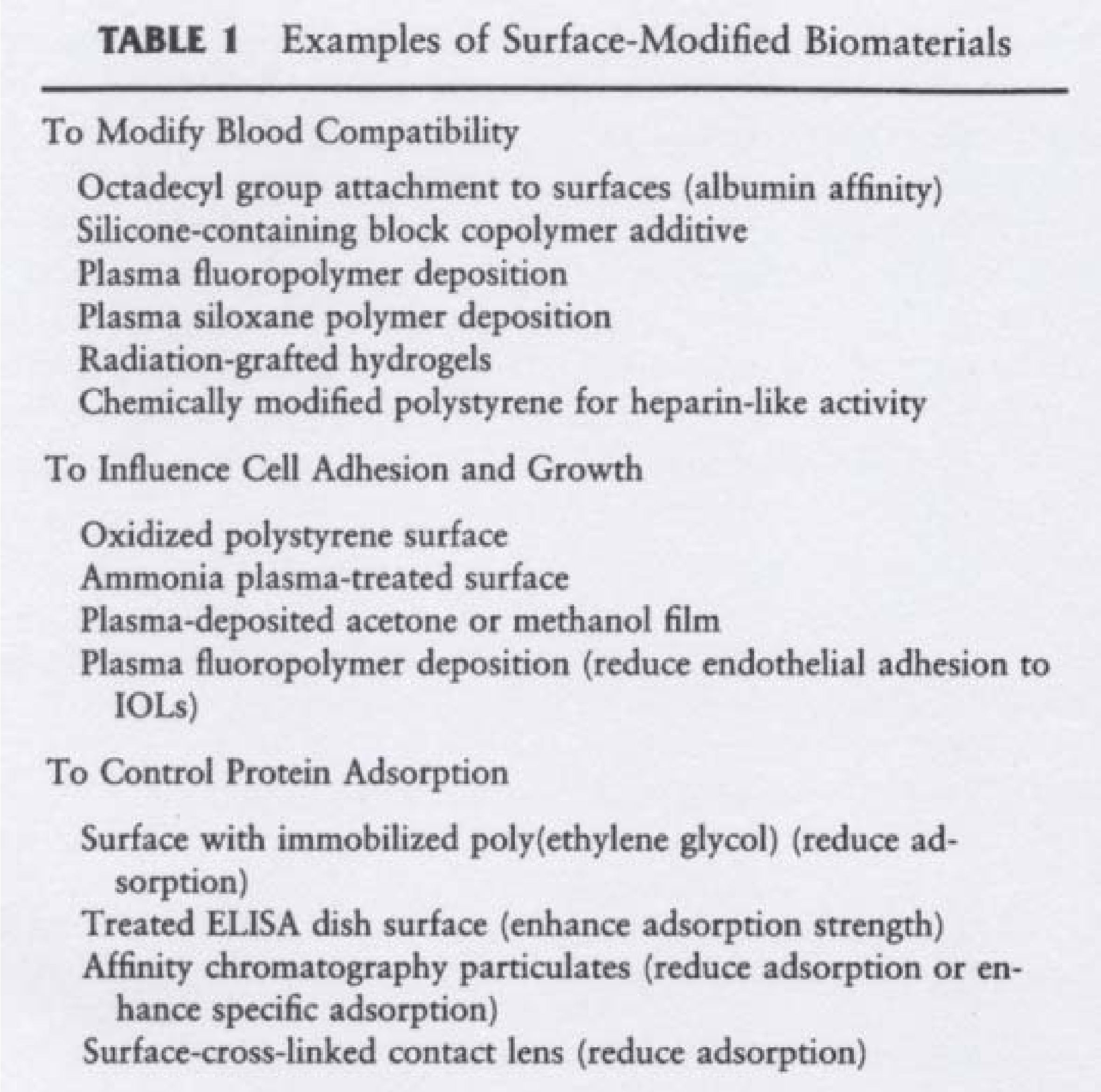


TABLE 1 Examples of Surface-Modified Biomaterials

To Modify Blood Compatibility

- Octadecyl group attachment to surfaces (albumin affinity)
- Silicone-containing block copolymer additive
- Plasma fluoropolymer deposition
- Plasma siloxane polymer deposition
- Radiation-grafted hydrogels
- Chemically modified polystyrene for heparin-like activity

To Influence Cell Adhesion and Growth

- Oxidized polystyrene surface
- Ammonia plasma-treated surface
- Plasma-deposited acetone or methanol film
- Plasma fluoropolymer deposition (reduce endothelial adhesion to IOLs)

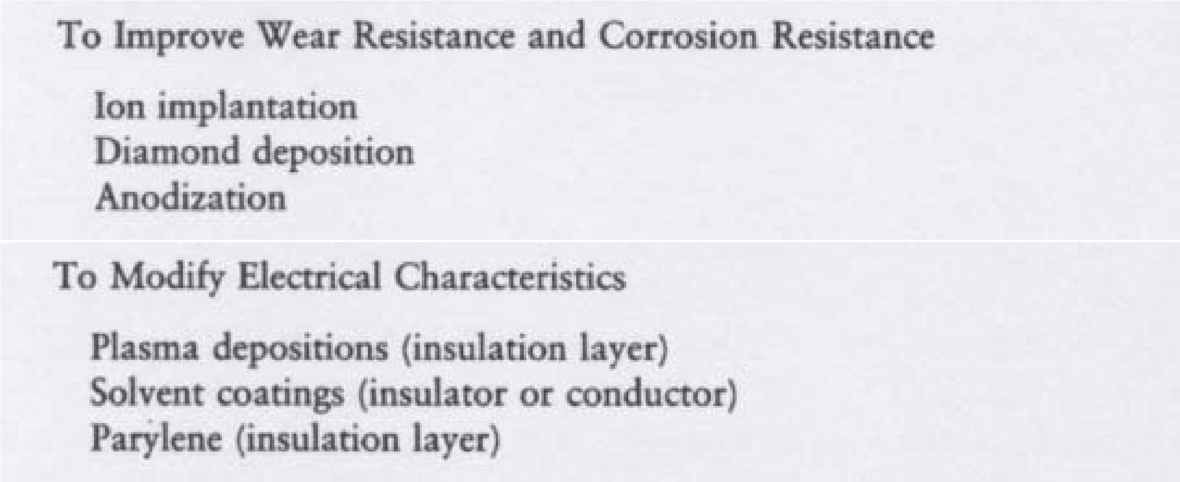
To Control Protein Adsorption

- Surface with immobilized poly(ethylene glycol) (reduce adsorption)
- Treated ELISA dish surface (enhance adsorption strength)
- Affinity chromatography particulates (reduce adsorption or enhance specific adsorption)
- Surface-cross-linked contact lens (reduce adsorption)

Courtesy R. Zenz

Surface Modifications

- Examples (cont.)



To Improve Wear Resistance and Corrosion Resistance

Ion implantation
Diamond deposition
Anodization

To Modify Electrical Characteristics

Plasma depositions (insulation layer)
Solvent coatings (insulator or conductor)
Parylene (insulation layer)

Courtesy R. Zenz

Surface Modifications

- General principles:
  - Chemically or physically altering the atoms, compounds, or molecules in the existing surface.
  - Overcoating the existing surface with a material of different composition.

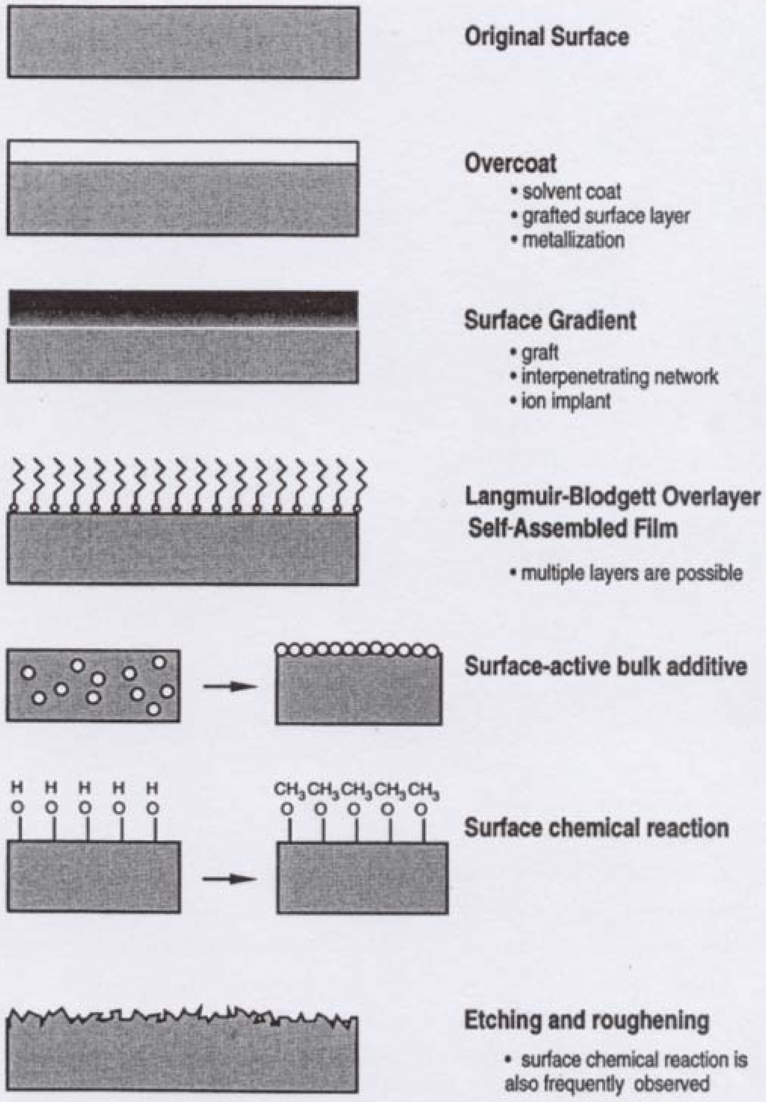


FIG. 1. Schematic representations of methods to modify surfaces.

Courtesy R. Zenz

Surface Modifications

- Chemical surface reactions:
  - Nonspecific - chemicals used to react with surface atoms.
    - molecules to leave functional/reactive groups on surfaces.
    - Acid treatment of materials, RFGD (Radiofrequencey Glow Discharge Deposition)
  - Specific reactions change only one group to another.
    - Alkylation, trifluoroacetic anhydride reactions, conversion to siloxane.

Courtesy R. Zenz

Surface Modifications

- The modified surface zone should be as thin as possible:
  - Thick surface can change the mechanical and functional properties of the material.
  - Thick coatings are also more subject to delamination.
  - Idealy: only the outermost molecular layer (3-10 Å).
  - In practice: thicker films are necessary (to ensure that all of the original surface is uniformly covered).
  - Some coatings intrinsically have a specific thickness:
    - E.g. LB-films (Langmuir-Blodgett deposition): the length of surfactant molecules is 25-50 Å.

Courtesy R. Zenz

Surface Modifications

- Radiation grafting:
  - Ionizing radiation (radiation, UV, e^-- beam) used to break chemical bonds in material surface to generate free radicals or reactive species.
  - Reactive surfaces exposed to coating material which reacts with surface species to create grafted surface layer.
  - Graft layers are thick (>1µm) but well bonded to the substrate (chemically bonded to surface).
  - Used to bond hydrogels to the surface of hydrophobic polymers.

Courtesy R. Zenz

Surface Modifications

- RFGD (Radiofrequencey Glow Discharge Deposition) and plasma treatments:
  - Low pressure ionized gases used to ablate (clean), etch, or deposit coating on substrate surface.
  - Advantages are many:
    - Coatings/surfaces are uniform and sterile
    - Metals, polymers, ceramics may be treated
    - Good film adhesion
    - Unique chemistries possible
    - Process easy
  - RFGD Disadvantage:
    - chemistry of coating is not well defined
    - Equipment is expensive ($10-100K)
    - Contamination of ionizing gas/atmosphere can be problematic

Courtesy R. Zenz

Surface Modifications

- RFGD applications:

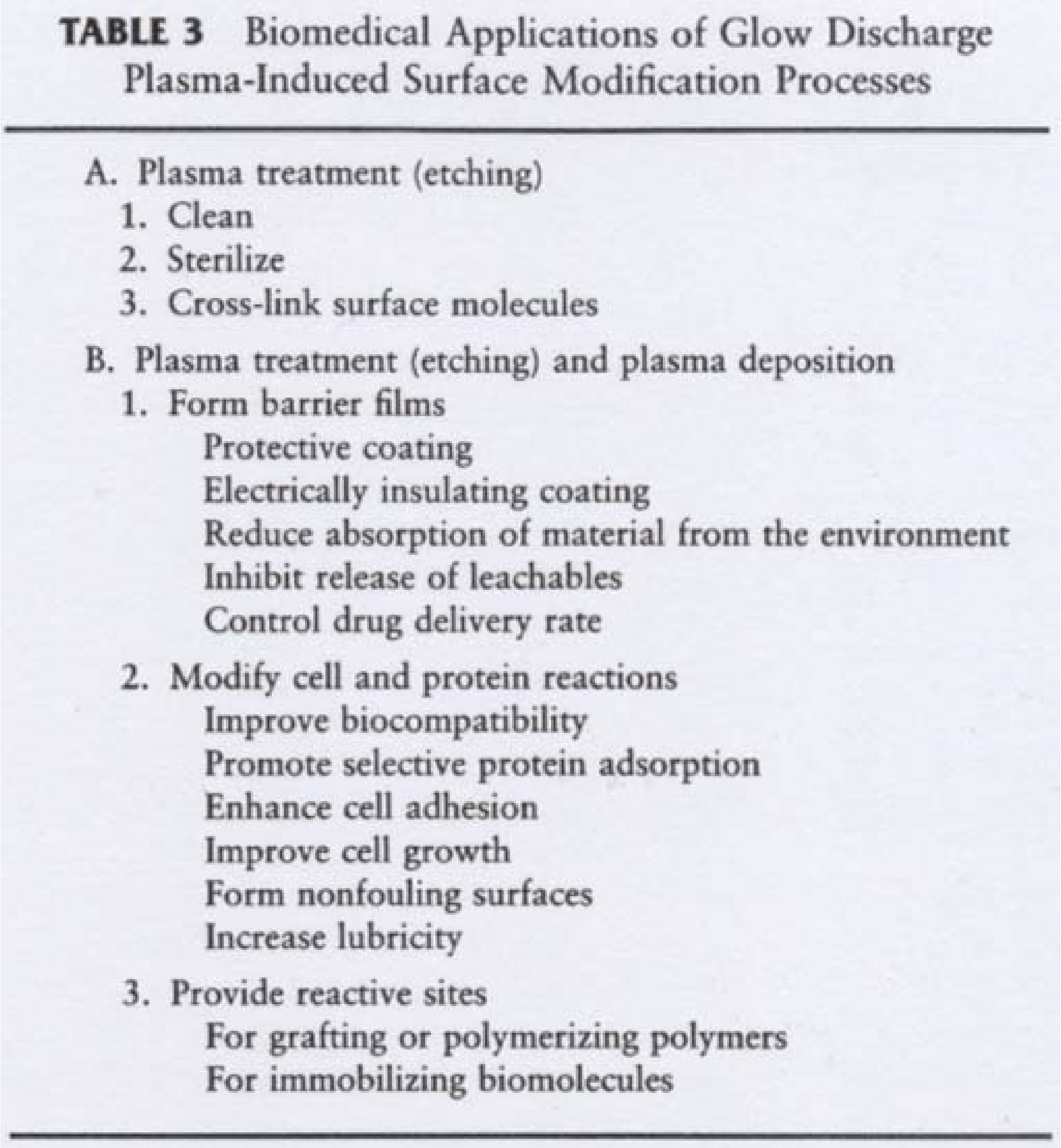


TABLE 3 Biomedical Applications of Glow Discharge Plasma-Induced Surface Modification Processes

A. Plasma treatment (etching)
  1. Clean
  2. Sterilize
  3. Cross-link surface molecules

B. Plasma treatment (etching) and plasma deposition
  1. Form barrier films
     - Protective coating
     - Electrically insulating coating
     - Reduce absorption of material from the environment
     - Inhibit release of leachables
     - Control drug delivery rate
  2. Modify cell and protein reactions
     - Improve biocompatibility
     - Promote selective protein adsorption
     - Enhance cell adhesion
     - Improve cell growth
     - Form nonfouling surfaces
     - Increase lubricity
  3. Provide reactive sites
     - For grafting or polymerizing polymers
     - For immobilizing biomolecules

Courtesy R. Zenz

Surface Modifications

- Silanization:
  - Used to modify hydroxylated or amine-rich surfaces (glass, silicon, many metal oxide surfaces).
  - A wide range of different silans is available.

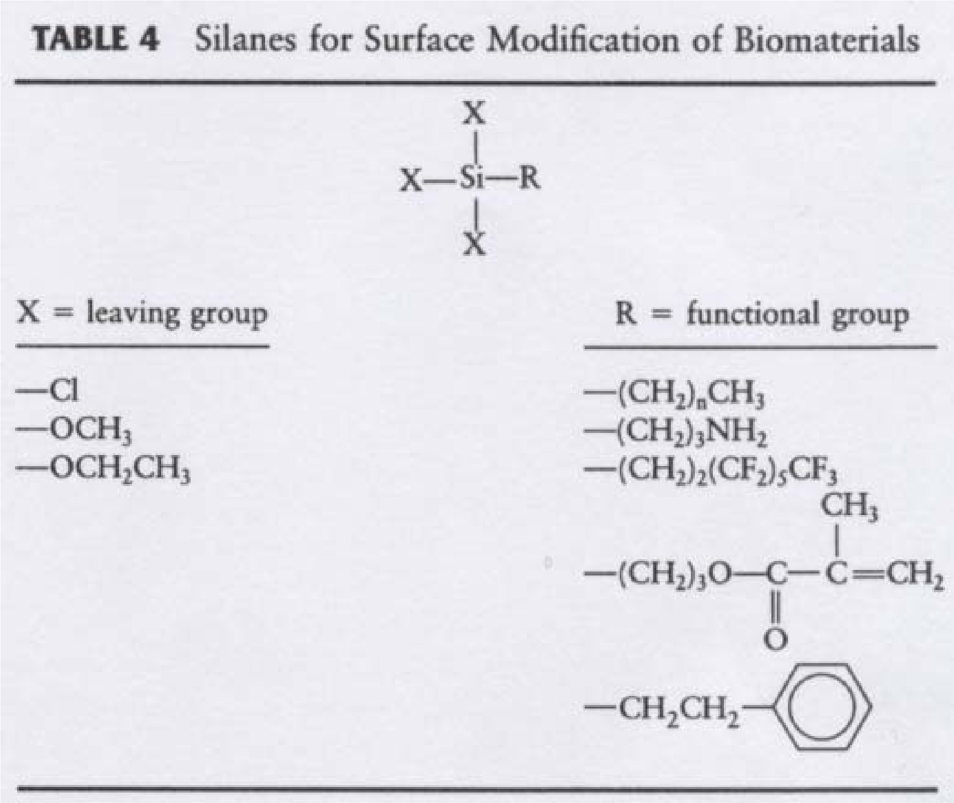


TABLE 4 Silanes for Surface Modification of Biomaterials

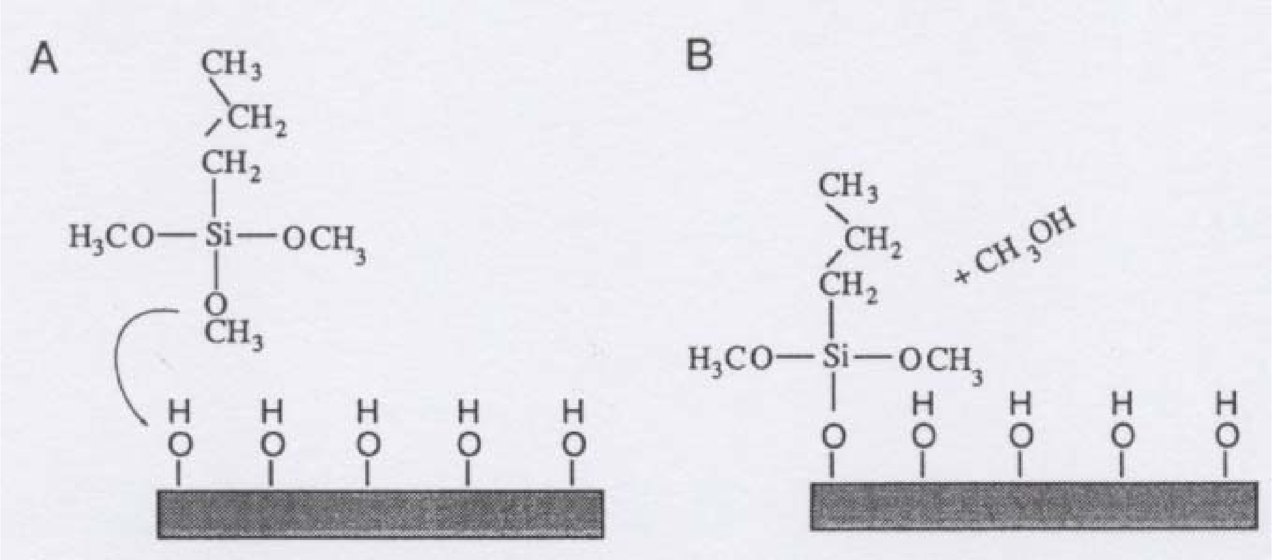
$$X-\overset{\displaystyle X}{\underset{\displaystyle X}{Si}}-R$$

X = leaving group	R = functional group
$—Cl$	$—(CH_2)_nCH_3$
$—OCH_3$	$—(CH_2)_3NH_2$
$—OCH_2CH_3$	$—(CH_2)_2(CF_2)_5CF_3$
	$—(CH_2)_3O—\underset{\displaystyle O}{\underset{\Vert}{C}}—\overset{\displaystyle CH_3}{\overset{\vert}{C}}=CH_2$
	$—CH_2CH_2—$

Courtesy R. Zenz

Surface Modifications

- Silanization (cont.)
  - Chemistry is simple and stable.
  - But: bond between Si and OH-group is also readily subjected to basic hydrolysis (film breakdown under some conditions must be considered.
    - cytokine immobilized on CoCr



Courtesy R. Zenz

Surface Modifications

- Ion beam implantation:
  - Ions accelerated at high energies to become embedded into the surface.
  - Mostly metals/alloys modified with C, N, B, Ir to increase hardness, wear resistance and corrosion resistance:
    - Iridium implantation to Ti-6AL-4V alloy to improve corrosion resistance.
    - Nitrogen implantation into titanium greatly reduces wear.
    - Boron and carbon implantation into 316L stainless steel improves high cycle fatique life.

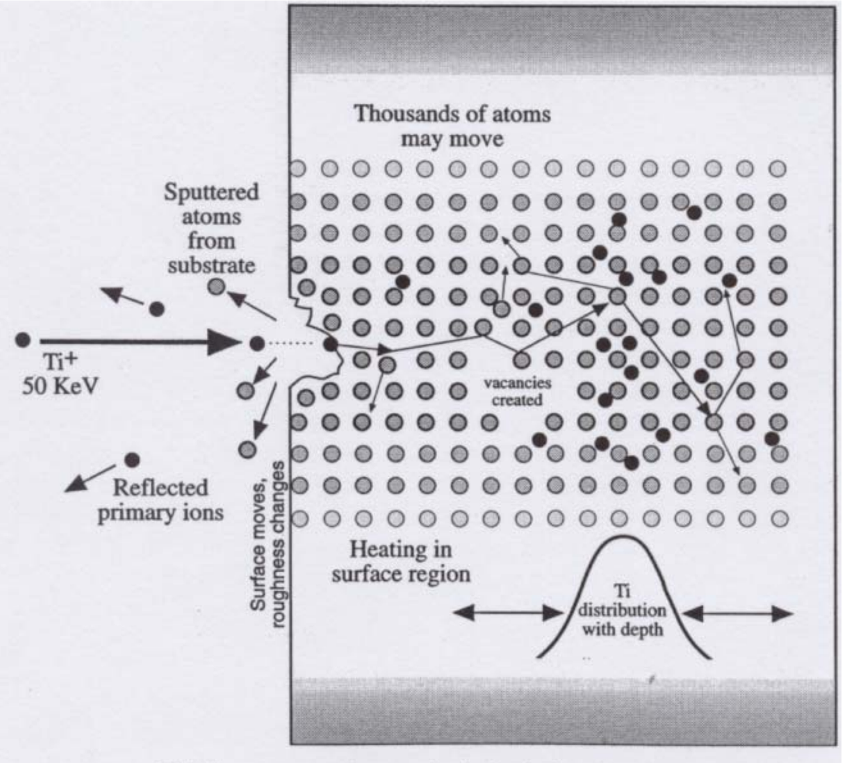


FIG. 5. Some considerations for the ion implantation process.

Courtesy R. Zenz

Surface Modifications

- Langmuir-Blodget Films - LB
  - Molecules with polar and nonpolar regions (phospholipids) coat surface to develop well ordered multilayers.
  - Wide range of chemicals can form LB films.
  - Stability can be improved by cross-linking or polymerization.

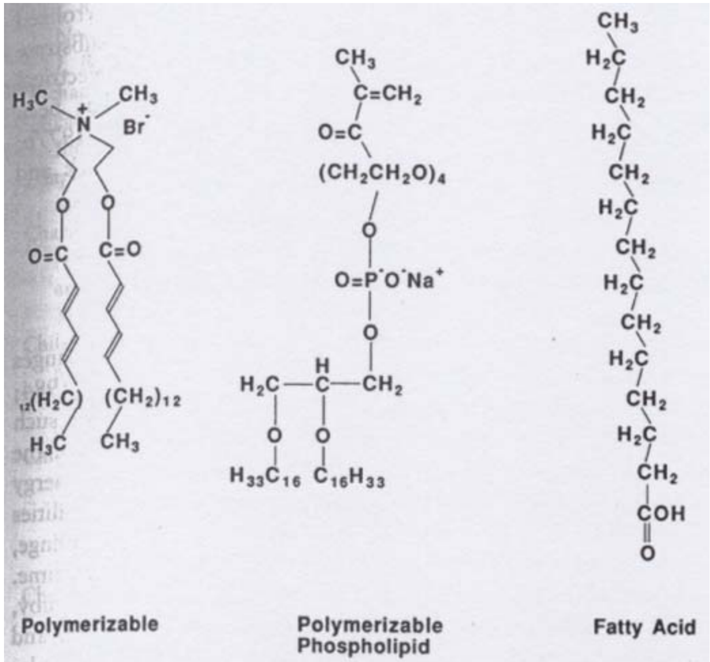
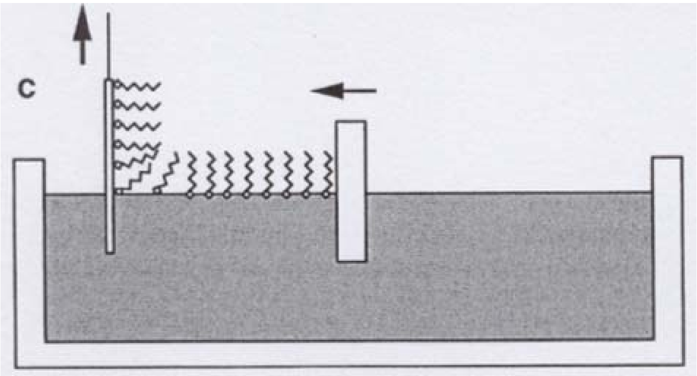


FIG. 7. Three examples of molecules that form organized Langmuir–Blodgett films.



Courtesy R. Zenz

Surface Modifications

- Self Assembled Monolayers (SAMs)
  - Films that spontaneously form highly ordered structures
  - Involve exothermic absorption reactions and significant van der Waal forces to form ordered ‘crystalline’ arrangements (tight packing).
  - Many options for changing the outer-most groups.
  - More stable than LB films.

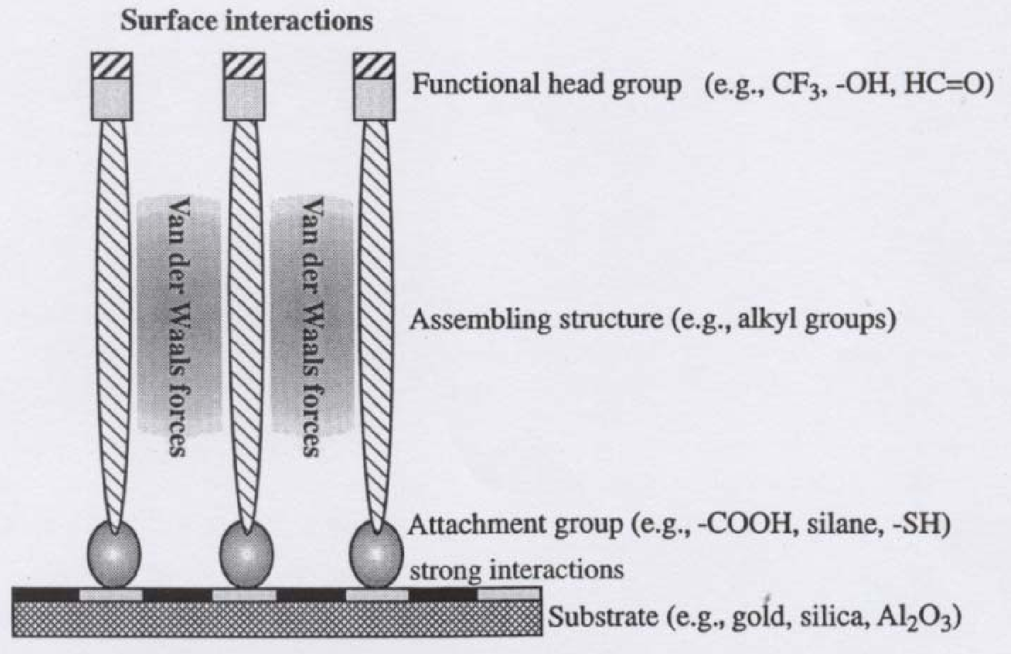


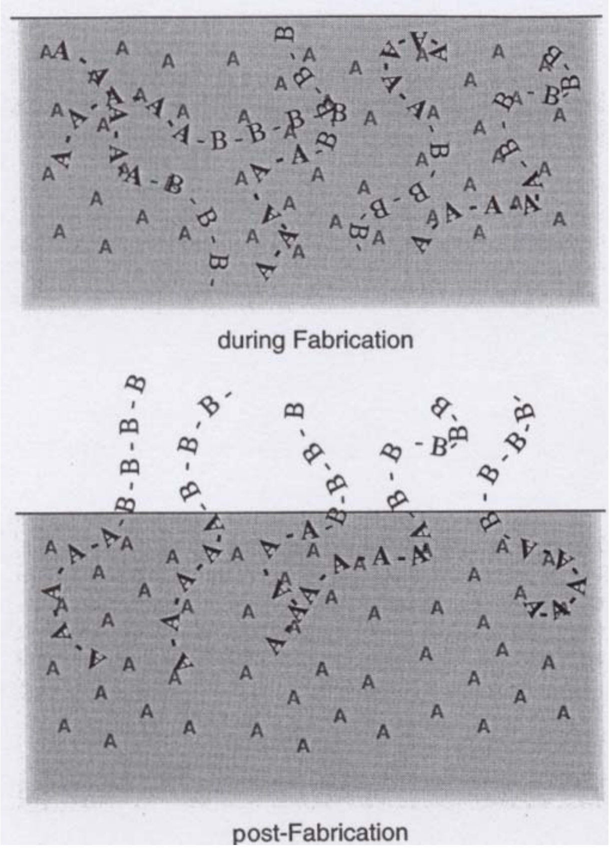
FIG. 8. General characteristics of molecules that form self-assembled monolayers.

Courtesy R. Zenz

Surface Modifications

- Surface-modifying additives (SMAs)
  - For organic and inorganic systems
  - E.g. Diblock copolymer
    - Block A will be soluble, or compatible with the material.
    - Block B will be incompatible.

During fabrication, the SMA might be distributed uniformly troughout the bulk; than the SMA will migrate to the surface.



Courtesy R. Zenz

Surface Modifications

- Conversion coating:
  - To modify the surface of a metal into a dense oxid-rich layer that imparts corrosion protection and enhanced adhesivity to the metal.
    - Steel is frequently phosphated or chromated (treatment with phosphoric acid or chromic acid).
    - Aluminum is electrochemically anodized in chromic, oxalic or sulfonic acid electrolytes.

Metall alloy systems are subjected to corrosion ($M \rightarrow M^+ + e^-$); this is reduced $10^3 - 10^6$ times by the presence of a minimal conductive, relatively inert oxide surface.

Courtesy R. Zenz

Surface Modifications

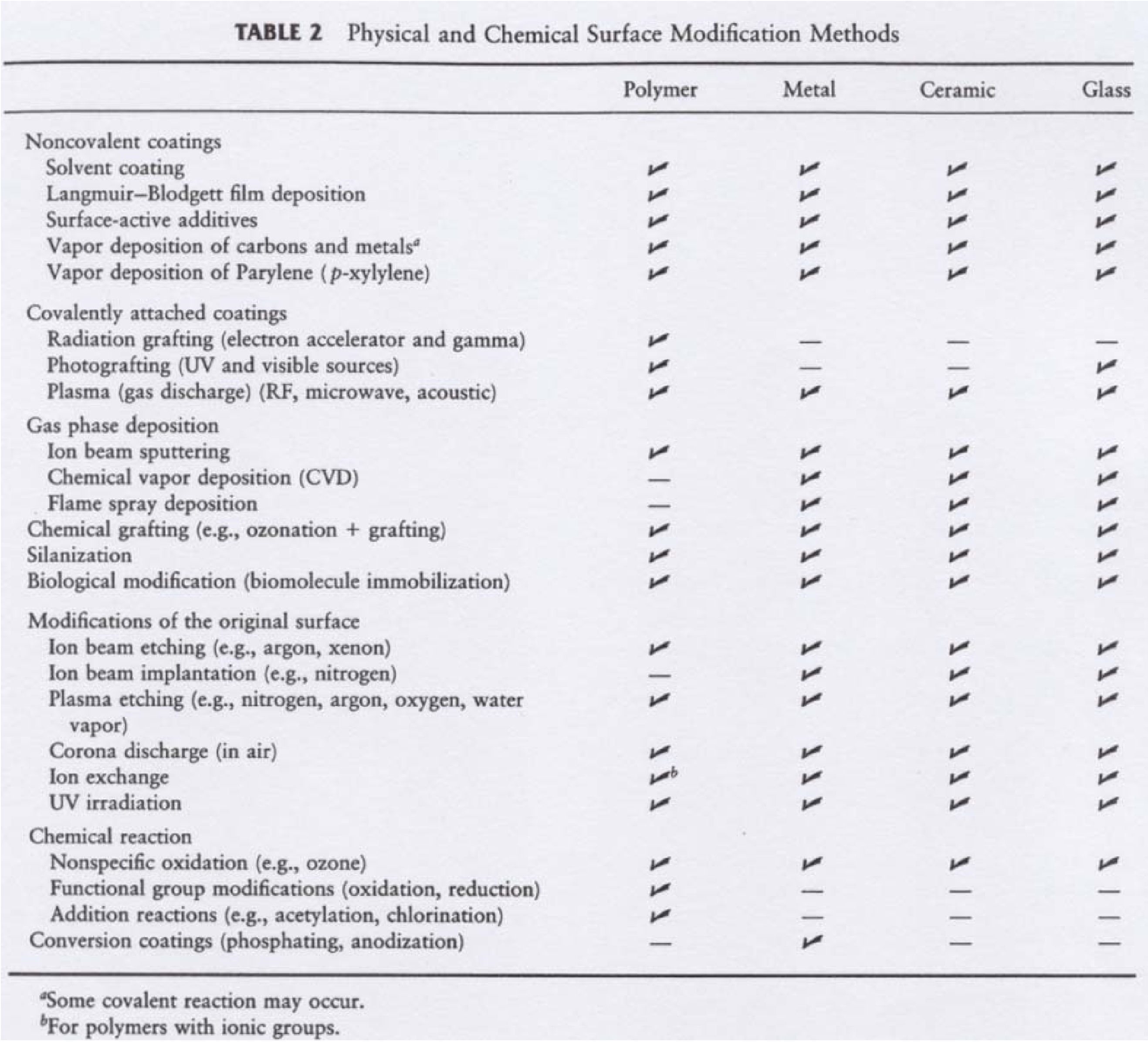


TABLE 2 Physical and Chemical Surface Modification Methods

	Polymer	Metal	Ceramic	Glass
Noncovalent coatings				
Solvent coating	✓	✓	✓	✓
Langmuir–Blodgett film deposition	✓	✓	✓	✓
Surface-active additives	✓	✓	✓	✓
Vapor deposition of carbons and metals[a]	✓	✓	✓	✓
Vapor deposition of Parylene (*p*-xylylene)	✓	✓	✓	✓
Covalently attached coatings				
Radiation grafting (electron accelerator and gamma)	✓	—	—	—
Photografting (UV and visible sources)	✓	—	—	✓
Plasma (gas discharge) (RF, microwave, acoustic)	✓	✓	✓	✓
Gas phase deposition				
Ion beam sputtering	✓	✓	✓	✓
Chemical vapor deposition (CVD)	—	✓	✓	✓
Flame spray deposition	—	✓	✓	✓
Chemical grafting (e.g., ozonation + grafting)	✓	✓	✓	✓
Silanization	✓	✓	✓	✓
Biological modification (biomolecule immobilization)	✓	✓	✓	✓
Modifications of the original surface				
Ion beam etching (e.g., argon, xenon)	✓	✓	✓	✓
Ion beam implantation (e.g., nitrogen)	—	✓	✓	✓
Plasma etching (e.g., nitrogen, argon, oxygen, water vapor)	✓	✓	✓	✓
Corona discharge (in air)	✓	✓	✓	✓
Ion exchange	✓[b]	✓	✓	✓
UV irradiation	✓	✓	✓	✓
Chemical reaction				
Nonspecific oxidation (e.g., ozone)	✓	✓	✓	✓
Functional group modifications (oxidation, reduction)	✓	—	—	—
Addition reactions (e.g., acetylation, chlorination)	✓	—	—	—
Conversion coatings (phosphating, anodization)	—	✓	—	—

[a] Some covalent reaction may occur.

[b] For polymers with ionic groups.

Courtesy R. Zenz