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Short Communication

Effect of annealing on the resistivity of copper oxide solar cells

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The effect of annealing on the resistivity of copper (I) oxides (Cu_2O) samples has been investigated in detail. The resistivity of the sample is a function of the power output of such Cu $_2$O solar cell. Results revealed that the annealing of Cu_2O samples improves the output performance compared to that of unannealed samples by about 36%. The results on the resistivity of the samples oxidized at different temperatures for different times but annealed for some duration at an identical temperature after proper quenching in deionizer water shows a lower and higher resistivities for annealed and unannealed samples respectively.

Key words: Annealed, unannealed**,** resistivity, quenching, Cu_2O Solar Cell.

INTRODUCTION

Historical perspective

Becquerel, in 1839, discovered that a photo voltage was developed when light was directed onto one of the electrodes in an electrolyte solution. Many years later, Adams and Day observed photovoltaic (PV) effects in solid selenium (William, 1998).Other researchers such as Lange, L.O Grondahl and Schottky also did pioneering work on selenium and cuprous oxide PV cells in 1920 (Olsen et al, 1982). During the 1920s and early 1930s, development efforts were carried out to correlate rectifier characteristics with fabrication techniques. Grondahl summarized these efforts in 1933 (Olsen et al, 1982). He also reported preliminary results on a photo cell made by reducing the surface of Cu_2O to form a Cu_2O/Cu Schottky barrier. Grondahl reported a photo response of about 50% at 500 nm. No effort was made to characterize the device as a solar cell; only the measured photo response at 500nm was mentioned.

At Bell laboratories in 1940s, Bardeen, Brattain and Shockley made an effort to develop a basic understanding of the copper oxide rectifier. During this time period, models for Schottky barriers were developed. Interest also began to move to silicon. Again, no effort was made to develop Cu_2O solar cells. In 1951, a review of the work done at Bell laboratories was published by Brattain (Walter, 1951).

The result concerning the photo response of front-wall Cu_2O / Cu cells was published in 1973 (Assimos and Trivich, 1973). By the end of 1975, two programs specifically aimed at Cu_2O solar cell fabrication and characterization were initiated by the National Science Foundation of United State of America, (USA) as part of the research applied to national needs program, one at Wayne state and the other at joint conference on general sciences, (JCGS).

Both programs were relatively small. Both groups investigated front-wall Schottky barrier cells. Power conversion efficiencies had approached 1% by 1978. Additional work conducted by the JCGS group has resulted in an increase in the Cu_2O solar cell efficiency to about 1.8% (Muller et al., 1963).

However, it is worthy of note that the conglomerative efforts devoted to Cu_2O solar cell research and development is very minute when compared with other materials at present being investigated. The so called “crude” investigations conducted on back-wall rectifiers in the early 1920s and late 1930s are often mistakenly regarded as work related to solar cell development. Despite the enormous amount of progress made in the semi conducting industries between 1979 and now, it is not an exaggeration to conclude that semiconductor physics has not yet been developed especially if one considers the

Table 1. Resistivity for annealed (Cu_2O) samples.

S/N	OxidationTemp (^0C)	Oxidation. Time(min.)	Thickness (mm)	$\rho_1\ (\Omega cm)$	$\rho_2\ (\Omega cm)$	$\rho_3\ (\Omega cm)$	Average $\rho(\Omega cm)$
1	950	7	0.12	356.90	360.900	361.26	359.69 ± 2.42
2	970	6	0.113	326.90	327.10	329.08	327.69 ± 1.21
3	980	5	0.108	301.00	298.90	300.34	300.08 ± 1.07
4	1000	4	0.107	292.9	292.60	292.69	292.73 ± 0.15
5	1050	3	0.106	291.2	292.10	291.56	291.62 ± 0.45

the increasing potentials of the devices yet to be harnessed.

In the present work, efforts have been made to investtigate how the resistivity of Cu_2O solar cell could be affected by proper annealing the samples of these oxides that is prepared by thermal oxidation technique in laboratory air, at elevated temperature and under atmospheric pressure (Onimisi, 2006).

Experimental procedure

Annealing and quenching

At the end of the oxidation period of Cu_2O samples, each sample was rapidly quenched by dropping in cold deionised water to stop further oxidation. This was further subjected to a second heat treatment (annealing) in air at a temperature of 500^oC for 1.5 h. At the end of annealing process, it was rapidly quenched in deionized water and dried. The annealing process was performed to lower the resistivity and increase the diffusion length of the minority carriers (Adrianus, 1978).

Resistivity measurement

Both the annealed and unannealed samples of oxidized copper (I) oxides (Cu_2O) were used for resistivity measurement for evaluating the effect of conducting layers on resistivity of Cu_2O . The four probe method was adopted for the resistivity measurement.

The four probe arrangement was placed in the oven, and the D.C micro voltmeter was switched on and allowed about 5 min for thermal stability. The zero of D.C micro voltmeter was adjusted with the knob provided for it.

Also, the constant current power supply/low current power supply was switched on and the zero reading of D.C micro voltmeter was again checked at zero current reading.

The current was gradually increased and the corresponding voltage reading recorded and tabulated in microampere and milivolt respectively, for different samples. In this experiment, current I was passed through the outer probes and the floating potential V was measured across the inner pair of four probes.

The floating potential V, a distance r from an electrode of resistivity ρ_0 , is given by

$$V = \frac{\rho_0 I}{2\pi r} \qquad (1)$$

From equation (1), the resistivity of a material is given by

$$\rho_0 = \frac{V}{I} 2\pi S = 2\pi SR \qquad (2)$$

Where S is the space between the probes.
But for a thin slice – non conducting bottom surface like the Cu_2O surface, the resistivity ρ is given by Onimisi (2006)

$$\rho = \frac{\rho_0}{G_7(W/S)} \qquad (3)$$

Where $G_7(W/S) = \frac{2S \ln 2}{W}$ and ρ_0 is given by equation (2)

So that equation (3) becomes

$$\rho = 2\pi SR \times \frac{W}{2S \ln 2} = \frac{\pi WR}{\ln 2} \qquad \rho = \frac{\pi WR}{\ln 2} \qquad (4)$$

Where ρ is the resistivity, W is the thickness of the sample and R is the measured resistance of the sample.

The samples were oxidized at different temperatures in the range 950 to 1050^oC for different time intervals and the most stable systems were chosen for investigation. For each oxidation temperature and time, three samples each of $A_{11},A_{12},A_{13},A_{21},A_{22}$,$A_{23},A_{31},A_{32},A_{33},A_{41},A_{42},A_{43}$,A_{51},A_{52},A_{53} were obtained. (Where A_{11},A_{12},A_{13}, are samples oxidized at 950^oC for seven minutes, A_{21},A_{22},A_{23} , are samples oxidized at 970^oC for six minutes, A_{31},A_{32},A_{33}, are samples oxidized at 980^oC for five minutes, A_{41} ,A_{42},A_{43}, are samples oxidized at 1000^oC for four minutes and A_{51},A_{52},A_{53} are samples oxidized at 1050^oC for three minutes. From each set of these samples, three measurements of the resistivity were taken from which the average was calculated so as to optimize the accuracy.

A total of forty five (45) sets of measurements were therefore conducted with the use of equation (4) for annealed Cu_2O samples alone. The whole procedure was repeated for all Unannealed samples.

Results of the resistivity value for annealed and unannealed copper (I) oxide samples

Tables 1 and 2 present the summary of the resistivity values for both annealed and unannealed samples of Cu_2O. It should be noted that at every oxidation temperature and time, three separate samples were used for the measurements.

Table 2. Resistivity for unannealed (Cu_2O) samples.

S/N	Oxidation Temp. (^0C)	Oxidation Time (min.)	Thickness (mm)	$\rho_1\ (\Omega cm)$	$\rho_2\ (\Omega cm)$	$\rho_3\ (\Omega cm)$	Average $\rho(\Omega cm)$
1	950	7	0.120	500.00	502.00	501.12	501.04 ± 0.56
2	970	6	0.113	506.00	507.00	502.48	505.16 ± 0.56
3	980	5	0.108	476.00	474.00	474.19	474.73 ± 0.63
4	1000	4	0.107	488.00	489.69	490.00	489.23 ± 0.98
5	1050	3	0.106	499.00	497.00	498.42	498.14 ± 0.76

DISCUSSION ON THE RESISTIVITY VALUES

The oxidized samples were annealed at 500^{o}C for 1.5 h. This annealing became necessary because of the disorder caused to the samples resulting from the high temperature oxidation and rapid quenching. 'Crystal defects' like point and line defects, dislocation, stacking faults may have resulted from the high temperature oxidation and rapid quenching. Consequently, the samples parameters such as charge carrier mobility, shunt and series resistances, and lifetime may have been severely degraded as a result. The annealing process was performed to achieve the following objectives:

(1) To heal the defects created in Cu_2O crystal lattices during the high temperature oxidation and quenching.
(2) To maximize the charge carrier mobility value and consequently minimize the resistivity values of the samples.
(3) To convert the polycrystalline Cu_2O obtained after oxidation to single or nearly single crystal.

Going by the result, the relatively high resistivity values obtained in Table 2 (Unannealed samples) could be due to the crystal defects of Cu_2O resulting from the high temperature oxidation. However, the low resistivity values noticed generally in all the annealed samples Table 1 reveal the fact that, the annealing process had the effect of healing those defects in Cu_2O structure created during the high temperature oxidation.

One of the primary aims of performing the annealing process was to improve on the conductivity of Cu_2O samples. It is also to minimize the internal voltage drop in solar cell materials, reduce the internal series resistant and hence reduce the resistivity. The resistivity of the solar cell material is also very crucial for maximum power conversion efficiency. Low resistivity will yield high electrical power conversion efficiency. Resistivity values in the range 100 – 200 Ω cm for thermally oxidized Cu_2O in the presence of $MgCl_2$ were measured in 1982 (Olsen et al, 1982) and Cu_2O oxidized at 970^{o}C for 4 min in the presence of HCl vapor exhibiting a resistivity in the range 200 - 400 Ω cm was measured by Musa, 2001, 1987).

Conclusions

The investigations have revealed that the annealing process carried out at 500^{o}C for 1.5 h has the effect of decreasing the resistivity of Cu_2O solar cell samples by nearly 36% of the value for unannealed samples oxidized under the same condition. The photo conducting properties of such system investigated have shown clearly that the output performance of annealed Cu_2O solar cells is much higher than that of unannealed samples. Further investigations being carried out by varying both annealing temperature and annealing time are expected to provide the optimum value for such parameters in determining the most efficient solar cell in such metal oxide systems.

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