Physical methods for the synthesis of low-dimensional nanomaterials

&

Tuning properties of PLD Magnetic Oxide Thin Films

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Which materials should be classified as Nano (Low dimensional)?

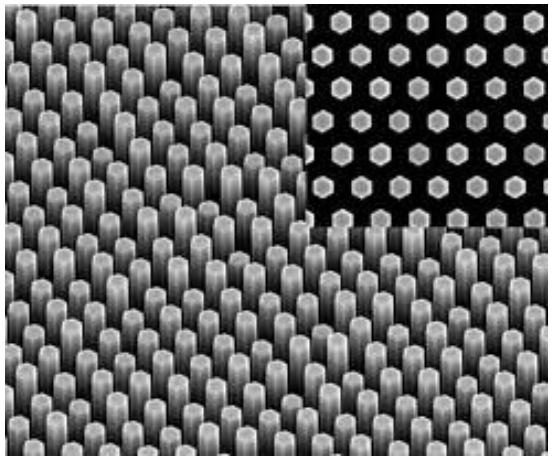
- Normal: 3D (bulk)
- Below 3D (i.e. **2D; 1D; 0D**): **low-dimensional**
  - **Definition:** Nanomaterials:
    - *At least* size in 1D should be *less than 100 nm (now ideally 10 nm)*

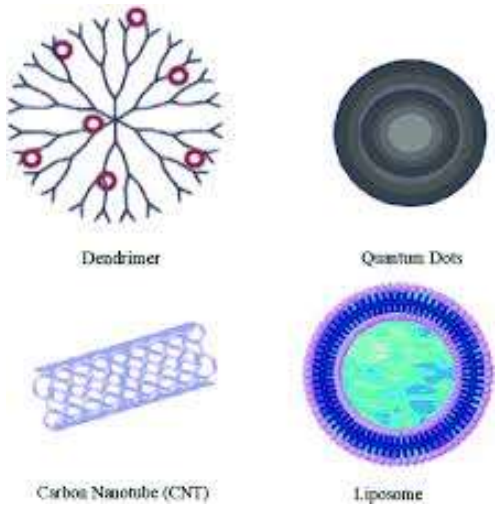
- *2D: in 1 dimension, size <100 nm (ultra-thin films)*
- *1D: in 2 dimensions, size <100 nm (nano-fiber: tubes or rods)*
- *0D: in all 3 dimensions, size <100 nm (nanoparticles-dots)*

Why are they important and interesting?

- Matters in nanosize behave differently
- Therefore, nanomaterials may have interesting properties that indeed do not exist in bulks of the same compounds
- Usually can be used widely in devices & modern applications including environment, energy & healthcare

Examples





How could they own remarkable properties?

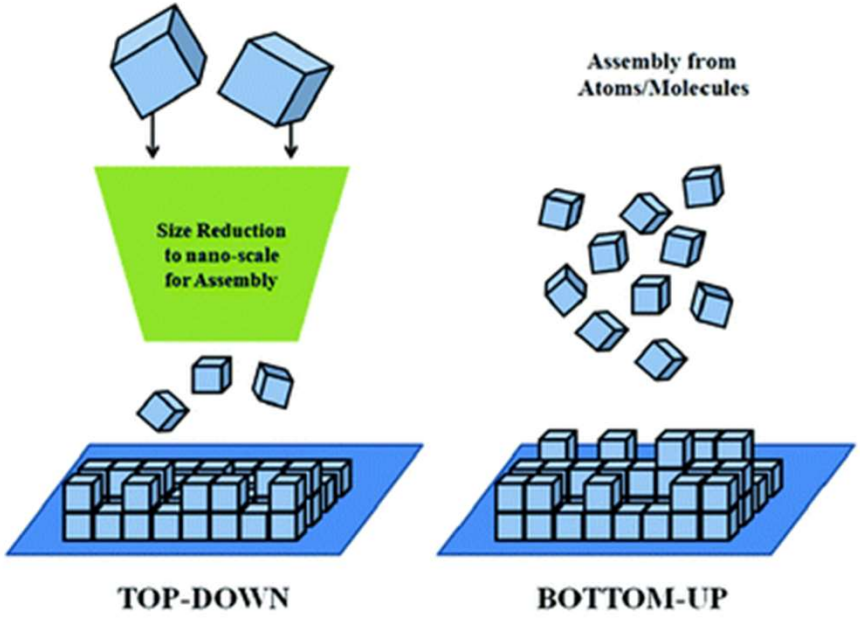
- Size, shape, specific surface area, aspect ratio
- Size distribution
- Surface morphology/topography
- Structure, including crystallinity & defects
- Solubility

Quantum confinement: can be observed once the diameter of a material is of the same magnitude as the de Broglie wavelength of the electron wave function.

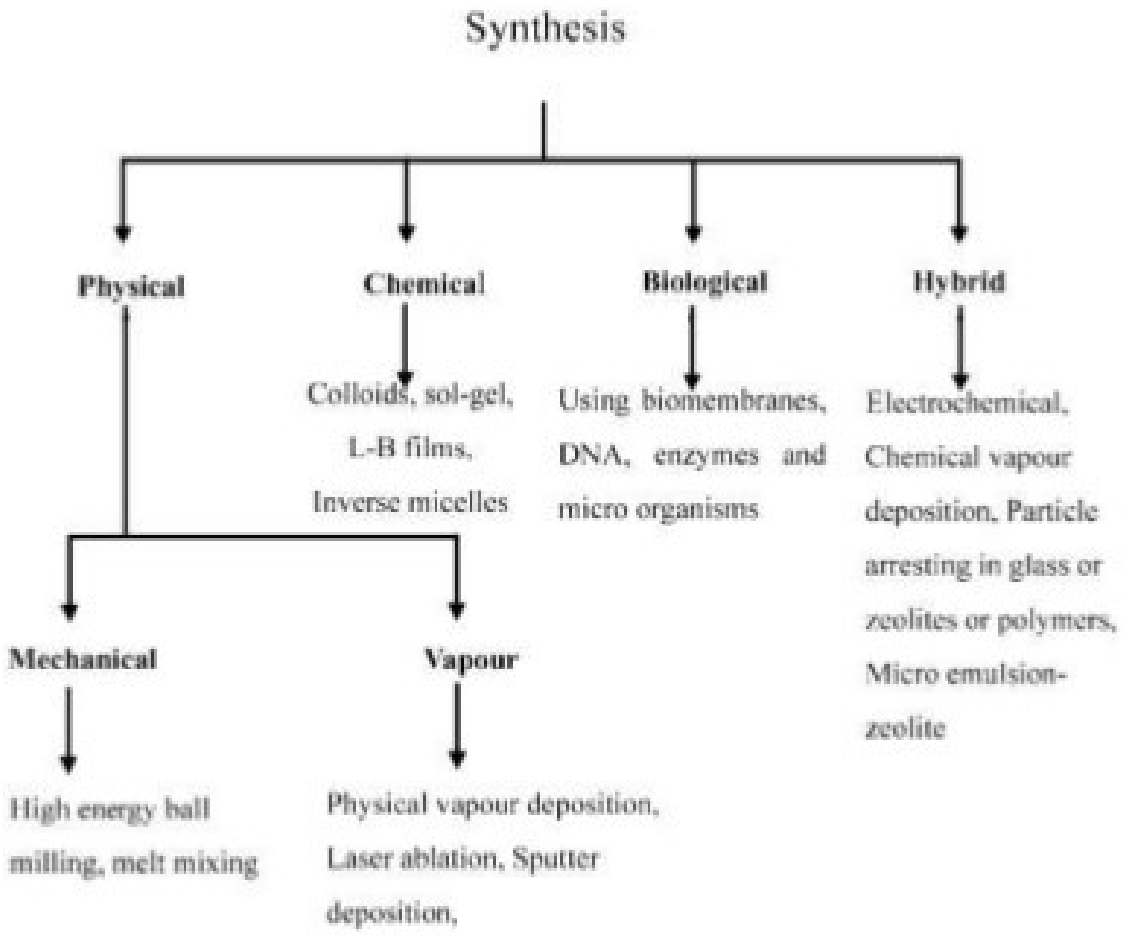
When materials are this small, their electronic & optical properties become different from those of bulk materials

Principles of synthesis

- The goal of any method intended for the synthesis of nanomaterials is to obtain a material that exhibits properties that originate from their characteristic length scale being in the nanometer range (1 – 100 nm).
- Accordingly, the synthetic method should exhibit control of size in this range.
- Physical methods of preparation often include top-down & bottom-up approaches.



Synthesis Of Nanomaterials



Pulsed Laser Deposition (PLD) method to fabricate thin films (mostly functional oxides)

- **Laser** is an electronic-optical device that produces coherent radiation. The term is acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation.

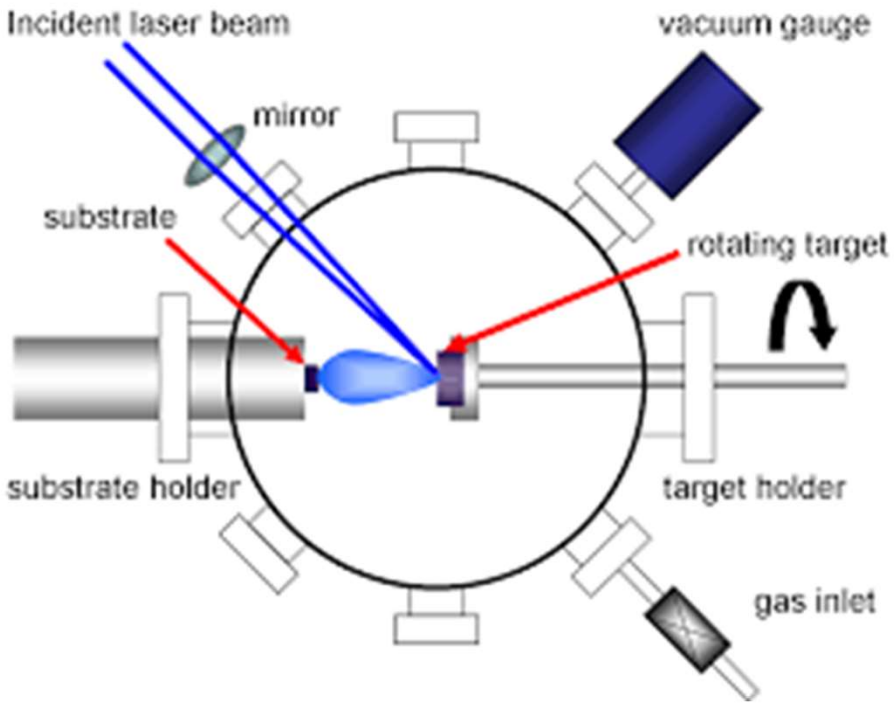
- **Pulsed Laser Deposition (PLD)** is a physical vapor deposition technique where a high-power pulsed laser beam is focused to shoot a target of the desired composition. Material is then vaporized & deposited as a thin film on a heated substrate facing the target. This process can occur in ultra high vacuum or in the presence of a background gas, such as O_2 when depositing films of oxides.

- One can alter the properties of functional materials by controlling the external parameters such as temperature (T) , electric & magnetic fields (E & H), pressure (PO_2) etc.!

Concept of PLD

PLD stages:

- laser ablation of target
- dynamic of plasma
- film nucleation and growth

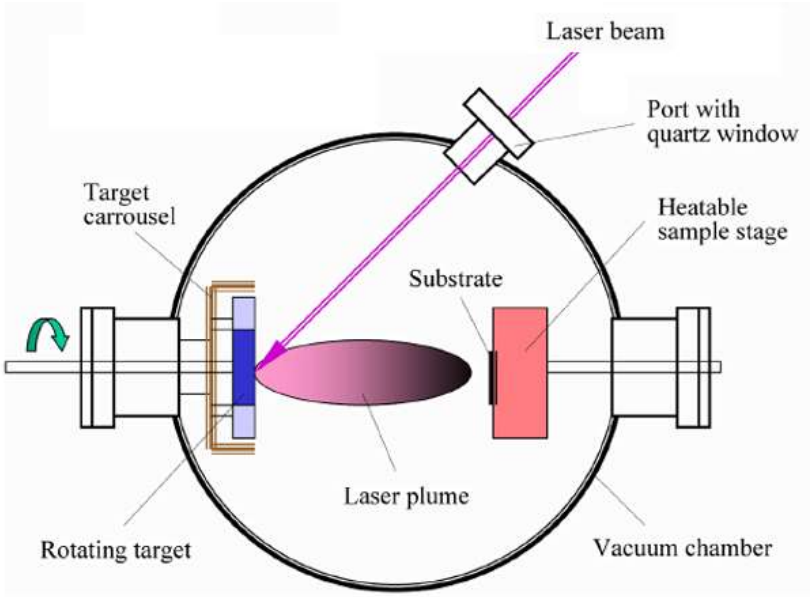


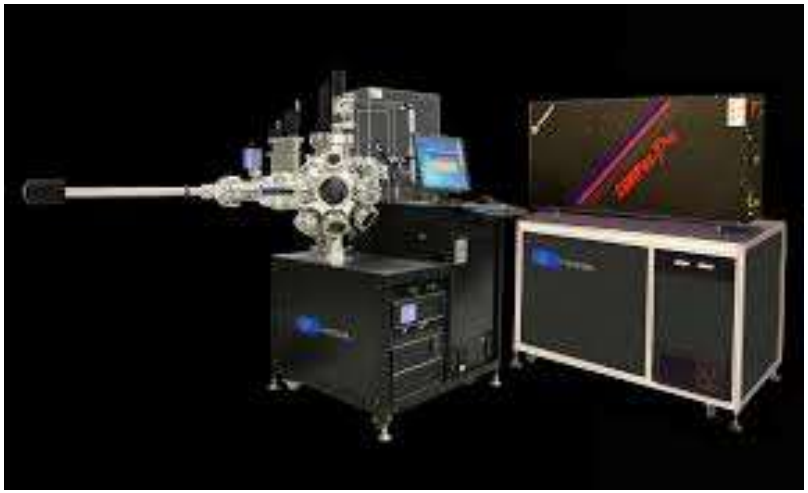
Advantage:

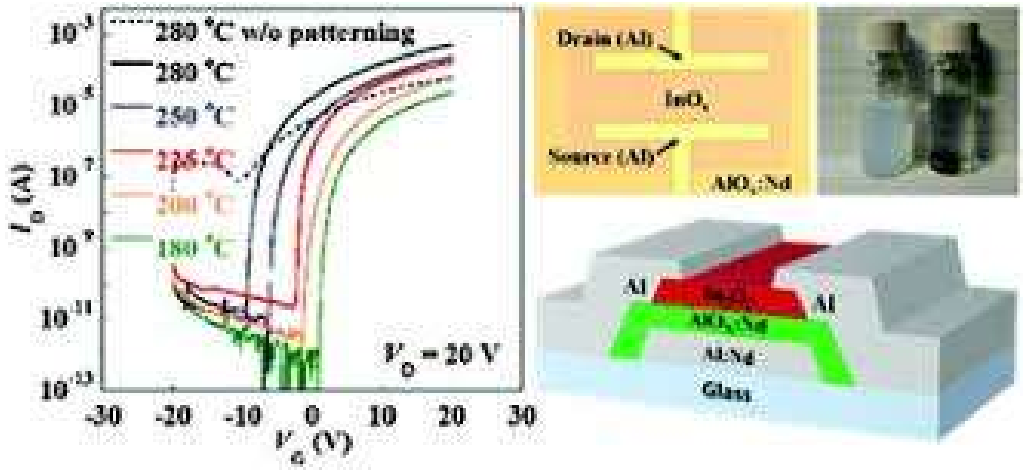
-film's stoichiometry is near to that of the target.
-versatile: many materials can be deposited in a wide variety of gases over a broad range of gas pressures.
-cost-effective: one laser source can serve many chambers.
-fast: high quality films can be grown in 10-15 minutes.

Important: Type of Eximer Laser; Beam alignement; **Energy density**; **Pulse repetition rate**; Time of shooting; Vacuum-**O_2 Pressure**; **Type of substrate; Substrate temperature;** Distance between target & substrate

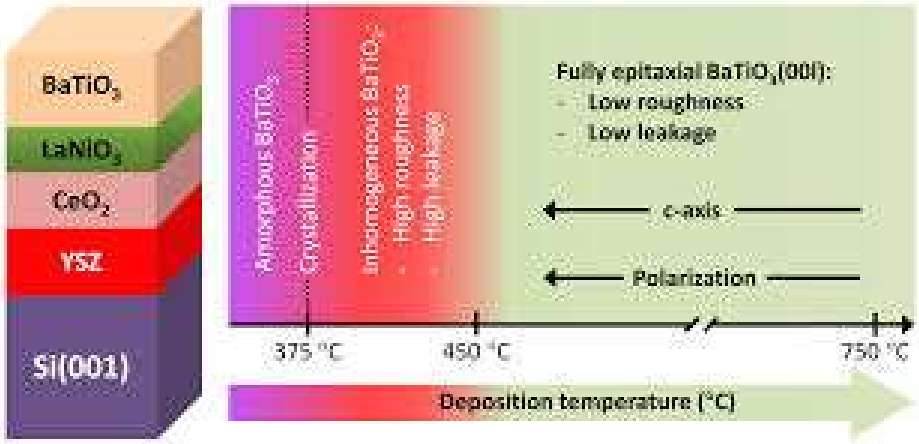
Growth of a film

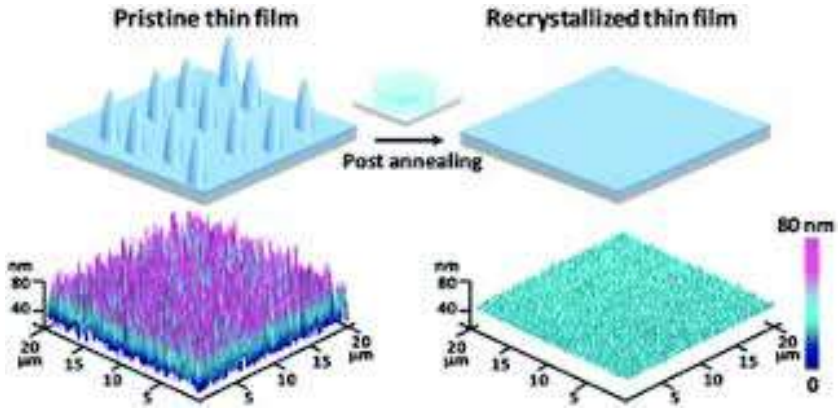


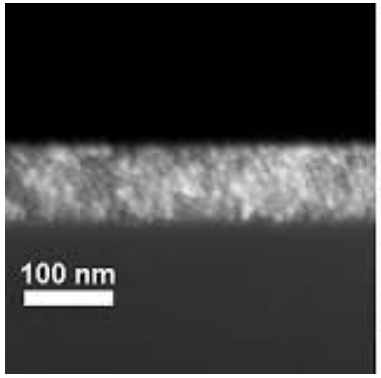


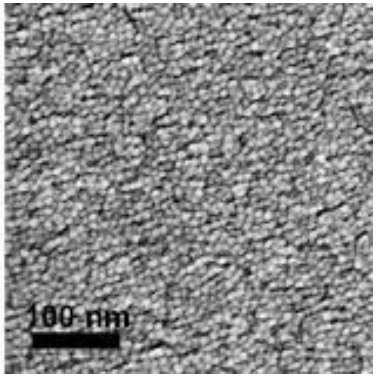


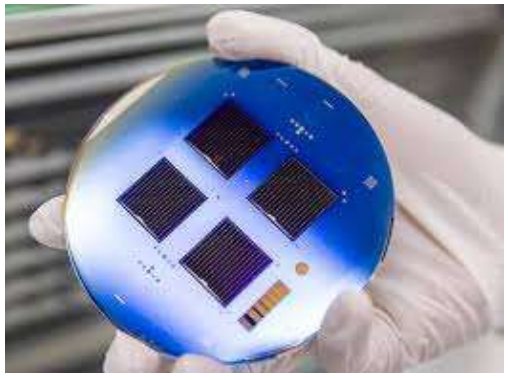
Fabrication Conditions (T, P, substrate, etc) play key roles in shaping up desired properties!


BaTiO3
LaNiO3
CeO2
YSZ
Si(001)
Amorphous BaTiO3
Crystallization
Inhomogeneous BaTiO3
- High roughness
- High leakage
Fully epitaxial BaTiO3(00l):
- Low roughness
- Low leakage
c-axis
Polarization
375 °C
450 °C
750 °C
Deposition temperature (°C)


Pristine thin film
Recrystallized thin film
Post annealing
nm
80
40
20 µm
15
10
5
80 nm
0


100 nm

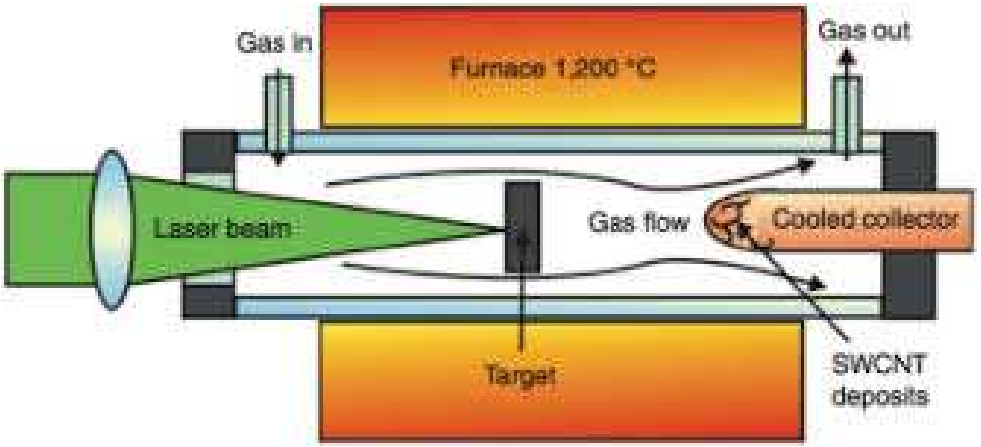

100 nm

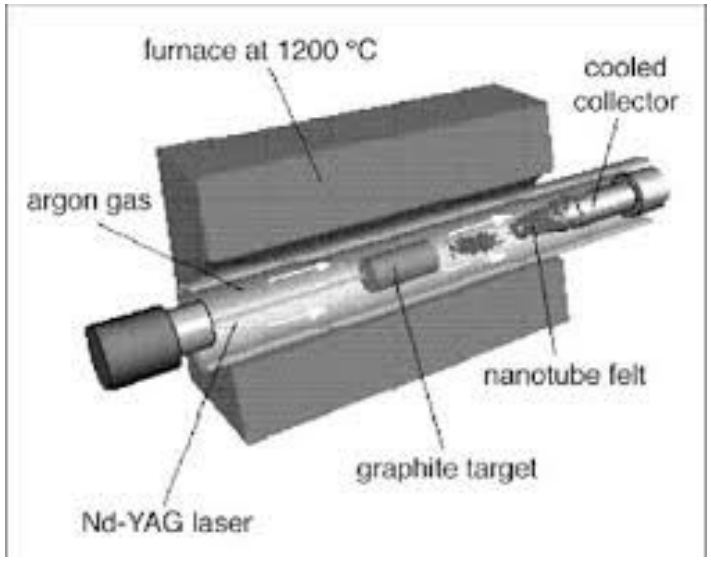


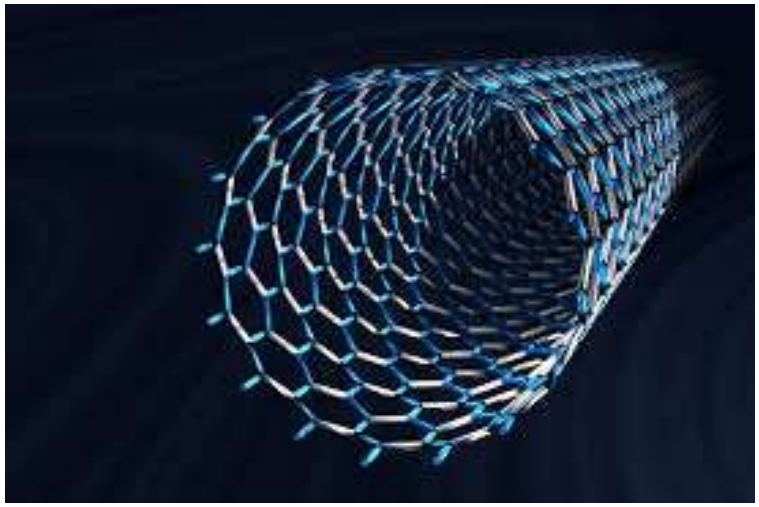
Laser ablation for synthesis of carbon nanotubes

- In laser ablation, a pulsed laser vaporizes a graphite target in a high-temperature reactor under the stream of an inert gas inside the chamber.
- Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses.
- A water-cooled surface may be included in the system to collect the nanotubes.

Diagram+Result







Fabrication Conditions play **key roles** in shaping up desired properties!

Laser ablation in liquid for the synthesis of nanoparticles

Laser ablation usually generates the nanoparticles from target placed inside the liquid.

Concentration of the ablated material (C_M) decreases, while the concentration of solution species (C_S) increases.

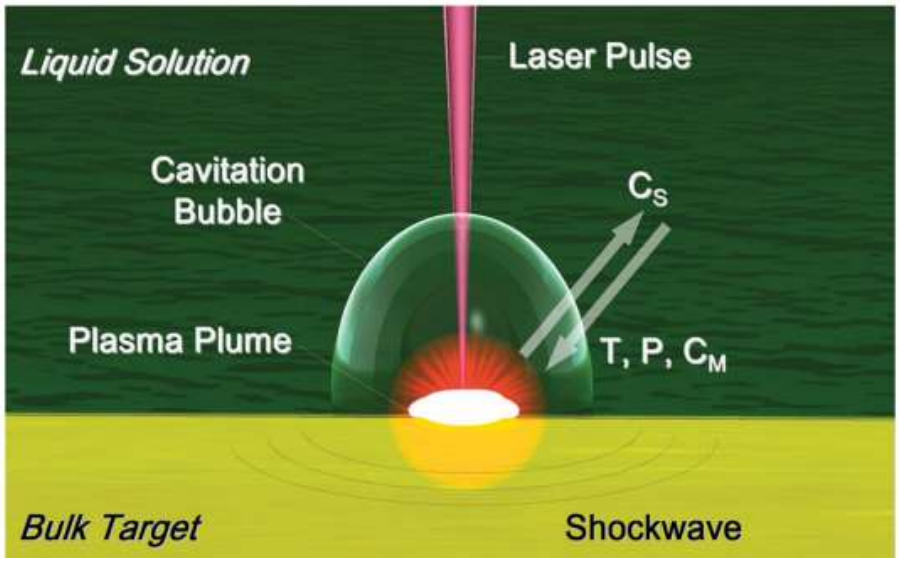
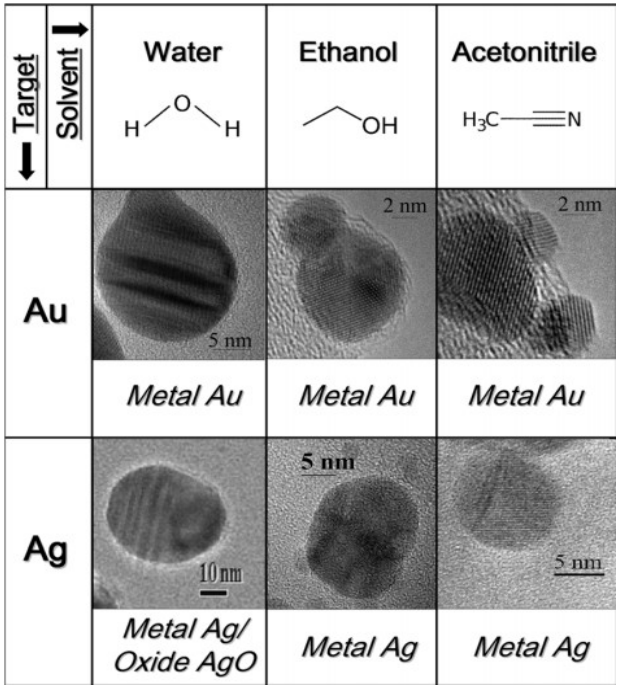


Figure from V. Amendola *et al.*/ Phys. Chem. Chem. Phys. 2013, 15, 3027-3046

Laser ablation in liquid is useful for the generation of metal & metal oxide nanoparticles. Typical parameters that should be controlled: pulse energy; repetition rate; wavelength; solution type; existence of other solutions, depth of target placement; purity of target.



In general, laser ablation in liquid generates quasi-spherical nanoparticles of metals!

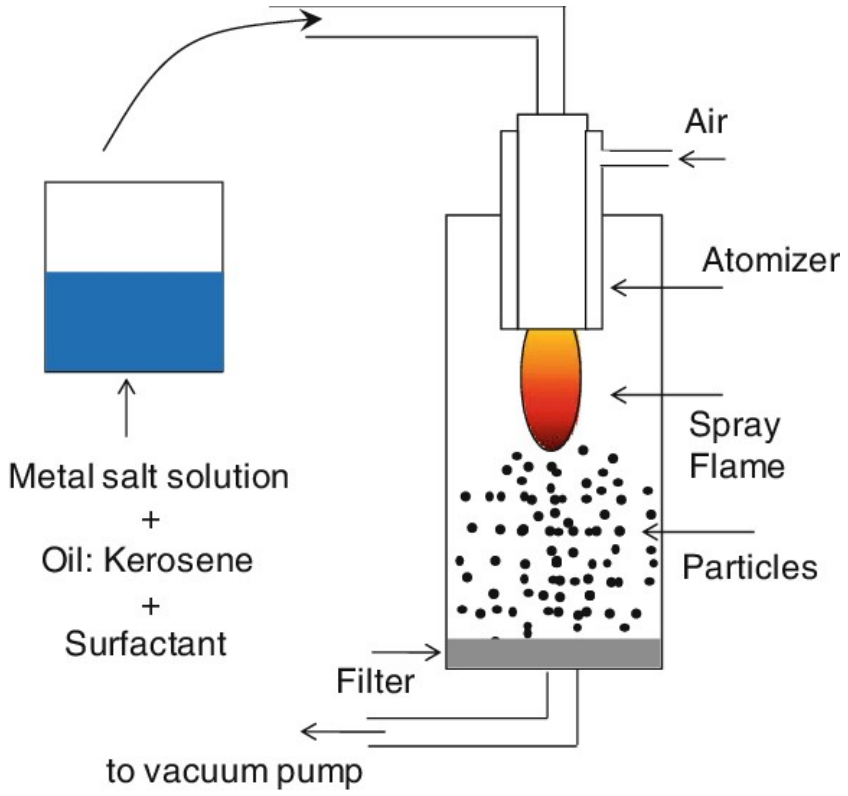
The following video demonstrates the laser ablation process:

https://www.youtube.com/watch?v=kOy0yuWpUzU

Figure from V. Amendola *et al.*/ Phys. Chem. Chem. Phys. 2013, 15, 3027-3046

Flame combustion method

In this method, a spray of precursor solution mixed with a gas carrier is burned in flame. In general, the method is suitable for fabrication of spherical metal oxide nanoparticles (undoped or doped).



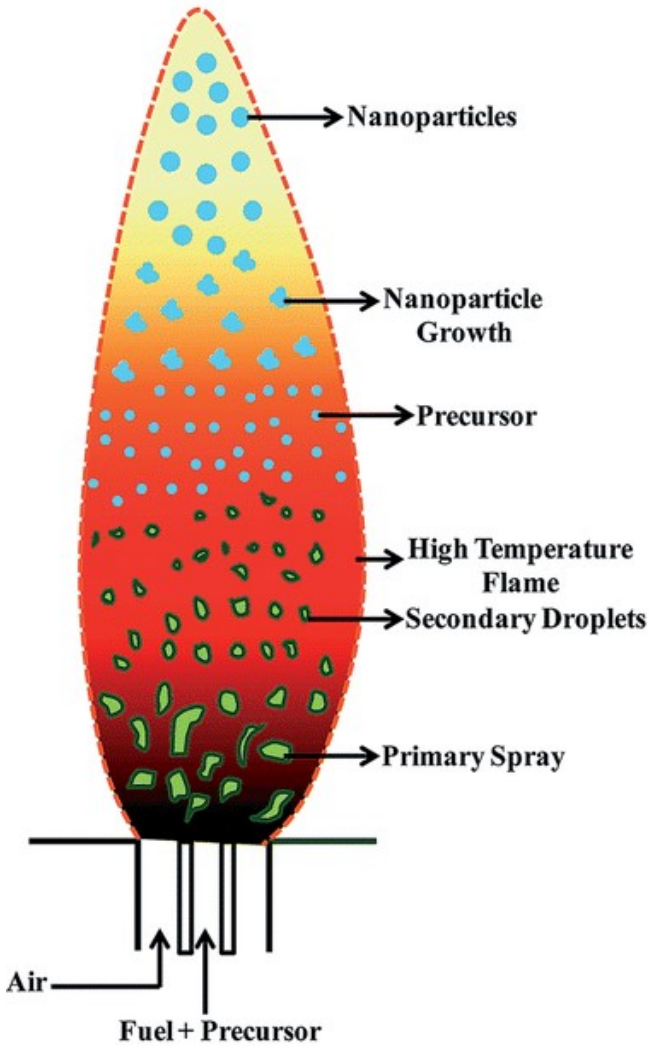
During the Flame combustion process,

size of nanoparticles can be controlled by means of:

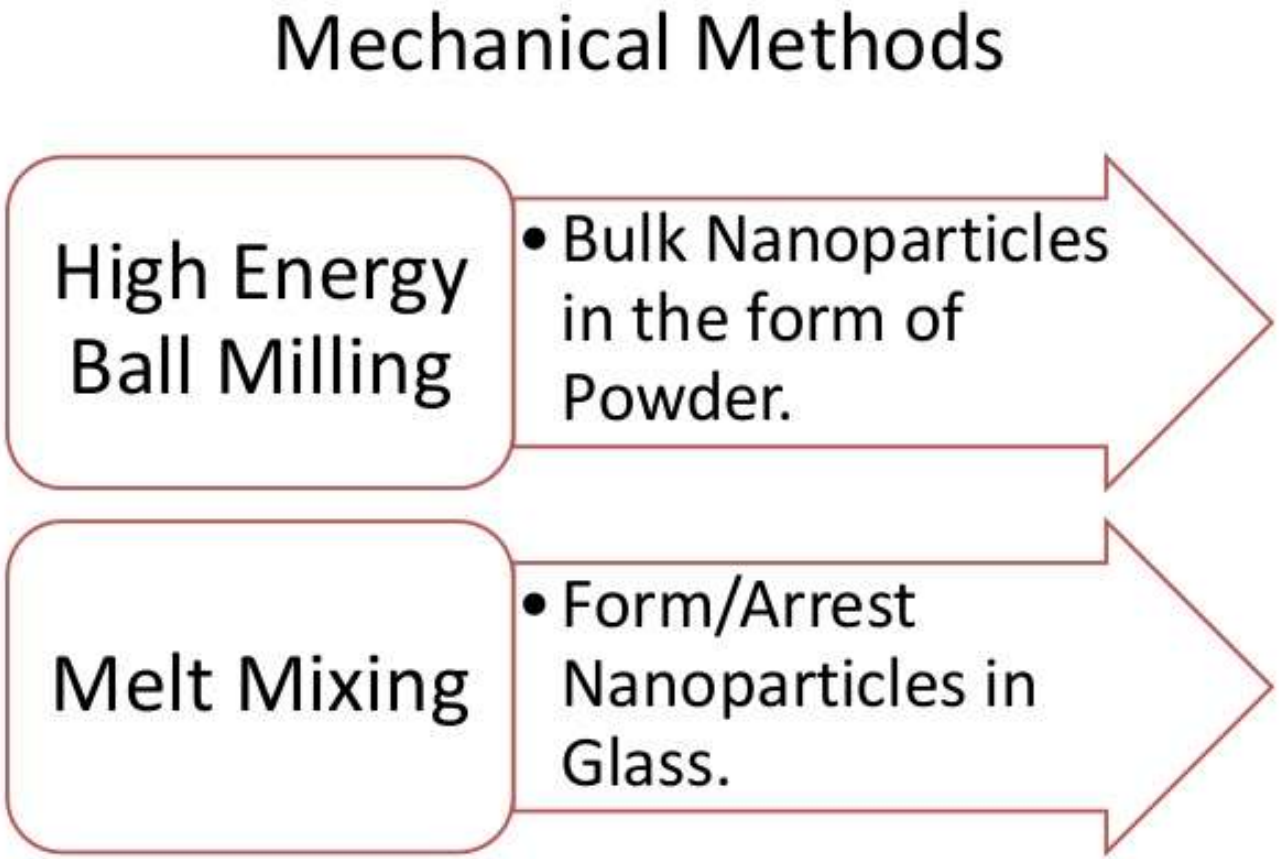
✓Salt concentration (lower concentration form smaller nanoparticles)

✓Addition of surfactants (restrict the growth of nanoparticles)

✓Precursor & gas supply rate, flame temperature, viscosity, etc.

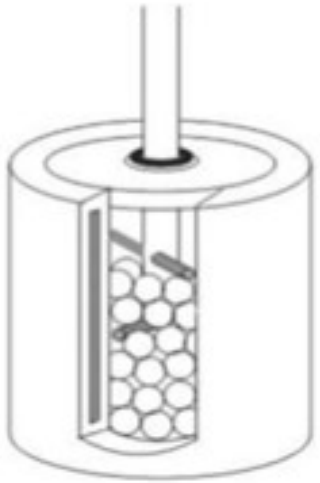


Mechanical method to make nanoparticles



High Energy Ball Milling

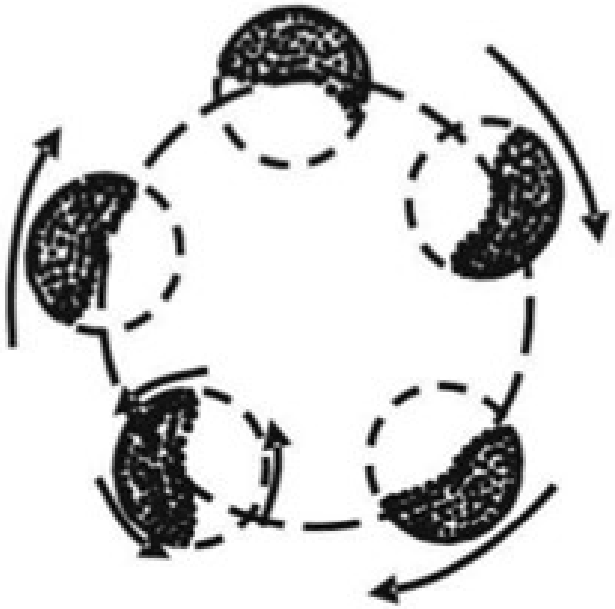
- Some of the materials like Co, Cr, W, Ni, Ti, Al-Fe and Ag-Fe are made nanocrystalline using ball mill.
- Few milligrams to several kilograms of nanoparticles can be synthesized in a short time of a few minutes to a few hours.
- One of the simplest ways of making nanoparticles of some metals and alloys in the form of powder.



- Usually 2:1 mass ratio of balls to material is advisable.
- If the container is more than half filled, the efficiency of milling is reduced.
- Heavy milling balls increase the impact energy on collision.

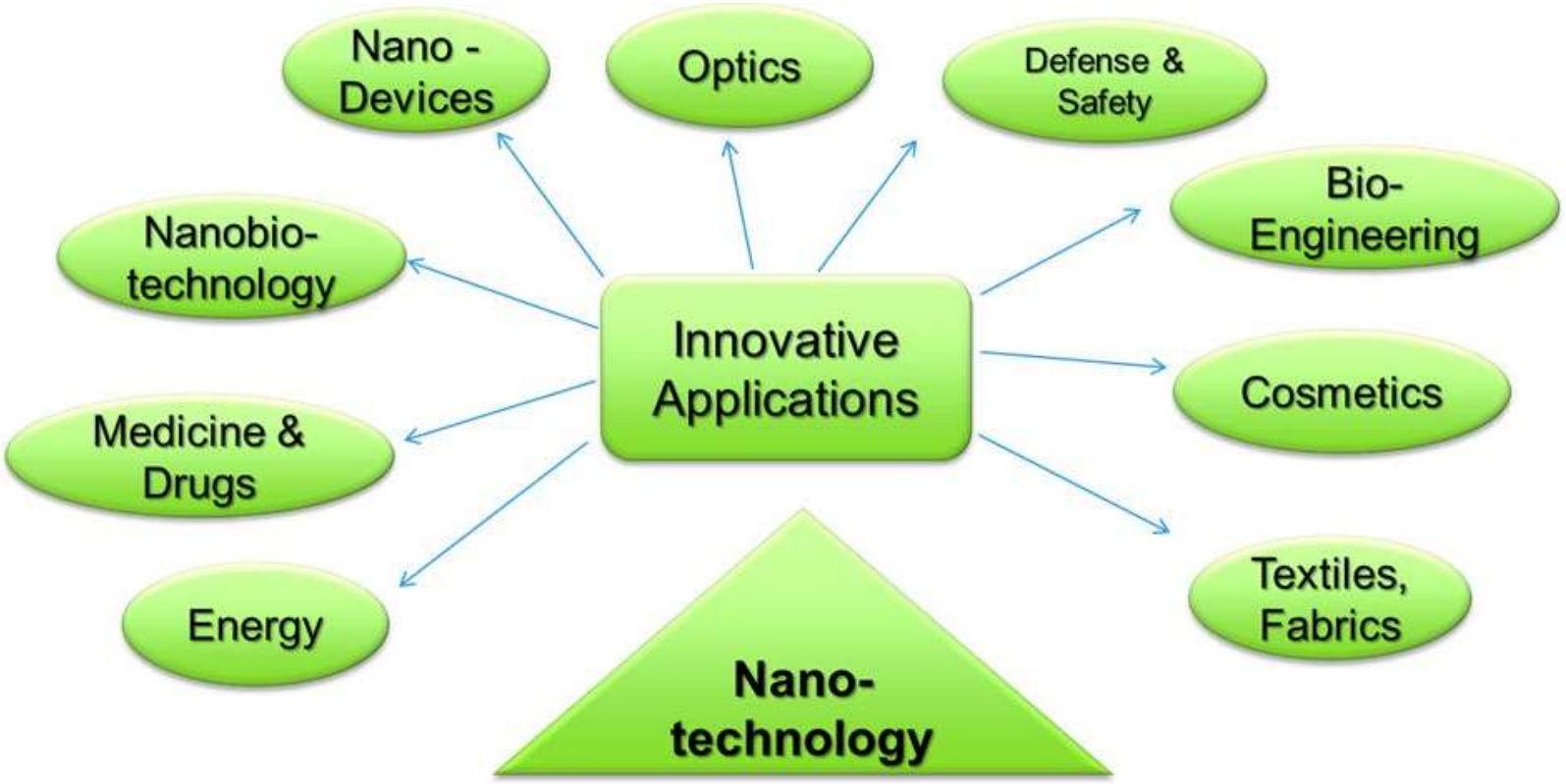
- To avoid any impurities from balls, the container may be filled with air or inert gas. However this can be an additional source of impurity, if proper precaution to use high purity gases is not taken.
- A temperature rise in the range of 100–1,100°C is expected to take place during the collisions.
- Lower temperatures favour amorphous particle formation.
- The gases like O_2, N_2 etc. can be the source of impurities as constantly new, active surfaces are generated.
- Cryo-cooling is used sometimes to dissipate the heat generated.

By controlling the speed of rotation of the central axis and container as well as duration of milling it is possible to ground the material to fine powder (few nm to few tens of nm) whose size can be quite uniform.



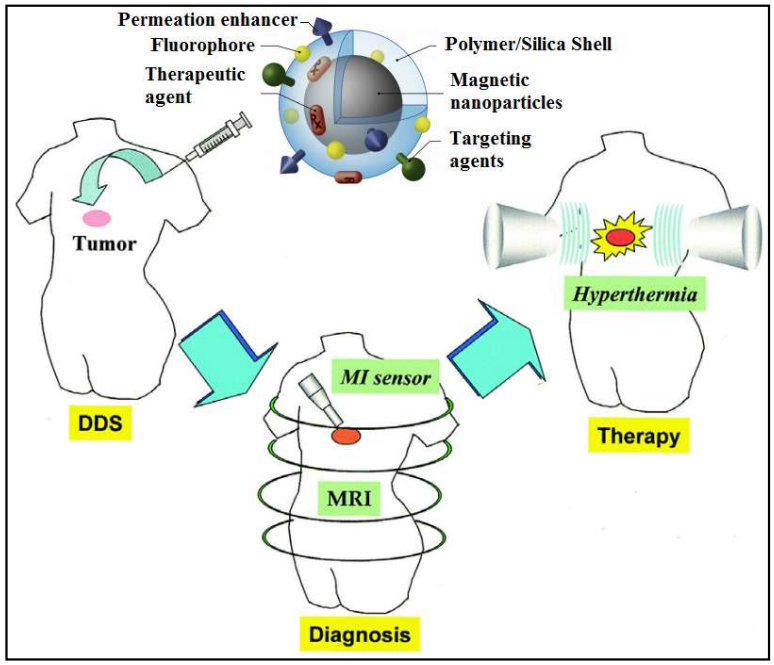
Physical methods of preparation can be *faster & more energy efficient* compared to conventional chemical methods.

Therefore, these methods can be easily scaled- up for *industrial production & commercialization*.

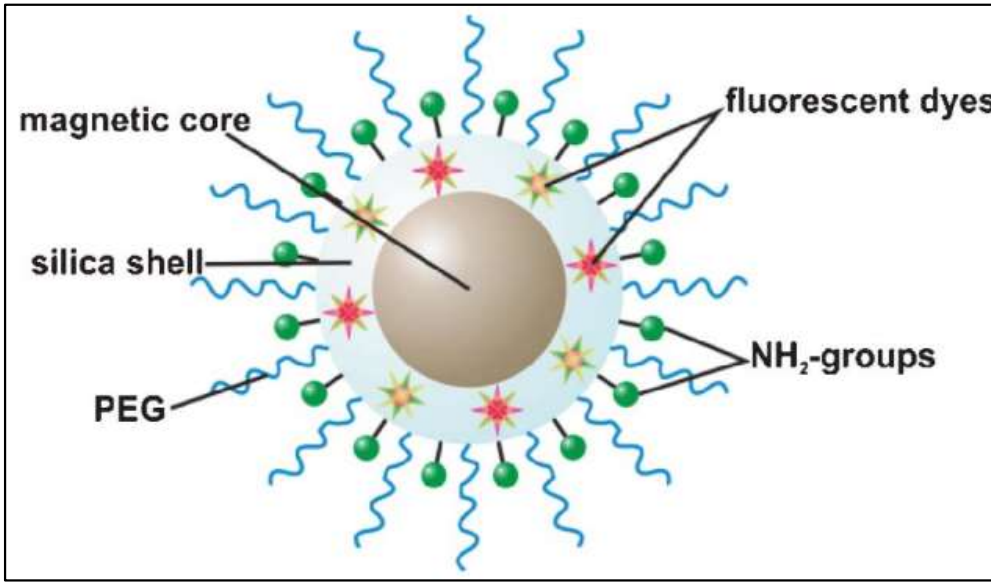


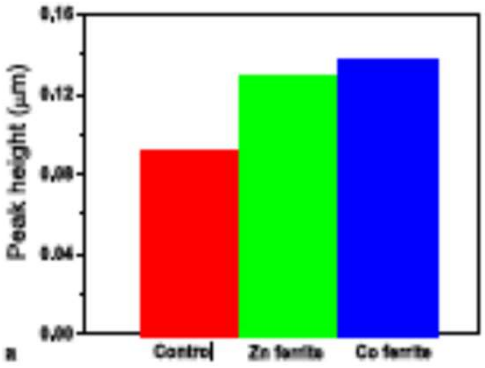
Nanoparticles for biomedical applications

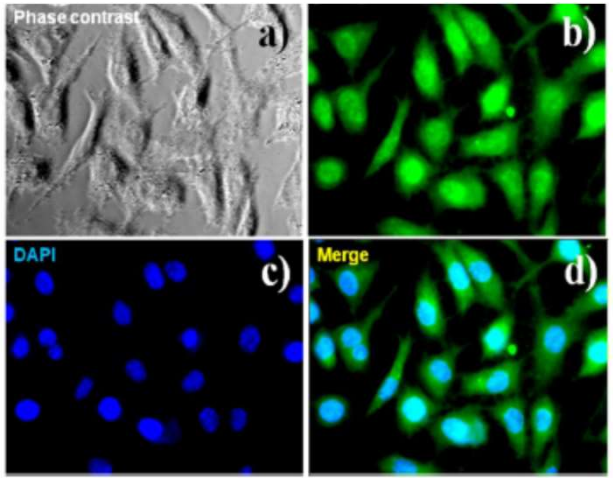
Therapeutics



Drug Delivery







Tuning Properties of PLD Magnetic Oxide Films

- Changing parameters of deposition

(type of substrate, heating temperature, O_2 pressure, repetition rate, energy density, distance between target & substrate)

- Varying thickness

(control by fixing time of deposition)

- Extra-annealing

- Multilayers

How could fabrication conditions influence films' properties?

- Type of substrates:

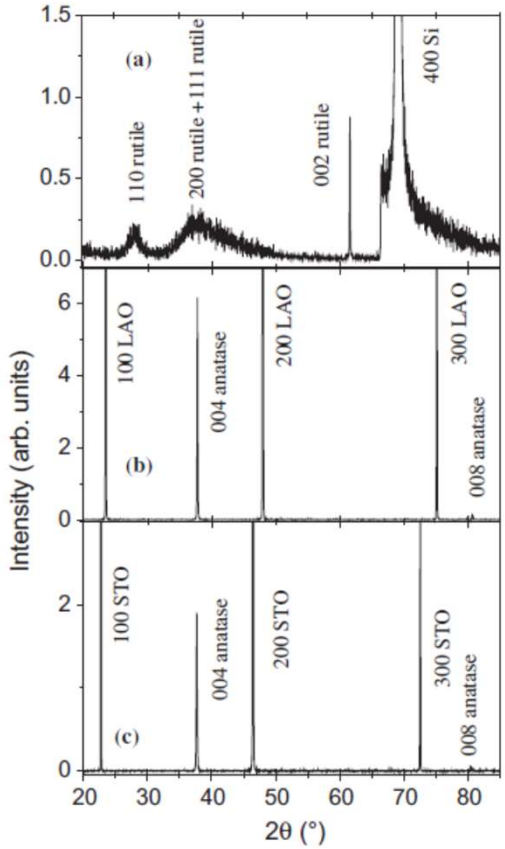


Figure 1. XRD pattern for a Co : TiO_2 film deposited at 700°C (*a*) on a Si substrate, under an oxygen pressure of 10^{-5} Torr; (*b*) on a LAO substrate under an oxygen pressure of 10^{-6} Torr and (*c*) on a STO substrate under an oxygen pressure of 10^{-5} Torr.

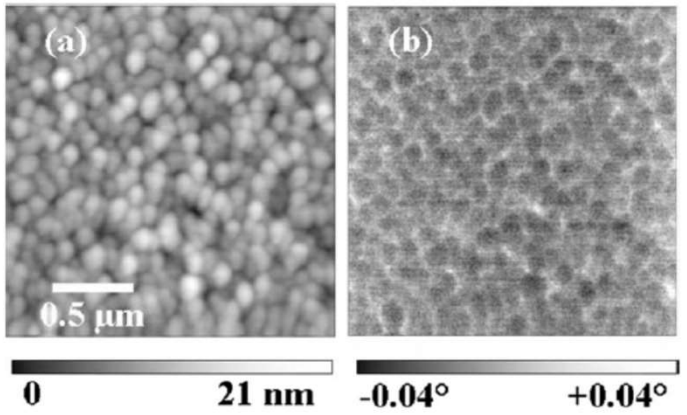


Figure 6. The topographic (*a*) and MFM (*b*) images obtained at room temperature on an area 2 × 2 μm^2 of the V : TiO_2 film grown on Si at 650°C. The tip was applied perpendicular to the film's plane.

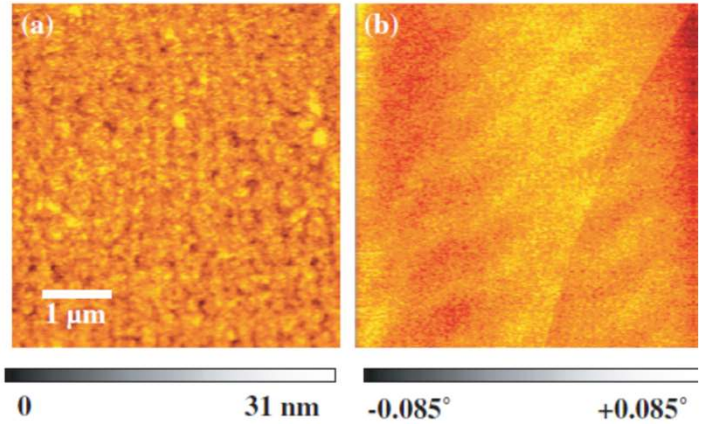


Figure 10. The topographic (*a*) and MFM (*b*) images taken at room temperature on the area 5 × 5 μm^2 of the V : TiO_2 film grown on LAO at 650°C. The tip was applied perpendicular to the film's plane

(This figure is in colour only in the electronic version)

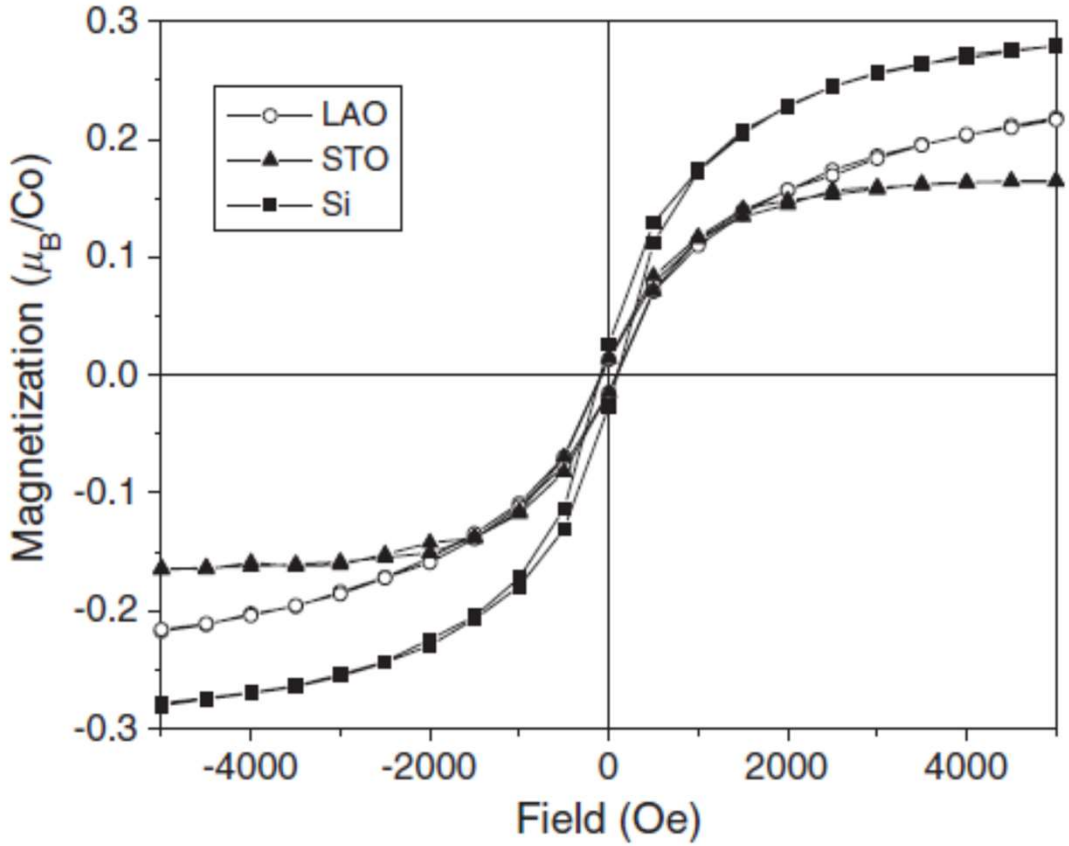


Figure 2. Magnetization versus magnetic field at 300 K for the Co : TiO_2 film fabricated at 700°C, under an oxygen pressure of 10^{-6} Torr on Si, LAO and STO substrates.

How heating temperature could change properties of films?

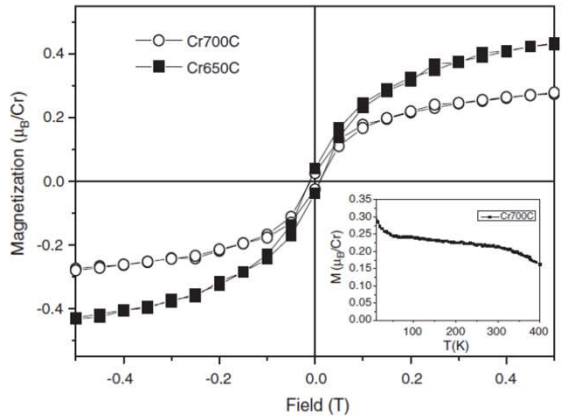


Figure 5. Magnetization versus magnetic field at 300 K for Cr : TiO_2 films grown on an Si substrate at 650°C and 700°C. The inset shows the $M(T)$ curve taken under 0.2 T for the film fabricated at 700°C.

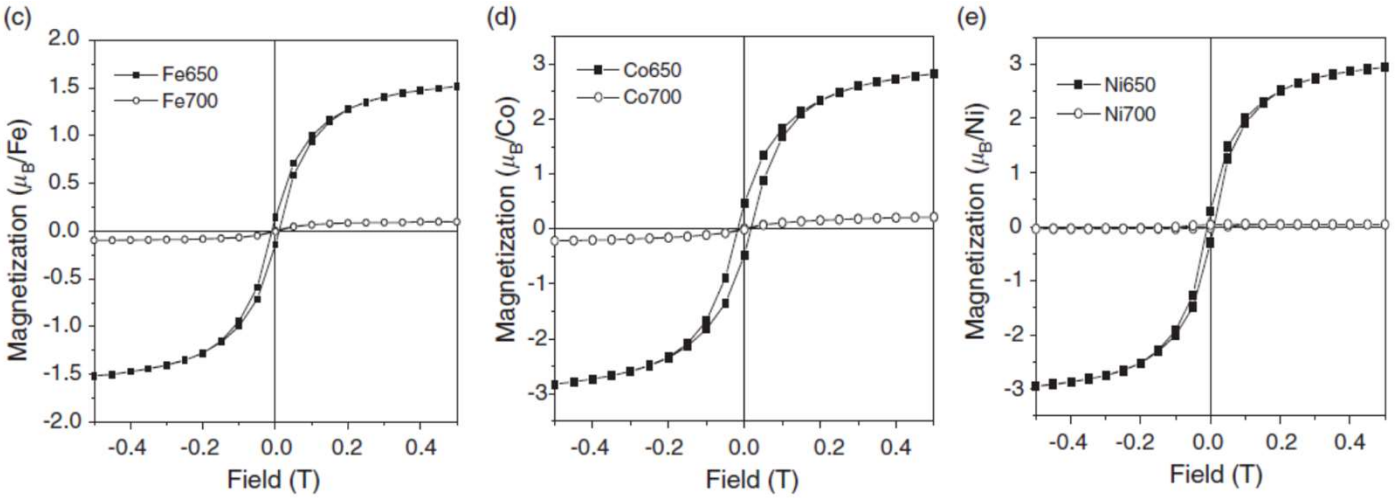


Figure 7. Magnetization versus magnetic field at 300 K for TM : TiO_2 films grown on LAO substrates at 650°C and 700°C: (*a*) V : TiO_2, (*b*) Cr : TiO_2, (*c*) Fe : TiO_2, (*d*) Co : TiO_2 and (*e*) Ni : TiO_2.

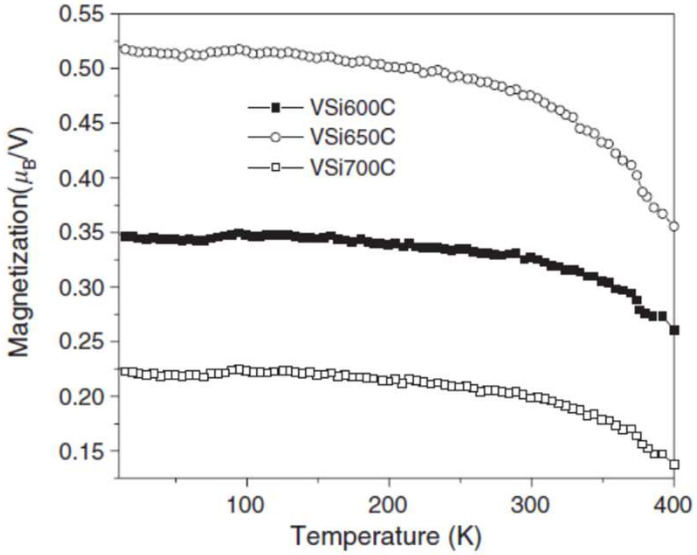


Figure 4. Magnetization versus temperature under 0.2 T for V : TiO_2 films grown on Si substrates at 600°C, 650°C and 700°C.

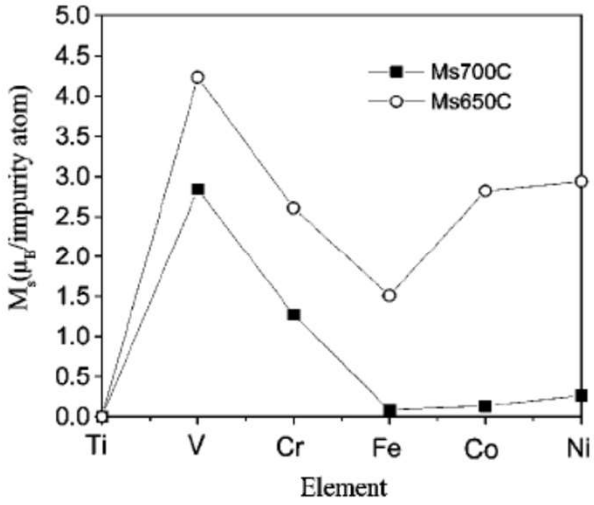


FIG. 8. Saturation magnetization vs element for TM: TiO_2 films fabricated at 700 and 650 °C {quantitative data taken from the saturated magnetic moments deduced from $[M(H)]$ curves measured at 300 K}.

How fabrication conditions could change properties of films?

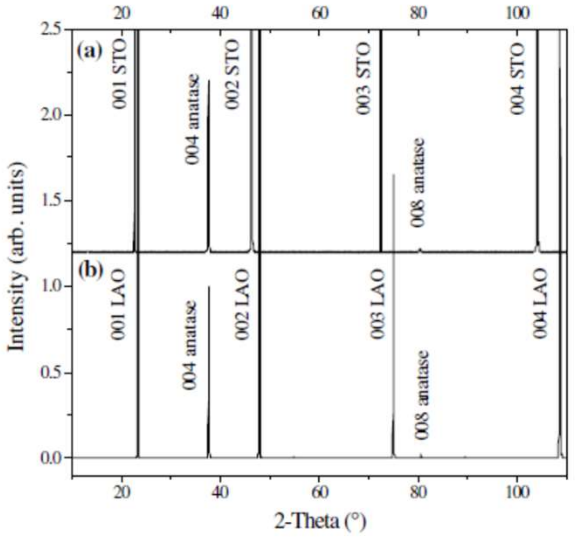


Figure 1. X-ray diffraction pattern (a) for a Co:TiO_2 film on STO under oxygen pressure of 1×10^{-5} Torr and fluence of 3 J cm^{-2} and (b) for a Co:TiO_2 film on LAO under oxygen pressure of 1×10^{-6} Torr and fluence of 1.5 J cm^{-2}.

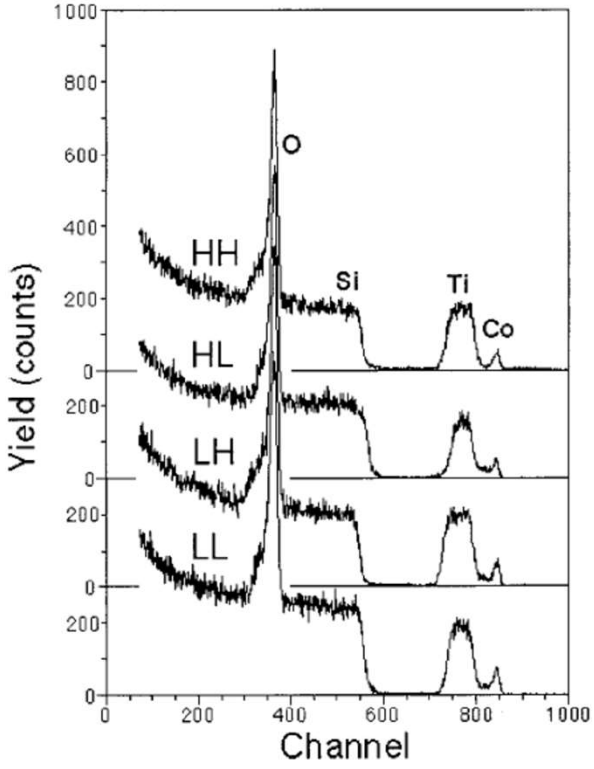


FIG. 4. RBS spectra of Co-doped TiO_2 films with four different conditions: (a) LL, (b) LH, (c) HL, and (d) HH.

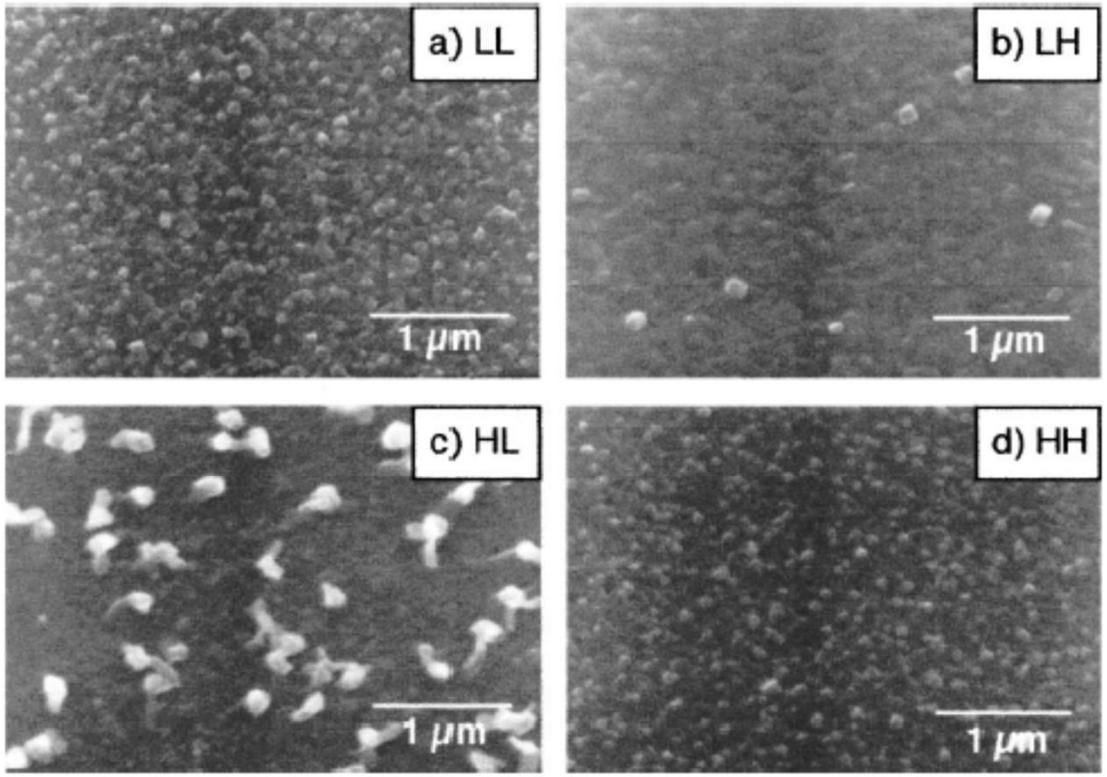
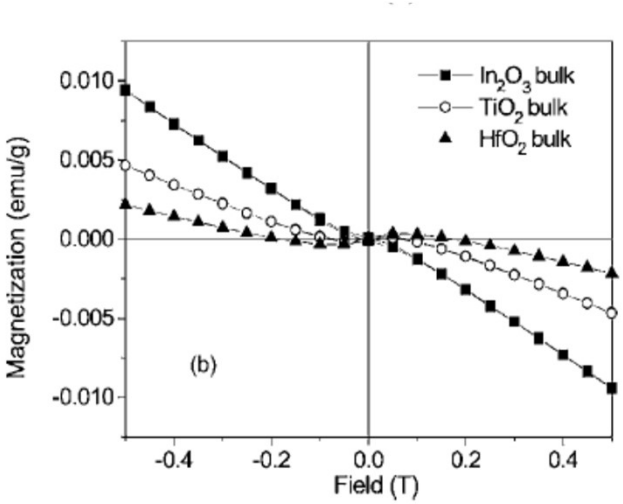


FIG. 3. SEM images of Co-doped TiO_2 films with four different conditions: (a) LL (P_{O_2} of 1×10^{-6} Torr and fluence of 1.5 J/cm^2), (b) LH (1×10^{-6} Torr, 3 J/cm^2), (c) HL (1×10^{-5} Torr, 1.5 J/cm^2), and (d) HH (1×10^{-5} Torr, 3 J/cm^2).

Thickness dependence



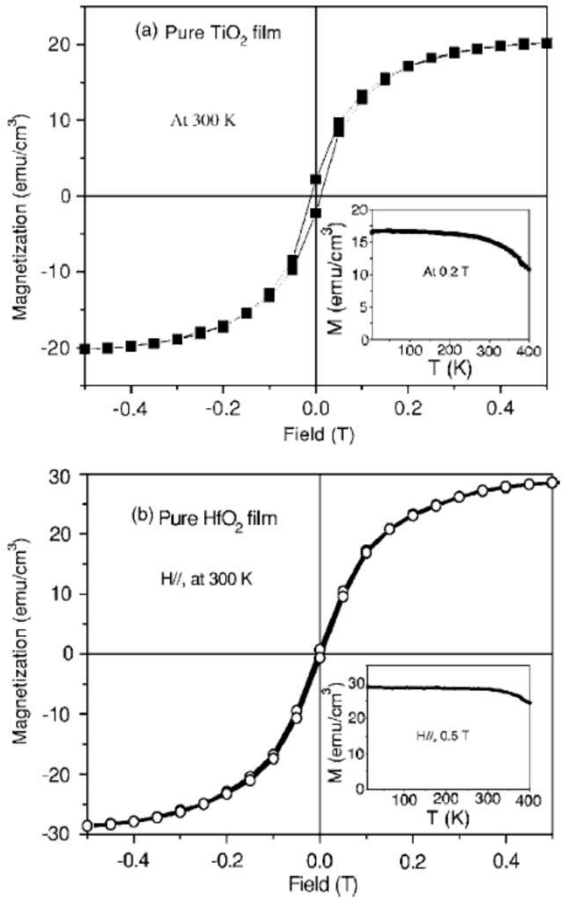
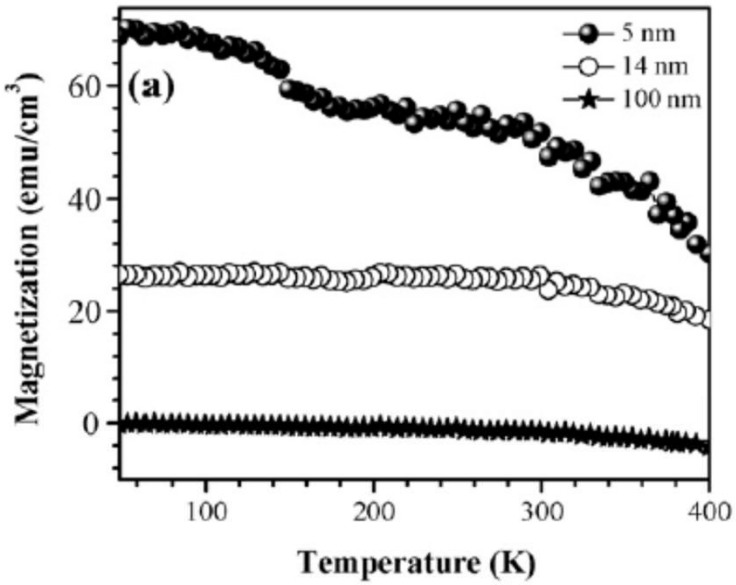
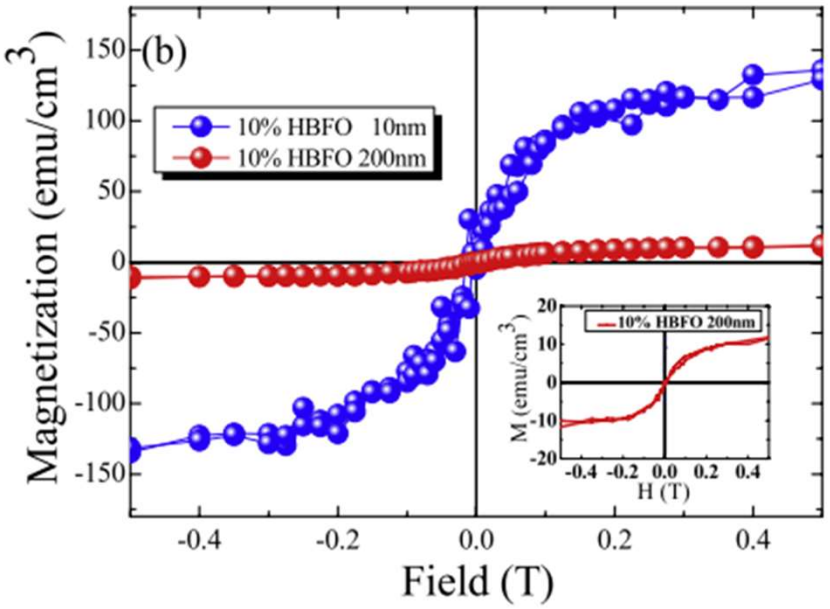
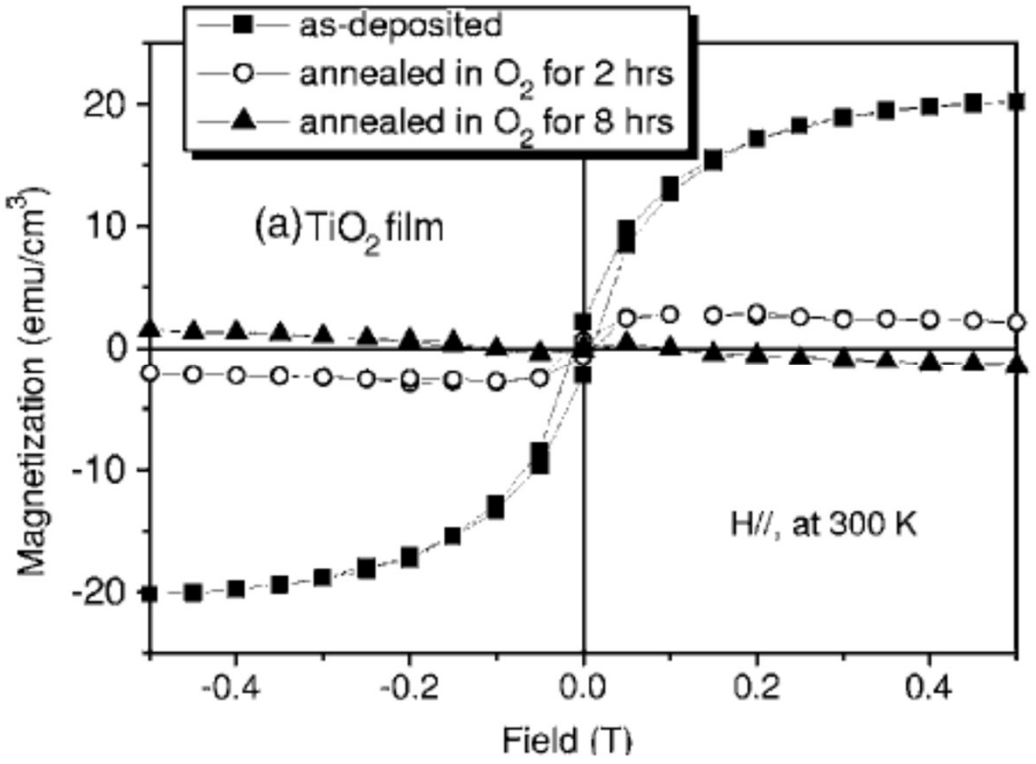


FIG. 1. Magnetization (a) versus magnetic field at 300 K for a pure TiO_2 film grown on a LAO substrate. The inset shows the *M-T* curve taken at 0.2 T and (b) versus magnetic field at 300 K for a pure HfO_2 film grown on an YSZ substrate. The inset shows the *M-T* curve taken at 0.5 T. (Note that the signals of substrates were subtracted already.)


(a)
5 nm
14 nm
100 nm
Magnetization (emu/cm3)
Temperature (K)
0
20
40
60
100
200
300
400


(b)
10% HBFO 10nm
10% HBFO 200nm
Magnetization (emu/cm3)
Field (T)
150
100
50
0
-50
-100
-150
-0.4
-0.2
0.0
0.2
0.4
M (emu/cm3)
H (T)
20
10
0
-10
-20

Annealing


as-deposited
annealed in O_2 for 2 hrs
annealed in O_2 for 8 hrs
(a)TiO_2 film
H//, at 300 K
Magnetization (emu/cm^3)
Field (T)
20
10
0
-10
-20
-0.4
-0.2
0.0
0.2
0.4

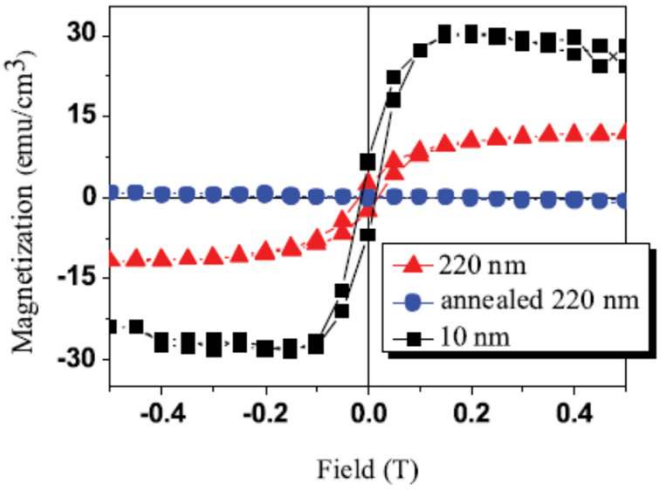


FIG. 2. (Color online) Magnetization versus magnetic field taken at 300 K as the magnetic field is applied parallel to the film's plane for the as-grown 10-nm-thick SnO_2 film, the as-deposited 220-nm-thick SnO_2 film, and the 220-nm-thick SnO_2 film postannealed under the O_2 atmosphere of 760 Torr at 700 °C for 10 hours.

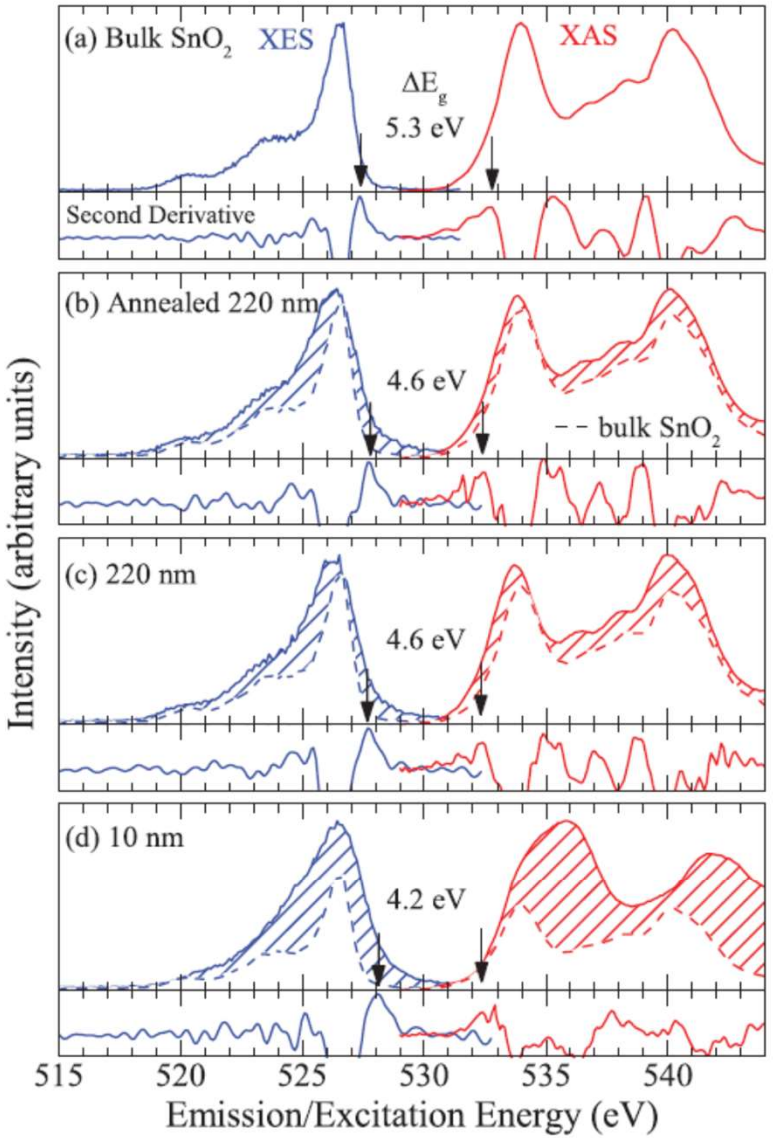


FIG. 3. (Color online) O K-edge x-ray emission (O $K\alpha$ XES) and absorption (O 1s XAS) spectra for bulk SnO_2 (a), the 200-nm-thick SnO_2 thin film with postannealing treatment (b), the 200-nm-thick as-grown film (c), and the 10-nm-thick as-grown film.