Application of Electrodeposited Nano/Micro Structured Metal Oxide Thin Films for Liquefied Petroleum Gas Sensing

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Abstract

A gas sensor is a device utilized to caution us of dangerous gases. As one of foremost utilized household fuel, the detection of possible leakages of Liquefied Petroleum (LP) gas from production plants, from cylinders during their storage, transportation and usage is of utmost importance. This PhD thesis sets out to examine novel electrochemically fabricated, both *n*-type and *p*-type Cuprous Oxide (Cu_2O) thin films for the detection of LP gas. The effect of the electrical resistivity change of Cu_2O thin film layer in the presence of LPG was used for gas sensing.

Nowadays, Cu_2O thin films are receiving an intense interest from the Scientific Community, due to their morphology, electronic, optical properties, and low fabrication cost, non-toxic and easy to process as a thin film which make them a promising candidate for many industrial applications including new gas sensors for the detection of toxic species.

The *n*-type Cu_2O films were grown in an electrolytic bath containing a solution of sodium acetate and cupric acetate whereas chlorine-doped Cu_2O thin films were prepared by adding a cuprous chloride ($CuCl_2$) into an electrolytic solution containing lactic acid, cupric sulphate and sodium hydroxide. The type of conductivity of the deposited films was determined using spectral response measurements and Mott-Schottky plots. The surface morphological, structural and compositional variation of every sample were done by using Scanning Electron Microcopy (SEM) and Energy Dispersive X-Ray Spectrometry (EDX) analysis. To identify the quality of roughness and wetting behavior of films, Atomic Force Microscopy (AFM) images with statistical data of roughness and Contact angle measurements was used.

The surface morphological, structural variation of *n*-type Cu_2O thin films deposited in the acetate bath with the deposition time was studied through SEM analysis and EDX analysis and gas response of bare *n*-type Cu_2O thin films was continued with 45 min deposited samples. The *n*-type Cu_2O thin films showed a response resulting in a maximum response around 85 °C with ~ 4.1% of LPG response. To obtain the surface modifications for improvement of gas response, the surface of electrodeposited *n*-Cu_2O thin films were modified by sulphidation using aqueous Na_2S followed by $(NH_4)_2S$ vapor treatment. Compared to untreated thin films, the resultant films showed enhanced response to liquefied petroleum (LP) gas at a relatively low operating temperature (~45 °C) with ~ 45 % of LPG response, as one of the lowest reported for a cuprous oxide based material. X-ray diffraction spectra confirmed that the films were of single phase. Observed by contact angle measurements and EDX data, $(NH_4)_2S$ vapor treatment converted the highly wetting sulphided films containing both Na and S to a partially wetting surface by forming sulphur on the film surface. This modification of the film surface,

enabled the sensor response to recover to ambient level after stoppage of LP gas flow, which sulphidation alone was inapt. Scanning electron micrographs complemented roughness measurements made by atomic force microscopy and showed a transformation of the polycrystalline morphology of bare *n*-Cu_2O film to one having highly porous structures, which thereby increased the surface area of the surface modified films. Therefore, this work demonstrates that the surface of the *n*-type Cu_2O thin films modified by $(NH_4)_2S$ vapor treatment and sulphidation can alter the surface wetting nature and increase the surface area to enhance LP gas sensing at a relatively low temperature.

Liquefied Petroleum Gas (LPG) gas response behavior of *p*-type cuprous oxide (Cu_2O) thin films fabricated by electrochemical deposition in the lactate bath was also investigated. The SEM and X-ray XRD measurements were performed to understand the crystalline structural variety of synthesized Cu_2O films deposited under the different pH conditions. According to the XRD patterns, the films had a preferred (200) orientation of cuprous oxide crystallites and thin films deposited at pH 10 shows high surface quality with sharp polycrystalline structures. For further confirmation of the quality of Cu_2O thin films of pH 10 samples, roughness analysis was done through AFM spectrums and statistical data of roughness measurements. Along the contact angle measurements, wettability variation of Cu_2O thin films with the increase of pH was observed as wetting, partial wetting and non-wetting. EDX was used for compositional analysis of films and Mott - Schottky plots and spectral response measurements were carried out to confirm the *p*-type conductivity of Cu_2O thin films. When exposed to a mixture of LP gas and dry air, the resistance of these films increased and under the off condition, it decreased up to the ambient value. LPG gas response was recorded for lowest LP gas concentration of 0.25 vol. % with ~ 30 s and ~ 40 s response and recovery time, respectively, at the room temperature with ~3.7% of gas response. The sensor responses were examined using LP gas in different dry air volume percentages (0.25% to 2.0%) at the room temperature. The optimum response of film observed at 60 °C with ~30% of sensor response to the flow rate of 0.25% of LPG: dry air. The device retained 95 % gas sensing stability after the period of 60 days, suggesting that the fabricated *p*-type Cu_2O thin films are reliable and promising for LPG sensing.

The effect of chlorine doping on the gas sensing behaviors of Cu_2O thin films fabricated in the lactate bath was investigated. Due to doping, the conductivity of the chlorine doped Cu_2O films increased by several orders of magnitude. The temperature dependent gas responses of the chlorine doped Cu_2O thin films to the LP gas was monitored at a constant gas flow rate of 0.005 ml/s. However, the chlorine doped Cu_2O thin films initially showed a positive response with increasing of resistance ($\Delta R > 0$) to the LP gas which then reversed its sign to give a negative response (resistance decreasing) which peaked at 52 °C (with 0.02M doped thin films). The positive response shown in the chlorine doped Cu_2O films vanished completely at 42 °C. Those investigations were continuing with the chlorine concentration, 0.02M doped Cu_2O thin films identified as best sample for gas sensing.

This work presents a facile and simple method to fabricate *p*- Cu_2O thin films which are active for LPG sensing at the room temperature. Also pH-dependent structural and morphological tuning ability of Cu_2O thin films deposited in lactate bath for best LPG response at room temperature was identified. Furthermore, the study introduces surface treatments of Cu_2O thin films by Na_2S and $(NH_4)_2S$ vapor and pH variation of deposition bath as wettability moderating methods for LPG sensing.