ABSTRACT

Copper (I) oxide (Cu2O) is a potential material for the fabrication of low cost solar cells for terrestrial application. A detailed survey on the previous work so far carried out on Cu2O based solar cells has been presented. The aspects discussed include the fabrication of Schottky (metal/semiconductor) barrier Cu2O solar cells, where different low work function metals are used to form the Schottky barrier solar cells. The problems associated with the Cu2O Schottky barrier solar cells and efforts made at improving the performance of these solar cells are highlighted. Discussions on heterojunction solar cells with Cu2O have also been presented. Various transparent conducting oxides (TCOs) used in forming the heterojunction cells are mentioned, and successes and failures of using them highlighted. The technological developments of these cells are still in their infancy and the performance remains very poor. The root causes of this poor performance are analyzed and possible areas for future research in the field are outlined.

Keyword: Copper (I) oxide, Solar cells, Solar cells, Schottky barrier solar cells

INTRODUCTION

The world’s major energy sources are non-renewable, and are faced with ever increasing demand, thus are not expected to last long. Besides being non-renewable, these sources, mainly of fossil fuels, contribute tremendously to the perennial problem of global warming. The eminent depletion and pollution problems of the above energy sources make the international community focus attention on alternative sources of energy, and solar energy appears highly promising. This energy is emitted from the sun primarily as electromagnetic radiation in the ultraviolet to infrared and radio spectral regions (0.2 to 3μm). The sun has a reasonable stable life time with a projected constant radiative energy output of over 10 billions (1010) years (Sze, 1981).

A solar cell performs two functions: photogeneration of charge carriers in a light absorbing material and separation of the charge carriers to a conductive contact that will transmit the electricity. In its simplest form, the solar cell consists of a junction formed between n-type and p-type semiconductors, either of the same material (homojunction) or different materials (Schottky or heterojunction).

Solar cells are electronic devices used for the direct conversion of solar energy to electricity, using the photovoltaic (PV) effect. In addition to other advantages, the method of converting solar energy to electricity is pollution free, and appears a good practical solution to the global energy problems; especially if practical economic means of direct conversion can be developed.

Cu2O is a non-stoichiometric defect p–type (walter, 1951) semiconductor and its potential for the design of solar cells have been recognized since 1920. This was before silicon, germanium and other potential semiconducting materials were discovered. The development of these materials for the fabrication of solar cells has reached advanced stages while that on Cu2O, as at the time of writing this paper, has been slow. However, interest in Cu2O was revived during the mid seventies by the photovoltaic community as a possible low cost material for solar cells. Several groups (Grondhal, 1933, Lange, 1938, Trivich et al., 1976) became interested in Cu2O solar cells in particular. This interest lasted for about eight years during which hardly a dozen research papers were published.

These drawbacks notwithstanding, Cu2O remains an attractive alternative to silicon and other semiconductors being favored at present for terrestrial applications. Its advantages are:

i) it is non – toxic,

ii) there is abundance of the starting material (which is copper), and

iii) its production process is simple.

Cu2O has a direct band-gap of 2 eV which is suitable for photovoltaic conversion. Theoretical calculations have predicted an electrical power conversion efficiency of approximately 12 %. The practical electrical power conversion efficiencies obtained by researchers, in the past, are below 2% (Noguet et al, 1977). However, recently efficiency of 2% has been reported (Mittiga et al., 2006).

The researches carried out during the mid-seventies and early eighties have now helped in revealing some of the mysteries surrounding this material and a perfect understanding of the various causes for the poor performance of Cu2O solar cells are now known. The purpose of this review is to survey the work done on Cu2O solar cells starting from the seventies to date. In what follows the methods of the production of Cu2O shall be discussed. Fabrication of and discussion on Cu2O solar cells are presented. Subsequently, a discussion on the performance of these cells is reported. Finally, various conclusions are drawn and suggestions for further work on Cu2O solar cells are provided.
Defects in Cu₂O
When a crystal of compound XY is formed it is usually thought of as having equal numbers of X and Y atoms. Such a crystal is said to be stoichiometric. However, this stoichiometry is not obeyed by many solids as the ratio of atoms in them is slightly different from the ratio in one mole. Such non-stoichiometric compounds balance their structures by the presence of defects: vacancies, interstitials or both (Sear and Fortin, 1984). Cuprous oxide is one of such non-stoichiometric materials with formula Cu₂O. The deviation from stoichiometry, δ is generally attributed to some imperfections. Sears et al. 1984 reported that an excess of oxygen, as a result of stoichiometry, is the major active impurity and gives a p-doped semiconductor.

Methods of Production Of Cu₂O
The most important methods for the production of Cu₂O are by thermal oxidation, electrodeposition and by sputtering.

Thermal Oxidation
This is by far the most widely used method of producing Cu₂O for the fabrication of solar cells. The procedure involves the oxidation of high purity copper at an elevated temperature (1000 – 1,500 °C) for times ranging from few hours to few minutes depending on the thickness of the starting material (for total oxidation) and the desired thickness of Cu₂O (for partial oxidation).

The oxidation process can be carried out either in pure oxygen or in laboratory air. Cu₂O has been identified to be stable at limited ranges of temperatures and oxygen pressure. It has been indicated that during oxidation, Cu₂O is formed first and after a sufficiently long oxidation time, CuO is formed. However, at temperatures below 1000°C and at atmospheric pressure, mixed oxides of Cu₂O and CuO are formed as observed from the X-ray diffraction (XRD) results. It has been suggested that the probable reactions that could account for the presence of CuO in layers oxidized below 1000°C are (Musa et al., 1998):

\[ 4Cu + O_2 \rightarrow 2Cu_2O \]
\[ 2Cu_2O + O_2 \rightarrow 4CuO \]

The unwanted CuO can be removed using an etching solution containing FeCl₃, HCl and NaCl.

The oxidation process is followed by annealing the sample at 500 °C and then stopping the process by quenching in cold water. This process leads to good quality polycrystalline Cu₂O with the bulk resistivity in the range of 10² -10⁴ ohmcm (Trivich et al., 1978 and Economou et al., 1982). The resistivity can further be lowered by oxidizing in the presence of chlorine gas. Resistivities below 100 ohmcm have been reported in the literature (Olsen et al., 1980 and Olsen et al., 1982) using this procedure.

It is also worthy of note that the purity of the starting Cu₂O material can have a significant impact on the quality of Cu₂O and the performance of the resulting solar cell. A number of pre- and post-oxidation treatments have been suggested in the literature (Olsen et al., 1982) which involves cleaning, etching, polishing and annealing the material prior to and after the oxidations.

Electro-deposition
Another method of producing thin films of Cu₂O is by electro-deposition. Thin films of Cu₂O can be electro-deposited by cathodic reduction of an alkaline cupric lactate solution, either on metallic substrates or on transparent conducting glass slides coated with highly conducting semiconductors (Noguet et al, 1977).

The properties of the electrodeposited films of Cu₂O are largely similar to those prepared by thermal oxidation. The grain sizes of the electro-deposits varies from 0.1 to 10µm. The major problem, however, is in the high resistivity (10⁷ - 10⁹ ohmcm) of the electrodeposited Cu₂O film ( Economou et al., 1982).

Sputtering
Cathode sputtering is essentially one of the methods used for the preparation of thin films. The method requires very low pressure in the working space and therefore makes use of vacuum technique. The material to be sputtered is used as a cathode in the system in which a glow discharge is established in an inert gas at a pressure of 10⁻¹ – 10⁻² torr and a voltage of a few kilovolts. The substrate on which the film is to be deposited is placed on the anode of the system.

The positive ions of the gas created by the discharge are accelerated towards the cathode (target). Under the bombardment of the ions the material is removed from the cathode (mostly in the form of neutral atoms or in the form of ions). The liberated components condense on surrounding areas and consequently on the substrates placed on the anode.

Reactive sputtering is used in the production of Cu₂O. A chemical reaction that occurs with the cathode material (Cu in this case) by the active gas (oxygen) either added to the working gas or as the working gas itself. The resistivity of the deposited Cu₂O film can be controlled over a wide range by simply varying the oxygen pressure. Cu₂O films of resistivity as low as 25 ohmcm have been reproducibly obtained (Drobny et al., 1979) by this technique.

Fabrication of Cu₂O Solar Cells
Even though Cu₂O was known since 1904, very little attention was paid to it. The few research works done on it were mainly concerning its photoresponse, as reported (Olsen et al., 1982 and Wikipedia, 2008). As a result of pioneering work in 1975 at National Science foundation and at the Joint Centre for Graduate Studies (JCGS) on fabrication and characterization of Cu₂O cells that Cu₂O solar cells of 1% efficiency were fabricated in 1978. Further works on the cell at JCGS yielded an efficiency of 1.8%. Experimental and theoretical studies conducted at JCGS group highlighted more on the potential viability of Cu₂O for low cost photovoltaic (PV) power generation.
Until recently, efforts in the past to fabricate efficient solar cells were confined to Schottky barrier solar cells (Herion et al., 1980 and Olsen et al., 1982). However, in recent times, single polycrystalline Cu₂O used for solar cells are obtained via any of the methods presented earlier in this paper. The Schottky barrier solar cells and the heterojunctions have been extensively investigated. Also, in the past, workers have not succeeded in producing n-type Cu₂O and therefore a homojunction cell structure (Trivich, 1982) could not be fabricated. Recently, Cu₂O homojunction solar cells have been fabricated (Longcheng and Meng, 2007 and Kunhee and Meng, 2009).

**Schottky Barrier Cu₂O Solar Cells**

A frontwall Schottky barrier solar cell (Olsen et al., 1980) is usually fabricated by evaporating a metal on top of Cu₂O in high vacuum chambers. A number of metals on Cu₂O have been tried and the best performance has been obtained with a natural Cu/Cu₂O junction.

A new method of obtaining Cu₂O has been reported (Iwanoski et al., 1985). This technique uses hydrogen ion bombardment of Cu₂O surface thus reducing the top surface to copper. Schottky barrier solar cells can also be fabricated in the back wall structure. This mode requires a natural junction using copper or any other material as the base and depositing a layer of Cu₂O on top of the metal base. The light then illuminates the junction through the semiconductor side. But back wall cells require thin layer of Cu₂O (<1μm) because of the high absorption coefficient and low diffusion length of the minority carriers (Trivich et al., 1978). Partial thermal oxidation can be used to produce the thin layer. Back wall solar cells of Cu₂O offer greater advantage over front wall cells because of the mechanical stability of the base materials and simplicity of fabrication.

**Heterojunction Solar Cells**

A heterojunction solar cell is fabricated by depositing n-type semiconductor of suitable band gap on Cu₂O. Methods like vacuum deposition, sputtering and electrodeposition have been used for the deposition. Several heterojunction solar cell structures have been studied and reported (Herion et al., 1980). Examples are the zinc oxide-cuprous oxide (ZnO/Cu₂O) and cadmium oxide-cuprous oxide (CdO/Cu₂O) solar cells.

Transparent conducting metal oxides, being n-type were used extensively in the production of heterojunction cells using p-type Cu₂O. Herion et al. (1980) have reported on a fairly detailed study of ZnO/Cu₂O devices. This was achieved due to the interest they had on metal oxides being generally stable compounds and the assumption that they are not likely to react with Cu₂O. Eventually, the cell exhibited poor performance. The cell characteristics were clearly influenced by the copper rich region adjacent to Cu₂O substrate. It was finally concluded that ZnO/Cu₂O heterojunction is essentially Cu/Cu₂O Schottky cell since Zn reduces Cu₂O to Cu. Hence reaction occurs with this type of cells too. Indium Tin Oxide (ITO) devices prepared by different techniques on Cu₂O were also reported (Herion et al., 1980 and Georgieva and Ristov, 2002). In all cases resistivity was found to be high and efficiency very low. Tanaka et al. (2004) have reported an intensive work on Cu₂O prepared with TCOs. They used TCO thin films such as indium oxide (In₂O₃), tin oxide (SnO₂) and multicomponent oxides like aluminium-zinc-oxide(AZO) and aluminium-zinc-indium-tin-oxide (AZITO), in addition to ZnO. Highest efficiency of 1.2% was obtained with AZO-Cu₂O devices prepared at 150°C and measured under air mass 2 (AM2) illumination. Others yielded disappointing results. A better cell was reported by Trivich et al. (1981) using CdO. It was found to generate an open circuit voltage, V<sub>oc</sub> = 0.4V and a short circuit current, I<sub>sc</sub> = 2mA cm<sup>-2</sup>.

There was no reduction of the Cu₂O layer observed, which shows the absence of any chemical reaction at the CdO/Cu₂O interface. This suggested a possibility of avoiding chemical reaction at the interface by the use of heterojunction, especially, of oxides on Cu₂O. However, the best solar cell, to date using TCO thin films is a multicomponent oxides, ITO/ZnO/Cu₂O solar cell. It was reported to have an efficiency of 2% (Mittiga et al., 2006). Copper (1) sulphide (Cu₂S) is another promising material for heterojunction devices for the formation of n-type Cu₂O/Cu₂S heterojunction solar cell since Cu₂S is a p-type semiconductor as grown. Works in the past were aimed at fabricating CdS/Cu₂S heterojunction devices. Fajinmi, 2000, reported on the deposition of Cu₂S, while Varkey, 1990, reported on copper (1) sulphide/crystalline silicon (Cu₂S/c-Si) solar cells.

**Homojunction Solar Cells**

In the past the low efficiency of Cu₂O cells was attributed to the lack of n-type Cu₂O, since an approach to achieving n-type doping has not yet been fully developed. Without it, the early studies had to rely on Schottky junctions and p-n heterojunctions for photovoltaic devices, which do not provide high efficiency. However, Fernando et al, 2002, has reported the possibility of obtaining n-type photoresponses from clean copper plates, immersed in CuSO₄ solution for a few days. Subsequently, the same researchers reported the n-type Cu₂O produced by heating copper sheets in CuSO₄ solution. The formation of the n-type Cu₂O on copper surface, by heating copper sheets in CuSO₄ solution, can be explained by the following chemical reaction:

\[ \text{Cu}^{2+} + \text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ \]

The long held consensus is that the best approach to improve cell efficiency in Cu₂O-based photovoltaic devices is to achieve both p- and n-type Cu₂O and thus p-n homojunction of Cu₂O solar cells. Experimental results in achieving both conduction types in electrochemically deposited Cu₂O by varying solution pH was reported by Longcheng and Meng, 2007. This enables p-type and n-type Cu₂O to be deposited electrochemically in sequence to form a p-n homojunction of Cu₂O. However, the first homojunction solar cell of Cu₂O using the electrochemical method was made by Kunhee and Meng (2009). The cell has only 0.1% efficiency due to high resistivity of the p- and n-Cu₂O layers (or substrate).
Performance of Cu₂O Solar Cells
The observed conversion efficiency of Cu₂O cells has remained far below the theoretical value, regardless of the method of growth of Cu₂O and the mode of fabrication of the cells. The best results obtained so far are in the range of 1-2 %. Many reasons have been advanced for this low performance.

Barrier height measurements in various Schottky barrier solar cells have shown that values are always in the range 0.7-0.9 eV regardless of the metal except for the case of gold and silver which form ohmic contacts with Cu₂O. This apparent plateau for the value of barrier heights is believed to be the principal cause of the low performance of the Cu₂O Schottky barrier solar cells. Studies on Schottky barrier solar cell indicate that there always exist a copper rich region at the interface between metal and Cu₂O regardless of the choice of the metal used. All Schottky type cells are therefore essentially Cu/Cu₂O solar cells and hence the constancy of the value of barrier height and the low electrical power conversion efficiency.

Papadimitriou et al. (1981) have reported the results of their study on ZnO/Cu₂O junction solar cells. The best values they obtained for open – circuit voltage (VOC) were of the order of 0.3 V. A copper rich region adjacent to the Cu₂O substrate was found to be responsible for dictating the cell characteristics. For the case of CdO/Cu₂O heterojunction formed at room temperature, no copper metal was found at the interface. The CdO/Cu₂O cell showed a short circuit current of 2 mAc⁻² and VOC of 0.4 V.

The method of electrodeposition is particularly attractive for its simplicity, low cost and possibility of making large area thin films (Wijesundara et al., 2006). But resistivity of electrodeposited Cu₂O films were reported to be quite high, of the order of 10⁵ – 10⁶ Ωcm (Economou et al. 1982 and Wijesundara et al., 2000), and therefore, the photovoltaic properties of the solar cells made with these films were poor. Several other production techniques of Cu₂O layer were later employed in order to improve on its resistivity. The various methods include thermal oxidation (Sear and Fortin, 1984, Musa, 1995 and Mittiga et al., 2006), chemical vapour deposition, or radio frequency magnetron sputtering (Akimoto et al., 2006). However, little improvements were recorded as the efficiency was still very low, less than 2%.

Surface analyses combined with barrier height studies (Olsen et al., 1979, Herion et al., 1980 and, Olsen et al., 1982) indicate that Cu₂O Schottky barriers made with low work function metals are essentially Cu/Cu₂O cells due to reduction of the Cu₂O surface. The copper rich region essentially determines the barrier height. Auger depth profiles showed the occurrence of chemical reaction of thermodynamically stable oxides at the interface and correspondingly to some reduction of the Cu₂O. Thallium is reported to be the only metal identified that would not reduce Cu₂O (Olsen et al., 1982). With 3.7 eV as its work function and theoretical value of a dark current, J₀ of the order of 10⁻¹⁴ Acm⁻², a Ti/Cu₂O Schottky barrier has a very large theoretical efficiency. Efficiency of 10% at air mass one (AM1) would be possible. However, deposition of Ti of reasonable sheet conductance is not possible on a substrate at room temperature. It was reported that Ti of adequate sheet conductance was deposited on cool substrate. Studies on the Ti/Cu₂O barrier represented only a slight improvement over the Cu/Cu₂O device. In fact studies on a number of metal/Cu₂O and metal/insulator/Cu₂O contacts (Trivich et al, 1981) showed that the barrier heights did not depend on the work function of metal.

Intensive work was done regarding deposition of Cu₂O and the dopant impurities (Musa, 1995 and Akimoto et al., 2006) but general observations show that the various dopants used to further lower the resistivity showed no significant improvement, with Cadmium as an exception. Nitrogen acts as a p-type dopant. Other methods of improving on the resistivity of the layer were then employed. Annealing of the Cu₂O layer at moderate temperatures, as reported by Noguet et al. (1977); Musa et al. (1998) and Wijesundara et al. (2006), showed some improvements. Another treatment followed; which is potassium cyanide (KCN) treatment as reported by Akimoto et al., (2006). The above treatments yielded little improvement since the efficiency, as at the time of this report, is still not more than 2%, for Schottky barrier Cu₂O solar cells.

The encouraging aspect of the above treatments is that, they revealed ways for further improvements. It was shown that the PV properties of Cu₂O Schottky cells are significantly affected by the surface treatment and crystallinity of Cu₂O (Fernando et al., 2002 and Tanaka et al., 2004). In particular, the deposition method and conditions are important when depositing a thin film on Cu₂O sheets.

Concluding remarks and suggestions for further work
Some reasons based on the analysis given can now be advanced for the low value of electrical power conversion efficiency of Cu₂O based solar cells.

(1) The high resistivity of the starting material. This problem contributes greatly to the performance of electrodeposited Cu₂O cells in particular. Further work need to be done to lower the resistivity of electrodeposited Cu₂O by doping.

(2) Non–existence of a technique of doping Cu₂O to get low resistivity n-type semiconductor before now so that conversion efficiencies greater than 2% for p-n homojunction Cu₂O solar cell could be fabricated. It is suggested that the work of Fernando et al, 2002 on production of n-type Cu₂O, Longcheng and Meng, 2007 and Kunhee and Meng, 2009, on p-n Cu₂O homojunction be pursued vigorously for the purpose of obtaining low resistivity Cu₂O homojunction solar cells. A better understanding of the stoichiometry of Cu₂O is desirable in this respect.

(3) A copper rich or oxygen deficient surface which makes all Schottky barriers essentially a Cu/Cu₂O structure. A suitable method of getting rid of the Cu-enriched region from the interface need to be explored.
It is therefore clear that a better understanding and remedy to the problems enumerated above demands more basic and applied investigation on Cu$_2$O.

REFERENCES


Lange, B. (1938): Photoelements and their Applications*, Reinhold publishing Corp; New York,


