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Effects of Surface Modification of n-Cu_2O/p-Cu_xS Thin Film Heterostructures for Enhanced Liquefied Petroleum Gas Sensing Properties

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Abstract

We report a novel mechanism to effectively detect LP gas based on surface modification through sulphidation followed by passivation of electrodeposited *n*-type cuprous oxide (Cu_2O), forming a thin film *n*-Cu_2O/p-Cu_xS semiconducting heterostructure. Electrochemically deposited *n*-type cuprous oxide (n-Cu_2O) thin films on Ti substrates in acetate bath were sulphided using Na_2S to fabricate n-Cu_2O/p-Cu_xS heterostructures. Subsequent passivation of these thin film structures using $(NH_4)_2S$ vapor enhanced the sensitivity (fractional change in thin film resistance) when exposed to liquefied petroleum (LP) gas.

Scanning electron micrographs (SEM) confirmed that typical unsulphided n-type Cu_2O thin films exhibit polycrystalline surface morphology, while SEM of both sulphided and passivated thin films revealed micro/nano-crystalline surface morphological features with porous structures. As expected, the thin film structures obtained through sulphidation followed by passivation of n-type Cu_2O films decreased the resistance (~100 kΩ) in comparison to the resistance (~1 MΩ) of the unsulphided n-type Cu_2O thin films. Upon exposure to LP gas, the resistance of these thin film structures increased while, sensitivity to LP gas depended on the sensing temperature. Exposure of thin film structures fabricated by electrodepositing *n*-

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type Cu_2O thin films for 45 min, sulphided and passivated for 5 s and maintained at a sensing temperature of 45 °C to LP gas with a flow rate of 2.5 ml/min recorded the highest sensitivity of 48 %.

Keywords: Cuprous oxide, Sulphidation, Surface passivation, Gas sensor, Liquefied Petroleum gas, electrochemical deposition

Introduction

Liquefied Petroleum (LP) gas is used worldwide for domestic, commercial and industrial purposes and is a highly flammable gas. Therefore, availability of efficient and low cost LP gas sensors are of importance with regards to ensuring user safety. Gas sensing properties of metal oxide semiconductor such as SnO_2, CdO, ZnO, In_2O_3, TiO_2 (Huang & Wan, 2009; Eranna, *et al.*, 2004; Yamazoe, *et al.*, 2003) have been extensively studied while many semiconducting materials have been considered for LP gas sensing applications (Yadav, *et al.*, 2013; Gunjakar, *et al.*, n.d.; Dhawale, *et al.*, 2008; Bulakhe & Lokhande, 2014; Shukla, 2012; Shinde, *et al.*, 2007; Bandara, *et al.,* 2014). There are many parameters of materials that are important for gas sensing applications, for example, adsorption ability, catalytic activity, sensitivity and thermodynamic stability are some of them. Many different metal oxide materials are favorable in some of these properties (Bochenkov & Sergeev, 2010; Korotcenkov, 2007; Wang, *et al.*, 2010; Shishiyanu, *et al.*, 2006). Due to this situation, more recent works focus on composite materials, such as, ZnO-CuO, SnO_2-ZnO andα-Fe_2O_3/ZnO (Yoon, *et al.,* 1998; De Lacy Costello, *et al.*, 1999; Chen, *et al.*, 2008). Not only the binary metal oxides, there are also numerous ternary, quaternary and complex metal oxides, which are of interest for gas sensing applications (Zhang, *et al.*, 2006; Meng, *et al.,* 2013; Meixner & Lampe, 1996). It is also important to note that the detection of simple gases, through semiconducting metal oxides often require elevated temperatures (Arafat, 2012; Gopel & Schierbaum, 1995; Sun, *et al.*, 2012; Bochenkov & Sergeev, 2010).

Electrochemical deposition of Cu_2O films has attracted increasing interest due to its associated low temperature assisted, relatively

simple and low cost technique (Siripala, *et al.*, 2009; Rahman, *et al.*, 2015). Also, it has the ability to control the crystal growth parameters, morphologies, compositions through a systematic variation of electrode potential/current, electrolyte concentration, bath pH and deposition time *etc.* (Schlesinger, *et al.,* 2010; Bijani, 2009; Jayathilaka, *et al.*, 2012; Jayathilaka, *et al.,* 2014; Jayathilaka, *et al.*, 2014; Teterycz, 2001; Siripala & Kumara, 1989). However, comparatively limited work has been done on Cu_2O and its ability to detect LP gas (Gunjakar, *et al.,* n.d.; Bulakhe & Lokhande, 2014; Shukla, 2012; Shinde, *et al.*, 2007; Janantha, *et al.*, 2009).

Recent work on Cu_2O thin films un-doped and doped with chlorine have shown their ability to be sensitive to LP gas at relatively lower operational temperatures of ~85 °C and 50 °C respectively (Bandara, *et al.,* 2014).

Furthermore, gas sensors based on the two components mixed together are more sensitive than the individual components alone (Yoon, *et al.*, 1998; De Lacy Costello, *et al.*, 1999; Chen, *et al.*, 2008).

Formation of n-Cu_2O/p-Cu_xS heterostructures through sulphidation of electrodeposited *n*-type Cu_2O using 0.01M Na_2S at 200 °C was previously demonstrated by Jayathilaka *et al.* (Jayathilaka, *et al.*, 2012). In subsequent work, they showed that, the sulphur passivation of p-type Cu_2O (Jayathilaka, *et al.*, 2014) and n-type Cu_2O (Jayathilaka, *et al.*, 2014) thin film defects, using 50 vol. % $(NH_4)_2S$ vapor improves the electrical transport properties and photo-response characteristics of these thin films. The work has also shown that the resistivity of the passivated films decreased while preserving the structural integrity of the thin films. Previous work on the fabrication of copper sulphide thin films showing gas sensing properties using solution growth technique has demonstrated its ability to detect ammonia gas at room temperature (Sagade & Sharma, 2008). But it has not been tested for detecting LP gas. Here we report a novel mechanism to effectively detect LP gas based on surface modification through sulphidation followed by passivation of electrodeposited n-type cuprous oxide (Cu_2O), forming a thin film n-Cu_2O/p-Cu_xS semiconducting heterostructure.

Materials and Methods

Electrochemical Deposition of Thin Films

Initially n-type Cu_2O thin films were deposited on Ti substrates. Before deposition, the substrates were cleaned with detergent, dilute nitric acid, HNO_3 acetone and finally rinsed with distilled water. The Cu_2O thin films were potentiostatically electro-deposited in a three-electrode electrochemical cell that contained aqueous solutions of 0.1 M sodium acetate (98%) and 0.01 M cupric acetate (98 %) (Acetate bath). Deposition was carried out for different durations as required at 60 °C under a potentiostatic condition of -200 mV. The n-type conductivity of the deposited films was verified using spectral response measurements. Prior to sulphidation, deposited thin films were thoroughly dried. Then the Cu_2O thin films were sulphided by placing a drop and spreading into a thin layer of 0.01 M Na_2S using a liquid droplet marker and drying at 200 °C.

Films were thoroughly cleaned with distilled water and allowed to dry before any measurements. Followed by sulphidation, the surface passivation was achieved by exposing the films to 50 vol. % $(NH_4)_2S$ vapor at 27 ºC for about 5 s.

Characterization of Thin Films

The surface morphological and structural characterization of the films was determined using SEM (Philips XL40) and XRD (SHIMADZU SSX -550) analysis.

Gas Sensing Measurements

In order to test the gas sensing properties when exposed to LP gas, the fabricated sensors were housed inside a gas sensing chamber made of stainless steel (Figure 1). The chamber contained two compartments; the top through which the gas was flown and the bottom where the heating element was housed. Electrical resistance was measured between the contacts probes placed on the surface of the film. The probes were externally connected to a multimeter that was connected to a computer data logger. The sensor surface temperature was controlled by using a thermostat with a

temperature controller. Thin films were placed approximately 2 cm away from the gas inlet. Inset above shows a detailed geometry of the thin film structures used for sensing LP gas with gold spring probes placed on the top surface.

All the measurements were made under atmospheric conditions (ambient) by using a flow through technique. The LP gas flow rate was maintained at a constant rate of 2.5 ml/min, till the film resistance reached steady state. Thereafter, the gas flow was stopped and allowed to recover till it reached the ambient resistance. The sensing temperature was varied between 30 °C and 150 °C, monitoring through a thermocouple (type K) which was in contact with the surface of the thin film. The electrical resistivity measurements were made using computer interfaced Keithley 2100 digital multimeter. Typically, the steady state maximum was reached within 50 s after the films were exposed to LP gas. The process was repeated several times (up to 4-5 times) for a given sensing temperature. Measurements were repeated at different sensing temperatures ranging from 30 °C to 150 °C.

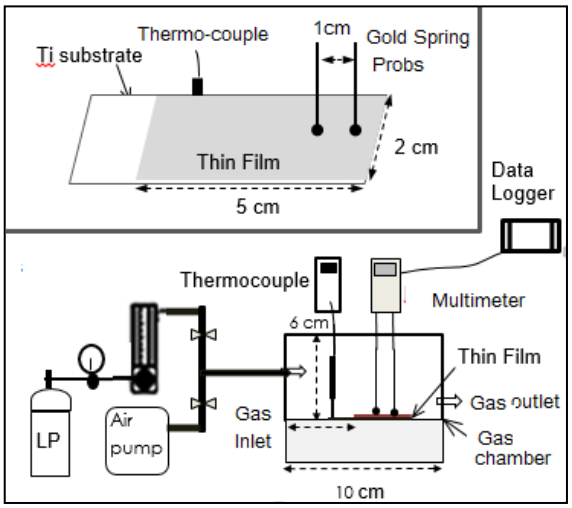

Figure1. Experimental setup used for testing thin film structures for its sensitivity to LP gas

Results

Structure and Morphology of Thin Films

Figure 2(a) shows the SEM view of a bare n-type Cu_2O thin film where there is a uniform coverage of polycrystalline grains. Figure 2(b) shows an SEM image of a sulphided and passivated thin film, confirming the porous micro/nanocrystalline surface morphological features.

Figure 2(c) indicates the XRD peaks of (i) untreated and (ii) sulphided and passivated n-type Cu_2O thin films. All the XRD peaks are due to Cu_2O and the Ti substrate. The sulphided and passivated n-type Cu_2O thin films do not show any Cu_xS peaks, presumably due to the extreme thinness of Cu_xS on the surface of the film. The formation of Cu_xS on the film surface has been verified by Jayathilaka *et al.* using X-ray photoelectron spectroscopy (XPS) measurements.

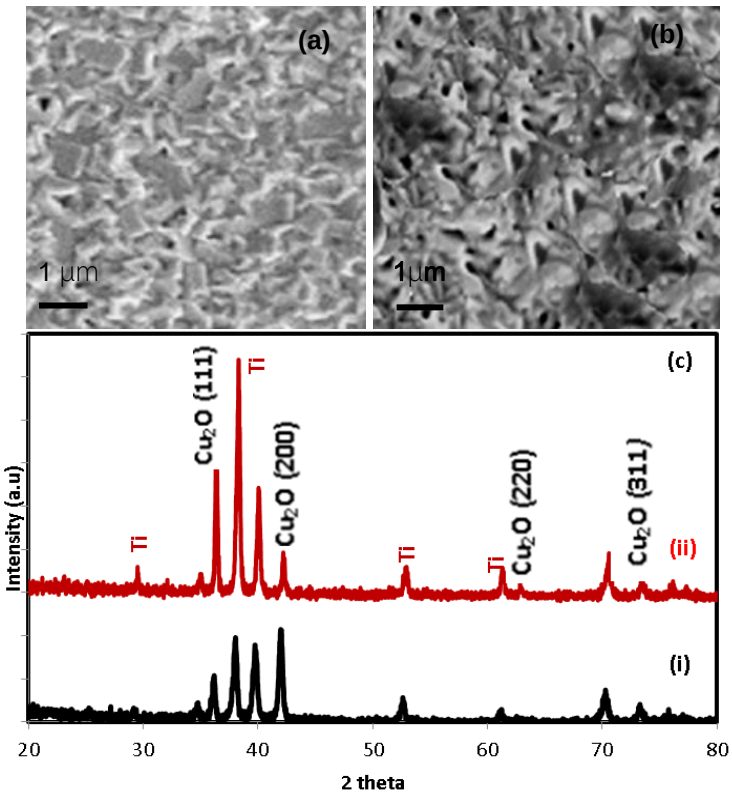

Figure 2. SEM picture of Cu_2O thin films
(a) n-type thin films fabricated in acetate bath
(b) sulphided and passivated (by placing a thin layer of 0.01M Na_2S at 200 °C and followed by exposure to 50 vol.% $(NH_4)_2S$ vapor for 5 s at 27 °C and
(c) XRD spectra for n-type Cu_2O thin film structures, (i) unsulphided (ii) sulphided and passivated by exposing to 50 vol.% $(NH_4)_2S$ vapor for 5 s at 27 °C.

Sensitivity of Thin Films to Liquefied Petroleum Gas

Untreated Cu_2O thin films showed a resistance ~1 MΩ which reduced down to ~ 100 kΩ after sulphidation and passivation. The sensor sensitivity (S) was calculated according to the following equation using the measured resistances.

$$S = \left|\frac{R_{LPG} - R_{Air}}{R_{Air}}\right| \times 100 \qquad (1)$$

where, R_{LPG} is the resistance of the film upon exposure to LP gas and R_{Air} is the resistance of the film under ambient atmospheric conditions.

Fabricated thin films were placed inside the gas chamber and resistance (hence the sensitivity) measurements were taken as a function of both time and sensor surface temperature. Upon exposure to LP gas, the resistance of the sulphided and passivated n-type Cu_2O films increased the film resistance. It gradually recovered to its initial ambient value when the LP gas flow was stopped**.** Figure 3(a) and Figure 3(b) show the resistance and the magnitude of sensitivity variations at sensor operating temperature at 45 °C obtained for sulphided and passivated n-type Cu_2O thin films upon repeated cycles of LP gas exposures. Response and recovery time of one cycle was completed around 100 s duration while, the sensor response was reproducible over all the LP gas exposure cycles. A steady state maximum sensitivity of 48 % was achieved when the sensor surface temperature was maintained at 45 °C, the optimum sensor operating temperature (see Figure 3c). Observations confirmed that the sensing temperature was a major

factor affecting the measured sensitivity. These films show greater sensitivity (~48 %) compared to unsulphided (~4 %) Cu_2O thin films (Bandara, *et al.*, 2014).

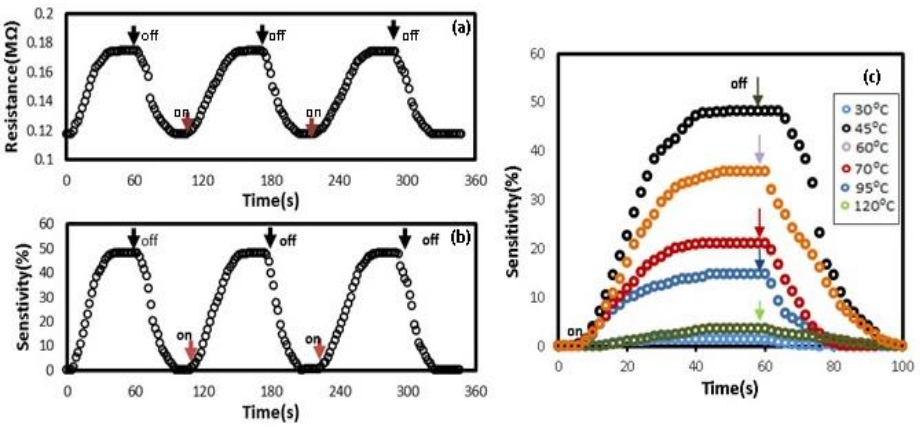

Figure 3: (a) Resistance and

(b) Sensitivity for a sulphided and passivated (by placing a thin layer of 0.01 M Na_2S at 200 °C and followed by exposure to 50 vol.% $(NH_4)_2S$ vapor for 5 s at 27 °C) *n*-type Cu_2O thin film structure operated at 45 °C. A gas flow rate of 2.5 ml/min was maintained during the ON cycle of gas flow to the thin film structure.

(c) Sensitivity measurements as a function of sensing temperature for the thin film structure used in (a), the arrows indicate the time at which the gas supply was turned OFF.

The LP gas reaction mechanism of the thin films showing LP gas sensing properties can be summarized as follows. The top surface of the thin films showing LP gas sensing properties gets exposed to ambient atmospheric oxygen. The top surface being p-type Cu_xS, chemisorbs oxygen to the surface, extracting electrons from the thin

film to form O_2^-on the film surface. This charge transfer process will increase the concentration of holes in the p-type Cu_xS, and thus will reduce the depletion region of the n-Cu_2O/p-Cu_xS heterostructure under ambient conditions. However, once exposed to LP gas, a reaction takes place that will remove the chemisorbed oxygen from the surface, giving the electrons back to the p-type Cu_xS region. The associated chemical reaction is given by the following equation (Shukla, 2012).

$$2C_nH_{2n+2}(ad) + O_2^- (ad) \rightarrow 2C_nH_{2n+1}\text{-}O + H_2O + 2e^- \qquad (2)$$

The newly released electrons will now go on to recombine with the majority carrier holes in the p-type Cu_xS region, which makes the film resistance increase, which was consistent with our observations. The decrease in holes in the p-type Cu_xS region will also allow the depletion region of the n-Cu_2O/p-Cu_xS heterostructure to increase. Therefore, the n-Cu_2O/p-Cu_xS heterostructure regulates the charge transfer processes discussed above. When the LP gas supply is stopped, chemisorbed LP gas molecules will gradually release from the surface and atmospheric oxygen will chemisorb back on the thin film, allowing the resistance to recover back to its ambient value and in the depletion region of the n-Cu_2O/p-Cu_xS heterostructure to recover back to its ambient condition.

Conclusions

In summary, a n-Cu_2O/p-Cu_xS heterostructure was realized by electrochemically depositing a n-type Cu_2O thin film on a Ti substrate, followed by sulphidation using Na_2S and passivation by $(NH_4)_2S$ vapor and was successfully used for the detection of LP gas. It can be clearly seen that the sulphidation with passivation has altered the gas sensing behavior of n-type Cu_2O thin films significantly. When exposed to LP gas, a maximum sensitivity (fractional change of resistance) as much as 48% at a relatively low sensing temperature of 45 ºC was recorded. Thus, the sulphidation has caused LP gas molecules to interact with the film surface more actively with a 10-fold increase compared to the maximum sensitivity of untreated Cu_2O films at 85 °C.

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