Chapter 5

Conclusions and future scope

5.1 Conclusion

The aim of the present research work is to develop a cost-effective, room-temperature operable, environment-friendly NO_2 gas sensor. In this study, the NO_2 gas sensor was developed employing two configurations- i) chemiresistive type and ii) OFET based. In both the implementations, PANi-Ta_2O_5 nanocomposite doped with CSA has been utilized as the sensing material.

A large no. of metal-oxide based gas sensors have been implemented with promising results. But they suffer from inherent disadvantages such as high operating temperature (200^0C-400^0C), poor selectivity and reproducibility. CPs have been successfully utilized in gas sensing applications with their numerous attractive features like flexible electrical and electronic properties, facile synthesis process, non-corrosiveness, light weight and low cost. In this endeavour, the use of organic/inorganic hybrid materials as the sensing element has attained great attention due to their adjustable physical and chemical properties, small grain size, high surface-to-volume ratio, porous structure and good stability.

CPs have been functionalized with inorganic metal oxides to achieve enhanced gas sensing performance. Among the CPs, PANi is found as one of the most promising candidate for gas sensing applications owing to its innumerable advantages such as relatively high conductivity (after doping), ease of synthesis, low cost and high environmental stability.

The present study started with the chemical oxidative polymerization of aniline monomer to obtain PANi in its emeraldine salt form. PANi, thus obtained, is blended with 50wt% Ta_2O_5 and subsequently doped with various percentages of CSA. Five samples, viz., pure PANi, PANi-Ta_2O_5, PANi-Ta_2O_5-CSA20%, PANi-Ta_2O_5-CSA30% and PANi-Ta_2O_5-CSA40% are thus obtained. All these five samples were subjected to material characterization and spectroscopic analysis using FESEM, TEM, XRD, UV-Vis and FTIR techniques. The FESEM study reveals highly aggregated nanostructures comprised of globular and flower-like morphologies of the CSA doped PANi nanocomposite. This kind of morphology possesses large surface-to-volume ratio and plenty of gas adsorption sites suitable for gas sensing applications.

The XRD results ensure the presence of Ta_2O_5 and CSA in the PANi nanocomposite with high crystalline nature with crystallite size of 12.49 nm. The UV-Vis and FTIR results elucidate the electronic absorption peaks and ascertain the presence of various functional groups related to Ta_2O_5 and CSA in the synthesized PANi nanocomposite. It is concluded that the CSA doped PANi-Ta_2O_5 nanocomposite possessed a large crystalline domain with enhanced PANi conjugation chain and aggregated globular morphology, making it a potential candidate for gas sensor applications.

In the first part of the current research work, chemiresistive thin film based device based on PANi and PANi-Ta_2O_5 doped with 20wt%, 30wt% and 40wt% has been devised. The PANi-Ta_2O_5-CSA40% nanocomposite demonstrated the best sensing behaviour. The sensor device based on PANi-Ta_2O_5-CSA40% depicted a high sensor response of 83% to 500 ppm of NO_2 gas at room temperature with a response time of 55 seconds and recovery time of 160 seconds. It is also found that the chemiresistive sensor is highly selective to NO_2 and its gas sensitivity was not influenced significantly by the atmospheric humidity. The device depicted a good stability over a period of 60 days.

In the last major work, the OFET based sensor was developed to study its electrical characteristics and NO_2 gas sensing properties. The PANi-Ta_2O_5-CSA40% was utilized as the sensing material and PMMA was used as the dielectric. The device showed a relatively good performance with carrier mobility of 0.12 cm^2/V-s, threshold voltage of -12.89 V, current ON/OFF ratio ~ 10^3 and subthreshold swing of 9.3 V/dec.

OFET research mainly seeks to optimize two parameters, viz., charge carrier mobility and current ON/OFF ratio. Organic semiconductors normally provide poor carrier mobility and possess low conductivity. This challenge can be overcome by wisely utilizing the advantages of hybrid materials made of organic and inorganic constituents. Here, PANi has been funtionalised with wide band-gap Ta_2O_5 and the inherently low conductivity of the polymer is improved by doping with CSA. It can be commented that the device demonstrates good performance in terms of carrier mobility and current ON/OFF ratio. High charge carrier mobility of the device can be ascribed to good synergy developed between the OSC and polymeric dielectric that enhanced the interface between the two. Charge transport of OFETs largely results from the narrow region comprising of a few molecular layers around the semiconductor/ dielectric interface. So, its quality significantly determines the carrier mobility. Another contributing factor is the larger crystalline domain the CSA doped PANi nanocomposite possessed which might have favoured better charge transport.

To achieve the best performing OFETs, the current ON/OFF ratio should be as large as possible. Neglecting the contact resistance at the source and drain electrodes, the ON current is determined mostly by the carrier mobility and the capacitance of the dielectric. The OFF current mainly depends on the gate leakage current. The use of low-k dielectric like PMMA causes a low off current by minimizing the gate leakage current and thus can contribute to having a high ON/OFF current ratio.

The threshold voltage of the OFET is determined by a no. of factors such as nature of the semiconductor/dielectric interface, built-in dipoles, impurities and charge traps. It can be lowered by increasing the gate capacitance and this can be possible with the use of high-k dielectric.

It is observed that the studied OFET suffers from two drawbacks- firstly, its high operating voltage and secondly, a high subthreshold swing of 9.3 V/dec. Both of these two factors could lead to high power consumption.

In practical gas sensing applications, it is highly desirable to use low-power (hence portable) devices. Many past reports have revealed that though OFETs exhibits high charge carrier mobility, they often operate at high voltage and normally show greater subthreshold swing. There have been several works which innovated novel means to minimize these issues.

The next generation technology utilizing organic electronics demands the realization of low-cost, low-power, light-weight and high-performance OFETs. One of the crucial steps towards achieving this is to implement OSCs with high charge carrier mobility and hybrid polymer gate dielectrics with solution processibility, compatibility with flexible substrates and high capacitance for high drain currents while operating at low voltage.

In the present work, PMMA was used as the gate dielectric with a dielectric constant 3.9. Polymeric dielectrics possess low value of k (<= 3.9) and hence low capacitance, and thus can exhibit high operating voltage and high threshold voltage. But they can provide high-quality smooth surface with enhanced semiconductor/dielectric interface owing to their low-temperature operability and solution processibility. On the other hand, high-k dielectrics can ensure low operating voltage and a steep subthreshold swing, but they are less effective in suppressing the gate leakage current. So, the desired result can be achieved by incorporating hybrid gate dielectric comprised of both high-k and low-k materials.

The OFET device fabricated here is based on top-contact architecture with a long channel of 1 mm in length and 1 cm in width. The top contact source and drain electrodes were thermally evaporated using hard mask. Due to the existence of the long conducting channel, there was a decrease in source and drain contact resistance that caused weaker influence of the channel resistance and resulted in high carrier mobility. Long channel reduces the possibility of channel "pinch-off" at the source end with further increase in drain-to-source voltage. However, the present work needs more research on reducing the channel length without compromising the device performance. Short channel devices facilitate faster operation, low power consumption and miniaturization.

The PANi-Ta_2O_5-CSA based OFET surpassed the chemiresistive type with superior gas sensing properties, low detection limit and, fast sensor response and recovery time. The sensor response was 68.7% towards 10 ppm NO_2, while it showed 82.5% response towards 50 ppm NO_2. The sensor was found to be reproducible and highly selective to NO_2.

The output characteristics of the OFET device showed increase in drain current with the increase in NO_2 concentration. The carrier mobility of the device showed an increasing trend with the increase in NO_2 concentration with positive shift in the threshold voltage. The changes in mobility and threshold voltage are indicative of improved gas sensing property of the device. The changing trend of ON current, carrier mobility and threshold voltage with the increase in the concentration of the analyte throws a better understanding of the sensing mechanism of the device and evaluation of the various sensing parameters.

The multiparameter accessibility of the OFETs makes them superior in the gas sensing field compared to the chemresistive implementation. The electrical parameters such as carrier mobility, threshold voltage, drain current, ON/OFF ratio, subthreshold swing etc. can be readily extracted and they can respond significantly to the gas exposure. This capability renders OFETs as a promising candidate for sensor devices, particularly electronic nose applications.

The fabricated OFET device presents high charge carrier mobility and an enhanced sensor response at a low detection limit with fast response and recovery time. The device operated reliably at ambient air, found to be highly selective and cost-effective. Taking these facts into account, it can be concluded that the PANi-Ta_2O_5-CSA based OFET is a promising platform for developing small-sized, low-cost, stable NO_2 gas sensors operable at room temperature.

5.2 Future scope of the work

The present thesis demonstrates room-temperature operable NO_2 gas sensor based on chemiresistive and OFET configurations. The OFET based sensor showed superior performance compared to the chemiresitive counterpart and is preferred for the gas sensing applications.

Compared to the two-electrode chemiresistors, the structure and operation of OFETs are more complex. The formation of the conducting channel at the semiconductor/dielectric interface is induced by the gate voltage and this enables to use ultrathin films of a wide variety of nanostructures as the active layer in the OFETs. The charge accumulation layer induced by the gate bias makes OFETs scalable and highly sensitive. Also, the enormous potential of using nanostructured thin films which facilitates high rate of adsorption/desorption and capture of analyte molecules with short response/recovery time opens up the road to use miniaturized, low-power yet high-performance sensor applications.

It is believed that the next-generation will strive for portable, small-sized, low power sensor devices. Therefore, there has been a constant demand for the development of low-voltage OFETs in the gas sensing field. However, it is a challenging task to obtain high performance OFETs with low voltage operability at the same time.

As the present device shows high charge carrier mobility, excellent gas sensitivity, good selectivity and air stability, there is ample scope to utilize the sensor in high-performance applications such as electronic nose devices. With further research on material engineering to fine tune the PANi based semiconductor and the gate dielectric with reduced thickness, low power operation and longer life time can be achieved. This will facilitate integrating the sensor device in low-cost, battery-operated portable circuits for continuous and effective monitoring of the environmentally toxic gas.

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