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THE EFFECTS OF PH VALUE ON THE PREPARATION OF COPPER OXIDE THIN FILMS BY DIP COATING TECHNIQUE

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ABSTRACT

Cupric oxide (CuO) thin films were deposited on the silicon substrate by dip coating technique. The starting material used was copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) which dissolved in de-ionized water and lactic acid while sodium hydroxide (NaOH) was used to control the pH of the solutions. Various pH values of solutions varying from 12.0, 12.3 and 12.5 were optimized in order to determine the optimum condition for dip coating process. The phase structure and morphology of the thin films were investigated by a X-ray diffraction (XRD) and a field emission scanning electron microscope (FESEM), respectively. Meanwhile, the thickness of the films was measured using surface profiler and confirmed with FESEM cross-section. The electrical properties were determined using a four-point probe instrument. The XRD pattern revealed that the deposited films are polycrystalline in nature with monoclinic CuO phase formation. Morphological studies revealed that the individual petals becomes larger, start to become more dense and then formed porous flower-like structure with completely covers over the substrate surface as the pH value increased. The film thickness was 19.6 µm at pH 12.0 which increased to 25.3 µm and 52.4 µm at pH 12.3 and pH 12.5, respectively. The film showed good resistivity at pH 12.5 with estimated value around 3.8019×10^3 Ω.cm compared to the others. Consequently, it was observed that various pH value has strong effects on the structural, morphological and electrical properties.

Keywords: copper oxide, P-type semiconductor, dip coating, pH value, thin film.

INTRODUCTION

Copper oxide is a p-type semiconductor which is categorized into transition metal oxide group. Copper oxide is one of the important metal oxide which has attracted recent research because of its low cost material, natural abundance of starting material (Cu), nontoxicity, excellent reactivity and reasonably good electrical and optical properties (Yang *et al*., 2013). It is also has many interesting characteristics such as super thermal conductivity, photovoltaic properties, high stability and antimicrobial activity. Recently, CuO have been widely investigated for various applications such as in solar cell technology (Kumar *et al.*, 2013), gas sensing devices (Aslani & Oroojpour, 2011; Li *et al*., 2008), magnetic storage media, lithium ion batteries, field emission devices, magnetic resonance imaging and photo catalysis (Nithya *et al*., 2014).

As an important p-type semiconductor, copper forms two well-known stable oxides which is cupric oxide (CuO) known as tenorite and cuprous oxide (Cu_2O) as a cuprite (Khojier, Savaloni, & Sadeghi, 2014). These two oxides have different physical properties, different colours, crystal structures and electrical properties. Both the tenorite and cuprite have a band gap energy of 1.21 eV to 1.51 eV (Armelao *et al*., 2003) and 2.10 eV to 2.60 eV (Zoolfakar, 2013), respectively. Compare to Cu_2O, CuO is more thermally stable materials because of stability of CuO with high oxidation number (Samarasekara, 2010). CuO is unique amongst the monoxides of 3d transition elements having a square planar coordination of copper by oxygen in the monoclinic structure with lattice parameter a = 4.6859 Å, b = 3.4283 Å, c = 5.1232 Å and β = 99.541°

(Marabelli, Parravicini, and Salghetti-Drioli, 1995). In the (100) plane, each copper atom is linked to four coplanar oxygen atoms at the corner of a rectangular parallelogram and each oxygen atom is linked to four copper atoms in the form of a distorted tetrahedron (Ravichandran, 2009). The chain traverse the structure in the [100] and [110] directions and alternate in the [001]. Each type of chains is arranged in the [010] direction with a separation between the chains of about 2.7 Å (Zoolfakar, 2013).

To date, various type of CuO thin film based gas sensors have been fabricated by the chemical vapour deposition, electrode position, thermal evaporation, spray pyrolysis technique, plasma evaporation, reactive direct current (DC) sputtering and radio frequency (RF) magnetron sputtering (C. Dhas, D. Alexendar, 2014). However, all these techniques requires sophisticated specialized setup and need a high temperature of deposition. Among of the thin films depositions method, dip coating technique is a very simple and low cost method (Ray, 2001). Dip coating technique also have other advantages such as easy control of film thickness, fine microstructure, low temperature sintering and possible to deposit a variety layers with good homogeneity of films (F.Ozyurt Kus, T.Serin 2009). In 2001, Ray *et al.* reported a sol-gel dip coating technique for CuO thin films on glass and quartz substrate (Ray, 2001). The sample were deposited with a withdrawal speed of 79.8 mm/min at different annealing temperature range from 360 °C to 500 °C. The films formed were uniform with black in colour and formed CuO phase at annealing temperature between 400 °C to 500 °C. While Armelao *et al.* prepared the CuO thin films on silicon substrates by dip coating technique

with a withdrawal speed of 70 mm/min (Armelao *et al.*, 2003). The CuO thin films results in tenorite phase at 900 ^{o}C of annealing temperature with average crystallite size less than 20 nm.

In this work, CuO thin film were prepared by dip coating technique and the effects of pH on the properties of these materials have been studied. Structural, surface morphological and electrical properties of the deposited films were investigated by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and four point probe instrument.

EXPERIMENTAL PROCEDURE

A flow diagram of the experimental procedure is given in Figure-1. In this experiment, copper (II) sulphate pentahydrate $(CuSO_4.5H_2O)$ were used as a starting material of the sol-gel method while de-ionized water and lactic acid were used as a solvent and the stabilizer, respectively. Several solutions with different pH are prepared to investigate the effect of pH on the thin films characteristics. To prepare the CuO thin films, copper (II) sulphate pentahydrate was dissolve in a mixture composed of lactic acid and deionized water. The solution was stirred in a reagent bottle on magnetic stirrer at a room temperature until it dissolved and completely mixed. Then, sodium hydroxide (NaOH) were added into solution in a specific quantity to control the pH of solution. The solution pH was measured using pH meter until the temperature is drop to 24 ^{o}C. Afterwards, the solution was kept for 24 hours at room temperature to ensure that the solution were completely mixed. A dip coating method was used to obtain the thin films in this experiment.

The silicon substrates were cleaned by dipping into dilute hydrofluoric acid (HF) and rinsed with deionized water before the deposition process. The silicon substrates is then dried with nitrogen gas (N_2). Next, the substrates were dipped and withdrawn from the precursor solution at a withdrawal speed of 180 mm/min under ambient conditions. The solution was stirred while the deposition process occurred. The as-coated gel film is then dried at 150 ^{0}C for 5-10 min on a hot plate to evaporate the solvent. The deposition and dried process were repeated for several times onto the same substrate. After coating, the thin films were annealed for 1 h at 400 ^{0}C in a furnace to make them polycrystalline.

Several fabrication tools were used to characterize the CuO thin films. The characterization tools are used to obtain the properties of the thin films. The structural properties of the CuO thin films were characterized by X-ray diffraction using a PANalytical X-Pert Powder with Cu Kα radiation of wavelength λ = 0.1540 nm, in the range of 20° – 80°. The surface
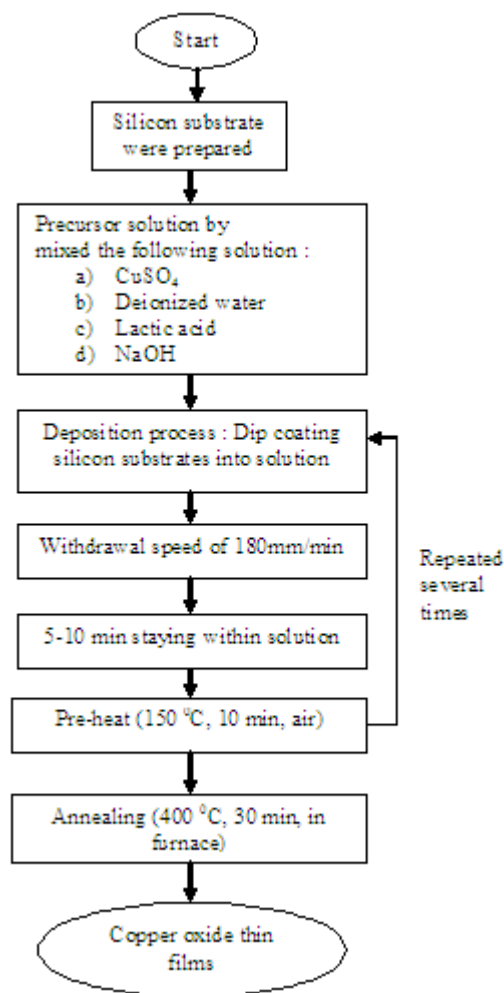

Figure-1. Flow diagram of the experimental procedure.

morphology and grain size of the CuO thin films were examined by a field emission scanning electron microscope (FESEM, model : JSM-7600F). The thickness of the CuO thin films were carried out by using a stylus profilometer while the resistivity of the CuO thin films were determined by using a four point probe instrument.

RESULTS AND DISCUSSIONS

Structural properties

The structural properties of CuO thin films are investigated by X-ray diffraction using Cu Kα radiation with λ = 0.1540 nm in the range of 2θ = 20° – 80°. The CuO thin films are prepared by the dip coating technique at various pH value of solutions. XRD pattern of CuO thin films at different pH value of solutions were shown in Figure-2.
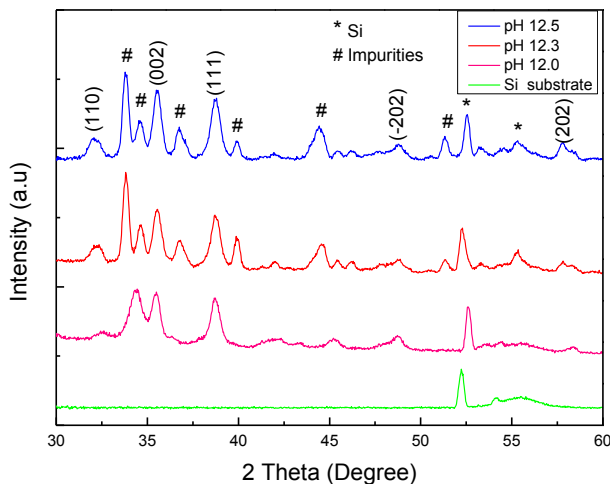
Figure-2. XRD pattern of CuO thin film at different pH value (a), pH 12.5 (b), pH 12.3 (c), pH 12.0.

It can be seen that the dominant peaks at 38.7° and 35.5° corresponding to the reflections from (111) and (002) planes. While there are other peaks which are 33.8°, 48.7° and 57.8°, respectively were indexed to (110), (-202) and (202) planes. These indicate that all samples are polycrystalline and matched the characteristics peaks due to monoclinic phase of CuO (ICSD 98-008-7124). Moreover, increases in pH value from 12.0 to 12.5 induce a stepwise increase in the diffraction peak intensities. XRD pattern of CuO thin film was narrower at major peak of 35.5° which corresponding to the reflections from (002) planes as the pH value increase to pH 12.5 due to improvement of the crystallinity in the films. Furthermore, it can be seen that the impurities peak formed at pH 12.3 and pH 12.5 while there is no impurities peak at pH 12.0. Hence, it is clear that the impurities peak formed as the pH value increased due to increase in sodium hydroxide (NaOH) while control the pH value of solutions. According to Debye Scherrer's equation, the crystallite size (D) of the films can be calculated using full-width at half maximum intensity (FWHM) expressed in radians,

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

Where
D = crystallite size
β = full width at half maximum (FWHM) of the strongest diffraction peak
θ = the diffraction angle
λ = the x-ray wavelength (0.145 nm)
κ = (~0.89) Scherrer's constant

The crystallite sizes of samples with pH 12.0, pH 12.3 and pH 12.5 were about 20 nm, 25 nm and 27 nm, respectively. From the patterns peak width, the lower crystallite size has been observed at pH 12.0. So, it is

observed that the crystallite size of CuO films increases as the pH value increase. The full-width at half maximum value was found to be decreased at each reflection with increasing in pH value of solutions. It is clear that pH 12.5 have the best crystallization level as compared to others. The results are summarized in Table-1. As seen from Figure-2, it can be concluded that the pH value of solutions mainly affect the microstructural properties of the deposited films.

Table-1. Microstructural properties of CuO thin films at different pH value of solutions.

pH value	d-spacing [Å]	FWHM (°)	Crystallite size (nm)
12.0	2.53024	0.4723	20.09
12.3	2.52641	0.3838	24.85
12.5	2.52507	0.3542	26.98

The film thickness is estimated using stylus profilometer and confirmed with FESEM cross-section. The variation of CuO film thickness with different pH value is presented in Figure-3. The lower value of film thickness is observed at pH 12.0 which is the estimated value is 19.6 µm. While the maximum thickness of the film is observed at pH 12.5 which is 52.4 µm. Based on this results, it can be conclude that the thickness of film is increases with increasing in pH value which can be related with the improvement of crystal quality based on XRD data.
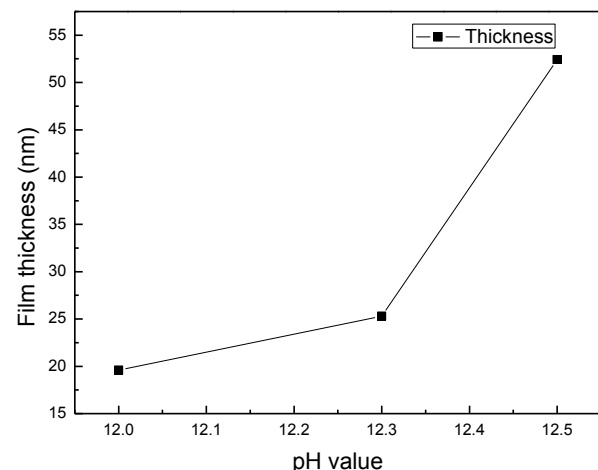

Figure-3. Film thickness of dip coated CuO thin films at different pH value.

Surface morphology

The pH value of solutions is one of the key factor to the growth of CuO thin films. In order to understand the
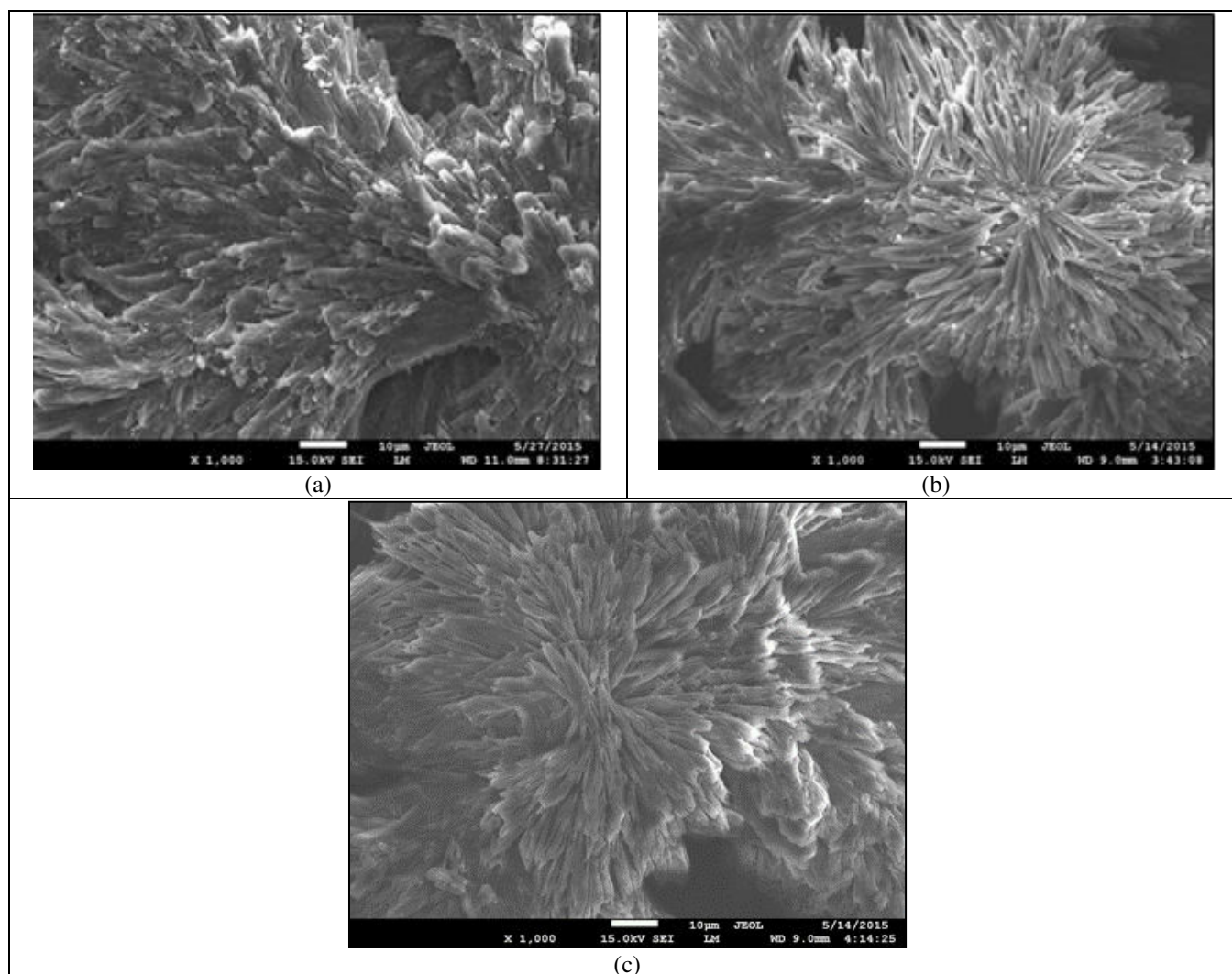
(a)

(b)

(c)

Figure-4. FESEM images of CuO thin films at different pH value (a) pH 12.0 (b) pH 12.3 (c) pH 12.5

influence of pH value on the process, a series of experiment were performed with different pH value. Surface morphology of CuO structures prepared at different pH value are shown above in Figure-4(a), 4(b) and 4(c).

Figure-4(a) represents a FESEM images observed for solution with pH 12.0. It shows that the surface of the deposited film was not completely formed and revealed an incomplete coverage of the substrate surface. The films surface shows an irregular morphology with typical more porous structure. Starting from pH 12.3 and onwards, there are growths of CuO flower like structure and the deposited film has complete coverage over the substrate surface as shown in Figure-4(b) and 4(c). The FESEM images in Figure-4(b) shows a quite uniform and individual petal like structure was formed. While in Figure-4(c), it can be seen that the petals start to become denser until it cannot be defined as individual petals. As the pH value of the solutions increased from pH 12.0 to pH 12.5, the morphology of structure remained the same and appeared to be flower like structure which is porous. It can be seen that the flower like structures were aggregated and the deposition film is not homogeneous. The formed of CuO flower like structures are bigger as the diameter of morphology is approximately 2 µm. Hence, the observed size increases with increasing of pH value as well as increased in crystallite size that can be confirmed from XRD data. It can be concluded that the pH value affect to the collisions, which leads to the formation of larger grains during the dipped in precursor of film formation. The larger grains are formed by agglomeration of the crystallites.

Electrical properties

A four point probe instrument was used for resistivity measurement of CuO thin film on silicon substrate. Figure-5 below shows the resistivity of CuO thin films at different pH value ranging from pH 12.0 to pH 12.5. Note that the obtained values were the averaged of the five measurements. The result show that the resistivity of CuO thin films with pH 12.0, pH 12.3 and pH 12.5 were about 0.489×10^3 Ω.cm, 0.5704×10^3 Ω.cm and 3.8019×10^3 Ω.cm, respectively. So, it is observed that the resistivity increases with increasing in pH value. Based on the electrical results obtained, it can be concluded that the sample is resistive.
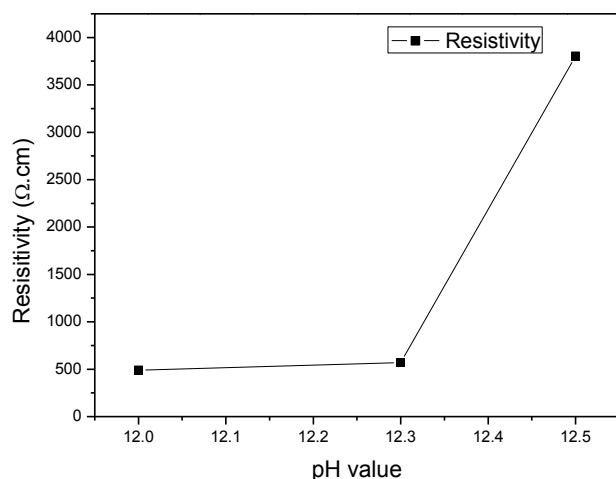
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Figure-5. Electrical properties of CuO thin films at different pH value of solutions.

CONCLUSIONS

Copper oxide thin films were deposited by using dip coating technique at various pH values varying at 12.0, 12.3 and 12.5. X-ray diffraction pattern showed that the intensity of dominant peak at 35.5° and 38.7° which corresponding to (002) and (111) planes and confirmed the monoclinic CuO phase formation. The dominant peaks which is 35.5° and 38.7° was more narrower at pH 12.5 as the full-width at half maximum value decreased with increasing in pH value of solutions. For that reason, it is confirm that pH 12.5 have the best crystallization level as compared to other pH value. For the surface morphology, the individual petals becomes larger, start to become more dense and then formed flower like structure porous with completely coverage over the substrate surface as the pH value of solutions increased to pH 12.5. The film exhibited a quite good resistivity at pH 12.5 with estimated value around 3.8019×10^{3} Ω.cm and the sample was found to be resistive. Hence, the pH values do influence the formation of thin films and pH 12.5 was the best condition observed.

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REFERENCES

Armelao, L., Barreca, D., Bertapelle, M., Bottaro, G., Sada, C. and Tondello, E. 2003. A sol-gel approach to nanophasic copper oxide thin films. Thin Solid Films, 442(03), 48-52.

Aslani, A. and Oroojpour, V. 2011. CO gas sensing of CuO nanostructures , synthesized by an assisted solvothermal wet chemical route. Physica B: Physics of Condensed Matter, 406(2), 144-149.

C. Dhas, D. Alexendar, A. C. *et al.* 2014. Preparation and Characterization of CuO Thin Films Prepared by Spray Pyrolysis Technique for Ethanol Gas Sensing Application. Applied Sciences, 8, 671-684.

F.Ozyurt Kus, T.Serin, N. S. 2009. Current transport mechanisms of n-ZnO/p-CuO heterojunctions. pdf. Journal of Optoelectronics and Advanced Materials, 11(11), 1855 -1859.

Khojier, K., Savaloni, H. and Sadeghi, Z. 2014. A comparative investigation on growth, nanostructure and electrical properties of copper oxide thin films as a function of annealing conditions. Journal of Theoretical and Applied Physics, 8, 116.

Kumar, V., Masudi-Panah, S., Tan, C. C., Wong, T. K. S., Chi, D. Z. and K, D. G. 2013. Copper Oxide Based Low Cost Thin Film Solar Cells. IEEE, 443-445.

Li, Y., Liang, J., Tao, Z. and Chen, J. 2008. CuO particles and plates: Synthesis and gas-sensor application. Materials Research Bulletin, 43(3), 2380-2385.

Marabelli, F., Parravicini, G. B. and Salghetti-Drioli, F. 1995. Optical gap of CuO. Physical Review B, 52(3), 1433-1436.

Nithya, K., Yuvasree, P., Neelakandeswari, N. and Rajasekaran, N. 2014. Preparation and Characterization of Copper Oxide Nanoparticles. Advanced Materials Research, 6(3), 2220-2222.

Ravichandran, R. 2009. Fabrication and Characterization of p-type CuO / n-type ZnO Heterostructure Gas Sensors Prepared by Sol-Gel Processing Techniques.

Ray, S. C. 2001. Preparation of copper oxide thin film by the sol-gel-like dip technique and study of their structural and optical properties. Solar Energy Materials and Solar Cells, 68, 307-312.

Samarasekara, P. 2010. Characterization of Low Cost P-Cu2O/N-Cuo Junction. GESJ: Physics, 2(2), 3-8.

Yang, C., Su, X., Wang, J., Cao, X., Wang, S. and Zhang, L. 2013. Facile microwave-assisted hydrothermal synthesis of varied-shaped CuO nanoparticles and their gas sensing properties. Sensors and Actuators, B: Chemical, 185, 159-165.

Zoolfakar, A. S. 2013. Tuning and Engineering of ZnO and Cu x O for Sensor, Solar Cells and Memory Devices Tuning and Engineering of ZnO and Cu x O for Sensor, Solar Cells and Memory Devices.