



A Review: Synthesis, Characterization and Cell Performance of Cu_2O Based Material for Solar Cells

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ABSTRACT

Low-cost thin film oxide/oxide heterojunctions based photovoltaic solar cells are one of the alternatives to silicon solar cells, among the potential photovoltaic devices based on semiconductor oxides. Cuprous oxide is a potential material for the fabrication of low cost solar cells for terrestrial application. In this article, firstly, we reviewed cuprous oxide Crystal structure, Band structure, different properties of cuprous oxide material such as electrical and transport properties and photoluminescence. Then we discuss in detail the synthesis techniques for the production of copper oxide such as Thermal Oxidation, Anodic Oxidation, Electrodeposition, Sputtering, Chemical vapor deposition etc. Latter on a detailed survey on the previous work so far carried out on Cu_2O based solar cells is presented. The fabrication and cell performance of based Solar Cells is also discussed.

Key words: Cell performance, Solar Cells, Low-cost thin.

INTRODUCTION

The need for sustainable power generation has encouraged research into a variety of photovoltaic materials and structures, with a greater emphasis being placed on a balance between performance and cost. The stability of many semiconducting oxides relative to other inexpensive solar cell technologies, such as organic¹ and dye-sensitized² cells, makes them an attractive alternative. Yet low-cost, non-toxic, inorganic solar cell technologies have received comparatively little attention. In a recent report, nine

inorganic semiconductors were identified as having both the potential for annual electricity production in excess of worldwide demand and material extraction costs less than that of crystalline silicon³. Further to materials costs, a recent study examined the high cost of modern vacuum deposition methods and highlighted the need for low-temperature, atmospheric, solution-based synthesis⁴⁻⁷. Copper has two stable oxides: cupric oxide (CuO) and cuprous oxide (Cu₂O). These two oxides are semiconductors with band gaps in the visible or near infrared regions⁸. These materials have several advantages: (i) availability and

abundance of the starting materials (ii) non-toxic nature (iii) Low production cost (iv) Band gaps lie in an acceptable range for solar energy conversion, and (v) n- and p-type conductivity⁹⁻¹¹. Copper and copper oxide (metal-semiconductor) are one of the first photovoltaic cells invented¹². Its semiconductor properties and the emergence of photovoltaic effect were discovered by Edmond Becquerel in 1839 while experimenting in the laboratory of his father, Antoine-César Becquerel. Copper (I) Oxide (Cu, O), in particular, has been synthesized extensively in polycrystalline form by electrodeposition from solutions near room temperature^{5,13,14}. Cu, O has a direct band-gap of 2.17 eV which is suitable for photovoltaic conversion. Theoretical calculations have predicted an electrical power conversion efficiency of approximately 9-12 %. The practical electrical power conversion efficiencies obtained by researchers, in the past, are below 2%¹⁵. However, recently efficiency of 3% has been reported¹⁶. 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 Cu, O solar cells are now known.

In this review the developments of Cuprous Oxide (Cu, O) solar cells are reviewed. We discuss the properties of Cuprous Oxide and the methods of the production of Cuprous Oxide. Subsequently, a discussion on the performance of these cells is reported. Finally, the conclusion and outlook to further improve Cuprous Oxide solar cell fabrication and performance are presented.

Crystal structure of Cu, O

The unit cell of Cu, O with a lattice constant of 0.427 nm is composed of a body centered cubic lattice of oxygen ions, in which each oxygen ion occupies the center of a tetrahedron formed by copper ions. The Cu atoms arrange in an fcc sublattice, the O atoms in a bcc sublattice. The unit cell contains 4 Cu atoms and 2 O atoms. One sublattice is shifted by a quarter of the body diagonal. The space group is Pn3m, which includes the point group with full octahedral symmetry. This means particularly that parity is a good quantum number. Figure 1 shows the crystal lattice of Cu, O. Cuprous oxide (copper (I) oxide Cu, O) is found in nature as cuprite and formed on copper by heat. It is a red color crystal used as a pigment and fungicide [17].

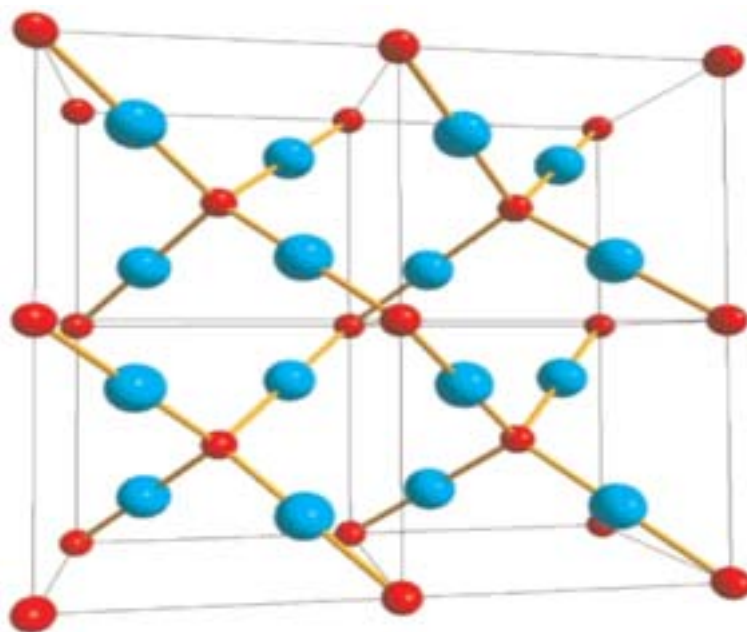


Fig. 1: Crystal structure of Cu, O shown by four unit cells. The big turquoise spheres represent copper; the small red spheres represent oxygen. As can be seen, each copper atom is linearly coordinated by two oxygen atoms

Band structure of Cu, O

Cuprous oxide (Cu, O) is a direct gap semiconductor with band gap 2.17 eV[11-19]. Cu, O crystals have a simple cubic lattice with two formulas unit per unit cell and have the symmetry of space group O_h^4 . There are two way of choosing the unit cell. In one, the oxygen atoms form a bcc lattice while in other, the copper atoms form fclattice. The site symmetries of the oxygen and the copper are Td and T 3d respectively. Several band structure calculations have followed the initial Augmented-Plan-Wave (APW) calculation by Dahl and Switendick²⁰. Band structure calculations show that the lowest energy band-to-band transition is

Direct at the \bar{A} point of the Brillouin zone as deposited in figure 2. The four transitions are named according to the wavelengths of their spectral positions yellow, green, blue, and indigo, respectively (see Figure 2). At the zone center the valence band is largely comprised of copper 3d orbitals and has Γ_7^+ symmetry, while the conduction band is made up of copper 4s orbitals²¹ and has Γ_6^+ . An optical transition between these band would be s- \rightarrow d in an atomic sense, making it parity forbidden ($\Gamma_7^+ \rightarrow \Gamma_6^+, \Gamma_8^+ \rightarrow \Gamma_6^+$). On the left of Fig. 2, the band dispersion is shown schematically. It has been studied by cyclotron resonance experiments²²⁻³⁴.

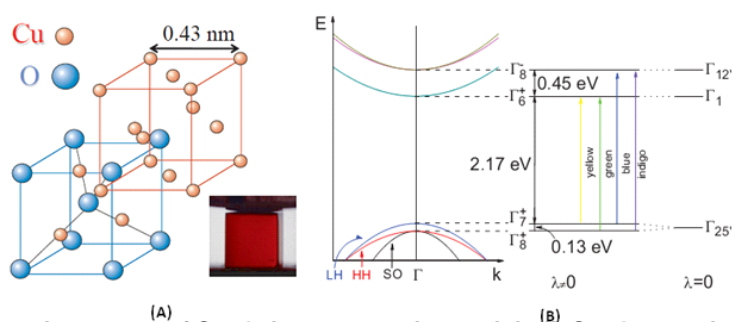


Fig. 2: (a) Crystal structure of Cu, O. Inset: natural-growth bulk Cu, O crystal. (b) Schematic of the Cu, O band structure near zone center. The red arrow denotes quadrupole transition³⁵.

Properties of Cuprous Oxide

Electrical and transport properties of Cuprous Oxide

Copper oxide is a defect semi-conductor but nowadays it is well established that Cu, O is a natural p-type semiconductor, whose carrier concentration depends on the amount of cation

deficiency³⁶, cuprous oxide is one of such non-stoichiometric materials with formula $Cu_{2-\delta}O$. The deviation from stoichiometry, δ is generally attributed to some imperfections. Sears *et al.* 1984³⁷ reported that an excess of oxygen, as a result of stoichiometry, is the major active impurity and gives a p-doped semiconductor.

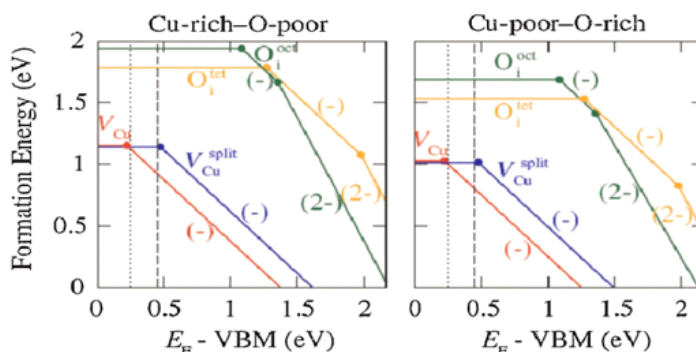


Fig. 3: Formation energies for intrinsic p-type defects in Cu, O in (a) Cu-rich-O-poor conditions and (b) Cu-poor-O-rich conditions. The solid dots denote the transition levels³

Theoretical studies³⁸⁻⁴⁵ on the role of intrinsic defects in Cu₂O agree that the simple copper vacancy and the vacancy in the so-called split configuration have the lowest formation energies (in Cu-poor and Cu-rich conditions, see Figure 3) compared to the other possible intrinsic acceptors, which are oxygen interstitials (in octahedral and tetrahedral coordination). The transition level (0/-) of VC_u is at 0.23eV. The formation energies of both defects are very similar (1.15 and 1.14 eV) and at least 0.7eV lower than that of oxygen interstitials.

Photoluminescence property of copper oxide

All copper oxides have one thing in common that they are weak luminescent or even

nonluminescent systems. In particular, CuO is "dark" black and luminescence data on this material have rarely been collected and reported⁴⁶⁻⁵⁰. Whoever unambiguously shows several luminescence signals, however, these are weak in intensity. The latter is due to the fact that optical transitions require parity change, which is not given between the energetic highest valence band and lowest conduction band of the direct semiconductor. The corresponding spin forbiddance of the transition resulting in the weak luminescence is partly broken by three possible effects: (a) defects within the crystal, (b) the decay of ortho-excitons, or (c) phonon assisted transitions.

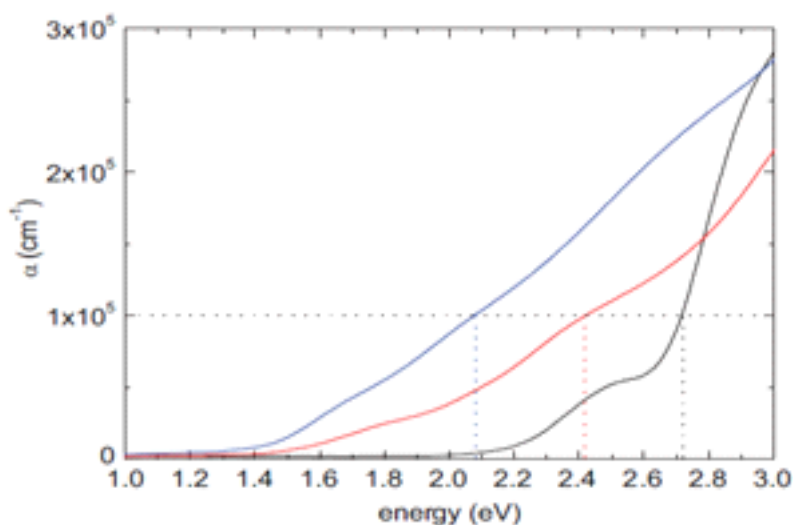


Fig. 4: Absorption spectra of Copper oxide. The horizontal and vertical dotted lines indicate the energies where the absorption coefficient reaches $1 \times 10^5 \text{ cm}^{-1}$ in the spectra[3]

The majority of the luminescence studies reported were performed on thermally oxidized copper (Figure 4), and they observed broad luminescence bands of Cu₂O have been assigned to doubly charged oxygen vacancies (V_{O}^{2+}) at 1.72 eV (720 nm) singly charged oxygen vacancies (V_{O}^{1+}) at 1.53 eV (810 nm) and copper vacancies (VCu) at 1.35 eV (920 nm). This assignment is very consistently used in literature⁵¹⁻⁵⁵, but the exact peak positions and especially the relative intensities strongly depend on the used growth process as well as sample processing. The two high-energy bands were only observed at low measuring

temperatures in the past, whereas the copper-vacancy band at low energies dominates the spectra at room temperature. In high-quality material, e.g., floating-zone grown single crystals, one can observe the additional recombination of the 1s ortho-exciton via an electric quadruple transition at temperatures of 4.2K at an energy of 2.03 eV (610 nm), and respective phonon side bands via electric dipole transitions.

Methods for the production of copper oxide

The optical and electrical properties of absorber materials in solar cells are key parameters

which determine the performance of solar cells. Hence, it is necessary to tune these properties properly for high efficient device. Electrical properties of , such as carrier mobility, carrier concentration, and resistivity are very dependent on preparation methods. Cuprous oxide thin films have been prepared by various novel techniques for the synthesis of cuprous oxide i.e. reactive sputtering, sol-gel technique, plasma evaporation, thermal oxidation, chemical vapor deposition, anodic oxidation, reactive sputtering, electrodeposition etc. Each of these methods has its own advantages and disadvantages.

Thermal Oxidation

This is by far the most widely used method of producing for the fabrication of solar cells. The procedure involves the oxidation of high purity copper at an elevated temperature ($^{\circ}$), 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 (for partial oxidation). The oxidation process can be carried out either in pure oxygen or in laboratory air. has been identified to be stable at limited ranges of temperatures and oxygen pressure. It has been indicated that during oxidation, is formed first and after a sufficiently long oxidation time, CuO is formed. However, at temperatures below 1000 $^{\circ}$ C and at atmospheric pressure, mixed oxides of and are formed as observed from the X-ray diffraction) results. It has been suggested that the probable reactions that could account for the presence of in layers oxidized below are⁵⁶.

The unwanted can be removed using an etching solution containing , HCl and . The oxidation process is followed by annealing the sample at and then stopping the process by quenching in cold water. This process leads to good quality polycrystalline with the bulk resistivity in the range of⁵⁷⁻⁵⁸. The resistivity can further be lowered by oxidizing in the presence of chlorine gas. Resistivity's below have been reported in the literature⁵⁹⁻⁶⁰ using this procedure. It is also worthy of note that the purity of the starting material can have a significant impact on the quality of and the performance of the resulting solar cell. A number of pre- and post-oxidation treatments have been suggested in the literature⁶⁰ which involves

cleaning, etching, polishing and annealing the material prior to and after the oxidations.

Anodic oxidation

Anodic oxidation of copper in alkaline solution is one of the standard methodologies for producing cuprous oxide powders used for marine paints and for plants preservation. Those powders are composed of particles of micrometer scale. However, solar cells, for their part, require particles or films of much smaller dimensions in order to achieve higher efficiency. Passive protecting layers formed on copper during anodic oxidation in alkaline solutions are widely investigated and described in electrochemical literature. The structure of those films formed on copper in neutral and alkaline solutions consists mainly of and or Stankoviae *et al.* (1998; 1999)⁶¹ investigated the effect of different parameters such as temperature, and anodic current density on powder preparation. The lowest value of average crystallite size was obtained at , whereas the highest value was obtained at . Singh *et al.*, (2008)⁶² reported synthesis of nanostructured by anodic oxidation of copper through a simple electrolysis process employing plain water as electrolyte. They found two different types of nanostructures. One of them belonged to particles collected from the bottom of the electrolytic cell, while the other type was located on the copper anode itself.

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 and a voltage of a few kilovolts. The substance 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 . 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 film can be controlled over a wide range by simply varying the oxygen pressure. Films of resistivity as low as has been reproducibly obtained⁶³.

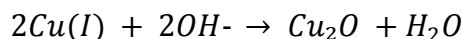
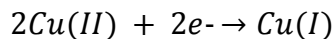
Chemical vapor deposition

Chemical vapor deposition is a chemical process used to produce high-purity, high performance solid materials. The films may be epitaxial, polycrystalline or amorphous depending on the materials and reactor conditions. Chemical vapor deposition has become the major method of film deposition for the semiconductor industry due to its high throughput, high purity, and low cost of operation. Several important factors affect the quality of the film deposited by chemical vapor deposition such as the deposition temperature, the properties of the precursor, the process pressure, the substrate, the carrier gas flow rate and the chamber geometry. Kobayashi *et al.* (2000)⁶⁴ investigated the high-quality thin films grown epitaxial on (110) substrate by halide chemical vapor deposition under atmospheric pressure. CuI in a source boat was evaporated at a temperature of , and supplied to the growth zone of the reactor by carrier gas, and was also supplied there by the same carrier gas. Partial pressure of CuI and O₂ were adjusted independently to. They found that the optical band gap energy of film calculated from absorption spectra is . The reaction of CuI and O₂ under atmospheric pressure yields high quality films.

Electrodeposition

Electrodeposition is a low temperature processing method where films are deposited from solution precursors. The advantages include the elimination of heat treatments which can be especially meaningful for nanostructures, an effective control of the deposition rate via over potential, the possibility to control the shape or crystallographic orientation via the pH or the precursor additives. It is a very low cost method since it does not require any vacuum processing can be electrodeposited between using a mixture of alkaline cupric sulfate, lactic acid and NaOH. Thickness ranges from. The potential must be properly controlled to allow electrodeposition of as

opposed to elemental Cu. Deposited films can be annealed. The reaction is



This technique typically yields a polycrystalline structure with the average grain size between . Electrochemical deposition technique is a simple, versatile and convenient method for producing large area devices. Low temperature growth and the possibility to control film thickness, morphology and composition by readily adjusting the electrical parameters, as well as the composition of the electrolytic solution, make it more attractive. At present, electrodeposition of binary semiconductors, especially thin films of the family of wide band gap II-IV semiconductors, from aqueous solutions is employed in the preparation of solar cells. A photovoltaic device composed of a p-type semiconducting cuprous (I) oxide () and n-type metal oxides has attracted increasing attention as a future thin film solar cell, due to a theoretical conversion efficiency of around 20% and an absorption coefficient higher than that of a Si single crystal⁶⁵.

The parameters of the solar cells, such the open circuit voltage, the short circuit current, the fill factor (I_{sc}), the diode quality factor (FF), serial and shunt resistant and efficiency were determined. The barrier height can also be determined from capacity-voltage characteristics.

Fabrication and cell performance of based solar cells

Fabrication of Solar Cells

The experimental and theoretical studies conducted at Joint Centre for Graduate Studies (JCGS) group highlighted more on the potential viability of for low cost photovoltaic (PV) power generation. However, in recent times, single polycrystalline 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 and therefore a homojunction cell structure (Trivich, 1982) could not be fabricated.

Recently, homojunction solar cells have been fabricated (Longcheng and Meng, 2007 and Kunhee and Meng, 2009).

Schottky Barrier Solar Cells

As a metal is in contact with a semiconductor, a Schottky barrier is formed. Theoretically, the Schottky barrier height is only determined by the work function of the metal and the electron affinity of the n-type semiconductor. For a p-type semiconductor, the higher the work function of the metal, the easier it is to form an ohmic contact. While for an n-type semiconductor, the lower the work function of the metal, the easier it is to form an ohmic contact. Copper is used as top metal contact for p-type cuprous oxide, while aluminum is used as top metal contact for n-type cuprous oxide. A front wall Schottky barrier solar cell (Olsen *et al.*, 1980) is usually fabricated by evaporating a metal on top of in high vacuum chambers. A number of metals on have been tried and the best performance has been obtained with a natural Cu/ junction. A new method of obtaining has been reported (Iwanoski *et al.*, 1985). This technique uses hydrogen ion bombardment of 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 on top of the metal base. The light then illuminates the junction through the semiconductor side. But back wall cells require thin layer of 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 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 . Methods like vacuum deposition, sputtering and electro-deposition 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 (/) and cadmium oxide-cuprous oxide (/) solar

cells. The / junction is an ideal abrupt heterojunction at thermal equilibrium and using the known measured values of electron affinities, band gaps and carrier densities in and , E_a is estimated approximately (as shown in Figure 5) [66, 67, 68] This value is approximately in the range of extracted activation energies. Thus, it is concluded that the interface recombination is the dominant current flow mechanism across the / heterojunction where the rate limiting step is diffusion of holes against the barrier established by band bending to recombine with electrons trapped in interfacial states. This mechanism is shown as path 1 in Figure 5.

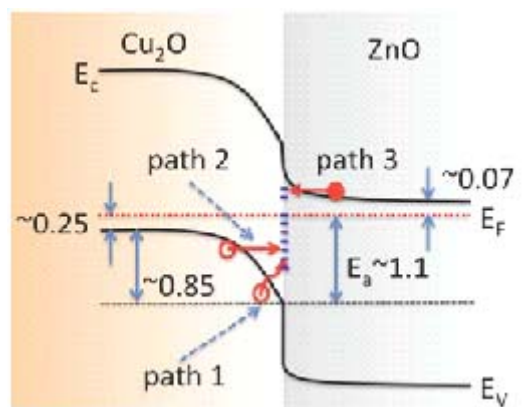


Fig. 5: Band diagram of the $\text{Cu}_2\text{O}/\text{ZnO}$ heterojunction. E_C , E_V , E_F and E_a are the conduction-band-edge, valence-band-edge, Fermi-level, & activation energies, respectively. Most of the band bending is shown to be on the side because of lower doping in compared to the side. Paths 1 and 2 indicate two possible hole recombination pathways through interface defects. Activation energy (E_a) is the barrier that the holes have to overcome to recombine. The approximate energy levels are based on the properties of bulk Cu_2O and ZnO . Electron affinities: 3.2 eV (ZnO) [66] and 4.2 eV [67] (ZnO); band gaps: 2.17 eV [68] (Cu_2O) and (); dielectric constants: 7.11 (Cu_2O) and 7.8 (ZnO), electron effective mass: 0.275 m_0 (ZnO) and hole effective mass in (Cu_2O) - where m_0 is free electron mass⁶⁸

Transparent conducting metal oxides, being n-type were used extensively in the production of heterojunction cells using p-type Cu_2O . 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. The cell characteristics were clearly influenced by the copper rich region adjacent to substrate. It was finally concluded that heterojunction is essentially Cu/ Schottky cell since Zn reduces to Cu. Hence reaction occurs with this type of cells too.

In all cases resistivity was found to be high and efficiency very low. However, the best solar cell, to date using TCO thin films is a multi-component oxides, ITO/ZnO/ solar cell. It was reported to have an efficiency of 2% (Mittiga *et al.*, 2006). Copper (I) sulphide (Cu₂S) is another promising material for heterojunction devices for the formation of n- / Cu₂S heterojunction solar cell since Cu₂S is a p-type semiconductor as grown. Works in the past were aimed at fabricating heterojunction devices. Fajinmi, (2000), reported on the deposition of Cu₂S, while Varkey, (1990), reported on copper (I) sulphide/crystalline silicon () solar cells.

Homo-junction 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 photo-responses from clean copper plates, immersed in CuSO₄ solution for a few days. Subsequently, the same researchers reported the n-type produced by heating copper sheets in CuSO₄ solution.

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 and thus p-n homo-junction of solar cells. This enables p-type and n-type Cu₂O to be deposited electrochemically in sequence to form a p-n homo-junction of . However, the first homo-junction solar cell of 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-layers (or substrate).

Cell characterization

Solar cell is a device that produces electricity from sunlight. Upon illumination, photons are absorbed by an active layer in a solar cell, and then electron-hole pairs are generated as excitons. The excitons need to diffuse to a donor–acceptor (DA) interface to dissociate into free charges. After that, electrons and holes need to transport to electrodes through their corresponding percolation pathway. During these processes, six main steps affect device performance:

- i) Photon absorption ,
- ii) Exciton generation ,
- iii) Exciton diffusion ,
- iv) Exciton dissociation ,
- v) Charge transport ,
- vi) Charge collection.

These six processes determining a solar cell performance can be better understood in a connection with external quantum efficiency (η_{EQE}) of a device. η_{EQE} is defined as a percentage of the number of charge carriers collected at the electrode under short-circuit condition to the number of photons incident on the device⁶⁸ can be expressed as the product of the above steps⁶⁹.

$$\eta_{EQE} = \eta_{ph} \times \eta_{ex} \times \eta_{diff} \times \eta_{ed} \times \eta_{tr} \times \eta_{cc} \quad \dots(1)$$

Solar cell efficiency can be calculated from its current density voltage ($J-V$) characteristic curves. From such curves, open-circuit voltage, short-circuit current density and fill factor can be obtained. Then energy conversion efficiency can be determined by:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_s} \quad \dots(2)$$

Where P_s is the incident light power density

Equivalent circuit of a solar cell is shown as Figure 6. A series resistance R_s originates from contact and bulk semiconductor, and a shunt resistance R_{sh} comes from poor diode contact. The J-V characteristics can be described as.

$$J = J_0 \left\{ \exp \left[\frac{q(V - J R_s A)}{n k_B T} \right] - 1 \right\} + \frac{V - J R_s A}{R_{sh} A} - J_{ph} \dots (3)$$

Where k_B is Boltzmann's constant, T is temperature, q is elementary charge, A is device area, n is ideality factor of the diode, J_0 is reverse saturation current density, J_{ph} is photocurrent, R_s is series resistance and R_{sh} is shunt resistance. The J-V curves and photovoltaic parameters including V_{oc} and FF strongly depend on the n ,. In the mid-1970s, gained renewed interest since it was considered as a low-cost material for solar cells. This renaissance took only about 10 years and the interest on decreased. The developments made during that period are collected in the review of Rai from 1988⁷⁰. It is worthwhile to have a look at his conclusions and suggestions for future work⁷⁰. The poor performances were linked to a few but essential issues: (i) Control of the conductivity of the p-type layer by doping – an issue that has been solved by nitrogen doping. (ii) Schottky barrier solar cells have copper-rich or oxygen deficient surfaces that limit the performance and will always suffer from this problem (Schottky-type solar cells with are today no longer of relevance). (iii) Heterojunction solar cells should be investigated by which the chemical reactions at the interface between the two materials can be controlled and the reduction of to Cu can be avoided. Indeed, in the last 8–10 years the investigations on cuprous oxide as a solar-cell material have put the focus on heterostructure systems and almost exclusively used ZnO as the n-type transparent window layer. Maximum values for the open-circuit voltage are around, short-circuit currents around 10 and fill factors FF at .

The limitations in the performance were in part attributed to interface defects, crystal orientation, and grain sizes, series resistance due to the high resistivity of the absorber layer, and in recent reports to the minority-carrier transport length^{71, 72}. It has been investigated that the open circuit voltage and the short circuit current density decrease with increase in temperature. Drops because of increase reverse current saturation with temperature because minority carriers increase with increase in temperature. Decrease because of increase the recombination of the charges.

Historical review on based Solar Cells

Even though was known since 1904, very little attention was paid to it. The few research works done on it were mainly concerning its photo-response, as reported⁶⁰. By 1927 the transferring capacity of another metal-semiconductor junction solar cell, made of copper and the semiconductor copper oxide, had been demonstrated. Towards both the selenium cell and the copper oxide cell were employed in light sensitive devices, such as photometers for the use in photography. These early solar cells, however, still had energy-conversion efficiencies of less than . As a result of pioneering work in at National Science foundation and at the Joint Centre for Graduate Studies (JCGS) on fabrication and characterization of cells that solar cells of efficiency were fabricated in . Further works on the cell at JCGS yielded an efficiency of

Experimental and theoretical studies conducted at JCGS group highlighted more on the potential viability of for low cost photovoltaic () power generation. Until recently, efforts in the past to fabricate efficient solar cells were confined to Schottky barrier solar cells. However, in recent times, single polycrystalline 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 and therefore a homo-junction cell structure could not be fabricated. Recently, homojunction solar cells have been fabricated.

Performance of Cu, O Solar Cells

The low efficiency was attributed to the naturally p-type conduction in , formed a copper-rich region at the metallurgical interfacial region of and other semiconductor or metal layer, which prevented a p-n junction in , the basic device structure in most inorganic solar cells. In this case, a homo-junction of is needed to achieve high efficiency solar cell Both p-type and n-type thin films prepared by electrodeposition have been reported by⁷³ they observed conversion efficiency of cells has remained far below the theoretical value, regardless of the method of growth of and the mode of fabrication of the cells. The best results

obtained so far are in the range of 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. This apparent plateau for the value of barrier heights is believed to be the principal cause of the low performance of the Schottky barrier solar cells. Studies on Schottky barrier solar cell indicate that there always exist copper rich regions at the interface between metal and regardless of the choice of the metal used. All Schottky type cells are therefore essentially solar cells and hence the constancy of the value of barrier height and the low electrical power conversion efficiency.

Papadimitriou *et al.*, (1981)⁷⁴ have reported the results of their study on junction solar cells. The best values they obtained for open-circuit voltage were of the order of 0.3 V. A copper rich region adjacent to the substrate was found to be responsible for dictating the cell characteristics. For the case of heterojunction formed at room temperature, no copper metal was found at the interface. The cell showed a short circuit current of cm^{-2} and of . The method of electrodeposition is particularly attractive for its simplicity, low cost and possibility of making large area thin films⁷⁵. But resistivity of electrodeposited Cu, O films were reported to be quite high, of the order of ^{58,76}, and therefore, the photovoltaic properties of the solar cells made with these films were poor. Several other production techniques of layer were later employed in order to improve on its resistivity. The various methods include thermal oxidation⁷⁷⁻⁷⁸, chemical vapor deposition, or radio frequency magnetron sputtering⁷⁹. However, little improvements were recorded as the efficiency was still very low, less Surface analyses combined with barrier height studies^{59, 80} indicate that Schottky barriers made with low work function metals are essentially cells due to reduction of the surface. The copper rich region essentially determines the barrier height. Auger depth profiles showed the occurrence of chemical reaction of thermodynamically more stable oxides at the interface and correspondingly to some reduction of the Cu, O. Thallium is reported to be the only metal identified that would not reduce⁵⁹. With

as its work function and theoretical value of a dark current, J_0 of the order of , a 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/Cu, O barrier represented only a slight improvement over the Cu/Cu, O device. In fact studies on a number of metal/Cu, O and metal/insulator/Cu, O contacts (81) showed that the barrier heights did not depend on the work function of metal. Intensive work was done regarding deposition of Cu, O and the dopant impurities^{79, 82} 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 layer at moderate temperatures, as reported by^{75, 83}, showed some improvements. Another treatment followed; which is potassium cyanide (KCN) treatment as reported by⁷⁹. 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 O 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 Schottky cells are significantly affected by the surface treatment and crystallinity of⁸⁴. In particular, the deposition method and conditions are important when depositing a thin film on sheets.

Summary and outcome

In this report, we summarized the potential and possibilities of copper oxide semiconducting material, its band structure, method the production of Cuprous Oxide () and its applicability in solar cells. Some reasons based on the analysis reveals that (1) the high resistivity of starting material is responsible for the low value of electrical power conversion efficiency of based solar cells. (2) Non-existence of a technique of doping to get low resistivity n-type semiconductor before now so that conversion efficiencies greater than for p-n homojunction solar cell could be fabricated. It is suggested that the work of Fernando *et al*, 2002 on production of n-type , Long cheng and Meng, 2007

and Kunhee and Meng, 2009, on p-n homojunction be pursued vigorously for the purpose of obtaining low resistivity homojunction solar cells. (3) A copper rich or oxygen deficient surface which makes all Schottky barriers essentially a structure. A suitable method to get rid of the Cu-enriched region from the interface need to be explored. The copper oxide-based semiconductors that clearly fulfill the most important criteria of the future: availability, sustainability, non-toxicity (elements of hope), and ease of synthesis. It is therefore clear that a better understanding and remedy to the problems

enumerated above demands more basic and applied investigation on .

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REFERENCES

- H. Y. Chen , J. Hou , S. Zhang , Y. Liang , G. Yang , Y. Yang , L. Yu , Y. Wu , G. Li , *Nat. Photonics*, **3**: 649 (2009).
- B. O'Regan , M. Gratzel, *Nature*. **353**: 737 (1991),
- C. Wadia , A. P. Alivisatos , D. M. Kammen , *Environ. Sci. Technol.* **43**: 2072 (2009),
- T.G. Gutowski , M. S. Branham , J. B. Dahmus, A. J. Jones , A. Thiriez , *Environ. Sci. Technol.* **43**: 1584 (2009).
- Y. Sheena Mary, C. Yohannan Panicker*, HemaTresa Varghese And Somi Sebastian., *Orien. J. of Chem.* **26**(3): 901-910 (2010)
- K. Anuar , Z. Zainal, M. Z. Hussein , N. Saravanan , I. Haslina, *Sol. Energy Mater. Sol. Cells*, **73**: 351. (2002).
- L. Wang , K. Han , M. Tao, *J. Electrochem. Soc.* **154**: D91 (2007).
- D.K. Zhang, Y.C. Liu, Y.L. Liu, H. Yang, *Physica B* **351**: 178 (2004).
- A.E. Rakhshani, *Solid State Electron.* **29**: 7 (1986).
- H. Raebiger, S. Lany, A. Zunger, *Phys. Rev. B* **76**: 045209 (2007).
- PeiweiLv, WeifengZheng, Limei Lin, FuchuanPeng, Zhigao Huang, *Fachun Lai, Physica B* **406**: 1253–1257 (2011).
- G.P. Pollack, & D. Trivich, *Journal of Applied Physics*, **46**(1): 163-172 (1975).
- P. E. de Jongh , D. Vanmaekelbergh , J. Kelly, *Chem. Mater.*, **11**: 3512 (1999).
- K. Mizuno , M. Izaki , K. Murase , T. Shinagawa, M. Chigane , M. Inaba , A. Tasaka , Y. Awakura, *J. Electrochem. Soc.*, **152**: C179 (2005).
- C. Noguét, M. Tapiero, C. Schwab, J.P. Zielinger, D. Trivich, R.J. Komp, E.Y. Wang, and K., Wang, 1 st European community *Photovoltaic conference proc.* P. 1170, (1977).
- B. K. Meyer, *et.al.*, *Phys. Status Solidi* **B249**, No. 8, 1487-1509 (2012)
- Hideki Ushio, Shunichi Matsuno, Tsuyoshi Hamada., *Theory of Copper Oxide Superconductors. Springer London.*, 214, (2005).
- Cuprite —Mindat directory (2010).
- A. F. Wells, *Structural Inorganic Chemistry*, 3rd edn (Clarendon Press, Oxford, 1984)
- J. P. Dahl and A. C. Switendick, *J. phy. Chem. Solids*, **27**: 931-942 (1966)
- R. J. Elliot, *J. phys. Rev.*, **124**: 340-345 (1961)
- E. F. Gross, *INuovo Cimento* **3**: 672 (1956).
- E. F. Gross and F. I. Kreihgol'd, *JETP Lett.* **7**: 218 (1968).
- E. F. Gross and F. I. Kreihgol'd, *JETP Lett.* **10**: 139 (1969).
- J. B. Grun, M. Sieskind, and S. Nikitine, *J. Phys. Chem. Solids* **19**: 189 (1961).
- R. J. Elliott, *Phys. Rev.* **124**: 340 (1961).
- R. J. Elliott, *Phys. Rev.* **108**: 1384 (1957).
- J. P. Dahl, *J. Phys. Colloq.* **28**: C3 (1967).
- J. P. Dahl and A. C. Switendick, *J. Phys. Chem. Solids* **27**: 931 (1966).
- A. Daunois, J. L. Deiss, and B. Meyer, *J. Phys.* **27**: 142 (1966).
- M. Balkanski, Y. Petroff, and D. Trivich, *Solid*

- State Commun.* **5**: 85 (1967).
32. V. T. Agekyan, *Phys. Status Solidi A* **43**, 11 (1977).
 33. R. A. Forman, W. S. Brower, Jr., and H. S. Parker, *Phys. Lett.* **A36**: 395 (1971).
 34. D. Frohlich, R. Kenklies, C. Uihlein, and C. Schwab, *Phys. Rev. Lett.* **43**: 1260 (1979)
 35. W. H. Brattain, *Rev. Mod. Phys.* **23**: 203 (1951).
 36. C. Carel, M. Mouallem-Bahout, and J. Gaude', *Solid State Ion.* **117**: 47 (1999)
 37. W.M. Sear, E.J. Fortin, *Solar Energy materials*, **10**: 93-103 (1984)
 38. D. Wu, Q. Zhang, and M. Tao, *Phys. Rev. B* **73**: 235206 (2006).
 39. H. Raebiger, S. Lany, and A. Zunger, *Phys. Rev. B* **76**: 045209 (2007).
 40. A. F. Wright and J. S. Nelson, *J. Appl. Phys.* **92**: 5849 (2002).
 41. M. Nolan and S. D. Elliott, *Phys. Chem. Chem. Phys.* **8**: 5350 (2006).
 42. D. O. Scanlon and G. W. Watson, *J. Mater. Chem.*, **21**: 3655(2011).
 43. M. A. Meki-Jeskari, *Model. Simul. Mater. Sci. Eng.* **14**: 207 (2006).
 44. D. O. Scanlon, B. J. Morgan, and G. W. Watson, *Phys. Rev. Lett.* **103**: 096405 (2009).
 45. Y. S. Lee, M. T. Winkler, S. Cheng Siah, R. Brandt, and T. Buonassisi, *Appl. Phys. Lett.* **98**: 192115 (2011).
 46. H. L. MicKinzie and M. O'Keeffe, *Phys. Lett.* **24A**: 137 (1967).
 47. G. P. Pollack and D. Trivich, *J. Appl. Phys.* **46**: 163 (1975).
 48. M. Zouaghi, M. Tapiero, J. P. Zielinger, and R. Burgraf, *Solid State Commun.* **8**: 1823 (1970).
 49. H. Shimada and T. Masumi, *J. Phys. Soc. Jpn.* **58**: 1717 (1989).
 50. J. Bloem, A. J. Van der Houven van Oordt, and F. A. Kroger, *Physica* **22**, 1254 (1956).
 51. Mehran Riazian And Ali Ramzannezhad., *Oriental Journal Of Chemistry* **28**(1): 73-82 (2012),
 52. C. Duvvury, D. J. Kenway, and F. L. Weichman, *J. Lumin.* **10**: 415 (1975).
 53. H. Solache-Carranco, G. Juarez-Díaz, A. Esparza-García, M. Briseno-García, M. Galvan-Arellano, J. Martínez-Juarez, G. Romero-Paredes, and R. Pen a-Sierra, *J. Lumin.* **129**: 1483 (2009).
 54. T. Ito and T. Masumi, *J. Phys. Soc. Jpn.* **66**: 2185 (1997)
 55. Musa, A.O., Ph.D Thesis, *University of Ilorin*, Nigeria. 108-136.,(1995):
 56. Trivich, D., Wang, E.Y. Komp, R.J. Kakar, A.S., 13th IEEE Photovoltaic Specialist Conf. Proc. 174 (1978)
 57. N.A. Economou, R.S. Toth, R.J. Komp and D. Trivich., 14th IEEE Photovoltaic Spec. Conf. Proc. New York: 1180-1185 (1982).
 58. L.C. Olsen, F.W. Addis and R.C. Bohara., 14th IEEE photovoltaic Specialist Conf. Proc., IEEE, New York, , p. 462. (1980)
 59. L.C. Olsen, F.W. Addis, and W. Miller., *J. Sol. Cells*, **7**: 247-279 (1982).
 60. EsmaeilBiazar*, Behnam Baghermanesh and K. SaeedHeidari., *Oriental Journal Of Chemistry* **27**(3) 953-958 (2011),
 61. D.P.Singh, J. Singh, P. R. Mishra, R. S. Tiwari, O. N. Srivastava., *J. Bulletin of Materials Science*, **31**(3): 319-325 (2008).
 62. V.F. Drobny, and D.L. Pulfrey., *J. Thin solid films*, **61**: 89-98 (1979)
 63. H. Kobayashi, T. Nakamura, & N. Takahash., *J. Materials Chemistry and Physics*, **106**(2-3): 292-295 (2007).
 64. M. Izaki, T. Shinagawa, K. Mizuno, Y. Ida, M. Inaba, and A. Tasaka., *J. Phys. D: Appl. Phys.* **40**: 3326-3329 (2007).
 65. S. S. Jeong, A. Mittiga, E. Salza, A. Masci, S. Passerini, *Electrochim. Acta* **53**: 2226 (2008).
 66. H. Kobayashi, H. Mori, T. Ishida, Y. Nakato, *J. Appl. Phys.*, **77**: 1301 (1995).
 67. V.A. Modhavadiya., *Oriental Journal Of Chemistry* **28**(2): 921-925 (2012).
 68. Mohammad Ramzan Parra, Padmini Pandey, Neha Singh, Hafsa Siddiqui and Fozia Z. Haque, *journal of material sciences*, **9**(1): (2012).
 69. Alireza Jafari, Masood Ghane*, Mehrdad Sarabi and Farhod Siyavoshifar., *Oriental Journal Of Chemistry* **27**(3): 811-822 (2011)
 70. B. P. Rai, *Solar Cells* **25**: 265 (1988).
 71. T. Minami, Y. Nishi, T. Miyata, and J.-I. Nomoto, *Appl. Phys. Express* **4**: 062301 (2011).
 72. Y. Liu, H. K. Turley, J. R. Tumbleston, E. T. Samulski, and R. Lopez, *Appl. Phys. Lett.* **98**: 162105 (2011).
 73. B.P. Rai, *J. Solar Cells*, 265-272 (1988).
 74. L. Papadimitriou, N.A. Economou, and D. Trivich., *J. Solar cells*, **3**: 73 - 80 (1981).

75. R.P. Wijesundara, M. Hidaka, K. Koga, and W. Siripala., *J.Thin solid films* **500**: 241-246 (2006)
76. R.P. Wijesundara, L.D.R.D. Perera, K.D. Jayasuriya, W. Siripala., K.T.L. De Silva, A.P. Samantilleke I.M. Dharmadasa., *J. Solar Energy Materials and Solar Cells*, **61**: 277-286 (2000).
77. KumariSapna1 ,Navin Kumar Sharma2 And Seema Kohli1., *oriental journal of chemistry* **28**(2): 969-974 (2012).
78. W.M. Sear, and E.J. Fortin., *J. Solar Energy materials*,**10**: 93-103 (1984).
79. A. Mittiga, A. Salza, E. Sarto, F. Tucci, M. and Vasanthi, R., *J. Applied physics letters*, **88**: 163 502-1 – 163502-2 (2006).
80. K.Akimoto, S. Ishizuka, M.Yanagita, Y.Nawa, K.G. Paul, T. Sakurai., *J. Solar energy*, **80**: 715-722 (2006).
81. MehranRiazian*, NaserMontazeri and Esmaeil Biazar., *Oriental Journal Of Chemistry* **27**(3): 903-910 (2011)
82. A. O. Musa, T. Akomolafe, and Carter, M. J., *Solar Energy Materials and Solar Cells, Pergamon*, **51**: 3-4 (1998).
83. H. Tanaka, T. Shimakawa, Miyata, T. Sato, H. Minami, T., *J. Thin solid films*, **469-470**: 80 - 85 (2004).
84. C.A.N. Fernando, P.H.C. de Silver, S.K. Wethasinha, I.M. Dharmadasa, T. Delsol, & M. C. Simmonds, *J. Renewable energy*, **26**: 521-529.,(2000).