ESP5403 Nanomaterials for Energy Systems

Synthesis and Characterization of Single Crystal, Bi-crystal, Poly-crystal and Nanocrystalline Materials

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- Synthesis of single crystal
- Synthesis of poly-crystals
- Impedance studies on single crystals
- Impedance studies on bi-crystals – role of grain boundaries
- Impedance studies on poly-crystals
- Synthesis of Nanomaterials:
  - Top down approach
  - Bottom up approaches
- Characterization of Nanoparticles

Synthesis of Single Crystal

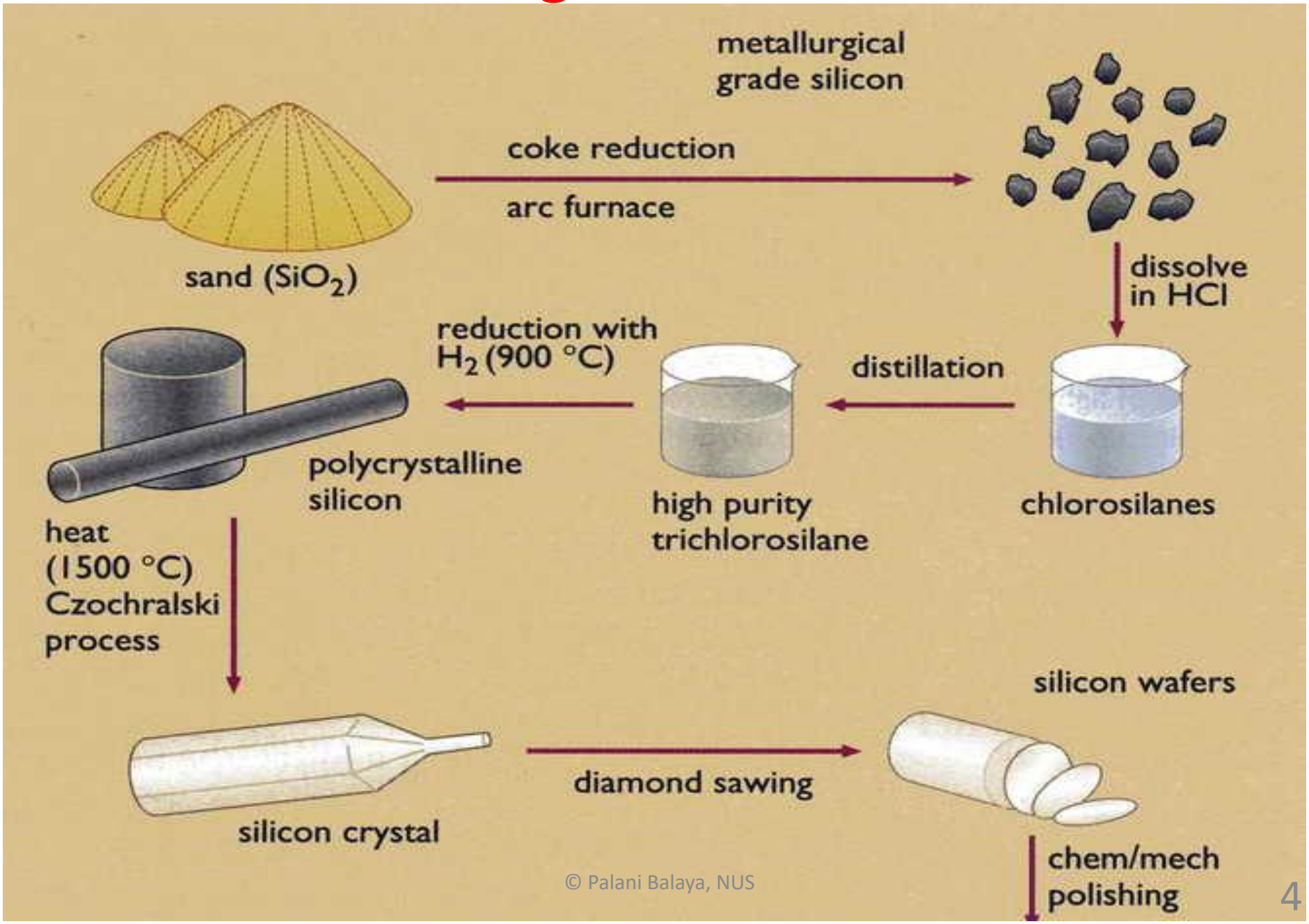
- Growing single crystalline silicon

– Czochralski process (single crystal is drawn slowly out of a melt)

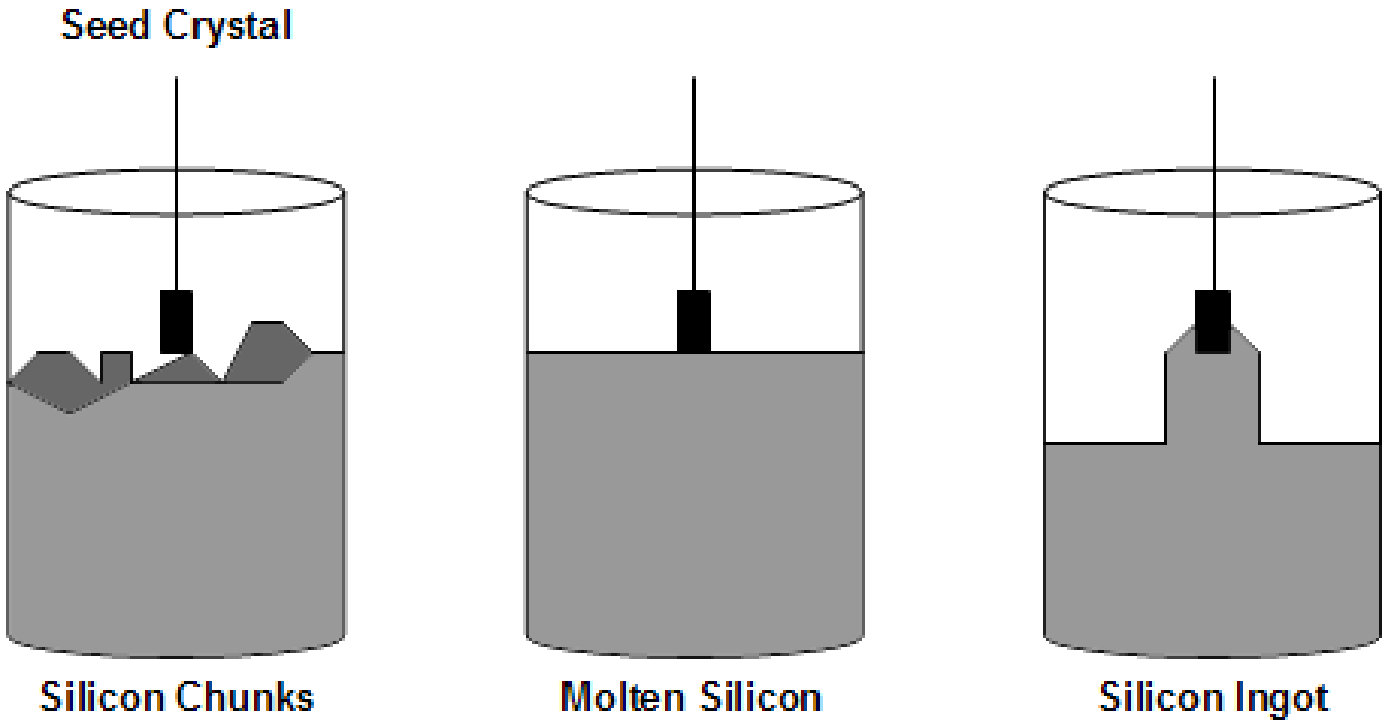
– Float zone process (formed from a polycrystalline silicon by passing a molten zone through it)

- In either case, the dopant is introduced during growth to produce p-type
- Solid crystal is sliced, etched to smooth the rough surface

Creating Silicon Wafers

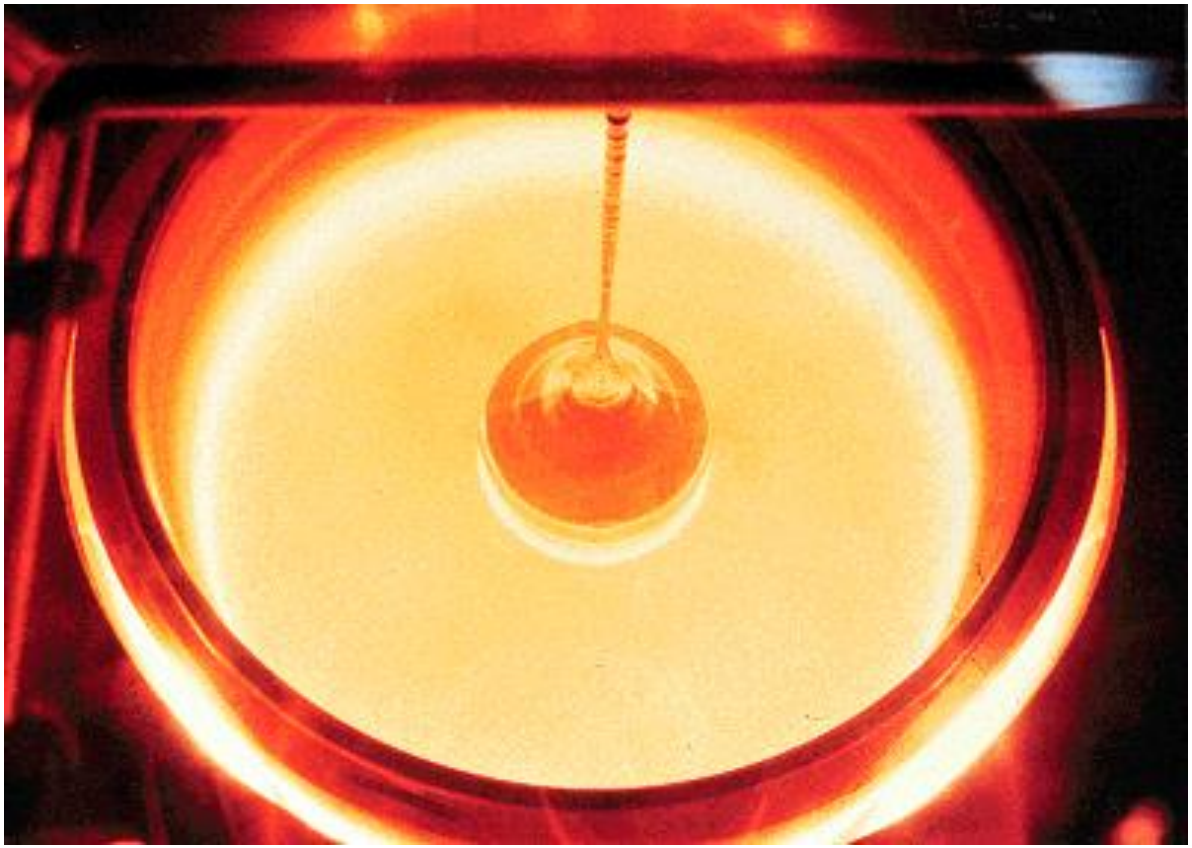


Growing Silicon Ingots



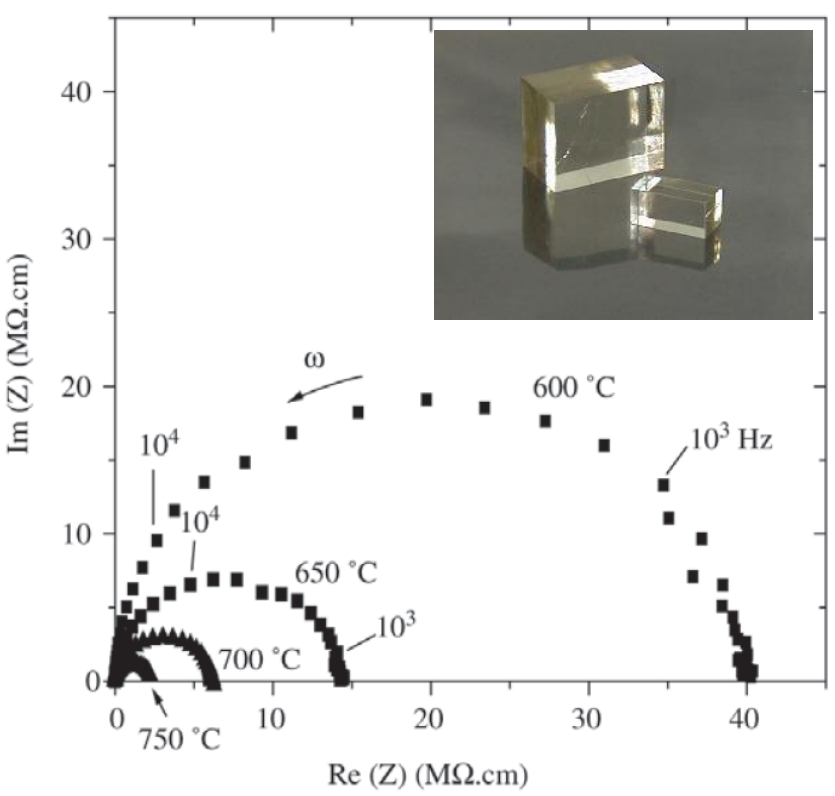
Czochralski Process

Drawing a Silicon Ingot

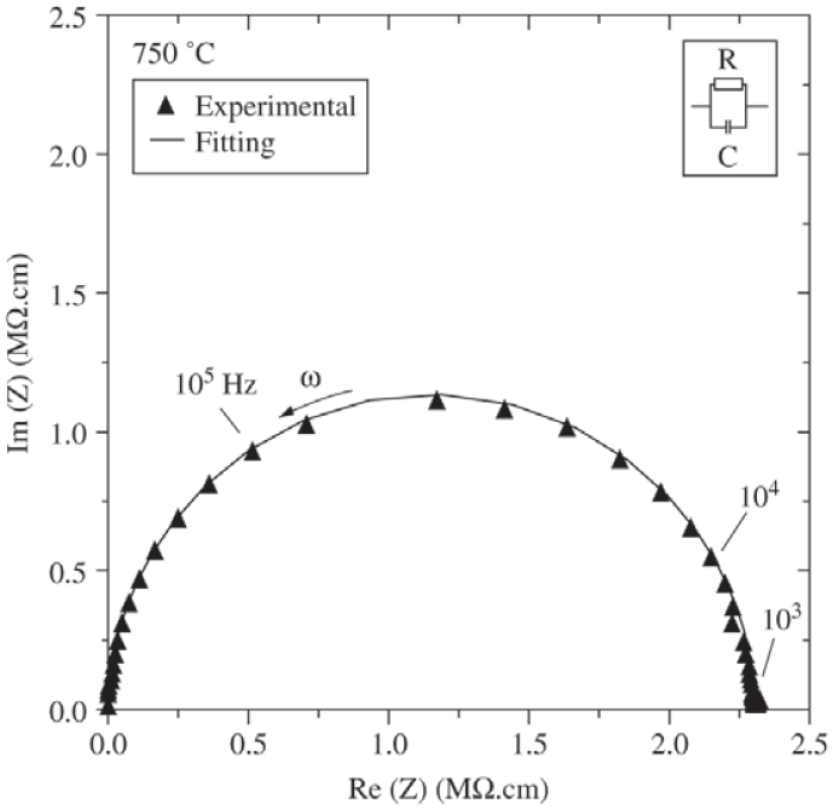


Silicon Ingots & Wafers

Impedance measurement on single crystals



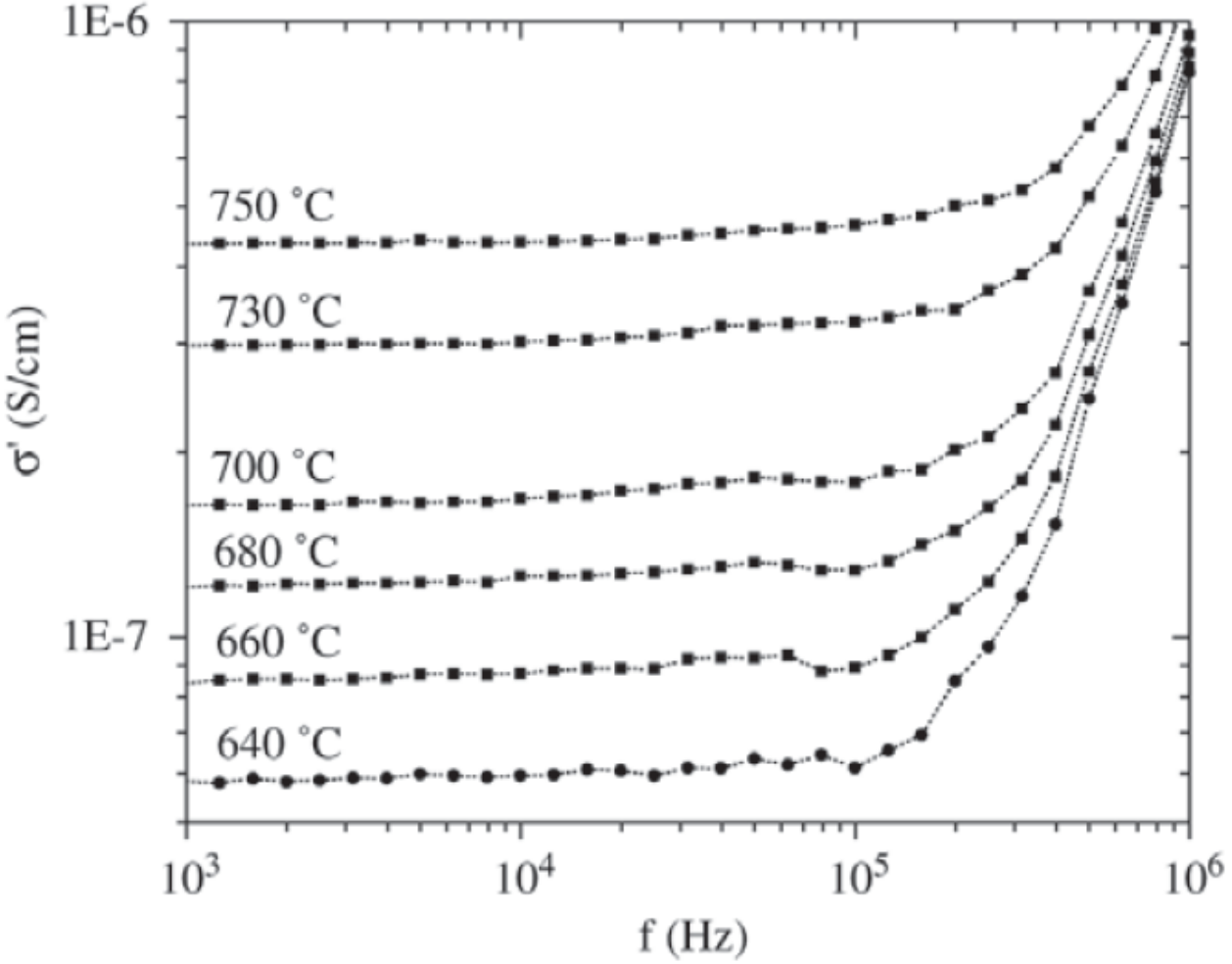
Complex impedance diagrams of $Bi_4Ge_3O_{12}$ single crystal, taken isothermally at 600, 650, 700 and 750 °C. The numbers indicate the signal frequency.



Complex impedance diagrams of $Bi_4Ge_3O_{12}$ taken at 750 °C, fitted to an equivalent RC parallel circuit. The numbers indicate the signal frequency.

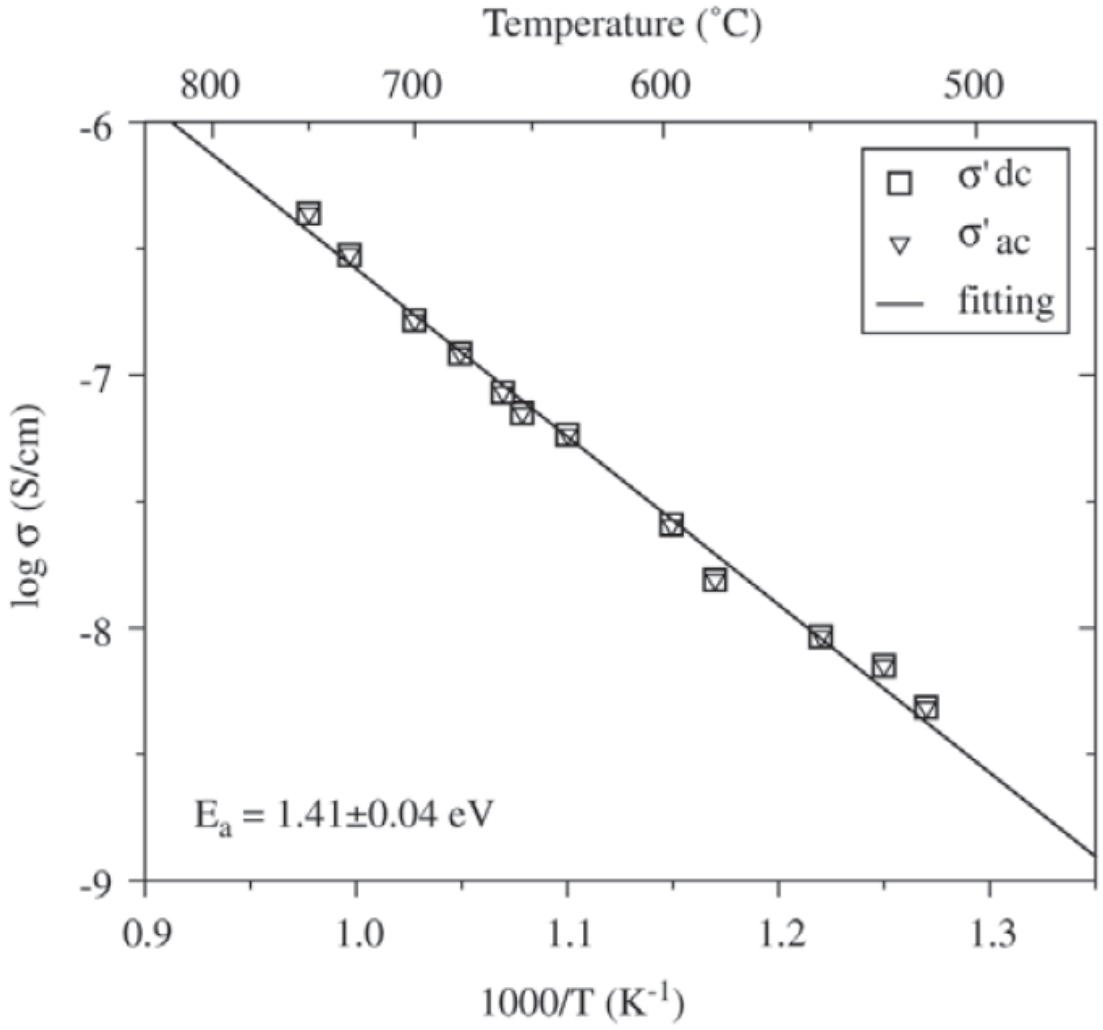
Macedo et al., Materials Research, 6 (2003) 577

AC Conductivity of BGO single crystal



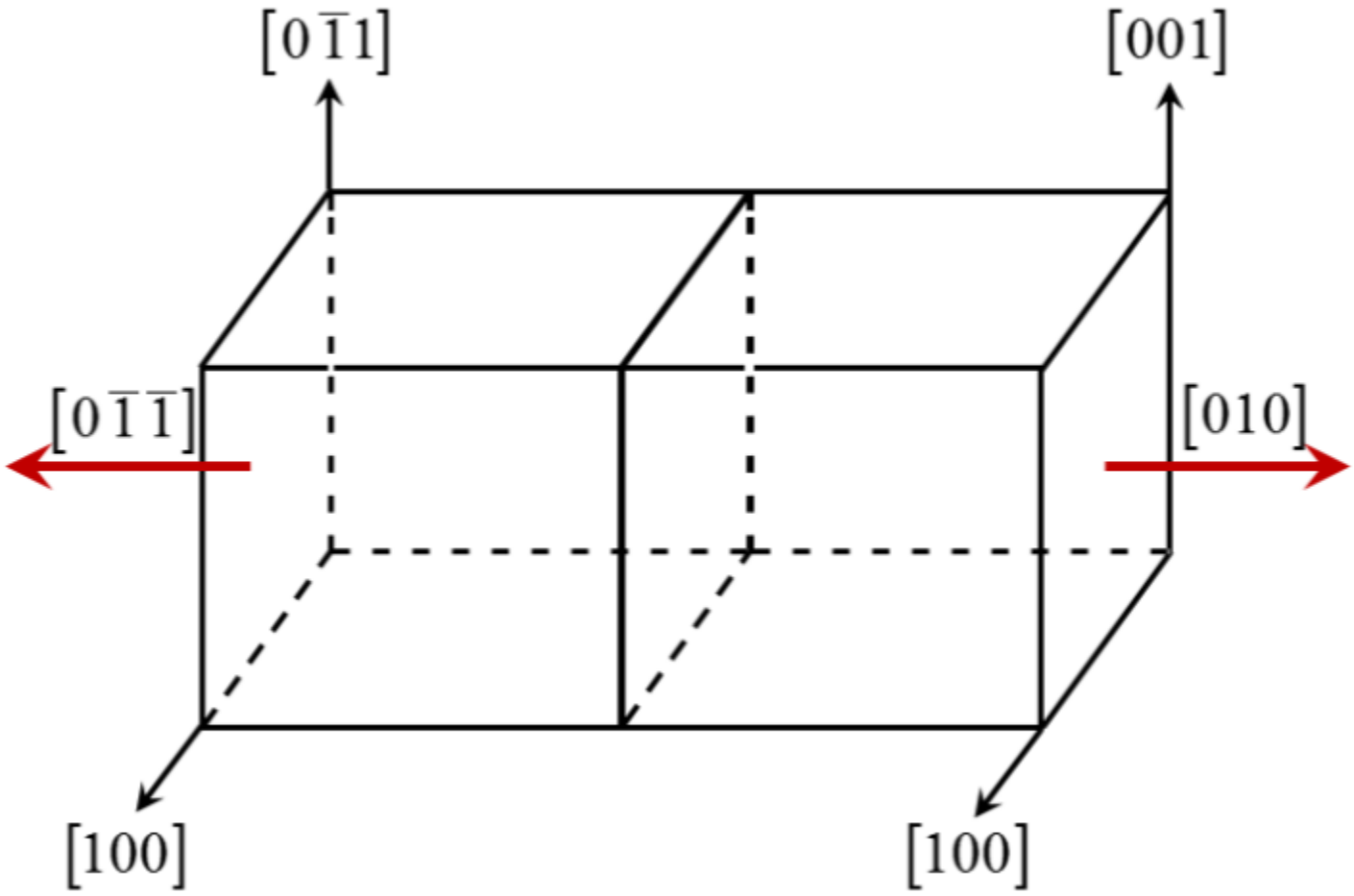
Conductivity σ' of BGO single crystal. The plateau at low frequencies accompanied by the dispersion at high frequencies is generally related to hopping processes in disordered solids[12].

DC and AC Conductivity of BGO single crystal

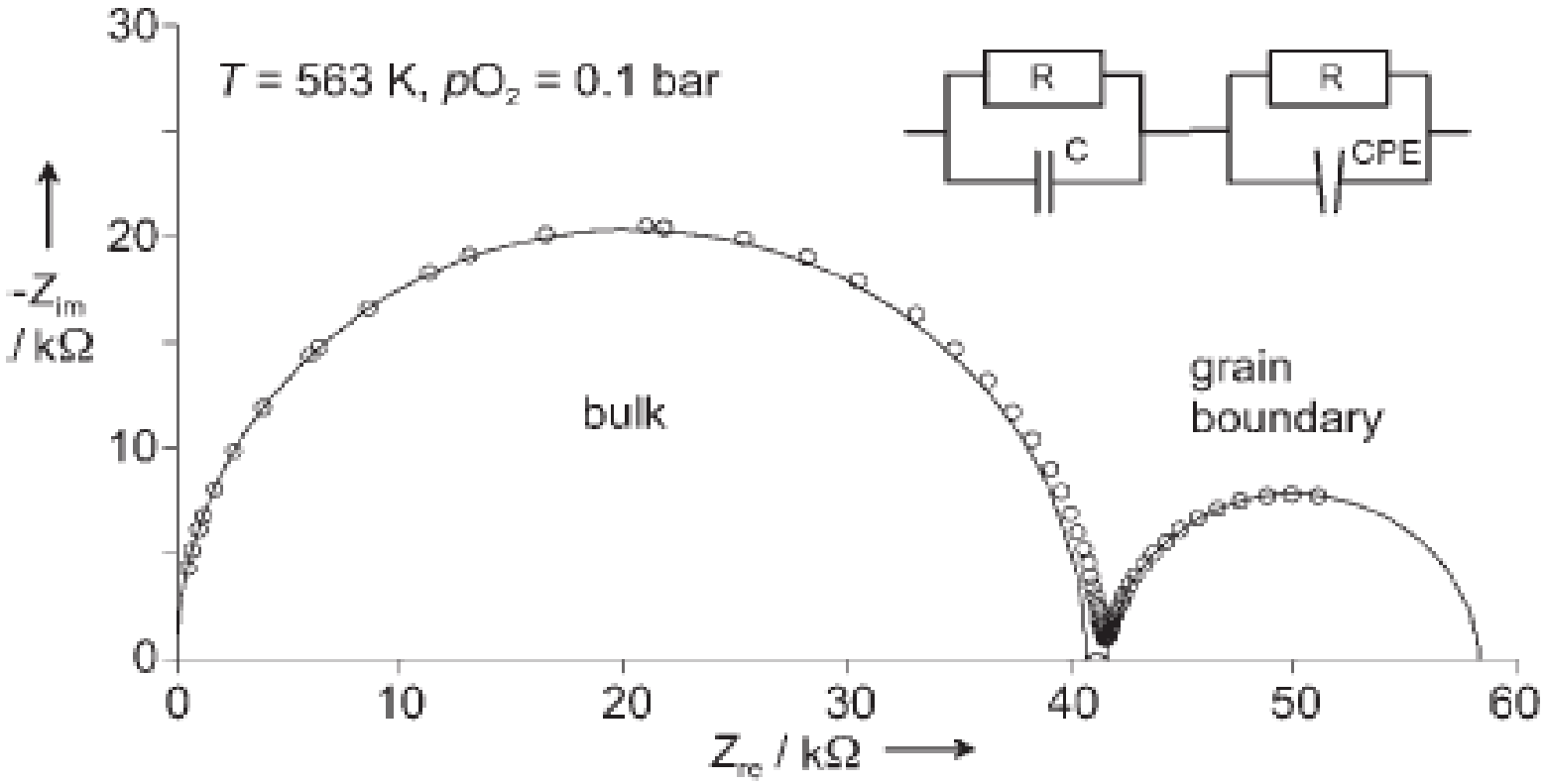


Arrhenius plots for dc and ac conductivities in BGO (σ'_{dc} and σ'_{ac}, respectively). The apparent activation energy indicated in the graphic was deduced from the slope of the linear regression of the data.

Schematic Representation of Bi-crystal

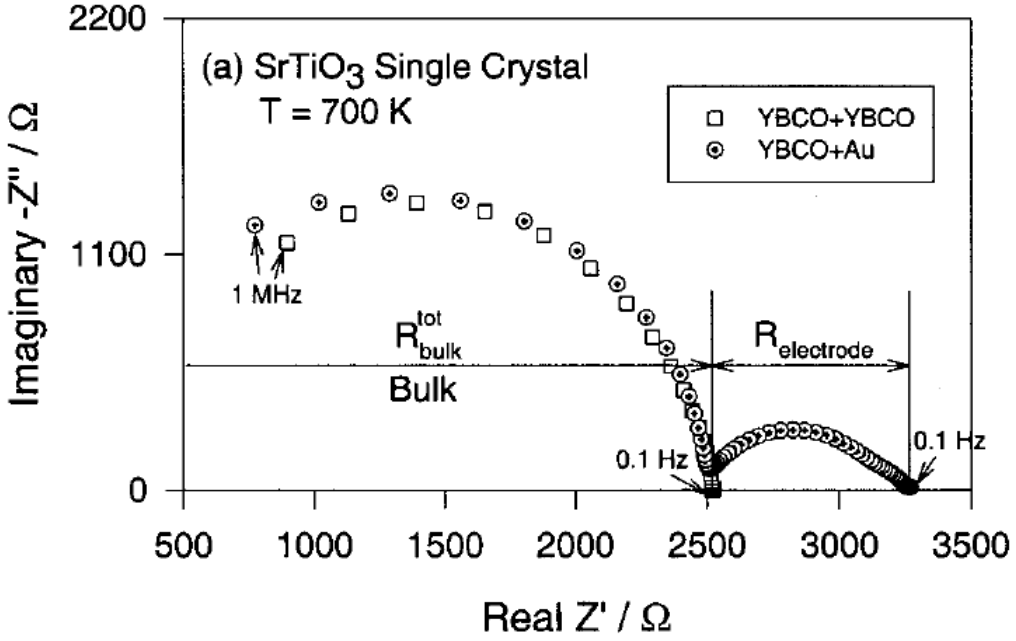


Impedance Measurement on Bi-crystal



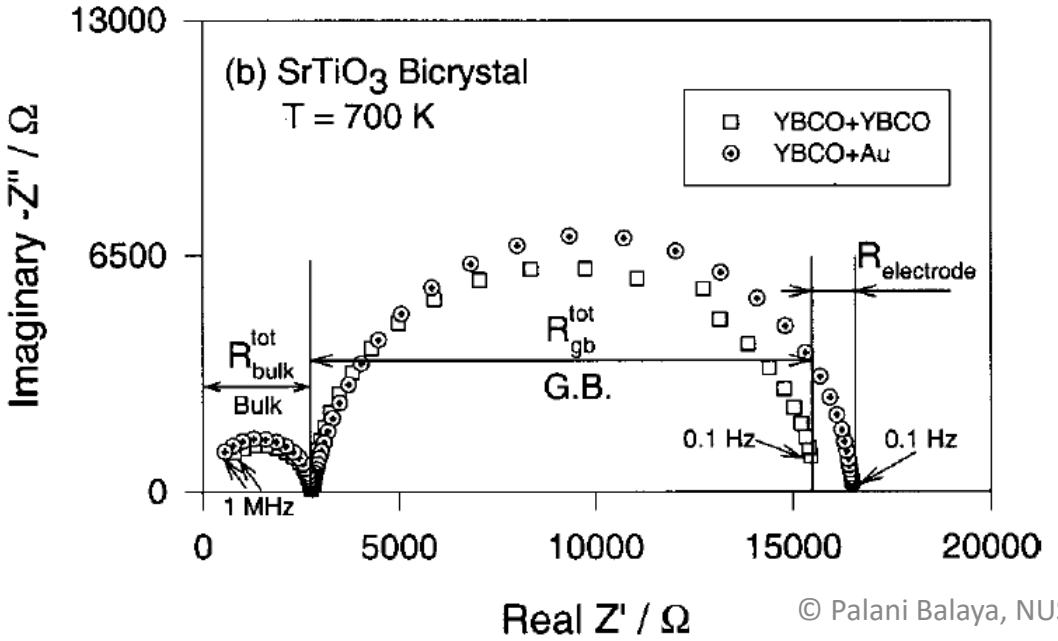
Impedance spectrum of the Fe-doped $SrTiO_3$ bicrystal with a tilt angle of 5.4° (reproduced from reference [126] with permission from the American Ceramic Society). In the corresponding equivalent circuit, the blocking grain boundary is represented by additional resistor and constant phase elements (the further R and CPE elements corresponding to the tiny electrode semicircle are omitted).

Impedance Measurement on Bi-crystal



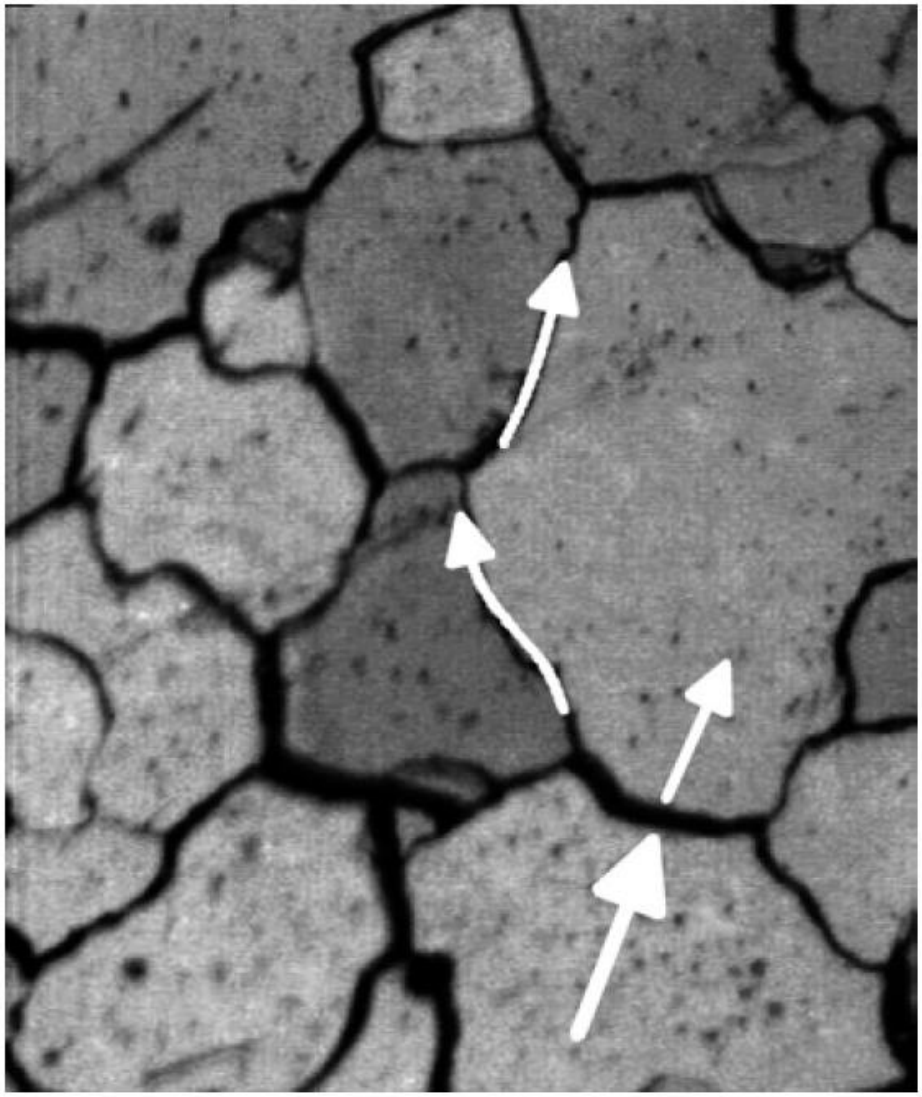
$(+)\ p_{O_2}$, YBCO/$SrTiO_3$/Au, $p_{O_2}\ (-)$

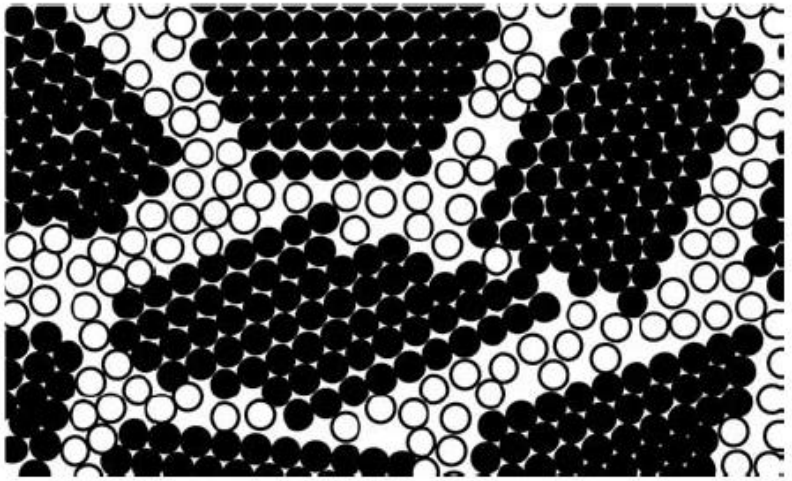
(+) YBCO/$SrTiO_3$/YBCO (-)



Journal of The Electrochemical Society, **148** (9) J50-J53, 2001

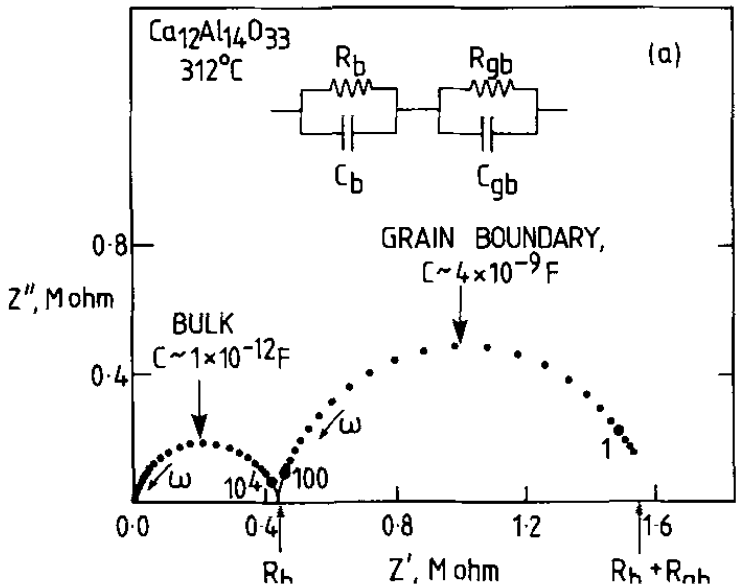
Micrograph of a Polycrystalline Material

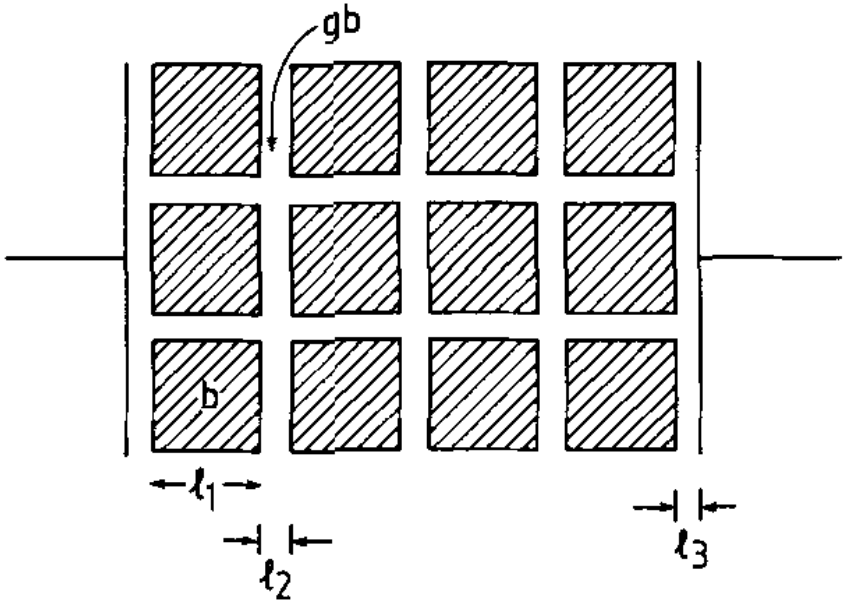




SEM image of a polycrystalline material where white arrows indicate possible grain boundary effects, as far as the transport is concerned.

Analysis of Bulk and Grain Boundary Contributions in Polycrystalline Materials





Impedance data for $Ca_{12}Al_{14}O_{33}$ presented in the complex impedance plane format, Z'' vs Z' where $Z^* = Z'\text{-j}\,Z''$, $j = \sqrt{-1}$, ω = angular frequency $2\pi f$. Selected frequency points, in Hz are marked. The equivalent circuit used to interpret the data is shown. It represents a series combination of crystal and grain boundary impedances.

Inverse relation exists between capacitance and thickness:

$$C = \frac{\varepsilon A}{l}$$

Hence, $$\frac{C_b}{C_{gb}} = \frac{l_2}{l_1}$$

Analysis of Bulk and Grain Boundary Contributions in Polycrystalline Materials

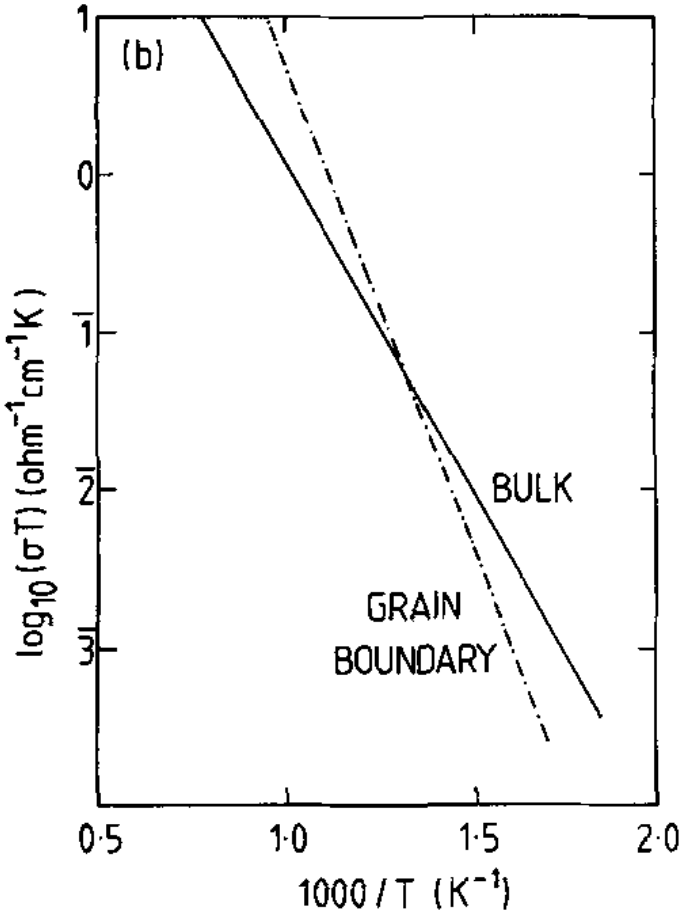


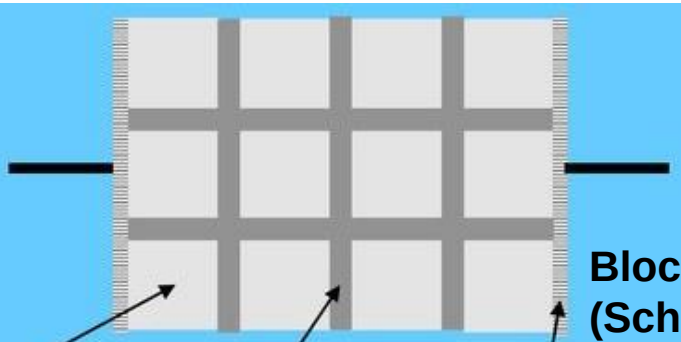
Table 1. Capacitance values and their possible interpretation.

Capacitance [F]	Phenomenon Responsible
10^{-12}	bulk
10^{-11}	minor, second phase
10^{-11}–10^{-8}	grain boundary
10^{-10}–10^{-9}	bulk ferroelectric
10^{-9}–10^{-7}	surface layer
10^{-7}–10^{-5}	sample-electrode interface
10^{-4}	electrochemical reactions

Temperature dependence of bulk and grain boundary conductivities for $Ca_{12}Al_{14}O_{33}$

Impedance Measurement on Polycrystalline Materials – Role of Brain Boundary and Electrodes

Composite Character of the Impedance Response of a Polycrystalline Sample



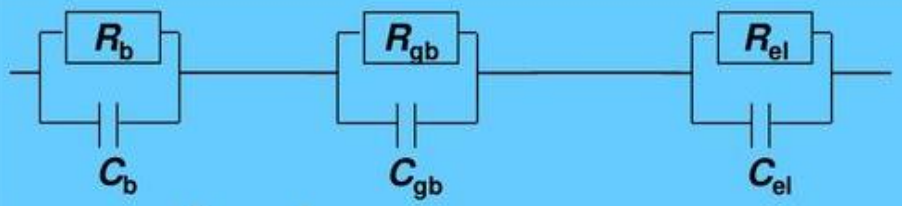
Blocking electrode (Schottky barrier)

Bulk $C_b \sim 1 \times 10^{-12}$ F

Grain Boundary $C_{gb} \sim 1 \times 10^{-9}$ F

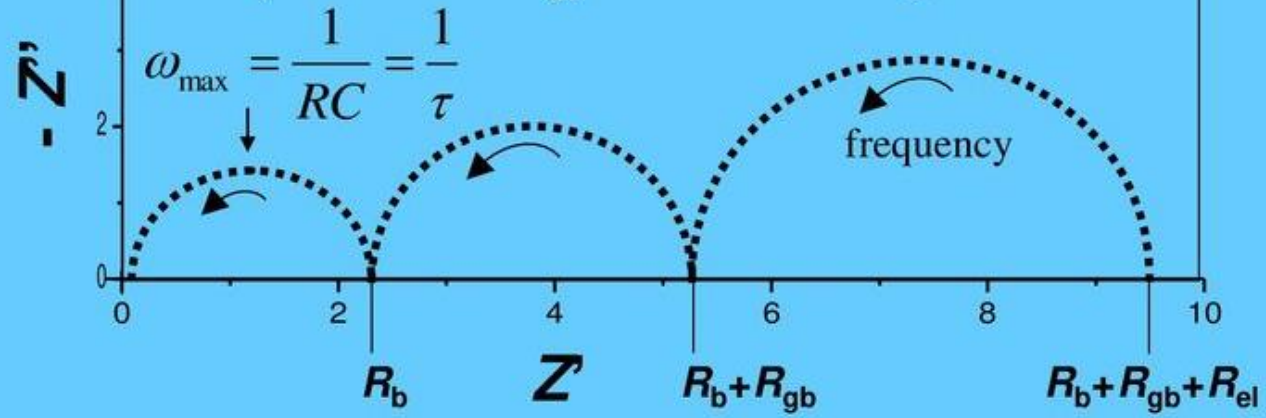
Electrode Interface $C_{el} \sim 1 \times 10^{-6}$ F

Equivalent Circuit

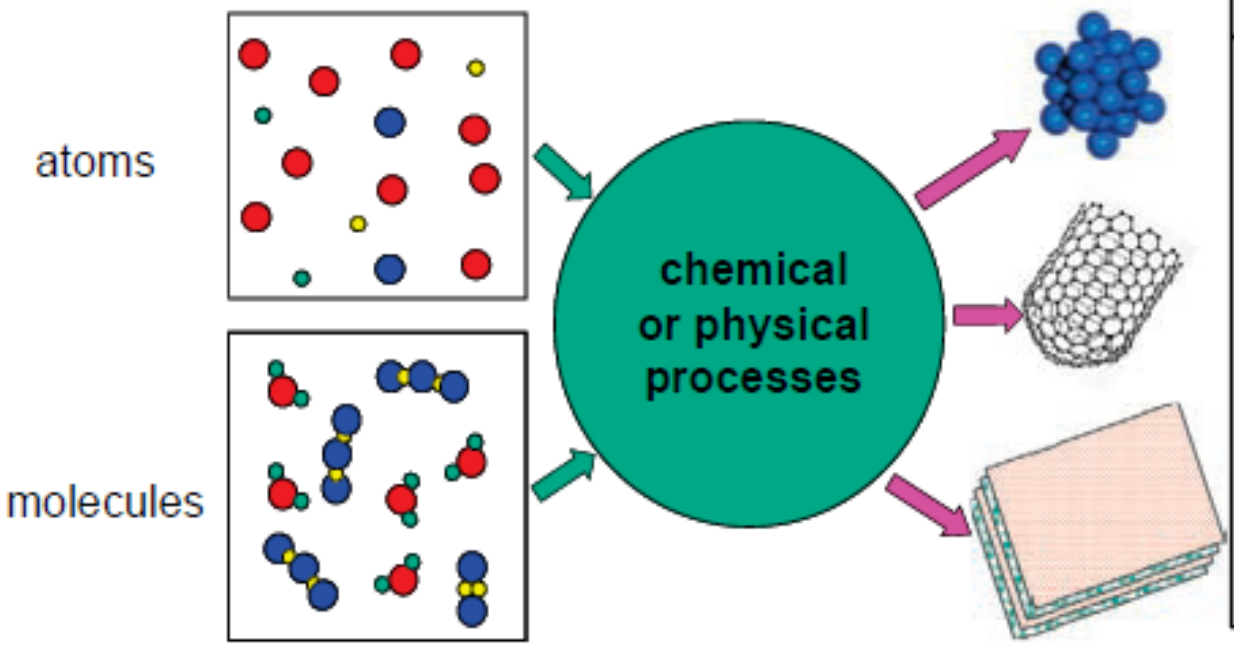


Nyquist Plot

Negative Imaginary Part of Impedance $-Z''$ vs Real Part Z'



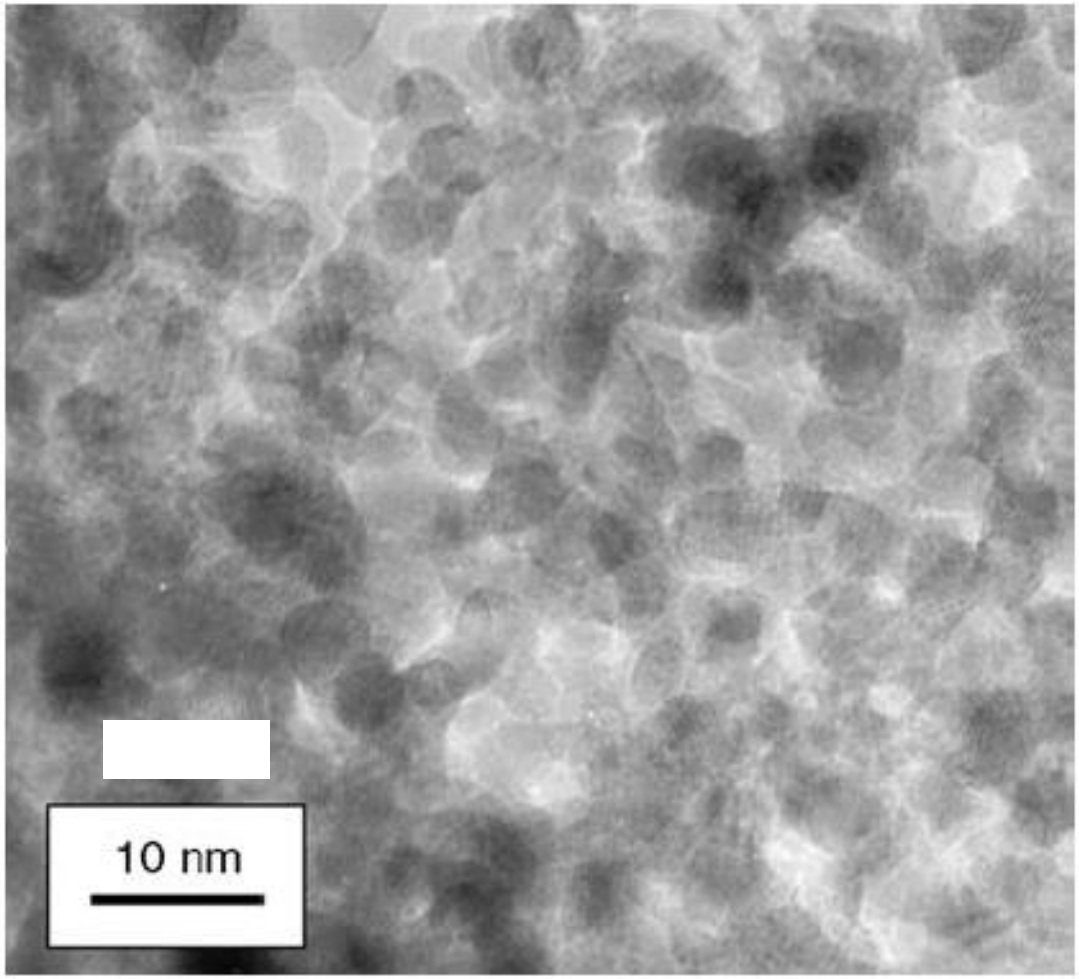
Formation of Nanomaterials – Dimensionality



product	dimen-sionality
particles	zero
nanotubes or rods	one
layers	two

Nanotechnologies are usually connected to bottom-up processes and are characterized by the use of atoms or molecules as building blocks. Bottom-up processes result in particles, nanotubes, nanorods, thin films, or layered structures. These products are also characterized by their dimensionality, as is also indicated.

Image of Nanomaterials



Transmission Electron Microscope image of ZrO_2 nanoparticles. This material has a very narrow grain size distribution; this may be important as the properties of nanomaterials depends on grain size.

Practice of Nanotechnology – Historical Evidences

Medieval stained-glass of an ancient church.

Nanotechnology has been applied by humans over a thousands years unknowingly from painting to making steel.

Medievel stained-glass in Europe:

Entrapment of nanoparticles in the glass matrix.

Ruby red color – gold particles (AuNPs) in the glass matrix

Deep yellow color – silver nanoparticles in the glass matrix

Practice of Nanotechnology – Historical Evidences

Deruta maiolica plate

Chinese ceramic porcelain

Deruta ceramics is an iridescent ceramic material developed in Italy during the early medieval age. The metallic glaze of this material was due to the presence of copper and silver particles in nanometer range **(see top)** . The Chinese used AuNPs to create a red color in the ceramic porcelains **(see right top).**

The Lycurgus Cup **(right)** is a dichroic cup made by Romans in the 4th century. The color of the cup changes with respect to the incident light. When it is looked at in reflected light or daylight, it appears green. However, when light is shown into the cup and transmitted through the glass, it changes to red. This color variation is due to the presence of gold and AgNPs

Lycurgus cup

Top-down vs. bottom-up

- **Top-down methods**

begin with a pattern generated on a larger scale, then reduced to nanoscale.

-By nature, aren't cheap and quick to manufacture

- Slow and not suitable for large scale production.

- **Bottom-up methods**

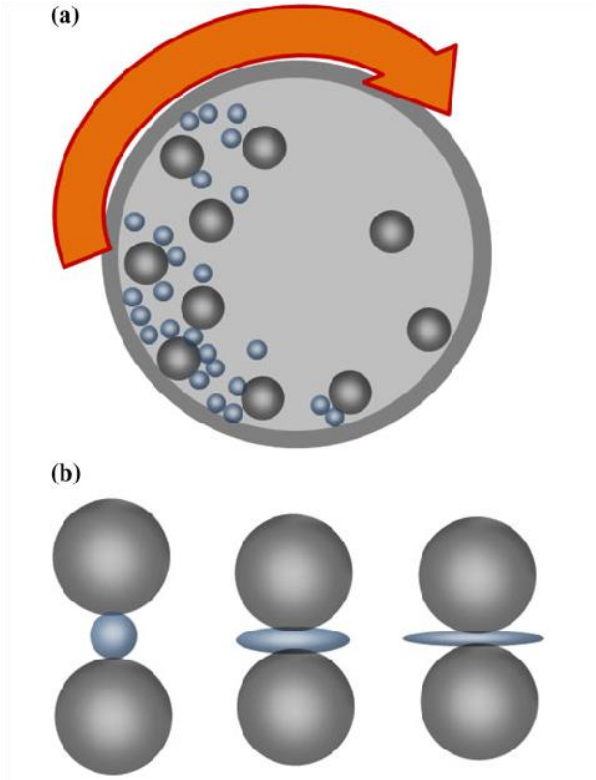
start with atoms or molecules and build up to nanostructures

-Fabrication is much less expensive

TOP DOWN: Physical Methods

Mechanical Milling:

Through this mechanical milling process, size of bulk material can be reduced to nanoscale.
Basic principle: Transfer of energy to the sample from the balls during the milling process.
Ball materials: Steel, Zirconia and Tungsten.
During milling process, local temperature increase – pay attention.
Final share and structure also depends on the strains causes during high energy collision process by the balls on the nanoparticles.
Usually nanomaterials are heat treated at slightly high temperature to relieve the strains.



Mechanochemical processing:

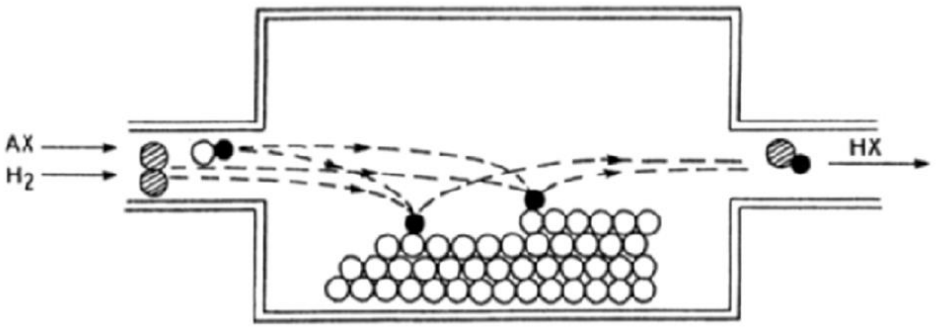
Mechanical milling process can be used to blend different starting (precursor) materials.
In the process size of submicron size of starting materials reduces to nanoscale.
Unqiue property of mechanochemical processing is the processing speed in yielding nanophase materials.
The nanosize precursors speed up reactions among them (increase of reaction kinetics) which induces chemical reaction (which basically requires high temperatures) to occur at low temperature.

BOTTOM UP: Chemical Methods

Chemical vapour Deposition:

In this method, a sample material is deposited in a vapor medium with the help of chemical reaction. The material is deposited in the form of thin film, powder or a single crystal. The advantages of the CVD is its excellent throwing power, thin films with uniform thickness with low percentage of porosity, and selective deposition on desired pattern. CVD is applied in thin films for dielectric, conductors, passivation layer, oxidation layer, conductive oxides, tribological and corrosion resistant coatings, heat resistant coatings, etc. Other applications include fabrication of solar cells and high-temperature fiber composites

Chemical vapour deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapour phase. It belongs to the class of vapour-transfer processes which is atomistic in nature, that is the deposition species are atoms or molecules or a combination of these.



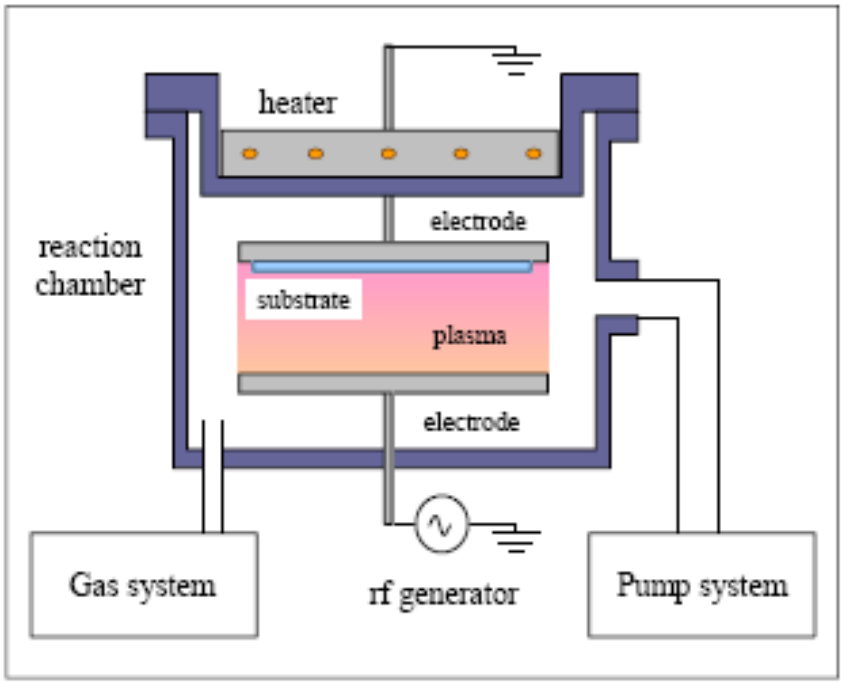
Schematic of a simple thermal CVD reactor

Amorphous Si Deposition-Plasma Enhanced CVD

Gases SiH_4, and H_2

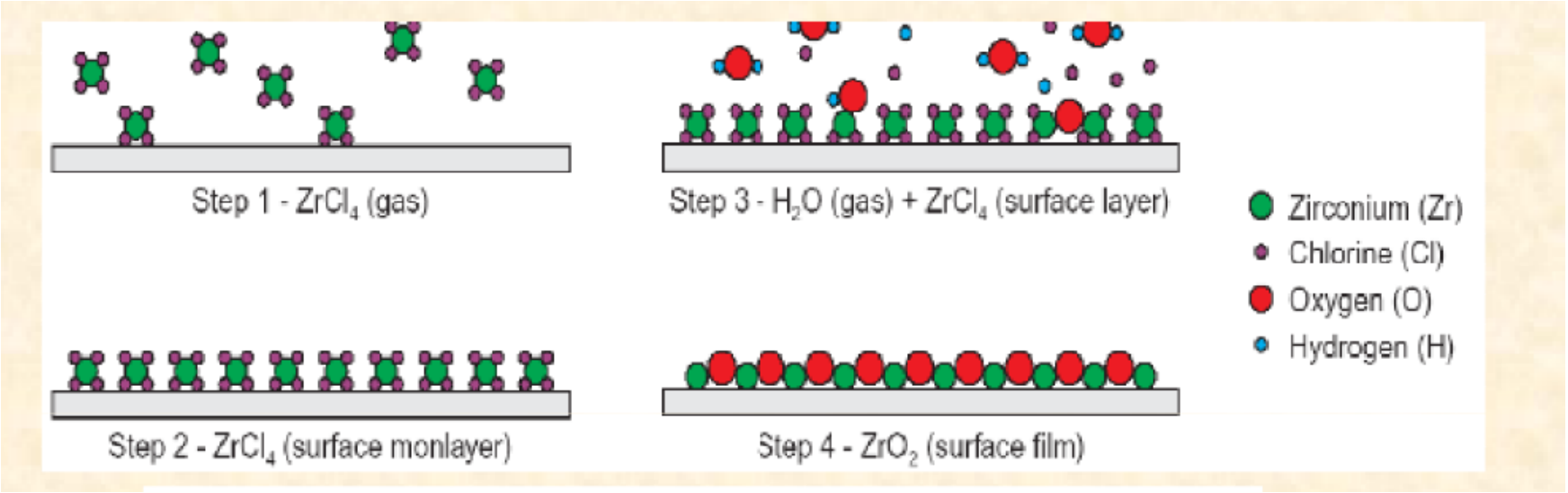
Dopant gases: trimethylborium ($B(CH_3)_3$) or diborane (B_2H_6)

phosphine PH_3



+ Low deposition temperature
+ Use of cheap substrates
+ Large area deposition
+ Easy doping and alloying
– Low deposition rate (1-2 Å/s)

Atomic Layer Deposition

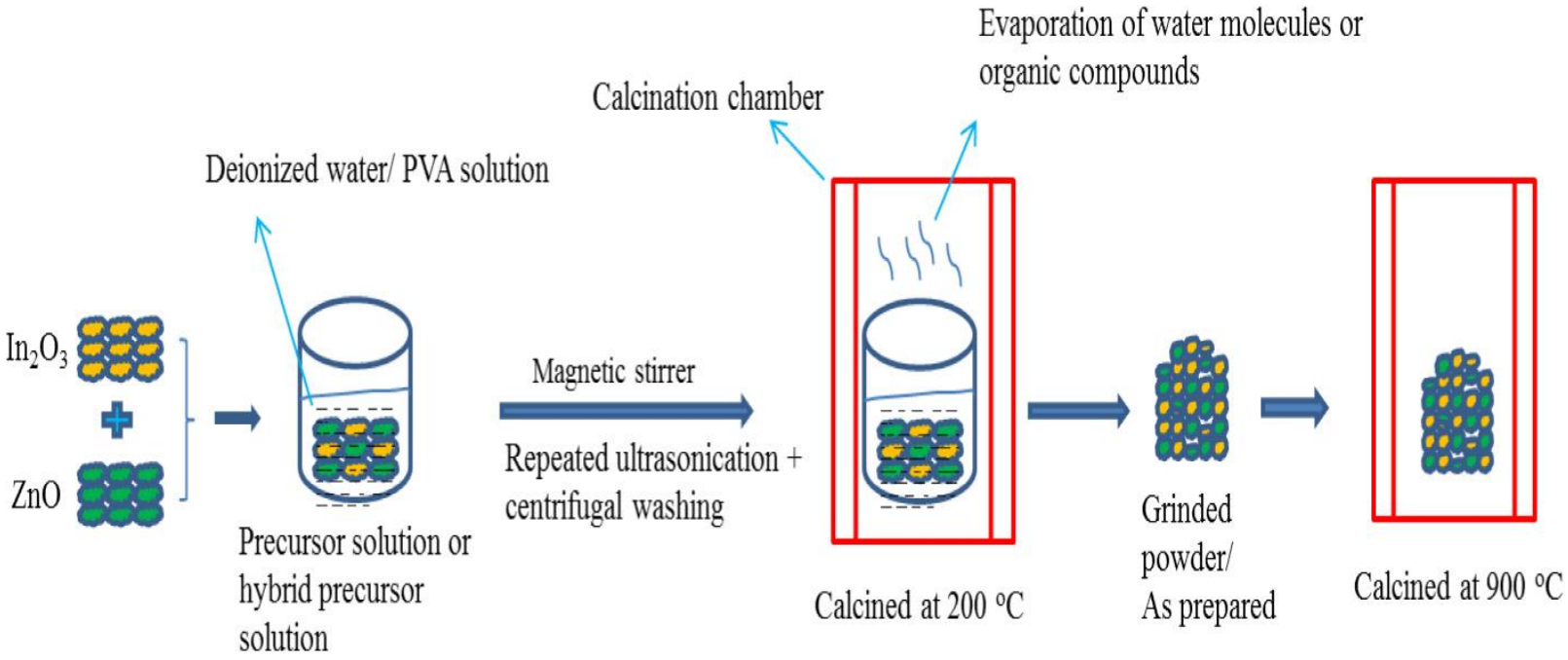


Atomic Layer Deposition (ALD) creates thin films from gas phase precursors. ALD provides the greatest possible control over the thickness of two-dimensional nanoscale structures. The core idea behind this control is to use the intrinsic properties of gaseous chemical compounds to enforce the desired physical architecture: a continuous coating that adheres to all available surfaces and can be grown with sub-nanometer precision.

Fig. forms the first layer of target material ZrO_2. This sequence is repeated until the desired thickness is reached

Wet Chemical Method

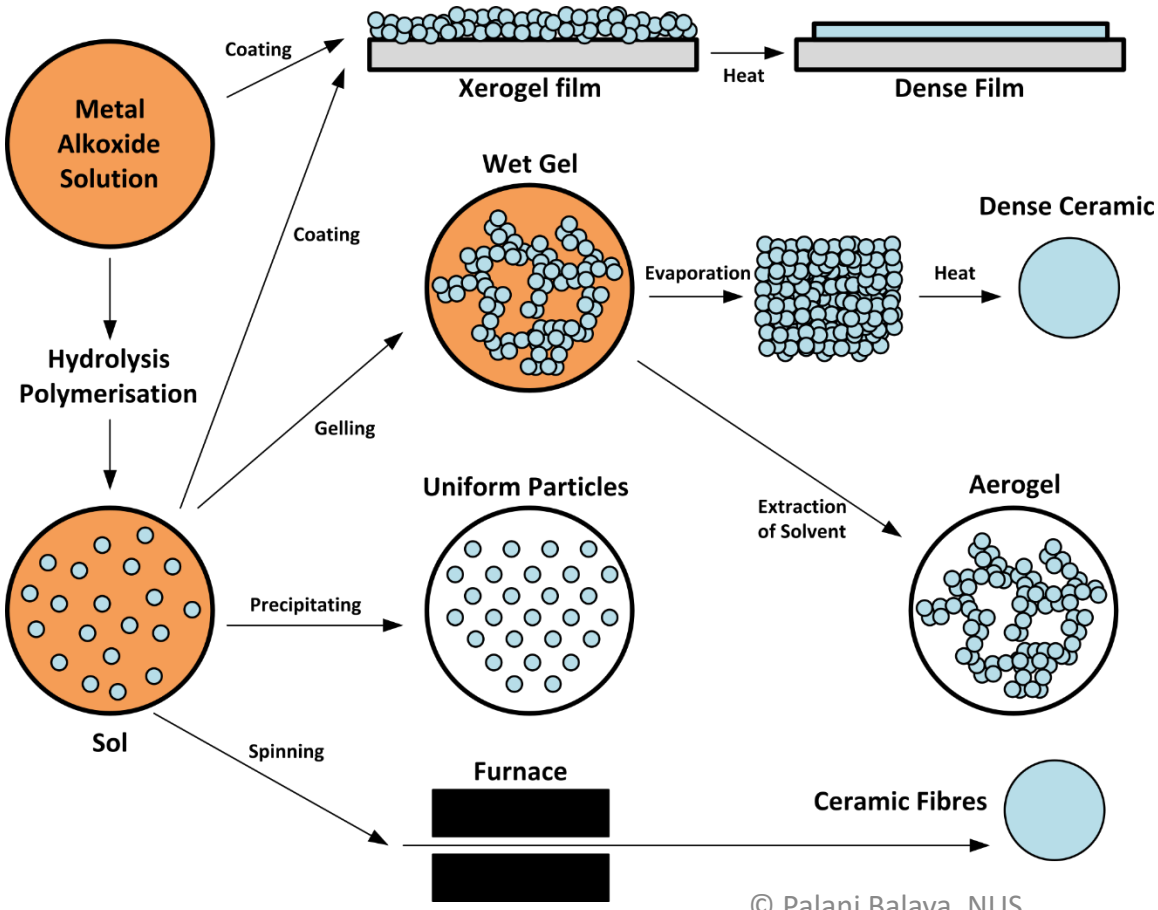
This method is used to synthesize uniform nanoparticles with desired size. This method achieved a great success because of the control over size, shape, and crystallinity. Wet chemical synthesis is mostly used to synthesize inorganic nanomaterials due to low cost and easy application. This method also has many disadvantages when it comes to the industrial scale due to long mixing time and uncontrollable nucleation and growth

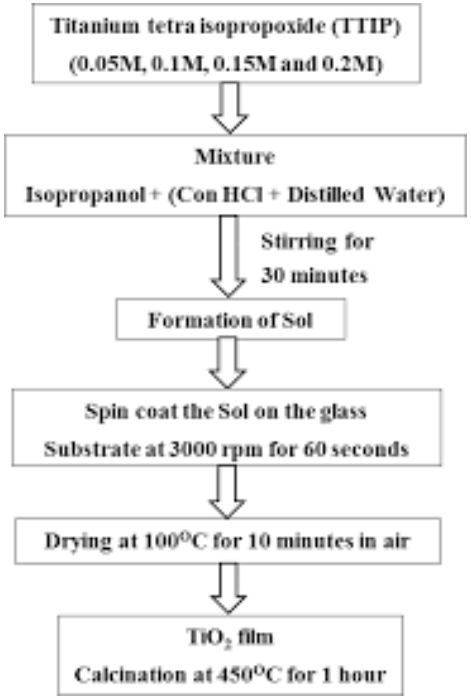


Wet chemical method of InZnO NPs.

Sol-Gel Method

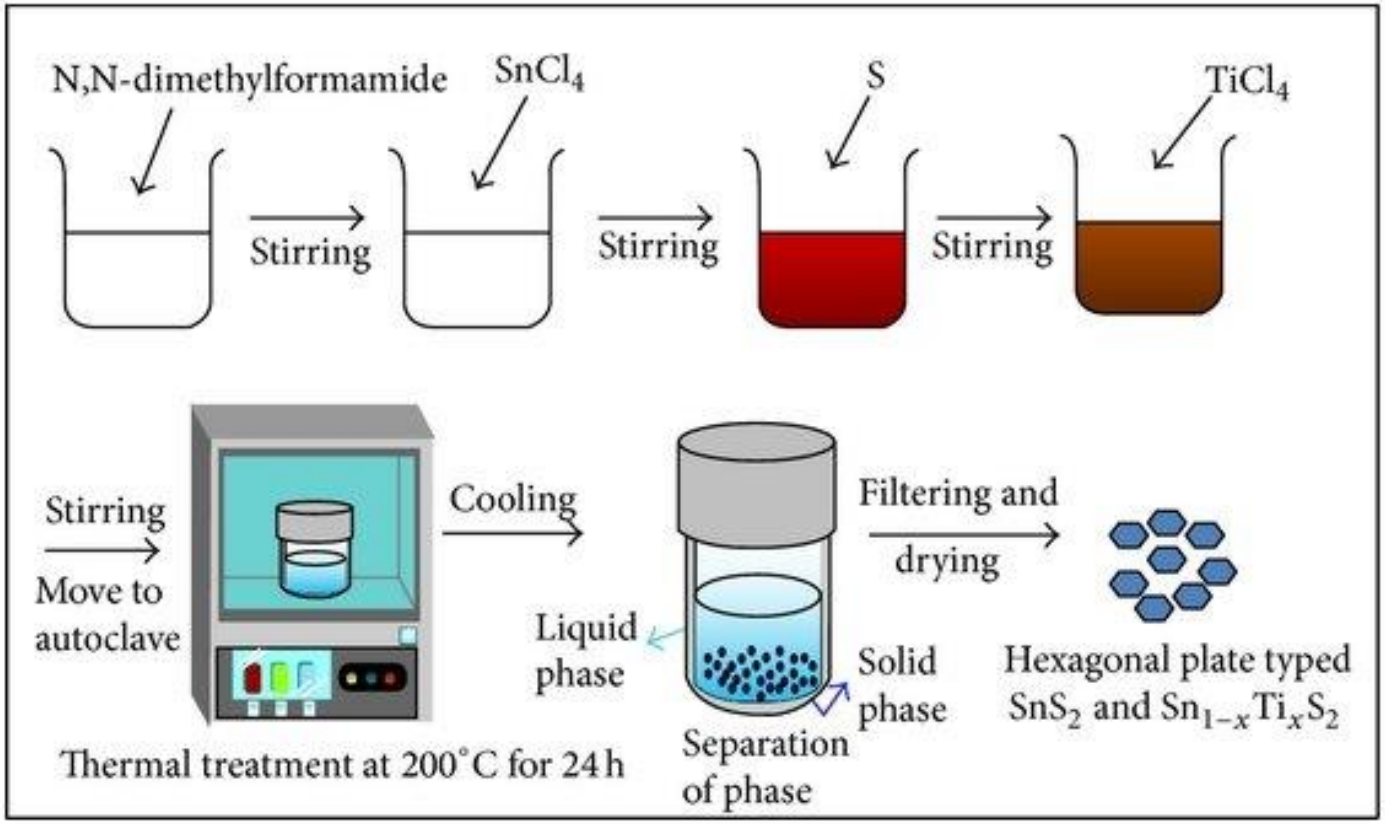
This method is mainly used to synthesize metal oxide NPs and mixed oxide composites with desired nanostructures. Typical sol–gel method includes the following steps: hydrolysis, condensation, and drying process. Initially, the metal precursor undergoes hydrolysis and yields metal hydroxide, followed by condensation to form gels. The final gel is dried and converted to xerogel/aerogel





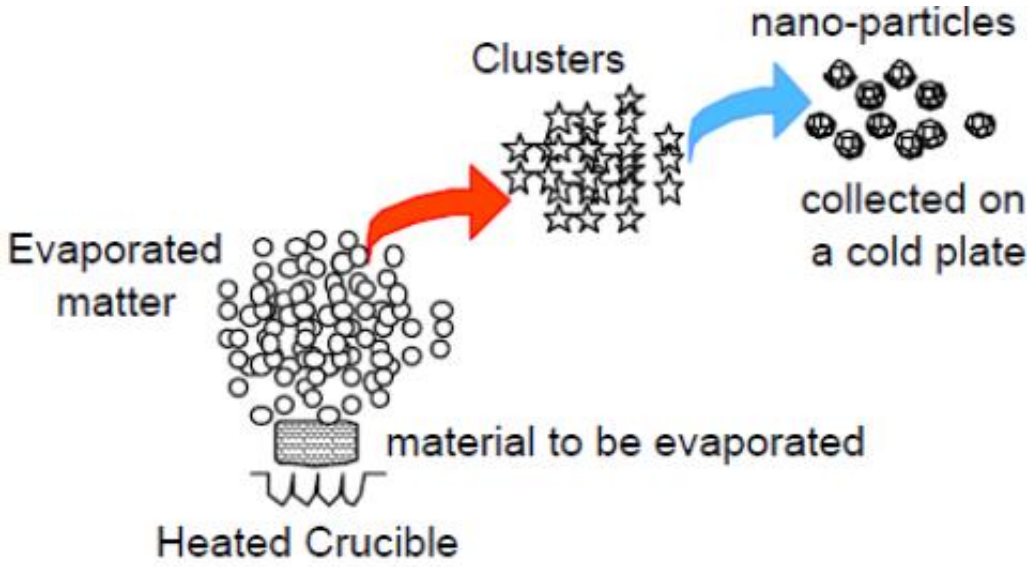
Solvothermal or Hydrothermal Method

The reaction occurring in solvents contained in sealed vessels by heating to their critical point under autogenous pressure is called hydrothermal/ solvothermal process. It is basically a crystallization process that consists of crystal nucleation and its growth. Particle morphology can be controlled by tuning the temperature, pH, and reactant concentrations :

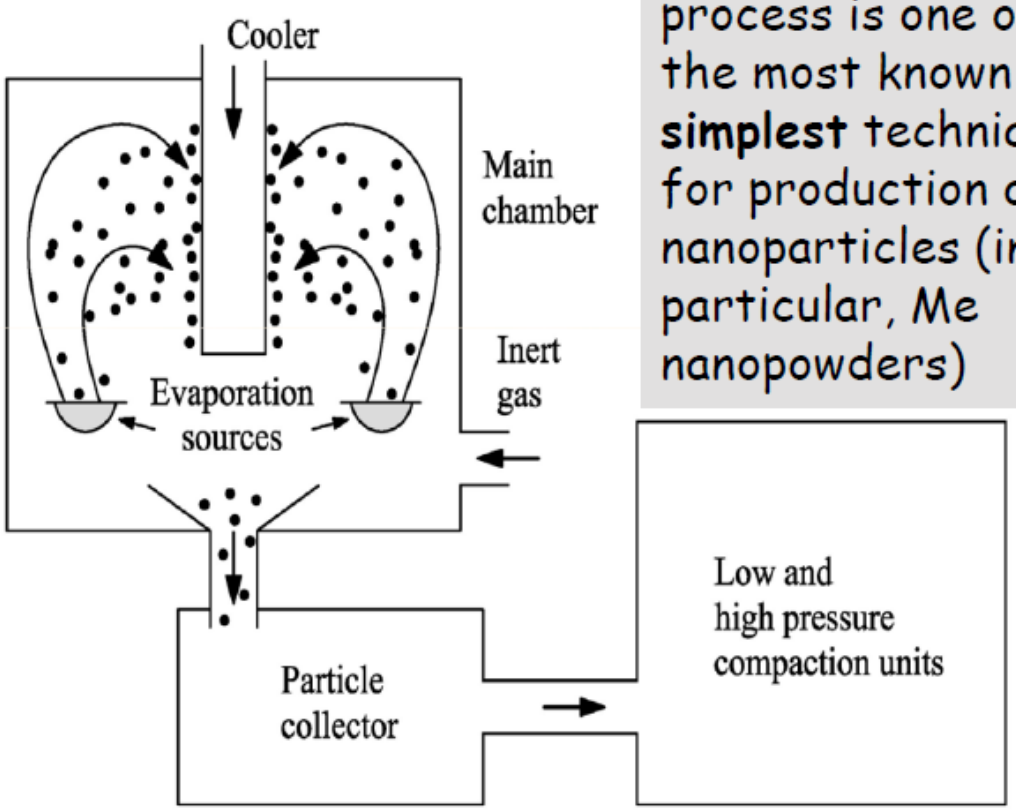


Methods for Synthesis of Zero Dimensional (Quantum Dots) Materials

- Nanoclusters are made by either gas-phase or liquid-phase processes.
- The commonest of which are inert-gas condensation and inert-gas expansion.
- Liquid phase processes use surface forces to create nanoscale particles and structures. There are broad types of these processes: ultrasonic dispersion, sol-gel methods, and methods relying on self-assembly.



Nanoparticle Condensation in Inert Gas



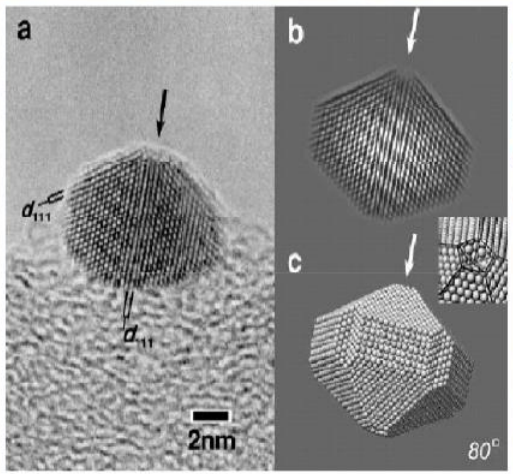
The inert gas condensation (IGC) process is one of the most known and **simplest** technique for production of nanoparticles (in particular, Me nanopowders)

An inorganic material is **vaporized** inside a **vacuum** chamber into which an **inert** gas (typically argon or helium) is periodically admitted.
Once the atoms boil off, they quickly lose their energy by colliding with the inert gas.
The vapor cools rapidly and **supersaturates** to form nanoparticles with sizes in the range 2-100 nm that collect on a finger cooled by liquid nitrogen.

Nanoparticle Condensation in Inert Gas

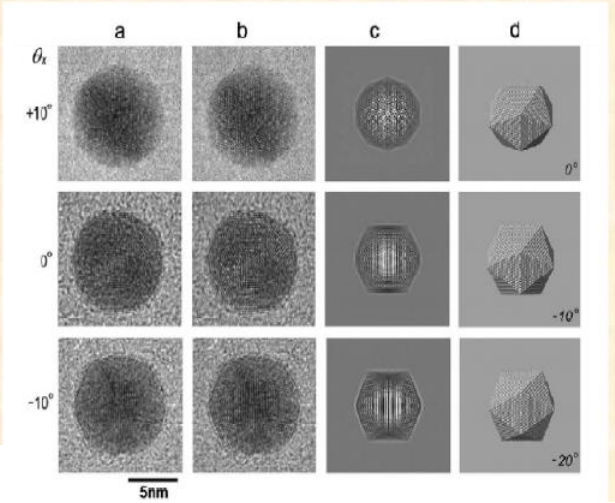
A material, often a metal, is evaporated from a heated metallic source into a chamber which has been previously evacuated to about 10^{-7} torr and backfilled with inert gas to a low-pressure.

Example of nanoparticles obtained by IGC

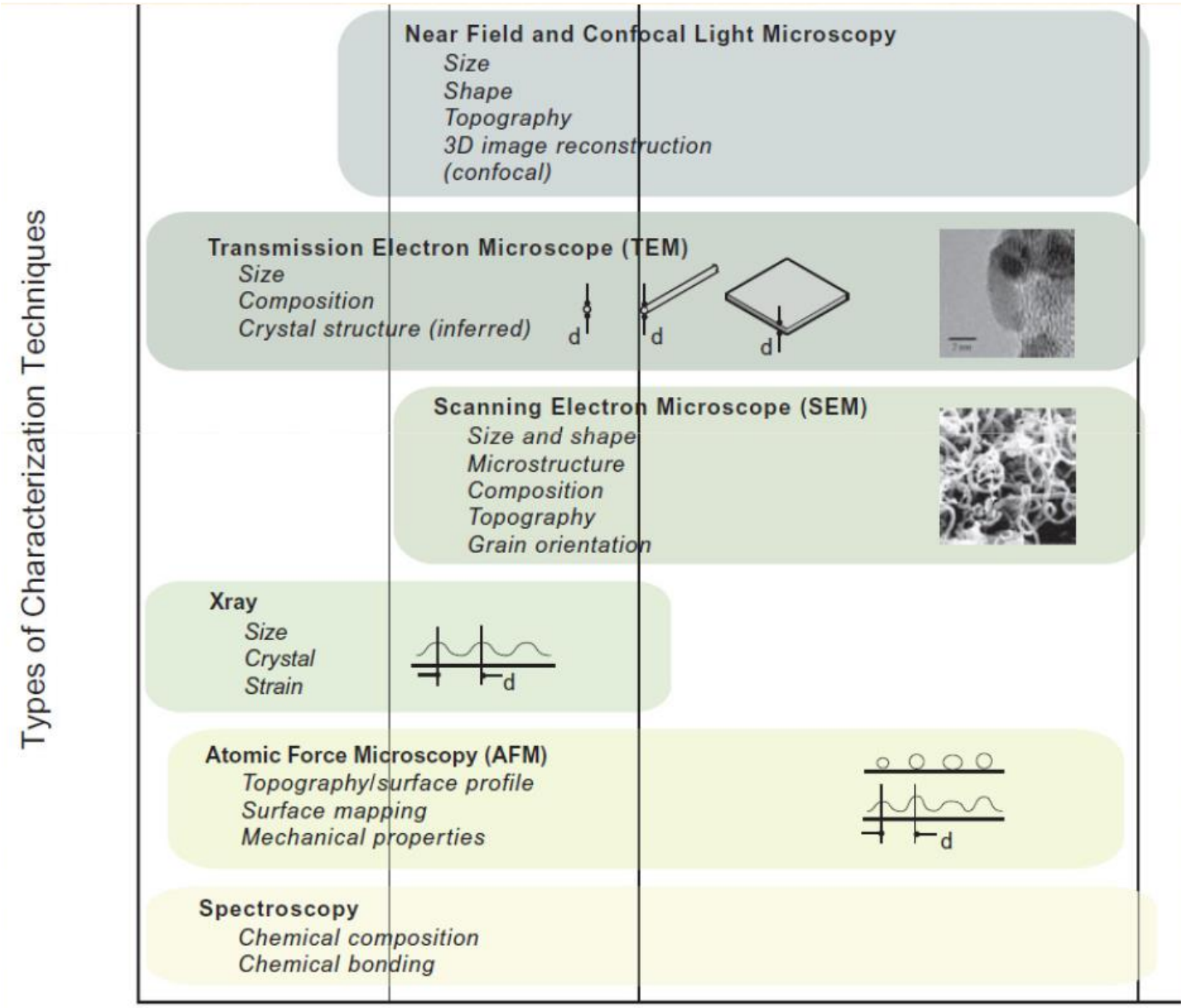


Decahedral gold nanoparticle generated from an inert gas aggregation source using helium and deposited on amorphous carbon film
[K. Koga, K. Sugawara, Surf. Sci. 529 (2003) 23]

Icosahedral gold nanoparticles generated from an inert gas aggregation source using helium and deposited on amorphous carbon film



Nanomaterials: Key Characterization Techniques



Nanomaterials: Key Characterization Techniques

X-ray diffraction (XRD) analysis:

X-ray diffraction is a conventional technique for determination of crystallographic structure and morphology. There is increase or decrease in intensity with the amount of constituent.

This Technique is used to establish the metallic nature of particles gives information on translational symmetry size and shape of the unit cell from peak positions and information on electron density inside the unit cell, namely where the atoms are located from peak intensities.

XRD patterns were calculated using X'per Rota flex diffraction meter using Cu K radiation and λ =1.5406 Å. Crystallite size is calculated using Scherrer equation CS= Kλ /β cos θ Where CS is the crystallite size Constant [K] = 0.94 β is the full width at half maximum [FWHM] Full width at half maximum in radius [β] = FWHM x π/180 λ = 1.5406 x 10-10, Cos θ = Bragg angle. X-ray diffraction analysis with various nanoparticles has been studied by various research workers to find the high crystallinity of the prepared sample

Scanning electron microscope:

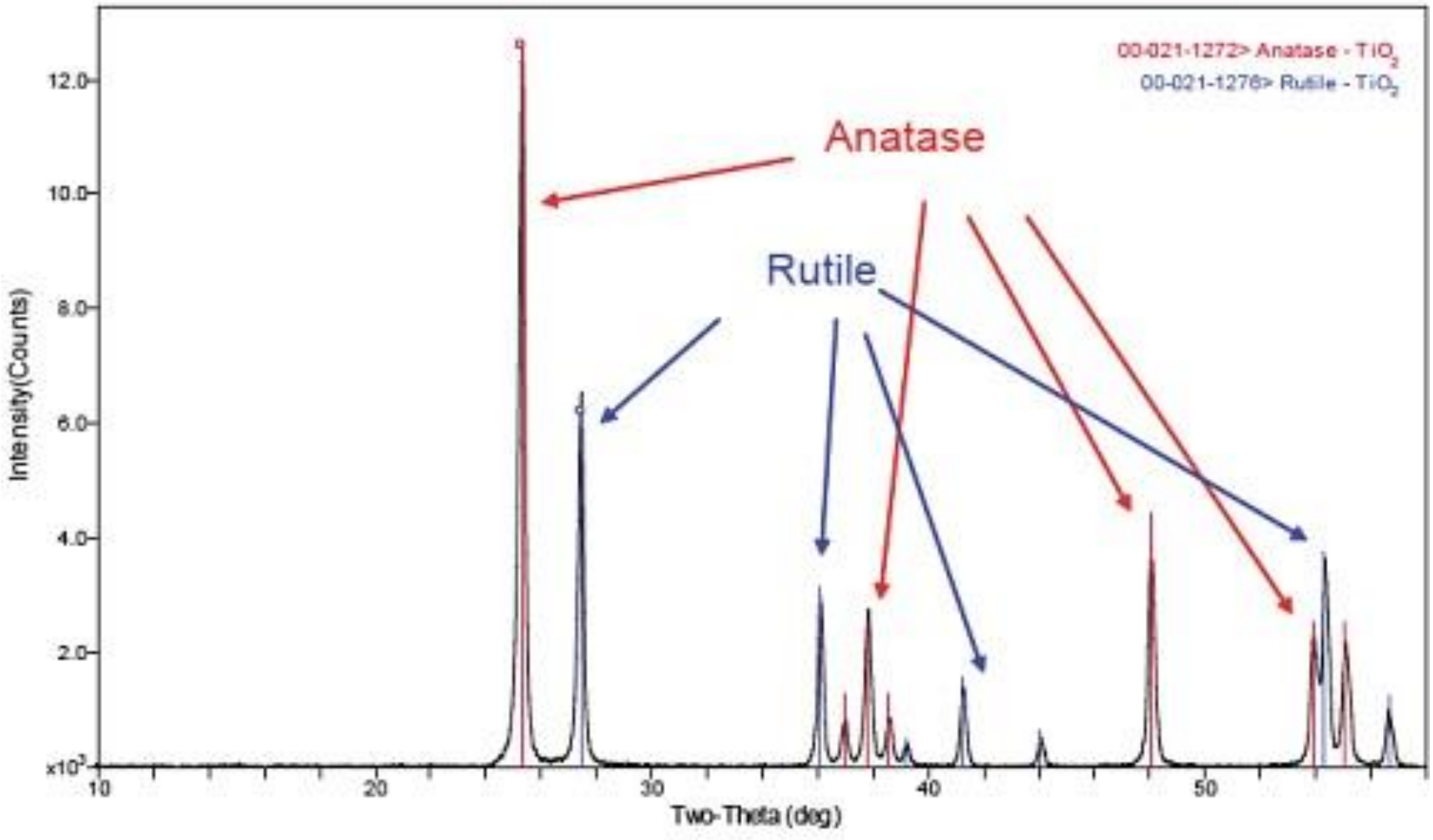
The characterization of Scanning electron microscope analysis is employed to determine the size, shape & morphologies of formed nanoparticle SEM gives high-resolution images of the surface of a sample is desired. The scanning electron microscope works as same principle as an optical microscope, but it measures the electrons scattered from the sample rather than photon. Because electrons can be accelerated by an electric potential, the wavelength can be made shorter than the one of photons. This makes the SEM capable of magnifying images up to 200.000 times. Measures the particle size and characterization, Conductive or sputter coated sample involved and the sensitivity down to 1nm

Transmission electron microscopy (TEM)

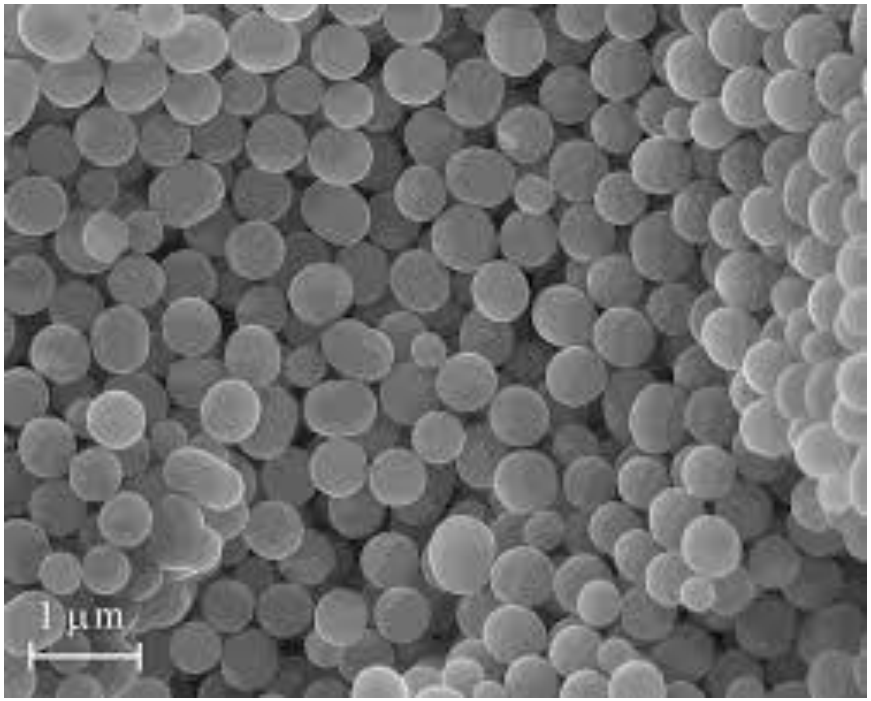
Transmission electron microscopy is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

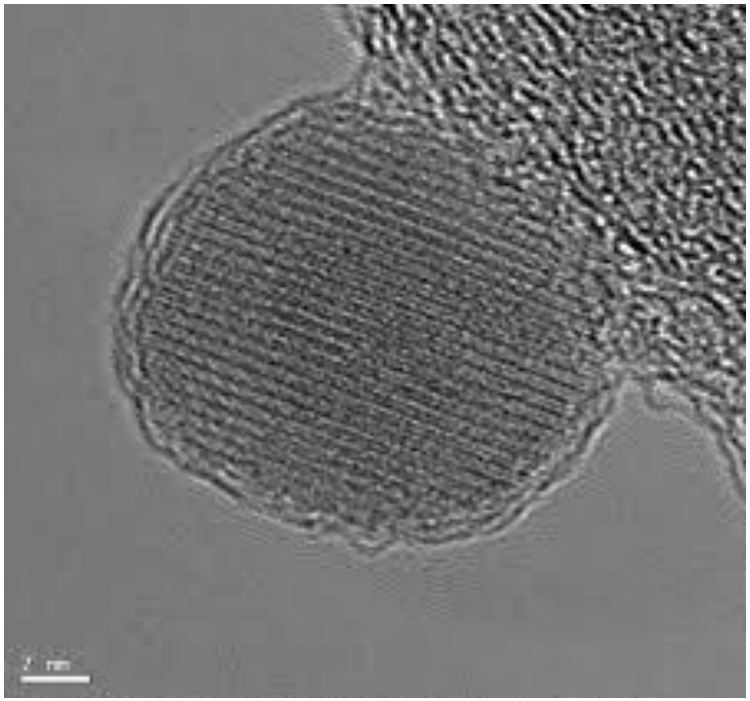
X-ray Diffraction: Structure Determination



Scanning Electron Microscopy & Transmission Electron Microscopy

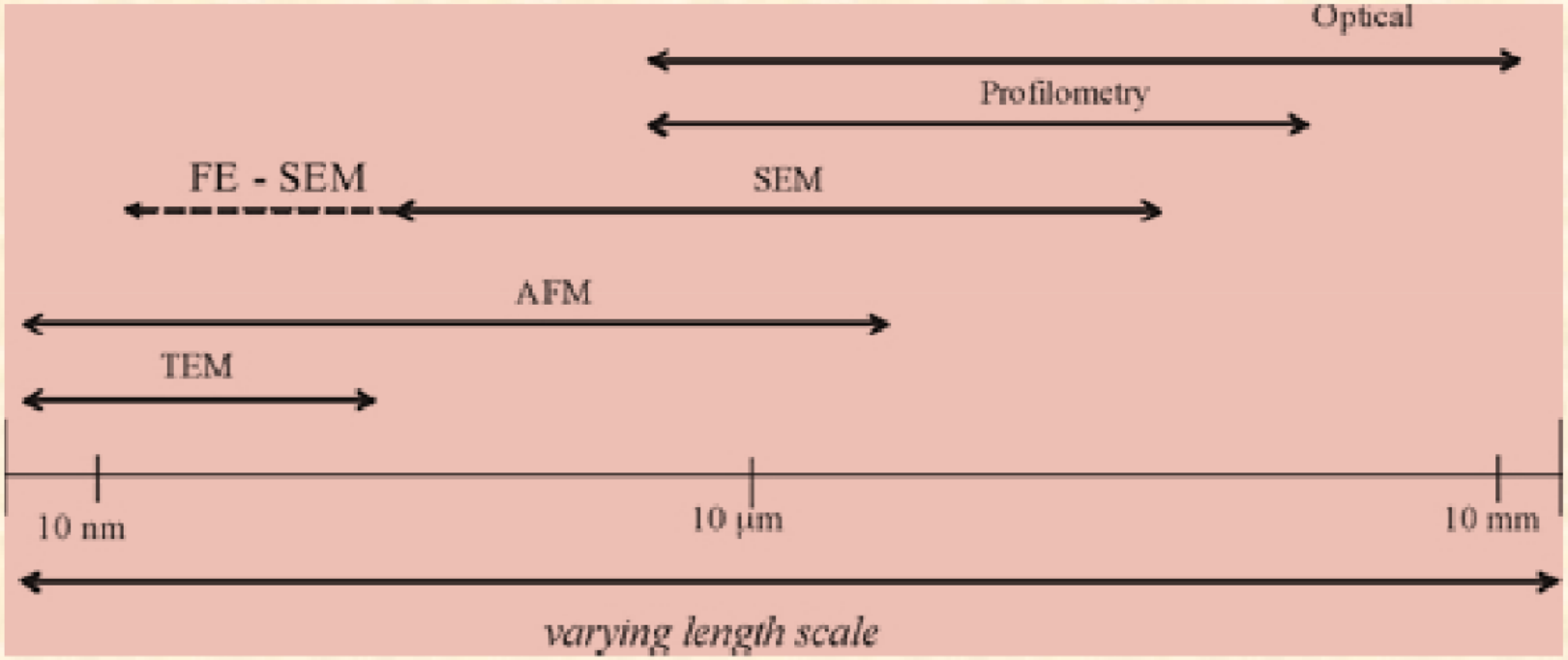


Scanning Electron Microscopy of Silica



Transmission Electron Microscopy of iron

Comparison of imaging techniques



An AFM is capable of resolving features in the dimensions of a few nanometers with scan ranges up to a hundred microns.