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Fabrication of CuO and ZnO Semiconductors using an Electrical Furnace

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Abstract: ***Zinc oxide (ZnO)/cupric oxide (CuO) is a heterojunction with promising applications in electronic devices such as solar cells, chemical gas sensors, among others. In the present work, it is reported the fabrication of a copper oxide (CuO) and zinc oxide (ZnO) semiconductors using a homemade electrical furnace. CuO was obtained by thermal oxidation (1000 °C) of Cu foils, which were previously thinned from 300 µm to about 100 µm in a ferric chloride solution. ZnO layers were obtained in two steps: firstly, Zn layers were obtained on quartz substrates by atmospheric pressure thermal evaporation of Zn shaves. Then, thermal oxidation was performed to the Zn layers. The CuO and ZnO semiconductors were characterized by Raman scattering and scanning electron microscopy techniques.***

1. Introduction

The p-n junction is a structure composed by a p-type and n-type semiconductors. It is used in the electronic technology for fabrication of several devices such as diodes, transistors, thyristors, led´s, solar cells, integrated circuits, laser´s, among others [1-5]. Since silicon is the semiconductor most used at the industrial scale, the non-optical p-n based devices are mainly fabricated as homojunctions of p-type and n-type silicon layers [6]. Nowadays, there are many efforts to fabricate heterojunction p-n devices composed by p-type and n-type layers of alternate semiconductors. For example, the use of ZnO and NiO has been reported for fabrication of a p-n junction [7]. A p-n junction using a ZnO and Al_2O_3 as the active layer in a solar cell has allowed finding the highest conversion efficiency [8]. In fact, there are some optical devices than can be fabricated using semiconductor metal oxides [9-12]. ZnO and CuO are metal oxides with interesting properties for fabrication of a p-n heterojunction. Although there are many techniques to fabrication of ZnO and CuO, the main issue is reproducibility of the samples, which is usually resolved with the use of expensive and complex techniques. In the present work, we report the methodology for fabrication of CuO and ZnO layers with the use of a resistive furnace. For fabrication of pure CuO layers, the furnace was used as thermal oxidation system. For deposition of ZnO layers, the furnace was initially used for thermal evaporation of Zn, and then as thermal oxidation of the Zn layers.

2. Materials and methods

Thermal oxidation and thermal evaporation techniques were used to obtain CuO and ZnO semiconductors. Å). SEM images were obtained by scanning electron microscopy (SEM, JEOL JSM-6510LV). Raman measurements were recorded using a micro-Raman LabRam HR-800 system. A He–Ne laser(λ = 632 nm) was used to induce scattering. The laser beam was focused using a 50× lens and also it serves to recollect scattered light. A 600 lines mm^{-1} grating was employed; 100 acquisitions were averaged with an exposure time of 5 s each one.

Fabrication of Cu films

Copper (Cu) foils of 99.999% purity were used to form CuO by thermal oxidation. Prior to oxidation, the copper sheets were rinsed in Xylene, Acetone, Methanol and Hydrofluoric Acid to remove impurities and the native oxide, respectively, as it is shown in Figure 1.

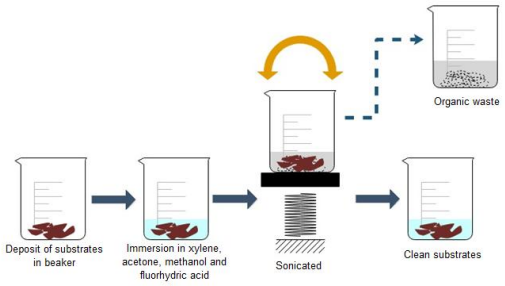


Figure 1: Preparation of copper substrates to remove impurities and native oxide over the surface of Cu

Oxidation of the Cu foils was carried out in a horizontal home-made resistive furnace for 24 hours at 1000 ° C using air flow, as shown in Figure 2. During oxidation, two types of copper oxide were formed: cuprous oxide (Cu_2O), which exhibits a p-type electrical conductivity and a band gap of 2.1 eV, and cupric oxide (CuO), which also exhibits p-type conductivity with a band gap of about 1.5 eV. It was found that when the temperature and time of oxidation increases, the CuO phase remains dominant until the Cu_2O disappears. The oxidation temperature was fixed to 1000 °C and the time of oxidation was fixed to 24 h. At end of the process, the samples showed a metallic gray color.

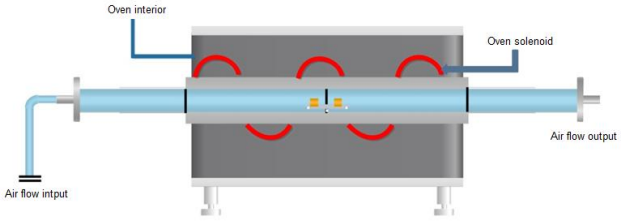


Figure 2: Home-made electrical furnace used for thermal oxidation of Cu

Cu foils (500 µm) oxidation

Cu foils (size of 10mm × 10mm) of 500 µm in thickness were used as substrates for thermal oxidation of Cu. The oxidation process is carried out at 1000 ° C for 24 h using 200 sccm flow of air, introducing the Cu foils with the furnace at room temperature (22 ° C). At the end of the oxidation, it was observed that the thickness of each sample increased about 300 µm, showing a thickness of 800 µm.

Cu foils (300 µm) oxidation

Since CuO samples obtained from Cu foils of 500 µm in thickness are very thick (800 µm), the second stage of Cu oxidation involved oxidation of Cu foils with a lower thickness (300 µm) than those Cu foils. As in the previous experiment, these foils were oxidized at the same conditions than the Cu foils with 500 µm in thickness. The new CuO samples exhibited a thickness of 500 µm. However, due to temperature effects, the layers became slightly concave. Although the final thickness of the oxide is smaller than in the previous experiment, the transport of the charges through a semiconductor could be limited due to parameters such as diffusion length of the charge carriers, which could promote a high potential barrier in a fabrication of a p-n heterojunction. Table 1 shows both thickness of CuO films and those of Cu foils with thicknesses of 500 and 300 µm.

Table 1: Thickness comparison between the thickness of a Cu foils of 500 and 300 µm and with their respective copper oxide

500µm		300µm	
Foil Thickness	Oxide Thickness	Foil Thickness	Oxide Thickness
517	819	315	516
519	819	310	513
515	817	318	518

Cu foils (100 µm) oxidation

Cu foils of about 100 µm in thickness were obtained by thinning Cu foils (size of 20 mm × 20 mm) of 300 µm thickness in a solution of 2:1 of ferric chloride: water. These foils were stirred in the solution for 60 to 90 minutes until the required thickness was achieved (showing a size of 5mm × 5mm and a thickness of 100 µm)(Figure 3).

Figure 3: a) Cu foil with size of 20 mm × 20 mm and 300 µm of thickness. b) Cu foil of 100 µm in thickness after thinning. c) Cu foil of 100 µm in thickness dimensioned at 5mm × 5mm.

The 100 µm in thickness Cu foils were oxidized at 1000 ° C for 24 hours using air flow (as in the previous experiments). After oxidizing the foils, the thickness of the oxide was about 150 µm. The experimental parameters for oxidation of Cu with foils of 100 µm in thickness are shown in Table 2.

Table 2: Experimental parameters for thermal oxidation of Cu

Sample number	Foil dimension		Oxidation temperature (°C)	Environ-ment	Flow (sccm)	Time (HH/ mm)
	Area (mm)	Thickness (µm)				
M1	5 x 5	100	1000	Air	200	24 hours
M2	5 x 5	92	1000	Air	200	24 hours
M3	5 x 5	97	1000	Air	200	24 hours

Fabrication of ZnO films

Thermal evaporation of Zn

Zn shaves with a purity of 99.999% were used as raw material. Thermal evaporation was carried out at a temperature of 800 ° C using Argon gas flow. Substrates were placed from the target at a distance in the range of 20-26 cm. The furnace was preheated to 300 °C before the Zn shaves were introduced into the quartz tube. Evaporation parameters are shown in table 3.

Table 3: Experimental parameters used for thermal evaporation of Zn

Sample number	Mass (mg)	Temperature (°C)	Time (HH/mm)	Drag gas	Flow (sccm)	Distance White/ Substratum (cm)
Zn-1	10	800	10 min	Argon	200	18
Zn-2	10		10 min	Argon	200	18
Zn-3	20		10 min	Argon	200	18
Zn-4	20		10 min	Argon	200	18

It was determined that to obtain a thin Zn film, the amount of mass of the Zn target, gas flow, and temperature need to be reduced. It was proposed to evaporate 10 mg of Zn using a gas flow of 200 sccm and a temperature between 700 and 800 ° C; the distance between the substrate and the target was 18 cm. This temperature range facilitated and speeded up evaporation. With a gas flow of 200 sccm, the transport of Zn vapor is slow and thus, the film was thinner than those of previous samples and showed more surface uniformity (figure 4). However, to make the Zn layer more structurally compact, the mass of Zn target was increased from 10 mg to 20 mg.

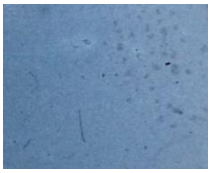


Figure 4: Zn film obtained by termal evaporation

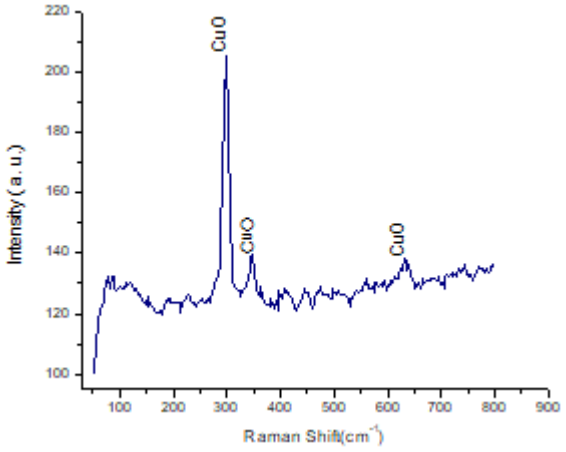
With the increase in mass of the Zn target, the film obtained exhibits a blue-light color and was observed to be more compact and uniform than the previous samples.

Thermal oxidation of Zn layers

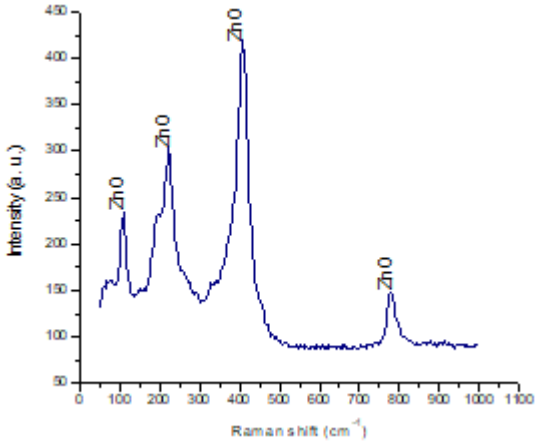
The Zn films were oxidized for 30 minutes at a temperature of 500 ° C using an air flow of 200 sccm. The oxidation process is relatively short because the Zn layer is relatively thin. To prevent cracking of the ZnO, it was cooled naturally from the oxidation temperature to room temperature. The result is a white, uniform and compact film about 30 µm in thickness. to promote surface film uniformity, the ZnO films were annealed for 2 hours at 500 ° C with an air flow of 200 sccm. The heat treatment modified the structure of the ZnO, reducing the porosity due to the grain growth.

3. Results

Figure 5 shows Raman measurements performed to the CuO and ZnO films. Fig 5a shows three peaks at 299, 399, and 633 cm^{-1}, which correspond to the Raman bands of the cupric oxide [13]. Fig 5b shows Raman spectrum of ZnO film. There are four bands centered at 104, 224, 406, and 779 cm^{-1} which correspond to the Raman modes of ZnO [14]. According to Raman spectra, the use of the resistive furnace as thermal oxidation and thermal evaporation system allows to fabricate pure CuO and ZnO samples.



(a)



(b)

Figure 5: Raman spectra: a) CuO film, and b) ZnO film.

Figure 6 exhibits SEM images of the CuO and ZnO films obtained by thermal oxidation and thermal evaporation techniques. Fig. 6a shows the top-view of a CuO film after thermal oxidation of Cu. The surface morphology of CuO can be seen as a compact and uniform film. On the other hand, the surface of the ZnO film (Fig. 6b) can be observed to be composed by grains of micrometer size.

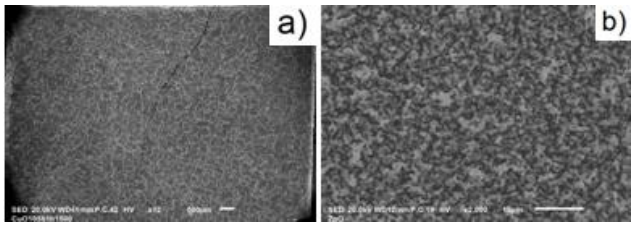


Figure 6: Sem images: a) CuO film, and b) ZnO film

4. Conclusions

CuO and ZnO films were obtained by thermal oxidation and thermal evaporation techniques. Both techniques were achieved using a home-made electrical furnace and controlling variables such as temperature of oxidation, time of evaporation or oxidation, and the gas flow. It was observed that pure CuO and ZnO films with surface uniformity can be obtained with a cheap and simple furnace.

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