Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 2458-9403
Vol. 4 Issue 7, July - 2017

The thickness effect of CuO thin films on electrical and gas sensing properties

Sameer Atta Maki & Ons Ahmed Mahmoud
Collage of education for pure science Ibn AL-Haitham university of Baghdad, Iraq

***Abstract*— Copper Oxide (CuO) thin films was prepared by thermal evaporation using Oxidation thermal at different thickness (100-150-200)nm, the structural properties examination by (XRD) reveals that this films have polycrystalline nature with monoclinic structure [1],the optical energy gap is to be found (2.1-2.35-2.4)eV for thickness (100-150-200)nm respectively in a previous research it is[1], the concentration and the mobility of carriers is calculated from Hall effect measurement , the activation energy is be found from the value of slope from plots of the variation in conductivity versus1000/T, these films applicated on gas sensor by studies relation the variation between the sensitivity and the time, Finally we conclude The (CuO) films at (200nm) showed slightly best sensitivity for gases than others films at (100,150nm) but it is not optimal, the aim of this studies utilization CuO thin films at low thickness in sensing (CO,CO2) gases.**

Keywords*— *Sensitivity, Conductivity, Hall effect, Mobility, concentration.

INTRODUCTION

Copper Oxide is naturally a p-type Semiconductors with a band gap in the visible or near infrared regions[2], have been studied for several season such as , natural abundant of starting materials Copper [3], Nontoxic nature, [1,2,4],economic and cheap[1,4],good electrical and optical properties[2], the easiness of production by copper oxidation, there are two Crystalline forms of copper oxides, cuprous oxide or cuprite(cubic Cu_2O) and cupric oxide or tenorite (Monoclinic CuO) [2,3], Both (CuO) monoclinic and (Cu_2O) curbic are p-type conductivity with a band gap of (1.3-2.1)eV[1] and (2.1-2.6)eV respectively [3,4], CuO thin films could be used in (Solar cells, photo sensor, Lithium – copper Oxide electrochemical cells, photo thermal and gas sensing application [5], superconducting devices[2,4], catalytic application [2], photovoltaic and electronic device fabrication[3]), In this paper we used CuO as gas sensor, the working principle of metal- oxide semiconductors based on change in resistance of gas-sensing materials result from changing in concentration of chemisorbed oxygen on surface gas sensor materials [6], depending on type of materials and gases ,for example reducing gases lead to increase of the conductivity for n-type semiconductors and a decrease for p-type materials respectively, whereas the effect of oxidizing gases is vice versa [6],Typically, chemical sensors consist of two main parts, a receptor and a transducer ,the receptor transforms chemical information into a form of energy, which can be measured by the transducer, the transducer converts this energy into a useful typically electrical, analytical signal [7], the improvement in performance of Copper Oxide for gas sensing by electron, Doping, annealing, Ultraviolet, plasma and irradiation[8] because this ways modified surface structure and the gas sensing properties are related to surface structure since this gases are react (adsorb) with surface[8],the gas sensing properties of these metal oxide semiconductors are influenced by many factors like the operation temperature, morphology and chemical composition [9] ,there are several method to preparation thin films some these deposition techniques (Thermal evaporation, sol-gel, pulsed laser deposition, spray pyrolysis)[1],(spin coating, dip coating) [10], SILAR [3,10], there are various types of metal Oxides used as sensing materials such as (NiO, ZnO, SnO_2 ,TiO_2, WO_3, In_2O_3, Fe_2O_3, and Y_2O_3)[11], Recently, CuO is used to enhance the gas sensor response more than the others common metal Oxides like (ZnO, SnO_2)[11],With regard to (CO_2)gas Detection have been used and studied mixed oxide composites like as ($BaTiO_3$ -CuO)by several research as in [12],as well the spinel oxides used to detection the gases such as (Cl_2, H_2, NH_3) but never ,one of these oxides (spinel ferrite) used for carbon dioxide detection [12], In this paper, We studied the variation of thickness on the electrical and gas sensing properties of (CuO)thin films to be used in fabricating gas sensor.

Experimental:

Firstly after cut and cleaned the slides with distilled water and alcohol in an ultrasonic cleaner for 15 min, before it we measured the thickness of this film by using gravimetric method, we recorded the mass of glass slides before and after deposition, we can calculate the thickness by using the mass law[13]

$$t = \frac{\Delta m}{\rho A} \dots \dots \dots (1)$$

Where ρ: is the mass density of the material($6.31 g/cm^3$), A is the film area on substrate in cm^2.

Secondly we measured deposited the metal Copper on glass and silicon(n-type) substrate by thermal evaporation technique in high vacuum system with thickness (100-150-200)nm at RT, Thirdly we put this substrate in Furnace type (Vectoreen) to get Copper Oxide thin films at (523K) for one hour with exist air at rate flow (1.5)liter/sec, Fourthly we made masks, put on this films in order to become ready to deposit Aluminum pure metal at RT by using thermal evaporation technique in high vacuum system using Edward coating unit model (E306) with Tungsten boat, the distance between substrate and boat was about (9cm) to made electrodes to measurement (D.C)conductivity, hall effect and gas sensing properties, We put this films on (glass &Silicon) substrate in system gas sensing , this system is consist from a homemade gas test chamber connected with Vacuum system represented in rotary pump used to discharge this chamber from gas by a valve made from stainless steel behind this chamber is considered outlet gas from the chamber, the Chemical reaction to produce gas was occurred in canister made from glass connected with plastic tube into system by another valve is located on nozzle this canister used to control the flow rate of gas ,the sensing process occurred under (500Mbar) at (25°C).

We used two gases prepared by the Chemical reaction such as (CO, CO_2)

1-$CO\ gas$:

We used (20Mlitter)from Formic acid (HCOOH) with (20Mlitter)from sulfuric acid (H_2SO_4) diluted 30% in Distilled water with heating(70°C) to produce $CO\ gas$

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

2-$CO_2 gas$:

We used (40Mlitter) from sulfuric acid (H_2SO_4) and ($2gm$)from Calcium Carbonate($CaCO_3$) to produce CO_2 gas and Calcium sulphate dissolved in water.

$$H_2SO_4 + CaCO_3 \rightarrow CO_2 + CaSO_4 + H_2O$$

Results And Discussion:

1- Hall effect:

We used the Hall effect measurement system (HMS-3000) equipped from Ecopia, two electrodes of films connected with insulted copper wires and the ends of these wires connected with D.C power supply type Tandem, they are connected in series with an Ammeter type Kithley-616 Digital Electrometer, while the other two electrodes are connected with copper wires to voltmeter type Kithley -177Micro Voh Dmm [14] ,we notes that when increasing the thickness the concentration of carriers increase and the mobility of the carriers decrease.

Table.1 The variation of concentration and mobility of carriers with variation of thickness.

thickness (nm)	Concentration (cm^{-3})	Mobility ($cm^2/V.s$)
100	$3.778*10^{11}$	8320
150	$1.243*10^{12}$	1816
200	$8.358*10^{12}$	205.3

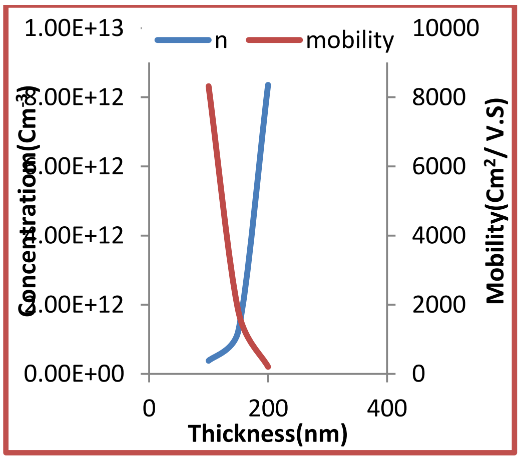

Figure.1 The Hall effect measurement for thickness(100-150-200)nm.

2-The electrical Conductivity measurement:

The electrical conductivity measurement by study the variation of resistivity with Temperature, we notes decrease resistivity with increasing temperature, and the Conductivity increased with the increase thickness of films, there are two activation energy at low and high temperature that confirmed the Polycrystalline structure ,The activation energy (E_a) is calculated from the slope of a curve lnσ versa (1000/T).we found CuO films,

Tabel.2 the values of the activation energy for (CuO) Thin films at different thickness.

Thickness(nm)	Ea_1 eV at (100-150)℃	Ea_2 eV at (50-100)℃
100	0.1725	0.0656
150	0.7676	0.0462
200	0.5175	0.0492

Tabel.3 the values of Conductivity for (CuO) Thin films at different thickness.

Thickness(nm)	
100	96.86
150	110.62
200	211.48

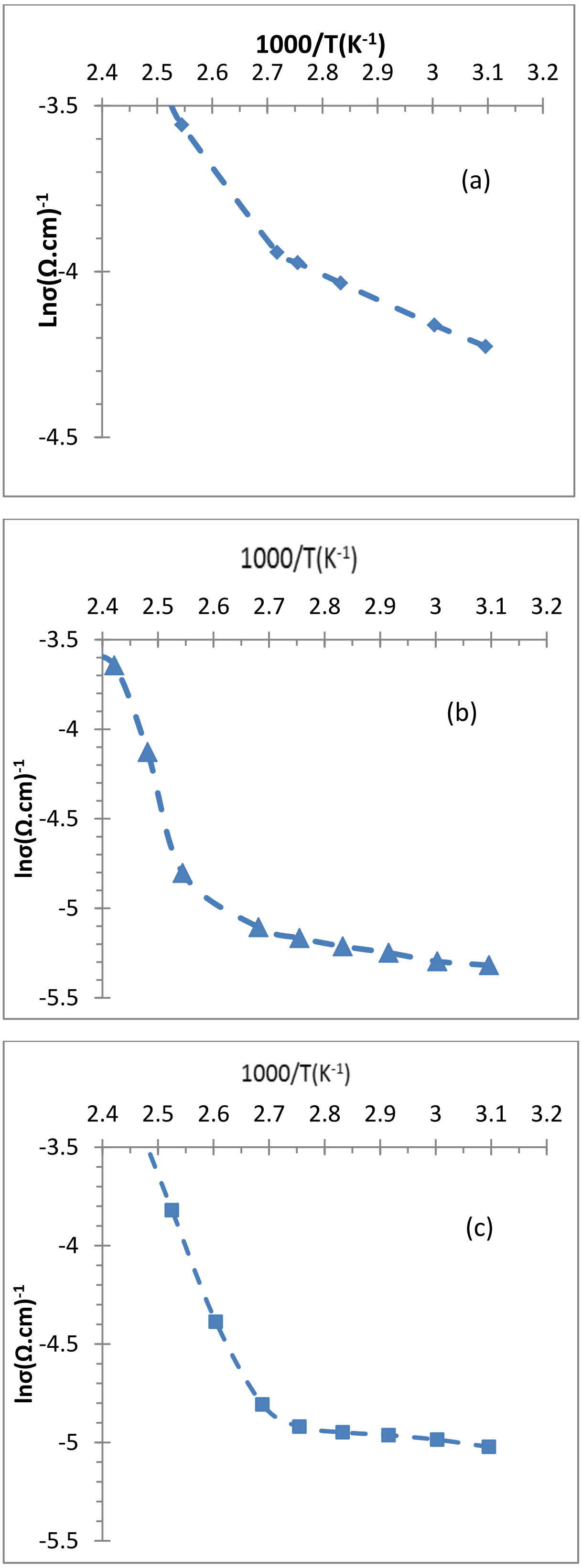

Figure.(2-a,b,c) The electrical conductivity (Lnσ) as a function of Temperature (1000/T)K for CuO thin films at (100-150-200)nm respectively.

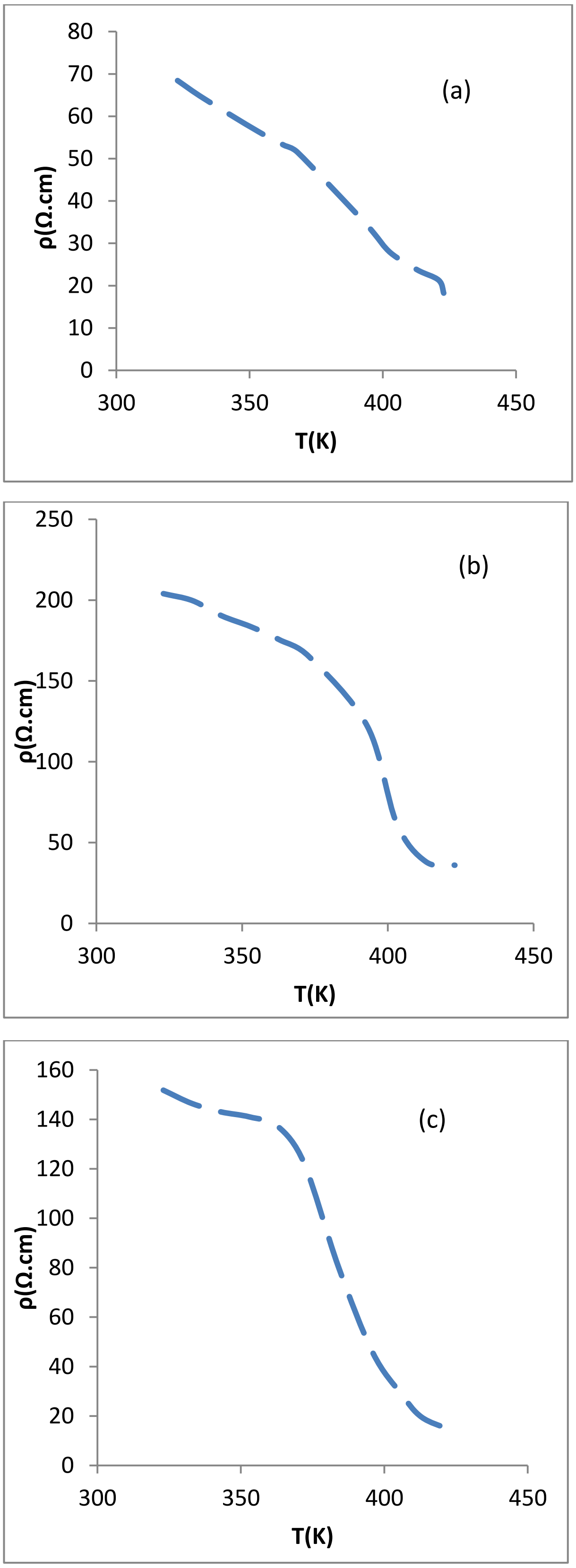

Figure.(3- a, b, c) The electrical resistivity as a function of Temperature (1000/T)K for CuO thin films at (100-150-200)nm respectively.

3- The gas sensing properties:

Gas Sensitivity Measurements.

The gas response ,sensitivity and selectivity of Oxide semiconductors depended on various factors such as (the dimensions, morphologies of the oxide nanostructures, composition of sensing material, donor concentrations, and charge carrier depletion or accumulation near the surface)[15], the gas sensitivity of these films were measured from recorded resistance was a function of time, It was observed that the resistance of CuO thin films increase when exposure to reducing gas(CO), and decreasing when exposure to oxidizing gas(CO_2). Gas sensor can be classified into three categories (a) solid electrolyte gas sensor,(b)catalytic combustion gas sensor,(c) semiconductor gas sensor[16], The sensitivity (S) is calculated from the equation.

$$Sensitivity = \left| \frac{R_{gas} - R_{air}}{R_{air}} \right| \times 100\% \ldots\ldots(6)$$

R_{gas}: the resistance of (CuO)thin film after exposure to gas.

R_{air}: the resistance of (CuO)thin film in air.

It was observed that the thin film at thickness (100nm),it showed slowly and negligible sensing for(CO) gas and non-sensitivity for gas (CO_2),also we noted the films have very week and negligible sensitivity at (150nm) for (CO, CO_2) respectively ,while the (CuO) films at (200nm) it showed slightly improvement in sensing for gas (CO, CO_2), So, in this case it was adopted that the optimizing (CuO) films for sensing gas at (200nm).

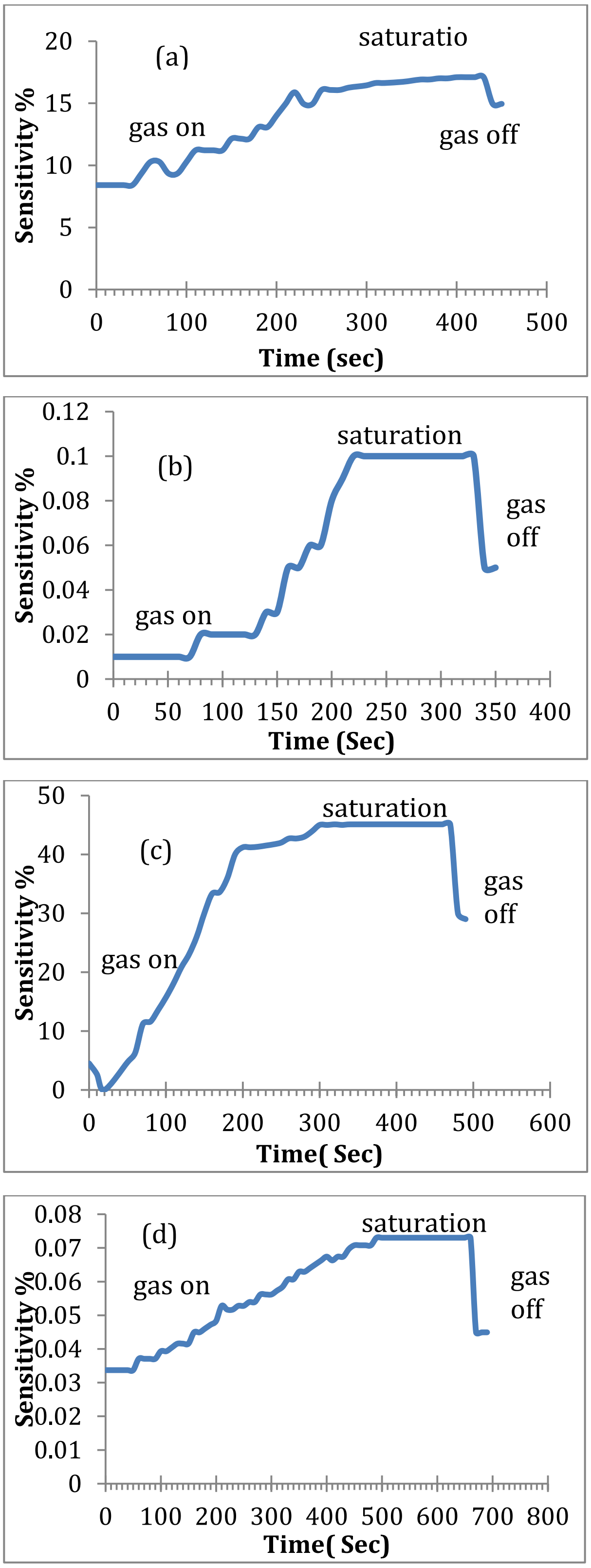

Figure.(4) (a, b)the sensitivity of CuO thin films on (glass, Si) substrate for (CO_2)gas and (c, d) showed the sensitivity of CuO thin films on (glass, Si) substrate for(CO) gas.

We notes from fig.3 the high response time of CuO thin films at 200nm on glass ,Si substrate for (CO_2) gas record (320sec)(230sec) respectively, for (CO) (290sec)(490sec) respectively, and we observed that all CuO films demonstrate response time and reach to saturation case, after discharge we note recovery time but didn't return to initial value before interaction.

Conclusion:

In Our research we studied the electrical and gas sensing properties of CuO thin films as prepared thermal Oxidation by using thermal evaporation in high vacuum, we observed the concentration of carriers and the Mobility of carriers, increase (decrease) with increasing thickness respectively, and the electrical conductivity varying with increase thickness, there are two activation energy for all thickness of CuO thin films this is confirmed the Polycrystalline structure of these films ,with regard to the gas sensing properties and the experimental data we concluded that the thin films of (CuO) at 200nm is the suitability for gas sensor Applications, since it's showed the high sensitivity for (CO)gas than (CO_2)gas, it was found (33%),(14%), In Futurity we suggest that this films of CuO with the same thickness doping by silver in order to improve the performance of these films about sensing gas properties or increasing thickness of (CuO) thin film above 500nm in order to develop commercial thin film gas sensor with high sensitivity.

Reference:

1- Sameer Atta Maki & Ons Ahmed Mahmoud (The thickness effect of CuO thin films on structural, Morphological and Optical properties), Journal of Multidisciplinary Engineering Science Studies (JMESS),vol.3(2017)(1555-1560).

2- Alireza Hojabri, Fatemeh Hajakbari, Nasrin Soltanpoor ,Maryam Sadat Hedayati,(Annealing temperature effect on the properties of untreated and treated Copper films with Oxgen Plasma),J Theor Appl Phys,(2014).

3- Kasim Uthman Isah, Muhammad Bakeko M.,Umar Ahmadu, Uno Essang Uno, Mohammed Isah Kimpa, Jibrin Alhaji Yabagi(Effect of oxidation temperature on the properties of copper oxide thin films prepared from thermally oxidized evaporated copper thin films),IOSR Journal of Applied Physics,vol(3),(2013),pp(61-66).

4- V.Figueiredo, E.Elangovan, G.Goncalves, P.Barquinha, L.Pereira, N.Franco, E.Alves, R.Martins, E.Fortunato, (Effect of post-annealing on the properties of copper oxide thin films obtained from the oxidation of evaporated metallic copper), applied surface science, vol.254(2008)(3949-3954).

5- C.Ravi Dhas, Dinu Alexander, A.Jennifer Christy, K. Jeyadheepan, A.Moses Ezhil, Raj and C.Sanjeevi Raja,(preparation and characterization of CuO thin films prepared by Spray Pyrolysis technique for ethanol gas sensing application), Asian Journal of Applied Sciences,vol.8(2014)(671-684).

6- G. Korotcenkov (The role of morphology and crystallographic structure of metal oxides in response of conductometric-type gas sensors), Materials Science and Engineering Reports : A Review Journal, Vol (61), (2008), pp(1-39)..

7- V. E. Bochenkov , G. B. Sergeev (Sensitivity , Selectivity and Stability of Gas - Sensitive Metal - Oxide Nanostructures), Metal Oxide

Nanostructures and their Applications, Vol (3), pages (31-52).

8- Dattarya Jundale, Shailesh Pawar, Manik Chougule, Prasad Godse, Sanjay Patil, Bharat Raut, Shashwati Sen, Vikas Patil,(Nanocrystalline CuO Thin Films for H_2S Monitoring: Microstructural and Optoelectronic Characterization),Journal of sensor Technology,vol.1(2011)(36-46).

9- Audrey Chapelle, Mohd H.Yaacob, Isabelle Pasquet, Lionel Presmanes, Antoine Barnabe, Philippe Tailhades, Johan Du Plessis, Kourosh Kalantar –Zadeh (Structural and gas-sensing properties of CuO-Cu_x Fe_{3-x} O_4 nanostructured thin films),Open Archive Toulouse Archive Ouverte,vol(153),(2010),pp(117-124).

10- S.S.Roy, A.H Bhuiyan, J.Podder (Optical and Electrical properties of copper Oxide Thin Films Synthesized by Spray pyrolysis technique),Sensors &Transducers,vol.191(2015),pp(21-27).

11- Mitesh Parmar and K.Rajanna (Copper(||)Oxide thin film for methanol and ethanol sensing),International Joural on Smart Sensing and Intelligent Systems,vol(4),(2011),pp(710-725).

12- A.Chapelle, F.Oudrhiri-Hassani, L.Presmanes, A.Barnabe, Ph.Tailhades,(CO_2 Sensing properties of semiconducting Copper Oxide and Spinel ferrite nanocomposite thin film),Open Archive Toulouse Archive Ouverte ,vol(256),(2010),pp(4715-4519).

13- Samir M Abdulalmohsin &Fouad Ajeel (study on structure and optical properties of CuO thin films prepared by chemical spray pyrolysis),Journal of Applied Physical Science International,vol.3 (2015)(178-184).

14- Zainab T.Abdulhamied (The Structural, Optical and electrical properties of NiO films prepared by RF-Sputtering as gas sensor), PHD.Thesis, Collage of education for pure science Ibn-Al-Haitham University of Baghdad.

15--kang-Min Kim, Hyun-Mook Jeong, Hae-Ryong Kim,Kwon-IL Choi, Hyo-Joong Kim and Jong-Heun Lee(Selective Detection of NO_2 using Cr-Doped CuO Nanorods),Sensors ,Vol(12),(2012),pp(8013-8025).

16- A.M.Azad, S.A.Akbar, S.G.Mhaisalkar, L.D.Birkefeld, and K.S.Goto (Solid – State Gas Sensors: A Review),Journal Electrochemical.Society, Vol(139),(1992).