Optical Imaging

NA $= \eta \sin\theta$(**Numerical Aperture**, refractive index, RI)

油镜:RI与玻璃类似,载玻片与介质之间几乎不发生折射,收集角度大

Resolution limits: ($R = \frac{\lambda}{2NA}$小)

Depth of field (Z): ~500nm

Resolution: ~200nm

Airy disk(衍射): Gaussian分布的光强度，当一个环的中心与另一个环的1st maximum ($\theta = \frac{1.22\lambda}{d} = \frac{1.22\lambda}{2R \cdot \mathrm{NA}}$)重叠时不可分辨

FRET

$$R_0{}^6 = \frac{9Q_0(\ln 10)\kappa^2 J}{128\pi^5\eta^4 N_A} \qquad E = \frac{1}{1+(r/R_0)^6}$$

Confocal Spectroscopy

对部分位置进行选择性地染色, 通过调对焦面调整被激发的分子, 扫描

Super-Resolution Microscopy

STORM(时间分辨)

在**不同的时间**点亮单个荧光分子。**Activator-reporter pair**, Activator荧光激发reporter, reporter被其他波长光quench. 单次发出600个光子, 光子数越多分辨率越高. Photo bleaching.

STED

scan, 高强度激光(破坏样品)， optical vortex产生donut-shaped images，双光子

STORM/RESOLFT	STED/PALM
多光子(Gaussian)	单光子
荧光分子的坐标	预先设定坐标
需要时间长(背景)	

AFM

平整面扫描，云母片、单晶硅

可以在水相中扫描(**原位**)

可以探测**绝缘材料**

Direct Mode:

Tapping Mode: 前端resolution取决于针尖粗细,后端取决于震动频率

Resolution: Scan rate(↓), Tapping frequency(↑),tip radius(↓), half angle(↓), force constant(↓), thermal noise, piezo response, dielectric of environment

通过对**针尖修饰**可以得到材料不同的性质

STM(Scanning Tunneling)

STM探测的是电子云密度，电子云密度高的地方电流大(**导电样品, 层状样品**)

TEM(Transmission e micro-)

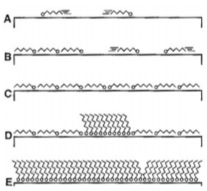
$$\lambda = \frac{h}{\gamma p} \quad \gamma = \frac{1}{\sqrt{1-(v/c)^2}}$$

$$\sigma_{elastic} = Z\pi\left(\frac{e}{V\theta}\right)^2 + \pi\left(\frac{Ze}{V\theta}\right)^2$$

$$Q_T = N\sigma_T = \frac{N_0\sigma_T\rho}{M}$$

$$\lambda_{mfp} = \frac{1}{Q_T}$$

$$P = \frac{t}{\lambda_{mfp}} = \frac{N_0\sigma_T\rho t}{M}$$



Structure: E gun, condenser lens, specimen, objective lens, projective lens, CCD

Limits: Small area, average, damage

BF-TEM

收集**透过电子与小角度散射**电子

3 contrast: mass-thickness, diffraction, phase contrast(Direct & diffracted undergo phase shifting in the material.)

Contrast in BF-TEM: composition, thickness, crystallinity

DF-TEM

收集某些特定的diffraction way对应的crystal plane

更好地分辨轻质与重质元素

HAADF

高角度散射，重质元素亮

STEM

HR-TEM

同时利用**衍射与透射电子**，可以清楚看到晶格条纹，亮暗场不代表原子位置，**调整焦平面**得到不同相

XPS

elemental composition, electronic states, chemical states, formula

Mass Spec-SIMS

Mas-charge ratio

EDS/EDX

外层电子跃迁到空穴放出X-ray，穿透能力强。可用于TEM，SEM

EELS

检测入射后能量损失的电子(Type, quantity, chemical state, collective interaction of atoms with neighbors)

EF-TEM

EELS+TEM,对不同组分染色

SEM

利用**二次电子+特征X线+背散射电子**

二次电子：表面形貌

背散射电子：不同元素contrast

specimen之后不用再聚焦

AES

内层电子跃迁激发外层电子电离

分析**表面**(~5nm)元素组成

常用于分析导体，用于SEM

Resolution: ~20nm

Plane Spacing

$$\left(\frac{1}{d_{hkl}}\right)^2 = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

Weiss Zone Law:

plane($h_1k_1l_1$)($h_2k_2l_2$)

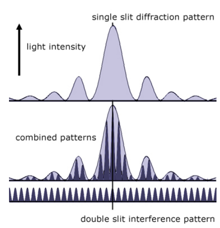
[UVW] =

$(h_1k_1l_1)\times(h_2k_2l_2)$

Single-Slit Diff

$$I = I_0 sinc^2\left[\frac{\pi x w}{\lambda L}\right]$$

$sinc(x) = \frac{\sin x}{x}$w: 缝宽



Double-Slit Diffraction

$$n\lambda = D\sin\theta = D\frac{x}{L}$$

SAED(Selected Area E Diff)

Back focal plane(衍射图像，非实像)

Single crystalline: diffraction pattern

Poly crystalline: 衍射环，没有取向，与objective lens高度相关

Amorphous: 没有环, 知distance between neighbors pdf(键长)

Raman

2 Kinds of scattering: Rayleigh, Raman(Stokes↓, anti-stokes↑)

SERS: electromagnetic, chemical +

DLS(Dynamic Light Scattering)

$D = \frac{k_bT}{6\pi\eta R_H}$ (**Input**: 黏度，温度)

Requirement: no stirring, narrow distribution, dilute, transparent, 溶剂不吸光, 溶剂折光系数不同, thermostable

Measure: D_T, Size(Z average), R_h, Polydispersity Index

Graph: Decay time(Size), Gradient (Polydispersity, more even larger)

$$G(\tau) = A(1+Be^{-2\Gamma\tau}) \quad \Gamma = D\left(\frac{4\pi n}{\lambda_o}\right)^2\sin^2\left(\frac{\theta}{2}\right)$$

Intensity $\propto r^6$, R↓ C↑, R↑ C↓ (1mL)

Static Light Scattering

Measure: Molar Mass(10^3-10^6), r_g, second virial coefficient, translational D_T, shape

Limitations: 1mL, R↓ C↑, non-turbid

Input: concentration C, Refractive index

SAS(Small Angle Scattering)

$I(Q) = N_pV_p^2(\rho_p-\rho_s)^2F(Q)S(Q)+B$

$F(Q)$: 单个粒子的作用(size shape, compo)

$S(Q)$: 颗粒之间的相互作用

用于probe重元素

SANS

Neutrons interact with **nuclei**(isotope)

截面积与原子序数没有明显的线性关系

通过调节Scattering length density(H_2O/ D_2O)调节contrast

probe**壳核结构**

	R(nm)		Invasiveness (high or low)	Elemental information	Vacuum
Confocal	200	Interior		N	N
TEM	0.005	Interior	High	With EDS, Y	Y
SEM	0.1	Surface	Low	AES and EDS, Y	
AFM	1	Surface	Low	N	N
STM	0.1	Surface	Low	N	Y
	Resolution	Origin of Contrast (RI, e density, nuclei cross- section)		Invasiveness (high, medium or low)	Typical angle range (estimate)
DLS	1-1000	Rayleigh scattering		Low	
SLS	1-1000	Rayleigh scattering		Low	
SAXS	1-200 nm	E density			8.84~0.044
WAXS	<1	E density		Low	2~160 (2θ)
SANS	1-200	Nuclei			
	Concentration	Probe Depth			Info. Aquired
		1-2nm	1-10nm	Microns	
XPS	1000ppm		Y		elemental composition, electronic states, chemical states, formula
SIMS	0.1ppm	Y			mass/charge ratio
EELS	10ppm		Y		轻质样品
EDS	1000ppm			Y	N

SAMs

M-S: ~150kJ/mol 断裂: 强酸，氧化

Odd-even effects: 偶数个C更亲水

Thiol可以通过部分氧化来调节与表面能的binding程度

Post Modification: Insertion at defect site, chemical reaction(光照生成PS后litho)

SAMs可以作为**spacer**介导粒子的自主装

不同的SAMs结构→**不同的自主装结构**

可以利用Microcontact print向基底印上thiol

SAMs: **HF with different moisture**(DNA)

SAMs: 可以作为resist

High E surfaces: silica, metals, MO_x

Low E: polymer, 小的分子晶体, graphene

Dynamic Measur: 变化越大, liquid-solid作用越弱

Block Copolymer

可以通过**活性聚合**得到

避免大范围分相, 但存在**microphase sep**.

Interaction Parameter(χ): 代表ΔH

Surface energy

Bubble: $\Delta P = 2\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$

Young-Laplace: $\Delta\mu = 2\gamma\Omega/r$:

$$\ln\left(\frac{P_c}{P_\infty}\right) = \ln\left(\frac{S_c}{S_\infty}\right) = \frac{\gamma\Omega\left(R_1^{-1}+R_2^{-1}\right)}{kT} = \frac{2\gamma V_m}{rRT}$$

Surface energy: $\gamma = \frac{1}{2}N\varepsilon\rho_a$

Surface Stabilization

Reducing surface energy: 表面弛豫, 表面重构, 表面吸附，composition segregation

P.Z.C: E = 0.06(p.z.c - pH)

产生表面电荷的方式: 离子的选择性吸附, 带点物种的解离, 离子替代, 电荷逃逸/累计, 物理吸附带点物种

Surface potential: $E = \frac{2.303RT}{F}\log(c/c_{zp})$

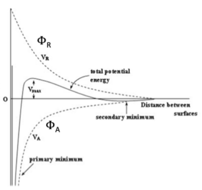
$E \propto e^{-\kappa(h-H)}$ H: double layer thickness

$\kappa = (F^2 I/\varepsilon\varepsilon_0 RT)^{1/2}$

DLVO theory:

$\Phi_R = 2\pi\varepsilon_r\varepsilon_0 r E^2\exp(-\kappa S)$

$\Phi_A = \frac{-Ar}{12S}$ if s<<r



双电层薄时可能出现 **secondary minimum**.

Electro stab. 动力学稳定

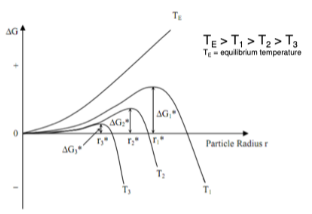
Steric stab. 动力学稳定

不良溶剂+低覆盖度: 先降后升

Homogeneous nucleation

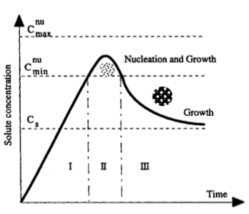
热力学: $\Delta G = -\frac{4\pi}{3}r^3 kT\ln\frac{C}{C_0} + 4\pi r^2\gamma$

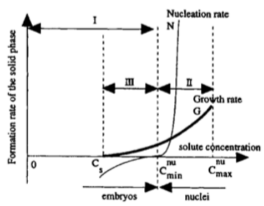
$r^* = -\frac{2\gamma}{\Delta G_v}$ $\Delta G_v^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$



Lamber Diagram:

Nucleation rate





$$R_N = \left\{\frac{C_0 kT}{3\pi d^3\eta}\right\}\exp\left(\frac{-\Delta G_v^*}{kT}\right)$$

Distribution:

diff. Controlled: $\frac{dr}{dt} = \frac{D(C-C_0)V_m}{r}$ D↓

Rxn. Controlled: $\frac{dr}{dt} = kr^2$ D↑

Multi layer: $\frac{dr}{dt} = k$ D↓

Heterogeneous Nucleation:

$\Delta G = a_3 r^3\Delta\mu_v + a_1 r^2\gamma_{vf} + a_2 r^2\gamma_{fs} - a_2 r^2\gamma_{sv}$

$a_1 = 2\pi(1-\cos\theta)$ $a_2 = \pi\sin^2\theta$ $a_3 = 3\pi\left(2 - 3\cos\theta + \cos^2\theta\right)$

$r^* = \frac{2\pi\gamma_{vf}}{\Delta G_v}\left\{\frac{\sin^2\theta\cdot\cos\theta + 2\cos\theta - 2}{2 - 3\cos\theta + \cos^3\theta}\right\}$

$\Delta G^* = \left\{16\pi\gamma_{vf}/(3(\Delta G_v))^2\right\}\left\{2 - 3\cos\theta + \cos^3\theta/4\right\}$

Top-Down

Photo Lithography (~10nm)

Positive resist: 光照后水溶 **Neg**: 光照后聚合，难溶

DRIT(Deep reactive ion etching, High): 低温形成直的孔道

Particle Etching(E beam lithography, fairly high)

Nanoimprint Lithograohy(NIL, ~5nm), Si stamp印poly

Plasma cleaning: O2去除有机物，Ar去除无机物

Nanosphere Lithograohy: PE小球, oxygen plas, CVD/PVD

Microcontact Printing: PDMS图章,比nanoimprint res低

AAO template(5~1000nm, hexagonal packing): 作为电化学还原的模板(Al_2O_3+HNO_3, Al+NaOH)

On-wire Lithography: Au/Niwire, 在wire一侧sputter Au

0D material

Au NPs

柠檬酸钠还原(>10nm, 80°C): T↑ R↓↑ D↓↑

Brust-Schiffrin(<5nm): Phase Transfer, $NaBH_4$ reduction, alkanethiol protection 丙酮ligand exchange可以得到>5nm

Seed Mediated Growth：多种形貌

Ag NPs

Polyol Synthesis: 醇(还原剂+stabilizaer)原位氧化生成醛，种晶介导生长，生成多种形貌的晶体(添加剂影响)

Pt NPs

NaOH + $H_2PtCl_6.6H_2O$, +HCl PVP stab.

Semiconductor

原子半径越大，**粒子尺寸越大** 对应的**band gap**越小

Brus's $E_g^* = E_g^{bulk} + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R}$

Bulk, 量子效应(空穴质量小时量子效应明显，半径小时量子效应占主导)，库伦引力

缺陷(**deep trap**)会导致电子能更好的地在价带与导带之间导通，改变吸光频率

Caps: TOPO不导电，很难隧穿; SnS2导电, 吸收λ变长

合成：TOPO溶液加热除气, Me_2Cd-TOP, TOP-Se(230°C) or (TMS)2Se (-100°C)生长温度低很多

不同形状: TOP+S→TOPS, CdO + HPA(酸,稳定)洗涤: 酸洗，+不良溶剂（大颗粒先沉淀）

Ball milling,

Electrospraying

LSPR

纳米粒子尺寸小于光波尺寸, quasi-static

Lateral dimension < δ_{diel}

影响因素: diameter(R↑λ↑), shape(nanoshell **scattering+absorption**, nanosphere+rod **absorption**)

三角形的nanoplate会有三个峰 (2个dipole+1个quadrupole)

粒子越小对应的**荧光效应**越强

Spectra: ligand&medium($\varepsilon_s - \varepsilon_m$)折光系数差距越大, ligand所占体积越大，波长变化越多

LSPR coupling: 间距越小，对应的波长越长

1D material

Electrospinning(非单晶), **Evaporation-Condensation**

VLS(Vapor-Liquid-Solid)

通常用于生长**Si纳米线**以及**半导体纳米线**(两者间溶解度低)，生长纳米线的宽度被droplet大小决定

Template Directed Growth

可用于生成金属, 金属氧化物, 或者Polymer

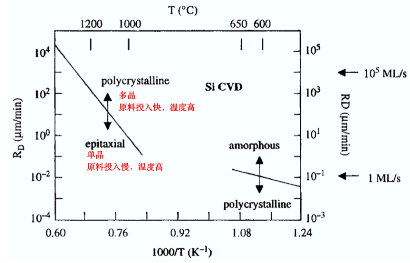
Electro chemical deposition:

Electroless chemical deposition: Polymer中空(实心polymer可以通过Nanosphere lithography)

2D Material

Island: $\gamma_{sv} < \gamma_{sf} + \gamma_{vf}$ **Layer**: $\gamma_{sv} = \gamma_{sf} + \gamma_{vf}$

I-L: $\Delta G^* = \left\{16\pi\gamma_{vf}/(3(\Delta G_v + w))^2\right\}\left\{2 - 3\cos\theta + \cos^3\theta/4\right\}$



PVD

蒸发(10^{-3}~10^{-10} torr)：LiF, Al, Ca, Ti, Cr, Au, C_{60}很难形成复合膜

Molecular Beam Epitaxy(10^{-10}torr): 元素供给枪，温度太高使其快速脱附，温度太低容易产生缺陷

Sputtering(100torr): 存在低压Ar，被电离轰击阴极

CVD(10~760torr)

复杂形貌材料的表面修饰: 金属，MOx, MCx, MNx,特别小的孔很难扩散进去

Metal Organic CVD: 通常生成**multilayer structure**

ALD

可以精确控制层数(0.5nm~几百nm)

Sol-gel process

金属前驱体水解生成colloidal suspension(sol)，sol之间发生condensation生成gel, 可以用于生成金属氧化物

Spin-Coating

Applying - rotating - drying - repeating