Use of Cu_2O microcrystalline thin film semiconductors for gas sensing

P.A. Praveen Janantha, L.N.L. Perera, K.M.D.C. Jayathilaka[b] , J.K.D.S.Jayanetti, D.P.Dissanayaka[a] and W.P.Siripala[b]
Department of Physics, University of Colombo
a – Department of Chemistry, University of Colombo
b – Department of Physics, University of Kelaniya

ABSTRACT

Gas sensors based on metal oxides are widely used for the detection of gases and organic vapors. Adsorption of gas molecules on the surface of a metal oxide semiconductor causes a significant change in the electrical conductivity of the material. This study was conducted to investigate the gas sensing properties of n-type microcrystalline cupreous oxide (Cu_2O) thin films, grown using electro-deposition. The variations in the resistance of thin film were observed for different gases, namely Oxygen, Nitrogen and Liquid Petroleum (LP) gas. The variations in resistance were measured with a higher resolution, for longer time durations and an analysis was conducted to find out how Cu_2O responded to these environments. Clear variations in the thin films' resistance were observed for O_2 while moderate responses were observed for LP gas. The changes in the resistance for fixed concentrations of O_2 were studied and a change in resistance of 5Ω was observed when O_2 concentration was increased from 0 to 0.311 (O_2:N_2) molar ratio in N_2 background.

1. INTRODUCTION

Currently numerous kinds of gas sensors are widely used for the detection of gases and organic vapours [1-3,5-7]. Because of their simplicity and low cost, semiconductor metal-oxide gas sensors standout among most of the other types of gas sensors. For more than five decades it has been known that the electrical conductivity of semiconductors varies with the composition of the gas atmosphere surrounding them [2]. Adsorption of gas molecules on the surface of a metal oxide semiconductor causes a significant change in the electrical conductivity of the metal. This is the operation principle of metal oxide gas sensors [3]. However, issues with sensitivity, selectivity and stability have limited their use, often in favour of more expensive approaches such as Gas Chromatography, spectroscopic sensors etc [2]. In this study electrically deposited Cu_2O was investigated for ascertaining its gas sensing properties. Cu_2O is one of the earliest studied metal oxide semiconductors, which was widely used in photo-voltaic applications due to its direct band gap of 2 eV. It is also a metal oxide which can be deposited in both n-type and p-types [4]. This study explores the potential of Cu_2O thin films in sensing gases while discussing its applications and limitations as a successful gas sensor. The study revealed that there was a clear change in conductivity in the Cu_2O thin films in the

presence of gases such as Oxygen, Nitrogen, and LP gas. Suggestions are also made to improve the use of Cu_2O films as a successful sensor which could be used in day-to-day applications. In this study a concentration of 0.311 O_2 to N_2 molar ratio was able to be sensed.

2. EXPERIMENTAL

In this study, n-type Cu_2O thin films were deposited on ITO (Indium Tin Oxide) coated glass plates using electro-deposition method. ITO plates were specially used since the ITO is of low conductivity and as such the change in conductivity upon gas adsorption on the Cu_2O thin films would be seen easily. Also its transparency makes it possible to check the type (n/p-type) of the Cu_2O thin film deposited.

Prior to the deposition, ITO glass plates were cleaned with dilute nitric acid and then rinsed with distilled water. Electro-Deposition was carried out in an electrochemical cell containing an aqueous solution of 0.1M sodium acetate and 0.01M Cupric Acetate. The temperature of the bath was maintained at 55^0C. Bath was stirred continuously using a magnetic stirrer (Both of these facilities were available in the magnetic stirrer heat bed used). The counter electrode was a platinum plate and the reference electrode was a saturated calomel electrode (SCE). Electro-deposition was carried out for about 60 minutes. This was the optimal time duration for depositing Cu_2O thin films in the apparatus which we have used. Deposition of Cu_2O is due to the following reaction

$$2Cu^+ + H_2O + 2e \rightarrow Cu_2O + 2H^+$$

Throughout the electro-deposition process, a cathodic potential of 200mV vs. SCE was maintained with the use of a potentio-stat device. This potential was selected to avoid the deposition of other phases of copper [4]. The chemical concentration and the potential were carefully controlled to obtain n-type thin films and the type was confirmed using the spectral responses mesurments [4]. The spectral response measurements were obtained in an electrochemical cell containing 0.1M sodium acetate solution. The photo response was measured using the phase sensitive detection method to monitor the photocurrent signal produced by the chopped monochromatic light beam. The experimental setup consisted of a lock in amplifier, monochromator, potentio-stat and PC.

Figure 1 shows some of the photo response graphs obtained for deposited Cu_2O thin films. As it could be seen the photo current has remained in the positive region for all the wave lengths. This confirmed that the thin film indeed was n-type. If it remained in the negative side it confirms that the thin film belongs to a p-type while if the current is not negative or positive for the entire spectrum band, then it is a mixture of both n and p-types [4].

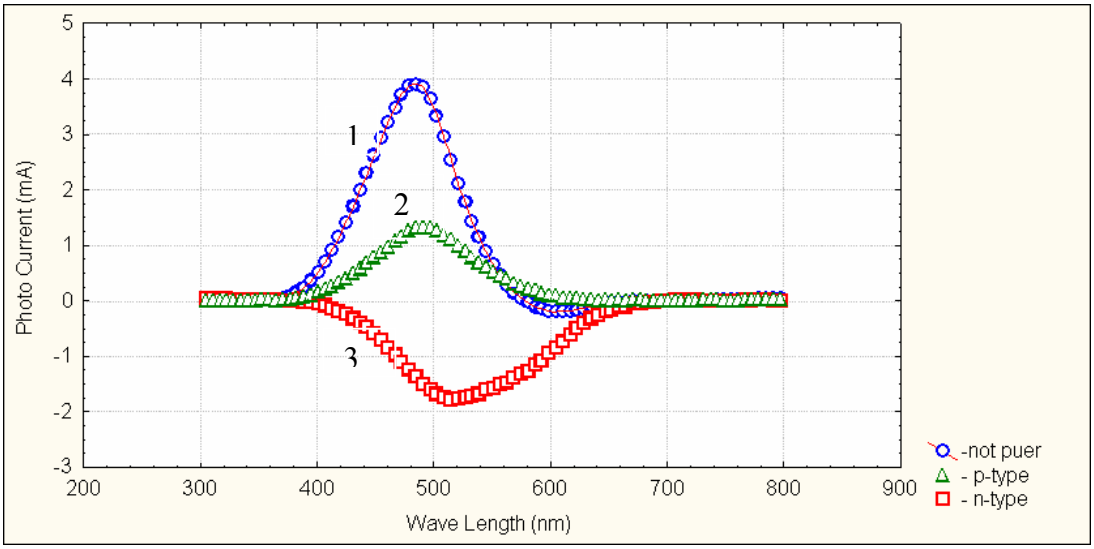

Figure 1. Curve 1 - The photo current is neither purely positive nor negative if the thin film is of both types. Curve 2- The photo current remains in the positive region if the thin film is of p-type. Curve 3– The photo current remains in the positive region if the thin film is of p-type [4].

In order to measure the resistance it was required to make the electrical connections on the Cu_2O film and in doing so, extra attention was taken to avoid short circuitry with the substrate (ITO plate). This task was accomplished by making the connections using a conductive silver ink (commercially available product under the brand "circuit works", product name – CW2200MTP). The paint consisted of Silver(7440-22-4), Polypropylene glycol methyl ether acetate(108-65-6), Ethylene glycol monobutyl ether acetate(112-07-2), n-butyl acetate(123-86-4) and Acrylic resin. The connections on the thin film with the use of the above mentioned conducting silver ink were made mainly using two methods.

In the first method Cu_2O thin film was deposited on ITO plate for long time durations (60-90mins) to make sure that the whole surface is coated with a strong Cu_2O film evenly. It was important to make sure that the electro-deposited part of the conducting surface is entirely covered with the deposited Cu_2O to avoid possible short circuitry which might occur after making the connections. This was done by visual inspection of the deposited film by placing it in front of a bright light and inspecting the deposition from the back side of the ITO plate. Then with the use of a small home made apparatus the connections were made on the thin film as shown in Figure 2.

Figure 2- Electric connections on the thin film, first method

As mentioned earlier, the conductivity of ITO plate is attributed to a very thin layer of ITO coating coated on one side of a high quality glass plate. In the second method of making the connection, a set of very thin lines were drawn on the ITO plate using a diamond pin (glass cutter) for removing the ITO layer on the top of these lines. This made several electrically isolated stripes on the plate. Then after the deposition of Cu_2O, the connections were made between the stripes by dropping conductive ink drops in the middle of the scratched lines, as there in Figure 3.

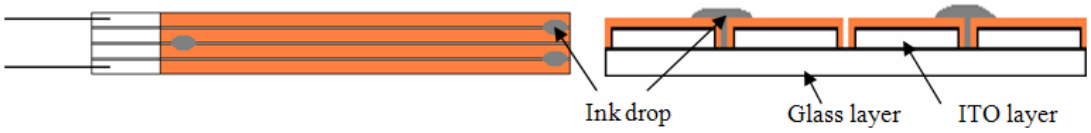

Figure 3 - Electric connections on the thin film, second method

As shown in the Figure 3, the wires were connected to the ITO sections on either side of the plate.

In order to create different environmental conditions in the vicinity of the Cu_2O thin film, the best method was to enclose the Cu_2O thin film in an air-tight chamber and to control the concentrations of gases inside that chamber. To accomplish this task, a Perspex gas chamber was made. Perspex is an Inert material (Does not react with most of the gases), transparent (Thin film could be illuminated) and a good thermal insulator (to keep steady temperatures inside the chamber).

To control parameters such as light (Cu_2O semiconductors have a direct energy gap of 2eV. This strongly implies the necessity for photo control over the period of experimentation.), the temperature (The conductivity of the semiconductors is very sensitive to the temperature. Therefore the temperature fluctuations must be kept to the minimum possible during the period of experimentation), and Gauss cage shielding (As the variations in the resistance could be quite small, powerful amplifying circuits were needed to be used. As a matter of fact all the efforts were made to avoid the possible sources of noises which could contribute to have signal distortions) a secondary enclosure was made. It was made out of regiform for better tempreture control for longer time durations. To form the Gauss cage, a thin conducting Aluminium foil was glued on to the inside wall of the box. The opening was made at the top of the box and messuers were taken to minimize the light leakages from in to and out of the enclosure.

3. RESULTS AND DISCUSSION

Gas flows

In order to check the reproducibility and to observe the conductivity changes, N_2 and O_2 were used. The thin films were subjected to alternate gas flows of N_2 and O_2 roughly a day after the deposition of the thin film and 7 weeks letter. The corresponding graphs are shown in Figure 4. The peaks correspond to O_2 whereas valleys correspond to N_2.

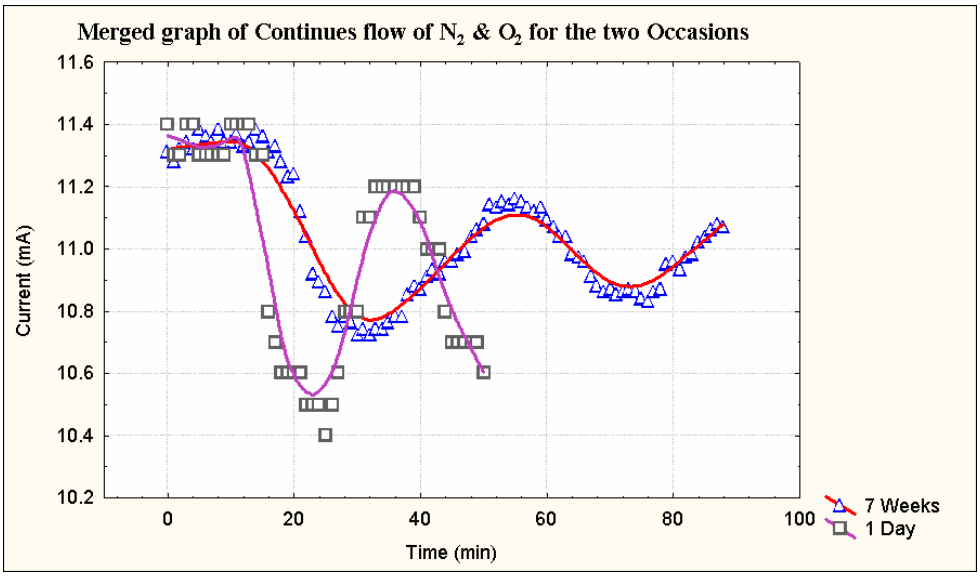

Figure 4 – Response to alternative gas flows of O_2 and N_2 in, one day after the deposition and 7 weeks later.

Fixed concentrations (O_2)

First the gas chamber was completely filled with N_2 and was left to stabilize for an hour. Then a measured volume of O_2 was inserted to the gas chamber and the changes in the resistance were measured and are given in Table 1. This behaviour is shown in Figure 5 and Figure 6.

Table 1. The change in resistance observed due to 15ml and 5ml gas flows of O_2.

Time left in N_2 to stabilize (min)	Volume of O_2 inserted (ml)	O_2-N_2 molar ratio	Increase in Resistance when exposed to O_2 (Ω)	Time taken to Stabilize when exposed to O_2 (min)
60	15	0.712	13	60
320	5	0.311	5	300

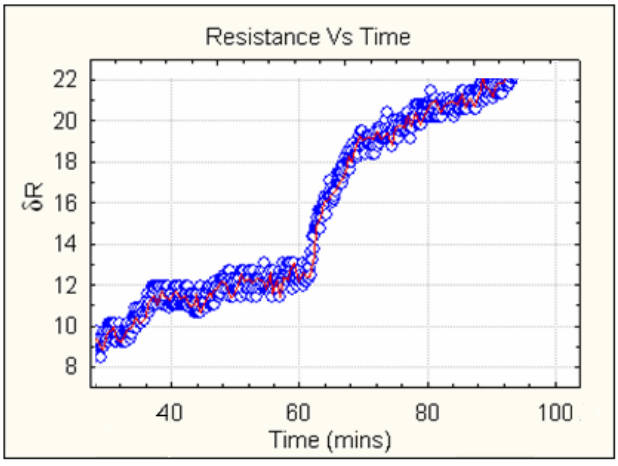

Figure 5. The change in resistance seen due to 15ml of O2

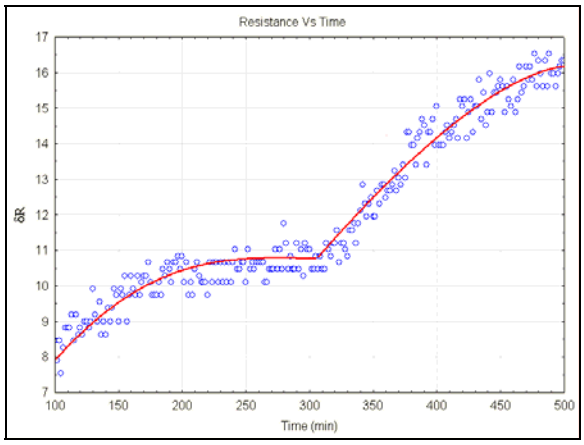

Figure 6 - The change in resistance seen due to 5ml of O2

The lowest volume of O_2 which produced an observable difference in the thin film resistance was found to be 5ml. The thin film produced a difference of nearly **5Ω** in the presence of 5ml of O_2 (in the gas chamber). The volume of the gas chamber was 21.07ml. The maximum error which could be present in the readings due to the technique and the instruments was found experimentally, and was found to be $\pm 0.8\ \Omega$.

LP gas

The thin films were found to be sensitive to LP gas too. Concentration of 0.311 molar ratio of LP gas: N_2 caused changes in the resistivity of the thin films. Due to some inconsistencies the study is still under way to analyse the response of these thin films to LP gas.

4. CONCLUSIONS

In this study, the sensitivity of n-type Cu_2O thin films was tested for both oxygen and LP gases. It was found that Cu_2O was sensitive to both of these gases. As the gas sensitivity is dependent on the grain size, the use of nanocrystalline films, are likely to improve the sensitivity further. The instability and the nature of the electric connection also imposed limitations in detecting smaller concentrations. The connections can be further improved by evaporating gold on to the thin film in the form of a mesh to increase the sensitivity.

Unlike most of the gas sensors that works only at high temperatures [2], n-type Cu_2O thin films were found out to be gas sensitive even at the room temperature. The material was also found to be sensitive to LP gas which is hazardous. Thus if the sensitivity of the n-type Cu_2O thin films can be further improved by improving the electric connections and also by making structural improvements, n-type Cu_2O thin films would have a promising future as a successful gas sensor.

REFERENCES

1. Chambell M, Sensor Systems for Environmental Monitoring, Springer, 149-152 (1997).
2. Kousuke Ihokura, Joseph Watson, The Stannic Oxide Gas Sensors, CRC Press, (1994).
3. Shiv K.Guptha, K.Ashwal Dinesh, Science and Technology of Chemiresistor Gas, Nova Science Publishers (2007).
4. SiripalaW, Weerasingha.W.J.L.D and Jayanetti J.K.D.S, Ceylon Journal of Science: Physical Sciences **12**, 67-72 (2007).
5. Radislav A. Potyrailo, Eric J. Amis, Contributor Radislav, A. Potyrailo, Eric J. Amis, High throughoutput analysis A tool for combinatorial materials science, Springer, (2004).
6. Cosandey Frederic, Skandan Ganesh and Singhal Amit, Materials and Processing Issues in Nanostructured Semiconductor Gas Sensors, JOM-e (2000).
7. Andreas Mandelis, Constantinos Christofides, Contributor Andreas Mandelis, Constantinos Christofides, Technology of Solid State Gas Sensors, Wiley-Interscience, (1993)