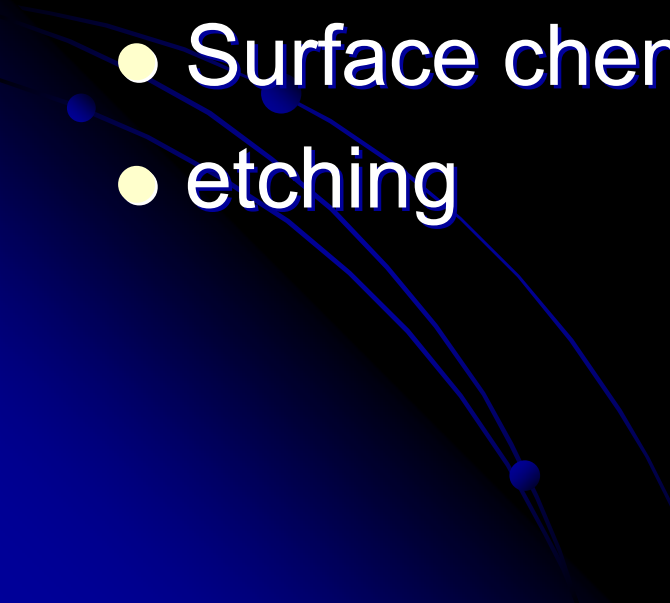


Malzeme ve Yüzey Kaplama Teknikleri 3. Hafta

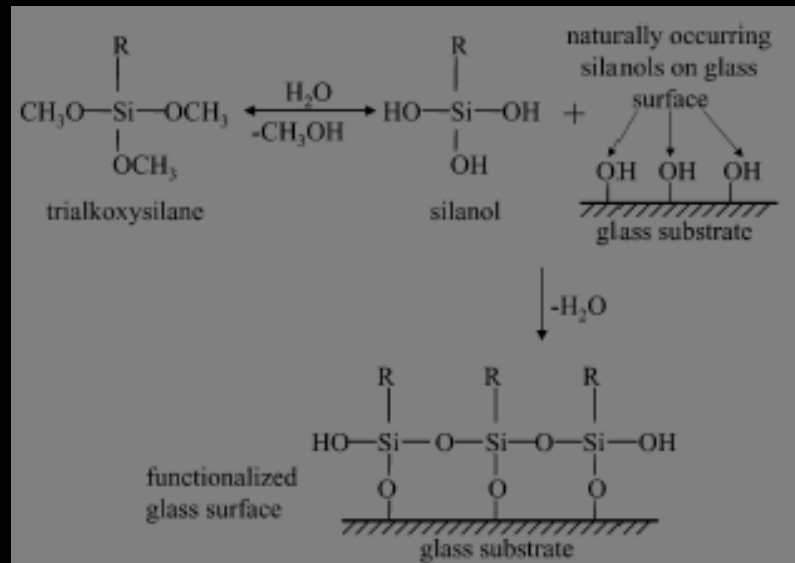


Başkent Üniversitesi
Endüstri Mühendisliği

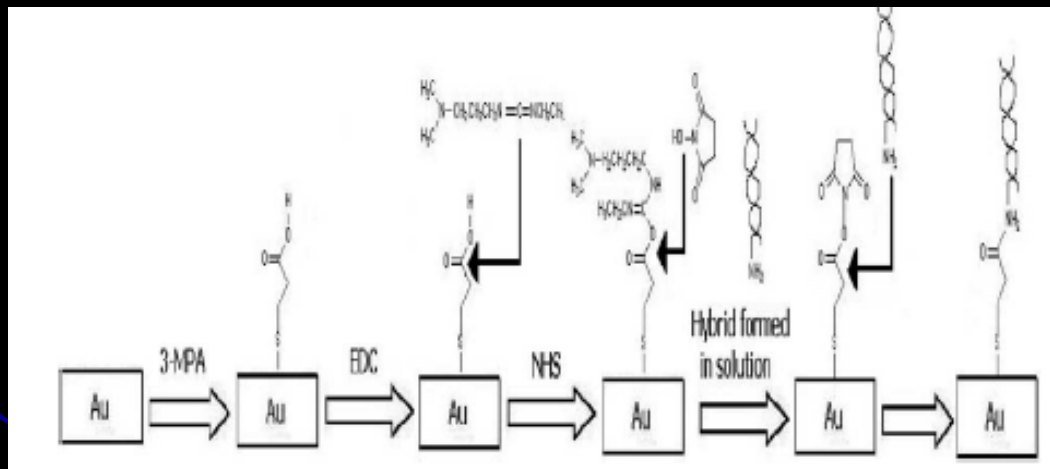
Yüzey Modifikasyon Yöntemleri

- Overcoat
 - Surface gradient
 - SAM
 - Surface active bulk additive
 - Surface chemical reaction
 - etching
- 

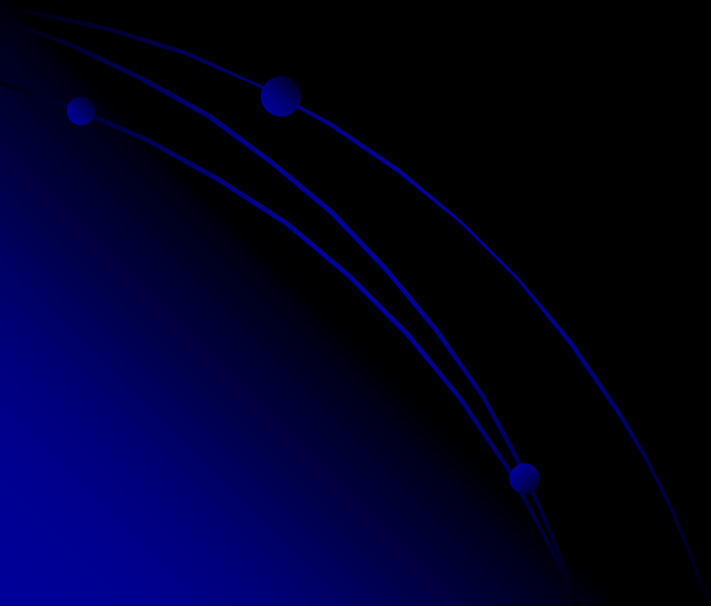
1. Silanizasyon



2. SAM



3. SMA

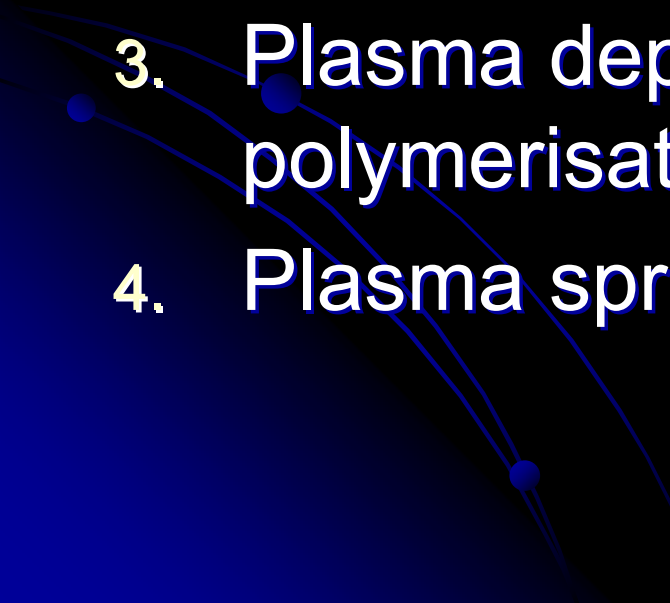


4. Yk Boşalım Teknikleri

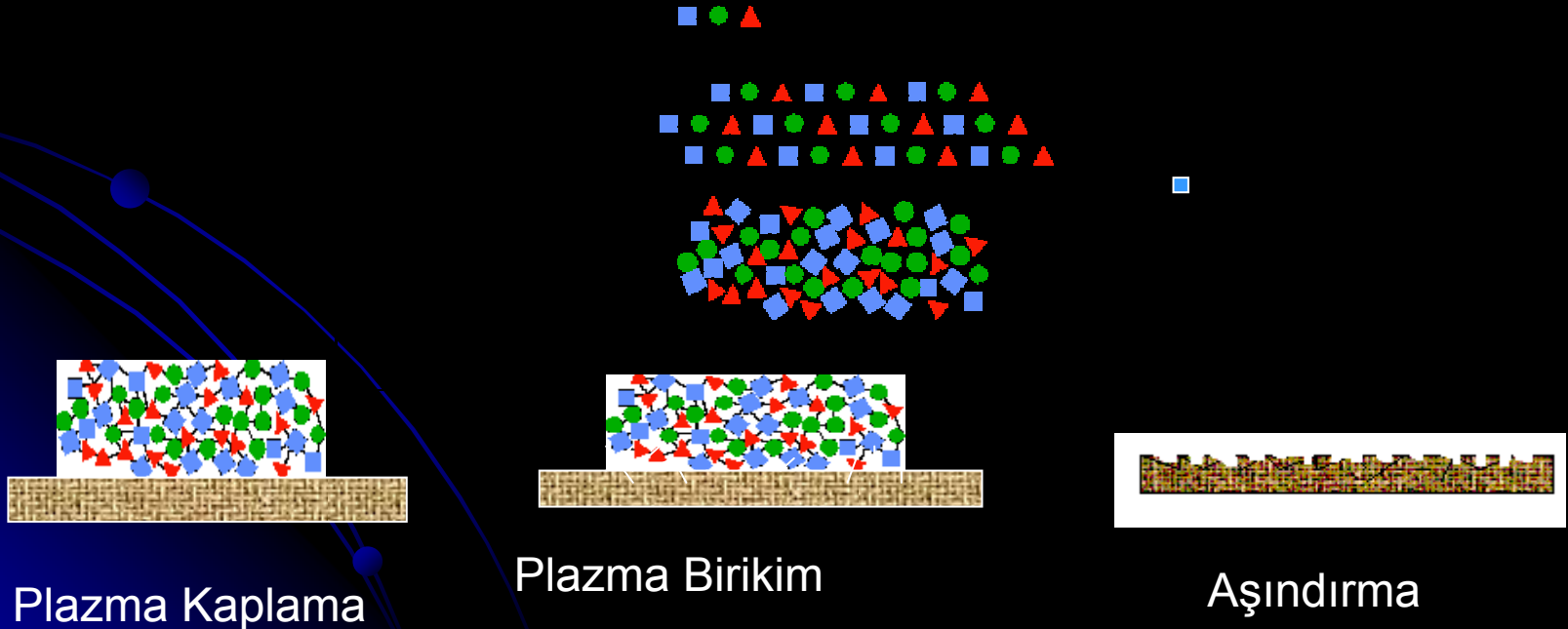
Çok farklı plazma kaynakları vardır:

1. Gaz plazma kaynakları: Radyo frekansı (rf) ya da mikrodalga (ECM), corona (uniform olmayan elektrik alanı), atmosferik arc
2. Laser plazma kaynakları

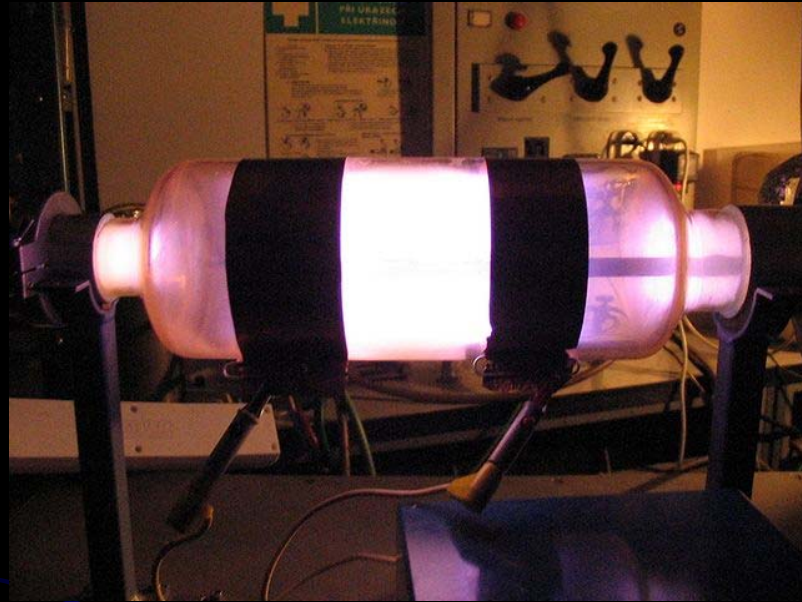
Farklı sonuçlar:

1. Plasma sputtering / etching
 2. Plasma implantation
 3. Plasma deposition (plasma polymerisation, grafting)
 4. Plasma spraying
- 

1. Uygulanan elektriksel boşalmanın türü (içten elektrodla kapasitif, dıştan elektrotla induktif gibi)
2. Uygulanan elektriksel boşalma ile ilgili diğer değişkenler (boşalmanın gücü, frekansı, monomer basıncı, monomer akış hızı)
3. Elektriksel boşalmanın uygulandığı reaksiyon kabı (reaktör) ile ilgili değişkenler (reaktör yatay boru ya da an şeklinde ayrıca monomerin giriş ve elektrotlara göre dağılışı geometrisindeki farklılıklar)
4. Polimerin üzerine kaplandığı ortamın yeri şekli yapısı vb. gibi bazı unsurlar rol oynamaktadır.



PLASMA POLYMERIZATION TECHNIQUE



A plasma which can be regarded as the fourth state of matter is composed of highly excited atomic, molecular, ionic, and radical species.

‘Cold plasma’ is typically obtained when gases are excited into energetic states by radio frequency (rf), microwave, or electrons from a hot filament discharge.

A plasma is a highly unusual and reactive chemical environment in which many plasma-surface reactions occur [2]

[2] Boddour, R.F., and Timmins, R. S., Eds. (1967), The application of plasmas to chemical processing, MIT Press, Cambridge, MA.

M

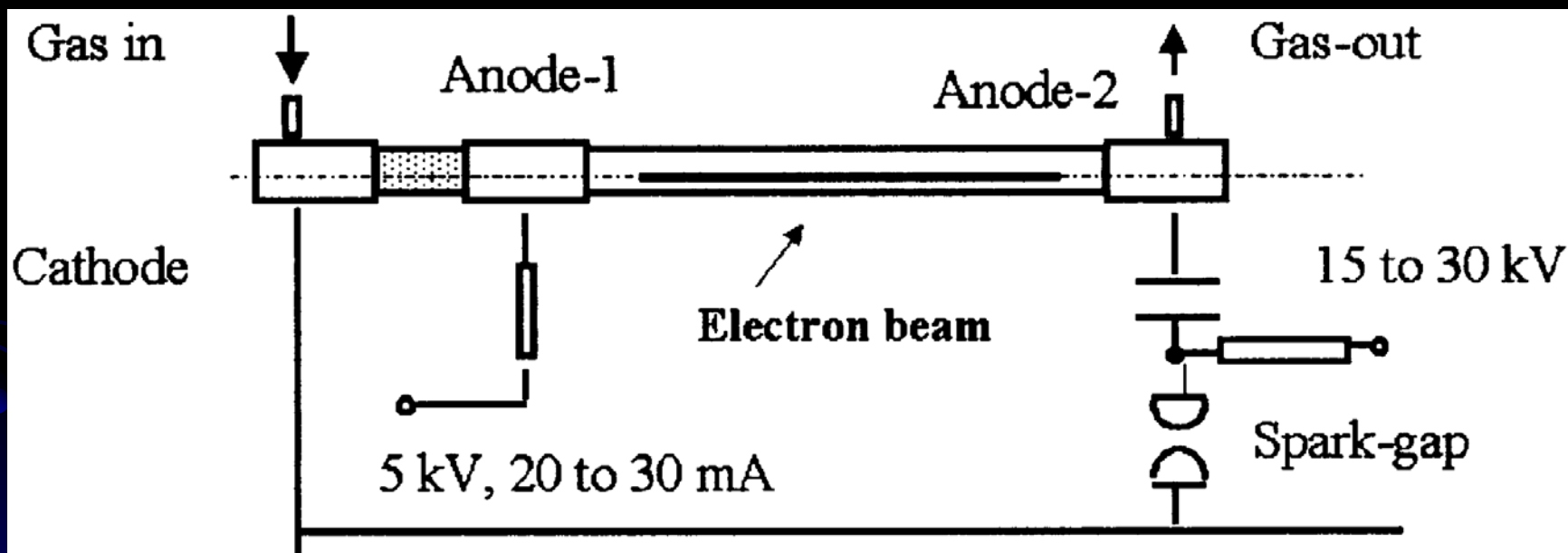


Plasma conditions

- Atmospheric pressure plasma
- Low pressure plasma

Plasma sources

- RF
- ECR
- CD
- Atmospheric arc
- Laser plasma sources



What is the plasma polymerisation technique used for?

Plasma-surface modification (PSM) is an effective and economical surface treatment technique for many materials and of growing interests in biomedical engineering, textiles, sensors [3] .

It is possible to change the chemical composition and properties such as wettability, metal adhesion, dyeability, refractive index, hardness, chemical inertness, lubricity, and biocompatibility of material surfaces.

- **Biomaterials**
- **Electronics, automotive industry**
- **Optics**
- **Drug delivery and packaging system**
- **Sterilization of materials , modification of membranes in seperation techniques, and sensor applications)**

[3] Yasuda, H., 1984, Plasma polymerization for protective coatings and composite membranes, Journal of Membrane Science, 18, 273-284.

Advantages

- extremely thin layer (A)
- good adhesion to the substrate
- pin-hole free surface
- modification of just the outer most atomic layers of a substrate
- mechanical strength of the substrate is maintained because of the highly cross-linked structure
- They allow selection of desired functional groups
- They are biocompatible and can be used for biological components such as enzymes and antibodies
- They minimize thermal degradation to the surface
- They have biocompatible characteristics
- They are an economical processing technique
- They have rapid treatment time

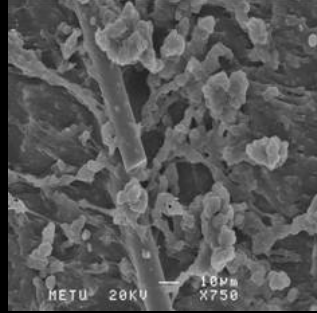
modification of just the outer most atomic layers of a substrate

selection of desired functional group

minimization of thermal degradation

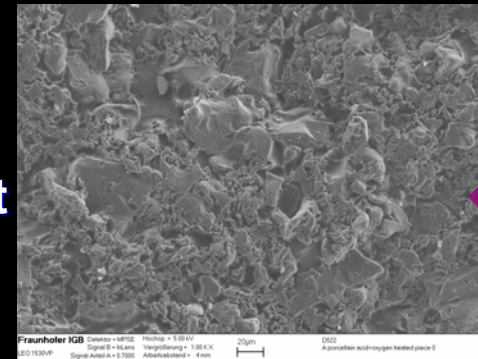
rapid treatment time

The Modification of Glass Fibres by Plasma Polymerization for Composite Glass Fibre/Acrylic Resin [4]



The quality
of the
fibre/matrix
coupling

A Novel Approach for Improvement of Interfacial Binding of Ceramics for Dental Materials Part I: Chemical Treatment and Oxygen Plasma Etching [5]



The interfaci
binding
of ceramics

Plasma Polymerization Technique to Overcome Cerebrospinal Fluid Shunt Infections, submitted to Surface and Coating Technology [6]

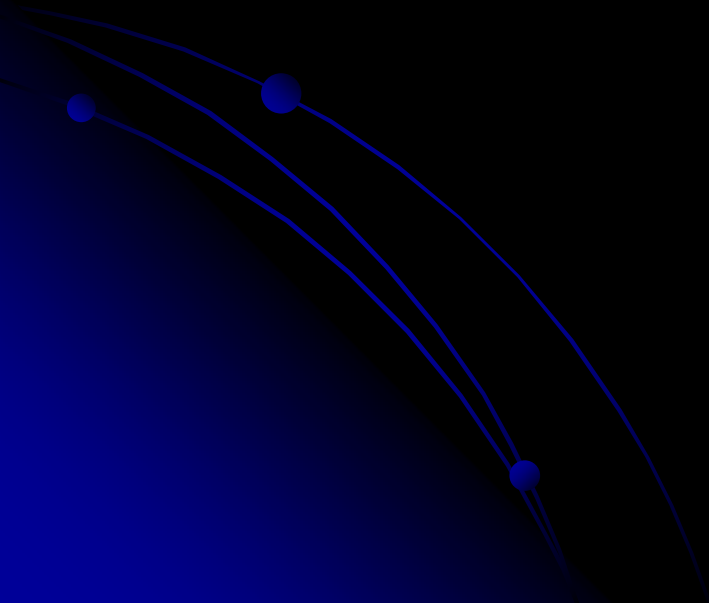
Bacteria
anti-fouling
surfaces

[4] Çökeliler, D., Erkut, S., Zemek, J., Biederman, H., Mutlu, M., The Modification of Glass Fibres to Improve Reinforcement Properties by Plasma Polymerization Technique, Dental Materials, Received 19 April 2005; accepted 05 Jan 2006, in press.

[5] Çökeliler D, Erkut S, Akdogan E, Shard A G, Özden N, Imirzalioglu P, Mutlu M, A Novel Approach for Improvement of Interfacial Binding of Ceramics for Dental Materials Part I: Chemical Treatment and Oxygen Plasma Etching, submitted to Dental Materials (May, 2006)

[6] Çökeliler D, Caner H, Zemek J, Choukourov A, Biederman H, Mutlu M, Plasma Polymerization Technique to Overcome Cerebrospinal Fluid Shunt Infections, submitted to Surface and Coating Technology (April, 2006)

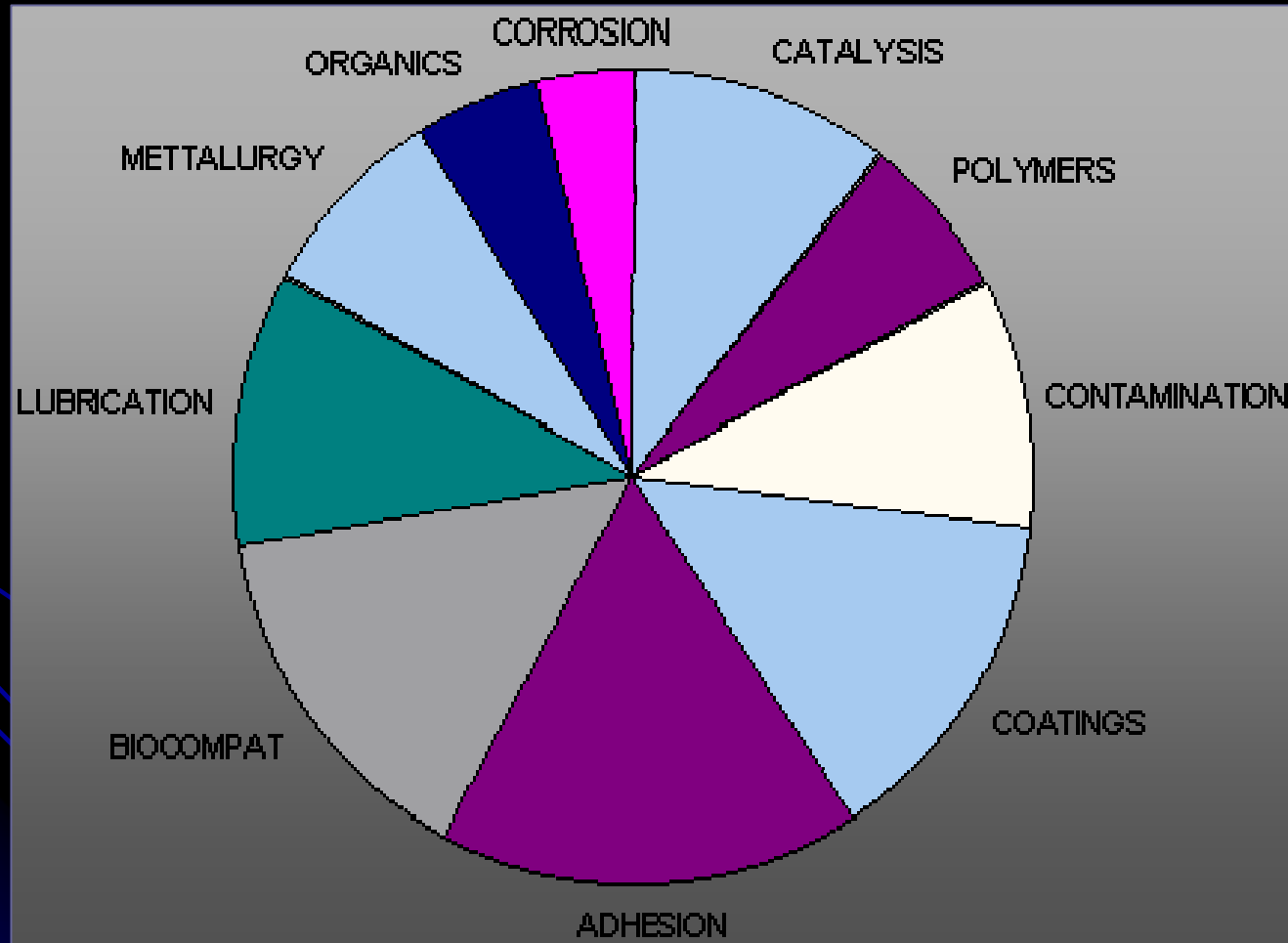
Yüzeydeki Etkileri Karakterize Edilmeli



Yüzeyin yapısı yığın yapıdan neden farklı olur?

- Doğal olarak değişebilir;
 - * Yüzeyde oksidasyon
 - * İç materyalin oksitleri yüzeyde oluşabilir.
- Fiziksel ve kimyasal olarak değiştirilebilir;
 - * Altınla ince kaplama
 - * Cu ve Zn ile kaplama
 - * Uçların sertleştirilmesi
 - * Biyomateryallerin, kan uyusabilirliğini, ıslanılabilirliği, hidrofilikliğini geliştirme

Yüzey Analiz Yöntemlerinin kullanıldığı Alanlar



Yüzey Analiz Yöntemleri

- **Spektroskopik yöntemler**

ESCA (Electron Spectroscopy for Chemical Analysis)
ya da XPS (X RAY Photoelectron Spectroscopy)

FTIR -ATR (Fourier Transform Infrared
Spectrometers with Attenuated Total
Reflectance)

- **Mikroskopik Yöntemler**

SEM (Scanning Electron Microscopy)

AFM (Atomic Force Microscopy)

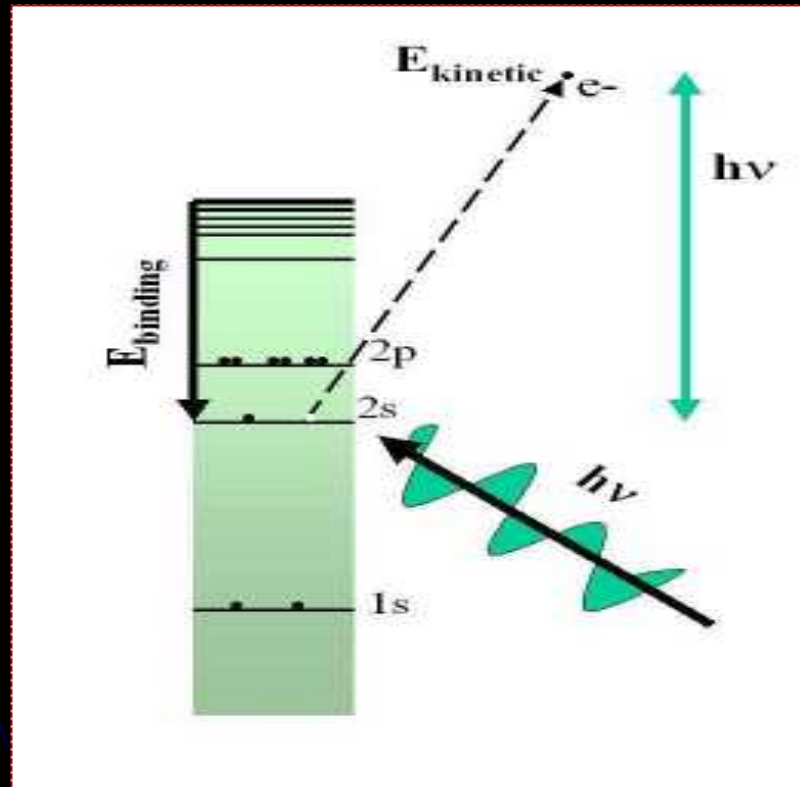
ESCA

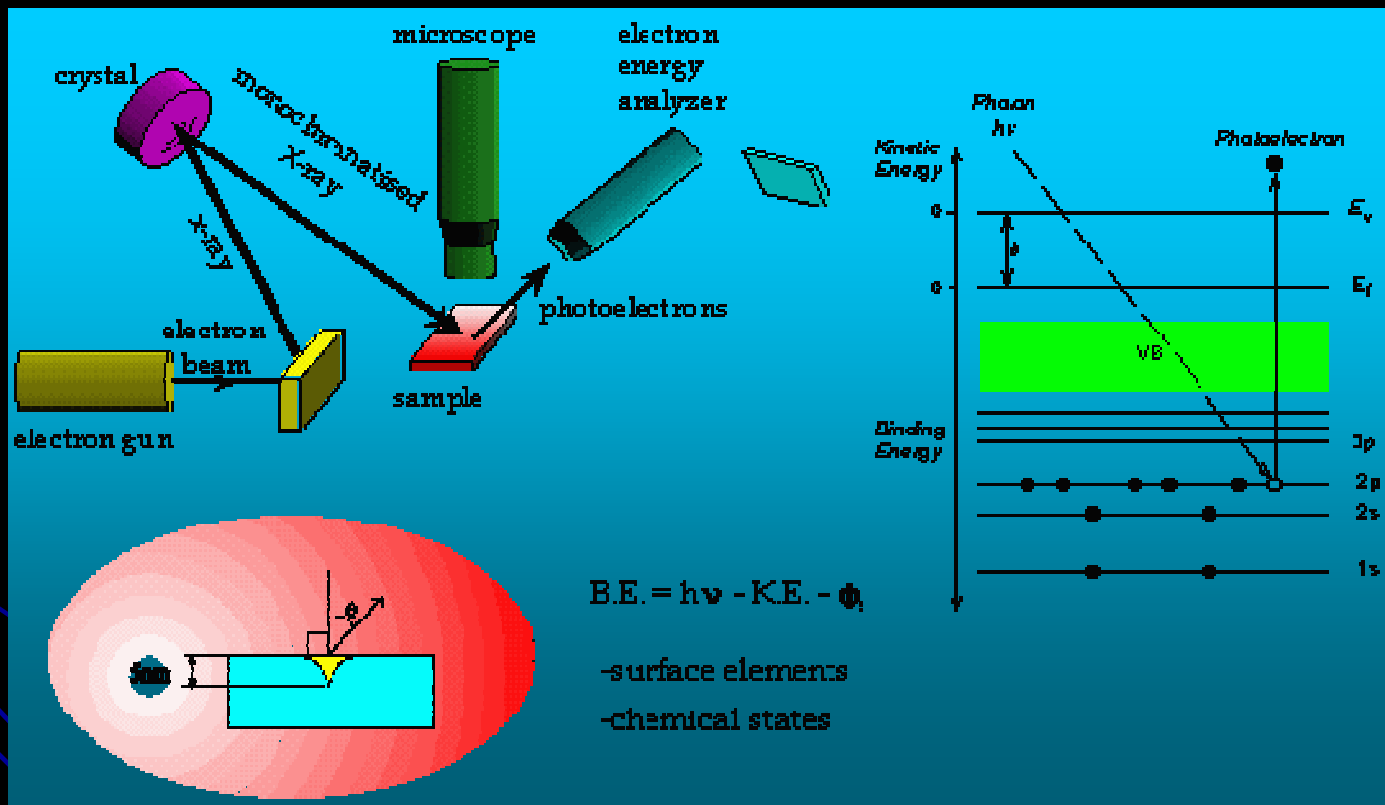
(Electron Spectroscopy for Chemical Analysis)(XPS)

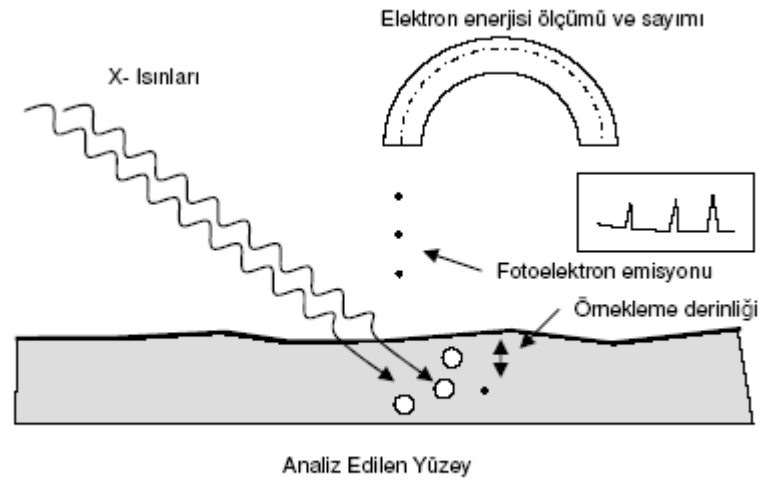
- Çalışma Prensibi

Yüzeye X ışını gönderiliyor

Kopan elektronun kinetik enerjisi ölçülüyor







Şekil 2. 6. XPS ile yüzey analizi

- Alet Ekipman

Örnek Bölümü

X ışın Kaynağı

Analizör

Manyetik Perdeleme

Dedektör

Vakum 10^{-9} torr

- Sonuç

10 nm-100 nm

H ve He dışında tüm elementler

Miktar Analizine uygun

FTIR -ATR (Fourier Transform Infrared Spectrometers with Attenuated Total Reflectance)

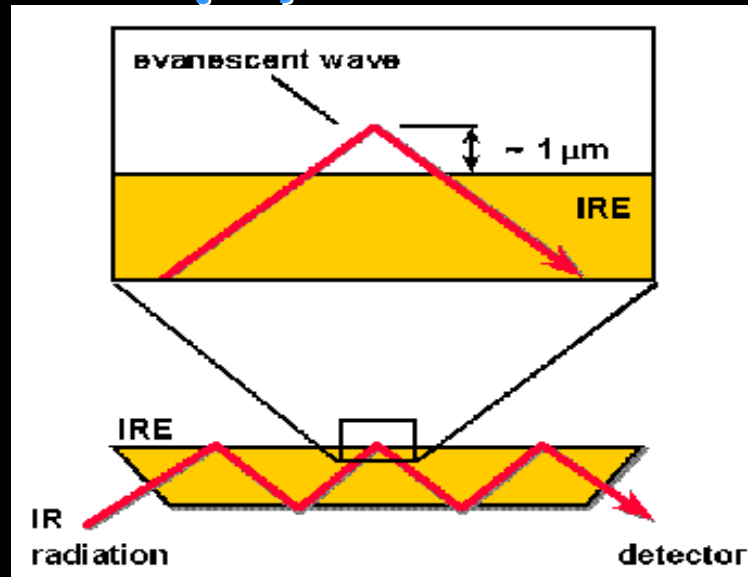
- Çalışma Prensibi

Infared ışını kullanılıyor

Örnek ATR kristali ile adapte durumda

Kristal yüksek kırılma indisine sahip, (zinc selenide, KRS-5(thallium iodide/thallium bromide), germanium and silicon)

Toz örneklerde ve sıvıda çalışılabilmektedir.

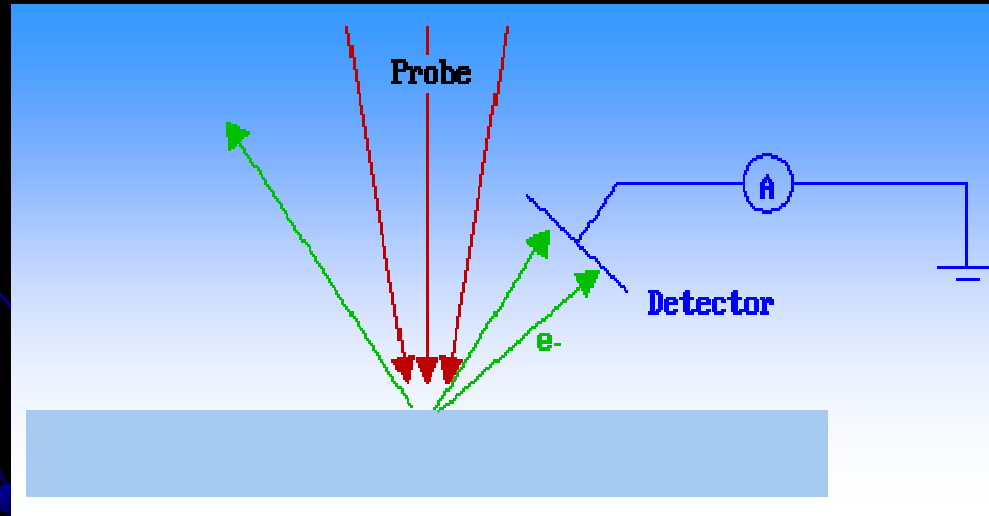


SEM (Scanning Electron Microscopy)

- Çalışma Prensipleri

Uyarılma elektron demeti ile olur.

Yüzeyden geri saçılan, ikincil elektronlar, x ışının floresansı ve fotonlarla görüntü oluşur.



■ Alet Ekipman

Örnek Bölümü(Altınla Kaplama)

Elektron tabancası

Geri saçılan ve ikincil e tutucu

Görüntü oluşturucu

Vakum(ısı ve yük)

■ Sonuç

10000 kez büyütme

3nm

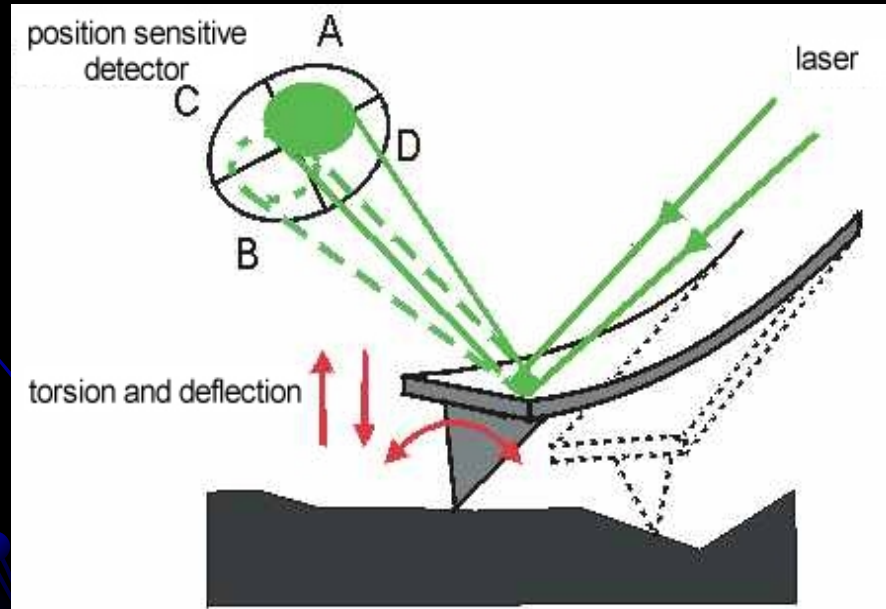
0.1-10000 um madde incelenebilir

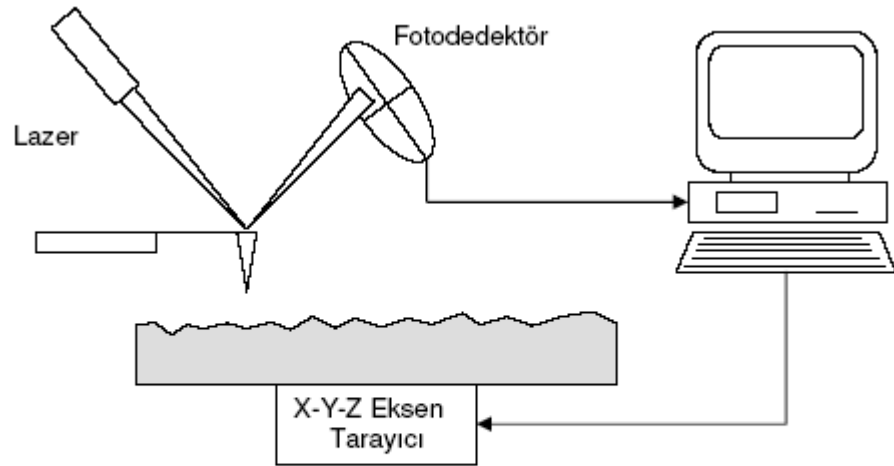
AFM (Atomic Force Microscopy)

- Çalışma Prensibi

Atomik boyutlarda kuvvet ölçülür.

Prob, yaylı kol üzerine monte ve yüzeyde 3 boyutlu hareket ettirilir





Şekil 2. 5. AKM yüzey analizinin şematik gösterimi

- Alet Ekipman

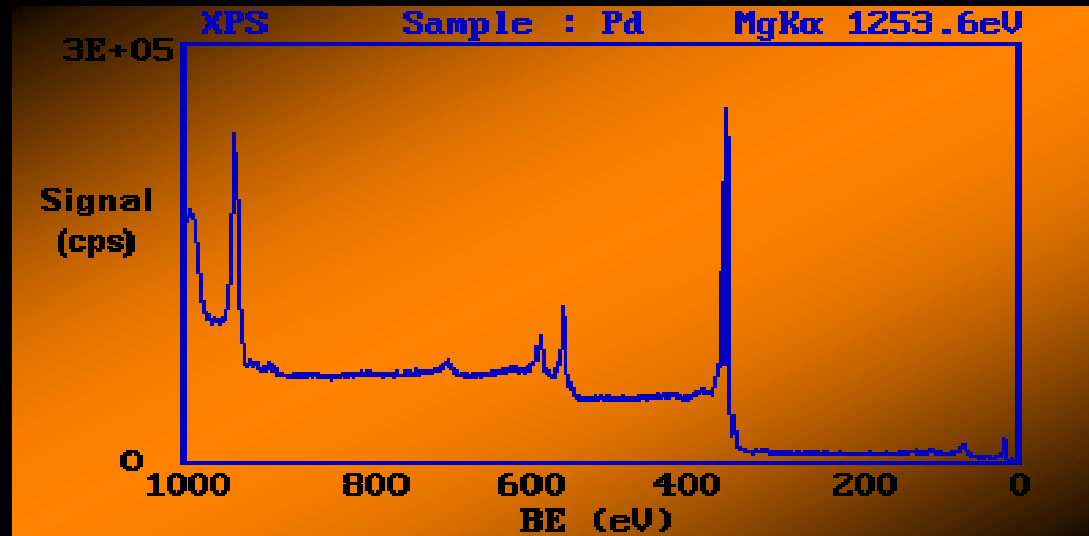
Prob (ince olmalı)
Görüntü oluşturucu
Vakum yok

- Sonuç

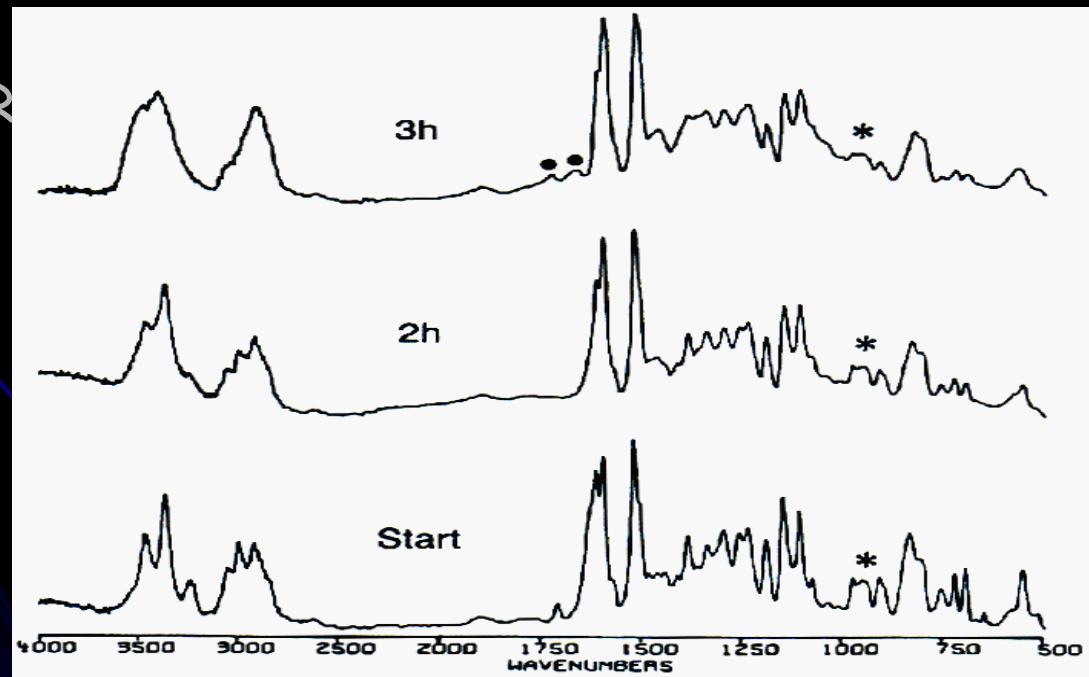
1-0.0001 um atomu görüntüleyebilir
Malzeme çok yumuşaksa deforme olabilir
Vakum yok

Spektroskopik Yöntemler

XPS

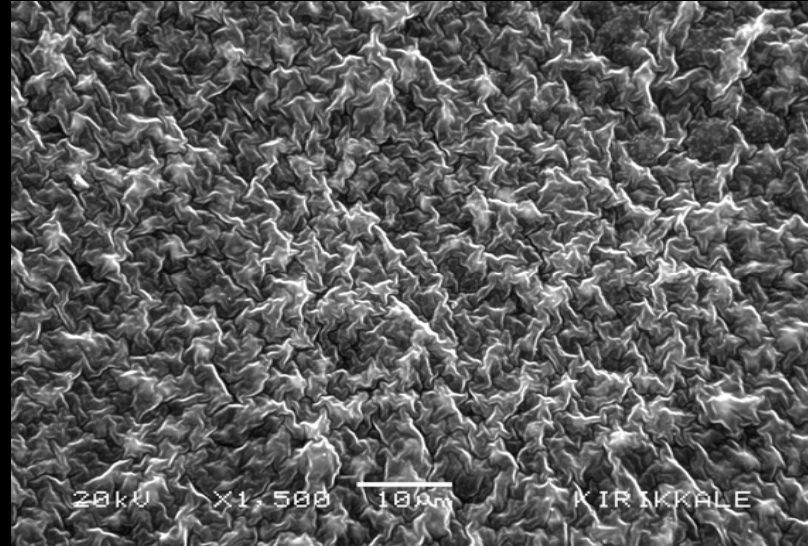


FTIR-ATR

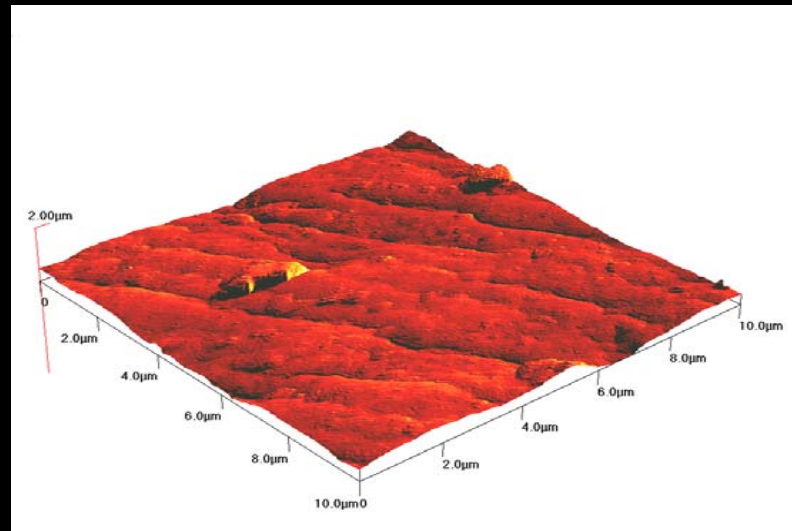


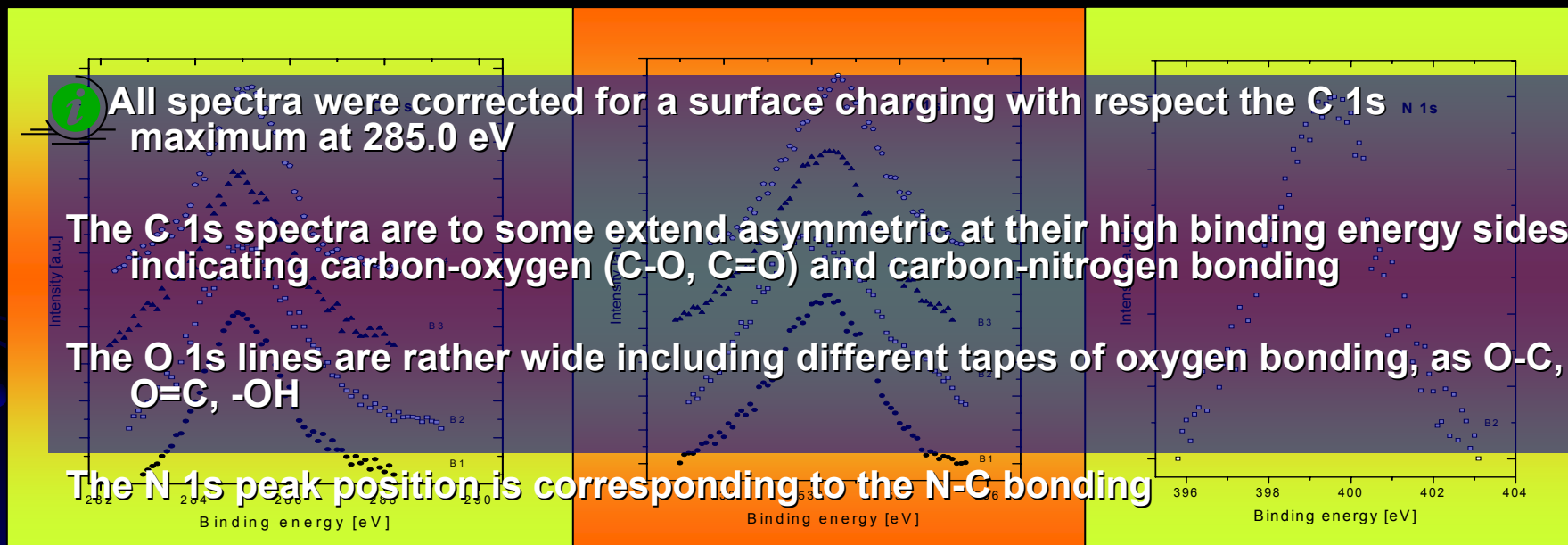
Mikroskopik Yöntemler

SEM



AFM





Core level spectra XPS of samples. B1: unmodified glass fibre

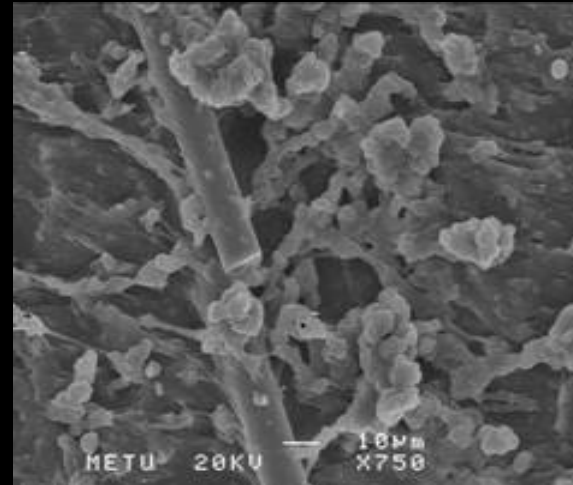
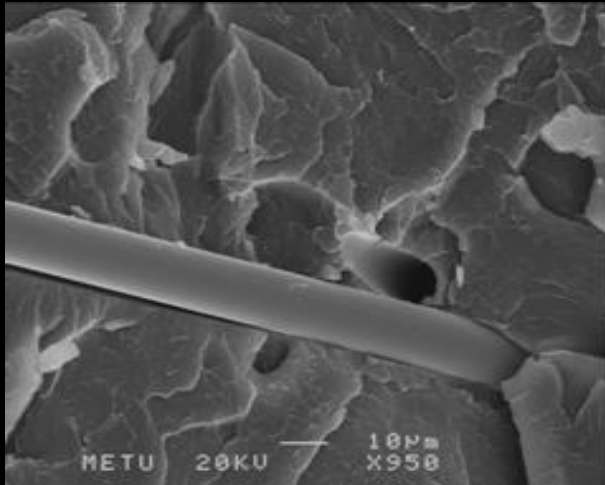
B2: modified glass fibre, monomer EDA

B3: monomer TEGDME

B4: monomer HEMA

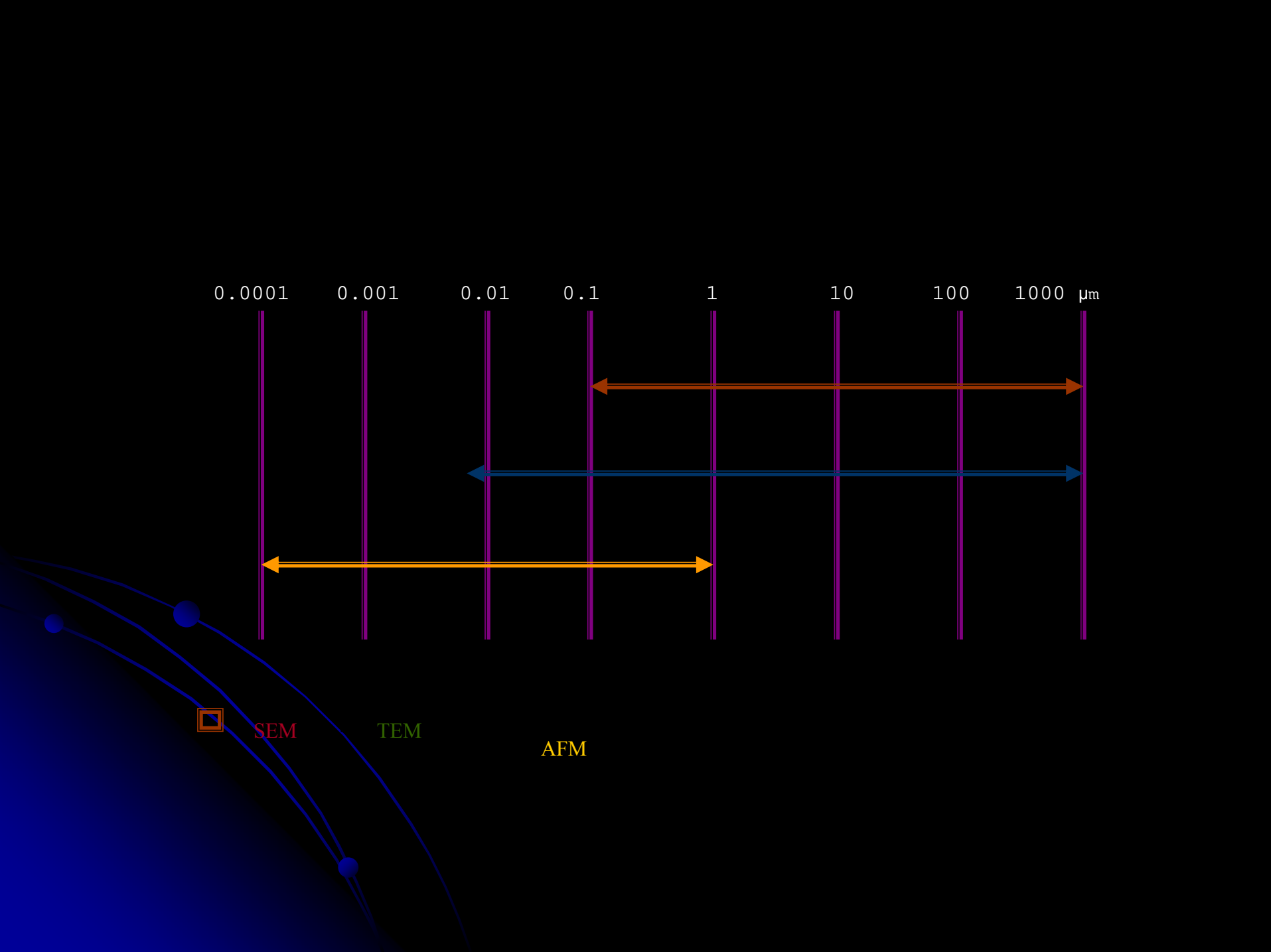


International Symposium on Plasma Chemistry, August 7th- 12th, 2005, Toronto, Canada



SONUÇ OLARAK..

<i>Technique Name</i>	<i>Analysis</i>	<i>Effective probing depth</i>
<i>X-ray Photoelectron Spectroscopy (XPS)</i>	Near surface composition. Chemical state analysis (not H and He)	100 Å
<i>FTIR - ATR</i>	Qualitative and quantitative elementary composition near surface	10000 Å



0.0001

0.001

0.01

0.1

1

10

100

1000

μm

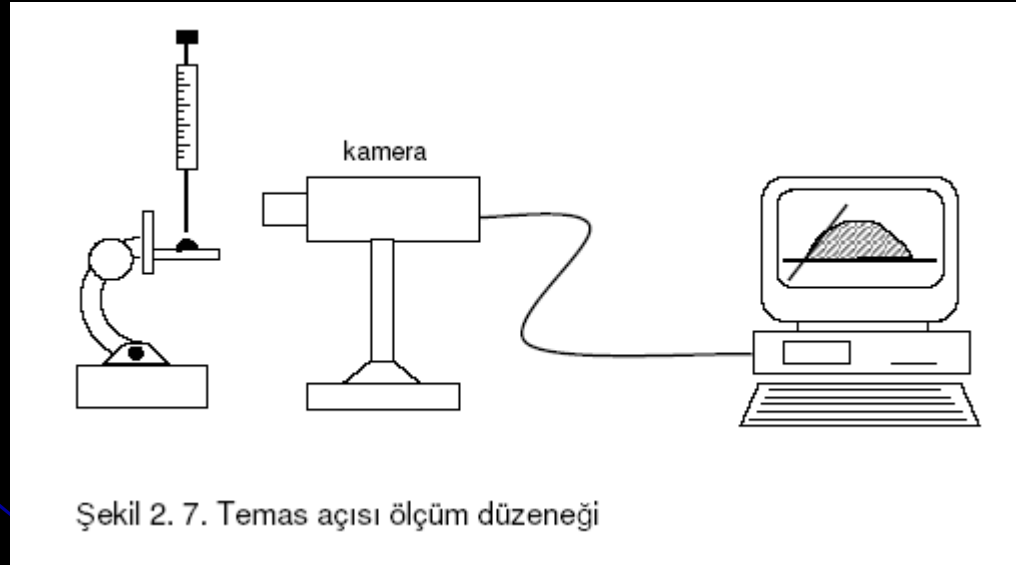
SEM

TEM

AFM



Temas Açısı Ölçümleri





The dispersive (γ_{sv}^d) and polar (γ_{sv}^p) components and total surface energy (γ_{sv}) for selected test liquids

Liquid	γ_{lv}^d (mJ/m ²)	γ_{lv}^p (mJ/m ²)	γ_{lv} (mJ/m ²)
Water	21.8	51.0	72.8
<i>n</i> -Octane	21.8	0	21.8

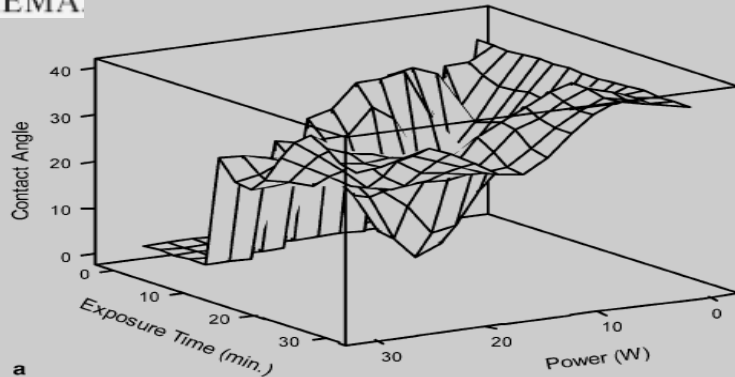
SFE components and IFE (mJ/m²) determined by contact angle measurements and geometric mean equation

Solid	SFE or IFE	Untreated	HEMA	EDA
Glass	γ_{sv}^p	37.08	48.59	47.73
	γ_{sv}^d	21.87	24.25	22.57
	γ_{sv}	58.95	72.83	70.30
	γ_{sw}^p	1.11	0.09	0.06
	$\frac{\gamma_{sw}^p}{\gamma_{sv}}$ (%)	62.89	66.71	67.90

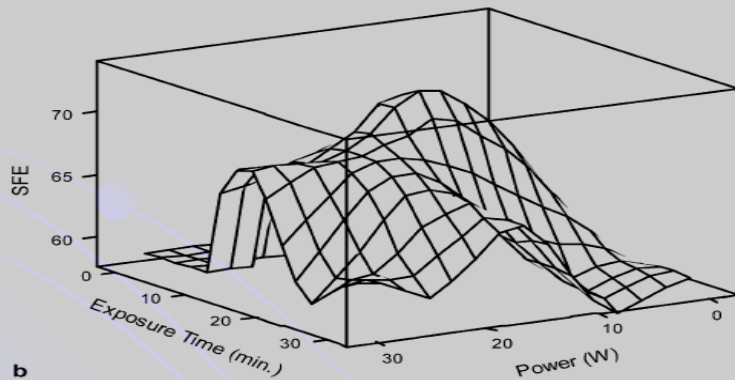
M. Mutlu et al.,
2005



HEMA

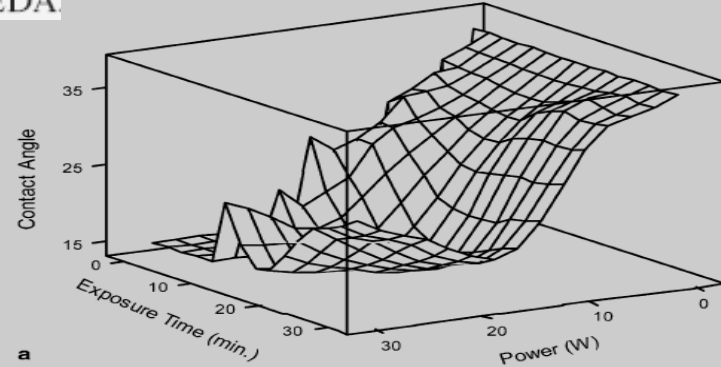


a

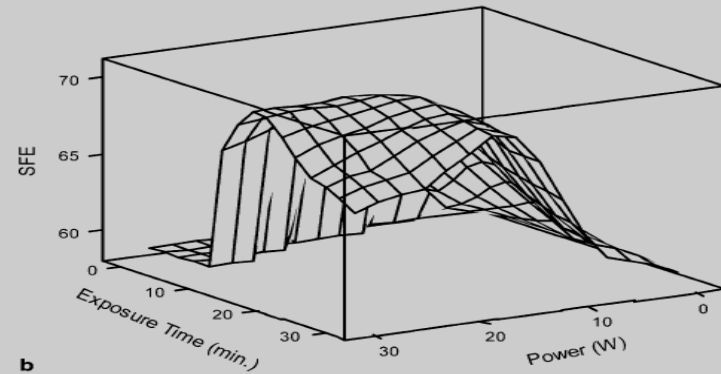


b

EDA



a



b

The effect of glow-discharge power and exposure time on contact angle (a) and surface free energy (b): substrate, glass;

The optimum plasma conditions with HEMA were determined as 15 W and 15 min for glass. The optimum parameters with EDA were determined as 20 W and 20 min for glass. PlzP-HEMA provided better hydrophilic surfaces than PlzP-EDA

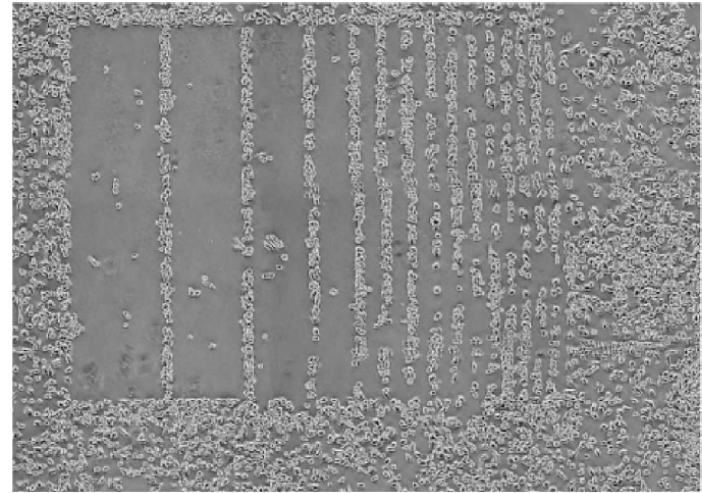
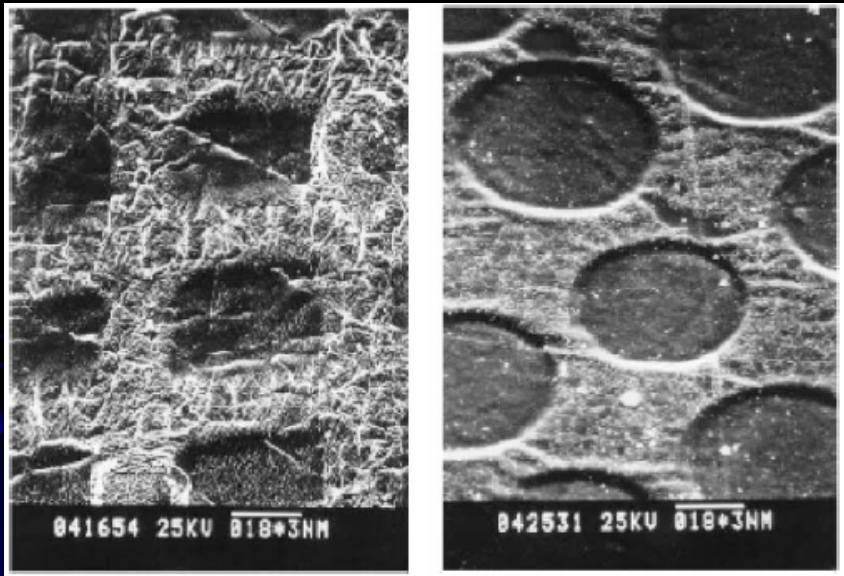


Fig. 17. Micro-patterned growth of epithelial cells (KB nasopharyngeal carcinoma cell line) on a logarithmic stripe pattern. The width of the bars is $50\ \mu\text{m}$ and their length varies between 30 and $50\ \mu\text{m}$ [10].

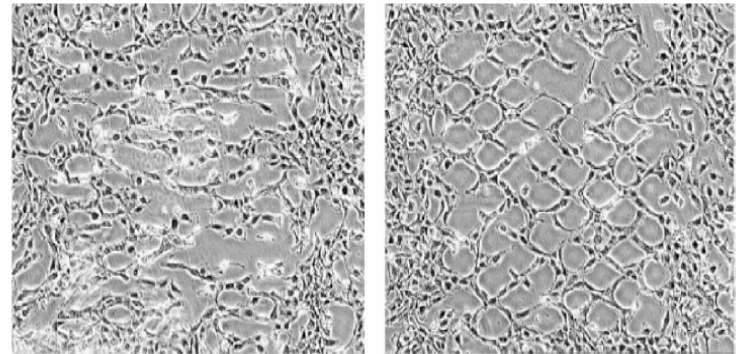


Fig. 18. Micro-patterned growth of fibroblasts (3T3 mouse fibroblast cell line) on different grid patterns. The characteristic dimension of the single pattern elements (free space) is $100\ \mu\text{m}$ and the width of the stripes is $30\ \mu\text{m}$ in each case [10].

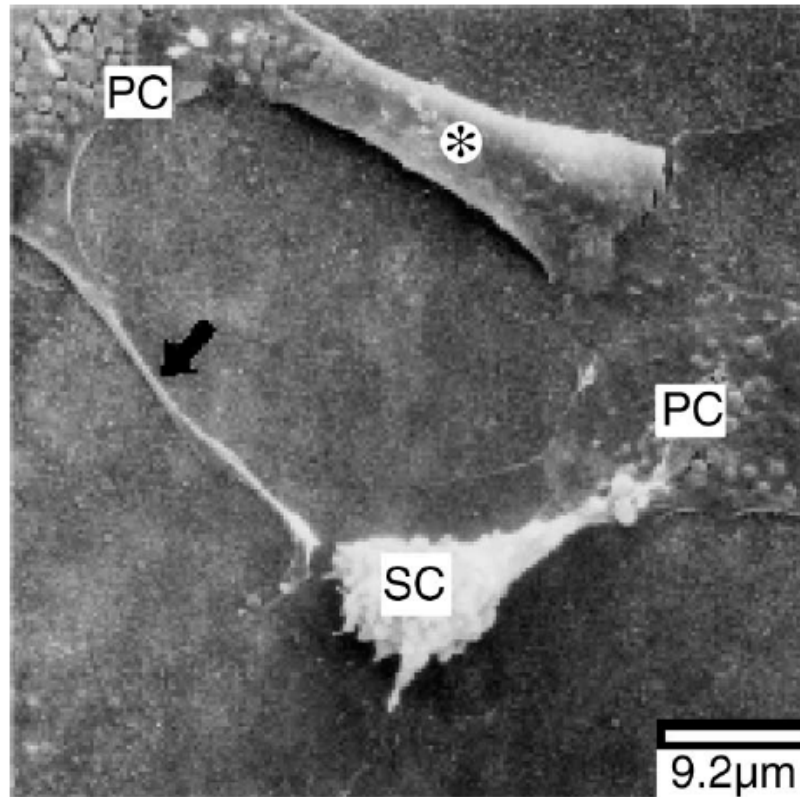


Fig. 24. SEM micrograph of osteoblast on amorphous CN film deposited on silicon after 1 week in culture. Spindle-shaped cells (SC) and well-spread polygonal cells (PC) maintain physical contact with each other through filopodia (arrow) or lamellopodia (asterisk) [126].

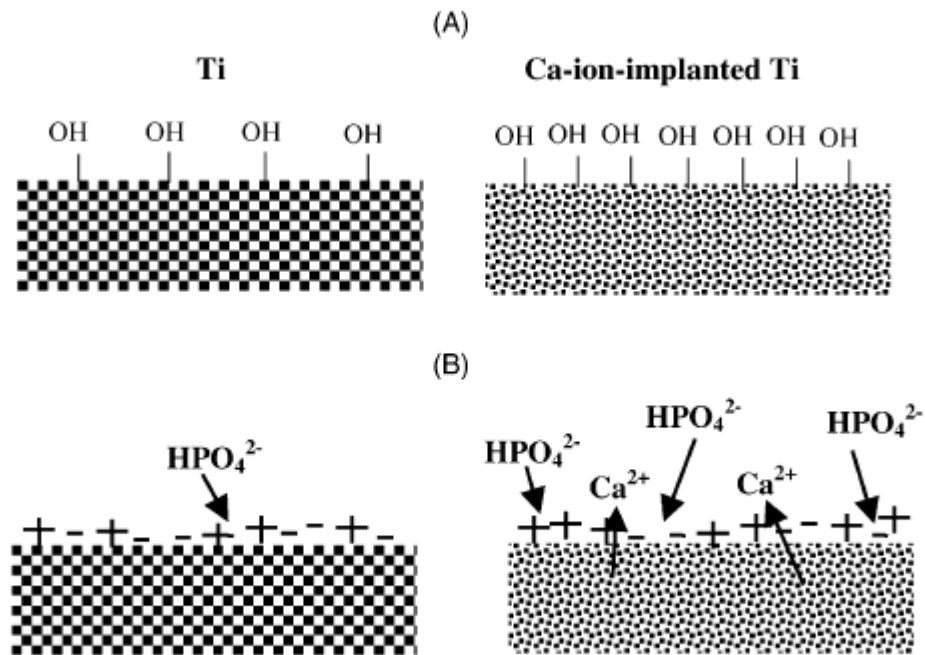


Fig. 36. Hydroxyl radicals on unimplanted and calcium implanted titanium: (A) in air, (B) in body fluid.

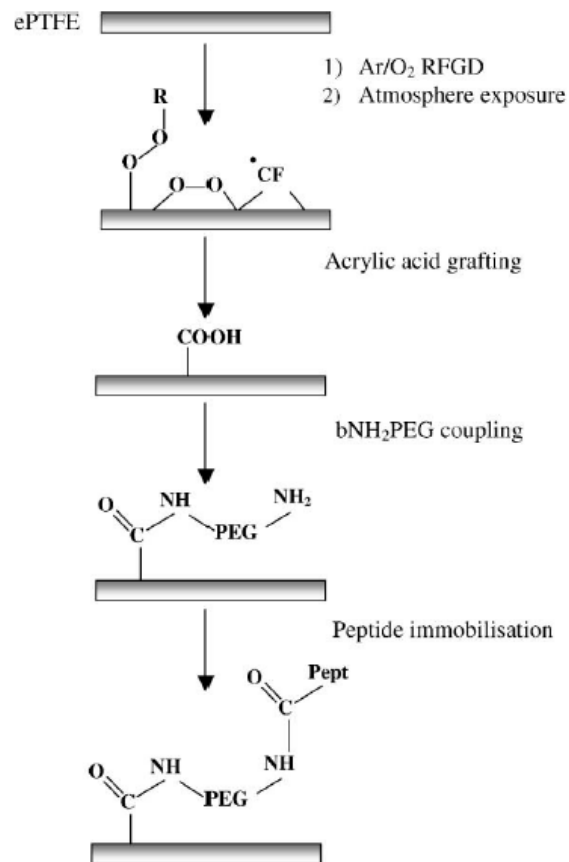


Fig. 39. Schematic of peptide immobilization [205].