Nano Sensors

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Methods for creating nanostructures

Important methods for the creation of nanomaterials and nanostructures are:

1. Top Down
   1. Mechanical grinding,
   2. Etching methods
      i. Without patterning
      ii. After patterning
         i. Optical lithography
         ii. Electron beam lithography
         iii. Nano imprint lithography (NIL)
         iv. Self-assembly and Anodized Aluminum Oxides
2. Bottom-Up techniques
   1. Sol-gel process
   2. Gas Phase synthesis of nanomaterials
   3. Others

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Sol-gel process

- The **sol-gel process**, involves **evolution** of inorganic networks through
  - the formation of a colloidal suspension (**sol**) &
  - **gelation** of the sol to form a network in a continuous liquid phase (**gel**).
- The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands.
- The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid.
- Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

https://www.youtube.com/watch?v=3XpuoVVzT1A

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Sol-gel process

- Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as Si(OEt) 4 (tetraethyl orthosilicate, or TEOS).
- The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR)z can be described as follows:

  MOR + H2O → MOH + ROH (hydrolysis)
  MOH + ROM → M-O-M + ROH (condensation)
- Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials.

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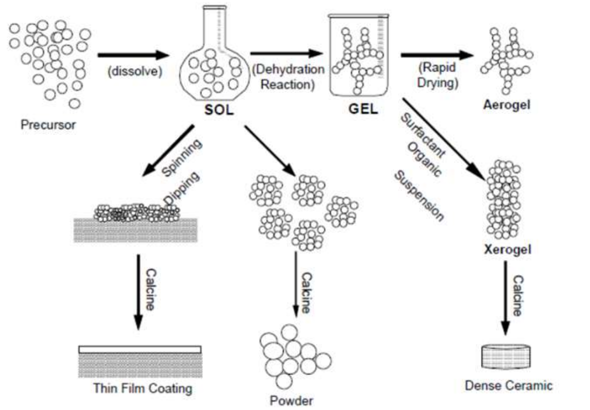
Sol-gel process

The sol-gel process steps:

- **Formation** of stable solutions of the alkoxide or solvated metal precursor.
- **Gelation** resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation reaction that results in increase in the viscosity of the solution.
- Aging of the gel (Syneresis), during which the polycondensation reactions continue **until** the gel transforms into a solid mass, accompanied by **contraction** of gel network & expulsion of solvent from gel pores.



Schematic representation of sol-gel process of synthesis of nanomaterials.

- Ostwald ripening (also referred as coarsening, where smaller particles are consumed by larger particles during growth process) & phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

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Sol-gel process

- Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel.
- The drying process is broken into four distinct steps:
  - the constant rate period,
  - the critical point,
  - the falling rate period,
  - the second falling rate period.
- If isolated by thermal evaporation, the resulting monolith is termed a ***xerogel***.
- If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an ***aerogel***.
- Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is achieved by calcining the monolith at up to 800°C.
- Densification & decomposition of the gels at high temperatures (T>800°C). The pores of the gel network are collapsed, & remaining organic species are volatilized.

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Sol-gel process

The interest in sol-gel synthesis method is due to:

- the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics.
- The major difficulties to overcome in developing a successful bottom-up approach is controlling the **growth** of the particles & then **stopping** the newly formed particles from agglomerating.
- Other **technical issues** are ensuring the reactions are complete so that no unwanted reactant is left on the product & completely removing any growth aids that may have been used in the process.
- The production rates of **nano powders** are very low by this process.
- The **main advantage** is one can get mono-sized nano particles by any bottom-up approach.

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Gas Phase synthesis of nanomaterials:

- The gas-phase synthesis methods are of increasing interest as they allow good control process parameters, to produce size, shape and chemical composition controlled nanostructures.

Some general aspects of gas-phase synthesis:

- In conventional chemical vapour deposition (CVD) synthesis, gaseous products either are allowed to react homogeneously or heterogeneously depending on a particular application.

1. In homogeneous CVD, particles form in the gas phase & diffuse towards a cold surface due to thermophoretic forces, and can either be
   1. **scrapped of** from the cold surface to give **nano-powders**, or
   2. deposited onto a **substrate** to yield what is called **'particulate films'**.
2. In heterogeneous CVD, the solid is formed on the substrate surface, which catalyzes the reaction and a dense film is formed.

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Gas Phase synthesis of nanomaterials:

To form nanomaterials several modified CVD methods have been developed. Gas phase processes have inherent advantages, some of which are noted here:

- An excellent control of size, shape, crystallinity & chemical composition
- Highly pure materials can be obtained
- Multicomponent systems are relatively easy to form
- Easy control of the reaction mechanisms

- Most of the synthesis routes are based on the production of small clusters that can aggregate to form nano particles (condensation).
- Condensation occurs only when the vapour is supersaturated and, in these processes, homogeneous nucleation in the gas phase is utilised to form particles.
- This can be achieved both by physical and chemical methods.

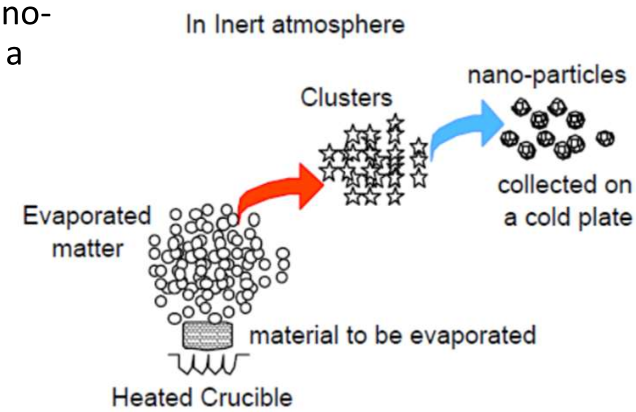
Gas Phase synthesis of nanomaterials:

The gas-phase synthesis methods

- Furnace
- Flame assisted ultrasonic spray pyrolysis
- Gas Condensation Processing (GPC)
- Chemical Vapour Condensation (CVC)
- Sputtered Plasma Processing
- Microwave Plasma Processing
- Particle precipitation aided CVD
- Laser ablation

Furnace:

- The simplest method to produce nano-particles, by heating the material in a crucible.
- Suitable for materials having high vapour pressure at the heated temperatures, that can be 2000°C.
- Energy is introduced by arc heating, electron-beam heating or Joule heating.
- The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound).



Gas phase process of synthesis of single phase nanomaterials from a heated crucible

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Furnace:

- For **reactive synthesis**, materials with very low vapour pressure have to be fed into the furnace as precursor such as organometallics, which decompose in the furnace to produce a condensable material.
- The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas & undergo condensation into small clusters via homogeneous nucleation.
- In case a compound synthesis, these precursors react in the gas phase and form a compound with the material that is separately injected in the reaction chamber.
- The clusters continue to grow if they remain in supersaturated region.
- To control their size, they need to be rapidly removed from the supersaturated environment by a carrier gas.

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Furnace:

- The cluster size and its distribution are controlled by only three parameters

1) the rate of evaporation (energy input),
2) the rate of condensation (energy removal), and
3) the rate of gas flow (cluster removal).

Because of its inherent simplicity, it is possible to scale up this process from laboratory (mg/day) to industrial scales (tons/day).

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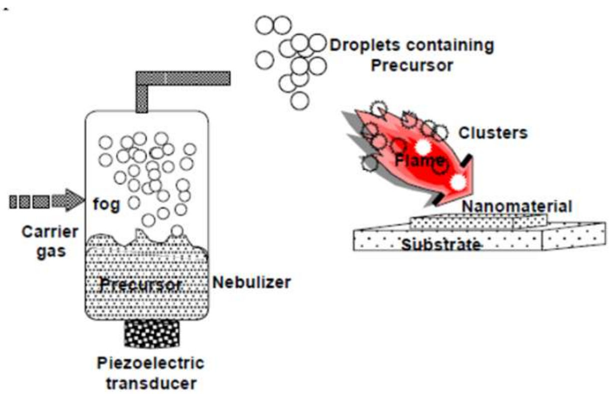
Flame assisted ultrasonic spray pyrolysis:

- Here, precursors are nebulized & then unwanted components are burnt in a flame to get the required material, e.g. ZrO_2 is obtained by precursor of Zr $(CH_3CH_2CH_2O)_4$.
- In combustion flame synthesis, the burning of a gas mixture, e.g. acetylene & oxygen or hydrogen & oxygen, supplies the energy to initiate the pyrolysis of precursor compounds; it is widely used for the industrial production of powders in large quantities, such as carbon black, fumed silica and titanium dioxide



Flame assisted ultrasonic spray pyrolysis

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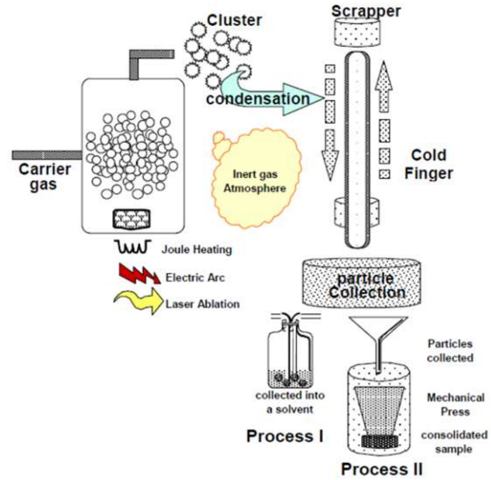
Gas Condensation Processing (GPC):

- In this technique, a metallic or inorganic material, e.g. a suboxide, is vaporised using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr).
- Cluster form in the vicinity of the source by homogenous nucleation in the gas phase & grow by coalescence and incorporation of atoms from the gas phase.



A typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.

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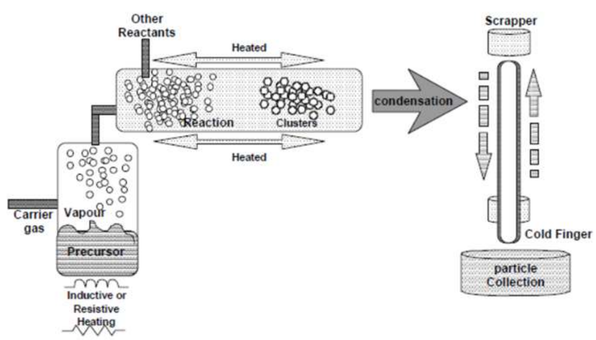
Chemical Vapour Condensation (CVC)

- Here, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation or the CVC process.
- Depending on the processing parameters nucleation of nano-particles is observed during chemical vapour deposition (CVC) of thin films & poses a major problem in obtaining good film qualities.



A schematic of a typical CVC reactor

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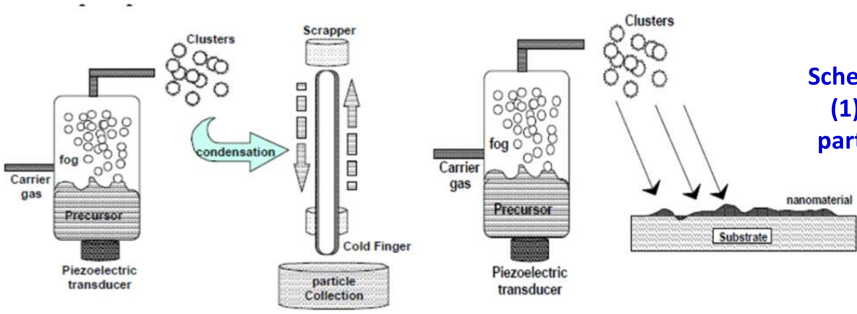
Particle precipitation aided CVD



(1) (2)

Schematic representation of (1) nanoparticle, and (2) particulate film formation.

- In this process, colloidal clusters of materials are used to prepare nanoparticles.
- The CVD reaction conditions are so set that particles form by condensation in the gas phase & collect onto a substrate, which is kept under a different condition that allows heterogeneous nucleation.
- Both nanoparticles & particulate films can be prepared.

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Questions!!

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