2009 spring

Microstructural Characterization of Materials

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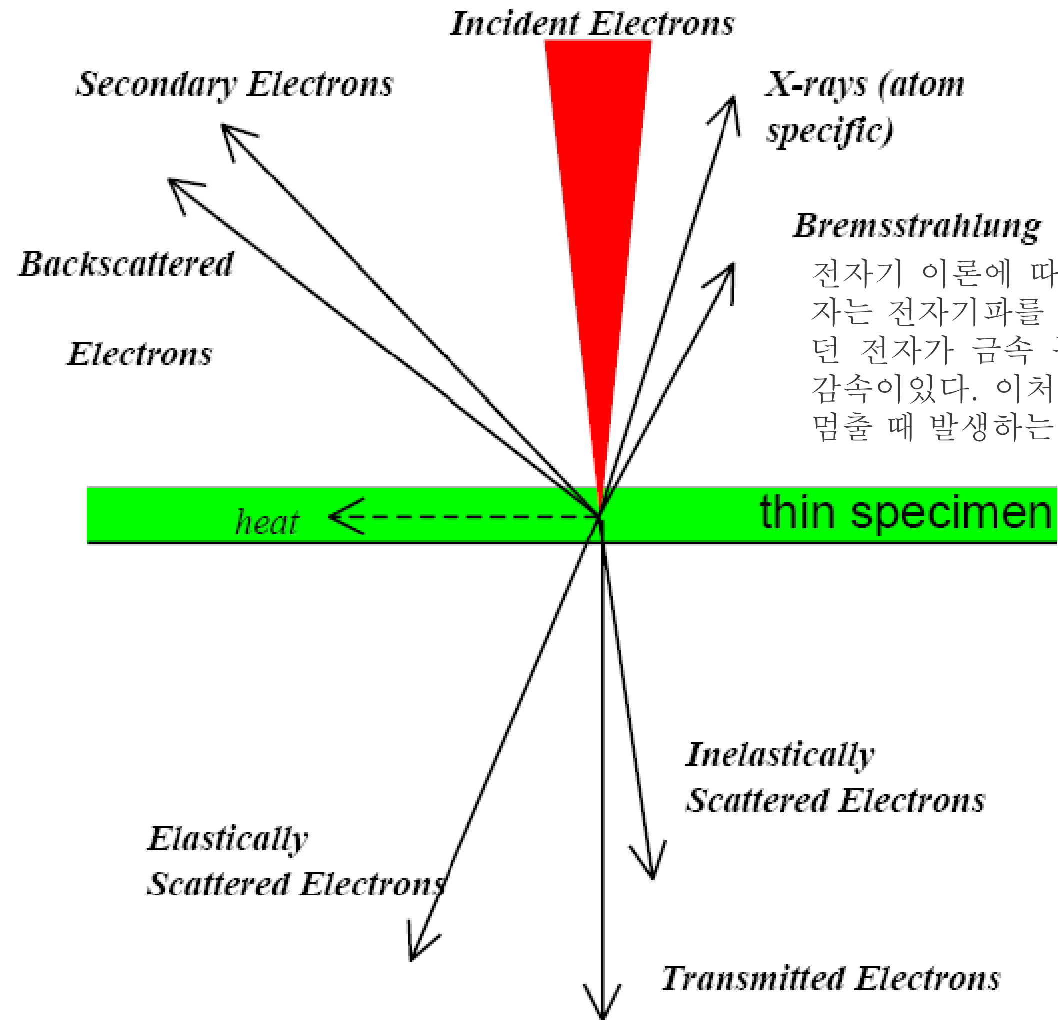
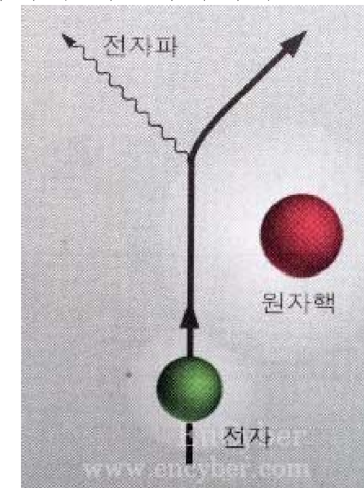
Interaction of high energy (~kV) electrons with (solid) materials-II

Interaction with a thin specimen (TEM & STEM)



제동복사 [制動輻射]

전자기 이론에 따르면 가속이나 감속되는 전자는 전자기파를 발생 시킨다. 빠르게 움직이던 전자가 금속 등에 부딛쳐 갑자기 멈추면 감속이있다. 이처럼 빠르게 움직이던 전자가 멈출 때 발생하는 복사가 제동복사이다.



The instruments and techniques

- Stationary Electron Beam

-- TEM: CTEM SAD/BF/CDF/WBDF, HRTEM

-- AEM: CBED, NBD, EDS, EELS, and EFTEM

- Conventional TEM/ Selected Area Diffraction/ Centered DF/Weak Beam DF

- Convergent beam ED/ nano beam D/ energy dispersive spectroscopy/ Electron energy loss spectroscopy/ Energy filtered TEM

- Scanning Electron Beam

-- STEM (BF, DF, and HAADF)

High-angle annular DF

-- SEM (SEI, BEI)

-- SEM + WDS = EPMA

Wave length dispersive spectroscopy/ Electron probe micro-analyzer

- Modern TEMs are all capable of HR works, but for some analytic works, attachments such as EDS and EELS must be added.

AEM vs. Conventional TEM

(Differences in aimed signals)

- CTEM and HREM deal mainly with the **elastically scattered** electrons.
- AEM deals mainly with the **in-elastically scattered** electrons and their resulting X-rays (by EELS or EDS) for the composition determination. But **elastically scattered** electrons are also collected to obtain structural information (by STEM).

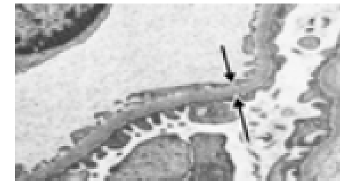
AEM vs. Conventional TEM

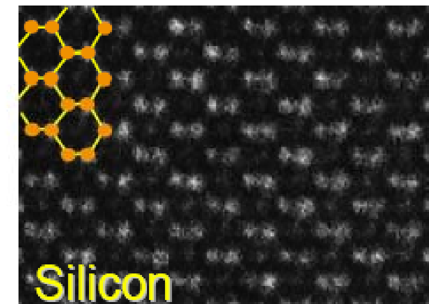
(Differences in Instrumentation)

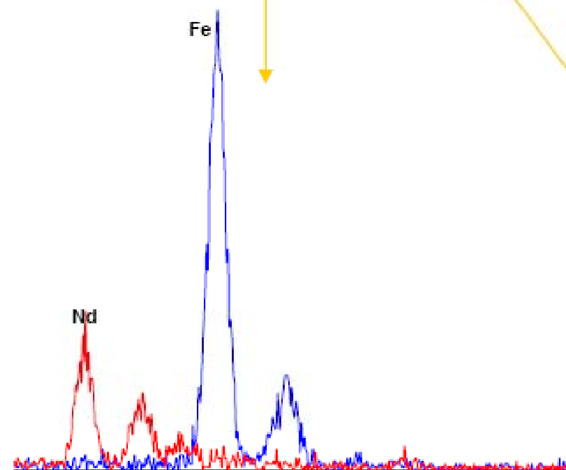
- Different illumination requirements: parallel illumination for CTEM (and HRTEM) but conical illumination for AEM
- Different designs for the objective lens to match the illumination system
- With analytical attachments: EDS for characteristic X-rays, EELS for in-elastic scattered electrons, and annular detectors for incoherent elastic electrons.

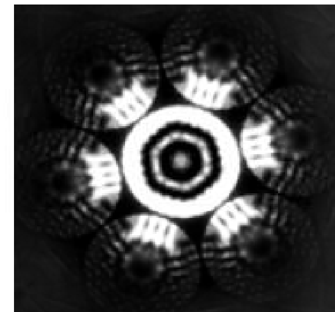
Types of Information from TEM

- Image
- Structure
- Chemistry





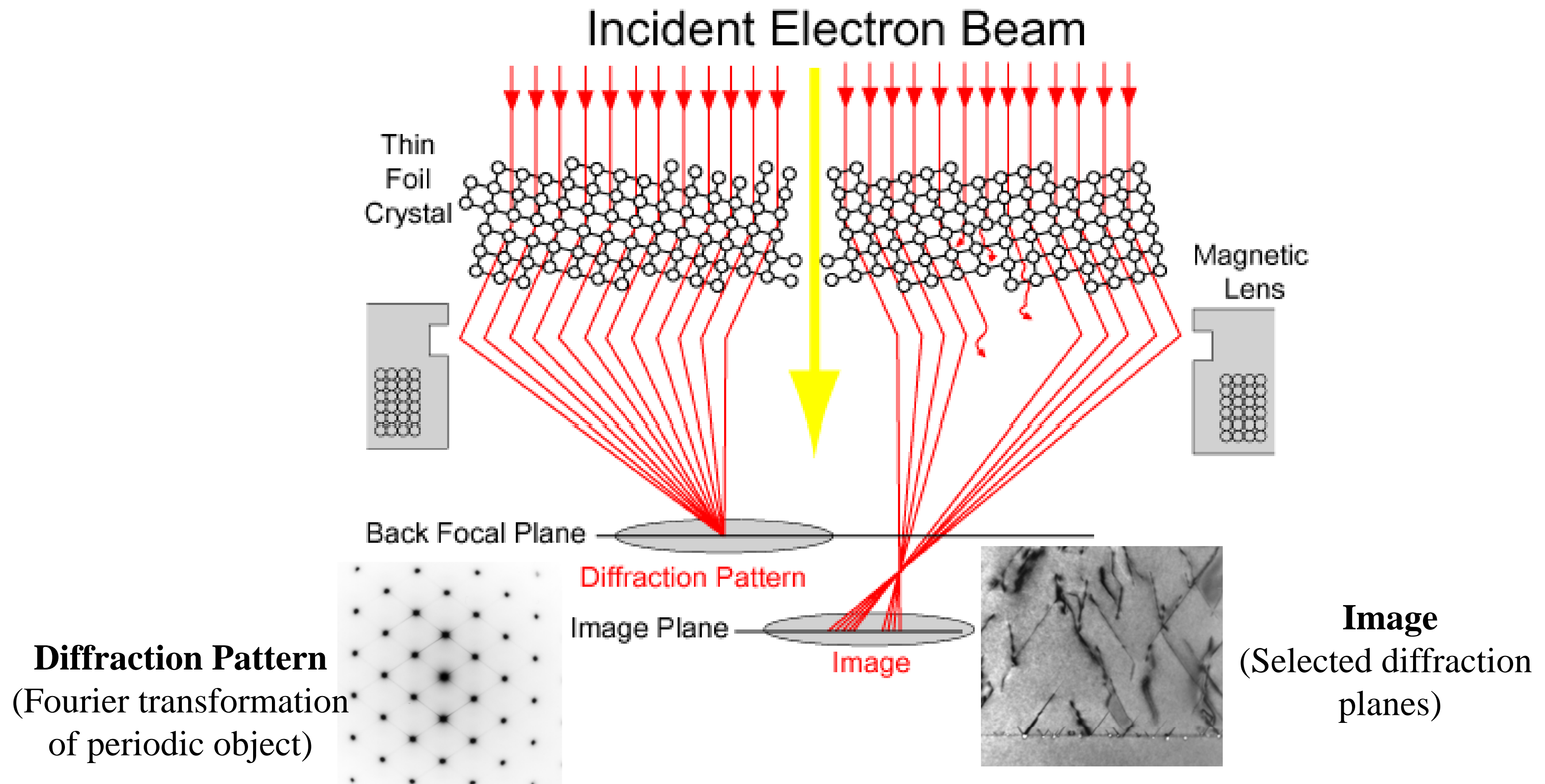




Examples of TEM applications to the characterization of Materials

- Morphology (imaging): CTEM (BF,DF), HRETM, and STEM (BF,DF, and HAADF)
- Crystal Structure (diffraction): SAED, NBED, and CBED
- Chemistry: composition (EDS,EELS, and STEM HAADF), chemical state (EELS)

Image and Diffraction



- **Diffraction occurs from the planes nearly parallel to the beam direction**

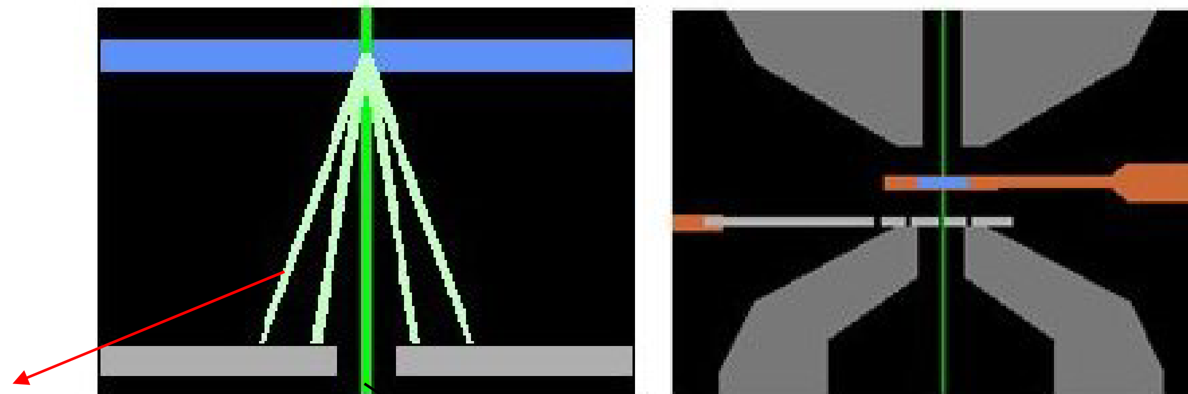
$$\lambda = 2d \sin\theta_B, \text{ where } \theta_B < 0.5 \text{ degree}$$

Bright-Field Image

✓TEM 관찰시 주로 많이 이용하는 방법으로서 대개 이미지가 밝기 때문에 명시야상으로 불리움

✓전자빔이 시편에 충돌하면 시편과의 상호간섭에 의해 광축으로 부터 벗어남

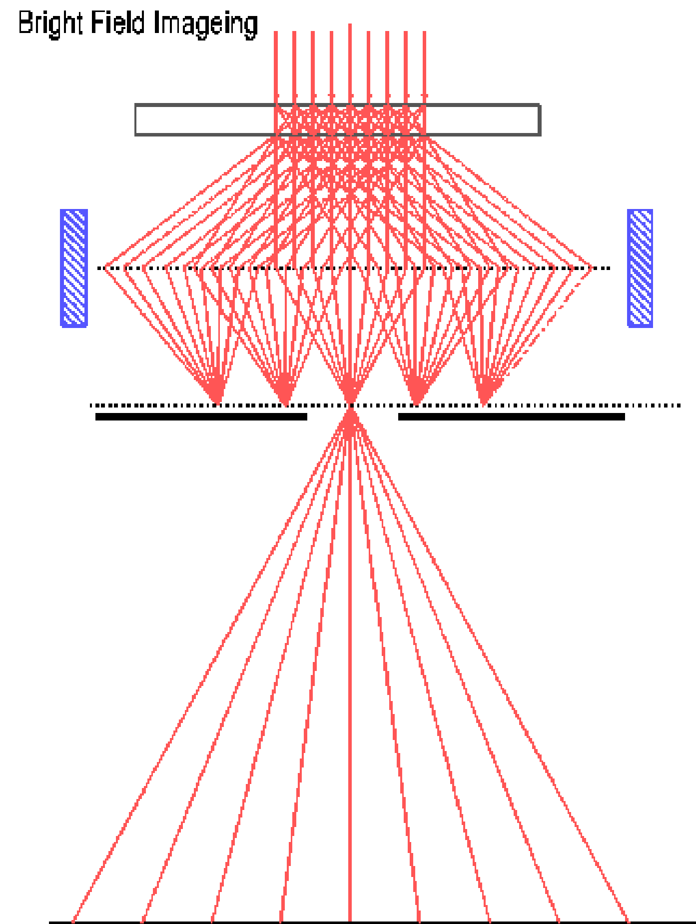
✓산란된 전자들은 조리개에 의해 차단되고, 광축에 가까운 투과된 전자빔만으로 image형성

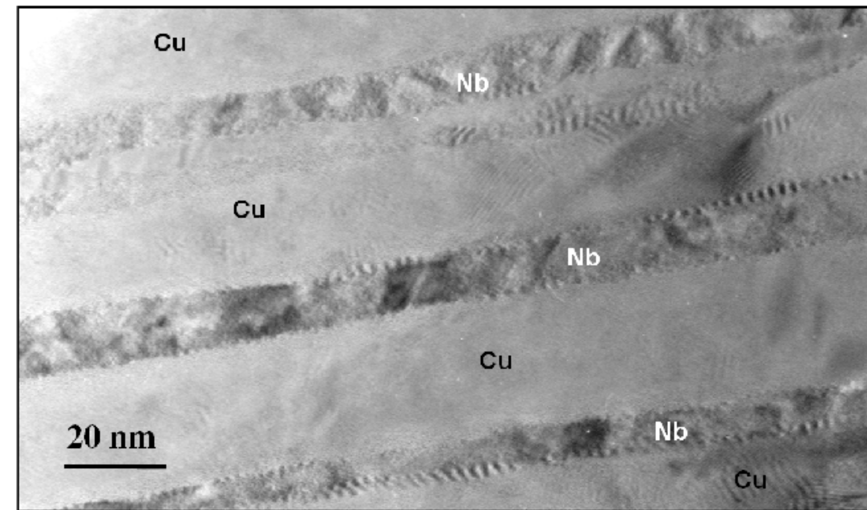


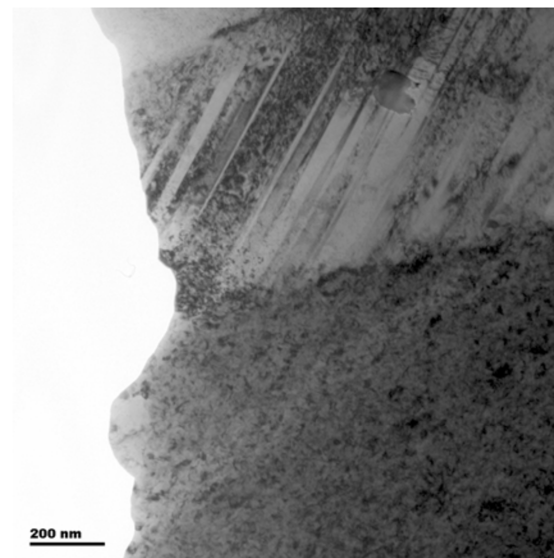
Refraction beam

Trasmission beam

Bright-Field Image

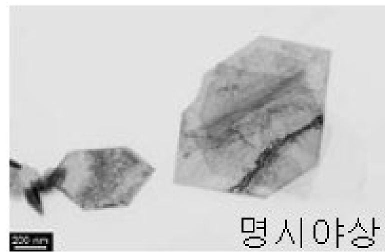


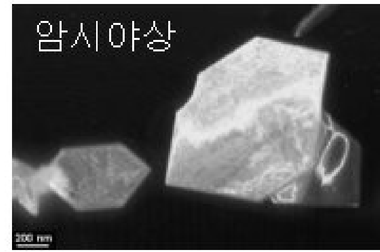


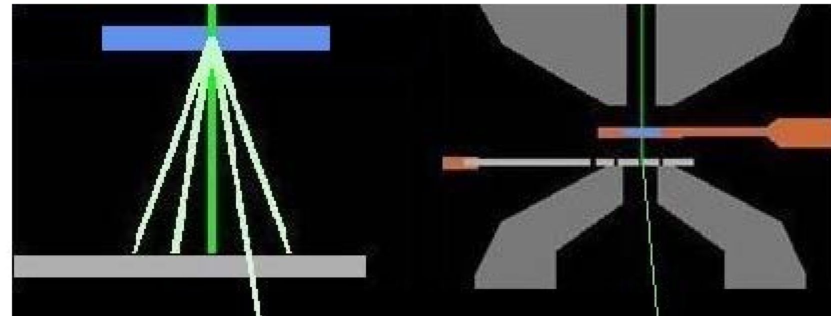


dark-Field Image

회절패턴이 형성되는 높이에 위치한 objective aperture를 이용하여 투과된 전자비임을 차단하고 회절된 전자비임을 이용하여 이미지를 형성하는 방법







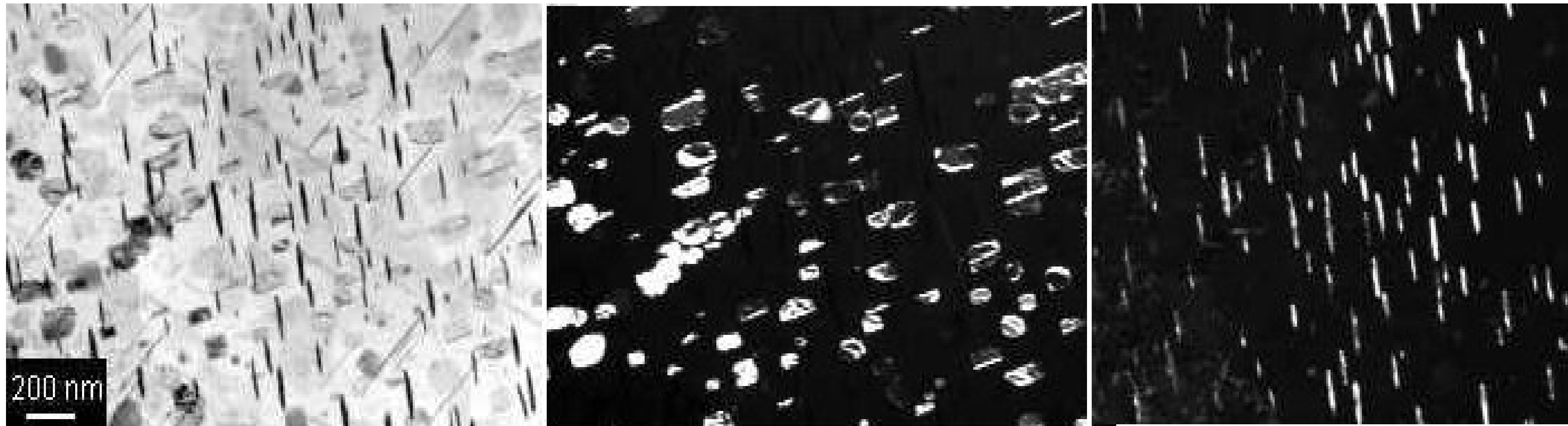
✓명시야상과 암시야상의 차이

결정이 굽어져 있고 입사 전자빔에 대한 결정면의 방향이 다르기 때문에 회절에 영향줌으로 발생

dark-Field Image

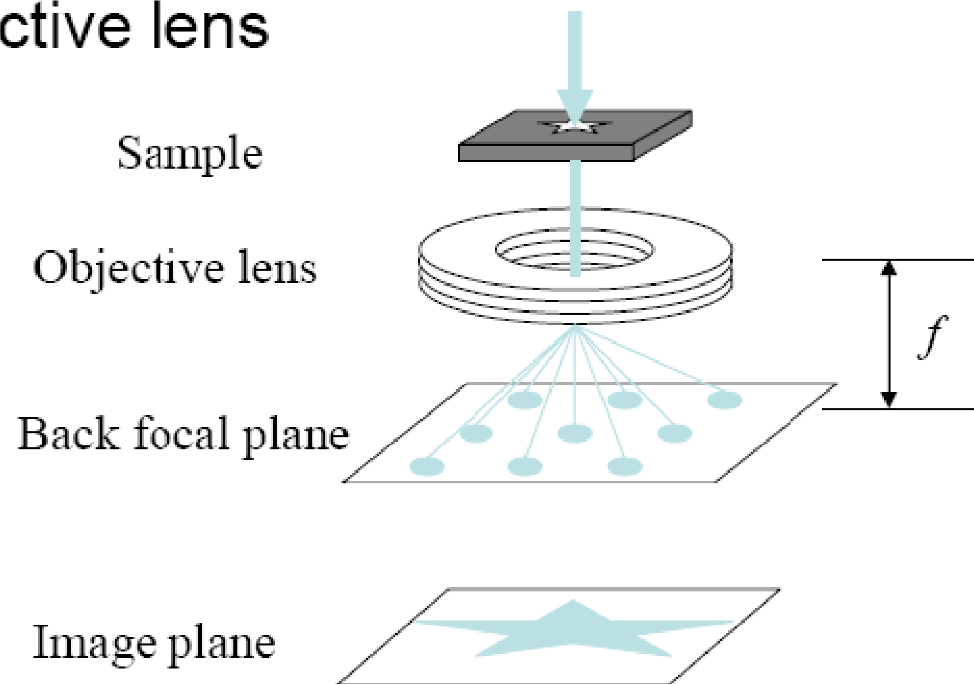
✓상세하게 보기 어려운 구조적 특징의 contrast가 선명해짐

✓시편의 전위(dislocation)이나 적층 결함(stacking fault)과 같은 결함구조(defect structure)를 분석할 때 유용



Electron diffraction

- Diffraction pattern locates at the back focal plane of the objective lens

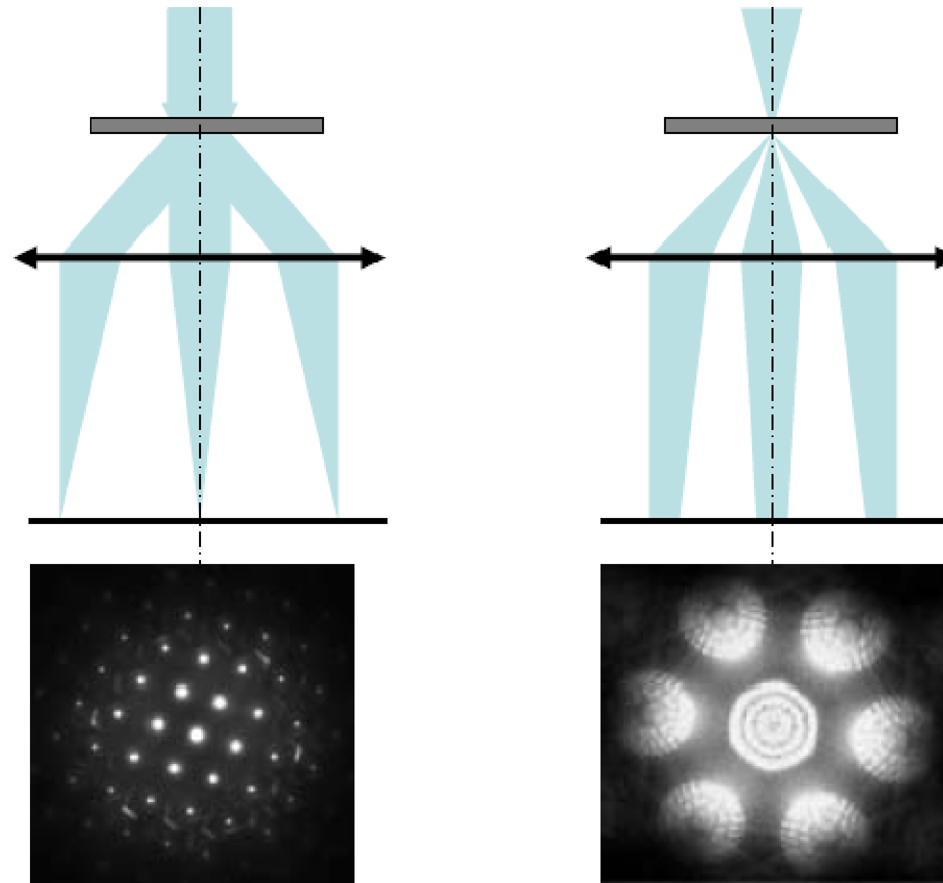


Diffraction in TEM

- Bragg’s law (< 0.5 ° scattering angle)
- All planes parallel to the incident beam
- Uniqueness of the pattern
- Structure determination
- Confirmation by the Simulation

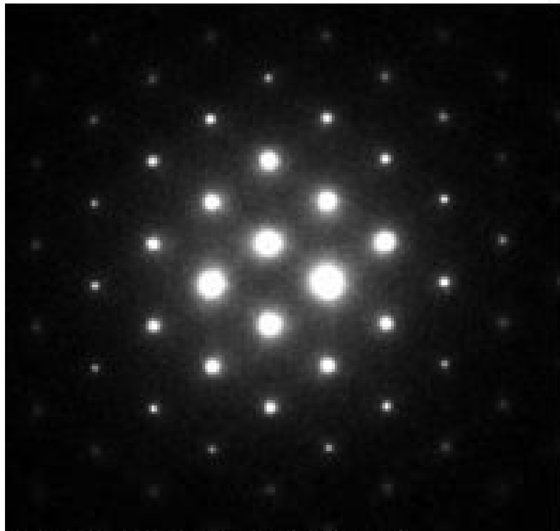
Diffraction with parallel illumination and conical illumination

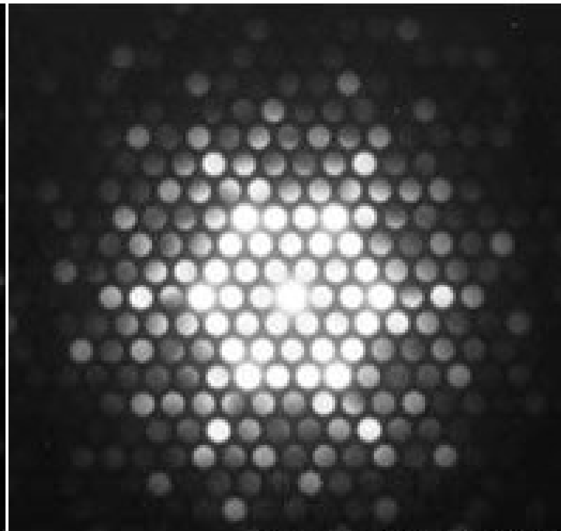
- Parallel beams are focused at the back focal plane
- Parallel illumination results sharp spots at the plane
- Conical illumination results discs at the plane

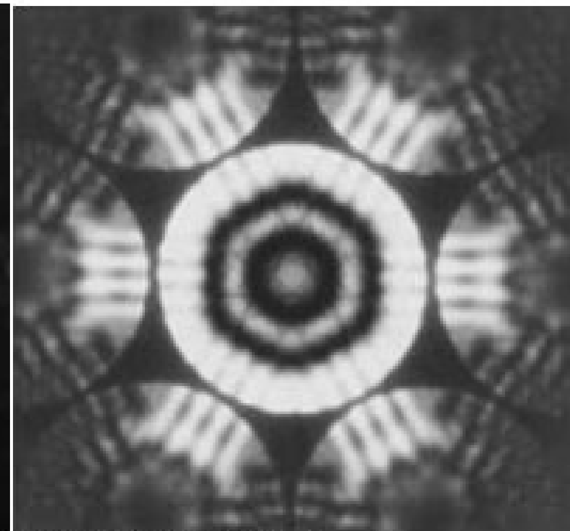


Diffraction pattern

회절패턴은 시편에 입사된 전자비임이 시편의 결정면에 의하여 회절된 3차원적 역격자 배열이 전자현미경의 back-focal plane높이의 평면에 의하여 잘린 면에 해당







Selected Area Diffraction

Convergent Beam Electron Diffraction

screen상에 보이는 grain이 어떠한 물질의 결정이고 격자상수가 얼마인지, 그리고 grain의 결정학적 방향(Miller 지수)이 어떠한지를 알기 위해서는 적어도 3개 이상의 zone-axis에서 회절패턴을 얻은 다음 회절 spot들 사이의 거리와 각도를 측정하여 물질의 종류와 격자상수를 분석한다

Spot pattern

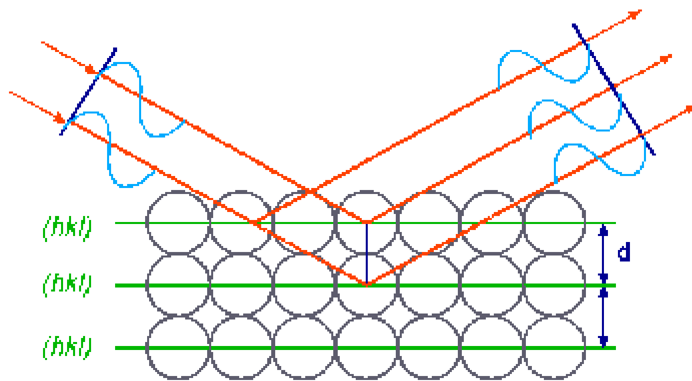
- Single crystal within the illumination area
- The regular arrangement of spots
- Spot brightness relates to the structure factor
- Spot position relates to the d-spacing

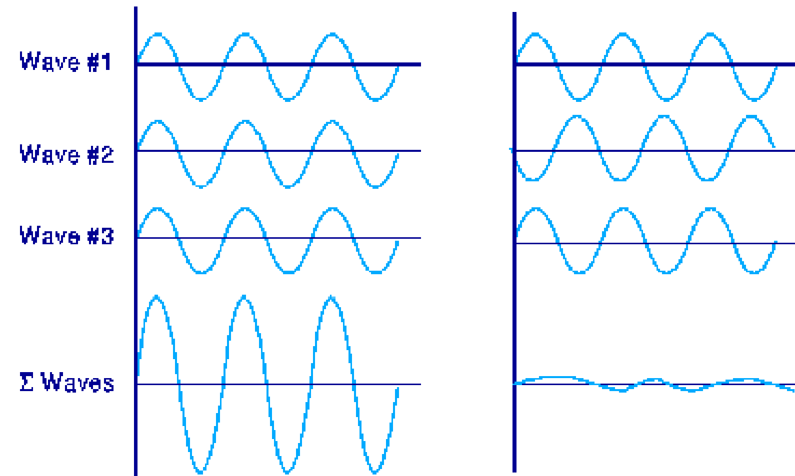
Diffraction pattern

✓ 단위세포의 형태와 크기, 그리고 시편 내 grain의 방향을 분석

✓결정은 Unit cell이 주기적인 반복 적층에 의해 형성되고 결정내 원자들이 형성하는 결정면에 의하여 전자빔이 회절

➡ Back-focal plane에 회절패턴이 형성

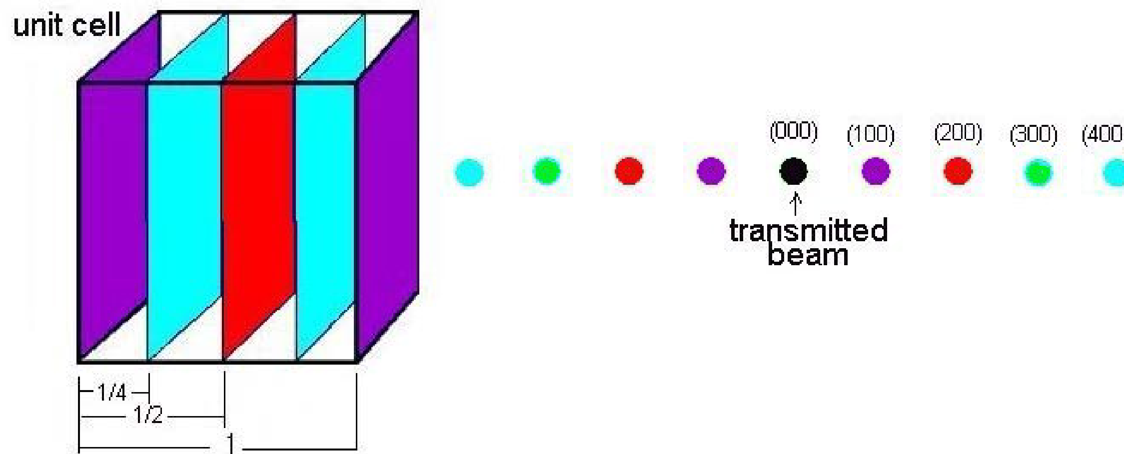




Diffraction pattern

✓역격자에서는 차원(dimension)이 실격자의 역수로 나타나며, 실격자에서의 결정면이 역격자에서는(즉, 회절패턴에서) 점으로 나타남

✓실격자에서의 결정면의 방향이 역격자에서는 면에 대한 법선으로 나타남

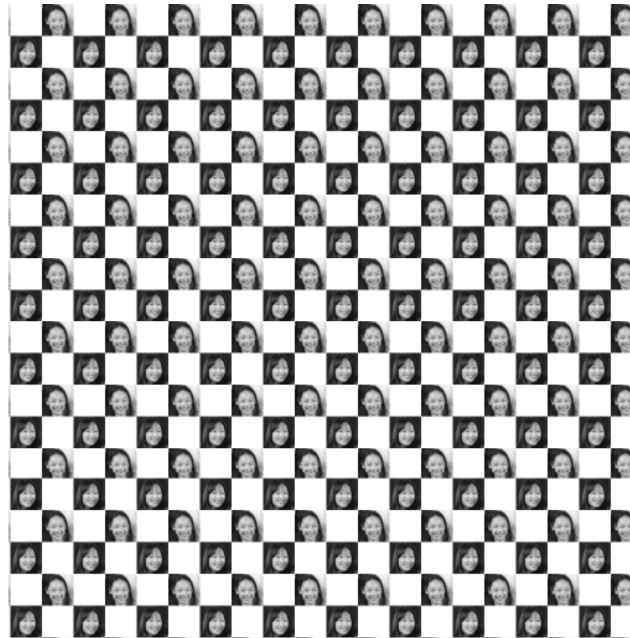


가로방향을 결정의 a축이라고 하고 격자상수가 1이라고 하면 (100)면(그림에서 보라색 결정면)은 역격자 혹은 회절패턴에서 1/1=1이므로 오른쪽 그림의 보라색 점에 나타나고 이러한 역격자점, 즉 회절패턴의 점들의 방향은 transmitted beam (000)을 출발점으로 하여 선을 그으면 모두 실제 결정면에 수직한 법선의 방향이 된다.

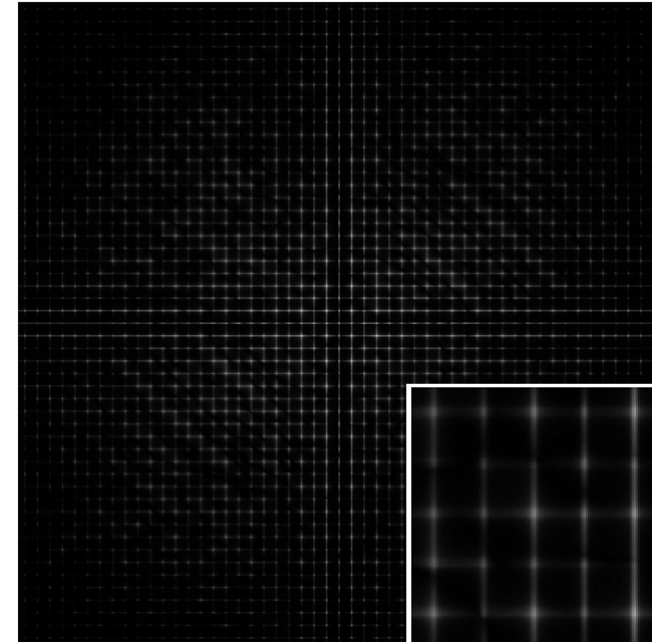
Diffraction from crystals
= Fourier Transformation of real space

(Atom A with scattering factor f_a)

(Atom B with scattering factor f_b)

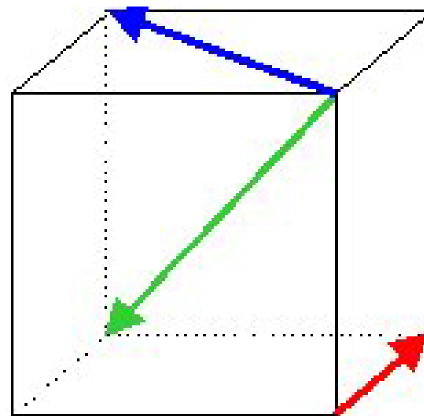
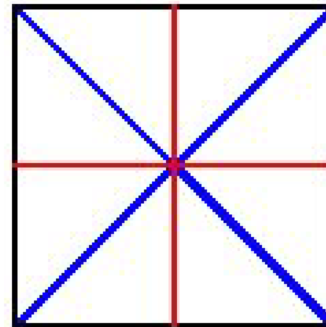
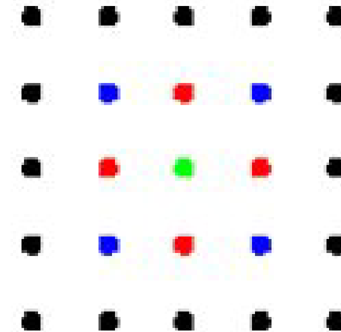
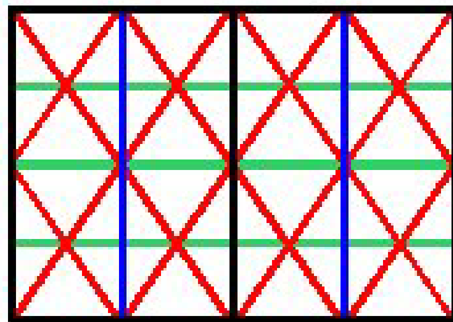


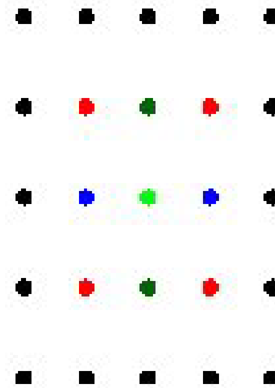
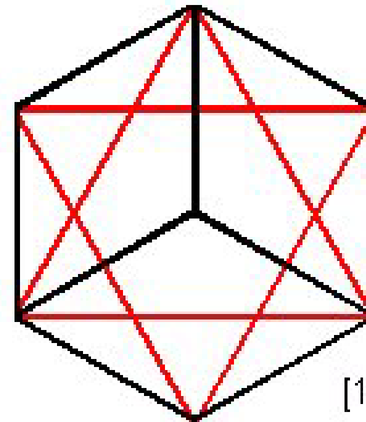
Real Space

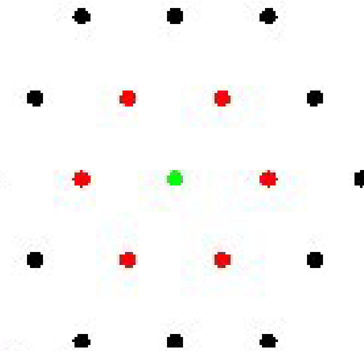


Fourier Transformation (= Diffraction)

Diffraction pattern

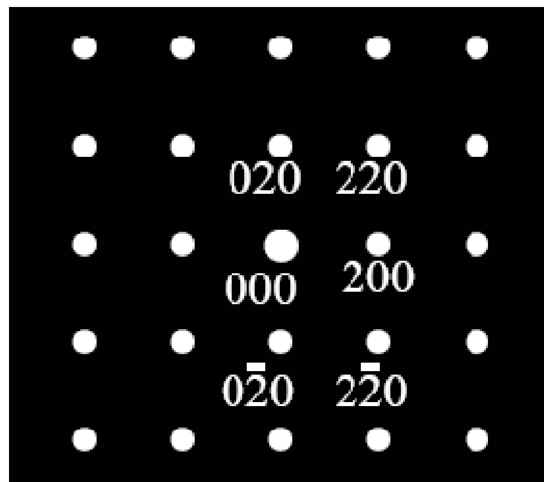







Standard spot pattern

- Example 1: f.c.c



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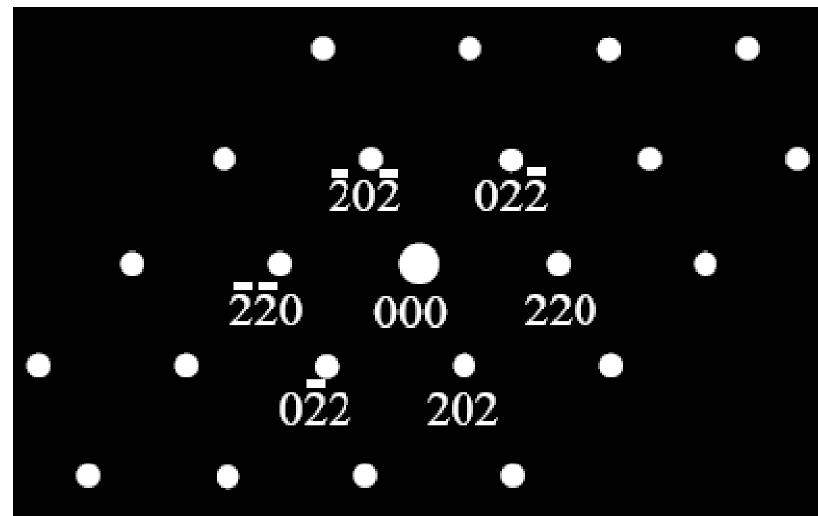
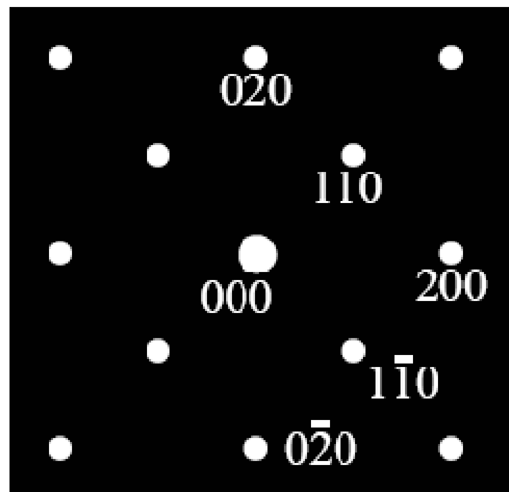


[$\bar{1}$11]

Standard spot pattern

- Example 2: b.c.c



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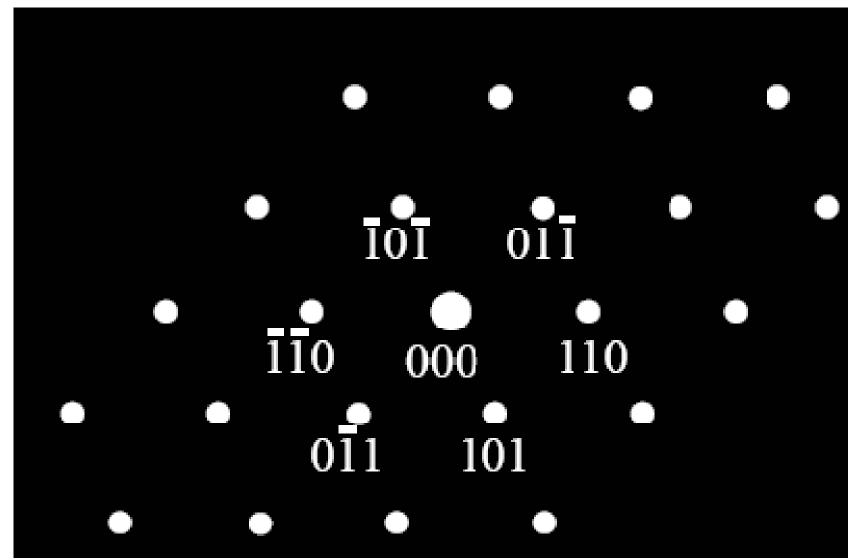
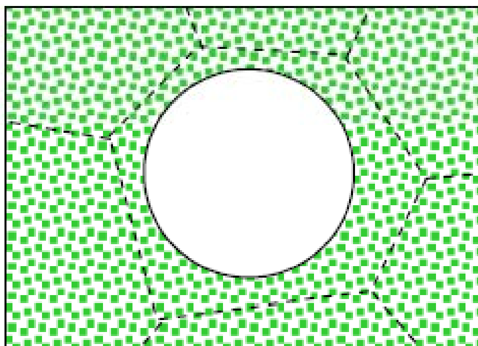
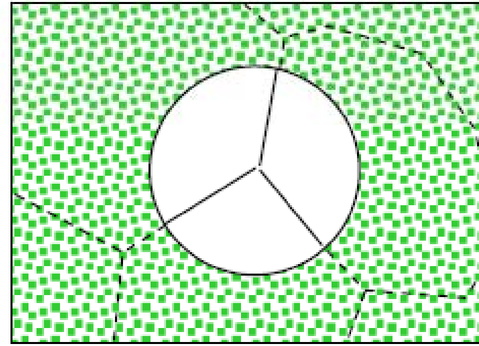
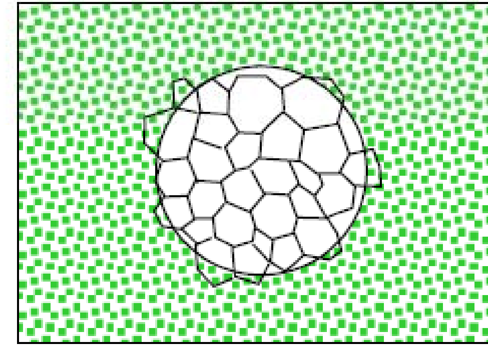


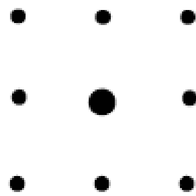
[$\bar{1}$11]

Electron Diffraction Pattern--Spot to Ring

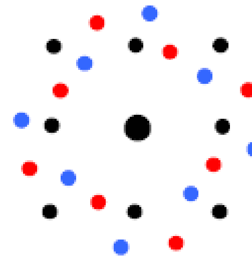




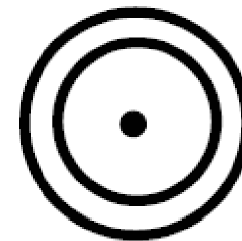




(a)

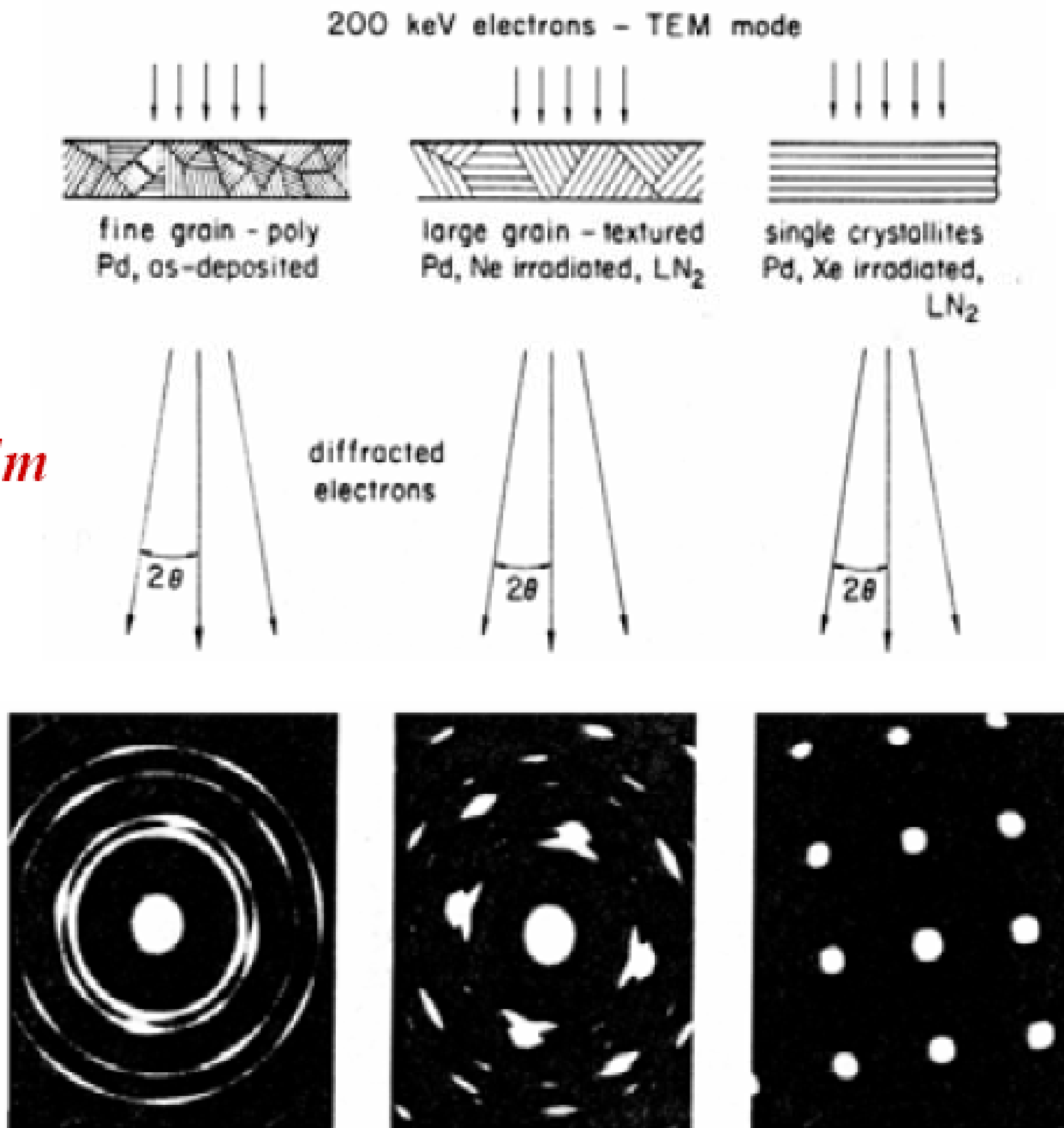


(b)



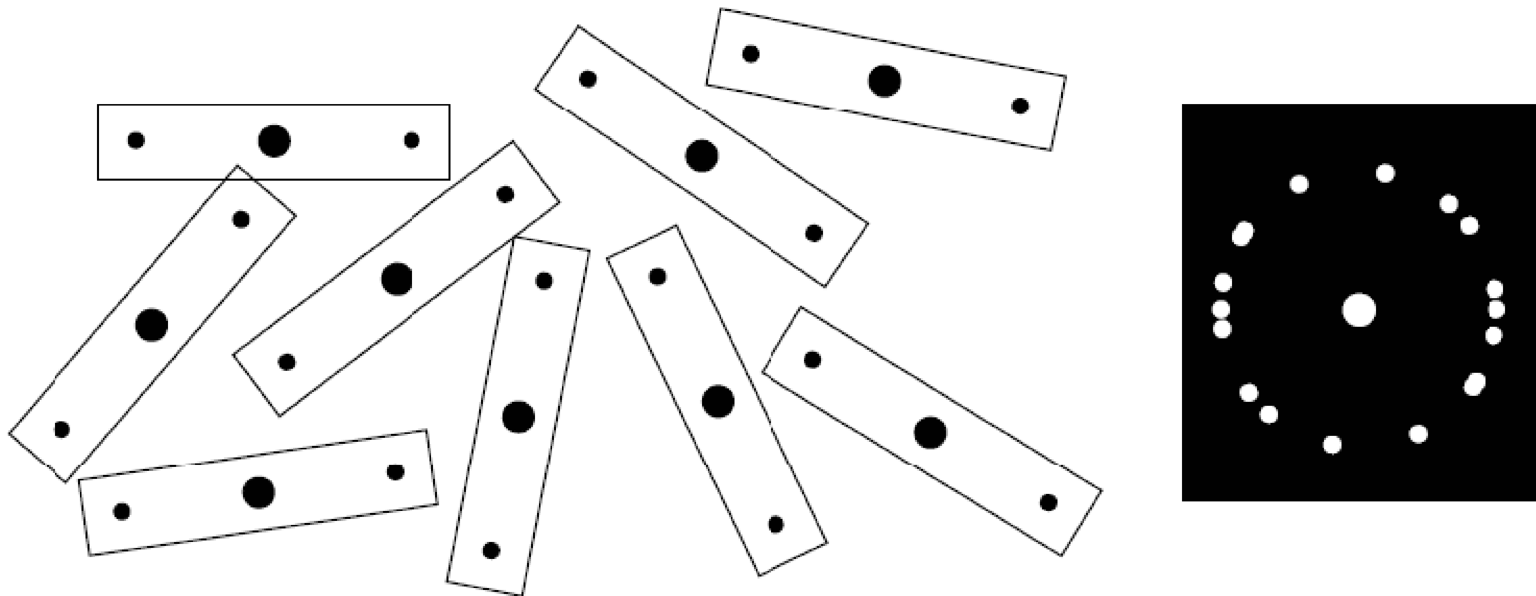
(c)

Electron Beam Diffraction of a Pd film

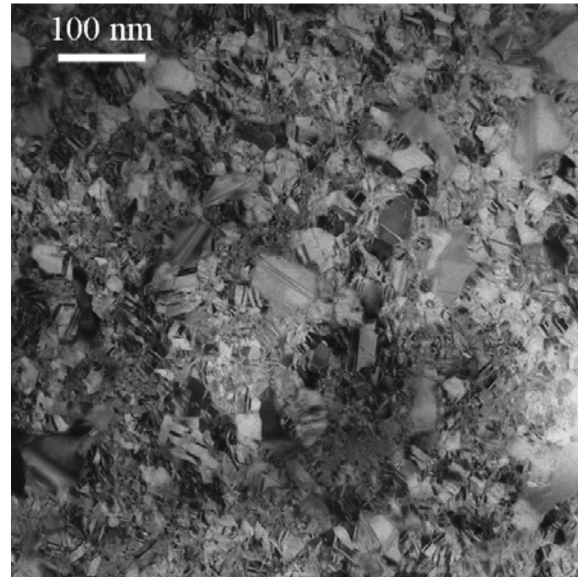


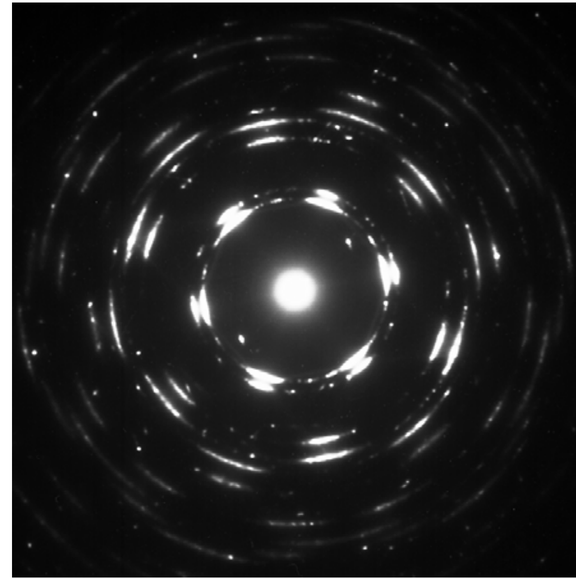
Ring pattern

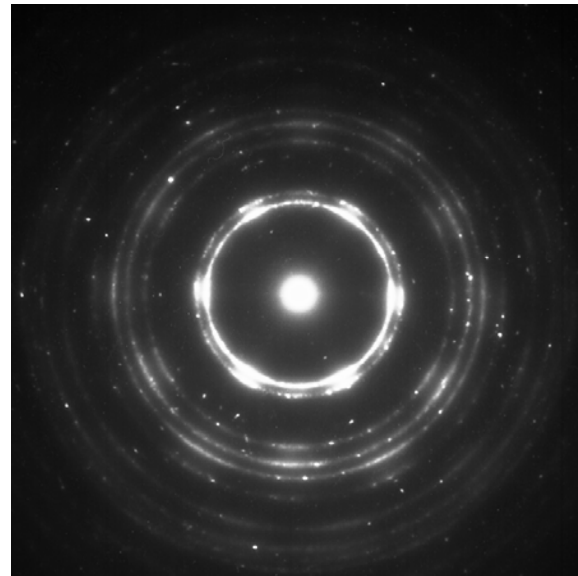
- Many fine particles in the illumination area, each of them is a single crystal and orientated randomly

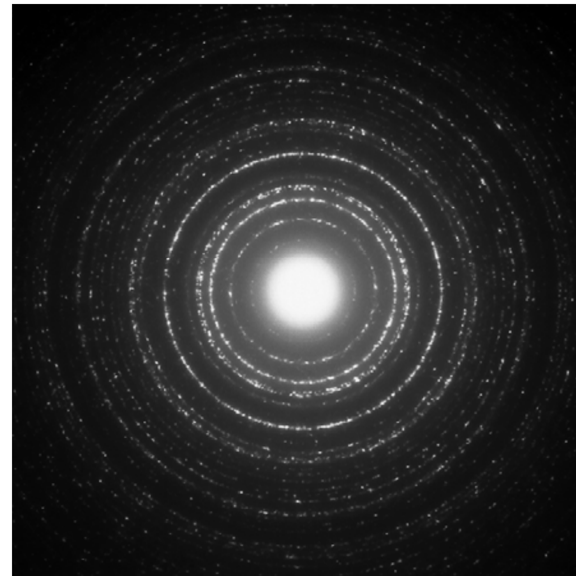


Diffraction from polycrystalline phase



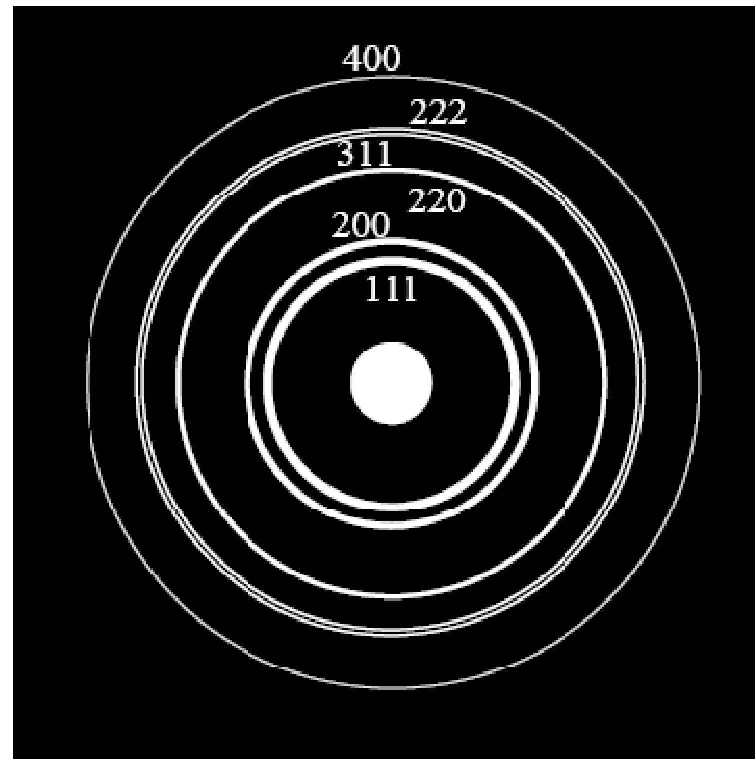






Ring pattern

- Typical polycrystalline Au diffraction pattern



Ring pattern: what can we obtain

- d-spacing

$$Rd_{hkl} = L\lambda$$

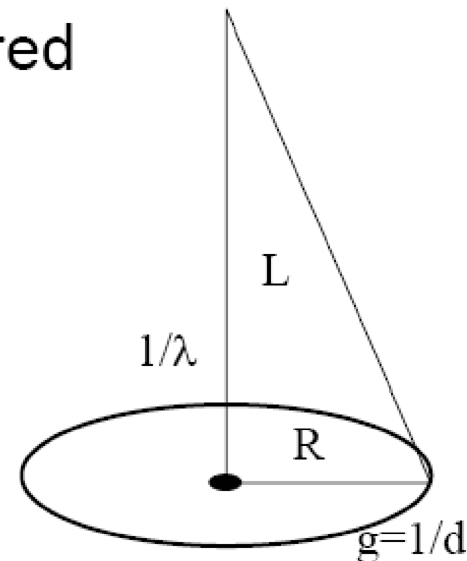
R: the measured ring radius

d_{hkl}: the d-spacing being measured

L: camera length

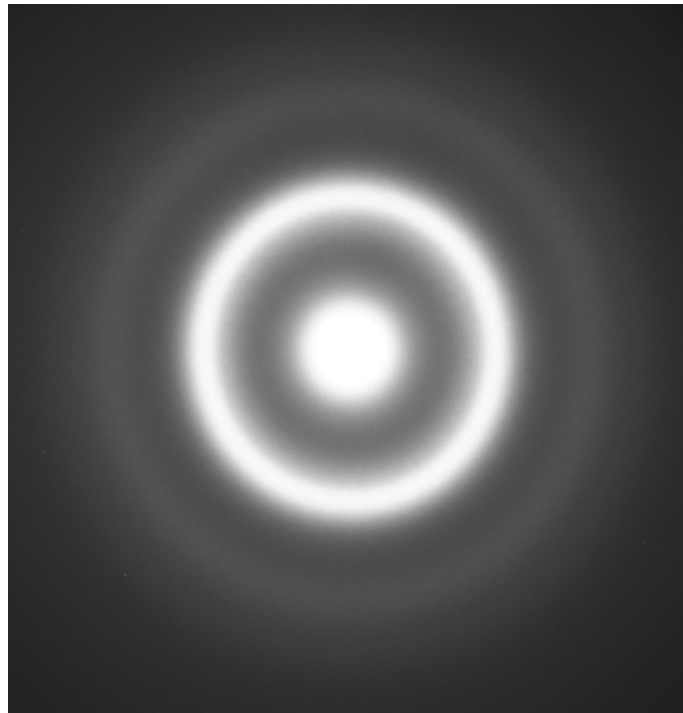
λ: wave length of electron beam

- Camera length calibration
- Crystalline / particle fineness

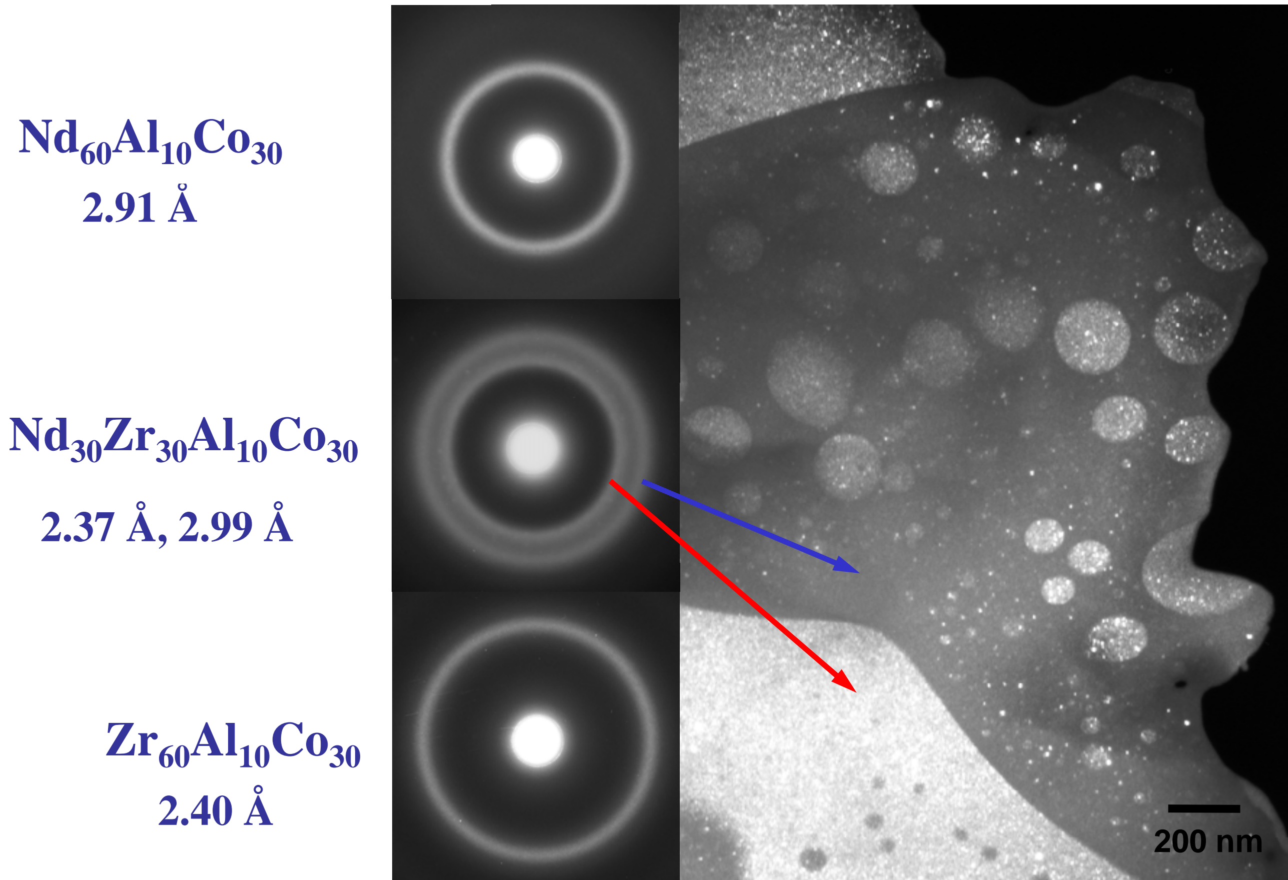


Amorphous materials

- Diffused ring pattern
- Reflecting the short range ordered structure
- Often seen at contamination layer or on carbon support film

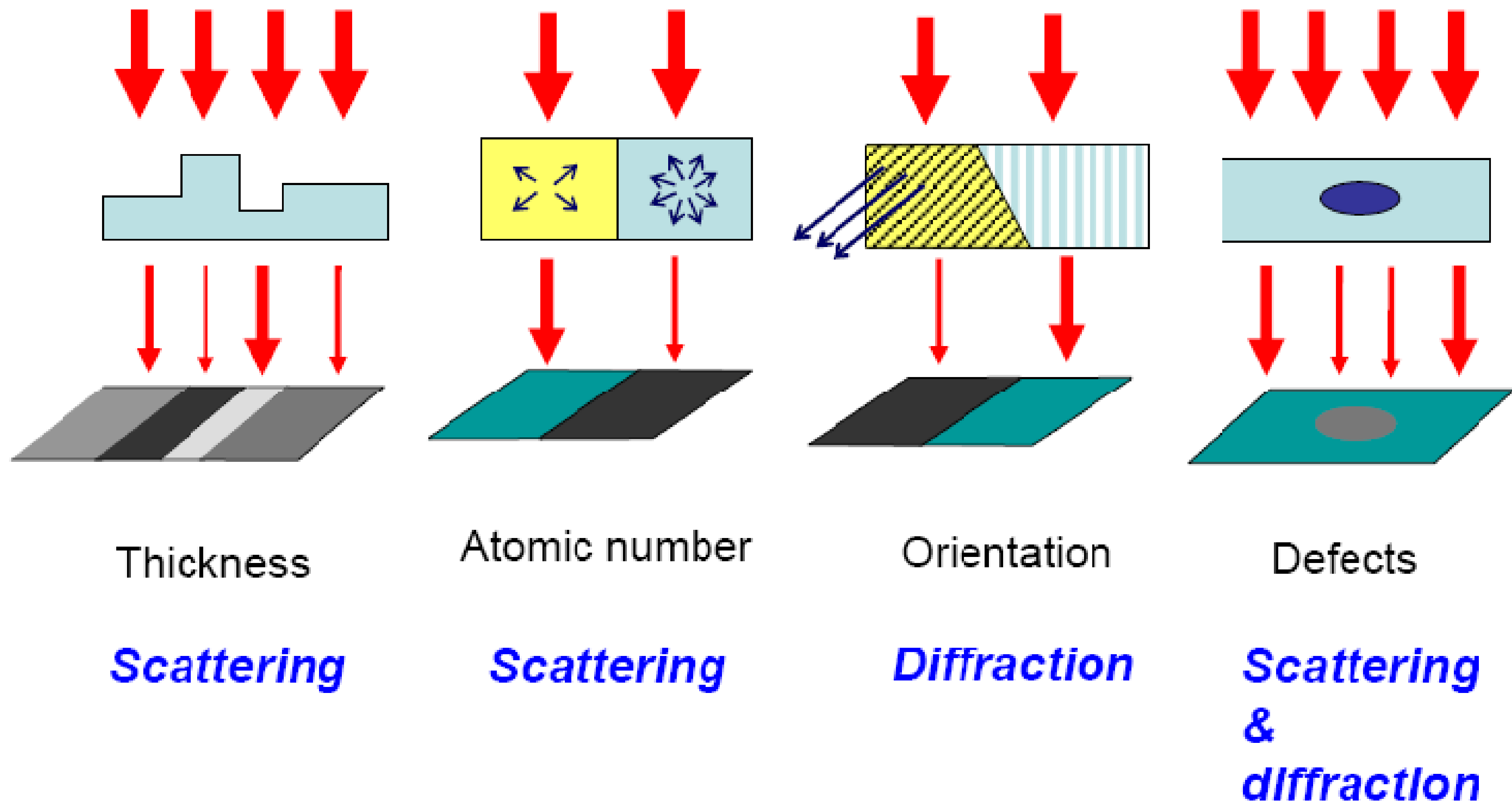


TEM results for $Nd_{30}Zr_{30}Al_{10}Co_{30}$ alloy



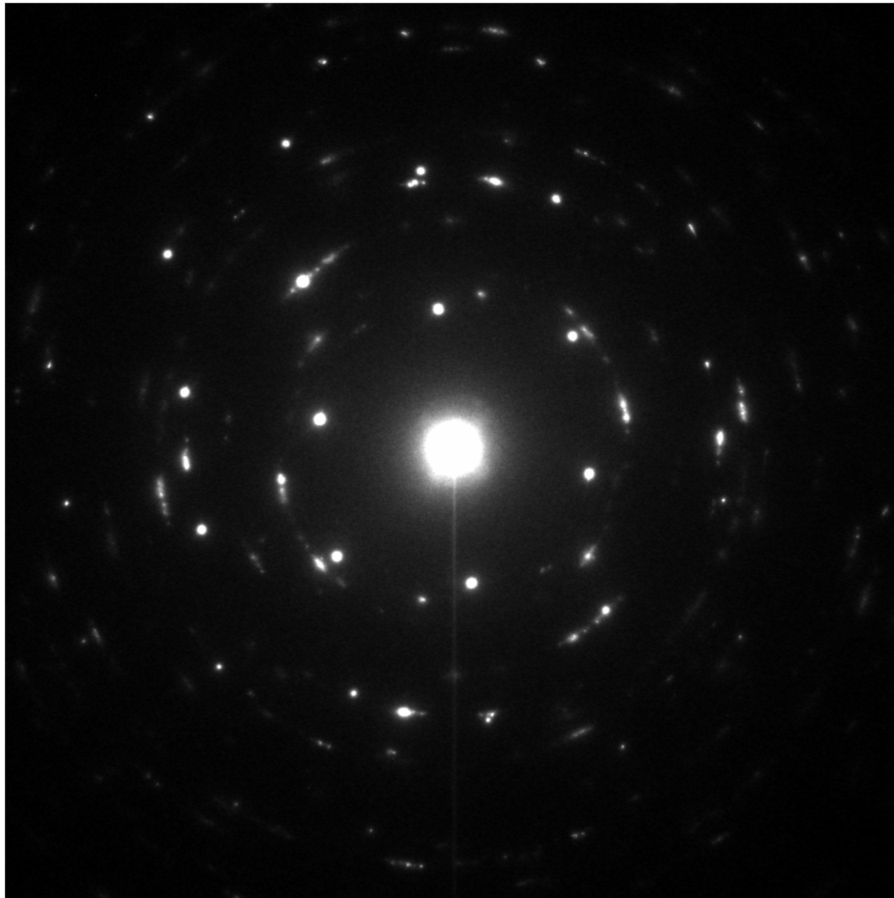
SADP and Dark-field TEM image

Major Factors affecting TEM Image Contrast

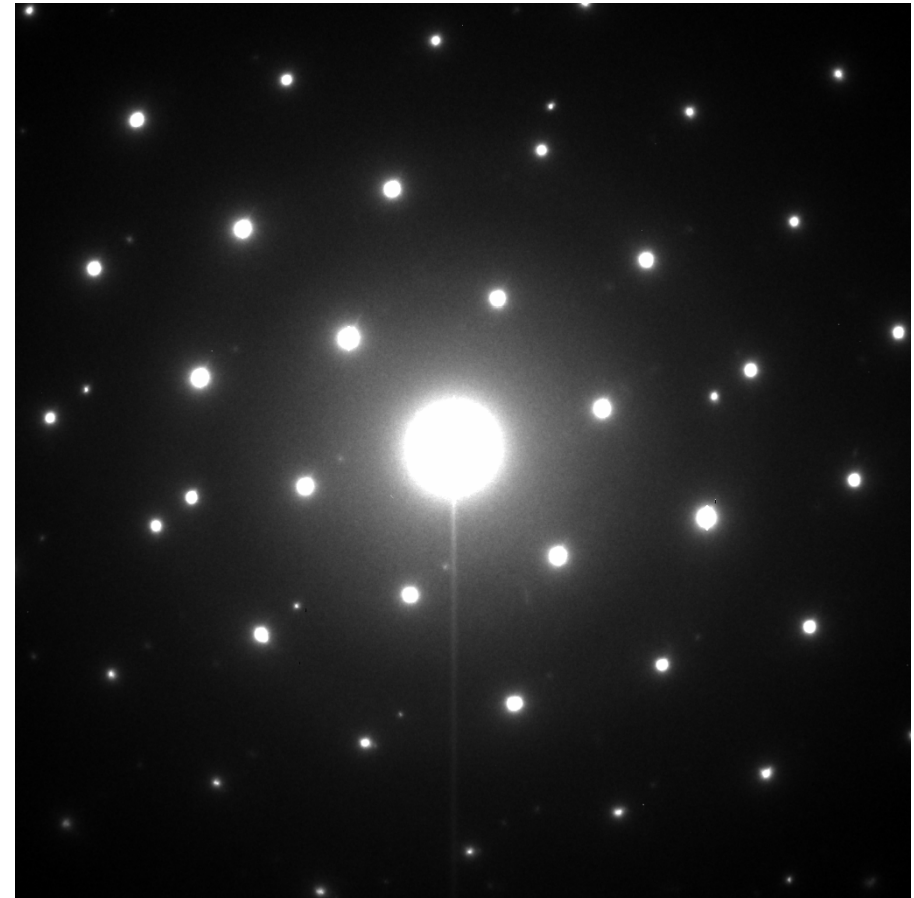


Selected Area Diffraction

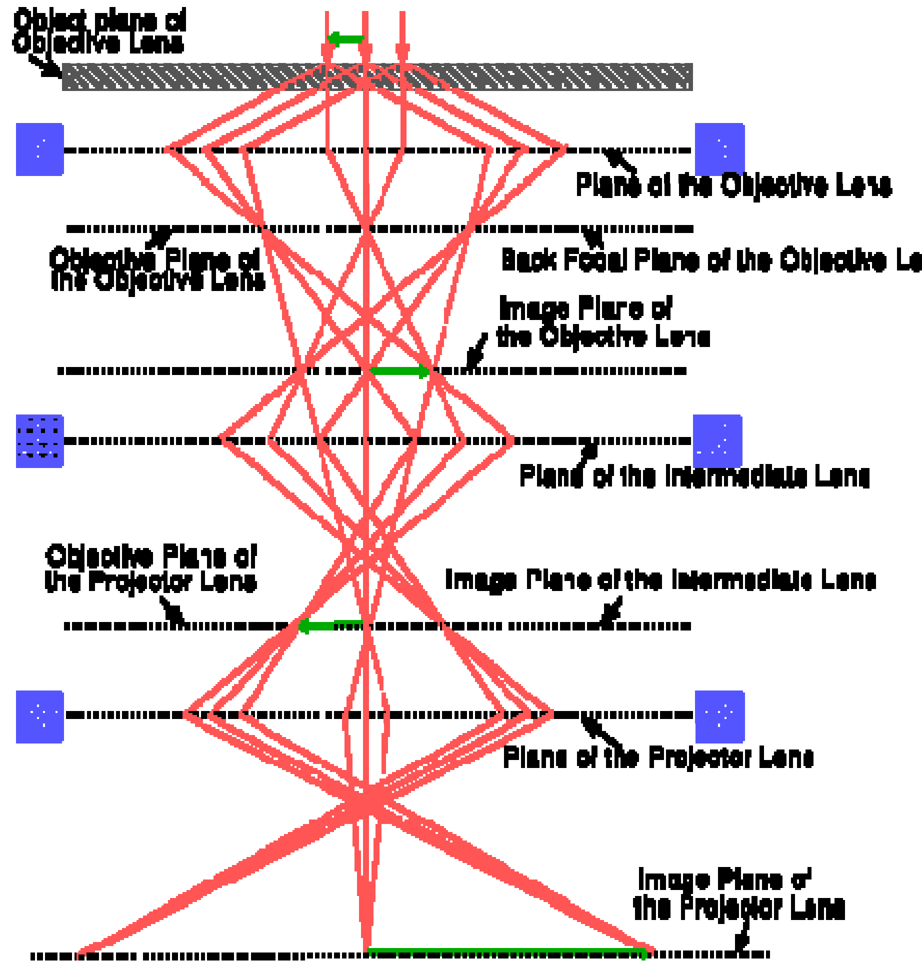
Tilted plate

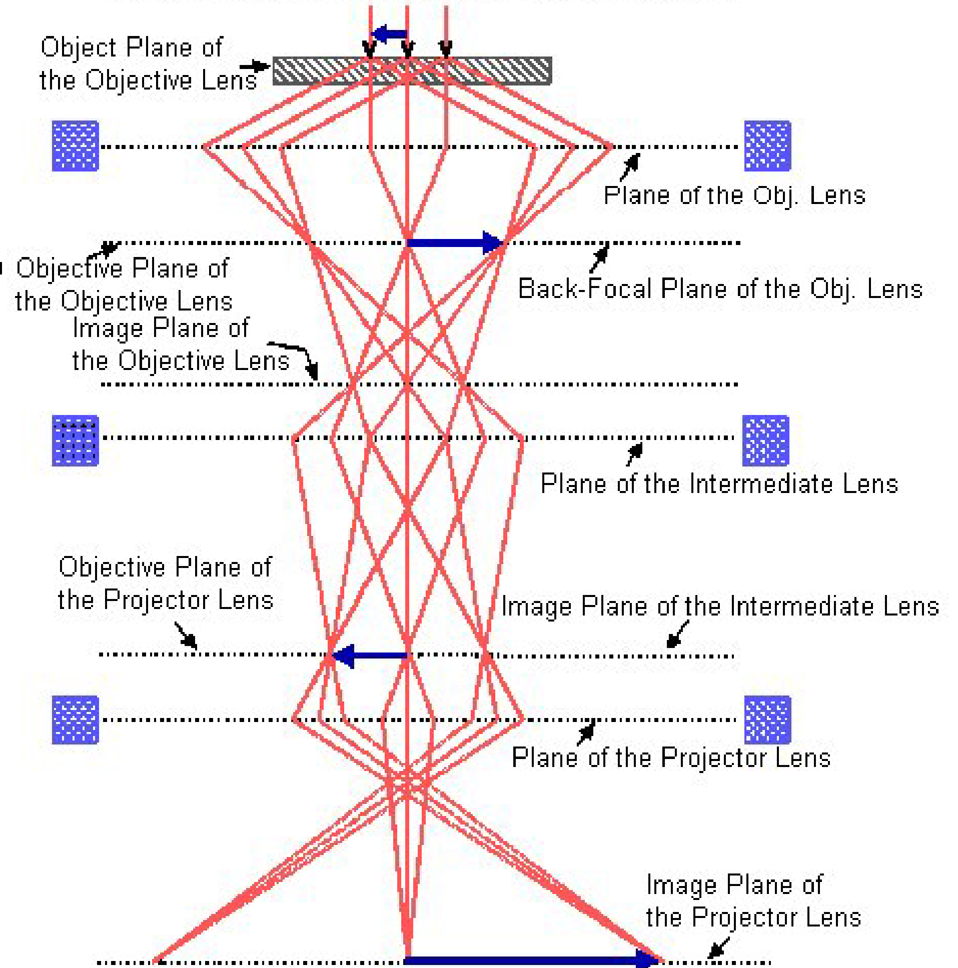


Normal to basal



영상을 볼때와 회절패턴을 볼때의 렌즈계 구성의 차이





Diffraction pattern 분석

Ring pattern의 Indexing

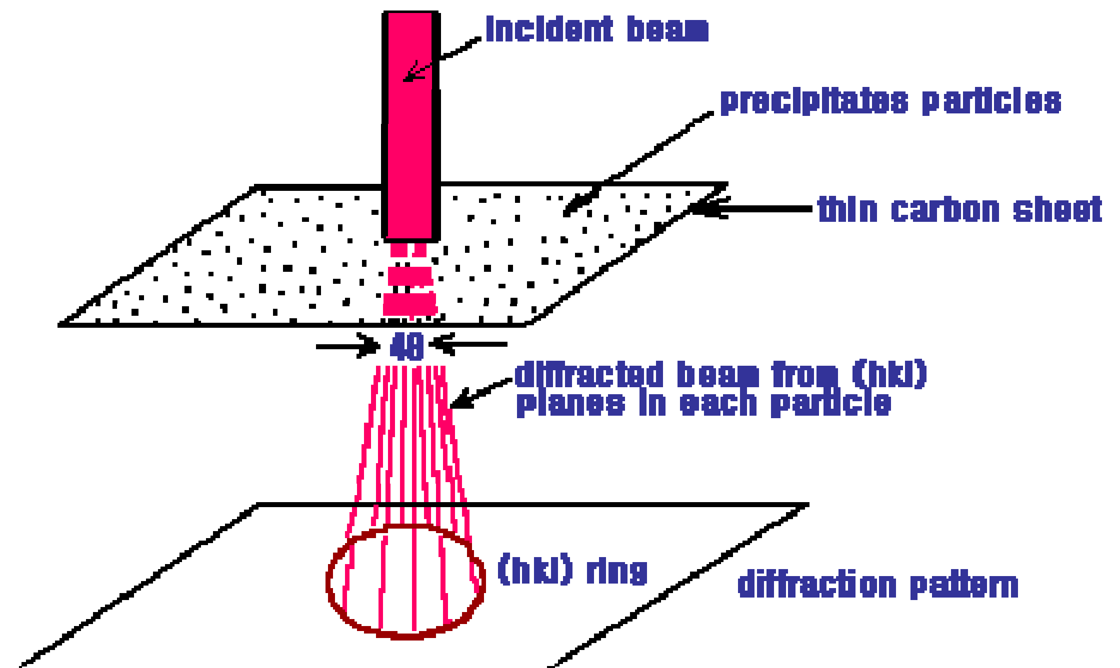
전자빔에 의해서 조사된 서로 다른 결정학적 방향을 가진 입자들이 각각 Bragg's law 를 만족하며 전자들을 회절시키면 ring pattern이 형성

$r/L = \sin\theta$, $r = R/2$ ---------(1)

$2\, d \sin\theta = n\, \lambda$ ---------(2)

$2 \sin\theta = 2\theta = \lambda/d = R/L$

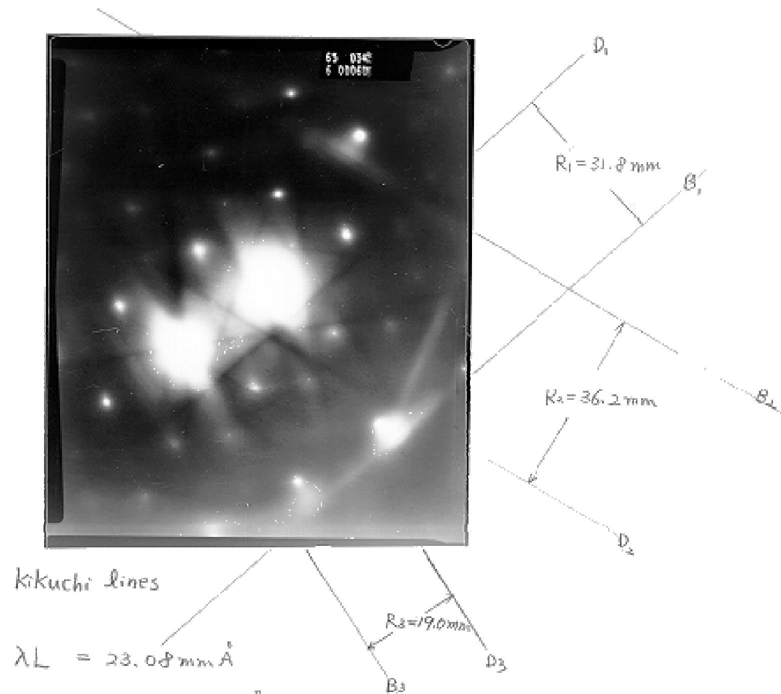
$\lambda L = Rd$



Diffraction pattern 분석

Kikuchi pattern

1. 결정학적 방향, 회절벡터, 시편의 방위(orientation), 상(phases)들 사이의 방위관계등를 결정할 때
2. 시편을 tilting시킬 때, Kikuchi map을 이용하여 쉽게 tilting방향 및 각도를 조절.
3. 정확한 Bragg's position으로부터 이탈된 정도를 나타내는 deviation vector **s**의 크기와 방향 결정
4. spot pattern과는 달리 실제 결정의 symmetry를 나타내므로 crystal symmetry를 정할때 사용.



spot-pattern의 index에 사용된 BCC구조를 가진 시편의 두꺼운 부분에서 얻은 회절패턴이다.

Rd = λL =23.08mmÅ를 대입하여 계산하면

$d_1 = \lambda L/R_1 = 23.08\text{mmÅ}/31.8\text{mm} = 0.7258\text{Å}$

$d_2 = \lambda L/R_2 = 23.08\text{mmÅ}/36.2\text{mm} = 0.6376\text{Å}$

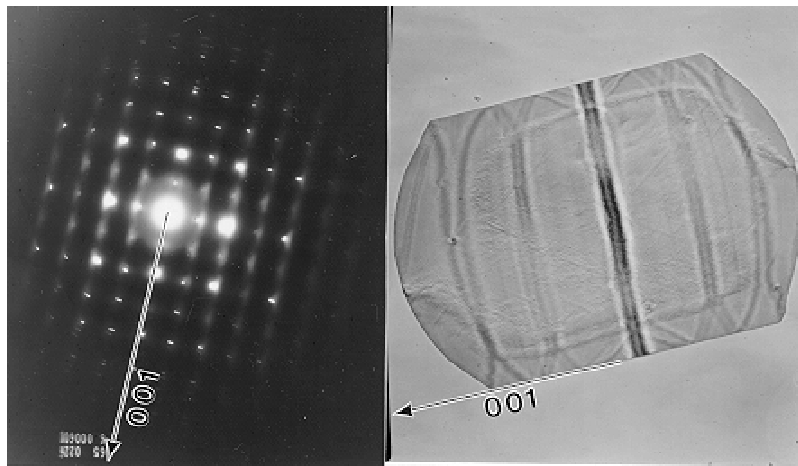
$d_3 = \lambda L/R_3 = 23.08\text{mmÅ}/19.0\text{mm} = 1.2147\text{Å}$

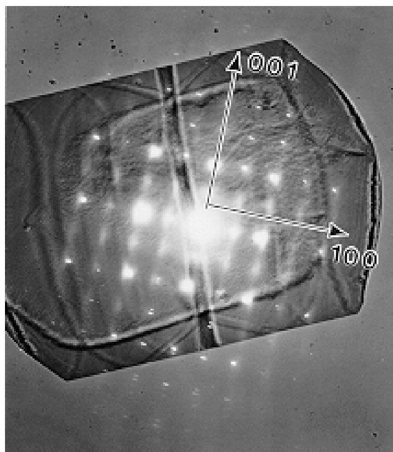
d_1과 d_2는 각각 {400}, {420}에 해당된다.

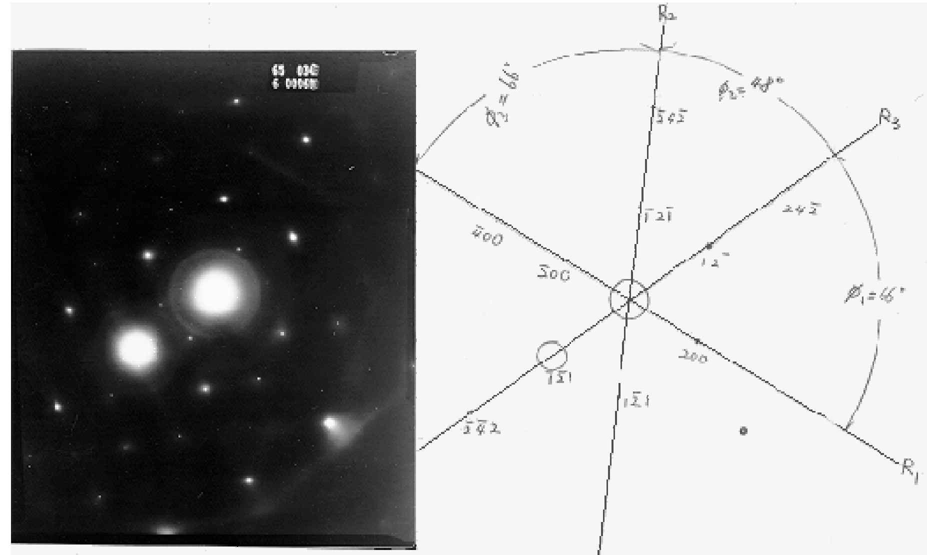
d_3는 {211}의 면간거리 값에 해당되고, 이는 Spot-pattern의 indexing에서 (-1 2 1)의 spot과 일치한다.

Diffraction pattern 분석

Spot pattern의 Indexing 미세조직상의 특정부위에 대한 결정학적 방향을 결정







$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{N}{a^2}$$

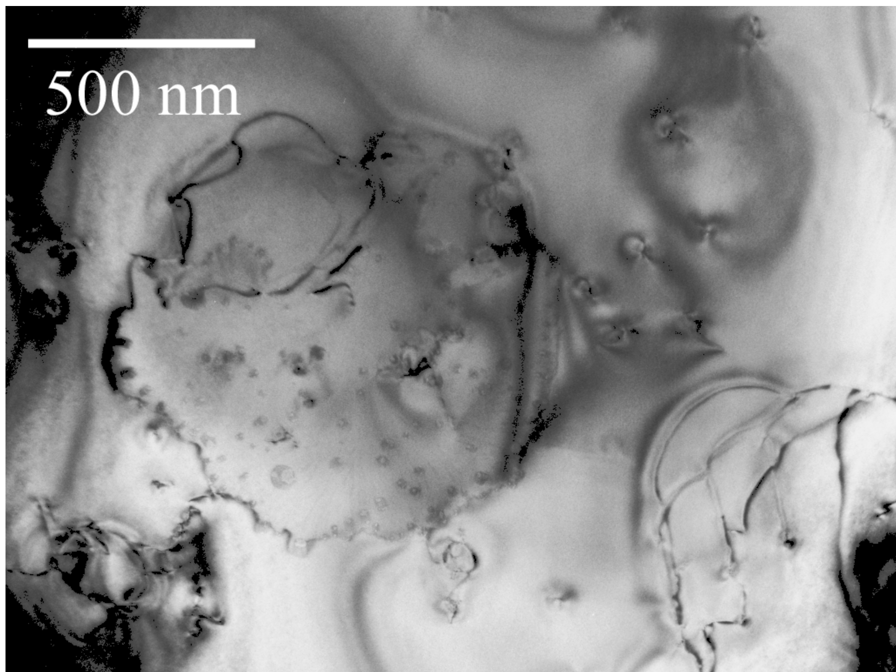
$$\cos\phi = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}$$

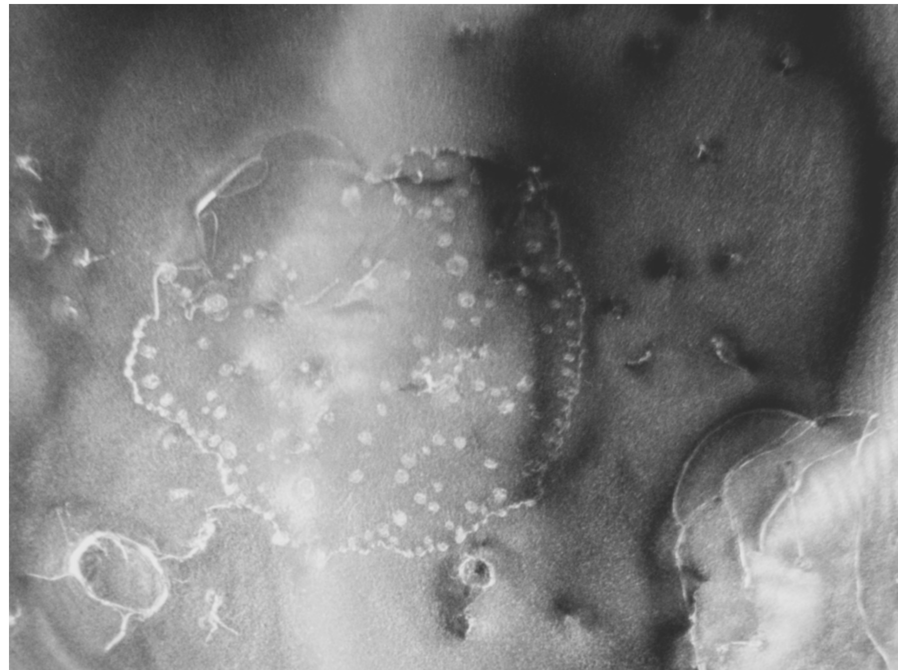
Image formation in TEM

- **Phase contrast**
- **Diffraction contrast**
- **Absorption contrast**

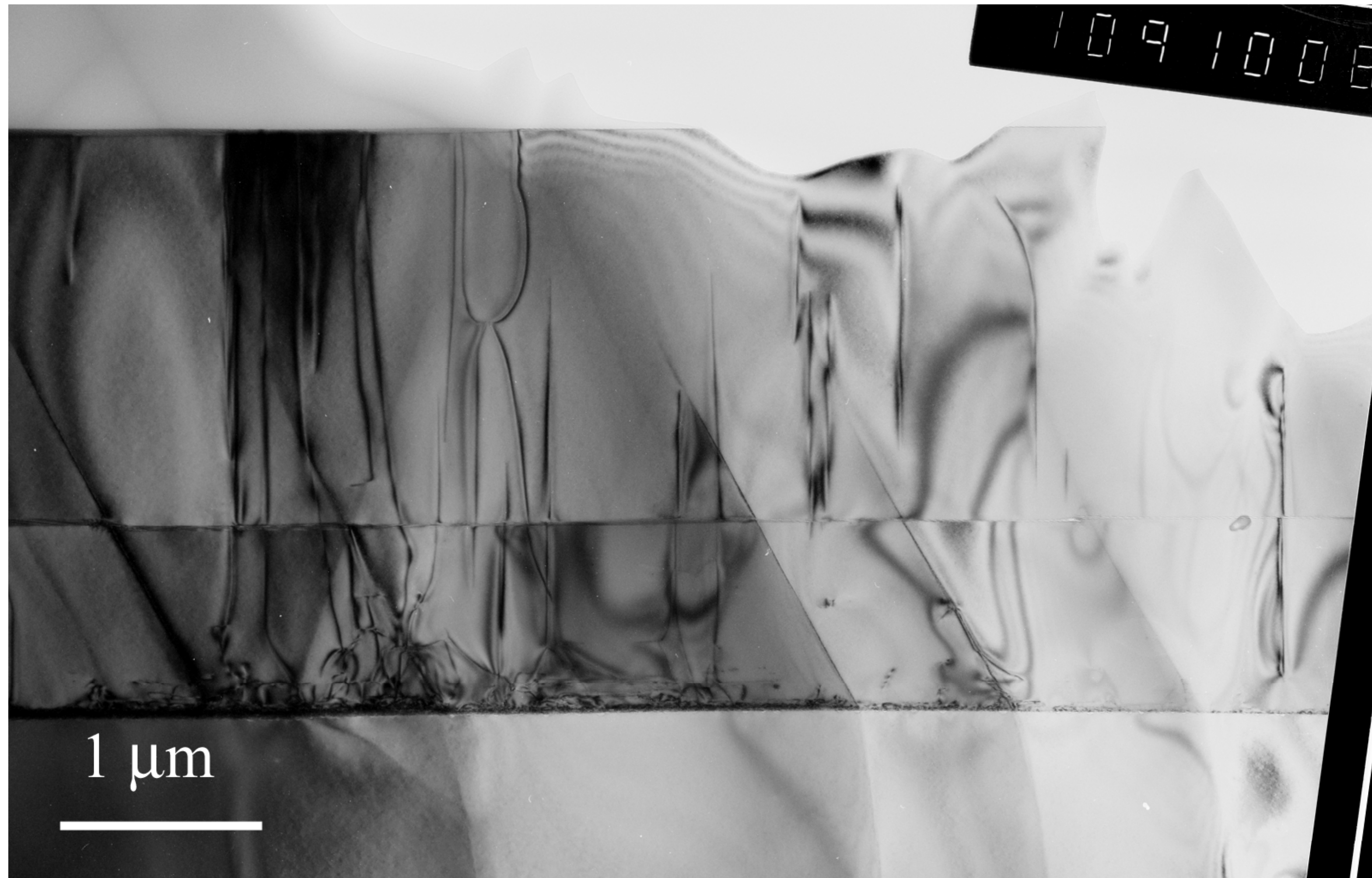
Weak beam darkfield

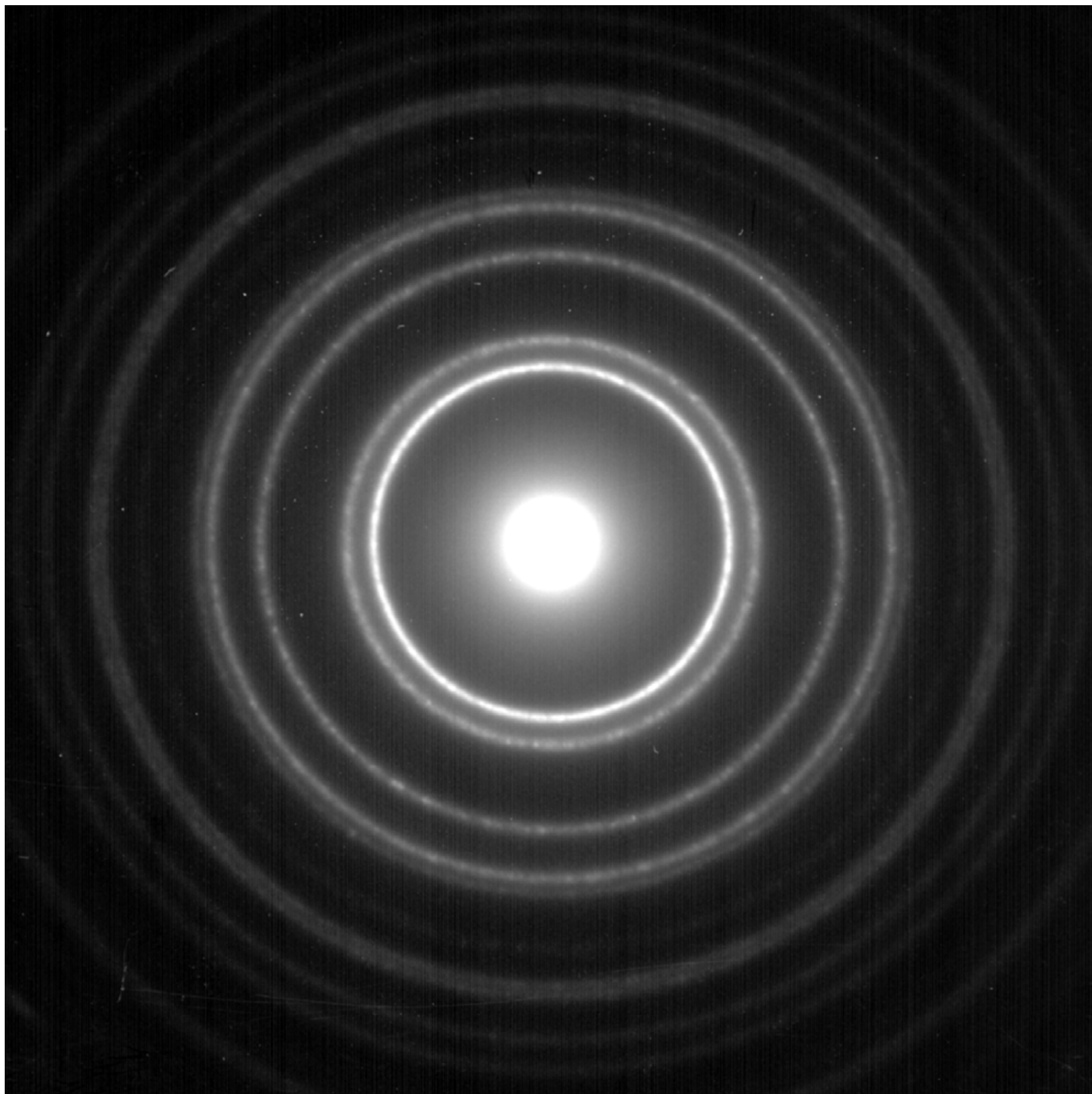
- Lattice defects generate strain field, which forms complicated image in normal brightfield image.
- WBDF reveals defect structure close to the core.





Dislocation images





Formation of ring pattern III