Chapter-1

Introduction

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This chapter includes a brief history of nanoparticles, their different technological applications and a discussion on their role in new physical phenomena and emerging technologies. Thin film deposition techniques, both chemical vapor deposition and physical vapor deposition have been described as well. The chapter is concluded with a brief discussion on the scope of the thesis work.
1.1 Brief history of nanostructures

Nanostructured materials are polycrystallites, that span the size range of 1 nm to 100 nm. Chronicles related to their existence unquestionably predate the recent fascination that they have earned of late. People used to colour glasses in ruby red by using gold foils when properly treated. Michael Faraday in 1850 attributed the origin of colours to the presence of the tiny particles of gold (gold fluid) [1]. In 1987, however, came the remarkable report of Haruta et al. [2], who found that nanoparticles of Au (2 to 4 nm in diameter), uniformly dispersed on an oxide support such as Fe₂O₃ or NiO, could catalyze the oxidation of carbon monoxide at temperatures as low as -77.8°C. Later, gold nanoparticles, acting alone, were found to catalyze the selective oxidation of alcohols [3] in water for the oxidation of carbon monoxide [4] at room temperature. Perhaps the most important, from the viewpoint of sustainable development, is the recent work of Christensen et al. [5], who showed how nanoparticles of gold, supported on the inert spinel MgAl₂O₄, very efficiently leads to the formation of acetic acid by aqueous-phase oxidation of ethanol in air. This transformation is of profound significance in the context of sustainability since materials such as acetic acid and ethylene (which are currently converted industrially by addition [6] to yield the important solvent ethyl acetate) are each fossil-derived. The synthesis of stable, isolable thiolate-monolayer-protected gold colloids and clusters by Schriffrin, Brust, and colleagues reported sixteen years earlier represented a seminal contribution in the development of modern metal colloid science [7]. These authors successfully demonstrated that the classical two-phase colloid preparation of Faraday could be combined with contemporary phase transfer chemistry to yield, in a simple procedure, very small colloidal gold particles coated/protected by a monolayer of functional thiolate ligands. Finally, Corbierre et al. have very recently described a fascinating new fabrication method for assembling 1D arrays of gold nanoparticles on surfaces [8]. This important new innovation
combines both top-down (electron beam lithography) and bottom-up (nanoparticle nucleation and growth) approaches, enabling thus the precise patterning of gold nanoparticles in true 1D array wherein the interparticle distances, as well as the patterns composed of nanoparticles, are precisely tunable. If the metal oxide nanoparticle research history is revisited, the following main reports deserve a special mention. Richard P. Feynman during 1958 gave a ground-breaking speech ‘There’s plenty of room at the bottom’ where he discussed the possibility of controlling materials at the level of atoms and molecules – this was the first vision of the possibilities of science and technology at the nanoscale. In 1974 the term ‘nanotechnology’ was coined by Norio Taniguchi of the University of Tokyo [9]. He used the word to refer to ‘production technology to get the extra high accuracy and ultra fine dimensions, i.e. the preciseness and fineness on the order of 1 nm (nanometre)’ [10]. In 1981 IBM invented a machine which can move single atoms around Gerd Binning and Heinrich Rohrer invented the Scanning Tunneling Microscope (STM) at IBM. This microscope allows atomic-scale three-dimensional profiles of surfaces to be obtained. The microscope relies on a tip that is positioned within 2 nm of the surface and measures the electron density of the surface. A new form of carbon is discovered: C_{60} in 1985 by Richard Smalley, Robert Curl and Harold Kroto while investigating the outer atmosphere of stars, for which they were awarded the Nobel Prize in 1996. Officially known as buckminsterfullerene, C_{60} is more commonly known as a buckyball as the 60 carbon atoms are arranged into a sphere made of 12 pentagons and 20 hexagons (exactly like a football). Carbon nanotubes discovered by Sumino Iijima in a process to make ‘graphitic carbon needles ranging from 4 nm to 30 nm in diameter and 1 micron in length’ [11]. The needle-like tubes he described consisted of multiple sheets of graphite rolled into hollow tubes, which have now become known as carbon nanotubes. In 1993 the first single-walled nanotubes (SWNT) were produced. During 1993 First high-quality quantum dots were prepared by Murray, Norris and Bawendi of
nearly monodispersed CdS, CdSe and CdTe [12]. Quantum dots are very tiny particles with interesting optical properties: they absorb normal white light and, depending on their size, emit a range of bright colours. This property arises directly from the very small size of the particle. During 1997 Nanotransistor was built. Lucent Technologies fabricated the ‘nanotransistor’ – a complete metal oxide semiconductor transistor. It was only 60 nm wide, consisted of source, drain, gate and gate oxide and improved the key measures of performance. This was the very first report related to metal oxide nanostructures. The key advance was being able to fabricate a 1.2 nm thick gate oxide layer. Since then the syntheses of metal and metal oxide nanostructures have attracted sustained efforts and as result, other companies have built nanotransistors that are even smaller.

1.2 Usefulness of nanoparticles

The physical and chemical properties of a material are determined by the type of motion that the constituent electrons are allowed to execute. The latter is determined by the space in which the electrons are confined due to the forces they encounter. Unbound (unconfined) electrons have unquantized motion and can thus absorb any amount of energy. Once an electron is bound in an atom or in a molecule, its motion becomes highly confined and quantization sets in. The allowed types of motions in atomic or molecular orbitals are found to have well defined energies. The smaller the space in which motion is bound, the stronger is the confinement and the larger is the energy separation between the allowed energies of the different types of motion. The atomic confinement is the strongest type of electronic confined motion.

In a metal, electrons are highly delocalized over a large space. This is a consequence of the fact that the separation between the valence and conduction bands vanishes, giving metals their conducting properties. As
the size of the metal cluster is decreased and its electronic motion is confined, the separation between the valance and the conduction bands becomes of the order of $KT$, and that cluster behaves as a semiconductor. Further confinement increases the energy separation, and the metal behaves as an insulator. In the size domain at which the metal–to–insulator behavior transition occurs, new properties possessed neither by the metal nor by the molecules or atoms forming the metal are expected to be observed.

The properties of nanoparticles are different from bulk materials due to following reasons

• defect and micro-structures are different as compared to bulk
• quasi - two dimensional (very thin films)
• strong influence of surface and interface

Because of these factors, nanostructures possess chemical, physical and mechanical properties that are unique as well as beneficial. As a result, nanostructures have lead to (i) discovery of new physical phenomena and (ii) new technological applications.

### 1.2.1 New physical phenomena

Some of the new phenomena observed in nanostructures are:

#### 1.2.1.1. Ferromagnetism in nanoparticles [13]

Ferromagnetism has been observed in nanoparticles of a large variety of non-magnetic inorganic materials such as non-magnetic Al$_2$O$_3$, TiO$_2$ and CeO$_2$, superconducting cuprates, metal nitrides and chalcogenides. Room-temperature ferromagnetism is exhibited by nanoparticles of these
inorganic materials although they are intrinsically non-magnetic. Nanoparticles of nitrides such as GaN and chalcogenides such as CdS and CdSe also exhibit ferromagnetism. Ferromagnetism of the nanoparticles is confined to the surface. This phenomenon has been utilized to render the classic ferroelectric BaTiO$_3$ to be multiferroic wherein surface ferromagnetism coexists with bulk ferroelectricity. Interestingly, nanoparticles of superconducting YBa$_2$Cu$_3$O$_7$ show surface ferromagnetism [13].

1.2.1.2. Density of states in nanomaterials.

Figure 1.1(a) illustrates the different systems in a general way, and figure 1.1(b) shows how the expected densities of states vary with dimensionality. Passing from three dimensions to two dimensions the density $N(E)$ of states changes from a continuous dependence $N(E) \sim E^{1/2}$ to a step-like dependence and so on.
1.2.1.3. Dielectric constant [14]

The refractive index $n$ changes markedly near surface plasmon resonance of a nanomaterial therefore the absorption features are not symmetrical in nanomaterials as compared to that of the bulk [14].

1.2.2 Technological applications

Nanostructures can be used for a wide variety of applications. These applications include, but are not limited to, the following:

1.2.2.1 Medicine

Researchers are developing customized nanoparticles of the size of molecules that can deliver drugs directly to diseased cells in human body. When perfected, this method should greatly reduce the damage which treatment such as chemotherapy causes to a patient's healthy cells.

1.2.2.2 Novel semiconductor devices

The dependence of the resistance of a material (due to the electron spin) on an external magnetic field is called magnetoresistance. This effect can be significantly amplified (GMR - Giant Magneto-Resistance) for nanosized objects, for example when two ferromagnetic layers are separated by a nonmagnetic layer, which is several nanometers thick (e.g. Co-Cu-Co). The GMR effect has led to a strong increase in the data storage density of hard disks and gigabyte range data storage is possible.

1.2.2.3 Space

Nanotechnology may hold the key to making space-flight more economically viable. Advances in nanomaterials make light weight solar
cells and a cable for the space elevator possible in principle. By significantly reducing the amount of rocket fuel required, these advances could lower the cost of reaching orbit and traveling in space. Lighter and stronger materials will be of immense use to aircraft manufacturers, leading to superior performance. Spacecraft where weight is a major constraint will also benefit from such developments. Nanotechnology would help to reduce the size of equipment and thereby decrease fuel-consumption required.

1.2.2.4 Food

Nanotechnology is having an impact on several aspects of food science, from food growth to packaging. Companies are developing nanomaterials that will make a difference not only in the taste of food, but also in food safety and the health benefits that food delivers. Bacteria identification and food quality monitoring using biosensors; intelligent, active and smart food packaging systems; nano encapsulation of bioactive food compounds are few examples of emerging applications of nanotechnology. A nanocomposite coating process could improve food packaging by placing anti-microbial agents directly on the surface of the coated film. Nanocomposites could increase or decrease gas permeability of different fillers as is needed for different products. They can also improve the mechanical and heat-resistance properties and lower the oxygen transmission rate. Research is being performed to apply nanotechnology to the detection of chemical and biological substances present in foods.

1.2.2.5 Fuel Cells

Nanotechnology is being used to reduce the cost of catalysts used in fuel cells to produce hydrogen ions from fuel such as methanol and to improve
the efficiency of membranes used in fuel cells to separate hydrogen ions from other gases such as oxygen. Probably the most prominent nanostructured material in fuel cells is the catalyst consisting of carbon supported noble metal particles with diameters of 1-5 nm. Suitable materials for hydrogen storage contain a large number of small nanosized pores. Therefore many nanostructured materials like nanotubes, zeolites or alanates are under investigation. Nanotechnology can contribute to the further reduction of combustion engine pollutants by nanoporous filters, which can clean the exhaust mechanically and by catalytic converters based on nanoscale noble metal particles or by catalytic coatings on cylinder walls and catalytic nanoparticles as additive for fuels.

1.2.2.6 Batteries

Companies are currently developing batteries using nanomaterials. As compared to conventional batteries, these batteries will have a very long shelf life and can be recharged in a shorter period. Moreover, the use of nano material may solve the battery disposal problem.

1.2.2.7 Fuels

Nanotechnology can address the shortage of fossil fuels such as diesel and gasoline by increasing the mileage of engines and making the production of fuels from low grade raw materials commercially viable.

1.2.2.8 Better Air Quality

Nanotechnology can improve the performance of catalysts used to convert vapors escaping from cars or industrial plants into harmless gasses. That's because catalysts made from nanoparticles have a greater surface area to interact with the reacting chemicals than catalysts made from larger particles. The larger surface area allows a larger quantity of chemicals to
interact with the catalyst simultaneously, which renders the catalyst more effective.

1.2.2.9 Hard and wear-resistant coatings

Hard coatings are often called metallurgical coatings and are a type of tribological coating. Hard coatings are used to increase the cutting efficiency and operational life of cutting tools and to maintain the dimensional tolerances of components used in applications where wear can occur, such as injection molds. In addition, the coatings can act as a diffusion barrier where high temperatures are generated by motion between surfaces or provide corrosion protection in aggressive environments. There are various classes of hard coating materials. They include: ionically bonded metal oxides (Al₂O₃, ZrO₂, and TiO₂) [15], covalently bonded materials (SiC, boron carbon [B₄C], diamond, diamond-like carbon [DLC] [15], TiC, AlN, CrC, mixed carbide, nitride and carbonitride compound alloys, and cubic boron nitride), and some metal alloys (cobalt chromium aluminum yttrium [CoCrAlY], NiAl, NiCrBSi). In some cases the coatings may be layered to combine different properties. Hard coatings are used to minimize fatigue-wear, such as the one found in ball bearings. Wear-resistant coatings also may be applied to surfaces where there is a light or periodic load. For example, hard coatings are deposited on plastics to improve scratch resistance. In some cases wear resistant coatings, such as SiO₂ or Al₂O₃, may be applied to already hard surfaces, such as glass, to increase the scratch resistance.

1.2.2.10 Electrically Active Films

Doped silicon films are used in semiconductor devices, and these films often are deposited by a very sophisticated PVD evaporation technique
called molecular beam apiary (MBE) or a CVD technique of vapor phase epitaxy (VPE). Amorphous silicon for solar cells is deposited by PECVD on webs and rigid substrates. Electrochromic films [16], which change optical transmission on the application of a voltage, depend on the diffusion of mobile species in the film under an electrical field. Films of a material such as selenium can become electrically charged when exposed to light. Such films are used to hold the toner in photocopying machines.

1.2.2.11 Gas sensors

Metal oxide (e.g. SnO₂, WO₃ etc.) [17-20] thin films have been widely used for the development of the sensors of various hazardous gases (H₂S, NH₃, NO, etc.)[21-23]. The sensing of the gas is possible because the resistivity of the metal-oxide film changes reversibly on interaction with gas. Nanocrystalline Pd metal films have been used for the sensing and storage of hydrogen gas.

1.2.2.11 Freestanding structures

Freestanding structures can be made by depositing a coating on a surface (mandrel), then detaching the coating from the mandrel surface or dissolving the mandrel. The technique is useful for fabricating very thin structures, complex surfaces, or foils or sheets of materials that are hard to deform by rolling. Examples are beryllium windows used for X ray transmission, boron thin-wall cones for high-frequency audio speakers, and Ti-V-Al metal alloy foils. A relatively new application is the production of micro electromechanical systems (MEMS) devices where very small structures are fabricated using deposition and etching processes.
1.3 Synthesis techniques

There are in principle, two distinct routes to create nanostructures. Physical OR chemical: The physical and chemical methods are having merits and demerits of their own such as in physical methods particles are grown by lithography or by evaporation techniques. The particles synthesized by this method are highly stable and can be handled easily, mostly due to the robustness of the substrates that are used as a support. In this method particles can be synthesized in large quantities and on large area. The physical techniques are quite repeatable and the systems are rigid. Chemical techniques have advantages of simple equipment and process. The technique enables synthesis of large quantity of nanomaterials at low cost. In chemical method particle growth occurs in various matrices or by the method of colloidal chemistry. This method also gives stable particles which can be handled as any other chemicals. The control over the process parameters is good hence the synthesis can be carried out with precise dimensions and size. However, due to simplicity and quality, physical vapor deposition and electrochemical route have gained recognition as promising techniques that address a large number of requirements related to the nanostructures production. In the present work the use of both the methods for synthesis is demonstrated. We have synthesized copper nanoparticles by thermal vapor deposition technique while the silver nanorods and branchlike structures are synthesized by the electrochemical route. In this method nanostructures with small dimensions and with very controlled morphology can be obtained. Colloidal metal preparation methods offer the possibility of developing synthetic protocols and the preparation of metals in nanostructured form with a control over the particle size distribution as well as particle morphology.

Sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and
hydrothermal treatment [24]. Size distribution of semiconductor, metal and metal oxide nanoparticles can be controlled by either dopant introduction [25] or heat treatment [26]. Better size and stability control of quantum-confined semiconductor nanoparticles can be achieved through the use of inverted micelles [27], polymer matrix architecture based on block copolymers [28] or polymer blends [29], porous glasses [30] and ex-situ particle-capping techniques [31,32].

Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing [33], microemulsion processing [34] and high-energy ball milling [35]. In sonochemistry, an acoustic cavitation process can generate a transient localized hot zone with extremely high temperature gradient and pressure [36]. Such sudden changes in temperature and pressure assist the decomposition of the sonochemical precursor (e.g. organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications.

In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution [33]. By rapidly pressurizing in a supercritical drying chamber and exposing to cavitational disturbance and high temperature heating, the sol-gel solution is mixed. The erupted hydrodynamic bubbles are responsible for nucleation, growth and quenching of the nanoparticles. Particle size can be controlled by adjusting the pressure and the solution retention time in the cavitation chamber. Microemulsions have been used for synthesis of metallic [34], semiconductor [37, 38], silica [39], barium sulfate [40], magnetic and superconductor [41] nanoparticles. By controlling the very low interfacial tension (~10^{-3} \text{ mN/m}) through the addition of a cosurfactant (e.g., an alcohol of intermediate chain length), these microemulsions are produced spontaneously without the need of significant mechanical agitation. The technique is useful for large-scale production of nanoparticles and requires a relatively simple and inexpensive hardware
High energy ball milling, the only top-down approach for nanoparticle synthesis, has been used for the generation of magnetic, catalytic and structural nanoparticles. The technique, which is already a commercial technology, has been considered imprecise because of contamination problems from ball-milling processes. However, the availability of tungsten carbide components and the use of inert atmosphere and/or high vacuum processes have reduced impurities to acceptable levels for many industrial applications. Common drawbacks include the low surface area, the highly polydispersed size distributions, and the partially amorphous state of the as-prepared powders.

1.4 Scope of the Thesis

On a piece of silicon chip of the size of ~1cm², hundreds of millions of transistors are fabricated. The chip is a building block of modern microelectronic devices and computers. To function together, the transistors are interconnected by metal thin film (Al or Cu) having thickness <0.25 micron. The process of making this metal interconnects is known as metallization. Thin-film aluminum is the most widely used material for metallization and is said to be the third major ingredient for integrated circuit (IC) fabrication, with the other two being silicon and SiO₂. Al is suitable for metallization with its very low resistivity and its adhesion compatibility with SiO₂. Al metal layers are usually deposited using physical vapor deposition (PVD) technique. The most serious and persistent reliability problem in Al interconnect metallization is it requires alloying for the deposition on Si substrates. These alloyed depositions are the most persistent and serious reliability failures in thin film integrated circuits. Besides alloying, a disadvantage of Al as a metallization material is its low melting temperature (660 °C) and the low Al-Si eutectic temperature (577 °C). These restrict the maximum processing temperature
once the Al layer has been deposited. Al also possesses lower conductivity than that of Copper.

In the futuristic ultra-large scale integration (ULSI) or giga-scale integration (GSI), the device miniaturization demands smaller and smaller interconnects [47]. This implies that the current density becomes higher and higher, so does the probability of circuit failure induced by melting of the lines. This is a subject, which has demanded and attracted much attention worldwide. The nanopatterns of various shapes of Cu on Si substrates may show different conducting properties. Our approach in this work involves synthesis of nanopatterns of Cu on Si by thermal vapor deposition technique with variable thickness (10-1000 Å) and see the effect on the morphology. These nanostructures may be used as template for the further growth.

The objective of the work is to explore the methods of thermal oxidation and chemical route for the synthesis of high quality nanoparticles of precise morphology. As the title of the thesis suggests, the synthesis of metal, metal oxide and bimetallic nanoparticles is carried out in the present study. The motivation of picking up a particular material is discussed in the respective chapters.

The metal oxide nanostructures are wide band gap semiconductors and are chemically stable. The metal oxides show large change in resistance with the change in varying atmospheric gases. SnO₂ is a wide band gap (3.6 eV) n type semiconductor widely used in gas sensing applications for gases such as hydrogen sulphide, ammonia, carbon monoxide, acetone, etc. SnO₂ based sensor (chemiresistors) are predominant solid-state gas sensors for domestic, commercial and industrial applications. However the major drawback of using these for gas sensing application is lack of selectivity. The addition of another metal oxide such as CuO has enhanced the sensitivity and selectivity in the film [48]. Along the same line, here the addition of WOₓ with SnO₂ is implemented in order to see its effect on gas sensing. WOₓ is an n type wide band gap (2.7 eV) semiconductor material
used in gas sensing devices for gases such as ammonia, chlorine, nitric/nitrous oxide, etc. Tungsten trioxide is a material with variety of application areas. For example the material is used within the thin film technologies as electrochromic material in smart windows as electrochemically functional materials in thermal control applications or as active layers in gas sensing application. The metal oxide nanowires were synthesized by using thermal vapor deposition technique. The formation of hierarchical heterostructures of these will increase effective area for gas adsorption. In case of thermal vapor deposition technique, the 99.9 % pure metal (Sn powder, W sheet) were used as source. The source metal was allowed to evaporate under the optimized conditions. The samples were collected by dry scratching or on templates. Depending on the process parameters the morphology and phase of the materials changes. Extensive study has been carried out and is undergoing for the shape controlled synthesis of metal, metal oxide nanostructures and hierarchical nanoheterostructures [49, 50]. However, precise control over the growth and morphology of synthesized nanostructures of these is yet a challenge. In the present study, two controlling parameters, namely growth temperature and growth time have been thoroughly checked for their impacts to monitor the optimum growth of SnO$_2$-WO$_x$ nanostructure. In order to substantiate these studies, preliminary gas sensing study of SnO$_2$-WO$_x$ nanowires heterostructures have been carried out. Thus, Synthesis of SnO$_2$ and SnO$_2$-WO$_x$ hierarchical nanoheterostructures by thermal evaporation technique is one of the objectives of the thesis. Experimentations included studying the effects of temperature (substrate temperature, source temperature and temperature gradient), time (growth time, heating- cooling rate, and gas pressure (vacuum, air pressure) on the formation of nanostructures. The prepared samples were tested for gas sensing applications in a static system.

In addition to metal and metal oxide nanoparticles; the bimetallic nanoparticles are synthesized as the addition of another metal may further
enhance the properties possessed by the metal nanoparticles. As the formation of a bimetallic bond leads to large changes in the band structure of the metal; the interactions between the metal-metal bonds are likely to be pronounced in nanomaterials as large surface area is available in nanoparticles than that of the bulk. During the chemical step, metal atoms formed will aggregate to form a nucleus. Nuclei that grow beyond a critical size will be stable, but a mechanism is needed to curb the growth of particles and to achieve a narrow size distribution. Different growth control mechanisms and strategies are used in the different types of nanoparticles synthesis. In the colloidal method, aggregation of nanoparticles is prevented either by electrostatic hindrance or the addition of a protecting agent, which will adhere onto the surface of the nanoparticles. In the microemulsion methods, surfactants are added and chemical reaction and mass-transfer processes are confined within the microdroplets engulfed by the surfactant molecules. A simpler strategy in the impregnation method is the early addition of the microporous support before the start of the chemical step. The support then acts as the confining medium to restrict reaction, diffusion and aggregation processes. We shall limit the discussion of these types of syntheses to those with distinct differences in the strategy of controlling the growth of nanoparticles. The organic protecting shell can be removed by washing in an appropriate solvent or by decomposition at elevated temperature in an inert atmosphere. Before the removal of the protecting agent, adsorption into a protecting microporous catalyst support is necessary to prevent agglomeration into larger metal particles. It would be desirable to use the alternative route of preparing colloidal nanometals without the use of protecting agents. This can be achieved for certain metals by appropriate combination of precursor, solvents, reducing agent and electrolyte.

In this particular study the colloidal synthesis methods namely electrochemical and chemical route for Ag /Au nanoparticles and their core shell are presented. Ag / Au are chosen particularly in order to study the
change in optical properties with the change in size of the particles. These materials show change in Uv-Vis absorption wavelength with the change in the size of the particles. These materials are inert and can be used for humidity sensing application if capped properly.

The optimization of the process parameters for the Ag nanoparticles by electrochemical route, by dispersing them in polymer matrix and by taking readymade core shell nanoparticles in PVP matrix; study their application for humidity sensing was the final objective of the present thesis.

In this thesis the experimental work, results, discussion, and conclusions are organized as follows. In Chapter-2 the experimental part and results on the morphology and gas sensing study of SnO$_2$-WO$_x$ hierarchical nanoheterostructures is presented. The synthesis is carried out using SnO$_2$ nanowires as template for the growth of WO$_x$ nanowires onto them. The synthesis is carried out by using thermal vapor deposition technique. WO$_x$ nanowires growth is optimized for the filament (source-tungsten) temperature, vacuum conditions and deposition time.

The results reveal that (i) hierarchical heterostructures are formed by vapor solid growth mechanism; (ii) with increasing time of deposition the length of WO$_x$ nanowires keeps on increasing and (iii) The morphology of WO$_x$ structures is dependent of the vacuum conditions.

The samples prepared, under optimized conditions are used for gas sensing applications. Three types of films are prepared for gas sensing application.

1. SnO$_2$ mat films (thick films); 2. SnO$_2$-WO$_x$ mat films and 3. single wire of SnO$_2$-WO$_x$.

The samples are tested for Cl$_2$ and H$_2$S gases. It is observed that the mat films show normal response to the oxidizing and reducing gas i.e. increase and decrease in resistance of the film, respectively. However, the single wire sensor shows anomalous response (decrease in resistance) in
presence of chlorine gas. The reasoning is discussed in this chapter. The films can be used as good Cl₂ sensors at room temperature.

In Chapter-3 the investigations pertaining to the Cu nanostructure formation on Si (with three different orientations) at high temperature in moderate vacuum conditions have been presented. For the optimization of growth of these nanostructures various substrate temperatures have been used. It has been shown that at 750 °C substrate temperature and at about 10⁻⁶ mbar vacuum triangular Cu nanostructures are formed on Si(111), square-like nanostructures are formed on Si(100) and rod shaped nanostructures are formed on Si(110) substrates. It has been observed that with the increasing thickness the density of the island keeps on increasing and at higher thickness a continuous film-like nature is seen. The diffusion of Cu in Si is revealed through characterization such as XRD and TEM. In XRD formation of Cu₃Si is clearly seen. The surface analysis is carried out by using XPS. These measurements reveal that there is formation of Cu on top surface of the film. From these characterizations, it can be inferred that at the interface between the Cu film and Si substrates, formation of copper silicide takes place while at the surface of the film copper is found to be in the metallic state.

In Chapter-4, in the first section the synthesis and results on nanostructures of Ag by electrochemical technique have been described. The morphology of the nanostructures is found to be strongly influenced by the surfactants Tetra Octyl Ammonium Bromide (TOAB) and Cetyl Trimethyl Ammonium Bromide (CTAB). The nanoparticles were dispersed in polymers such as PVA and PVP and their humidity sensing studies are presented. In the second section the particles of Ag and Au were grown in-situ in polymer such as PVP by using reducing agents in polymers. The humidity sensing range is found to go on increasing with the thickness of the film. The samples have proved that they can be used as very good humidity sensors.
The summary of the thesis work and main conclusions are presented in Chapter-5. The Chapter is concluded by bringing out the future scope of the research work related to the topic of the thesis.

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