Abstract

One dimensional (1-D) TiO_2 nanostructures are considered to be a promising material for gas sensing applications owing to its intrinsic properties like high surface to volume ratio, low activation energy, non-toxic, biodegradable, and low cost. Therefore, it is imperative to study 1-D TiO_2 nanostructures thoroughly, so that a reliable and cost-effective technology for gas and vapor sensing applications can be realized. In this thesis, an attempt is made to find new techniques for selective detection of volatile organic compounds like methanol, ethanol, etc. using 1-D TiO_2 nanostructures.

The sensors investigated in this work were made up of different 1-D TiO_2 nanostructures which were synthesized over the Ti substrate. TiO_2 nanostructures like nanotubes, multi-layer nanotubes, and nanorods were grown using electrochemical anodization, step voltage assisted electrochemical anodization, and hydrothermal method, respectively. The morphological, structural, topographical, chemical, and electronic properties of TiO_2 nanostructures were studied extensively using Field Emission Scanning Electron Microscopy, X-ray Diffraction, Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy, and Photoluminescence Spectroscopy, respectively. Also, the basic device structure of all fabricated sensors was kept similar for symmetry. In this work, a typical TiO_2 based sensor consisted of the following three components: (i.) a sensing layer of 1-D TiO_2 nanostructure, (ii.) top electrode of Au, and (iii.) bottom electrode of Ti substrate. Thus, the sensor has a very simple design with a sensing layer sandwiched between two electrodes. For all fabricated sensors, both resistive and capacitive sensing upon exposure to various VOCs were investigated systematically and their sensing mechanism was established based on the experimental results.

Firstly, the effect of various physical parameters like temperature, vacuum and reducing ambient on the impedance of 1-D TiO_2 nanostructures-based sandwich

structure sensor was investigated using Nyquist plots. By virtue of this, an equivalent electrical circuit for this type of sensor was modeled and various factors governing resistive and capacitive changes were identified. For all TiO_2 nanostructures, it was observed that resistance and capacitance of the sensor were decreased and increased, respectively upon exposure to reducing vapor ambient. In general, the resistive response of the sensor was found to be dependent upon the adsorption/desorption of VOC molecules on the surface of nanostructures. This response can be modulated with surface carrier concentration and thickness of TiO_2 nanostructures. On the other hand, the capacitive response was noticed due to the change in the dielectric medium of the sensor upon exposure to VOCs. This response majorly relies on the volume of void region/free space available in between two electrodes, and dielectric constant of TiO_2 nanostructures and test VOC species.

In the case of TiO_2 nanotubes based-sensor, resistive and capacitive responses were found to have a natural logarithmic relation with VOC concentration (100-300 ppm). This characteristic of the sensor was used to develop a new measurement technique involving the measurement of both resistive and capacitive response simultaneously for detecting a range of VOCs with their concentration with high selectivity. The sensor was tested successfully at room temperature to identify and quantify VOCs like methanol, ethanol, acetone, and 2-propanol.

The other kinds of 1-D nanostructures like multi-layer nanotubes and nanorods were also explored with a view to enhance the selectivity of the sensor. Multi-layer nanotubes were synthesized using step voltage assisted electrochemical anodization and experimental results demonstrated that sensitivity (in resistive mode) and selectivity (in capacitive mode) of the sensor was increased with an increase in the number of layers of TiO_2 nanotubes. This behavior was attributed to the benefits of (i.) incremental effective surface area, and (ii.) Schottky barrier lowering effect at interlayer junctions. In another approach, the hydrothermal synthesis recipe was optimized for obtaining highly ordered and stable TiO_2 nanorods on a Ti substrate.

For TiO_2 nanorods based sensor, the selectivity of the sensor was found to get degraded with VOCs concentration in resistive mode. However, capacitive sensing was found to be more effective for selective detection of VOCs for higher concentration levels (above 100 ppm).

Finally, a capacitive type sensor based upon TiO_2 nanotubes was tested at room temperature to detect methanol with high selectivity in the presence of other volatile organic compounds especially ethanol. Capacitive response magnitudes of 123%, 234%, 327%, and 564% were measured for 200 ppm of pure ethanol, 10% methanol in ethanol, 25% methanol in ethanol and pure methanol, respectively. Thus, the sensor exhibited excellent capacitive selectivity towards methanol with respect to ethanol due to the significant difference in their dielectric constant values. Also, the sensor exhibited excellent stability, repeatability and fast response/recovery times (< 1 min). Moreover, the fabricated sensor was successfully integrated with an IC-based signal processing circuit and hence, making the complete sensor system portable, low cost and simple to handle.

Thus, the research elucidated in this thesis involved synthesis, characterization and, fabrication of 1-D TiO_2 nanostructures-based sensors for selective detection of VOCs. An in-depth analysis of physical, chemical and electrical parameters of TiO_2 nanostructures was the key to explore new solutions to the problem of inadequate selectivity of metal oxides/TiO_2 based sensor. It was shown that selective detection of VOCs can be enhanced by using 1-D TiO_2 nanostructures with a sandwich structure configuration and measuring both resistive and capacitive changes of the sensor upon exposure to VOCs. Apart from achieving better selectivity, the sensor in this work exhibited other worth noticeable properties like excellent stability in terms of baseline resistance and capacitance values, facile and fewer fabrication steps, and low operating temperature.