7
Conclusion and Future Work

In this Thesis, a systematic investigation is performed on the structural, morphological, electrical, and gas sensing properties for MO_x sensors such as TiO_2, ZnO and V_2O_5 nanostructures. Throughout the research, the prime concern was to enhance the sensing response towards MO_x based gas sensors towards target gases. Flammable and toxic gases were studied in this Thesis; especially, hydrogen gas which is known to be a futuristic fuel and acts as an energy source. The detection of toxic and explosive gases is highly essential even at extremely low concentration of the gas to save lives and material belongings. The proposed hydrogen gas sensor (ZnO as a sensing layer) not only showed enhanced sensing performance, but also operated at low temperature. Improvement in sensing response was made possible by applying several techniques like doping of transition metal element into MO_x, and formation of p-n heterojunction using p-type materials (rGO and carbon nanofibers) on n-type MO_x. Based on the investigations carried out for compiling the Thesis, the major points are listed as below.

TiO_2 nanoplates of anatase dominated phase have been deposited on p-Si substrate by RF magnetron sputtering. Schottky barrier height between metal and semiconductor is modulated by different metal electrodes (Ag, Ni, and Au) on TiO_2 nanoplates to enhance the sensing response towards hydrogen gas. The effective barrier height is calculated as ~0.15 eV for Ag, ~0.17 eV for Ni, and ~0.19 eV for Au electrodes at 175˚C. Highest effective barrier height is observed for Au electrode which corresponds to a large change in relative response ~77%. For Au electrode, fast response and moderate recovery times are observed as ~7 and 114 sec, respectively. This proves that the Schottky barrier height strongly affects the relative response of the sensor.

Undoped and Ni doped (2, 4, and 6% Ni) ZnO nanostructures have been grown by RF magnetron sputtering system. XRD pattern reveals hexagonal wurtzite structure for undoped and Ni-doped ZnO. In undoped ZnO, preferential growth is observed along with the c-axis. Moreover, FESEM shows a columnar structure having conical tips of very dense packed ZnO nanorods for undoped ZnO nanostructures. Surface morphology transforms with Ni doping, and highest relative response is observed for 4% Ni-doped ZnO nanostructures. Lower limit of detection down to 1ppm (~10%) is also possible at moderate operating temperature (75 ºC), the stability of which sustains up to 150 days without reduction in relative response for 4% Ni-doped ZnO sensor. Excellent relative response is observed for 4% Ni-doped ZnO sensor, due to large surface sites for adsorption of oxygen on nanoplates and lowest activation energy ~6.47 KJ/mol. However, reduction in relative response of 6% Ni- doped ZnO is due to the modification in growth direction of ZnO crystal structures.

Highly sensitive hydrogen gas sensor based on rGO decorated 4% Ni-doped ZnO nanostructures has been studied. Different concentration of rGO (0-1.5 wt%) on Ni-doped ZnO is used to study the hydrogen sensing behaviour. Initially, the resistance increases with rGO concentration at low concentration of rGO (from 0 wt% to 0.75 wt%) decoration, and decreases when the concentration of rGO reaches to 1.5 wt%. The hydrogen gas sensor exhibits maximum relative response of ~63.8% for 100 ppm at 150°C with 0.75 wt% of rGO decorated on Ni doped

ZnO nanostructures. Further, the sensor shows excellent selectivity towards hydrogen gas in comparison to CH_4 and CO_2 gases, even for low gas concentrations (1ppm to 100 ppm). Enhancement of relative response is mainly attributed to the existence of synergistic effects of maximum number of p-n heterojunction having large Schottky barrier height variations with more oxygen ions adsorption site availability on rGO for hydrogen gas. However, the decreased relative response with 1.5wt% decoration of rGO can be attributed to the formation of interconnected rGO between electrodes, reducing the total resistance and allowing the current flow directly through the interconnected rGO between electrodes.

Then, improved NO_2 gas sensing properties based on rGO decorated V_2O_5 thin film has been carried out. DC sputtering system has been utilized to fabricate V_2O_5 thin film, and later, rGO is decorated on V_2O_5 thin film by drop cast method. Initially, the current of rGO decorated V_2O_5 reduces as compared to V_2O_5 thin film, and later current is found to increase in the rGO film on glass substrate. Moreover, a comparison has been made for the relative response of all sensors. Surprisingly, it is found that only rGO decorated V_2O_5 sensor marked highest NO_2 gas sensing response for 100 ppm at 150°C. Additionally, the above specified rGO decorated V_2O_5 sensor gives approximately 61% times more sensing response over the V_2O_5 thin film based sensor. Extremely high sensing response is due to the formation and modulation of p-n heterojunction at the interface of rGO and V_2O_5. Moreover, the presence of active sites like oxygenous functional groups on rGO surface also increases the sensing response.

Hydrogen sensing has been performed on PAN/PAN-b-PMMA derived electrospun nanoporous CNF loaded on ZnO nanostructures. Different concentrations of CNF (0.1 – 0.5 wt%) are loaded on sputter grown ZnO nanostructures by drop cast method. FESEM images of all sensors have been extracted systematically after loading different concentrations of CNF on ZnO surface. XRD characterization reveals that CNF and ZnO have good crystalline nature. Initially, loading of small amount of CNF (0.1 – 0.2 wt%) leads to decrease in current as compared to pure ZnO nanostructures, but the current increases significantly for high amount of CNF (0.3 – 0.5 wt%). Maximum relative response is observed for 0.2 wt% CNF/ZnO nanostructures than all sensors towards 100 ppm hydrogen at 150˚C. In fact, improved sensing response is mainly due to large reaction sites available for hydrogen molecules while diffusing through the nanoporous CNF, the creation of numerous p – n heterojunctions at the interface of CNF and ZnO, and the occurrence of additional oxygen functional groups at the CNF surface. Moreover, the sensing response decreases for high amount of CNF loaded on ZnO nanostructures, which is due to the fact that current passes directly through the partial bridges of CNF network between the electrodes, making p – n heterojunctions less effective.

These investigations shows that sensing response for MO_x based gas sensors highly depend upon the Schottky barrier height. Moreover, sensing response, long term stability, response time, and selectivity for MO_x can be enhanced by using additional nanomaterials (e.g. rGO and CNF), which reduces the operating temperature of gas sensor. In order to obtain further amendment in MO_x based gas sensors, some future work are listed below:

- Long term stability of MO_x based gas sensor is a challenging task which is due to the changes in environmental conditions such as, different temperatures and different humidity levels. Such types of effects should be minimized by keeping the same environmental conditions near the gas sensors in real-time monitoring.

- Fabrication of highly selective gas sensors based on MO_x is one of the prime concerns. However, an array of different sensing materials could be realized to improve the selectivity issue by measuring and comparing the data obtained from different individual sensors.

- For flexible wearable MO_x gas sensors, a cracking of sensing layer on a flexible substrate is also a key issue and needs to be rectified in the future. Thus, a cost-effective, flexible, wearable, and reliable gas sensor is the foremost need.

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