Chapter -5

Summary

SnO$_2$ nanostructures capable of sensing small concentrations of oxidizing and reducing gases at low operating temperatures have been synthesized by non aqueous sol gel and ultrasonic spray pyrolysis (USP) techniques. The samples synthesized under different experimental conditions have been investigated for their thermal, structural, optical, electrical and gas sensing properties by various characterization techniques. The brief summary of the results obtained in various sections is given below.

Nanostructured SnO$_2$ powder has been synthesized by a simple non aqueous sol gel method using SnCl$_2$.2.H$_2$O and ethanol as precursors. TGA/DTA analysis of gel shows the absence of any major weight loss and endo-exothermic reaction regions beyond 500$^\circ$C which indicates that the gel has been completely decomposed to SnO$_2$ powder. The structural development of SnO$_2$ powder has been studied by calcining the gel in the temperature range of 500-700$^\circ$C. XRD studies confirms the formation of tetragonal rutile type SnO$_2$ in these samples. The powder material calcined at higher temperatures is found to be more crystalline. FESEM analysis reveals the formation of weakly aggregated secondary particles forming a highly porous network in case of sample calcined at 500$^\circ$C, whereas hard aggregates without any visible pores are observed at higher temperatures. TEM investigations indicate that these aggregates are comprised of spherulitic nanostructures with an average size ranging between 34.6-40.3 nm. The energy dispersive X-ray analysis of the powder samples shows the presence of Sn and oxygen with a small oxygen deficiency. The optical band gap evaluated from the absorption coefficient is found to increase from 3.50 to 3.67 eV with an increase in calcination temperature. The electrical studies of 32± 0.1 $\mu$m thick SnO$_2$ films prepared from these samples show their semiconducting nature. The gas sensing behaviour of the films towards 50ppm of ammonia, acetone, ethanol and chlorine has been studied in the operating temperature range of 25-250$^\circ$C. It is found that the films based on SnO$_2$ powder synthesized at a calcination temperature of 500$^\circ$C are highly sensitive and selective to ammonia at room temperature (25$^\circ$C) and exhibit a response as large as 694 %. Whereas the response exhibited by films based on powder samples synthesized at higher calcination temperatures is observed
to be much suppressed. This clearly indicates that small sized nanostructures with high crystallinity and loosely aggregated porous structure promotes ammonia sensing at low temperatures. The densification of agglomerates and destruction of intercrystallite pores at higher temperatures hinders gas diffusion and hence suppresses the response.

SnO$_2$ films have been prepared onto glass substrates by ultrasonic spray pyrolysis technique using 0.25M ethanolic solution of stannous chloride. The deposition has been carried out for a fixed duration of 20 minutes at substrate temperatures of 350-450°C to identify the right morphology for gas sensing applications. The thickness of the films is observed to increase with substrate temperature and is found to lie between 387-510 nm. XRD analysis of the films shows prominence of different film orientations at different substrate temperatures with average crystallite size lying in the range of 24.4-36.5 nm. FESEM analysis reveals significant changes in morphology of films with increase in the substrate temperature. The films deposited at a substrate temperature of 350°C are found to be composed of densely packed spherical crystallites, whereas cuboidal and pyramidal shaped crystallites are observed in case of films deposited at 400°C and 450°C, respectively. The presence of voids in these films suggests an increase in porosity at high substrate temperatures. Compositional analysis further shows that the films are oxygen deficit with slight variation in oxygen deficiency at different substrate temperatures. The optical band gap energy is found to lie in the range 3.67-3.94 eV. The gas sensing studies on films reveal that the films are highly sensitive to chlorine at 150°C. Films deposited at 400°C show a maximum response of 287% towards 50 ppm of chlorine with response time of 12 seconds and recovery time of 73 seconds.

Films deposited at 400°C have been subjected to post deposition annealing at temperatures of 400 and 500°C for two hours. XRD studies indicate comparatively higher degree of crystallinity of annealed films with preferred orientation along (211). The average crystallite size of films annealed at 400 and 500°C is found to be 33.4 and 33.7 nm respectively. FESEM analysis of the films shows a remarkable change in film morphology due to re-orientation and aggregation of the crystallites upon annealing at different temperatures. Films annealed at 400°C show a highly porous network of platelet like nanostructures, whereas bipyramidal crystallites with comparatively larger size are observed in films annealed at 500°C. The compositional analysis indicates that the films annealed at 400°C are more oxygen deficit as compared to those annealed at higher temperature. The optical band gap of
the films is found to lie between 3.89-3.93 eV. Films annealed at 400°C show an improved response of 388 % towards 50 ppm of chlorine as compared to as deposited films. Thus, post deposition annealing can be used as a potential tool for improving the gas sensing properties of SnO$_2$ films.

Modification of properties of gas sensitive films deposited at 400°C has been further carried out by swift heavy ion irradiation by 100 MeV Ni$^{2+}$ ions at different fluence (1x10$^{11}$-5x10$^{13}$ ions/cm$^2$). The XRD analysis of films shows variation in intensities and orientation of peaks at different fluence. The crystallite size for irradiated films is found to lie in the range 32.7 – 43.2 nm which is comparatively higher than the unirradiated ones. FESEM analysis of films reveals the formation of well defined octahedral crystallites at higher fluence dose beyond 1x10$^{12}$ ions/cm$^2$. The optical properties of films show band gap lying in the range of 3.66 to 3.98 eV. Films are found to be sensitive to chlorine and exhibit response maxima at different operating temperatures beyond 150°C. Interestingly, the films irradiated at fluence of 1x10$^{11}$ and 5x10$^{12}$ exhibits a response of 307 and 345 % at operating temperatures of 200 and 250°C, respectively which is comparatively higher than that observed in case of unirradiated ones. However the recovery achieved for these films is about 48 to 52 % as compared to 90% in case of unirradiated films.

To improve the properties of SnO$_2$ based materials, the precursors are modified with cationic, anionic and non-ionic surfactants namely cetyl-trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and polyethylene glycol-400(PEG). TGA/DTA analysis of modified gel show that thermal stabilization is achieved at 500°C. XRD analysis of surfactant modified SnO$_2$ powder sample reveals that the material is composed of smaller crystallites as compared to unmodified one. FESEM and TEM analyses show that the addition of surfactants lead to the formation of highly porous structure with macrosized agglomerates comprising of spherulitic nanostructures with an average size lying in the range of 3.5-12.2 nm. An oxygen deficiency ranging between 1.83- 2.13% has been observed in the EDAX analysis of the synthesized powder material. The optical band gap of samples depicts a blue shift towards higher energies as compared to unmodified SnO$_2$ powder. The gas sensing investigations made on surfactant assisted thick films reveal a good sensitivity towards ammonia and chlorine at different operating temperatures. Thick films based on SDS modified powder sample exhibit a response as large as 978% and 471 % towards 50 ppm of ammonia.
and chlorine at operating temperature of 100 and 200°C respectively. These results suggest that the structural evolution in SDS based powder samples is more effective in improving the gas sensing behaviour as compared to CTAB and PEG modified ones.

Surfactant modified SnO$_2$ films have been deposited onto glass substrates kept at temperature of 400°C. Surface morphology and porosity of films appear to be strongly dependent on the concentration of surfactants. XRD patterns depict variation in peak intensities and preferred orientations as compared to films prepared from unmodified precursors. Crystallites as small as 15.6 nm have been observed in case of CTAB modified films. EDAX and FESEM analyses reveal the formation of oxygen deficit films with significant variation in porosity, shape and size of nanostructures. The films modified with high concentration of SDS and CTAB show comparatively higher response of 431% and 303% towards 50 ppm of chlorine. The response and recovery time of these films are found to lie between 23-34 and 45-51 seconds, respectively.

To study the effect of antimony (Sb) doping on the properties of SnO$_2$ nanostructures, the precursor solution has been modified by the addition of antimony chloride (SbCl$_3$). TGA/DTA analysis of antimony doped SnO$_2$ gel with highest doping concentration of 6 mol% show complete decomposition of the gel at 500°C. XRD investigations of the gel calcined at 500°C confirm the formation of ATO powder samples. FESEM and TEM analyses indicate that 2 and 4 mol% doped ATO are formed of very fine loosely agglomerated secondary particles comprising of spherulitic nanostructures. Crystallites as small as 7.5nm have been observed in case of 4 mol% Sb doped SnO$_2$ powder samples. Optical studies reveal a blue shift in the band gap energies as compared to pure SnO$_2$. Thick film prepared from SnO$_2$ powder sample with 4 mol% Sb show an exceptionally high response of 4316 % and smaller response time towards 50 ppm of ammonia. Thus optimum doping concentration of antimony in SnO$_2$ can be effectively used to enhance the room temperature ammonia sensing characteristics.

Sb doped SnO$_2$ thin films with Sb doping percentage of 2-6 mol% and thickness of 447±4 nm have been deposited by ultrasonic spray pyrolysis. XRD results indicate that crystallinity of films decreases with increase in dopant concentration. FESEEM analysis of the films show a change in shape of crystallites from cuboidal to polygonal type with antimony doping. The band gap of the films is found to lie between 3.91 and 3.98 eV. The gas sensing
studies reveal that the films with 2 mol% Sb doping has a maximum response of 12% towards 50 ppm of chlorine at an operating temperature of 250°C. This response is found to be much lower as compared to that of undoped SnO$_2$ film and ATO thick films.

Although there are numerous factors which control the properties of the n-type semiconducting SnO$_2$ films yet it is hoped that the present investigations would be worth consideration for the utilization in gas sensing devices. A systematic study of the synthesis parameters and the effect of different pre and post synthesis modifications on the gas sensing behaviour of nanostructured SnO$_2$ would also constitute an interesting area of investigation.