# SYNTHESIS OF LOW COST COPPER ZINC TIN SULFIDE (CZTS) MATERIALS USING SURFACTANT FOR EFFICIENT AND SUSTAINABLE SOLAR HARVESTING.

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**ABSTRACT**
Increase in power consumption and environmental pollution has necessitated research into alternative energy sources such as solar cells and other renewable sources. Within different types of solar cells, thin films which are considered as second generation technology have attracted reasonable attention in the last decade as a result of serious quest for clean, renewable and sustainable energy sources. Fossil fuels in the form of oil, gas, coal and other non-renewable sources are the major energy sources for human consumption in the last century, their method of production and combustion have affected our ecological environment adversely as a result of carbon dioxide ($CO_2$) emission, the major cause of global warming. Here in this work, development and characterization of low cost Copper Zinc Tin Sulfide (CZTS) thin films is proposed which aim at growing cost effective nanoparticle thin films for solar cell application using earth abundant materials, surfactants polymers and chemical bath deposition techniques. However, CZTS has gained significant attention because of its low cost, nontoxic nature, good bandgap of 1.45eV and environmental friendly. Recently, use of new materials and surfactant in thin films has shifted the interest of solar cell researchers and manufacturers from the use of rare and toxic materials to inexpensive, earth abundant and non toxic materials.

## 1.0 INTRODUCTION.

The rapid growth in power consumption, population and increase in environmental pollution caused by human activities, have necessitated research and applications of alternative energy sources such as solar cells unlike before. Like many developing countries in Africa, Nigeria has experienced a significant increase in its electricity needs as it is developing. Since coal is one of the sources of its energy for power generation. Its combustion process has led to an increase in pollution and environmental destruction (David, Abioye 2013). A nations access to a clean, sustainable and efficient (in all ramifications) electric power generation system goes a long way in determining that nations destiny. However, being products of nature ourselves it is only natural that our major sources come from nature itself (David et al 2013). In should be noted that 70% of the GHG emissions come from fossil fuel combustion from electricity generation (David 2017). In cases where the supply is much lower than the demand, alternate sources of energy using fossil fuel are used thereby raising the carbon footprint. This rapid growth in power consumption, population and increase in environmental pollution caused by human activities, have necessitated research and applications of alternative energy sources such as solar cells unlike before. Nowadays there are lots of concerns about photovoltaic systems because they can generate electricity on-site where it is needed, avoiding transport losses and complete reduction in $CO_2$ emission. Solar energy is a renewable energy resource and is converted to electrical energy in two ways thus using a photovoltaic material which generates an electrical potential when exposed to light or using a thermal process which uses the energy from the sun to heat a working fluid in an electricity generating cycle (Ezukwoke 2017)

Among different types of solar cells, second-generation solar cells thin film technology have attracted considerable research effort, mainly due to the increasing demand for earth abundant and inexpensive materials for solar cell fabrications. Cost-effective solar cell production not only requires the use of earth abundant materials, such as CZTS, but also needs economical fabrication processes. Fabrication processes of CZTS absorber layers can be generally classified into vacuum- and non-vacuum-based techniques. The non-vacuum processes have the advantage of a low cost and a high throughput compared to the vacuum-based techniques. The main different among the most popular solar cell technologies lies in their constituent materials and the choice of fabrication process. This could be critically seen by an excellent and concise review of solar cell technologies. The indisputable king of solar cell materials is silicon (Si), which is at the same time the best understood and the most earth-abundant material in the world (Xia et al 2013). Solar cells based on single-crystal or multi-crystalline Si are wafer-based technologies, meaning that the material is manufactured in the form of a big chunk (a couple of meters tall) then cut into thin slices, called wafers which is the building block of Si solar cells (Kumar et al 2018). Wafers are thin but not that thin a typical Si solar cell employs a rigid 200 µm-thick wafer. Crystalline silicon solar cell has many drawbacks like low energy gap of 1.2eV, cost for bulk production, poor light energy absorption co-efficiency and requires mechanical glass support (Bello, Awodele 2018). The current need of energy at low cost is one of the many driving forces for the renewable energy industry. Due to this, researchers focus on materials that can be fabricated easily using cheap techniques with less materials consumption, so that PV can cost less and be more convenient than fossil fuels. This causes most of the photovoltaics industries to grow rapidly, materials other than silicon crystals are being explored for solar cells applications. Some of these materials include cadmium, copper, tellurium, selenium, indium, tin, zinc and among others. However, researchers are looking into promising thin films semiconductor material that consists of only abundant and inexpensive elements for solar cell application. Among the generation of the solar cell technologies, thin film solar cell technology has been more successful owing to the advantage of being cheap and efficient. Currently, the main thin film solar cells include the amorphous Silicon thin film, Cadmium Telluride (CdTe), Copper Indium Selenium (CIS), Copper Indium Gallium Selenium (CIGS), Gallium Arsenide (GaAs), and Copper Zinc Tin Sulfide ($Cu_2ZnSnS_4$ which will hereafter referred to as CZTS), etc. GaAs and CdTe contain toxic elements (cadmium and arsenic) while CIGS system contains rare indium element therefore, these two types of solar cells cannot meet the future development in thin film solar cells (Patel et al 2013), (Sharma et al 2015). However, this work reports synthesis and fabrication of low cost CZTS thin films solar cells materials for solar harvesters using chemical bath deposition techniques.

## 2.0 ENVIRONMENTAL IMPACT

Fossil fuel dominated electricity generation in most of the developing countries in the world has posed enormous environmental consequences globally. The growing concern about our environment and sustainable development focuses attention on renewable energy sources currently. One of these sources is the direct conversion of sunlight into electricity by means of photovoltaic cells. Solar energy has the potential to fulfill an important part of the sustainable energy demand for future power generations (Xia et al 2013). Thereby, low-cost organic photovoltaic systems have come into the international research focusing on the synthesis and development of low cost solar cell materials for energy and environmental sustainability. Currently the world consumes an average of 13 terawatts (TW) of power (Kumar et al 2018). By the year 2050, as the population increases rapidly and the standard of living in developing countries improve; this amount is likely to increase to 30 TW.

For example, the University of Nigeria, Nsukka (UNN) consumes approximately 3000KWh, which amounts to about 26MWh annually. However, the University receives approximately only 50% of electrical energy from the National Grid (David 2015). The remaining 50% of the required is generated using fuel generators which apart from being expensive, affect the environment adversely with a direct impact on global warming.

If burning fossil fuels provides this power, the concentration of carbon dioxide in the atmosphere will be more than double, causing substantial global warming, along with many other undesirable consequences. Therefore, one of the most important challenges confronting scientists and engineers is to device a means to provide the world with 30 TW of power without releasing carbon into the atmosphere. This could be achieved through deployment of thin film materials for solar cell applications. Figure 1 describes a graph showing the $CO_2$ emissions of solar power relative to other sources of energy. While they are lower than most other sources, in $CO_2$ emissions to the environment. This is mainly due to the process of mining the silicon. Thin-film solar panels therefore generate fewer lifetime $CO_2$ emissions than silicon-based solar panels, so as thin films gain popularity, the average $CO_2$ emissions to atmosphere will likely reduced drastically.

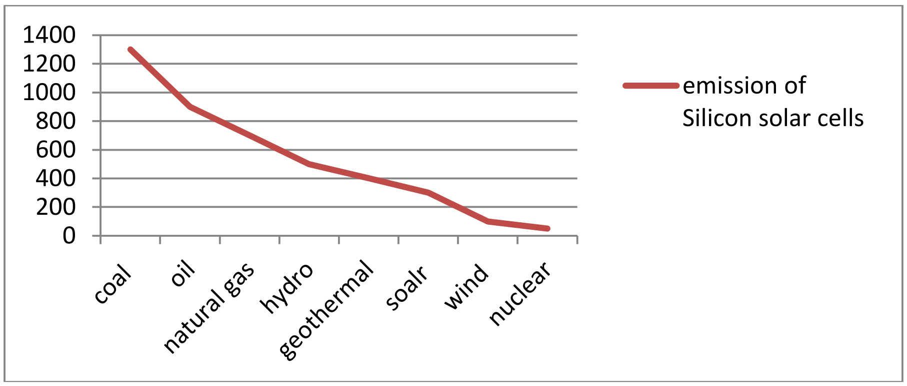



*Figure 1 showing the Carbon IV Oxide Emission of the Different Electricity sources.*

## 3.0 MATERIALS AND METHOD

CZTS solution was prepared by dissolving Copper II Sulfate 0.02M, Zinc Sulfate 0.01M, Tin Chloride 0.02M and Thiacetamide 0.10M as sources of Sulfur in different beaker containing 100ML of distilled water respectively. Each beaker was placed on a magnetic stirrer for 20minutes to ensure complete dissolution of the salt. During stirring, it was observed that the salt particles dissolved and formed a colourless solution. The surfactant material to be used in the deposition was prepared by dissolving 0.02M of Cetyltrimethyl Ammonium Bromide (CTAB) in a beaker containing 100M of distilled water. The surfactant was dissolved differently in a beaker and was stirred to obtain a uniform mixture using a magnetic stirrer. To grow the film, precursor solution of 0.02M Copper Sulfate, 0.01 Zinc Sulfate, 0.02M Tin Chloride, 0.16M of Thiacetamide, and 0.02 CTAB in equal combining volume were mixed together in a beaker with the following ratio:

**Cu : Zn : Sn : S : CTAB = 2 : 2 : 2 : 2 :1**

Later, pre-cleaned glass substrates were immersed in the beaker containing the precursor solution. The beaker was thereafter heated in air for one hour maintaining maximum temperature of 325K and allowed for cooling and deposition for another twelve hours. After one hour of heating, it was observed that the solution became blurred and light dark precipitate formed in the beaker containing the substrate. It was also observed that after twelve hours of deposition, heterogeneous reaction occurred and deposition of CZTS took place on the substrate. Finally, the film was annealed to maximum temperature of 3500°C to obtain a polycrystalline CZTS. The structural, morphology of the film were investigated. X-rays diffractometer and Rama spectroscope were used to record X-ray diffraction (XRD) pattern and Raman spectrum of the films in order to exam the their crystalline structure.

## 4.0 MORPHOLOGICAL CHARACTERISATION

Several routes and methods have been used in preparation and deposition of $Cu_2ZnSnS_4$ thin films, however, in this work we aimed to grow kesterite type CZTS thin films using CBD and the figure 2 shows the kesterite structure of CZTS deposited with CTAB surfactant. However, the Scanning Electron Microscope (SEM) analysis revealed uniform kesterite structure in the presence of the surfactant material just like pure CZTS morphology without surfactant materials.

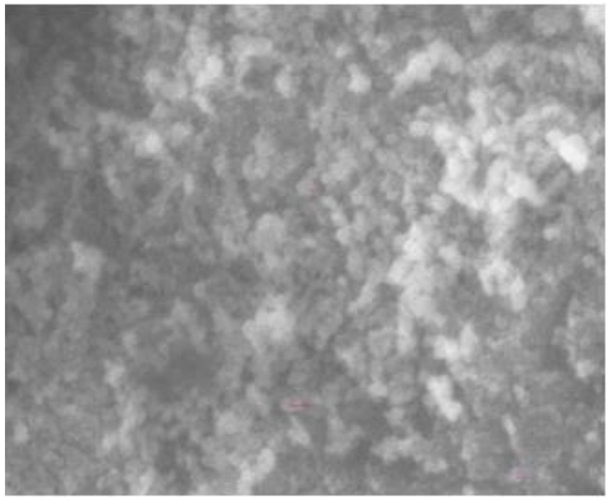
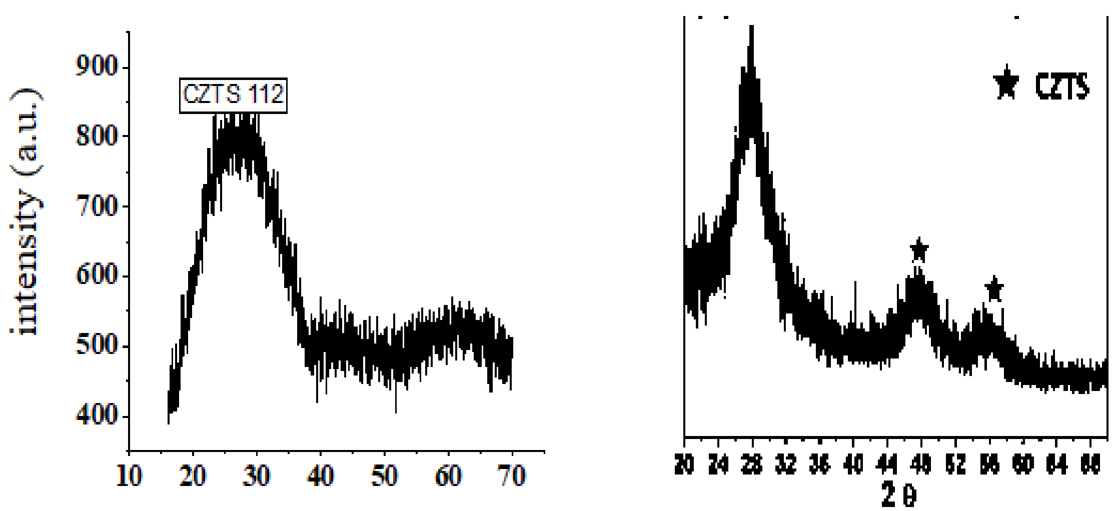


*Figure 2: Morphological structure of CZTS using CTAB Surfactant SEM image.*

## 4.1 RESULT AND CHARACTERISATION

In Figure 3 the X-rays diffraction pattern of CZTS with surfactant CTAB deposited on a glass substrate materials and the film was annealed at 3500C for 30minutes. From the XRD, it was observed that the deposited CZTS film was armorphous in nature but the crystalline nature came after annealing. In general, the films shows 2Ɵ values of 28.30°C and 47.60°C corresponding to (112) and (220) kestrite plane respectively as shown in the figure 3(a) and 3(b). This confirms that pure kestrite of CZTS could be achieved by simple CTAB surfactant capping.




(a) (b)

*Figure 3 XRD Pattern (a) and (b) of CZTS thin films Obtained after Depositing with CTAB.*

Figure 3a and 3b shows the XRD pattern for the film annealed at 350°C for 30 minutes. The film is of polycrystalline type showing peaks located at 28.3°C and 47.6°C corresponding to the (112) and (220) directions. The film shows also a sudden directional rise along (112) which is characteristic of pure crystalline CZTS kesterite pattern. The low intensity of these peaks can be as a result of short annealing time and thin in material thickness since the time has not been sufficient to allow the compound to grow completely.

## 5.0 CONSLUSION

The $Cu_2ZnSnS_2$ (CZTS) thin films have been synthesized using cost-effective and convenient chemical bath deposition (CBD) techniques in the present of surfactant material. XRD studies revealed that the pattern of CZTS deposited without surfactant shows the same peaks at the same location after deposition with CTAB surfactant material. Also it worth noting that CZTS film is amorphous in nature therefore annealing at relatively high temperature gives sharper diffraction peaks at (112) and (220) of kesterite crystal structure with uniform and densely packed surface morphology which gives exact pattern like CZTS. The adoption of thin film solar will give absolute reduction to excessive gaseous emission from other renewable energy source including solar energy. Renewable energy industry, with a focus on economic viability, sustainability and environmental responsibility should invest more in the synthesis of low cost and carbon free thin film solar cell material.

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