



**Physical methods for the synthesis of  
low-dimensional nanomaterials**

**&**

**Tuning properties of PLD Magnetic  
Oxide Thin Films**

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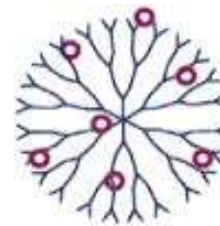
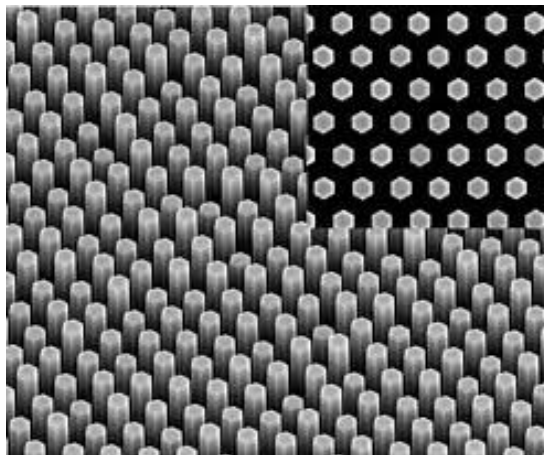
## Which materials should be classified as Nano (Low dimensional)?

- 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 they are important/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



Dendrimer



Quantum Dots



Carbon Nanotube (CNT)



Liposome

# How could they have remarkable properties?

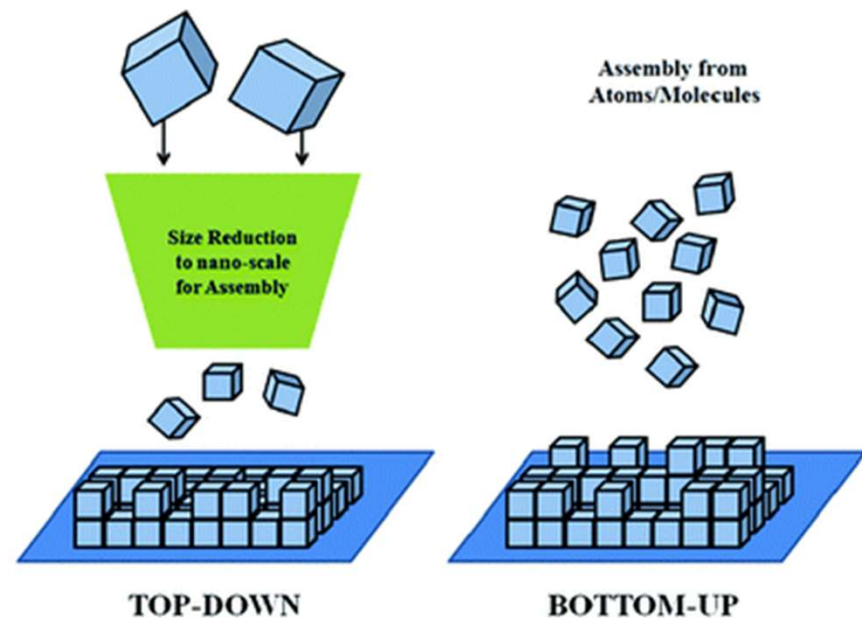
- Size, shape, specific surface area, aspect ratio
- Size distribution
- Surface morphology/topography
- Structure, including crystallinity & defects
- Solubility

**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.

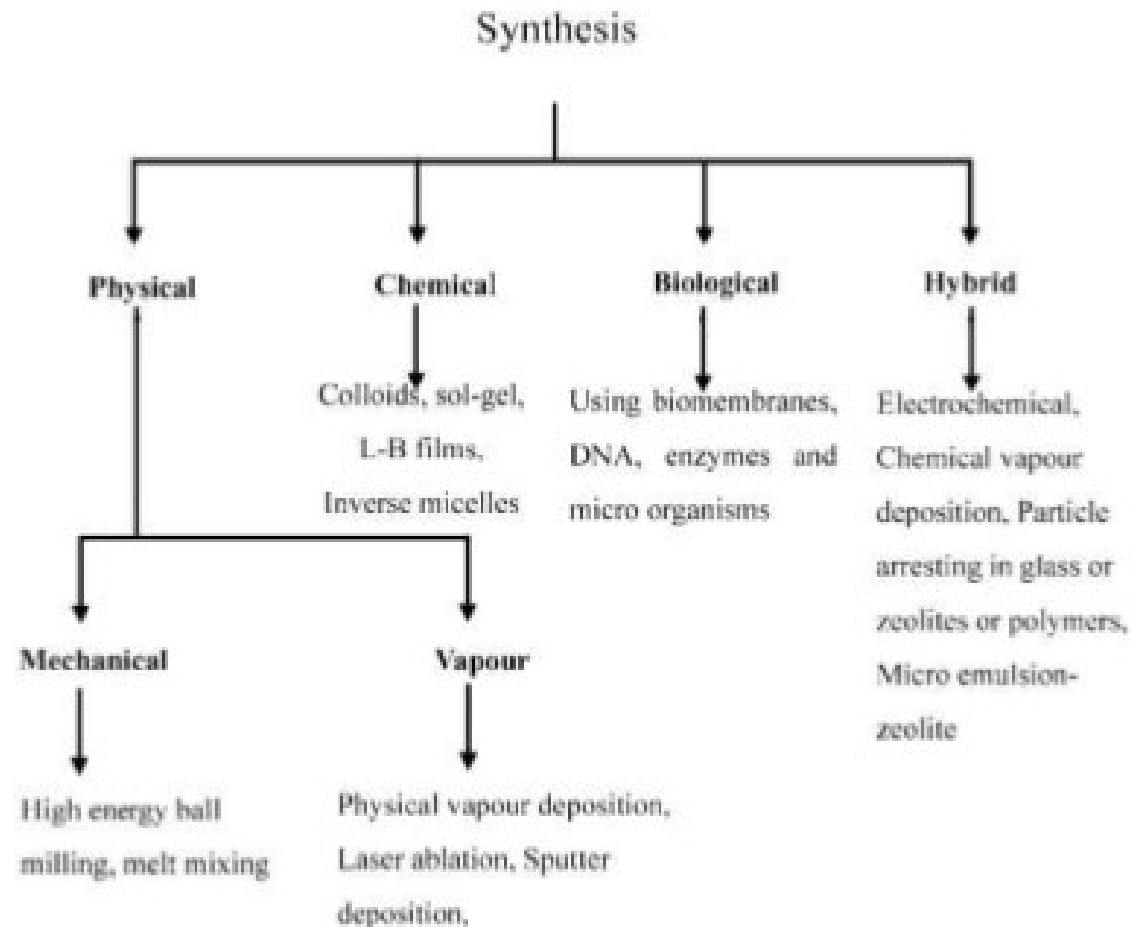
When materials are this small, their electronic & optical properties deviate substantially from those of bulk materials

# Principles of synthesis

- The goal of any method intended for the synthesis of nanomaterials is **to yield a material** that exhibits properties that are results of 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)

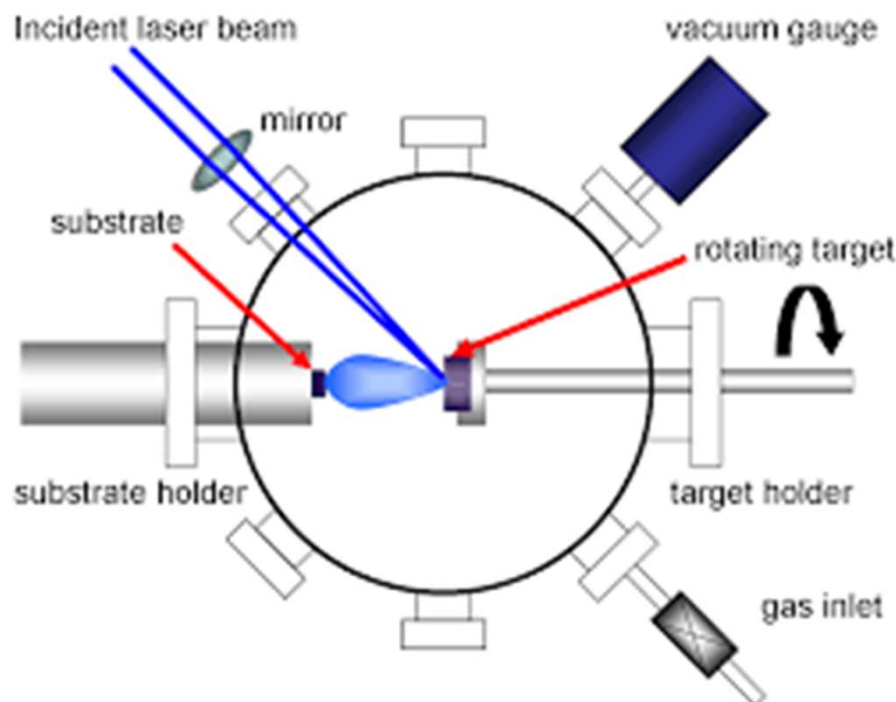
- **Laser** is an electronic-optical device that produces coherent radiation. The term is acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation.
- **Pulsed Laser Deposition (PLD)** is a physical vapor deposition technique where a high power **pulsed laser beam is focused to shoot a target** of the desired composition. Material is then vaporized and 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<sub>2</sub>** when depositing films of oxides.
- One can alter the properties of functional materials by controlling the external parameters such as temperature, electric and magnetic fields, pressure etc.!



# Concept of PLD

## PLD stages:

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

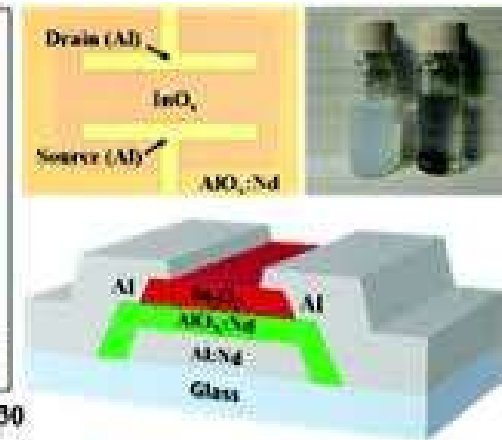
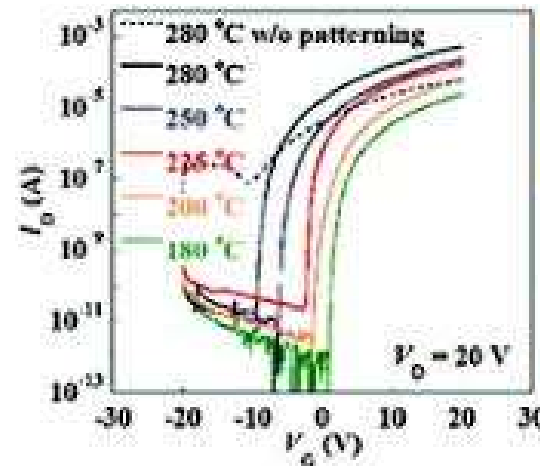
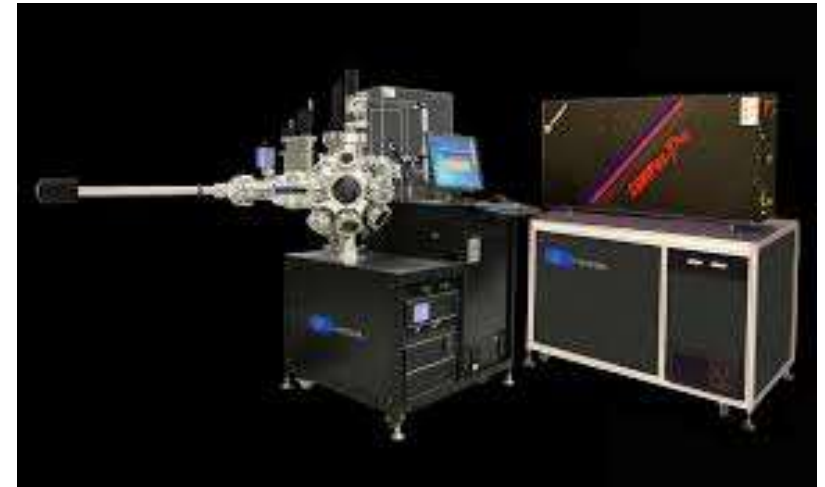
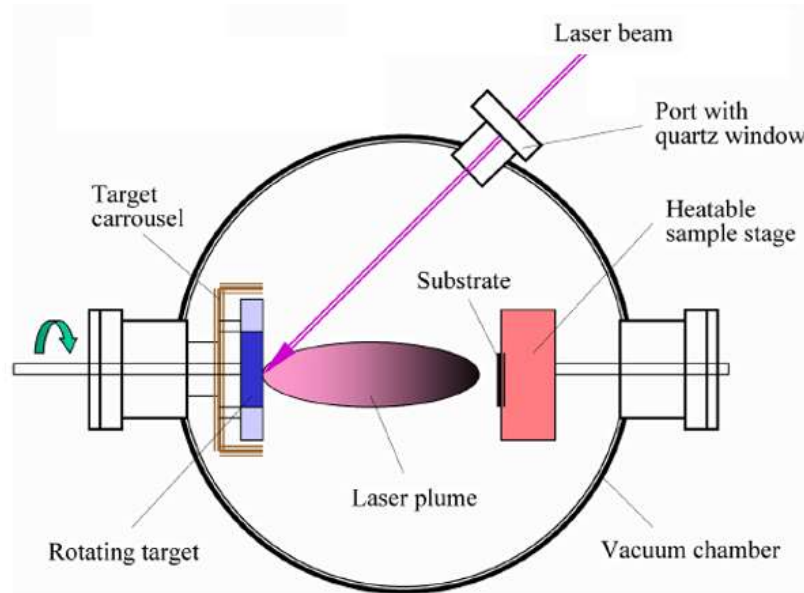


## Advantage:

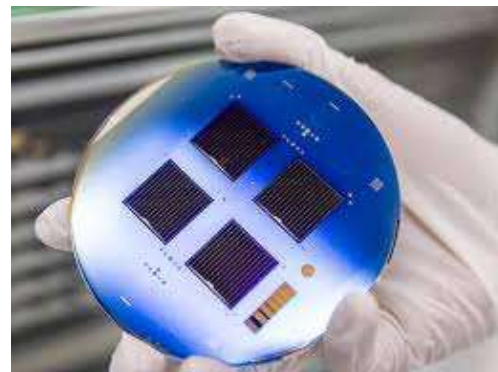
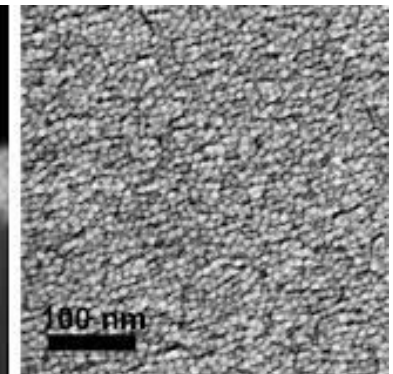
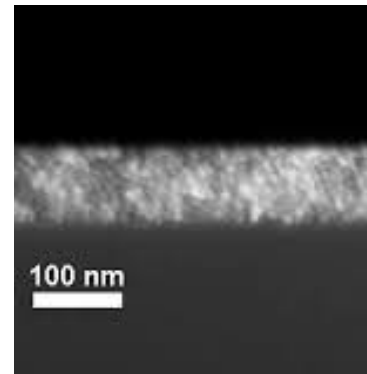
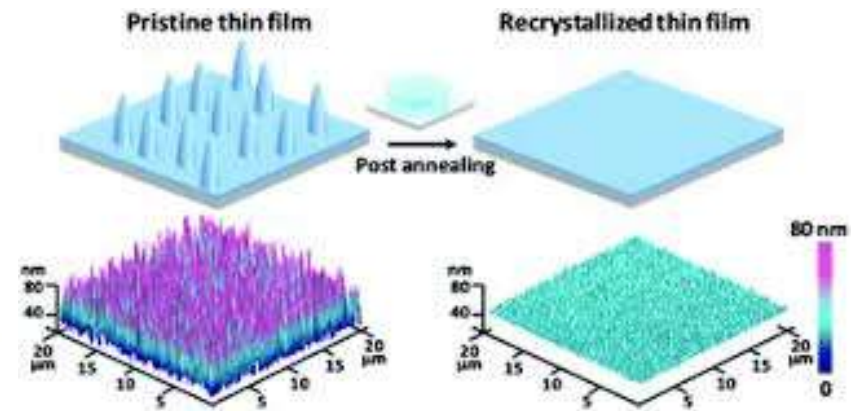
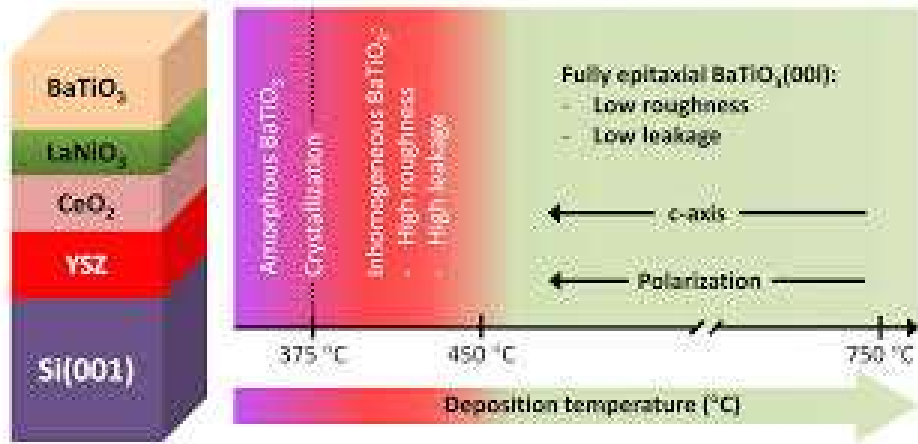
- film's **stoichiometry** is near to that of the target.
- versatile**: many materials can be deposited in a wide variety of gases over a broad range of gas pressures.
- cost-effective**: one laser source can serve many chambers.
- fast**: high quality films can be grown in 10-15 minutes.

**Important:** Type of Eximer Laser; Beam alignment; **Energy density;**  
**Pulse repetition rate;** Time of shooting; Vacuum-**O<sub>2</sub> Pressure;**  
**Type of substrate; Substrate temperature;**  
Distance between target & substrate

# Growth of a film



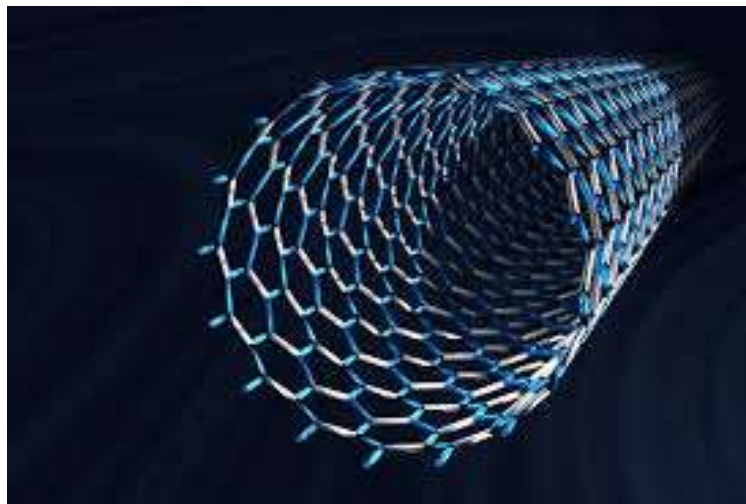
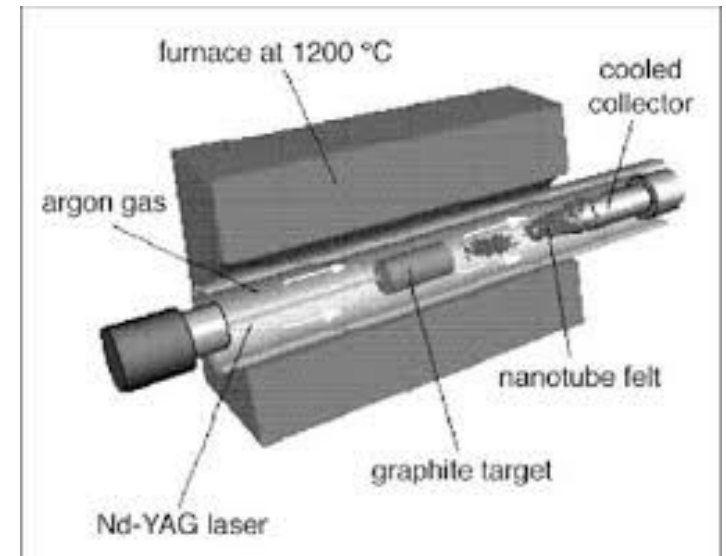
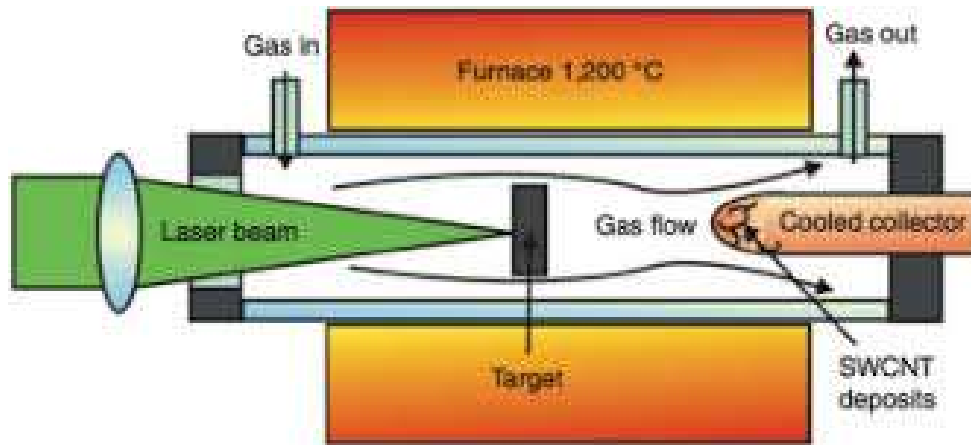
**Fabrication Conditions (T, P, substrate, etc) play key roles in shaping up desired properties!**



# 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.

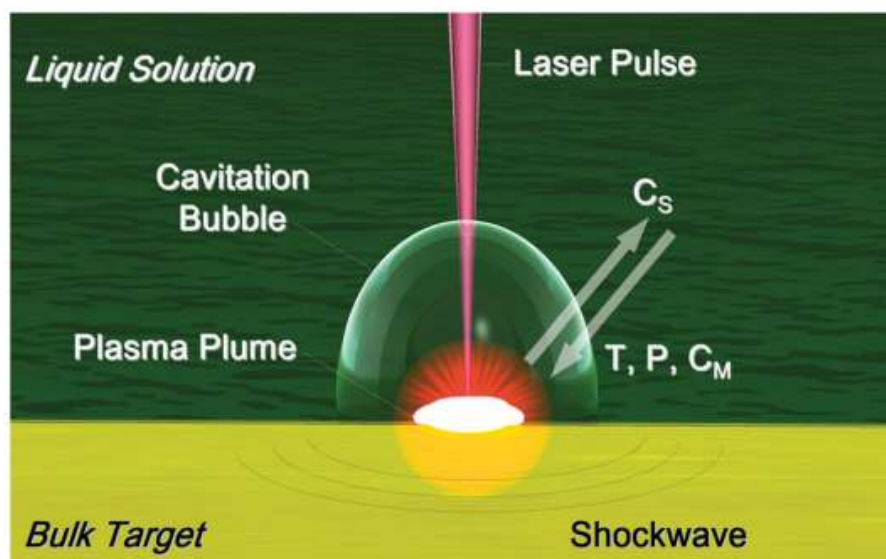


Figure from V. Amendola *et al.*/ Phys. Chem. Chem. Phys. 2013, 15, 3027-3046

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.

Target ↓	Solvent ↓	Water	Ethanol	Acetonitrile
		<chem>O</chem>	<chem>CCO</chem>	<chem>CC#N</chem>
Au				
	<i>Metal Au</i>	<i>Metal Au</i>	<i>Metal Au</i>	
Ag				
	<i>Metal Ag/ Oxide AgO</i>	<i>Metal Ag</i>	<i>Metal Ag</i>	

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

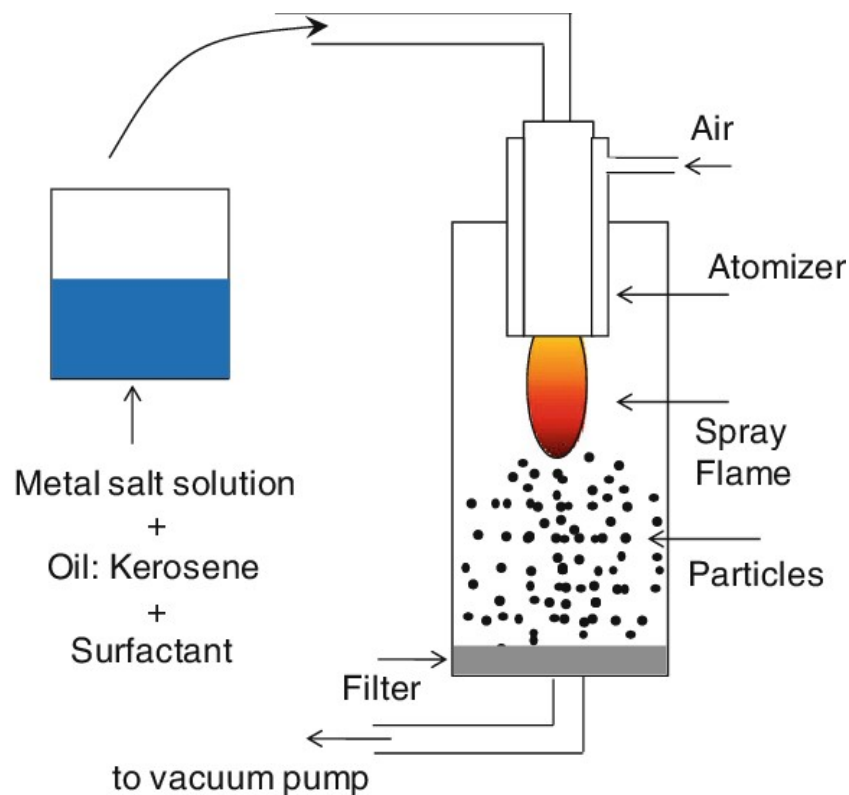
The following video demonstrates the laser ablation process:

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

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

## Flame combustion method

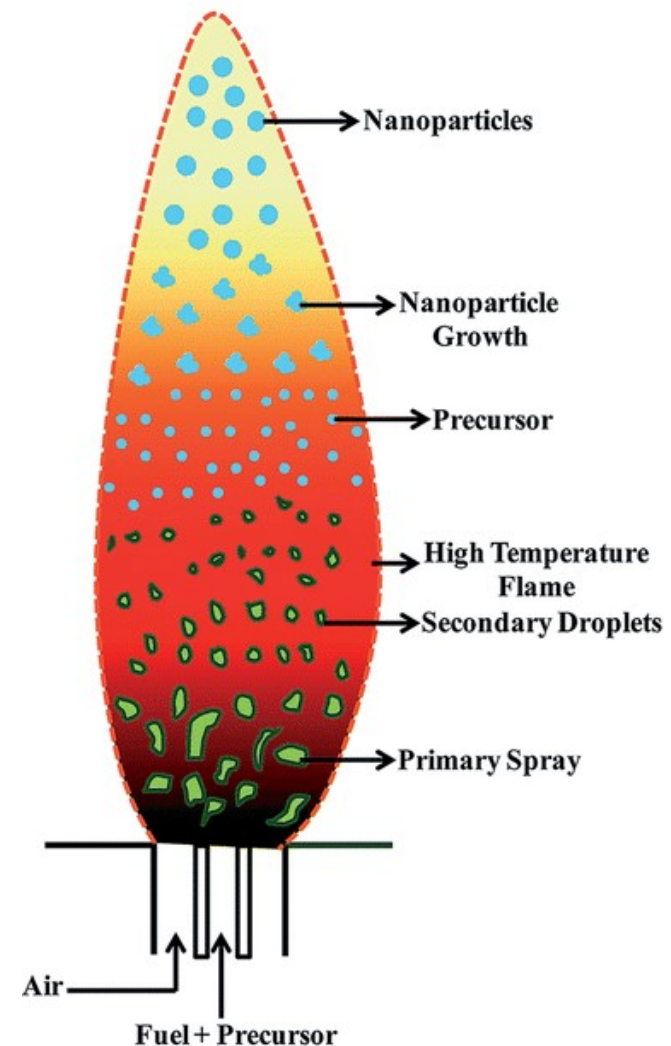
In this method, a spray of precursor solution mixed with a gas carrier is burned in flame. In general, the method is **suitable for fabrication of spherical metal oxide nanoparticles** (undoped or doped).





During the Flame combustion process the 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 and gas supply rate, flame temperature, viscosity, etc.



# Mechanical method to make nanoparticles

## Mechanical Methods

High Energy  
Ball Milling

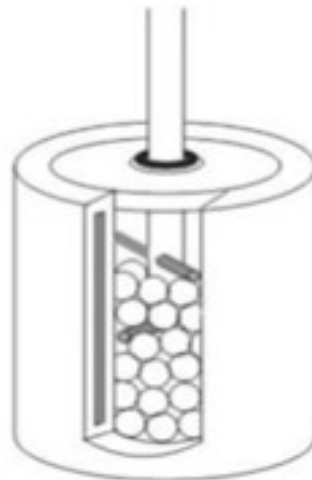
- Bulk Nanoparticles in the form of Powder.

Melt Mixing

- Form/Arrest Nanoparticles in Glass.

## High Energy Ball Milling

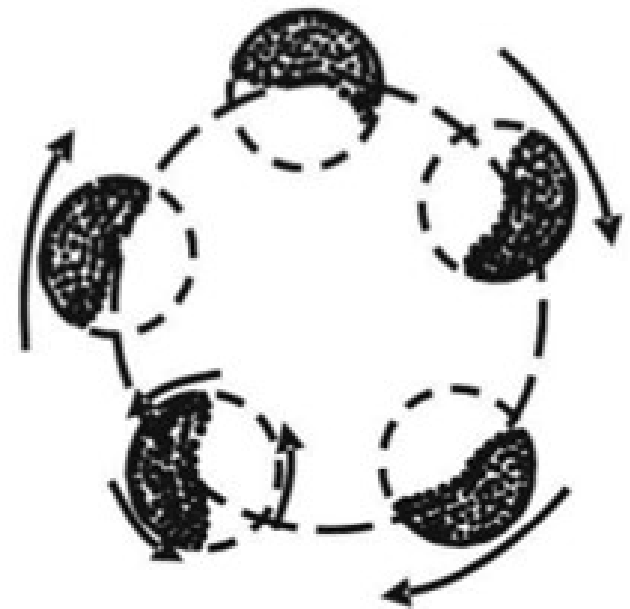
- Some of the materials like Co, Cr, W, Ni, Ti, Al-Fe and Ag-Fe are made nanocrystalline using ball mill.
- Few milligrams to several kilograms of nanoparticles can be synthesized in a short time of a few minutes to a few hours.
- One of the simplest ways of making nanoparticles of some metals and alloys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

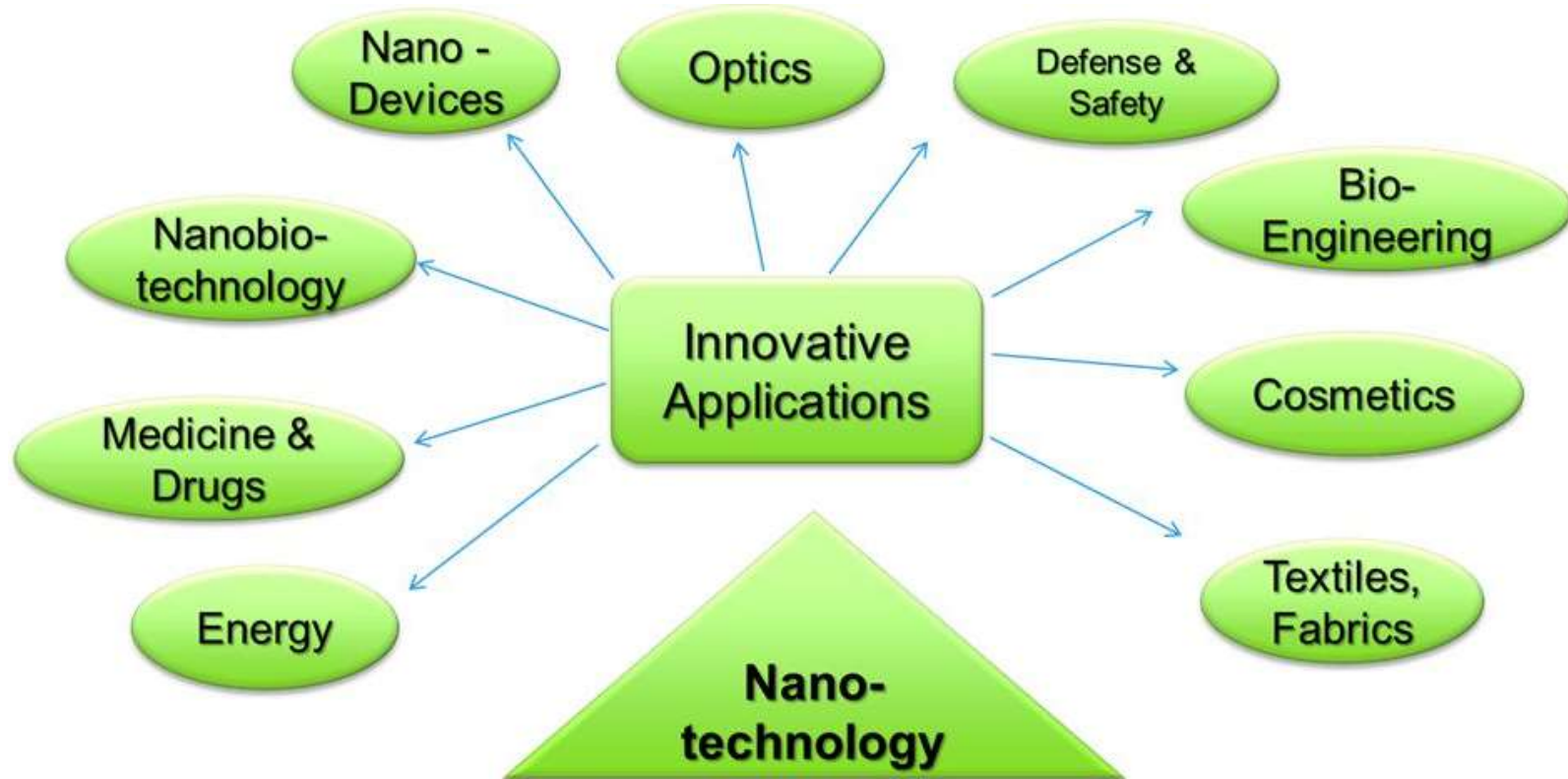
- To avoid any impurities from balls, the container may be filled with air or inert gas. However this can be an additional source of impurity, if proper precaution to use high purity gases is not taken.
- A temperature rise in the range of 100–1,100°C is expected to take place during the collisions.
- Lower temperatures favour amorphous particle formation.
- The gases like O<sub>2</sub>, N<sub>2</sub> 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.

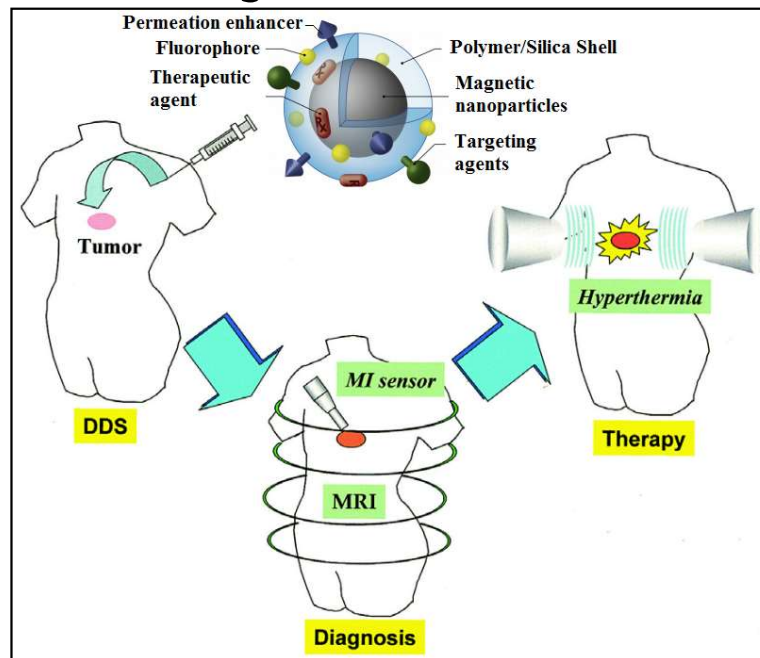
Therefore, these methods can be **easily scaled-up** for **industrial production & commercialization**.



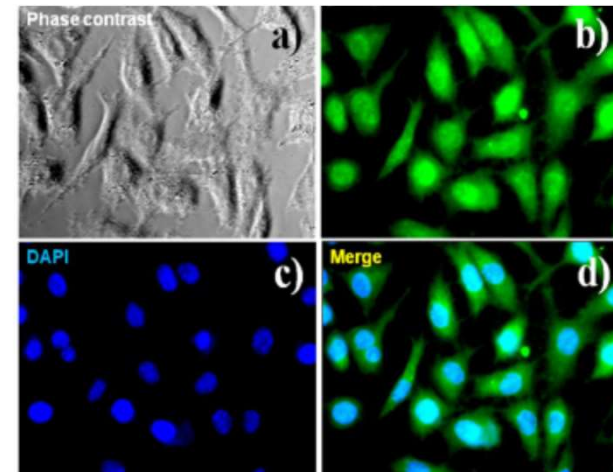
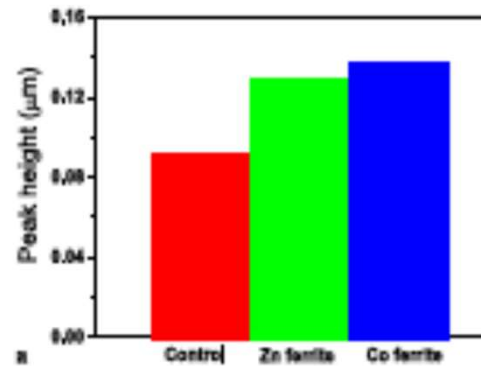
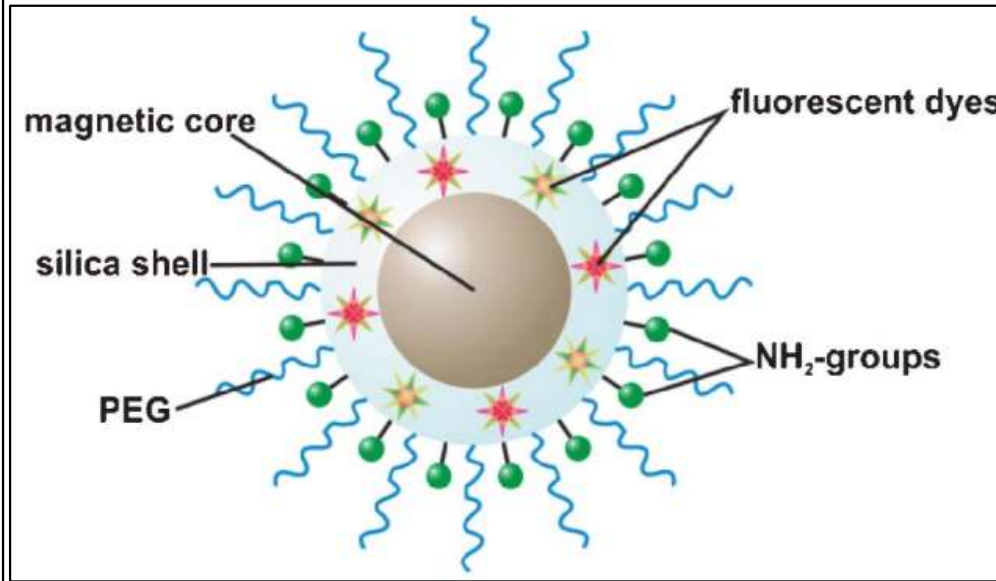
# Nanoparticles for biomedical applications

## Therapeutic

S



## Drug Delivery



# Tuning Properties of PLD Magnetic Oxide Films

- **Changing parameters of deposition**

*(type of substrate, heating temperature, O<sub>2</sub> pressure, repetition rate, energy density, distance between target and substrate)*

- **Varying thickness**

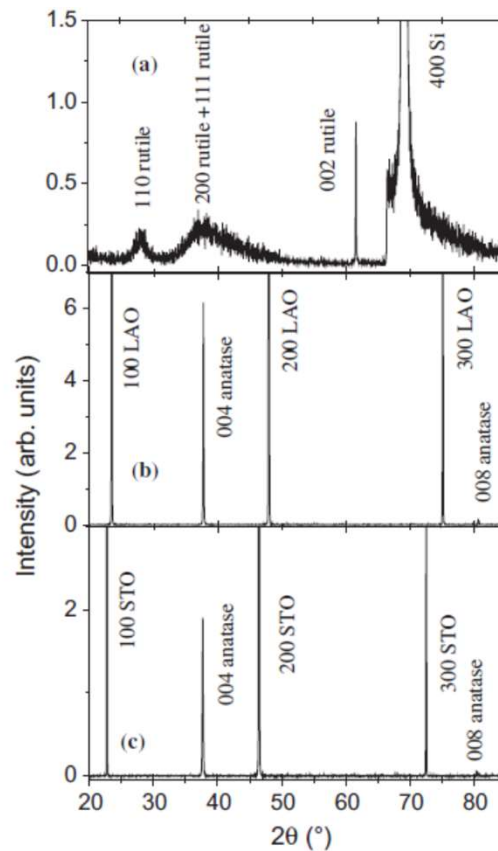
*(control by fixing time of deposition)*

- **Extra-annealing**

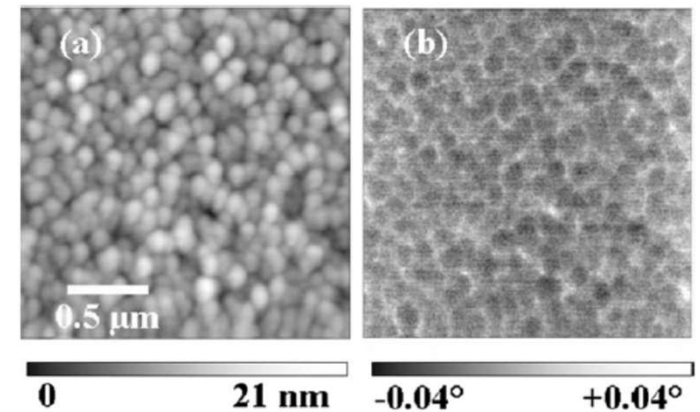
- **Multilayers**

# How fabrication conditions could change properties?

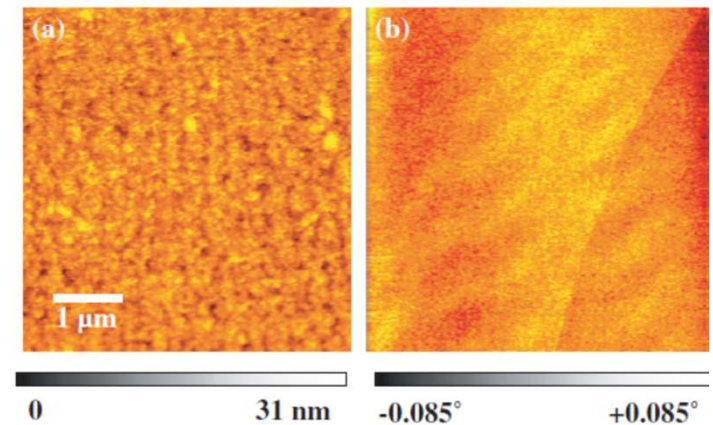
- Type of substrates:



**Figure 1.** XRD pattern for a Co:TiO<sub>2</sub> film deposited at 700°C (a) on a Si substrate, under an oxygen pressure of 10<sup>-5</sup> Torr; (b) on a LAO substrate under an oxygen pressure of 10<sup>-6</sup> Torr and (c) on a STO substrate under an oxygen pressure of 10<sup>-5</sup> Torr.

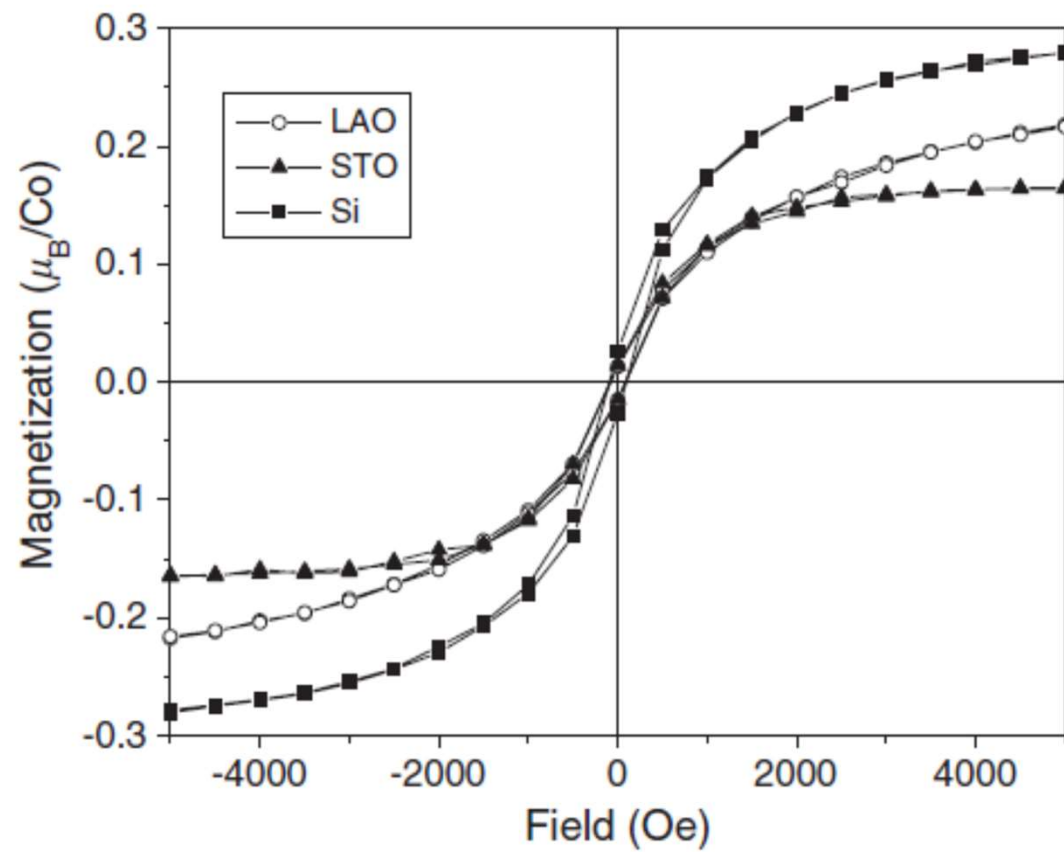


**Figure 6.** The topographic (a) and MFM (b) images obtained at room temperature on an area 2 × 2 μm<sup>2</sup> of the V:TiO<sub>2</sub> film grown on Si at 650°C. The tip was applied perpendicular to the film's plane.



**Figure 10.** The topographic (a) and MFM (b) images taken at room temperature on the area 5 × 5 μm<sup>2</sup> of the V:TiO<sub>2</sub> 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<sub>2</sub> film fabricated at 700°C, under an oxygen pressure of 10<sup>-6</sup> Torr on Si, LAO and STO substrates.

# How heating temperature could change properties of films?

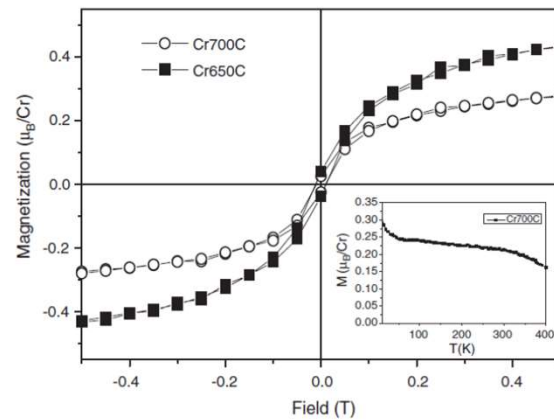


Figure 5. Magnetization versus magnetic field at 300 K for Cr: TiO<sub>2</sub> films grown on an Si substrate at 650°C and 700°C. The inset shows the  $M(T)$  curve taken under 0.2 T for the film fabricated at 700°C.

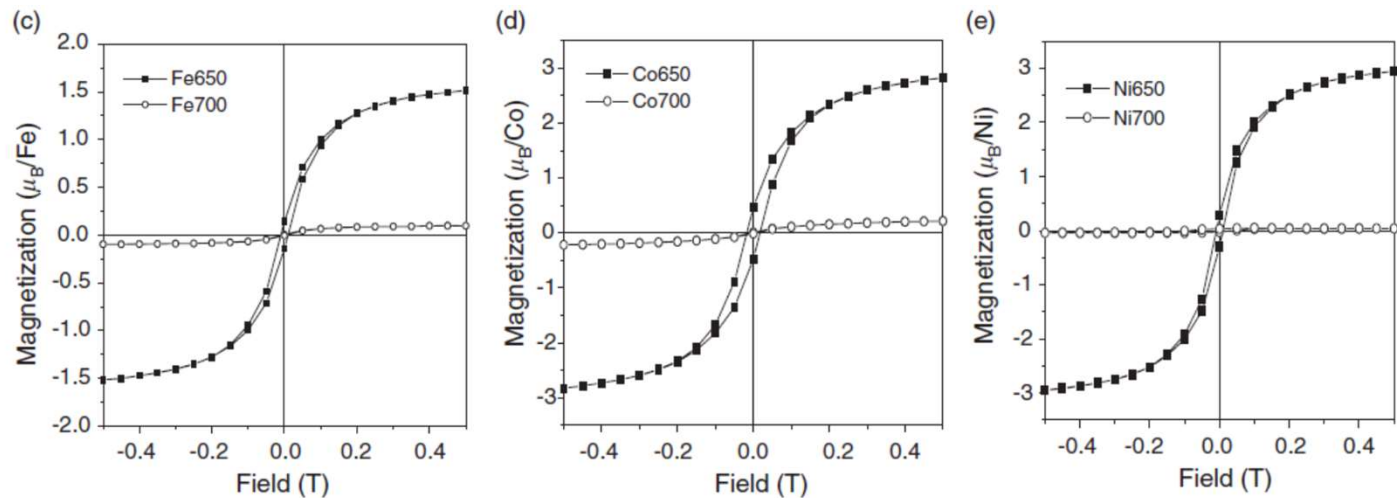


Figure 7. Magnetization versus magnetic field at 300 K for TM: TiO<sub>2</sub> films grown on LAO substrates at 650°C and 700°C: (a) V: TiO<sub>2</sub>, (b) Cr: TiO<sub>2</sub>, (c) Fe: TiO<sub>2</sub>, (d) Co: TiO<sub>2</sub> and (e) Ni: TiO<sub>2</sub>.

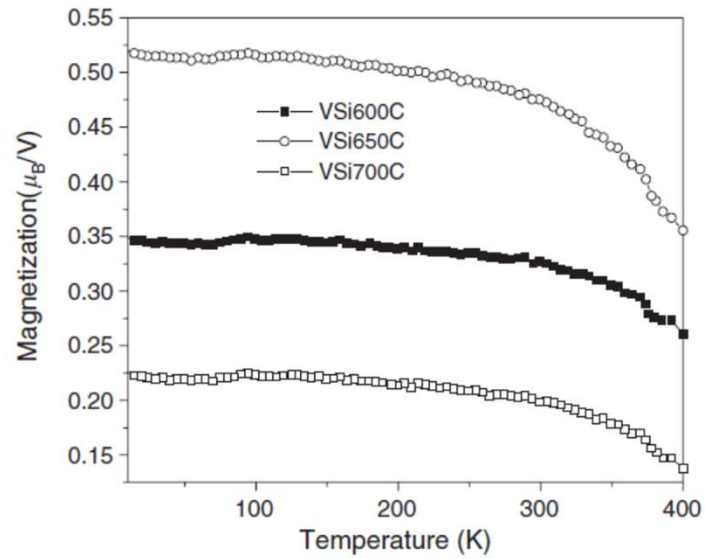


Figure 4. Magnetization versus temperature under 0.2 T for V:TiO<sub>2</sub> films grown on Si substrates at 600°C, 650°C and 700°C.

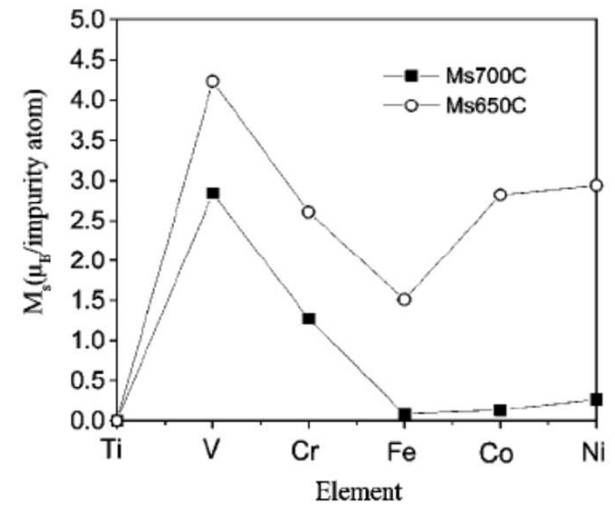


FIG. 8. Saturation magnetization vs element for TM:TiO<sub>2</sub> films fabricated at 700 and 650 °C {quantitative data taken from the saturated magnetic moments deduced from  $[M(H)]$  curves measured at 300 K}.

# How fabrication conditions could change properties of films?

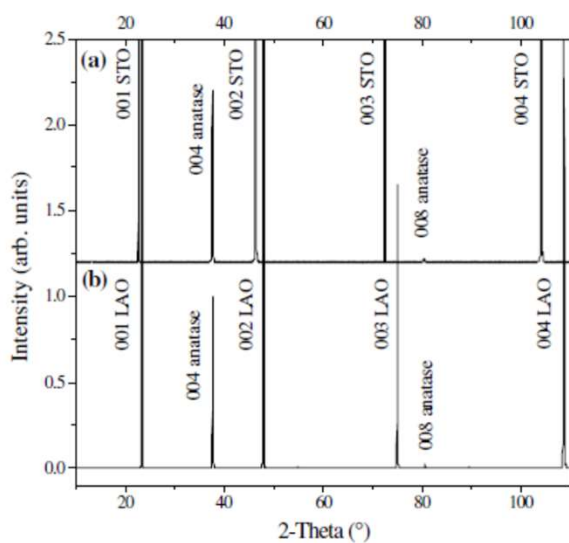


Figure 1. X-ray diffraction pattern (a) for a Co:TiO<sub>2</sub> film on STO under oxygen pressure of  $1 \times 10^{-5}$  Torr and fluence of  $3 \text{ J cm}^{-2}$  and (b) for a Co:TiO<sub>2</sub> film on LAO under oxygen pressure of  $1 \times 10^{-6}$  Torr and fluence of  $1.5 \text{ J cm}^{-2}$ .

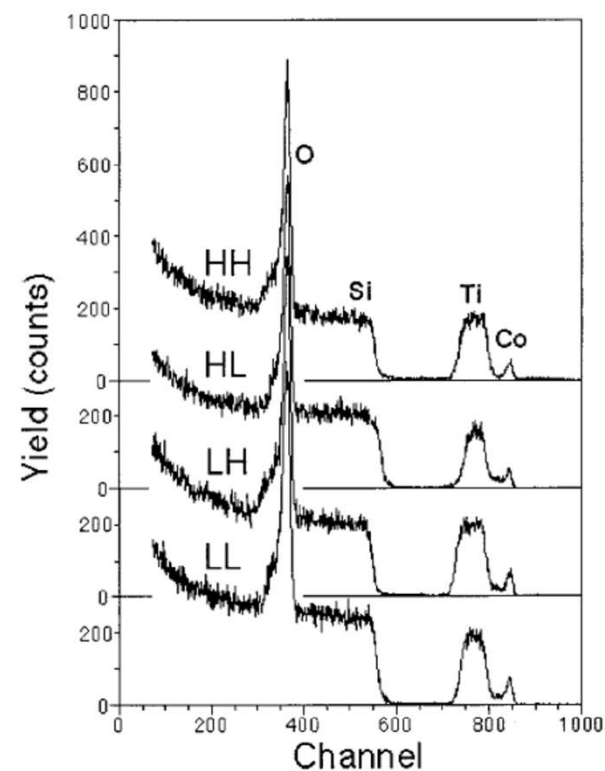


FIG. 4. RBS spectra of Co-doped TiO<sub>2</sub> films with four different conditions: (a) LL, (b) LH, (c) HL, and (d) HH.

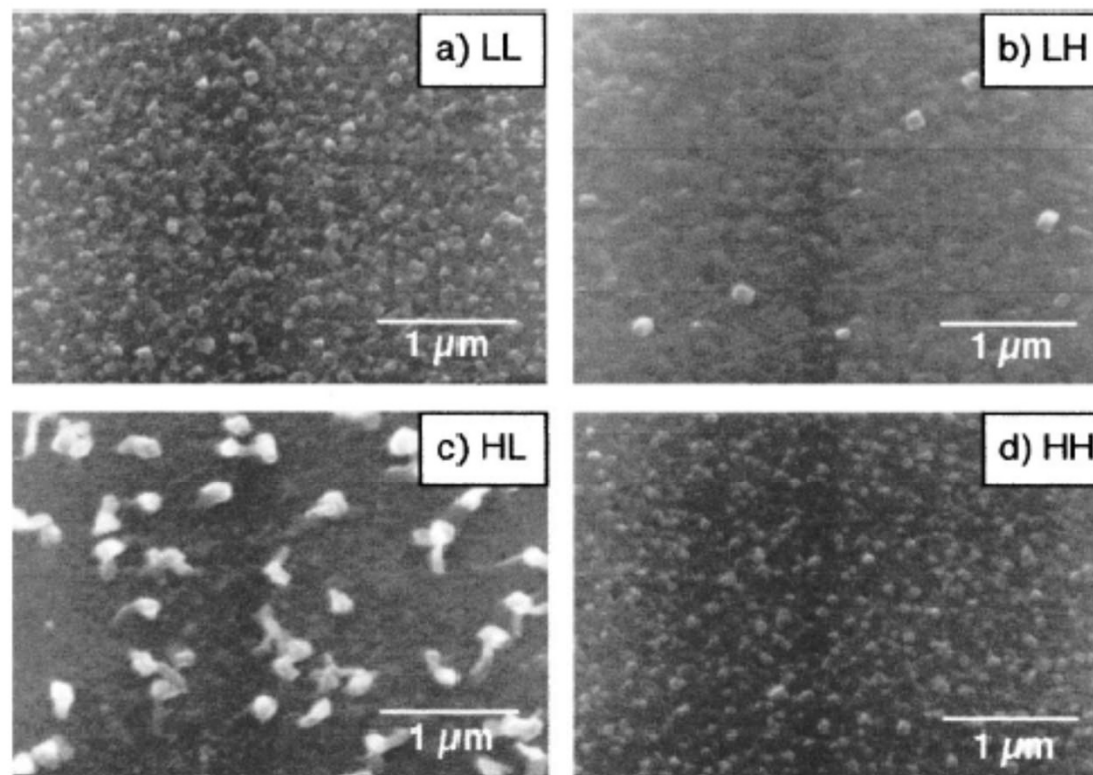


FIG. 3. SEM images of Co-doped TiO<sub>2</sub> films with four different conditions: (a) LL ( $P_{O_2}$  of  $1 \times 10^{-6}$  Torr and fluence of  $1.5 \text{ J/cm}^2$ ), (b) LH ( $1 \times 10^{-6}$  Torr,  $3 \text{ J/cm}^2$ ), (c) HL ( $1 \times 10^{-5}$  Torr,  $1.5 \text{ J/cm}^2$ ), and (d) HH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

# Thickness dependence

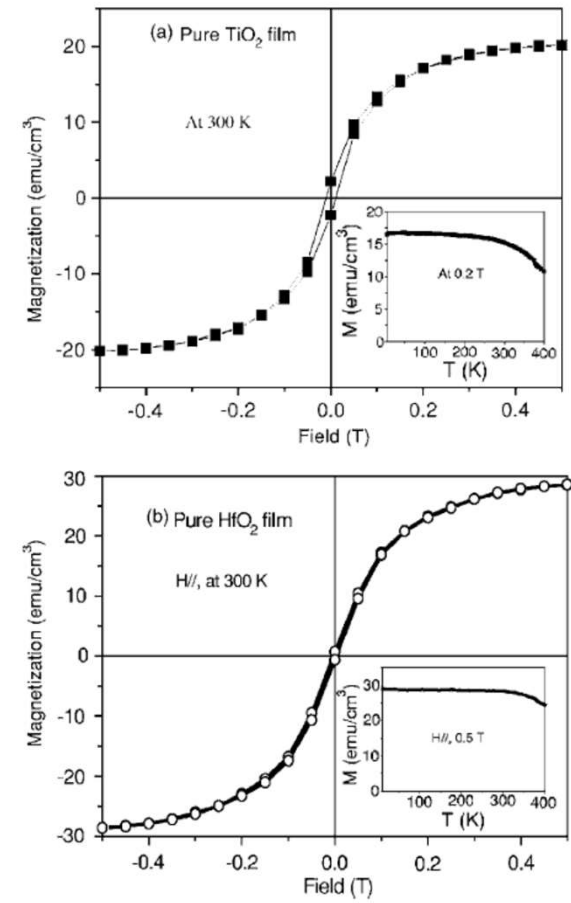
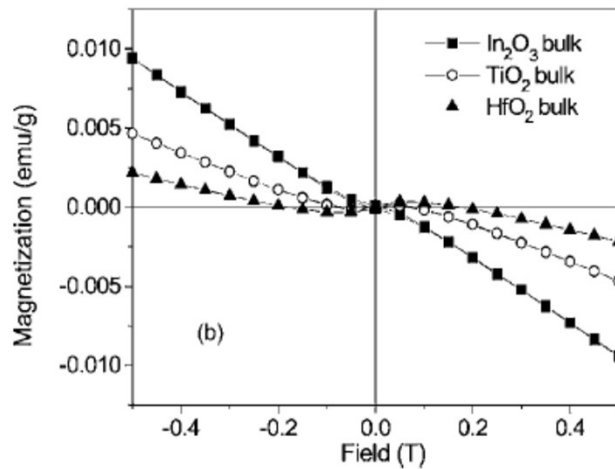
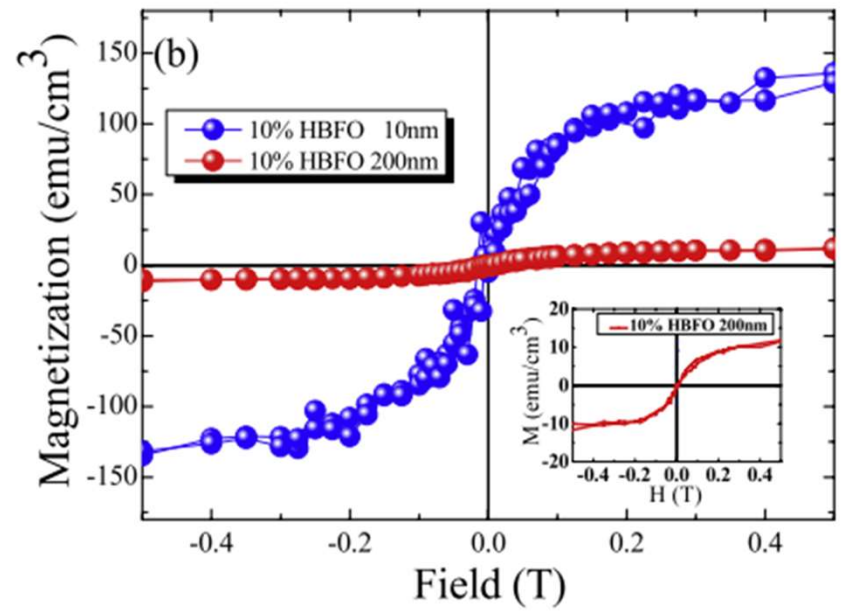
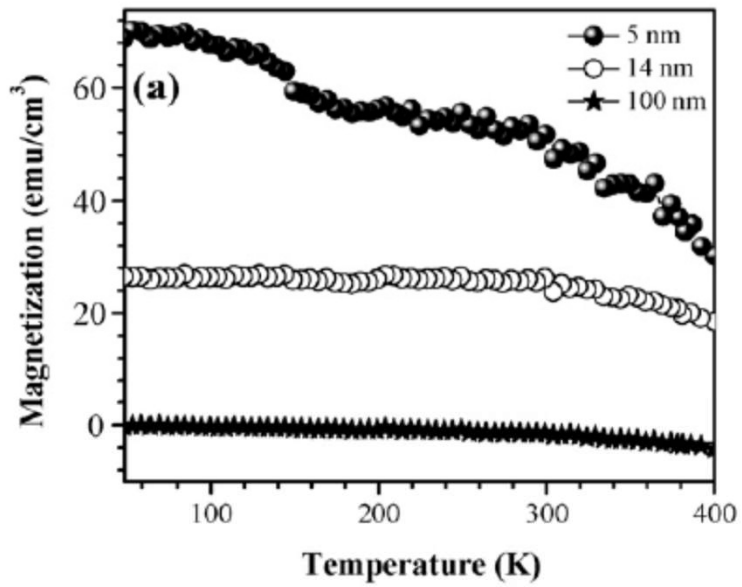
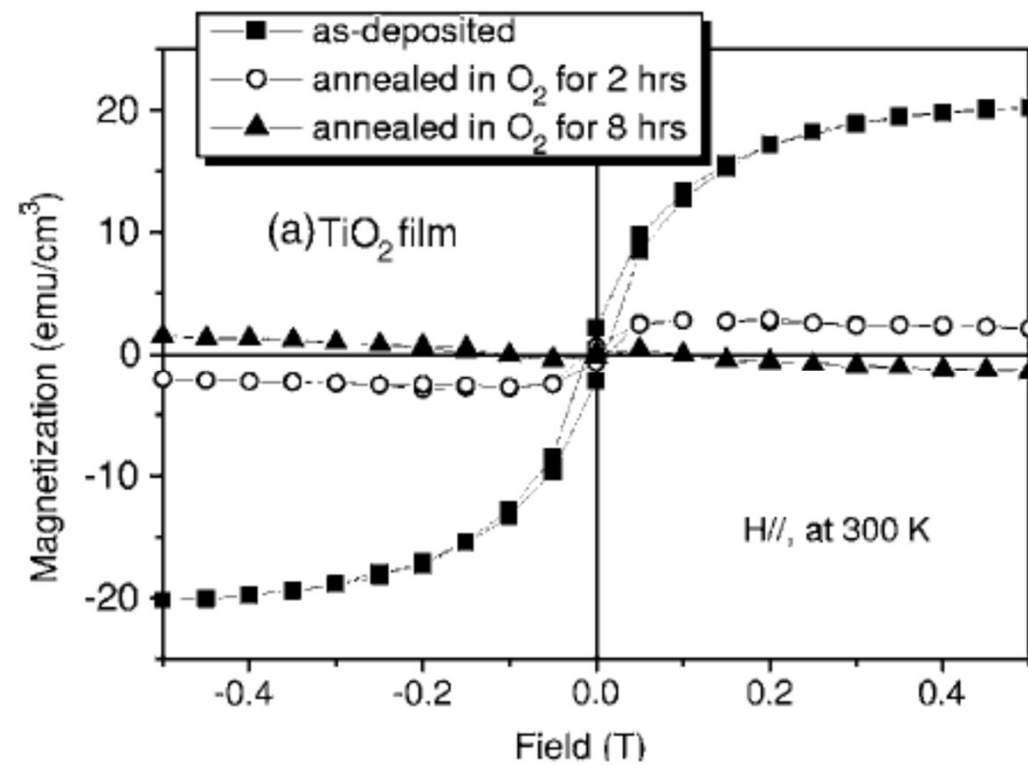


FIG. 1. Magnetization (a) versus magnetic field at 300 K for a pure  $\text{TiO}_2$  film grown on a LAO substrate. The inset shows the  $M-T$  curve taken at 0.2 T and (b) versus magnetic field at 300 K for a pure  $\text{HfO}_2$  film grown on an YSZ substrate. The inset shows the  $M-T$  curve taken at 0.5 T. (Note that the signals of substrates were subtracted already.)



# Annealing





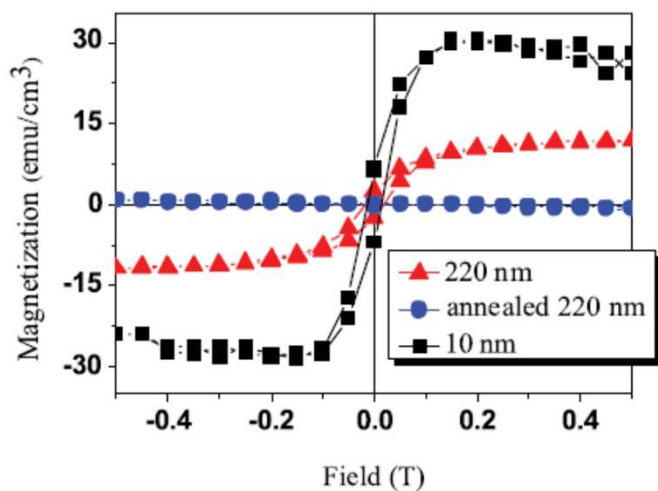


FIG. 2. (Color online) Magnetization versus magnetic field taken at 300 K as the magnetic field is applied parallel to the film's plane for the as-grown 10-nm-thick SnO<sub>2</sub> film, the as-deposited 220-nm-thick SnO<sub>2</sub> film, and the 220-nm-thick SnO<sub>2</sub> film postannealed under the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

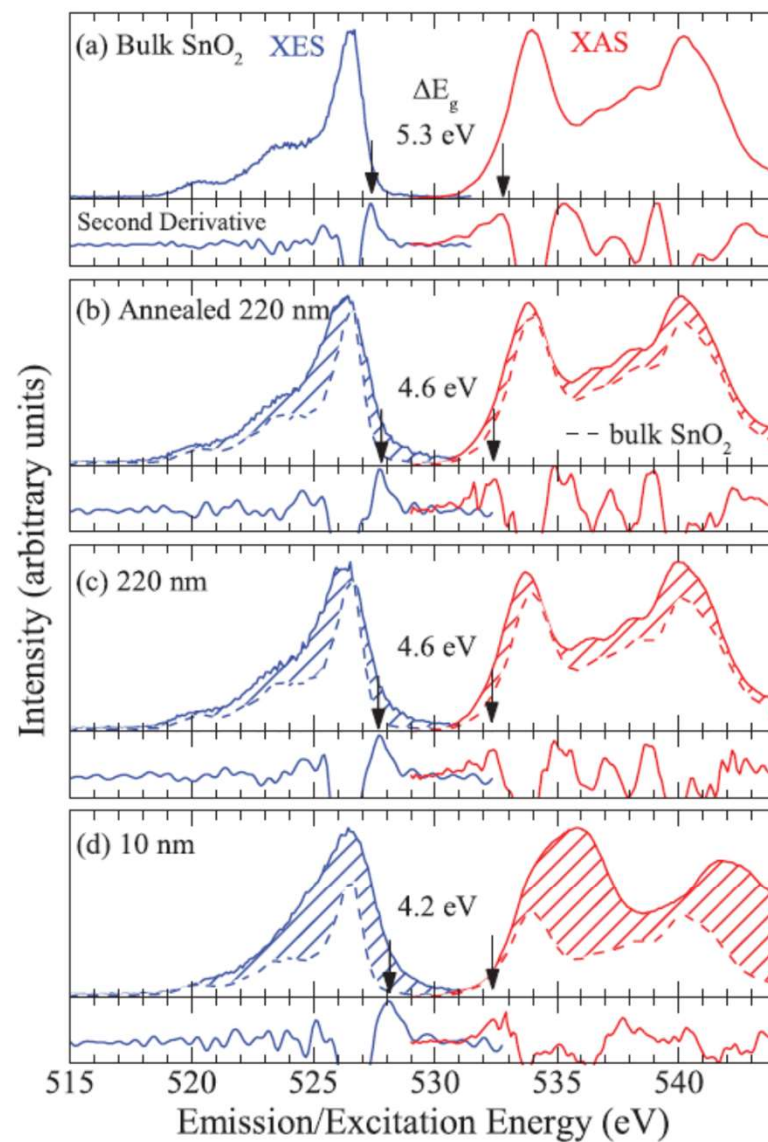


FIG. 3. (Color online) O *K*-edge x-ray emission (O *K* $\alpha$  XES) and absorption (O 1*s* XAS) spectra for bulk SnO<sub>2</sub> (a), the 200-nm-thick SnO<sub>2</sub> thin film with postannealing treatment (b), the 200-nm-thick as-grown film (c), and the 10-nm-thick as-grown film.