HRTEM

High Resolution Transmission Electron Microscopy

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CHEM-E4205

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Introduction

- **Microscopy techniques used to reveal small objects beyond visual capacity**
  - Without the help of any instrument, the resolution of naked eyes is only about 0.1 mm, or 100 μm
- **The early developed light microscope (LM) magnify objects by optical lenses using visible lights**
  - resolution of LM can be improved to below 1 μm at several hundred nanometers
- **After the LM technique, it was discovered that electrons could be used as the illumination source to improve the imaging resolution**
  - Several microscopy (EM) techniques have been developed
  - Ernst Ruska developed the first electron microscope, a TEM, with the assistance of Max Knolls in 1931
- **In these techniques, various detected signals come from the electron–specimen interactions**
- **If the sample is thin enough, the electrons can penetrate right through the samples to form images using electromagnetic lenses.**

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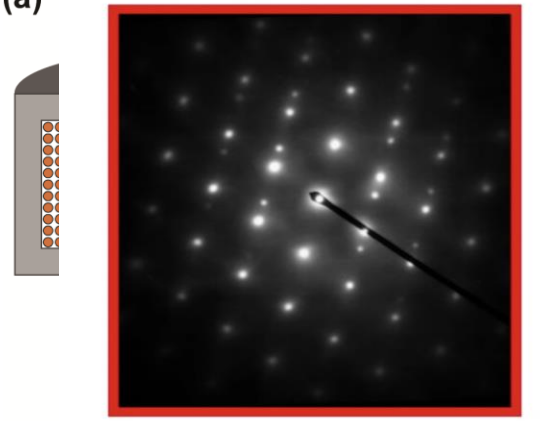
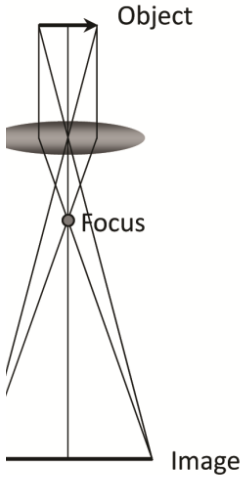
- Luo, Z. *A Practical Guide to Transmission Electron Microscopy: Fundamentals*; Momentum Press: New York, UNITED STATES, 2015.

Principles of TEM & schematic



spot intensity determined by energy of electron



Objective Lens and Objective Aperture → The objective lens is used for focusing and magnifying the object.

Projector Lens → The projector lens is used to further magnify the images formed by the intermediate lens. The projector lens has a great depth of focus.

Viewing Screen and Camera → The viewing screen is coated with phosphorescent powders, which emit visible lights upon being bombarded by high-energy electrons. Recording can be done by a film camera or a CCD camera. If a CCD camera is available, the TEM data are recorded directly to digital files.

Wehnelt, and these electrons are accelerated by a high voltage (the TEM working voltage) between the Wehnelt and anode plate. A crossover is formed in this gap.
A LaB6 filament can provide about 10 times brighter beam than a W filament with several times extended lifetime, while a higher gun vacuum level is required.

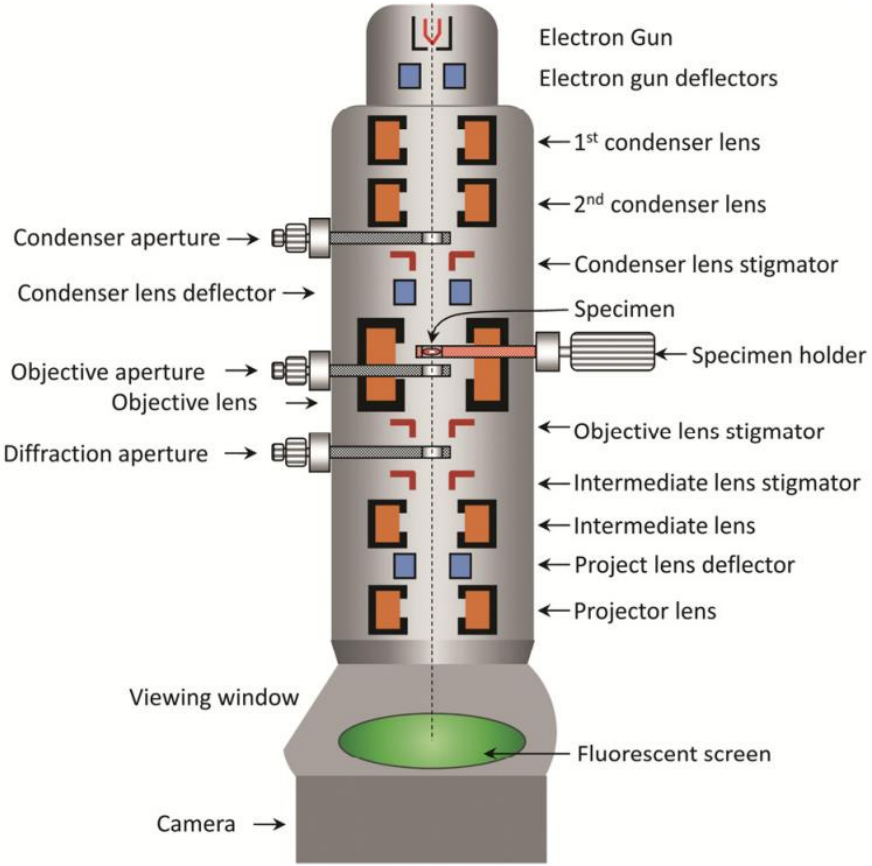


Fig. 3.1 Schematic construction of a TEM.

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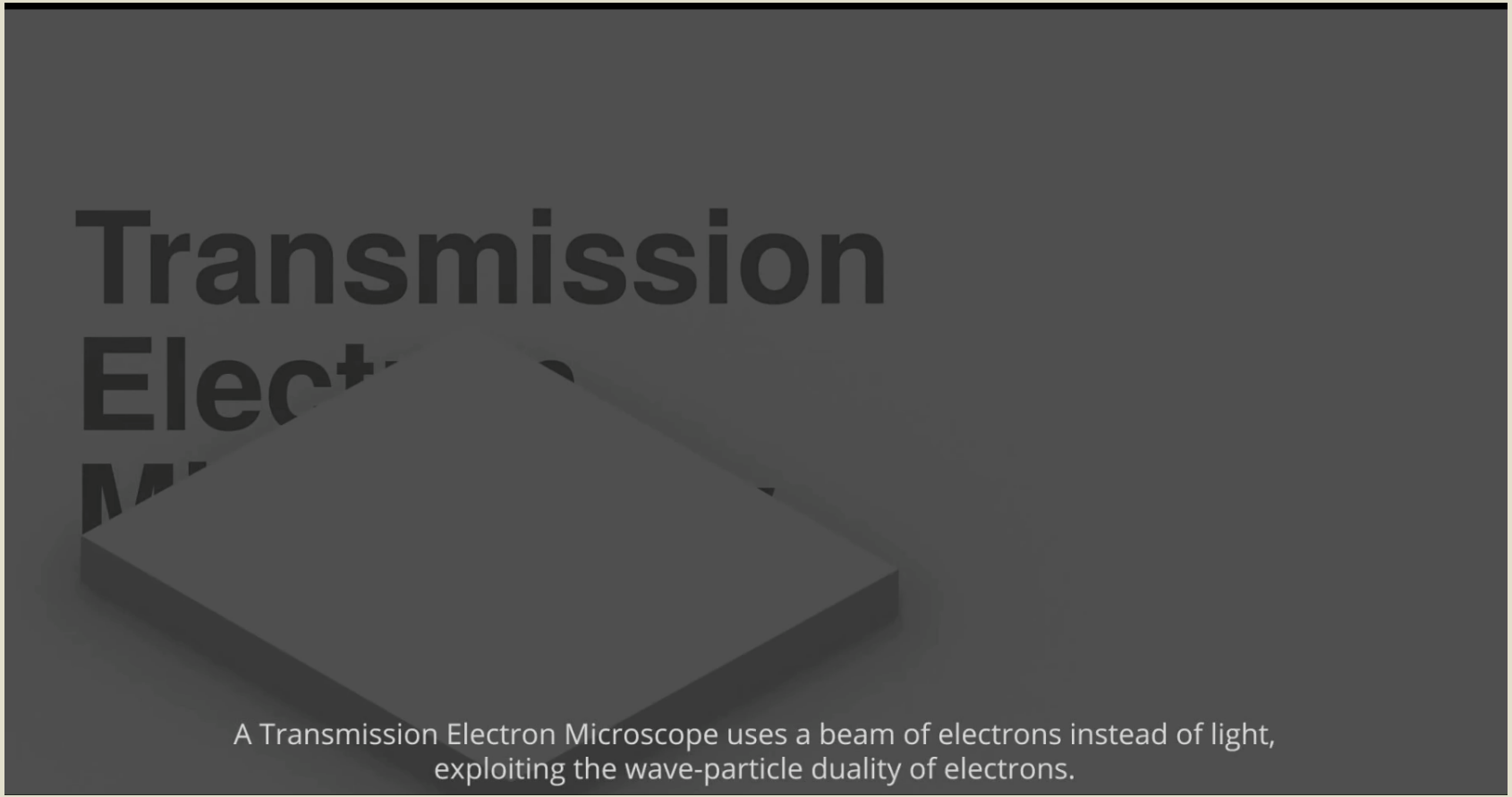
Luo, Z. *A Practical Guide to Transmission Electron Microscopy: Fundamentals*; Momentum Press: New York, UNITED STATES, 2015.

Principles of HRTEM



Jubobroff. *English: Operating Principle of a Transmission Electron Microscope (TEM)*; 2016. https://commons.wikimedia.org/wiki/File:Transmission_Electron_Microscope_operating_principle.ogv (accessed 2023-05-02).

Utilization of HRTEM – Sample preparation

Sample preparation is one of the most critical step to get meaningful TEM results:

1. To preserve the original structure of the sample;
2. To be as thin as possible, typically at least less than 100 nm to be transparent to electron beam;
3. To be dehydrated or stay in a frozen state, so that it does not evaporate or release much vapor or gas during the observation inside the TEM vacuum chamber;
6. To be preferably electrically conductive to avoid beam charging effect causing beam damage;
7. To be surface clean with minimum contaminations.

To particle or powder samples, TEM grids should be used to provide the support.

Includes cutting, grinding, polishing, and punching into 3-mm disks.

Table 2.1 TEM sample preparation of material samples.

	Grids	Ion milling	Electropolishing	FIB	Microtomy
Metal and alloy	No	Yes	Yes	Yes	No
Ceramic	Not common	Yes	No	Yes	No
Rock/ mineral	Not common	Yes	No	Yes	No
Polymer and polymer composite	No	Yes	No	Yes	Yes, if not too hard
Metal or ceramic composite	Not common	Yes	Yes if conductive	Yes	No
Solid thin film	No	Yes	Not common	Yes	No
Powder	Yes	Yes (with embedding)	No	Yes (with embed-ding)	Yes (with embedding)
Particles for fibers in liquid solu-tion	Yes	No	No	No	No

Luo, Z. *A Practical Guide to Transmission Electron Microscopy: Fundamentals*; Momentum Press: New York, UNITED STATES, 2015.

Data Retrieved

- Different types of information can be gained including point defects, packing, particle size, lattice planes, angles and distances between planes/lattices

- It can provide not only a high imaging resolution down to angstroms or even sub angstrom level but also structural information through electron diffraction

- Due to high resolution, minimal crystal lattice imperfections can be seen
    - Resolution is sub-ångström level at best
- Also, provides chemical composition information through the interactions of high-energy electrons with core electrons of the specimen

W. Wan ORCID logo, J. Su , X. D. Zou ORCID logo and T. Willhammar, Transmission electron microscopy as an important tool for characterization of zeolite structures., Inorg. Chem. Front., 2018, 5, p. 2836-2855 DOI: 10.1039/C8QI00806J

Data Retrieved

Causes for incorrect data:

- **Particle size: Orientation effects, since it's a 2D projection of a 3D property**

- **Thickness of sample can cause problems:**
  - **Can lead to difficulty of interpretation due to multiple scattering of electron beams.**

Zhou, W.; Greer, H. F. What Can Electron Microscopy Tell Us Beyond Crystal Structures? European Journal of Inorganic Chemistry 2016, 2016 (7), 941–950. https://doi.org/10.1002/ejic.201501342.

Data Retrieved

- **In order to get sample thickness, imaging has to be done of the cross section → Data interpretation might be difficult, due to both sides of the interface needing to diffract strongly**

- **Statistics:**
  Images are of a tiny area →either need lots of pictures or can't say much about the structure in general.

Reason for high resolution

- **Add definition of resolution "smallest size that can be identified"**
- **Theoretical limit of resolution:**

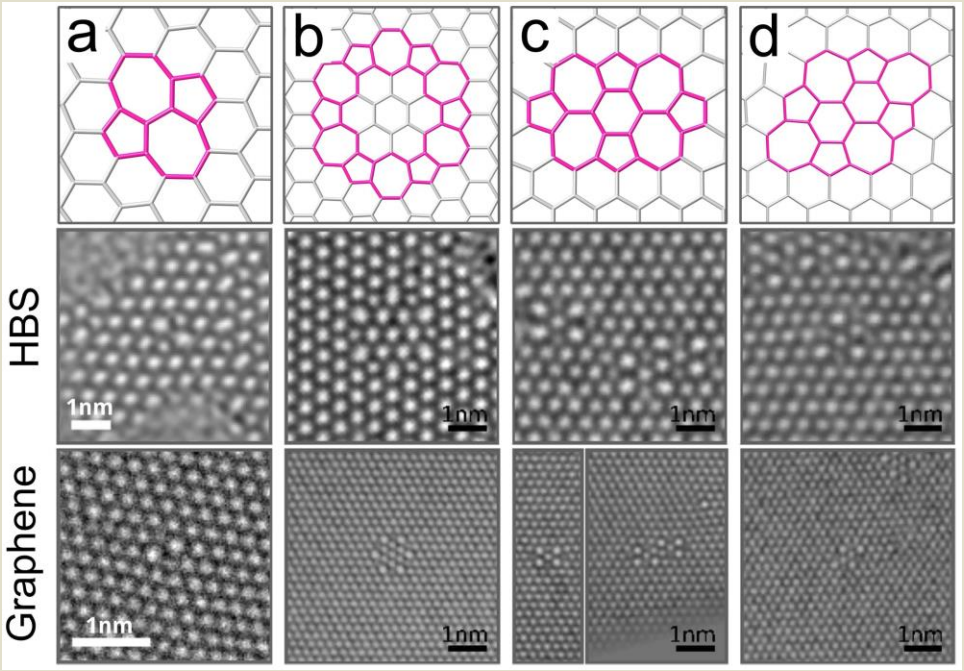
$$\delta = \frac{0.61\lambda}{\mu \, sin\beta}$$

(Rayleigh criterion)

- **This comes from the diffraction limit**
- **Shorter wavelength leads to higher resolution (resolution limit when intensities overlap)**
- **In practice: the limit is higher due to factors such as spherical aberration from the lens and chromatic aberration from the electron gun**
- **Electron pathway position through the lenses would present different outcomes according to the spherical aberration.**
    - For example, passing through the middle vs. edge
- **Intensity depends on interaction between electrons and the sample**

Data interpretation

- Typical HRTEM image
- In this case, light areas are denser with electrons vs. darker
- All examples mostly symmetrical, structures but..
- A few distinct spots with different pattern
- Picture D shows both vacancies and extra atoms.



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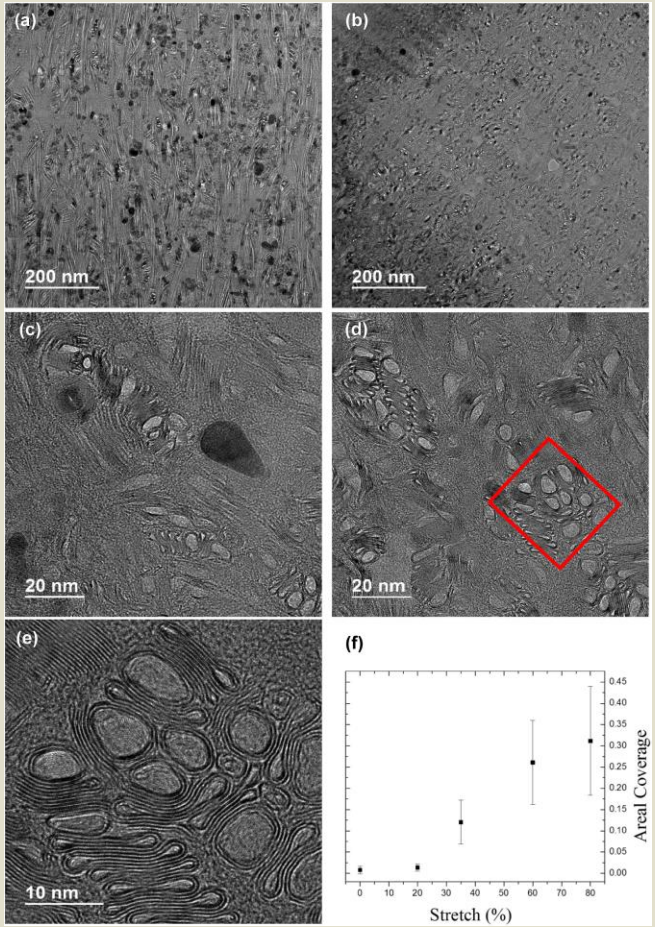
Data interpretation

- **The more you magnify, the more detailed information can be obtained**
- **Picture B: 2 different colored areas, packing density results in different colors → Different phases**
- **Picture D & E: CNT's, when magnified, reveals double walled structure**



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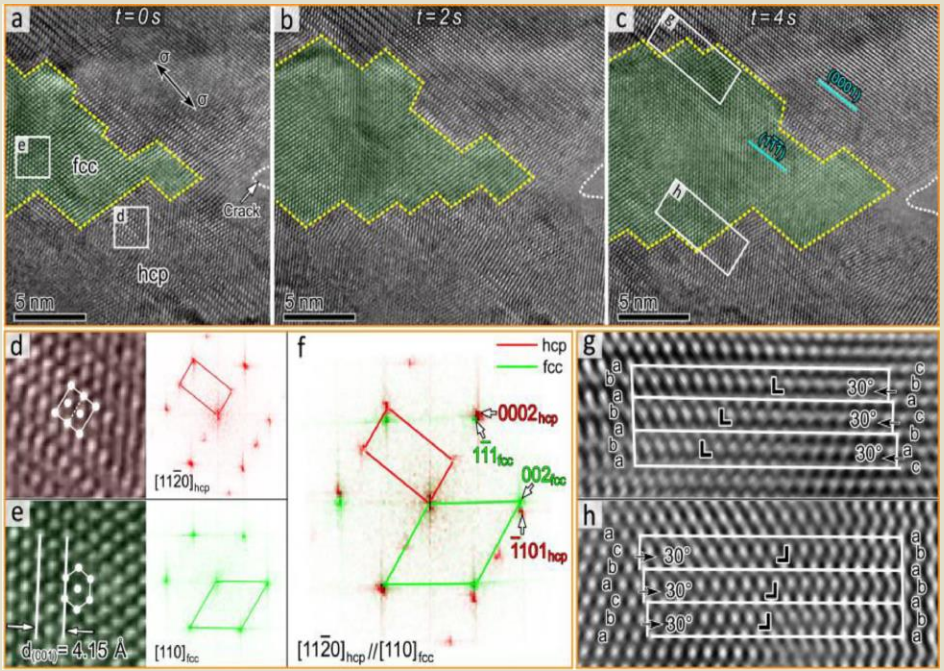
Jolowsky, C.; Sweat, R.; Park, J. G.; Hao, A.; Liang, R. Microstructure Evolution and Self-Assembling of CNT Networks during Mechanical Stretching and Mechanical Properties of Highly Aligned CNT Composites. Composites Science and Technology 2018, 166, 125–130. https://doi.org/10.1016/j.compscitech.2018.04.003.

Data interpretation

- 2 different types of structures in one sample
- Deduce which packing according to the pattern

- Picture D showing hcp packing
- Picture E showing fcc packing



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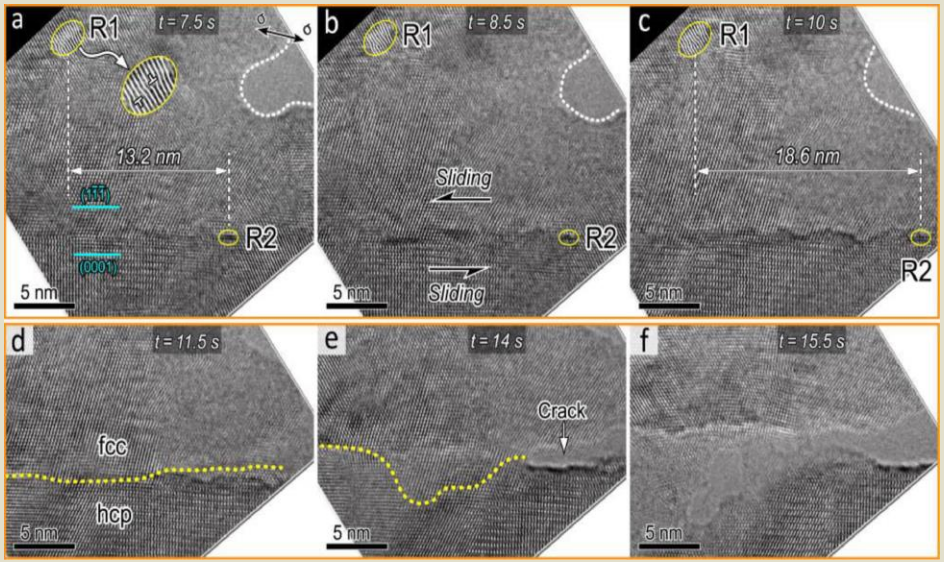
Kou, Z.; Li, X.; Huang, R.; Yang, L.; Yang, Y.; Feng, T.; Lan, S.; Wilde, G.; Lai, Q.; Tang, S. Stress-Induced Phase Transformation and Phase Boundary Sliding in Ti: An Atomically Resolved in-Situ Analysis. Journal of Materials Science & Technology 2023, 152, 30–36. https://doi.org/10.1016/j.jmst.2022.12.029.

Data interpretation

- **Areas R1 and R2 (Fig. A-C) move as a function of time**
- **→ Phase sliding**

- **Boundary between FCC and HCP (Fig. D-F) moves**
- **→ Cracking**



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Comparison of TEM

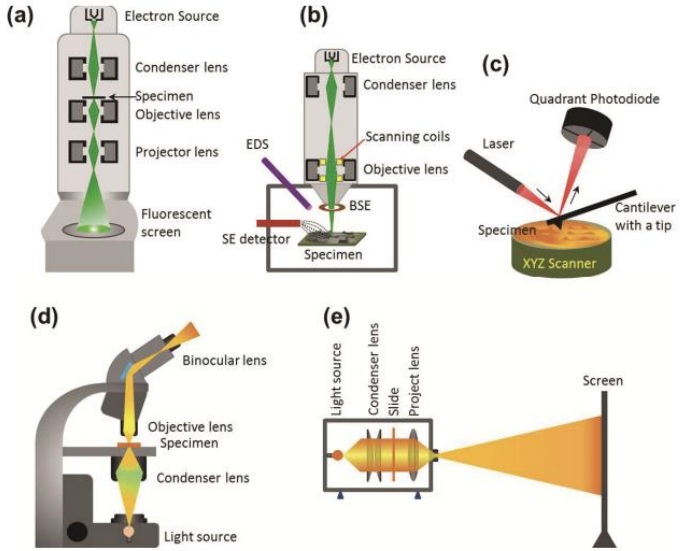

Fig. 1.3 Comparison of different magnifying methods: (a) TEM; (b) SEM; (c) AFM; (d) LM; and (e) projector.

(e) Slide projector. From left to right, the ray path is light source → condenser lens (two pieces of lenses combined together) → slide (specimen) → projector lens → screen. The ray path is similar to LM and TEM, except the objective lens that is missing since there is no need to focus down the beam. The magnified image is a 2D projection of the slide, which is similar to the TEM image.

TEM Fig.(c).

profilometer.

Table 1.1 Comparison of TEM with LM, SEM, and AFM.

	TEM	LM	SEM	AFM
Sample preparation	Samples must be very thin (<100 nm). Solid or thin sliced samples should be dehydrated and preferably conductive (carbon coating needed for nonconductive samples). Liquid can be prepared by cryo-EM method.	No restriction.	Normally dehydrated and surface is coated with a thin carbon or metal layer if nonconducting. Hydrated samples can be done using low-vacuum mode, special capsules, or cryo-SEM.	No restriction.
Resolution	Angstroms or sub-angstroms.	Sub-micrometers.	Nanometers.	Vertical: angstroms to 1 nm; Lateral: nanometers
Imaging	Mass-thickness contrast imaging, diffraction-contrast imaging, Z-contrast imaging in STEM, and phase-contrast in HRTEM; 2D only, except 3D reconstruction by electron tomography.	Low-magnification imaging. 2D for thin sections, or 3D using stereoscope or optical sectioning.	3D sample surface observation.	3D sample surface imaging by profiling at high resolution.
Structure	By electron diffraction or atomic imaging.	No.	By EBSD.	No.
Chemical analysis	By EDS, EELS, or STEM.	No.	EDS or WDS, while spatial resolution is lower than TEM.	No.

Luo, Z. *A Practical Guide to Transmission Electron Microscopy: Fundamentals*; Momentum Press: New York, UNITED STATES, 2015.

Pros & Cons

Pros:

- TEMs offer the most powerful magnification, potentially over 50 million times or more
- TEMs have a wide-range of applications (educational and industrial fields)
- TEMs provide information on compound structure, defects and unit cell properties
- Images are high-quality and detailed
- TEMs are able to yield information of surface features, shape, size and structure

Cons:

- TEMs are large and very expensive
- Laborious sample preparation
- Operation and analysis requires special training
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber
- TEMs require special housing and maintenance
- Images are black and white
- Statistically relevant data is an issue

Luo, Z. *A Practical Guide to Transmission Electron Microscopy: Fundamentals*; Momentum Press: New York, UNITED STATES, 2015.

- **Sample grown by ALD/MLD**
- **Samples prepared for TEM by Cu layer, further protected by a carbon layer and sample prepared with focused ion beam (FIB) milling**
- **Structure analyzed by XRD and verified by TEM**
  TEM results compared with XRR, showing promise as XRR is a faster method in gaining density information

IOP Publishing Semiconductor Science and Technology
Semicond. Sci. Technol. 36 (2020) 025012 (7pp) https://doi.org/10.1088/1361-6641/abcee2

Characterization of ZnO/AlO$_x$/benzene thin-film heterostructures grown through atomic layer deposition/molecular layer deposition

Fabian Krahl[1], **Yanling Ge**[1,2] **and Maarit Karppinen**[1]

[1] Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, Espoo, Finland
[2] VTT, Espoo, Finland

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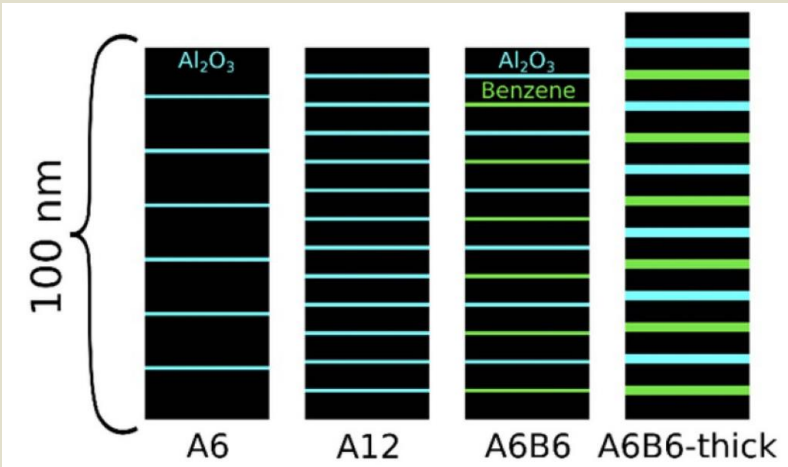

Figure 1. Cross section sketches of the present multi-layered thin-film samples.

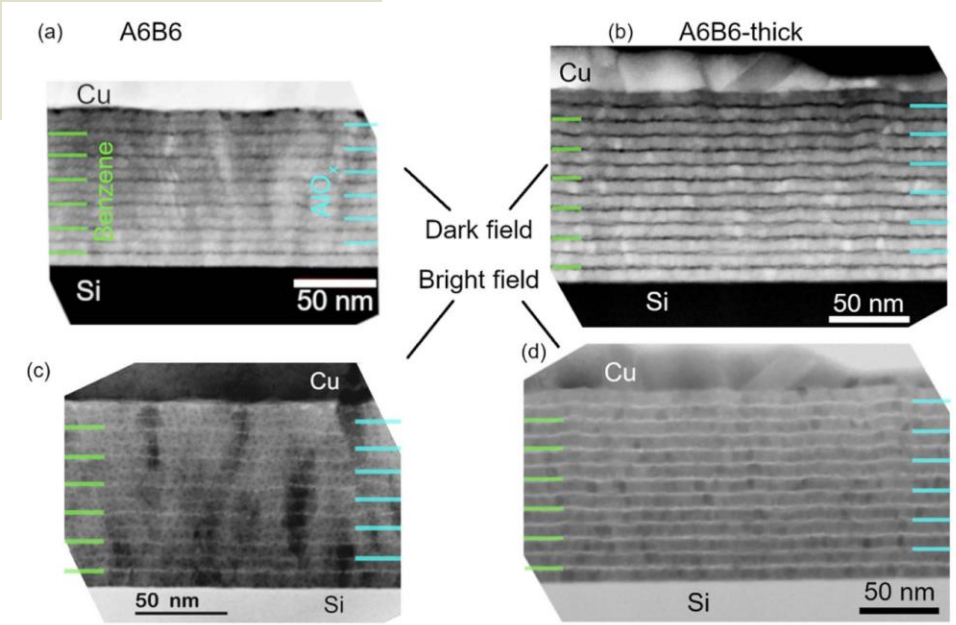

Figure 3. Bright and dark field TEM images of samples A6B6 and A6B6-thick.

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Krahl, F.; Ge, Y.; Karppinen, M. Characterization of ZnO/AlO $_x$ /Benzene Thin-Film Heterostructures Grown through Atomic Layer Deposition/Molecular Layer Deposition. *Semicond. Sci. Technol.* **2021**, *36* (2), 025012. https://doi.org/10.1088/1361-6641/abcee2.

- **Solid state synthesis, mixing Sr and Co oxides.**
- **HRTEM used for identification of new phase, “supercell” dimension, monoclinic distortion**

Chem. Mater. **2006,** *18,* 155−158

Parent of Misfit-Layered Cobalt Oxides: $[Sr_2O_2]_qCoO_2$

H. Yamauchi,† K. Sakai,† T. Nagai,‡ Y. Matsui,‡ and M. Karppinen*,†

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

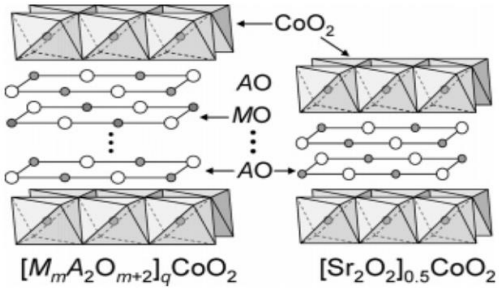

Figure 1. Crystal structures of misfit-layered cobalt oxides, $[M_mA_2O_{m+2}]$ CoO_2, in general and of the new “zero” phase, $[Sr_2O_2]_{0.5}CoO_2$. The form contains hexagonal CoO_2 layers coupled incoherently with square-plan *A*O and *M*O layers along the sequence, $AO-(MO)_m-AO-CoO_2$, where the latter lacks the $(MO)_m$ “charge reservoir”. All the layers should l considered potentially nonstoichiometric, at least in terms of oxygen.

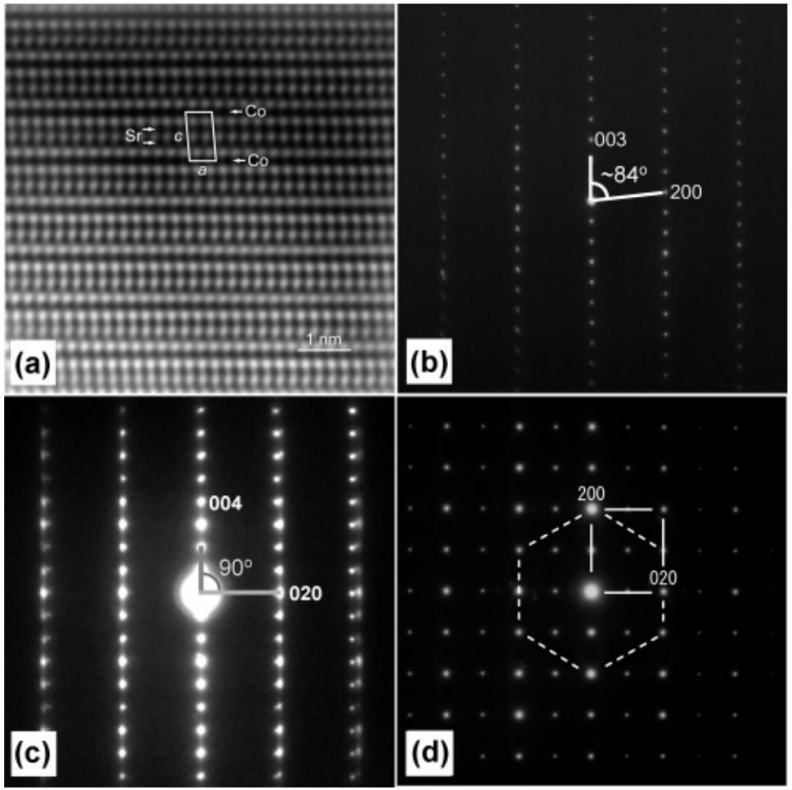

Figure 3. HRTEM image and ED patterns for $[Sr_2O_2]_{0.5}CoO_2$. (a) The HRTEM image represents the *ac* plane, exhibiting the layer sequence of $SrO-SrO-CoO_2$ and a monoclinic distortion. The ED patterns are taken with the electron beam along (b) [010], (c) [100], and (d) [001]. The first ED pattern confirms the monoclinic distortion and the last shows that the phase is commensurate, i.e., q $(=b_H/b_S) = 0.5$.

Yamauchi, H.; Sakai, K.; Nagai, T.; Matsui, Y.; Karppinen, M. Parent of Misfit-Layered Cobalt Oxides: $[Sr_2O_2]_qCoO_2$. *Chem. Mater.* **2006**, *18* (1), 155–158. https://doi.org/10.1021/cm0519176.

High-T_c superconductivity in three-fluorite-layer copper oxides. II. (Cu,Mo)Sr_2(Ce,Y)$_3Cu_2O_{11+\delta}$

Y. Morita,[1] T. Nagai,[2] Y. Matsui,[2] H. Yamauchi,[1] and M. Karppinen[1,*]
[1]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
[2]*National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
(Received 19 February 2004; revised manuscript received 22 April 2004; published 17 November 2004)

- **Solid state synthesis by mixing oxides, Calcinated (950˚C) and sintered (1020˚C).**
- **HRTEM used for structure confirmation and to check for stacking faults and other defects**

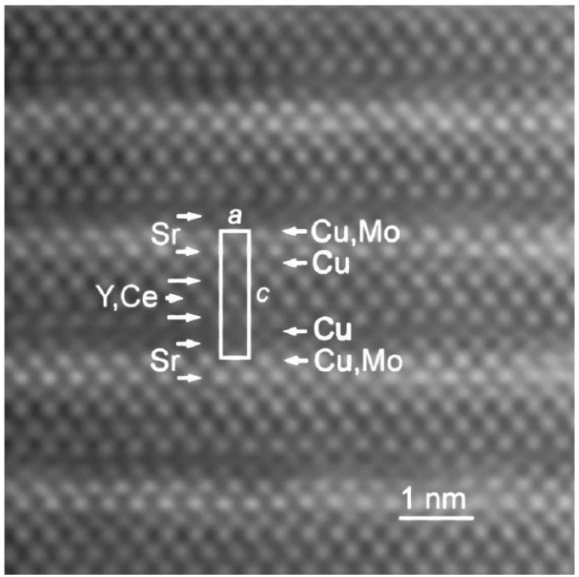

FIG. 2. HRTEM image for the HPO-100 sample.

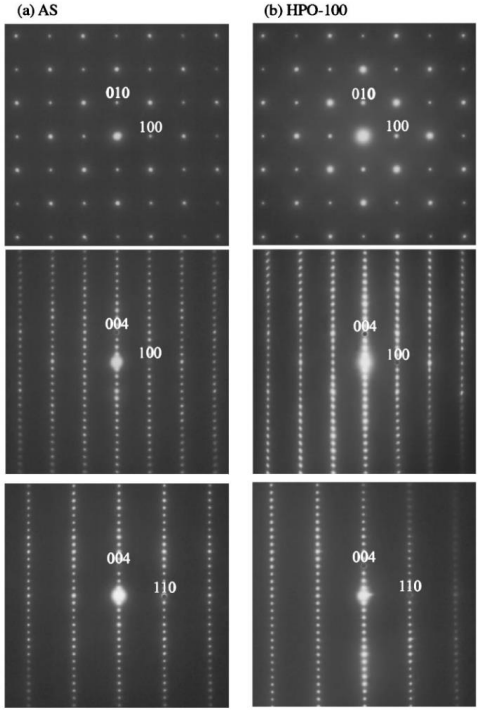

FIG. 3. ED patterns for the AS (a) and HPO-100 (b) samples with the incident beam along the directions, [001], [010], and [1−10] (from the top to the bottom).

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Morita, Y.; Nagai, T.; Matsui, Y.; Yamauchi, H.; Karppinen, M. High- T c Superconductivity in Three-Fluorite-Layer Copper Oxides. Ⅱ. (Cu , Mo) Sr 2 (Ce , Y) 3 Cu 2 O 11 + δ. *Phys. Rev. B* **2004**, *70* (17), 174515. https://doi.org/10.1103/PhysRevB.70.174515.

Questions ?

Questions are allowed but discouraged … ☺

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