Chapter 5

Summary and conclusions
The present work is mainly based on the synthesis of nanostructures (SnO$_2$-WO$_x$, CuSi by physical method and Ag nanoparticles and Ag-Au core shell in polymer matrix by chemical route) and their possible applications in gas sensing. The first chapter is for the brief introduction to the topic. The synthesis of metal oxide (SnO$_2$) and the controlled synthesis of hierarchical heterostructures of metal oxide (SnO$_2$-WO$_x$) are presented in the second chapter. The synthesis is carried out by a two step thermal evaporation technique. The diameter of SnO$_2$ nanowires is 50-170 nm and length is in few μm. These nanowires are used as templates for growth of WO$_x$ nanowires onto them. WO$_x$ nanowire structures are formed on SnO$_2$ nano wires in thorn like fashion. The length of WO$_x$ nanowires is about 2 μm and the diameter is about 50 nm. The structural characterizations reveal that the structures are present in two distinct forms i.e. SnO$_2$ and WO$_x$ and no mixed phases are present in the sample. The usefulness of the samples is exploited for preliminary gas sensing application for mat films and single wires. The films of SnO$_2$, WO$_x$ and hierarchical heterostructures are tested for H$_2$S and Cl$_2$ gas and it is confirmed that the heterostructures are becoming selective for chlorine gas at room temperature. The functional tests performed on single wires show interesting results for detection of chlorine with detection limit upto 0.5 ppm level and relatively fast response and recovery times. The mechanism for gas sensing for a single wire based sensor is proposed. The suitability of using Si orientations as substrates for the formation of nanostructures of Cu is demonstrated. The synthesis is carried out by thermal evaporation route using a vacuum system of rotary pump backed by Turbo Molecular Pump (TMP); vacuum level achieved in it was $10^{-6}$ mbar. The shapes of the structures were triangular, squarelike and rodshaped on Si(111), Si(100) and Si(110) substrates respectively. The shape of the nanostructure is dictated by the Si substrate orientation. The
formation of particular shape of the island is attributed to the diffusion of Cu into the oxide layer due to high substrate temperature. In ultra large scale integration (ULSI) and giga scale integration (GSI) technologies the thickness of the interconnects is expected to be <100 nm. Cu is low resistivity material and has got high melting point than Al. Therefore is attempted in the studies. The application of these nanopatterned structures is attempted as a template for the growth of carbon nanostructures onto them; the study needs to be carried out further.

In the third section the synthesis of silver nanobranch like structures by using electrochemical route is presented. The surfactant of Tetra Octyl Ammonium Bromide (TOAB) and Cetyl Treimethyl Ammonium Bromide (CTAB) are used. The synthesized nanostructures are dispersed in polymer Polyailine (PANI) for humidity sensing applications. The humidity sensing is carried out by optical route. The film shows high sensitivity in low humidity range (0-20 %RH) which is important from the application point of view.

Humidity sensing study is carried out for Ag, Au and core shell particles of Ag core and Au shell samples grown insitu by chemical route in polyvinylpyrolidone matrix (PVP) is presented. The comparative humidity sensing study of Ag-PVP and Au-PVP samples shows that the Ag-PVP films are highly sensitive than that of Au-PVP films. This is attributed to much smaller size of Ag particles (50 nm) in PVP and mobility of Ag particles is higher than that of Au (few μm) particles. Preliminary study of Ag core and Au shell particles in PVP matrix is also presented and further study is needed on the same.

We attempt to compare the synthesis method viz. chemical and physical for the nanoparticle synthesis.

The physical route gives high yield of nanoparticles and the particles are stable upto few months. The particles formed are of size of about 200 nm diameter or edgelength. In electrochemical or chemical method however a control over the synthesis can be achieved. The chemicals can be used in
appropriate proportion. However precise control over the size and shape can be achieved in chemical method as compared to physical route.

In overall conclusions, the techniques for synthesis of metal oxide, metal and bimetallic nanostructures are developed. The synthesis techniques allow precise control over size and shape of the nanostructures. Depending on the application point of view synthesis techniques can be chosen.

The synthesized structures are used for gas and humidity sensing applications. The materials show promising sensing properties for the development of a new generation of gas sensors. Some of the novel results observed out of the study are,
(i) A "hierarchical nanoheterostructures" of SnO\textsubscript{2}-WO\textsubscript{x} are formed by using thermal vapor deposition technique.

(ii) Cu islands of triangular, squarelike and rodlike structures are obtained on Si substrates at comparatively low substrate temperature and under moderate vacuum conditions (10\textsuperscript{-6} mbar).
(iii) Ag nanoparticles by using electrochemical route can be synthesized. When these particles are dispersed in polymers such as PANI and PVP the films show very good humidity sensing properties and the films can be used for humidity sensing.
(iv) The size and morphology of the structures can be controlled by varying synthesis parameters.

1) We have demonstrated how controlled growth of hierarchical heterostructures of SnO\textsubscript{2}-WO\textsubscript{x} structures can be obtained. The key finding is that a simple two step thermal evaporation can be employed for hierarchical heterostructure formation. It is not demonstrated but, the same procedure can be employed for the nanoheterostructure formation of other metal oxide structures [1]. The structures can be employed for gas sensing applications. These nanostructures may provide selectivity for a particular gas, which can be useful from application point of view.
We have developed a crude but simple method for single wire isolation of nanowires. This method can be used and modified further for making single wire films. These single wire films show very efficient response and selectivity.

2) The synthesis of CuSi patterned structures on Si substrate is demonstrated. The thickness dependence of the films is also presented. The different shapes of the nanopatterns may contribute to the conduction in the films in different ways which can be applied in interconnects and as field emitters. An attempt is made to use these patterned structures as templates for growth of another structure onto it. The method can be modified to get nanowires onto the patterns. The structures can be used for various applications such as nanocantilevers, gas sensors, etc.

3) The synthesis of metal nanoparticles is important from the optical studies point of view. The nanosize provides increased surface to volume ratio. When the shape of these is changed the effective surface area for interaction with the surface is increased. The particles can be dispersed in various polymers and study the properties can be studied. It is not presented here but in the scope one can say that the interaction inside the polymers i.e. Metal nanoparticles-metal nanoparticles interaction, polymer-polymer and metal nanoparticle-polymer interactions can be understood by using these films. The films can be used for gas sensing as well as humidity sensing applications.

4) Many novel applications can be brought forward by the combination of any two or all of the methods which will change the properties of the nanomaterial owing to its nanosize and shape and polymeric binder.

References

1. Hae-Ryong Kim, Kwon-II Choi, Jong-Heun Lee, Sheikh A. Akbar