

Conclusion

6.1 Summary of Results

This thesis work is mainly involved in studies of semiconducting metal oxide (SMO) nanostructures, with a special focus towards the understand of their growth mechanism, various analytical characterizations to explore their structure and properties and finally correlate these properties towards the gas sensing and catalytic applications. Two types of semiconductor such as (i) p-type copper oxide and (ii) n-type zinc oxide based nanostructures have been investigated here which are widely known for their gas sensing and catalytic properties. Moreover, growth mechanism of a mixed oxide phase using these two SMOs has also been studied. Mostly, physical growth routes such as vacuum assisted evaporation of thin metal films followed by thermal oxidation and reactive sputter deposition of oxide thin films were used as growth techniques. Additionally, chemical synthesis of mixed oxide nano-particles using sol-gel method has also employed. As major application, carbon monoxide is used as a target gas for various gas sensing studies towards the optimization of the CO sensor fabrication. In addition, photo-catalytic activity of copper oxide thin films has been explored through dye degradation process using Methylene blue. Moreover, ethanol vapour sensing of ZnO nan-rods at room temperature has also been tested. Finally, all findings are explained in terms of surface kinetics and thermodynamics, thermal diffusion and surface free energy related to the structure, morphology and chemistry of the nanostructures. All oxide materials are mainly grown through the physical route and thermal oxidation process for sufficiently long duration, which confirms their thermodynamic stability.

The first part of the present work (**Chapter 3**) is concerned about the growth of a single oxide phase of copper oxide (**p-type semiconductor**) thin films using thermal oxidation of thin Cu film. The effect of many growth parameters such as oxidation

temperature, oxidation time (duration), oxygen partial pressure, film thickness and crystal orientation have been investigated towards the formation of single oxide phase of Cu_2O and CuO nano-structures. Oxide phase purities and various analytical properties of the CuO_x films have been investigated using various characterization techniques mainly XRD, SEM, EDS, SPM, XPS and Raman Spectroscopy, I-V and Hall measurements etc. These nano-structured thin films are further explored for the CO gas sensors and photo-catalytic MB degradation applications. Thermal oxidation process is found to be highly sensitive to the diffusion kinetics and reaction dynamics. Thermal diffusion of Cu and oxygen species play a very crucial role here. However, after sufficient duration of thermal oxidation (up to 25 hr), final copper oxide phase is found to be determined solely by the oxidation temperature, which can be treated as thermodynamic equilibrium. Within this saturation limit, the completion of the oxidation process is mostly determined by the diffusion kinetics which further depends on the duration of oxidation and the thickness of initial Cu layers. In addition, final oxide state may also depend on O_2 partial pressure which can influence the reaction dynamics. Overall XRD results suggest the formation of highly crystalline copper oxides films. I-V measurement indicates that the initial surface oxidation of Cu film starts at 150°C . However, lower oxidation temperature range (250°C - 320°C) results in a crystalline phase of Cu_2O growth under air ambient condition. Higher oxidation temperature (330°C and above) results in the starting of CuO phase and within the range of diffusion limit, longer duration of annealing can lead to the completion of CuO phases. Under oxygen ambient, formation of Cu oxide phases start to appear at slightly lower temperatures (Cu_2O between 140°C - 270°C , CuO above 280°C) as compared to air ambient oxidation. Raman and XPS results are found complementary with the XRD findings and have also confirmed the oxide phase purity for both cases. Single oxide phase of Cu_2O thin films appear with a faceted surface morphology directed by its materialistic properties and exhibit an optical band gap of about 2.2 eV, which makes it a visible light active material suitable for the photo-catalytic applications. CuO films appear with large granular structures where a gradual increase in grain size with the oxidation temperature is also observed. Within a narrow temperature window, strong growth asymmetry and formation of CuO nano-rods has also been observed, both in air as well as oxygen ambient thermal oxidation. Moreover, the surface resistivity of the CuO films strongly depends on the oxidation temperature and steadily decreases with it. Hall measurement studies indicate that this is mainly related to the carrier (hole) concentration and the XPS analysis finally

confirmed that it is originated from the unintentional Cu vacancy model of the oxide layer which further controls the stoichiometry issue of the CuO film. All these findings are explained in terms of oxidation of Cu films through surface diffusion controlled by the thermodynamic and diffusion kinetics as well as chemical free energy.

Present studies indicate that a nano-structured Cu₂O thin film has the potential for photo-catalytic activities, which has successfully been used for the degradation of MB under visible light irradiation. The dye degradation results show that the single phase Cu₂O film has a clear superiority over the CuO film and exhibit a significantly high photo degradation efficiency of 98% within 15 min. On other hand, nano-structure CuO thin films have successfully been tested as a CO sensing material at lower operating temperature. Gas sensing results is found to be very much promising for CuO thin films grown at relatively lower oxidation temperature (for 3hrs). It provides a CO sensing platform with a low operating temperature as low as 150°C and with a very high sensitivity down to 25 ppm. These findings are explained in terms of surface adsorption possibility as well as its surface electrical transport properties. Finally, CuO thin film prepared at 350°C oxidation temperature is found to be able to sense 25 ppm CO gas with reasonably fast response and recovery times. These findings are of high practical importance for the fabrication of CO sensors with lower operating temperature (reduced power consumption) to detect low concentration CO poisoning.

The next part of the thesis work (**Chapter 4**) is related to the growth and morphological modulation of Zinc oxide (**p-type semiconductor**) based nanostructure thin films. ZnO thin films of various surface morphologies were achieved by systematical controlling the thermal oxidation process. Thin Zn films were thermally oxidized in air ambient at different oxidation temperature (RT – 1000°C). The oxidation temperature is found to be very much sensitive towards the formation of ordered nanostructures and by systematically controlling the surface kinetics and diffusion thermodynamics different growth morphology of ZnO nanostructure, starting from vertical nano-wall growth to anisotropic nano-rods formation can be achieved. I-V measurement shows the initial surface oxidation at about 130°C, slightly lower than the temperature of copper oxide formation. However, crystalline ZnO formation actually starts above 400°C. Vertical growth morphology of ZnO nano-wall/ sheet structures is usually formed at relatively lower oxidation temperature (below 450°C). These vertical wall structures are mostly controlled by the surface kinetics and the initial morphology of the metallic

Zn film. With increase in oxidation temperature, thermal diffusion of the oxide species is significantly enhanced. A transition from vertical to lateral growth morphology of 2D layered structure is observed at around 500°C, which is mostly dominated by the thermodynamics. Another transition from homogeneous 2D growth to asymmetric 1D growth front is found for oxidation above 650 °C. This transition is mostly originated from the lowering of surface free energy by formation of different crystal facets/planes. Finally, highly dense 1D ZnO nano-rods/ wires has been obtained at 700°C. TEM results revealed that ZnO nano-rods are basically of pyramid and prism shaped, with growth direction of (001), along the c-axis of wurtzite ZnO crystal lattice. I-V results and Hall measurements have confirmed a significant increase in surface resistivity for ZnO films oxidized at higher temperature. XPS results show a relative enhancement of O₂ composition within the ZnO layer for higher oxidation temperature. Both findings are explained in terms of O₂-vacancy model and reduced carrier concentration at higher oxidation temperature. A correlation between structure, morphology and chemistry of different ZnO nanostructures has also been established and a possible formation mechanism of various ZnO nano-structures is schematically presented.

Two different ZnO nanostructures based CO gas sensors have successfully been fabricated and their sensing performances are compared. CO sensing result for ZnO nano-rods grown at relatively higher oxidation temperature (700 °C) is found to be superior over the porous nano-sheets structure. Nano-rods based CO sensor looks very much promising as 19% sensitivity was obtained at a relatively lower temperature of 200°C for 220ppm of CO concentration. All sensing mechanisms are also explained in terms of surface adsorption as well as its electrical transport properties. Finally, this study can provide a CO sensing platform with a high sensitivity and low operating temperature with very good reproducibility. Moreover, these ZnO nano-rods are able to sense ethanol vapour, even at room temperature which can drastically reduce the power consumption.

At the last part of this thesis (**Chapter 5**), mechanism behind the formation of doped and nano-composite mixed oxide (CuO and ZnO) have been investigated by exploiting the structural, morphological, chemical and optical properties. Two different growth methods such as reactive sputtering process and chemical sol-gel method have been employed to form the MOs hetero-junctions and nano-composites. In case of sputtering, thin films were grown on glass or silicon substrates with different Zn target

powers whereas for sol-gel method nano-particles are synthesized using various concentrations of Zn precursor.

In physical growth route, up to a Zn target power of 40W, Zn-doped CuO films are formed. Afterwards CuO-ZnO nano-composite starts to form which turned to Cu-doped ZnO formation above 70W. Doped samples usually appeared in granular cauliflower-like islands whereas; nano-rods are found on top these granular islands for nano-composite. For sol-gel growth process, Zn-doped CuO nano-particles are formed up to a Zn precursor concentration of 0.07M and nano-composite of ZnO-CuO starts to form above 0.08M. Cu-doped ZnO nano-particles appear in large granular islands whereas nano-composites are having tiny flakes on these granular structures. For cased, optical and electrical properties of these mixed oxides are drastically modified. The optical energy band gap for composite structure increased from 1.8eV for CuO to about 3.6eV for CuO-ZnO nano-composite. The dopant atoms can effectively enhance the gas-sensing performance as well as photo-catalysis activities by altering the nano-structure surface morphology as well as energy band diagram. Therefore, it is expected that mixed oxides may very much be useful for various catalytic and selective gas sensor applications. At the end, all oxide materials are mainly grown through the physical route and processed through a sufficiently long thermal oxidation, which confirms their thermodynamic stability.

Among various gas sensing parameters, selectivity is the most challenging issue as the sensing material reacts with several gases simultaneously during the exposure. Hence, the minimization of the cross sensitivity of the sensors towards other gases remains as an open question. To address the poor selectivity, so-called electronic nose (EN) with an array of different chemi-resistors would be a complicated but useful method [1]. Other option would be single output multivariable sensors, exploiting various physical, chemical, electronic and optical properties of the surface [2]. However, both approaches require a very complex processing unit to recognize the desired pattern for selective detection of target gas. Apart from this complicated technological approaches, another option would be to explore the materialistic properties of a single sensor and their correlation towards the selective sensing. The sensor operating temperature can significantly modulate the surface chemical reaction and hence the sensitivity for a particular target gas, which may largely differ for the background gases. Hence by proper choice of the operating temperature selectivity issue of a particular

sensor can partially be addressed. It is also expected that the sensitivity of any metal oxide based gas sensor may strongly depend on the nature of the crystal plane exposed to the gas species. This finding can further lead to a selective sensing of a particular target gas using specific nano-scale morphology of the MOx. Another important approach leading to a better selectivity would be the tailoring of the surface properties by introducing impurities/dopants. This process can generally impact in two ways: (a) modify the surface diffusion and free energy during the growth process, leading to a different surface morphology (crystal plane) and (b) modulation of surface electronic properties due to dopants or metal nano-particles decoration. Both process have significant impact on effective surface area as well surface interaction sites of the sensing layer and hence a selective response for the target gas/vapour. Finally, exploitation of the capacitive impedance in combination with usual surface resistance may also be a useful approach.

However, the resistive mode gas sensing mechanism of any metal oxide based sensor is solely a surface active chemical process. Hence, to improve the detection limit of any sensor material it is quite obvious to enhance the effective surface area i.e., surface to volume ratio of the sensing layer. Therefore, nanostructured surface morphology is one of the most common features of any gas sensor. In addition, modification of the surface interaction sites for the target gas molecules would also be a useful approach. In this aspect, unintentional doping by varying the growth/oxidation temperature of the film is found to be very useful. Within this study we found that the lower oxidation temperature for CuO is more effective whereas for ZnO film it is towards the higher oxidation temperature. Both effects are related to their unintentional Cu and O₂ vacancy models, respectively. Finally, the operating temperature can also influence the surface chemical reaction and enhance the sensitivity when it operates in the reaction limited regime.

Apart from the selectivity, sensor response time is also a very crucial parameter and needs a great attention. In general, the response time is an inbuilt property of any MOS based gas sensor which is largely controlled by the choice of the sensor material and the target gas/vapour. Apart from this, enhancement of the surface charge carrier mobility by controlling the external parameter (temperature, dopant) can also lead to a faster response of the sensor. Another useful approach to reduce the response time is to reduce the surface interaction site for the target gas molecules. This method would be

useful for a faster response for very low concentration of target gas as limited interaction sites got easily saturated. At the same time, this method also restricts the working range of the target gas concentration.

The gas sensing mechanism for SMO based sensor is found to be significantly different for mixed oxides layers as compared to the individual layer mainly due to their nano-composite formation. A possible explanation of this mechanism related to heterojunction network formation and its impact on sensing performance is discussed here. This explanation suggests that the composite materials are highly sensitive as compared to the individual oxide layers. Hence, by a proper selection of the mixed oxide layers along with their composition ratio a preferable composite structure can be achieved. In addition to this, by optimizing the operating conditions the overall sensing performance of the SMO based sensor can drastically be improved for mixed layer. In addition, depending of the relative material compositions of compatible oxide materials (ZnO:CuO), structural format of the mixed layer can be divided into two parts either doped semiconductor or semiconductor nanocomposites. Similarly, the gas sensing mechanism can also alter with its nanoscale structures as discussed in the following. In case of a doped semiconductor, the gas sensing mechanism is to some extent similar to an individual layer, apart from its modulated surface morphology and surface electronic properties. The surface conductivity is mainly controlled by the carrier density and grain boundary and their modulation during exposure to the target gas molecules. However, in case of nano-composite materials many hetero-junctions are formed between different nano-clusters and appear with a network of different series and parallel combinations. This heterojunctions network significantly contributes towards the surface conductivity of the sensing material and also gets modulated during its exposure to various target or background gases/vapours. Therefore, it can be concluded that the sensing mechanism of mixed layer is vastly different from that of a single layer.

6.2 Further Research Plans

Some future research work plans are highlight here:

1. Majority of the pure metal oxide (SMO) gas sensors suffer from the selectivity issues. In this aspect mixed oxide can play a deciding role due to its improved electrical properties. Therefore CO sensing studies of the mixed oxide (CuO:ZnO) would be great technological potential.
2. Gas sensing studies of these oxide nano-materials (CuO, ZnO) were solely confined to the reducing gas (CO and ethanol vapour), therefore sensing reaction on oxidizing gas/vapours would be of high scientific interest.
3. Properties of various ZnO crystal facets are found to be significantly different from each other. Hence, the gas sensing ability could also be very much dependent of the crystal planes. Therefore, orientation dependent selective sensing behaviour of ZnO nanostructure may address the selectivity issue more effectively.
4. Photo-catalytic activities can significantly be enhanced using mixed/doped/ oxides hetero-junctions and metal decorated nano-composites. This knowledge of mixed oxide formation can be exploited towards efficient catalytic application such as water splitting for H₂ generation.
5. Optical and electronic properties of Cu₂O films confirmed its ability towards absorption of visible light which can be potential candidate for photo-voltaic. Moreover, the fabrication hetero-junction solar cell using copper and zinc oxide would also be promising footstep approach towards the green energy source.