

EFFECT OF OXIDATION TEMPERATURE AND OXIDATION TIME ON THICKNESS OF COPPER (I) OXIDE (Cu_2O) SOLAR CELL

*M. Y. Onimisi, N. Hariharan** and A.O Musa***

*Department of Physics, Nigerian Defense Academy, Kaduna, Nigeria.

**Department of Physics, Ahmadu Bello University, Zaria, Nigeria

***Department of Physics, Bayero University, Kano, Nigeria.

(Submitted: 20 December, 2006; Accepted; 28 April, 2007)

Abstract

Investigation has been made concerning the effect of oxidation temperature and time on the thickness of copper (I) oxides solar cells prepared by thermal oxidation method. The samples were oxidized at different oxidation temperatures and time. The different oxidation temperatures and lengths of time were employed in order to find which oxidation temperature and time would result in the least thickness and stability of Cu_2O on Cu which is a factor of the sample resistivity and output performance of a solar cell. Result shows that samples oxidized at the following temperatures and times gave the least thicknesses and stable oxides when compared with other samples at the different oxidation temperature and time: 950°C for 7minutes, 970°C for 6minutes, 980°C for 5minutes, 1000°C for 4minutes and 1050°C for 3 minutes. It was further observed that samples oxidized above or below these temperatures and times do not only exhibit poor performance when used in solar cell fabrication, but also stand the risk of breakage during chemical etching process as a result of the oxides being fragile.

Keywords: Annealing, etching, copper (I) oxide, thermal oxidation.

Introduction

Before the intensive research on copper (I) oxide, the potential for the oxide to be used in semiconductor devices had been recognized before 1920 (Olsen et al, 1982). It has been observed that Cu_2O is one of the earliest known materials to be used as semiconductor devices. The oxide is observed to be an attractive starting material for the production of solar cells for low cost terrestrial conversion of solar energy to electricity. Copper (I) oxide is one of the earliest known photovoltaic materials and the first in which the photovoltaic effect was successfully explained (Fortin and Sears, 1981). When the performance of Cu_2O was compared with those of well developed silicon and germanium solar cells, it was observed that the later was relatively high Adrianus (1978). Also observed was that the best Cu_2O solar cells efficiencies obtained have been of the order of 1% (Nognet,

Taperiom, Schrab, Jielinger, 1982). This efficiency was observed to be caused primarily due to the general low value of the barrier heights of all Schottky barrier solar cells, which are in the range of 0.7-0.9eV irrespective of the choice of the metal (Olsen, Addis, and Miller, 1982). However, this oxide is still considered as an attractive solar cell material due to its easy availability, non-toxicity and relatively low-cost of its constituents (Musa et al, 2001).

Copper (I) oxides have direct band gap of 2eV, optimum conversion efficiencies of the order of 12% at room temperature was mentioned to be a possible material for photo voltage solar cells. The researches carried out in the mid-seventies and early eighties have helped in unveiling some of the mysteries surrounding this material and a perfect understanding of the various causes for the poor performance of Cu_2O solar cells. These include methods of producing Cu_2O (thermal oxidation, electro deposition,

Sputtering, thermal evaporation and methods of fabrication of the cells), the oxidation temperature and time. It is my believed that if the exact oxidation temperature and time at which a stable oxide and very low thickness is known for this structure, then the efficiency of the cell might be enhanced once more. The different oxidation temperatures and lengths of time used is intended to find which oxidation temperature and time would result in the least thickness and stability of Cu_2O on Cu which is a factor of the sample resistivity and output performance of a solar cell.

This work is aimed at determining which oxidation temperature and time would result in the optimal response of the properties of each of our samples in order to direct research efforts in the search for high efficiency in the limitless potentials of these materials that could provide high efficient solar cells to provide electricity and other power source in military operations and cadets bush exercise where access to national grid is a bit difficult.

Sample Preparation

Thermal oxidation:

The samples were placed in a ceramic crucible boat and introduced with the aid of a long tong into the furnace, as soon as the oxidation temperature was attained. Timing commenced with a stop watch as soon as the samples get inside the furnace. The oxidation was performed in free air at an atmospheric pressure. At the end of the oxidation period, the samples were brought out of the furnace and immediately quenched in deionised water.

The samples were oxidized at the following temperatures: 950°C, 970°C, 980°C, 1000°C and 1050°C each at the following time durations in the furnace 2 minutes, 3 minutes, 4 minutes, 5 minutes, 6 minutes, 7 minutes, 8 minutes, and 9 minutes, respectively. That is, at every temperature stated above, four sets of samples were oxidized for 2 minutes; another four sets of the same samples were also oxidized for 3 minutes and so on. These were repeated for all the temperatures. The different oxidation temperatures and times used were intended

to find which oxidation temperature and time will give the least thickness and stability of Cu_2O on Cu which is a factor of resistivity and output performance of a solar cell.

Annealing and Quenching

At the end of the oxidation period, 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°C for $1\frac{1}{2}$ hours. Consequently, the

best samples, that is, the samples that gave the least thickness were selected and these were annealed at the following temperature and time: 500°C for $1\frac{1}{2}$ hours. 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).

Thickness Measurement

The thickness of Cu_2O on Cu could be measured either directly from the cross-sectional SEM micrograph or by measuring the mass loss of Cu_2O on Cu. In this work, the thickness of copper(I) oxide was measured by measuring the mass loss of Cu_2O on Cu that is, by observing the mass loss of Cu_2O/Cu structure after the Cu_2O layer had been dissolved in concentrated HCl. This was obtained by the following procedures:

- (i) The samples were weighed on a digital meter balance to obtain the mass of Cu_2O/Cu . This mass was taken as M_1
- (ii) The samples were then dipped in a concentrated Hydrochloric acid solution to remove the Cu_2O layers i.e.,



- (iii) The samples were again weighed to obtain the remaining mass M_2 of Cu the difference between these two masses i.e., $(M_1 - M_2)$ gives the mass M of Cu_2O on Cu. The measured mass of Cu_2O and the known density of Cu_2O was used to compute the required thickness of Cu_2O on Cu using equation (1).

$$\text{Volume} = \text{Mass}/\text{density}$$

$$\Rightarrow \text{Thickness} = \frac{\text{mass}}{\text{density} \times \text{area}} \quad (1)$$

Results and Discussion

Tables 1 to 5 show the results of different oxidation temperatures and times of oxidation for copper (I) oxide sample. These tables show the thickness of Cu_2O on Cu at various oxidation temperature and oxidation time. It also indicates which oxidation temperatures and at what oxidation time gives the least thickness and stability of Cu_2O on Cu which is a factor of the resistivity and output performance of a solar cell.

Table 1: Sample A_{11} (Cu_2O)

Oxidation temperature: $950^{\circ}C$
 Oxidation times: 9,8,7,6,5,4,3, (minutes)
 Annealing temperature: $500^{\circ}C$
 Annealing time $1\frac{1}{2}$ hours

S/N	Oxidation time(minutes)	Thickness of Cu_2O on Cu (mm)	Area of the cell (mm) ²
1	9	0.123	210
2	9	0.123	210
3	9	0.122	210
4	9	0.123	210
5	8	0.122	210
6	8	0.122	210
7	8	0.123	210
8	8	0.122	210
9	7	0.121	210
10	7	0.120	210
11	7	0.120	210
12	7	0.120	210
13	6	0.120	210
14	6	0.121	210
15	6	0.121	210
16	6	0.121	210
17	5	0.121	210
18	5	0.121	210
19	5	0.122	210
20	5	0.122	210
21	4	Oxides are not stable	210
22	4	Oxides are not stable	210
23	4	Oxides are not stable	210
24	4	Oxides are not stable	210
25	3	No oxidation	210
26	3	No oxidation	210
27	3	No oxidation	210
28	3	No oxidation	210

Table 2: Sample A_{21} (Cu_2O)

Oxidation temperature: $970^{\circ}C$
 Oxidation times: 9, 8, 7, 6, 5, 4, 3, 2(minutes)
 Annealing temperature: $500^{\circ}C$
 Annealing time: $1\frac{1}{2}$ hours

S/N	Oxidation time(minutes)	Thickness of Cu_2O .(mm)	Area of the cell (mm) ²
1	9	0.120	240
2	9	0.120	240
3	9	0.119	240
4	9	0.119	240
5	8	0.117	240
6	8	0.116	240
7	8	0.116	240
8	8	0.115	240
9	7	0.114	240
10	7	0.113	240
11	7	0.114	240
12	7	0.113	240
13	6	0.113	240
14	6	0.113	240
15	6	0.113	240
16	6	0.113	240
17	5	0.114	240
18	5	0.115	270
19	5	0.115	270
20	5	0.114	270
21	4	0.116	270
22	4	0.116	270
23	4	0.115	270
24	4	0.116	270
25	3	Incomplete oxidation	270
26	3	Incomplete oxidation	270
27	3	Incomplete oxidation	270
28	3	Incomplete oxidation	270

Table 3: Sample A_{31} (Cu_2O)

Oxidation temperature: $980^{\circ}C$
 Oxidation times: 9, 8, 7, 6, 5, 4, 3, 2(minutes)
 Annealing temperature $500^{\circ}C$
 Annealing time $1\frac{1}{2}$ hours

S/N	Oxidation time (minutes)	Thickness of Cu_2O (mm)	Area of the cell (mm) ²
1	9	Samples are fragile	240
2	9	Samples are fragile	240
3	9	Samples are fragile	240
4	9	Samples are fragile	240
5	8	Samples are fragile	240
6	8	Samples are fragile	240
7	8	Samples are fragile	240

8	8	Samples are fragile	240
9	7	0.112	240
10	7	0.112	240
11	7	0.112	240
12	7	0.112	240
13	6	0.110	240
14	6	0.111	210
15	6	0.110	210
16	6	0.110	210
17	5	0.109	210
18	5	0.108	210
19	5	0.108	210
20	5	0.107	210
21	4	0.110	210
22	4	0.110	210
23	4	0.111	210
24	4	0.111	210
25	3	0.112	210
26	3	0.112	210
27	3	0.112	210
28	3	0.112	210

Table 4: Sample A_{41} Cu_2O Oxidation temperature: $1000^{\circ}C$

Oxidation time: 7, 6, 5, 4, 3, 2, (minutes)

Annealing temperature: $500^{\circ}C$ Annealing time: $1\frac{1}{2}$ hours

S/N	Oxidation time (minutes)	Thickness of Cu_2O (mm)	Area of cells (mm) ²
1	7	Fragile samples	210
2	7	Fragile samples	210
3	7	Fragile samples	210
4	7	Fragile samples	210
5	6	Oxides are not stable	210
6	6	Oxides are not stable	210
7	6	Oxides are not stable	210
8	6	Oxides are not stable	210
9	5	0.1086	210
10	5	0.1087	210
11	5	0.1086	210
12	5	0.1086	210
13	4	0.1074	210
14	4	0.1073	210
15	4	0.1073	210
16	4	0.1073	210
17	3	0.1088	210
18	3	0.1087	210
19	3	0.1088	210
20	3	0.1087	210

Table 5: Sample A_{51} (Cu_2O)

Oxidation temperature:	1050 ^o C
Oxidation times:	6, 5, 4, 3, 2(minutes)
Annealing temperature:	500 ^o C
Annealing time:	1 $\frac{1}{2}$ hours

S/N	Oxidation time(minutes)	Thickness of Cu_2O (mm)	Area of cell (mm) ²
1	6	Fragile sample	240
2	6	Fragile sample	240
3	6	Fragile sample	240
4	6	Fragile sample	240
5	5	Oxides are not stable	240
6	5	Oxides are not stable	240
7	5	Oxides are not stable	240
8	5	Oxides are not stable	240
9	4	0.1065	240
10	4	0.1066	240
11	4	0.1065	240
12	4	0.1065	240
13	3	0.1063	210
14	3	0.1062	210
15	3	0.1063	210
16	3	0.1062	210
17	2	0.1075	210
18	2	0.1075	210
19	2	0.1073	210
20	2	0.1073	210

Discussion

The higher thickness observed on 9 and 8 minutes oxidation periods tables 1 and 2 shows that there may be probably traces of CuO measured along with Cu_2O . This is because of short period of time the sample spent in the etching solution. If the sample oxidized at this period is allowed a longer time in the etching solution, the sample becomes fragile to touch.

The samples were oxidized at different temperatures and different lengths of time, but with constant annealing temperature and time. The different oxidation temperatures and lengths of time used is intended to find which oxidation temperature and time would result in the least thickness and stability of Cu_2O on Cu which is a factor of the samples resistivity and output performance of a solar cell. Going by the results obtained in tables 1 to 5, it can be seen that in (table1), samples

oxidized at 950^oC for seven minutes and those oxidized at 970^oC for six minutes (table2), at 980^oC for five minutes (table3), at 1000^oC for four minutes (table4) and at 1050^oC for three minutes in (table5) gave the least thicknesses and stable oxides when compared with other samples in the same oxidation temperature and time.

It was observed that samples oxidized above these temperatures and times or below this oxidation temperature and time do not only exhibit poor performance when used in solar cell fabrication, but also stand the risk of breakage as a result of the oxides being fragile during chemical etching process.

Also observed was the fragile nature of the samples that were oxidized at a very high temperature above (1000^oC) for a longer time above (5 minutes). This resulted in breakage into smaller pieces during the etching process. Also samples oxidized at 950^oC, 970^oC for four minutes and below

have an unstable oxides structures that is, the oxides peels off during the etching process due to incomplete oxidation resulting from short time spent in the furnace. However, the oxidation of the samples requires high temperatures like (950, 970, 980, 1000, 1050)^oC and relatively shorter period of time (7, 6, 5,4and3) minutes for partial thermal oxidation tables 1 to 5.

Copper (I) oxides have been identified to be stable at limited ranges of temperature and high oxygen pressure Kittel C, (1981). During thermal oxidation, Copper (I) oxide was formed first and after sufficiently long oxidation time, Copper (II) oxide was also formed on top of Cu_2O Kittel C, (1981).

In 2001, Cu_2O was oxidized at 970^oC for 4 minutes in the presence of HCl vapor exhibiting a thickness of 0.115mm and a resistivity in the range 200-400 Ω cm, Musa et al, (2001). This result is in agreement with the result obtained in table2 of this report.

Conclusion

In this work, the best solar cells fabricated were those of Copper (I) oxides (Cu_2O), produced by partial thermal oxidation at the following temperatures and times:

950^oC for seven minutes, 970^oC for six minutes, 980^oC five minutes, 1000^oC for four minutes and 1050^oC for three minutes It was observed that samples oxidized above these temperatures and times or below this oxidation temperature and time do not only exhibit poor performance when used in solar cell fabrication, but also stand the risk of breakage as a result of the oxides being fragile during chemical etching process.

Also observed was the fragile nature of the samples that were oxidized at a very high temperature above (1000^oC) for a longer time above (5 minutes). This resulted in breakage into smaller pieces during the etching process. Also samples oxidized at 950^oC, 970^oC for four minutes and below have an unstable oxides structures that is, the oxides peels off during the etching process due to incomplete oxidation resulting from short time spent in the furnace. However, the oxidation of the samples requires high temperatures like 950, 970, 980, 1000, 1050, ^oC and relatively shorter period of time 7, 6, 5,4and3 minutes for partial thermal oxidation.

References

- Adegboyega G. A (1990): Solar Cell Materials, Nigerian Journal of renewable energy 21-23.
- Adrianus D.K (1978): Solid State Physics, Prentice-Hall Inc., N.Y., 349-350.
- Assimos J.A and Trivich D. (1973): Photovoltaic Properties and Barrier Heights of Single Crystal and Polycrystalline Cu_2O Contacts, J Applied physics 44, 1687pp.
- Banshah, R.F (Ed.) (1991): Hand Book of Deposition Technologies for Films and Coatings (2nd edition, Noyes Publications) U.K. 87-90
- Bardeen, J. (1947): Metal oxide semiconductor, Phys. Rev. 717-727.
- Brattain W.A, (1951): The copper oxide rectifier, Review of Modern Physics 103-106.
- Brillson, L.J, (1982): Surface Science Report2, 123-326.
- Brillson, L.J, (1992): Handbook of Semiconductors (Ed. P.T. landsberg, Elsevier) N.Y 281-417.
- Brillson, L.J (1994): Surface Science, Cambridge University Press U.K .909-927.
- Bunshah R, (1991): Deposition Methods, Ed. R. F Bunshasha, Noyes Publications, N.Y 554-555.
- Carlson, J.O (1991): Handbook of Deposition Technologies for Films and Coatings (Ed. R.F Bunshasha, 2nd edn, Noyes publications) N.Y, 374-433
- Chark J; (1978): Solar Energy Materials, Applied Physics Letters 32, 43-45.
- Economon N.A, Toth R.S and Trivich D. Komp R. J (1982): 14th IEEE Photovoltaic special conference procedure New York, 1180-1182.

- Elwell D. and Pointon A.J (1986): Physics for Engineers and Scientists, John Willey and sons N.Y, 268-277.
- Fortin E. and Sears W.M; (1981): Thin film Cu_2O/Cu Photovoltaic Cell Conference, Canada, 901-910.
- Greenwood N.N and Earnshaw A., (1984): Chemistry of the Elements, Department of Inorganic and Structural Chemistry, university of Leeds UK pergamon press, 1373-1376
- Herion J. and Natsch B. (1980): IEEE Photovoltaic Specialist Conf. Proc IEEE, N.Y.
- Kittel C. (1981): Introduction to Solid State Physics 6th edition, John Wiley and Sons Inc. N.Y, 508-522.
- Musa, A. Oand Akomolafe, T. (2001): Thin film Backwall Schottky Barrier Solar Cells of Cuprous Oxide (Cu_2O). Ife Journal of Technology, Vol. 10, No. 1, 41-47.
- Noguet C. Taperion M. Schrab C Jienger S.P, (1982): Cuprous Oxide as a Photovoltaic Converter, Solar Energy Journal, 1172-1178.
- Olsen L.C, Addis F.W, and Miller; (1982): Experimental and Theoretical Studies of Cu_2O Solar Cell, 14th IEEE Photovoltaic Conference, 250-269.