and Nano-materials might explain why reduction to the size range of nanometers leads to great changes in the Physical and chemical properties of the materials.

3. Quantum Confinement effect

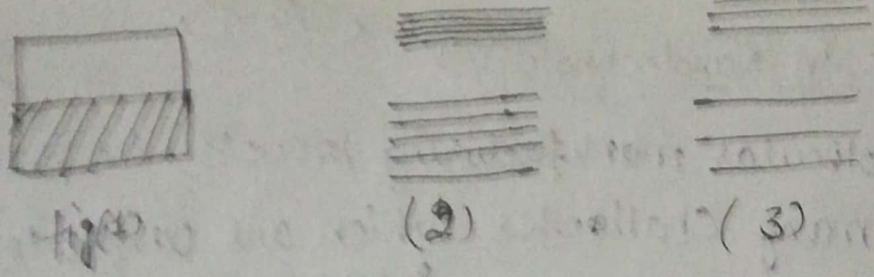
Semiconductors with all three dimensions in the 1-10nm size range are referred to as "quantum dots"

In this size range electrons exhibit quantum mechanical effects. The quantum effects such as quantization energy levels can be observed in principle and band gap energy 'Eg' becomes correlated with size; as the dimensions of the particle decreases, 'Eg' increases.

- Size-dependent properties are observed such as quantum confinement in semiconductor particles, and super-paramagnetism in magnetic materials etc.

Electronic Structure :-

In bulk materials (metal), the conduction band is partially filled with electron or the conduction and valence band partly overlap each other and no forbidden energy gap in between. But when its size is reduces to hundred atom, the continuous bands in (fig(1)) are replaced by the set of energy levels [fig(2)]. which may have gap in energy > $k_B T$ (Thermal energy) and with the decreases in size this gap may increases further. The electron structure changes to cluster of atom [fig(3)]. This is similar to a molecule having discrete energy bonding and antibonding orbits.




Reactivity :-

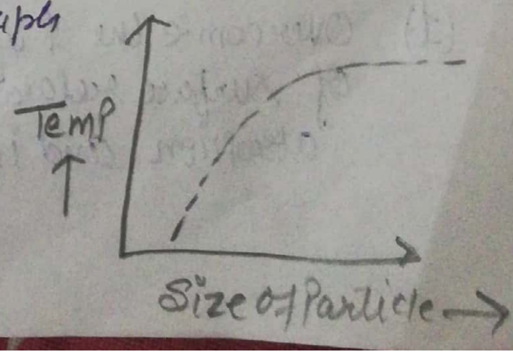
As electronic structure of nano Particle depends on the size of the particles hence ability of cluster to react depends on the size of cluster.
e.g In Gold if size of particles is 3-5 nm then its catalytic activity is very high.

Optical properties :-

If by using laser evaporation of silicon, nanoparticles of silicon are obtained then large clusters are obtained. The mass to charge ratio is measured by spectrometer. In semiconductor nanoparticles there is significant shift in the optical absorption spectrum towards the shorter wavelength (blue) as the size of particle is reduced i.e; there is change in the colour of the particle

melting point :-

It is observed that if size of the cluster is less than 100 atoms, then amount of energy is needed to ionise it is different from ionisation energy required for bluk. for gold; temp vs. size of particle is shown in the graph



## Challenges in Nanotechnology:-

In molecular manufacturing process, researchers face many challenges which are unique to nano-structure and nanomaterials.

- Nano structured materials possess a huge surface energy and thus are thermodynamically unstable or metastable. So it is necessary to overcome the surface energy.

- As one shift from bulk material to nanoscale the electronic structure undergoes a major changes i.e there is a opening of bands into clusters having discrete energy levels.

- As the Particle size is reduced; there is a significant shift in optical absorption spectra i.e there is change in colour.

- Doping become extremely important at nanometer scale. Fluctuation of doping concentrations can not be tolerated in the nanometer scale; because it would lead to totally different function of Nano-device.

Therefore for the fabrication processing of Nano materials and Nanostructures, the following challenges must be met:

(1) Overcome the huge surface energy by means of surface relaxation, surface restructure, surface absorption and impurity enrichment

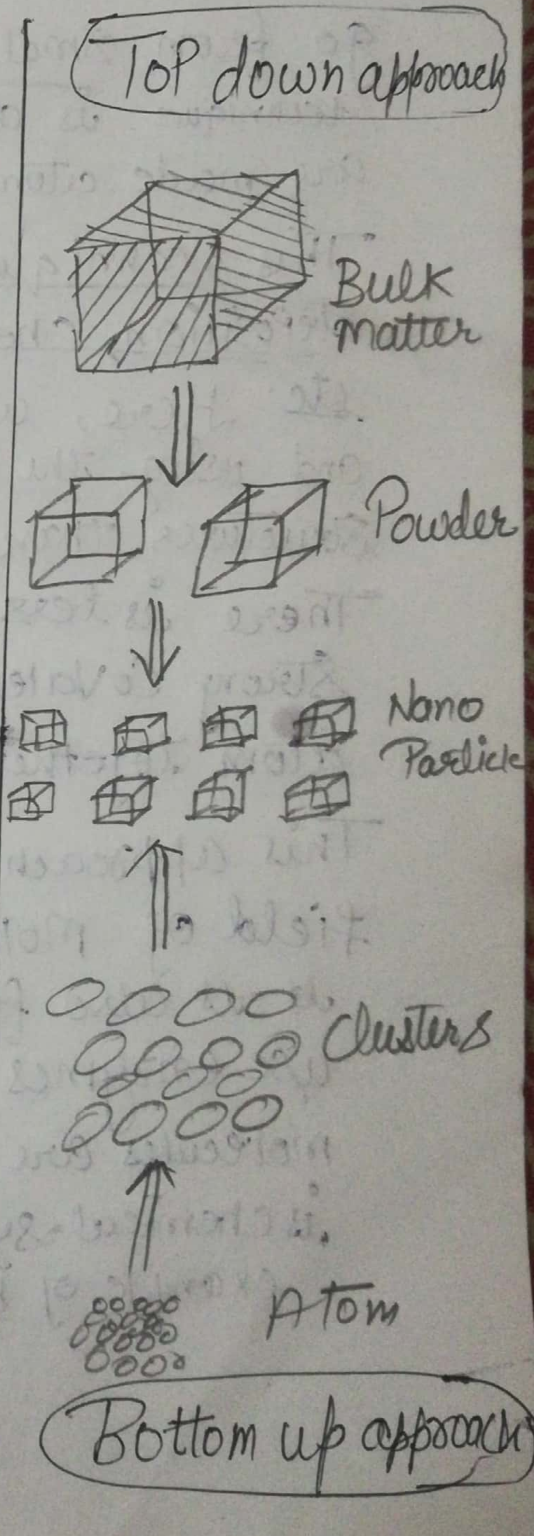
(ii) for desired Physical properties, uniform size distribution, morphology and chemical Composition

## * Manufacturing Technique of Nanomaterials (fabrication)

There are number of techniques available for manufacturing (fabrication) of Nanomaterials, mainly two main approaches

(i) Top-down approache

(ii) Bottom-up approache.




**Top-down approache:→**

In top down approach we go from larger size to smaller size. This approach is similar to making a stone statue. This is achieved by taking a bulk piece of stone which is then brought to the desired shape and size. But the limit of the smallest features sizes depends on the tool being used. In this method, there is a lot of wastage of the material and limit of resolution depends on the tool is use. The Schematic diagram of the process shown in fig Right side.

**for Example:-**

This kind of approach include the various type of lithographic techniques (Such as Photo-Ion beam, electron beam of X-rays lithograph), cutting, etching and grinding (ball milling).

**Bottom-up-approaches:-**

In this technique we go from smaller size to larger size. This technique is also ~~used~~ called as larger structures are made atom by atom or molecule by molecule. This technique is involved chemical synthesis, deposition, chemical sol-gel technique and sputtering etc. Here, we start from an atom or a molecule and using the process of assembling go to the larger structures than started. [as show in fig see Page (9)] There is less wastage with this technique, and strong covalent bonds will hold the constituent atom together.

This approach will play a big role in the field of molecular manufacturing & and it is also found in nature; all cells are use enzymes to produce DNA. Here component molecules are bounded together and final structure is chemical synthesis and molecular fabrication are example of bottom's up technique