1. Introduction and Motivation

Energy is one of the vital basics for human society and its maintenance on Earth. Furthermore, energy consumption increases each year to pursue the technological and industrial development all over the world. Fossil fuels such as oil, coal, and gas are still the dominant energy sources and also will remain the main source of energy in the future as shown in Figure 1-1. It is clear from this forecast that energy consumption from the renewables increased in the past and is expected to increase in the future compared with other energy sources.

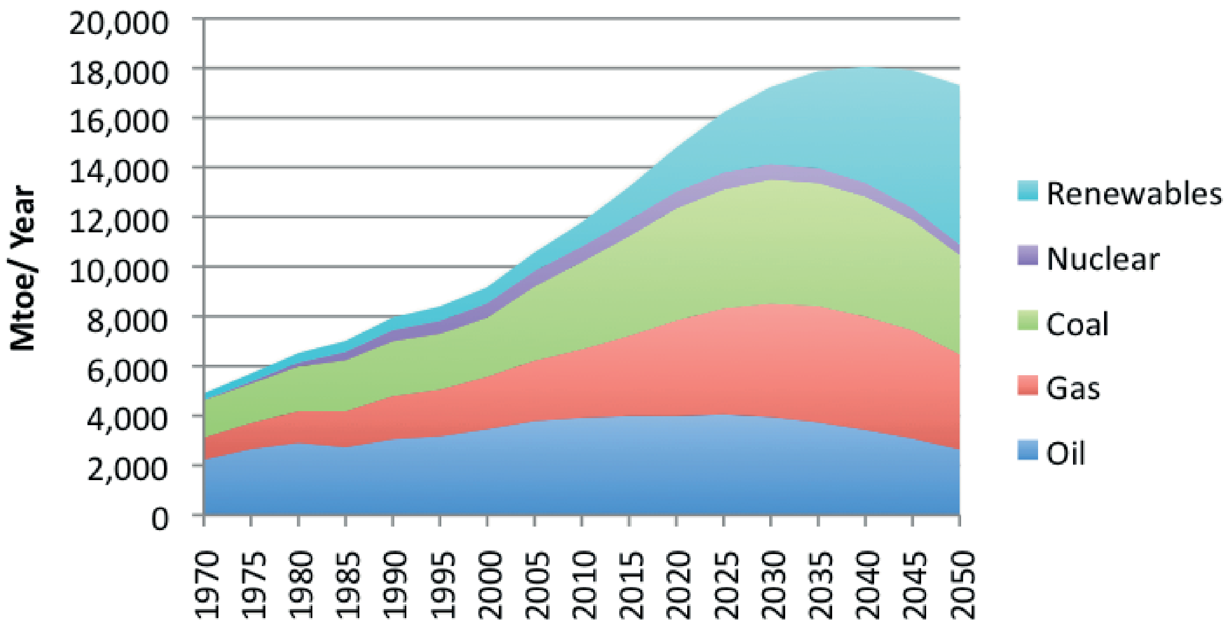

Figure 1-1: A global forecast of energy consumption rate [1].

To produce energy from fossil fuels is intrinsically problematic as their reserves are limited and almost of them will be depleted in the near future if the consumption rate remains as it is today. The emission of carbon dioxide (CO_2) produced from fossil fuels consumption becomes also a big environmental issue as it is the main source of the climate change problem. Therefore, there is heightened attention to green energy which uses renewable energy resources such as wind, geothermal, biomass, tidal, and solar energy. The renewable energy will secure vital energy supplies as well as keep our planet livable for the next generations.

Solar energy is in some sense the most sustainable energy resource for future energy supplies. The Sun provides earth with a huge amount of energy; it delivers energy of about 10^{17} joules to Earth in one second. The energy of 1.7×10^{22} joules which the Sun supplies to Earth in 1.5 days equal to the amount Earth's ultimate recoverable resources of oil. The energy of about 4.6×10^{20} joules which is used annually by humans is almost the same energy that Earth receives from the sun in one hour. This is a convincing argument towards solar energy being the best candidate for future energy supplies in terms of potential capacity [2].

There are mainly three different ways using solar energy as illustrated in Figure 1-2. First of all, solar radiation can be converted to heat energy. This heat energy is transferred to a thermal storage medium for space heating or to produce the electricity (indirect way). Secondly, solar fuels can be obtained from the solar energy through photosynthetic processes by the generation of excited electron-hole pairs in biological or chemical systems. The natural photosynthesis (biomass) in plants produces fuel in the form of sugar and other carbohydrates. Water can be split by the photosynthetic process with artificial molecular assembly to produce fuel in the form of hydrogen. Thirdly, solar energy can be converted directly to electricity by photo-induced charge carriers (electron-hole pairs) in semiconductors compound photovoltaics (PV) [2]. In other words, photovoltaic (solar) cells are electronic devices which convert the sunlight photons directly into electricity.

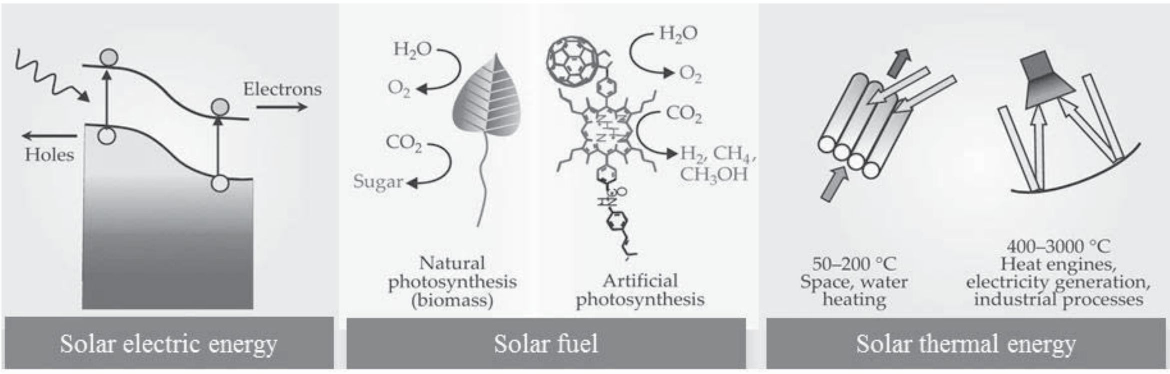

Figure 1-2: The three main different ways to use solar energy [2].

PV is one of the most advanced technologies for clean power production keeping low concentrations of CO_2 in the atmosphere as well as becoming a promising renewable energy source instead of fossil fuels to meet the global energy demand. There are different types of solar cells depending on the semiconductor materials used to fabricate the devices. When the junction is made from one type of semiconductor, it will be known as a Homojunction solar cell, for example crystalline silicon solar cell. If two different semiconductors used to fabricate the solar cell, it will be called Heterojunction cell. Copper indium diselenide ($CuInSe_2$ or CIS) solar cells are examples of this type. By inserting a middle intrinsic layer in between, the junction, p-i-n structures will be formed such as amorphous silicon thin film cells and n-i-p structures will be formed such as cadmium telluride (CdTe) cells.

Solar cells can also be divided into four major categories; crystalline, thin film, compound and nanotechnology PV. Crystalline PV includes crystalline silicon solar cells which are fabricated from single crystalline and multi-crystalline silicon. Amorphous silicon, Cadmium Telluride (CdTe) and Copper Indium Diselenide (CIS) solar cells are examples for thin film cells. Examples of compound PV are dye-sensitized solar cells (DSSC), organic solar cells, Gallium Arsenide (GaAs) solar cells, and tandem solar cells (such as triple-junction GaInP/GaAs/Ge). Carbon nanotubes to produce solar cells and quantum dots solar cells (QDSCs) are two examples of solar cells that based on nanotechnology [3]. PV can be also classified by using the concept of different generations. The first generation of solar cells is based wafers which are made of crystalline silicon such as single crystalline silicon and polysilicon. The second generation is based mainly on the optimization of single junction devices to reduce materials costs by using thinner films such as CdTe, CIGS and amorphous silicon. In contrast, the third generation includes double, triple junction and nanotechnology to increase the devices efficiencies and also to lower costs [3,4].

The power conversion efficiency of solar cells is limited by the material bandgap that determines the photon absorption rate. Figure 1-3 presents the maximum theoretical efficiency for some of the potential materials in an ideal single p-n junction structure, which was calculated according to the Shockley-Queisser detailed balance limit [5,6]. Solar cells based on crystalline silicon (c-Si), cadmium telluride (CdTe), and copper zinc tin sulfide (CZTS) are predicted to have efficiencies higher than 30%. Therefore, PV based on these materials became the majority of solar cells on the market.

It has been reported that the installed capacitance of PV increased from 2.6 GW to 139 GW from 2004 to 2013. Nevertheless, by the end of year 2013, only 0.7 % of the consumed electricity was produced from photovoltaics [7]. This number is in stark contrast to the huge amount of radiative energy that the planet Earth receives from the Sun. Therefore, to increase the energy from the PV sector, a save supply of elements and compounds are required to produce and fabricate more solar cells. Popular elements used in the currently PV market are silicon for crystalline silicon (c-Si), tellurium and cadmium for cadmium telluride (CdTe), and indium, gallium and selenium for copper indium gallium diselenide (CIGS) solar cells. Research sponsored by the U.S. Department of Energy claims that PV based on CdTe and CIGS have problematic prospects for scaling up as they employ metals which are not available in huge amounts on the earth and as they are only byproducts of mining of other materials, and moreover these materials are toxic [8].

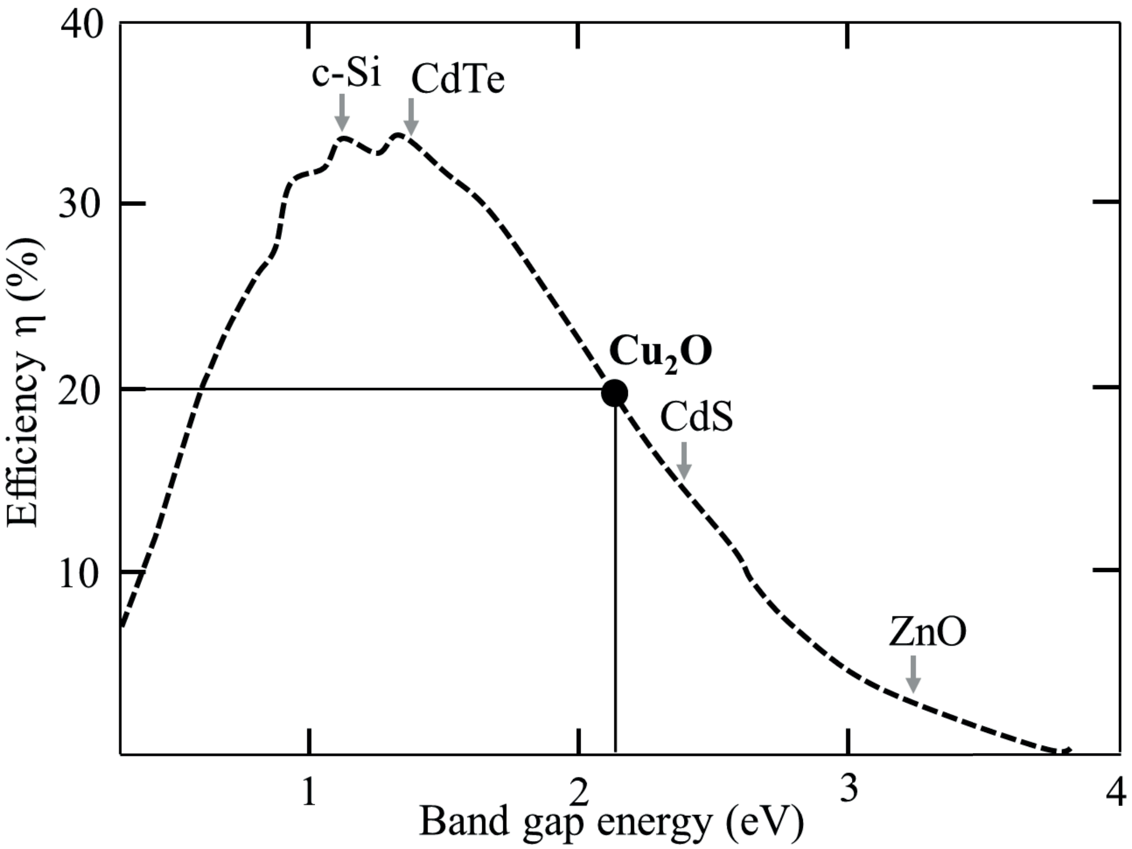

Figure 1-3: Maximum theoretical efficiency (Shockley–Queisser limit) for solar cells with different materials such as c-Si, CdTe, and Cu_2O as an absorber layers and materials CdS and ZnO as a window layers [5,6].

On the other hand, although silicon-based solar cells are the majority of PV on the market and have relatively high energy conversion efficiencies, their fabrication and production needs high temperatures leading to expensive processes and extreme energy consumption [9].

At present, the main challenges to realize major and scalable energy sources are based on finding suitable materials and cost-effective techniques to fabricate photovoltaic systems. Furthermore, the reduction of module costs and in increase of energy conversion efficiencies are important. Therefore, photovoltaic materials should be based on abundant source materials, inexpensive, and non-toxic. Also they should have a direct band gap with proper size as well as reasonable physical and chemical stability. They should be produced by simple preparation methods that are suitable for a large area production. Earth-abundant elements become one of the most promising materials for photovoltaic applications due to their non-toxicity, chemical stability and availability for low cost manufacturing techniques [10].

Cuprous oxide (Cu_2O) is found to be one of the most promising earth abundant alternatives to traditional thin film PV materials since it can provide solar cells with maximum theoretical efficiency of about 20% as presented in Figure 1-3. It has the advantages of being an abundant source material and follows the requirements to produce such low cost PV. Besides, electrochemical deposition is one of the most attractive methods for Cu_2O thin films growth. This is a low cost and low temperature technique based on chemical solutions, providing large area thin films manufacturing [11,12].

The aim of this work is thus to fabricate and characterize low cost photovoltaic devices based on Cu_2O thin films which are produced using electrodeposition. The effect of electrodeposition modes on the devices properties is investigated as well as the effect of Cu_2O thin films thickness on the basic parameters of solar cell and heterojunication properties is studied in order to determine the optimum thickness of Cu_2O as absorber layer for solar cells. Furthermore, the dependent of the solar cells properties on the illumination time and temperature will be discussed. The effect of inserting ZnO as buffer layer on the solar cell basic parameters will be studied.

The outline of the thesis is as follows; Chapter 1 presents the introduction for our work and the motivation. Chapter 2 describes the theoretical background of photovoltaic concepts including the junction formation and the basic solar cell parameters as well as the fundamental properties of Cu_2O, its applications, and growth methods of Cu_2O. In chapter 3, the attention will be given to basics of experimental methods including electrodeposition and sputtering as well as the characterization methods including Raman spectroscopy, scanning electron microscopy (SEM), EBIC, I- V, C-f, C-V, and EQE measurements which will be employed in this work. Experimental processes to deposit Cu_2O thin films and fabrication steps to produce solar cells as well as the effect of deposition modes and the deposition time on their structural properties, morphology, and basics parameters of the solar cells will be the subject of chapter 4. In chapter 5, the effect of illumination time on the solar cells performance and the temperature dependence on the basic parameters of the devices will be discussed. Effect of inserting ZnO buffer layer by Atomic Layer Deposition

(ALD) on the basic parameters of AZO/ZnO/Cu_2O flexible solar cell on plastic substrate will be investigated in chapter 6. Finally, conclusions and critical analysis of the obtained results are presented in chapter 7.

2. Theoretical Background

In this chapter, attention will be given to the main concepts of energy generation in solar cells. Also an overview of cuprous oxide (Cu_2O) properties and preparation methods as well as several efforts to use it for the photovoltaic applications are presented.

2.1. Basic concepts of solar cells

To understand the basic parameters [including open circuit voltage ($\boldsymbol{V_{oc}}$), short circuit current density ($\boldsymbol{J_{sc}}$), fill factor ($\boldsymbol{FF}$), and efficiency ($\boldsymbol{\eta}$)] of the photovoltaic devices and the junction properties we will present a brief overview of the principles concepts of solar cell.

2.1.1. Semiconductor-metal/semiconductor junctions

In the simplest case, the solar cell device is based on p-type semiconductors and n-type semiconductors with two metallic contacts. So we will start with semiconductor-metal junctions and then semiconductor-semiconductor junctions. When a metal and semiconductor are brought together to form a junction, electrons diffuse from higher concentration regions to the lower ones by a charge carrier exchange from one side to the other. In the case of p-type semiconductors with a work function higher than that of the metal ($\boldsymbol{\phi}_p > \boldsymbol{\phi}_m$), electrons will flow from the metal into the semiconductor which gives a negative net charge region in the semiconductor as shown in Figures 2-1 a and b. While for n-type semiconductor with $\boldsymbol{\phi}_n < \boldsymbol{\phi}_m$, electrons will move from the semiconductor to the metal resulting in a region of positive charges in the semiconductor as shown in Figures 2-1 c and d. Such flow of charges produces a region within the semiconductor known as the depletion region. There is a large amount of free charge in metals in which any flow of electrons into or out of the metal is easily compensated, and, therefore, the depletion region within a metal is negligible [13].

Figure 2-1 shows the process in which a Schottky junction is formed between the metal and semiconductor. The work function of materials is defined as the potential required removing the least tightly bound electron and in a metal it is always the same as the electron affinity and in a semiconductor equal to the Fermi level energy. In a semiconductor the electron affinity (χ) is the difference in energy between conduction band energy and the vacuum energy. The metal and semiconductor have independent Fermi levels ($\boldsymbol{E_f}$) before the contact process. In the p-type semiconductor the $\boldsymbol{E_f}$ is $\boldsymbol{\phi}_p$ below the