Fabrication and performance characterization of nano-structured semiconducting metal oxide thin films for gas/molecular sensing

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Abstract

Development of nano-scale materials have been intenselly researched in the field of sensors. The intimate correlation between nanostructured materials and sensor performance has led to multidisciplinary state-of-art technological development in sensors technology. Metal oxide semiconductors in particular, are of great interest in the development of gas sensors and biomedical nanodevices. The experimental work reported in this dissertation outlines the fabrication of nanostructured Cu_2O and ZnO thin films using electrodeposition and their applicability in sensing liquefied petroleum (LP) gas and glucose. The surface morphological properties and the structural properties of the fabricated thin films were evaluated using scanning electron microscopy and X-ray diffraction and energy dispersive X-ray spectroscopy. The photo-response properties were assessed using photocurrent spectral response measurements and the electrical properties were studied by Mott–Schottky measurements. LP gas sensing was performed under a controlled environment using a custom made gas chamber. Sensor performance was measured in a conductometric mode where the resistance-time measurements were used to evaluate sensitivity of the material to LP gas. Chronoamperometric and cyclic voltammetric measurements were used to evaluate the electrochemical performance for the non-enzymatic glucose sensing.

Firstly, a surfactant free template assisted electrodeposition method was used to fabricate thick *n*-type Cu_2O films having cubic nanostructures and were used for the detection of liquefied petroleum (LP) gas at low concentrations. Templates were fabricated by initially electrodepositing a *p*-type Cu_2O thin film on a Ti substrate followed by annealing that changed conductivity of the film to *n*-type, as confirmed by Mott–Schottky and spectral response measurements. SEM measurements of resulting films showed nano-cubic crystals having sizes of 150–300 nm. When exposed to a mixture of LP gas and dry air, the resistance of these films increased and the maximum response was recorded when films were maintained at 180°C for all concentrations and it was independent of the surface morphology. At 180°C, at the lowest tested LP gas concentration of 2 vol%, a twofold increase in response was observed in the nano-cubic films compared to the micro-crystalline *n*-type Cu_2O films. This improvement in gas response was attributed to the increased effective surface area of the nanostructured films. Compared to other LP gas sensing materials, these films showed improved response and recovery times of ~120 s and ~90 s, respectively.

Secondly, Cu_2O and ZnO based nanomaterials having different morphological structures were developed and used in non-enzymatic glucose sensing. Amperometric sensing measurements of glucose were performed using *n*-Cu_2O nano-cubic films fabricated on Ti using a surfactant

free template aided electrodeposition method. Amperometric measurements for these films yielded a sensitivity of 28.4 μA mM^{-1} cm^{-2} with a lower detection limit (LOD) of 15.6 μM and a linear range of detection from 17 to 11,650 μM which were significantly better than the microcrystalline *n*-Cu_2O films. Further, by optimizing the electrodeposition parameters, *p*-type nanocubic Cu_2O nanostructures were electrodeposited on Cu substrates. These Cu_2O thin films were later modified to form copper nanoclusters, with their shapes determined by the electrodeposition time and the applied potential. Better glucose sensor performance was yielded by dendrite-like Cu nanoclusters deposited on *p*-Cu_2O NCs/Cu electrode with a sensitivity of 45.32 μA mM^{-1} cm^{-2}, wide linear detection range of 92 to 24,420 μM and a LOD of 31.38 μM and with a fast response time of less than 3 s. Moreover, to further enhance performance of non-enzymatic glucose sensing, 3D Cu foam (CF) and 2D Cu plates were used to form binder free 1D $Cu(OH)_2$ nanostructures. Thereafter, following an annealing process $Cu(OH)_2$ structures were converted to Cu_2O nanostructures with diameter of ~ 200 nm and length exceeding 1 μm. The CF based nanostructures showed a heterogeneous distribution of nanowires, nanotubes or nanorods while, Cu plate based nanostructures consisted of ripple-like structures on the outer surface of the Cu_2O nanowires. Cu_2O/CF electrodes yielded a significant improvement in the sensor performance with a sensitivity of 5,792.69 μA mM^{-1} cm^{-2}, an ultralow detection limit of 15 nM and a much faster response time of less than 1 s. This outstanding performance can be attributed to the rough surface of Cu_2O nanostructures enriched with nano-pores in size of around 20 nm. At the same time, in the perspective of Langmuir isothermal, ultra-wide linear detection range of up to 60 mM with a high sensitivity of 1565.19 μA mM^{-1} cm^{-2} was measured for the same electrode. These electrodes provide a better platform for non-enzymatic glucose detection with high specificity and reproducibility having relative standard deviation (RSD) of 2.8%.

The study was further extended to ZnO nanorods modified with Cu nanoparticles for non-enzymatic glucose detection. Following co-electrodeposition, fabricated wurtzite structures of ZnO NRs/ITO electrode with hexagonal facets were modified with Cu NPs in size of less than 100 nm. A sensitivity of 142.41 μA mM^{-1} cm^{-2}, linear detection range of up to 5,968.1 μM and a very low LOD of 130 nM was measured for these electrodes. This LOD is one of the best ever reported for ZnO nanomaterials based on non-enzymatic amperometric glucose sensing.