

# FABRICATION OF THIN – FILM CU/CU<sub>2</sub>O SCHOTTKY DIODE PHOTOVOLTAIC CELL BY THERMAL OXIDATION



ISSN: 2141 – 3290  
www.wojast.com

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## ABSTRACT

A thin film copper/cuprous oxide (Cu/Cu<sub>2</sub>O) Schottky barrier cell has been prepared by thermal oxidation of copper sheet (1mm thick) in air at a temperature over one thousand degree Celsius (>1000°C) with corresponding time in minutes. The junctions on Cu<sub>2</sub>O were prepared by graphite carbon paste method obtained from used dry cells. The dependence of oxide thickness on oxidation temperature and time were investigated and presented. It is also observed that the growth law for thin film formation is a power law of the form  $d = At^m$ ; with  $d$  as oxide thickness in microns,  $A$  and  $m$  are constants which depends on oxygen concentration, temperature intensity and time in minutes. The results obtained indicate that cells of possible practical interest will have an oxide of a micron grown at relatively high temperatures. It was also deduced that the copper/cuprous oxide fabricated by the thermal oxidation method is a metal – semiconductor (or Schottky) diode with all the characteristics. Oxide films formed between 900°C and 1050°C were observed to consist entirely of Cu<sub>2</sub>O and showed p-type semiconductor while those grown below 900°C consists of a mixture of cupric oxide (CuO) and Cu<sub>2</sub>O. The CuO layer formed was found to be also p-type semiconducting.

## INTRODUCTION

Copper –cuprous oxide (Cu/Cu<sub>2</sub>O) has been considered as a useful material for photovoltaic solar energy conversion. The obvious advantages of Cu/Cu<sub>2</sub>O are the ready availability, non – toxicity and relatively low cost of its constituents. The early work (Lange, 1938) has almost invariably been done on ill-defined polycrystalline samples of Cu<sub>2</sub>O with only a few exceptions of studies on single -crystals. These early works have been reviewed (Sears and Fortin 1984), in effect large single crystals and polycrystalline of cuprous oxide of the material can now be grown by thermal oxidation of copper to form metal/semiconductor (Schottky).

However cuprous oxide has been shown to be a p-type semiconductor with a band gap of 2eV and optimum conversion efficiency of 12%. (Musa, *et al* 1998) Several approaches have been used to grow Cu<sub>2</sub>O based solar cell of reasonable efficiencies with disappointing results in most cases. (Sanja, *et al*, 2011) The Schottky barrier approach has been shown to be feasible with only one metal, Copper. Most Schottky barrier cells have been of the front-wall variety and were based on thick brittle, mono crystalline Cu<sub>2</sub>O with the associated problems of low mechanical stability, high series resistance and poor barrier characteristics. (Fortin. and Masson 1982) However, work has been done on Cu/Cu<sub>2</sub>O back wall cells because little is known about the growing of thin oxide on copper in the micrometer range back-wall cell, which however, offers great advantages over a front wall;

- a) Simplicity of preparation and material stability even in thin form.
- b) A junction which is never exposed to the atmosphere after its preparation.

It is essential however that the Cu/Cu<sub>2</sub>O layer be thin because of the high optical coefficient and low diffusion length of minority carriers in cuprous oxide. Indeed, a number of techniques have been employed for the fabrication of this thin oxide contact (Ikata, 1987). One of these is

the anodic oxidation which requires electrolyte of different concentration, less energy and it is potentially easy to control. This work however is based extensively on back-wall Cu/Cu<sub>2</sub>O thin cells grown by thermal oxidation in high temperature (>1000<sup>0</sup> C). In addition, the preparation under which Cu/Cu<sub>2</sub>O cells can be expected to yield optimum efficiency involved some relevant experimental details such as the treatment of the starting copper (substrate), the oxidation procedures and the measurement of the oxide thickness. (Ohajiana and Abumere 2013)

### METHODOLOGY

The fabrications of most semi-conductor devices employ the planar diffusion techniques. The technique used in this work is the thermal oxidation techniques which is part of a planar diffusion technology. Before the introduction of the impurity, the substrate surface is prepared as described thus:

First, 1 mm thick industrially graded copper plates are cut to appropriate dimension of 1.0cm x 1.0cm for thermal oxidation

This step involves immersion of the copper plates in a strong oxidizing agent such as dilute Nitric acid (HNO<sub>3</sub>). In this solution the rough copper plates which are characterized by scratches littered with crystal particles are etched to smoothness. Besides, the etchant also removes the surface layer of the copper to a desired thickness. This is followed by a rinse in deionize water and dried. It has been shown that high purity copper in the neighborhood of 99.9% has been achieved by this simple water cleaning process, (Jayatissa, 2009)

Manual polishing was used. It involves subjecting the rough copper surface to various grades of emery paper. The polished copper plate is now rinsed in deionized water and dried. In the hope of getting oxide layer, additional pre-oxidation treatments were also tried for some thermal oxidation cells. In this case, the copper plate was first pre-oxidized at lower temperatures (200 – 500<sup>0</sup>C) before thermal oxidation at 1000<sup>0</sup> C.

#### Thermal oxidation process:

Among other processes, such as electrochemical, anodic oxidation, plasma reaction etc., thermal oxidation process was used in this work. The clean copper samples were mounted on the ceramic holder and oxidized in the high temperature furnace. (Fig. 1)

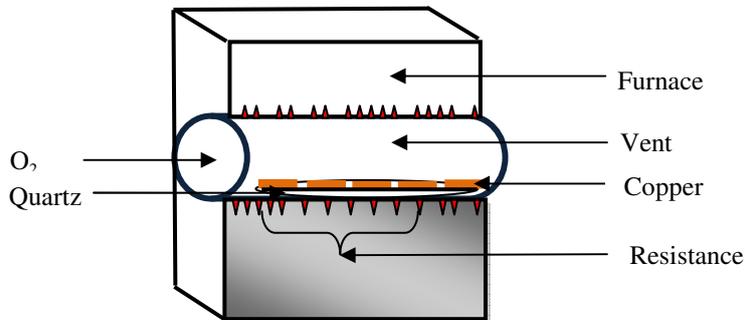


Fig. 1. High temperature furnace for thermal oxidation

The reactor tube made of quartz consists of resistance heated furnace and a cylindrical fused – quartz tube containing the copper wafers. The Cu samples were oxidized by admitting oxygen manually from a reservoir or allowed to oxidize in air at temperature from 900<sup>0</sup>C -1050<sup>0</sup>C for one and a half hours. When oxidation was over, the temperature was raised to a value between 1080<sup>0</sup>C and 1120<sup>0</sup>C. This made possible the conversion of Cu<sub>2</sub>O sheet to single crystal by annealing at these temperatures for points ranging from 5hrs to 48hrs. After annealing the samples are quenched in water by quick withdrawal from the furnace, a process which requires less than 10secs. The cooling is rapid so that only thin layer of cupric oxide (CuO) is formed on

the surface. The black cupric oxide is removed by etching in dilutes HNO<sub>3</sub> or by grinding and polishing. The Cu<sub>2</sub>O showed the grain boundaries and characteristic ruby red colors of Cu.

**The oxide thickness measurements:**

The oxide layer thicknesses in the micrometer range were grown at a relatively high temperature. In effect, the growth rate of Cu<sub>2</sub>O on Cu as a function of temperature and oxidation time was investigated. The growth of the thickness of the oxide layer was determined by a gravimetric method. This involves observing the mass loss of Cu<sub>2</sub>O –Cu cell after the Cu<sub>2</sub>O layer has been dissolved in hot ammonium hydroxide by considering the area, A, and assuming a density, ρ for the Cu<sub>2</sub>O. To determine the mass loss of Cu<sub>2</sub>O, the finished samples obtained at various temperatures and times of oxidation were weighed using the mettle balance model H80 of sensitivity 0.1mg; after which it was dipped in hot NH<sub>2</sub>OH solution (about 78°C) for five minutes to dissolve out the cuprous oxide only and re-weighed.

The change in mass Δm is equal to the mass of cuprous oxide deposited. The film thickness, d is given by

$$d = \frac{\Delta m}{2\rho A} \tag{1}$$

where the factor 2 divides the change in mass since only one side of the oxide thickness is needed, d is thickness of Cu<sub>2</sub>O on Cu, ρ is the density of Cu<sub>2</sub>O (= 6.0gcm<sup>-3</sup>) and A is surface area of copper sheet 1cm then thickness of Cu<sub>2</sub>O on Cu is calculated for all the samples used. (Noguet, *et al.*, 1982).

**RESULTS**

Tables 1 – 3 give summary of oxide thickness of the samples with oxidation time at temperatures varying from 900°C to 1050°C, while Table 4 shows the oxide thickness and corresponding temperature at fairly constant time. Figures 2 - 4 show the graphs of oxide thickness with temperature. Figure 4 indicates the oxide thickness variation with oxidation temperature. The graphs are identical which reveals the growth law for thermal oxidation of thin film barrier power law of the form

$$d = At^m \tag{2}$$

with d in microns and t in hours and m is the slope.

Logarithm of both sides of equation 2 gives; log d = log A + m log t

Table 1: Oxide thickness (in microns) with respective T ~ 900°C

Samples	Thickness (μm)	Oxidation time (hrs)
1	3.80	5.00
2	6.20	10.00
3	8.50	15.00
4	11.00	20.00
5	14.00	25.00
6	15.30	30.00
7	17.00	35.00
8	18.00	40.00

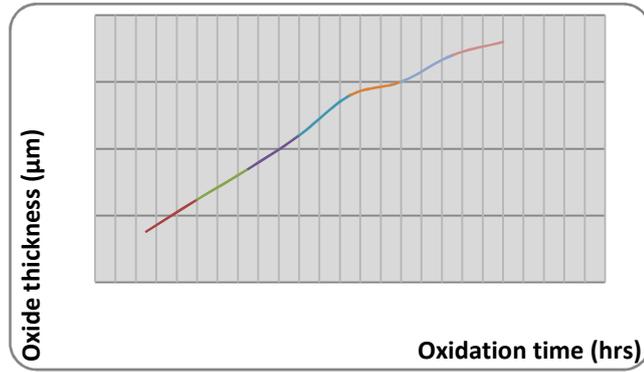


Fig. 2. Oxide thickness versus Oxidation time

Table 2. Oxide thickness (in microns) with respective T ~ 1000°C

Samples	Thickness (µm)	Oxidation time (hrs)
1	7.50	5.00
2	15.00	10.00
3	17.50	15.00
4	17.00	25.00
5	20.00	25.00
6	24.00	30.00
7	25.00	35.00s

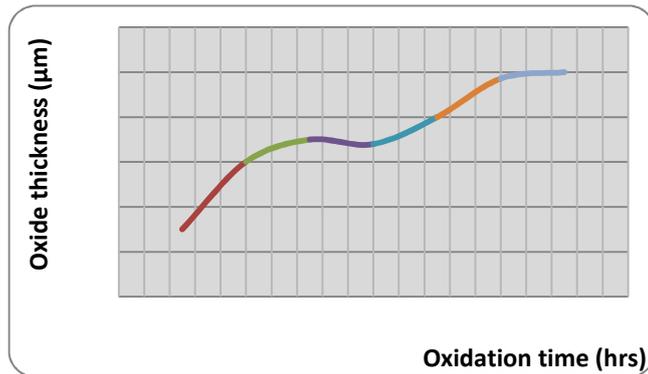


Fig. 3. Oxide thickness versus Oxidation time at T ~ 1000°C

Table 3. Oxide thickness with respective T ~ 1000°C

Samples	Thickness µm	Oxidation time (hrs)
1	21.10	5.00
2	33.50	10.00
3	38.50	15.00
4	45.00	20.00
5	47.00	25.00
6	52.00	30.00
7	58.50	35.00

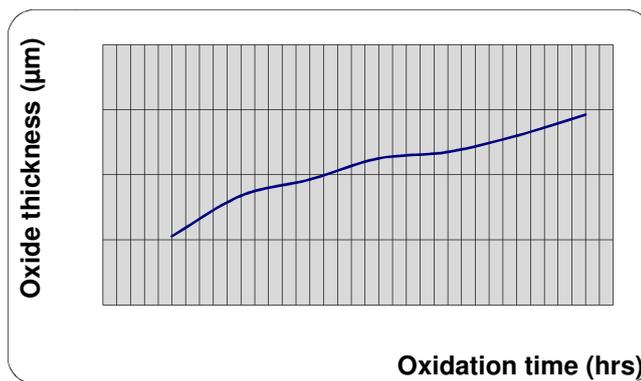


Fig. 4. Oxide thickness versus Oxidation time at T ~ 1050°C

Table 4. Oxide thickness versus Oxidation temperature at t = 60s

Samples	Oxidation thickness (µm)	Oxidation temp (°C)
1	5.00	800.0
2	5.30	800.0
3	5.50	800.0
4	7.30	850.0
5	7.50	850.0
6	9.00	900.0
7	9.50	900.0
8	15.00	950.0
9	14.00	950.0
10	17.00	950.0
11	22.30	1000.0
12	23.00	1000.0

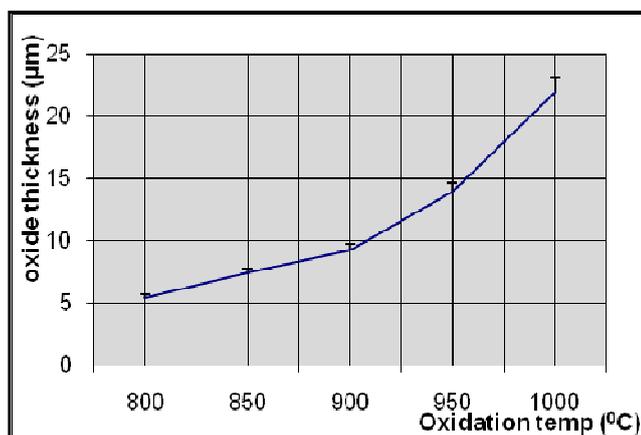


Fig. 5. Oxide thickness versus oxidation temperature at t = 60s

A plot of log thickness against log time gives a straight line whose slope is derived from the growth law (Fig 5).

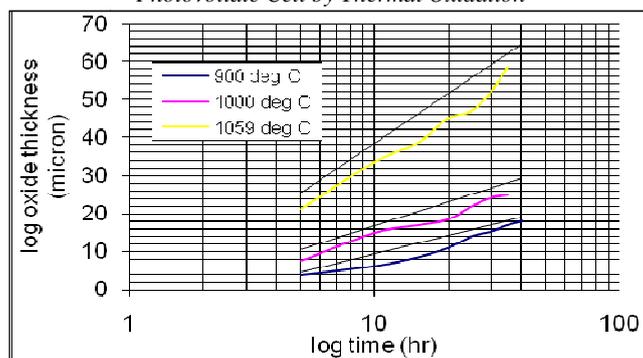


Fig. 6. Log oxide thickness versus log oxidation time

### DISCUSSION AND CONCLUSION

In this work the dependence of Cu<sub>2</sub>O/Cu photovoltaic cell on the oxide film thickness was established. The efficiency of the cell was found to increase as the oxide film-thickness increases with temperature. From Table 3, a large amount of oxide thickness of about 58.30 μm at oxidation time of 35hrs were observed in the sample prepared at 1050 °C, whereas in Table 1 the sample prepared at 900 °C has oxide thickness of 17.0μm at the same oxidation time of 35hrs. It is obvious that the morphology of these samples oxide thickness is observed to increase with increasing oxidation temperature and time.

The plots of oxide thickness against temperature shows similar pattern of growth law. It can be inferred that oxide thickness later in micrometer range requires reasonable time and relatively high temperature of the order of 900°C to remain in the Cu<sub>2</sub>O region. This implies that to obtain a thickness of say 60 μm by oxidation at 1000°C requires well over 35hrs. It can also be inferred that once the growth process has stopped, further annealing has no noticeable effect on the grain size hence the oxide thickness is fairly constant.

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