CHAPTER 1

Introduction

In the introduction part, we have talked about important background of this thesis, research objective and literature review of materials that is Zinc Oxide and Cuprous Oxide. Moreover, the basic principle of these material, research plan and expecting benefits are included in this chapter.

1.1 Historical background

Nowadays, energy has become the most important to human being, especially electric energy. Generally, the electric energy is mostly produced from the process that comes with producing carbon dioxide and another gases, especially coal power plant. They affect to environment, animals, human and global warming. In order to decrease those problems, at present alternative energy are chose to produce electricity widely. It is a clean energy and environmental friendly.

Solar energy is a resource of energy and offers a clean, climate-friendly, very abundant and inexhaustible energy resource to humanity. Its availability is better in warm and sunny countries. Solar cell is a kind of renewable energy, and it is a device that converts the solar energy directly into the electricity by photovoltaic effect. Silicon based solar cells, which is a type of p-n junction solar cell, currently play the important rule on solar cell market because its energy conversion efficiency is still high [1] as well as the cost is expensive.

To develop the solar cells which are low cost and high efficiency is an important goal for managing the growing global energy demand and decreasing the carbon dioxide gas and greenhouse gases emission [2]. In the present, semiconducting oxide materials plays important rule for many application in wide range of technologies such as chemical gas sensors, photodetector, diode and solar cells. Semiconductor oxide solar cell is one of nanotechnology application because the cost is so effective.

1.2 Research Objectives

1.2.1 To fabricate and characterize of ZnO and Cu_2O film prepared by sparking process

1.2.2 To study the effect of Al doping on ZnO layer prepared by sparking process for Cu_2O solar cell application

1.3 Literature Review

In 1956, Loferski JJ reported the conversion efficiency of semiconductor that has band gap energy of 2.1 eV is expected to be 18 % [3]. Cu_2O is a semiconductor material with energy band gap of 2.1 eV and a p- type semiconductor. It was used to build a solar cell based on p – n junction because of high hall mobility and hole concentration of 90 cm^2/Vs and 4 x 10^{14} cm^{-3} respectively. In contrast, ZnO is an n-type semiconductor material which was used widely as an acceptor layer for solar cell based on Cu_2O because the Cu_2O is suitable to form hetero junction solar cell with n-type ZnO [4, 5, 6, 7, 8, 9]. The 0.054 % efficiency of ZnO/Cu_2O solar cell was obtained by successive ionic layer adsorption and reaction deposition method (SILAR) [7]. The efficiency of the Cu_2O solar cell was improved to 0.117 % by electrodeposition [4]. The efficiency value of 0.41 % by the same method [9]. The efficiency of ZnO/Cu_2O solar cell is still low since there are factors that affect to change the efficiency of the solar cell such as optimization of the cell structure, method of film preparing and so on.

In order to improve the efficiency of the Cu_2O based solar cell. The n-type ZnO film has been doped with many metal elements. Impurity doping such as Al, In, Ga, B affected to high electrical conductivity [10]. Among these elements, Al doped ZnO (AZO) are considered as an alternative for transparent conducting oxide material (TCO) for solar cell. The atomic substitution of Al to Zn in ZnO crystal structure has occurred a free electron in conduction band, which provides a reduction in its electrical resistivity [11]. This material exhibits high transparency and low resistivity [12]. Efficiency in structure of AZO/Cu_2O was 0.24 % from 2%-Al doped in ZnO prepared by Magnetron-

Sputter Deposition method [6]. The efficiency value was 1.09% using 5% of Al doped on ZnO layer prepared by the same method [13]. From the study of M. Mozibur Rahman et al. [14] shown that increasing percentage of Al doping on ZnO affected to decrease the resistivity of the film, and this reason has indicated that Al doping on ZnO affect to efficiency of solar cell based on Cu_2O increasing.

1.3.1 External quantum efficiency (EQE) of the Al-ZnO/Cu_2O solar cells

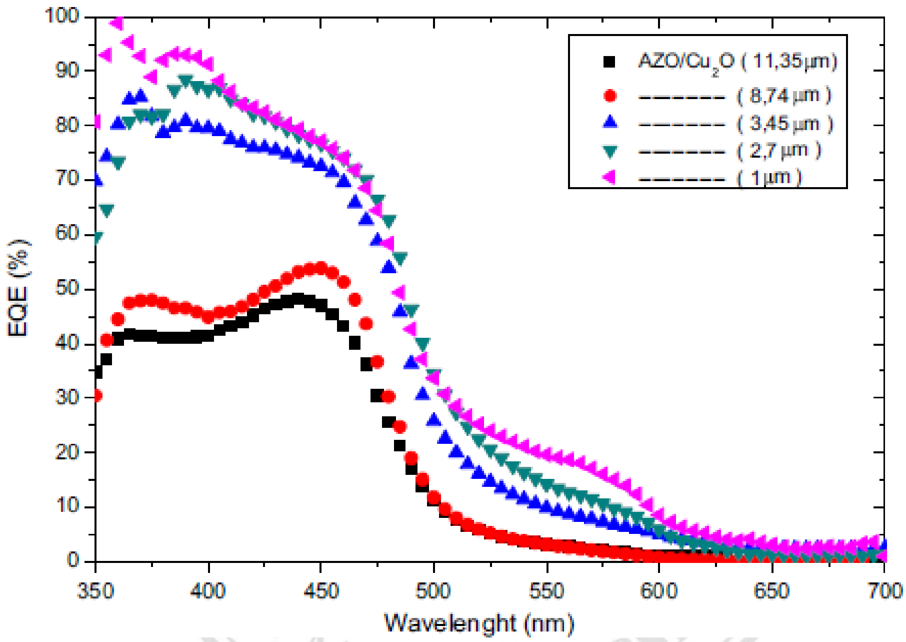

Figure 1.1 EQE of the Al-ZnO/Cu_2O solar cells under room temperature [13].

From figure 1.1 shows that for all solar cells the photocurrent generated for the region from 350 nm to 500 nm, and the thickness of Cu_2O had affected to photocurrent generation, which 1 µm of Cu_2O film thickness can produce photocurrent to be higher than others. Moreover, they indicated that photocurrents were mostly generated by Cu_2O absorber because its absorption is mostly in wavelength range of 300 nm to 600 nm which is shown as figure 1.2

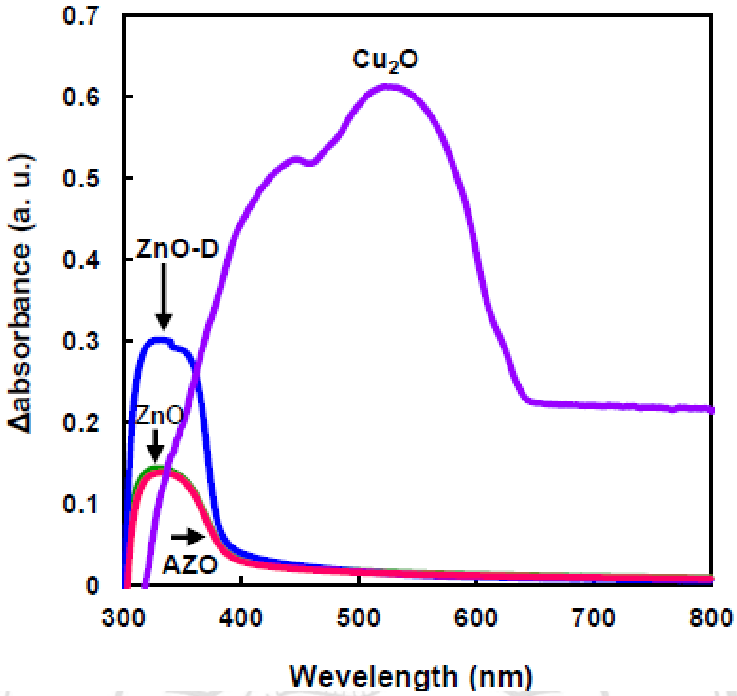

Figure 1.2 Optical absorption of Cu_2O, ZnO, Al-ZnO (AZO) and ZnO-dipcoating [15].

1.3.2 Al doping on ZnO layer

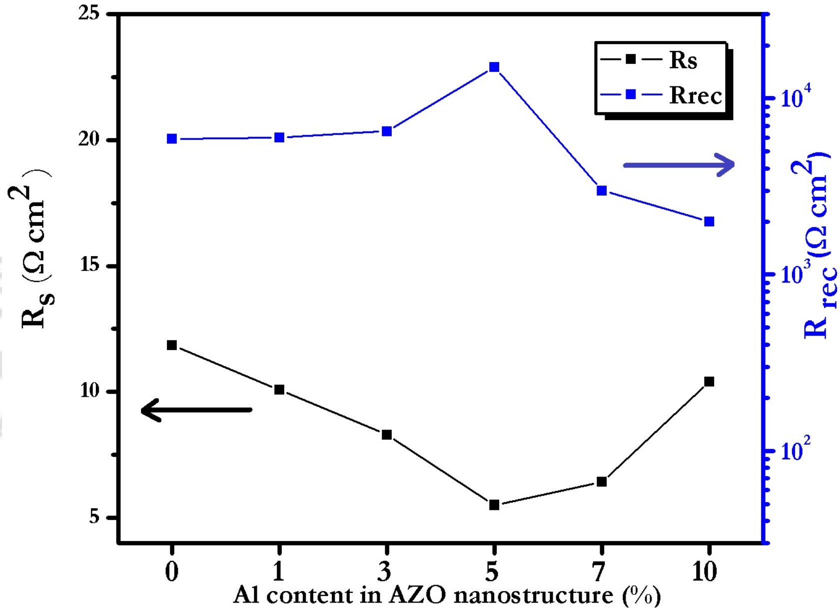

Figure 1.3 Effect of Al doping (%) on ZnO prepared by spary pyrolysis method to the resistivity [16].

From figure 1.3, they indicated that the doping of Al in ZnO nanostructure leads to decreasing a film series resistance (R_S) and to increasing a recombination resistance (R_{rec}). However, there are optimize of Al content in ZnO at 5 %, considering that futher enhancement of Al doping content has affect to decrease the recombination resistance because of increasing of the point defect and electron trap states in ZnO nanostructure.

1.3.3 Influence of Cu_2O thickness on power conversion efficiency

A study of Kevin P. Musselman et al [17] reported that increasing Cu_2O thickness affected to short circuit current (J_{SC}). This study indicated that 3 µm of Cu_2O thickness made highest J_{SC} for ZnO-Cu_2O bilayer structure. Furthermore, Kam Tongleung et al. calculated the optimized thickness of p-type Cu_2O film of 2.5 – 3.0 µm to maximize their open circuit voltages (V_{OC}) [8]. Mahmovd Abdelfantah et al. [13] supported the details that the power conversion efficiency will be highest while Cu_2O thickness is 2.5 – 3.0 µm, which is shown as figure 1.4

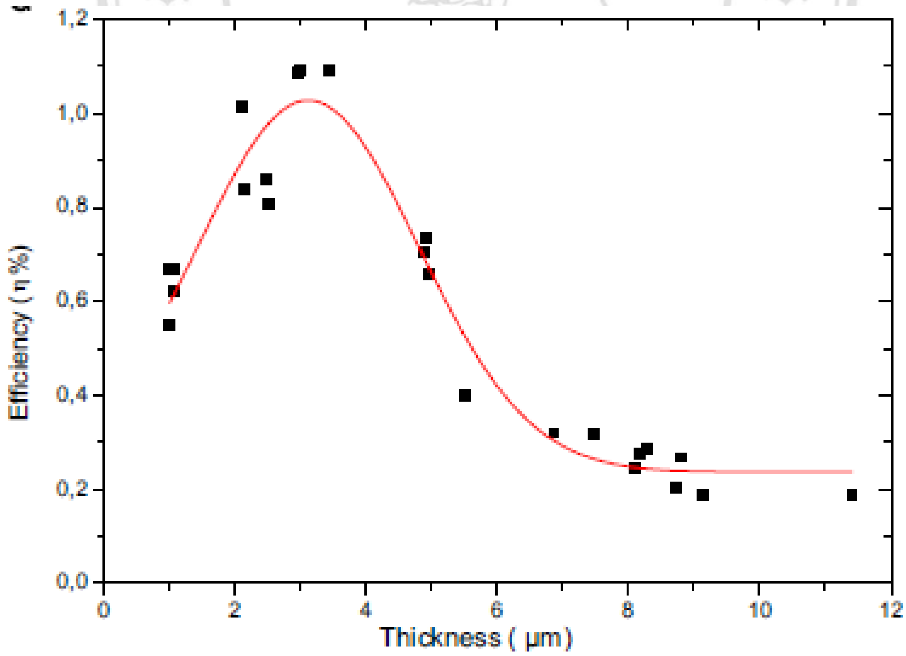

Figure 1.4 Effect of different Cu_2O absorber layer thickness to efficiency of solar cell [13].

A number of research has concentrated to improve efficiency of solar cell based Cu_2O by studying effect of Cu_2O thickness and Al doping content in ZnO by using different film deposition methods. However, each deposition method has difference of advantage and disadvantage. Moreover, film deposition techniques are the process that come with high cost of technology. In order to develop the low cost process of the solar cell, sparking process [18] is one of method to prepare metal oxides. It is cheap and easy to produce the semiconductor films. This research, sparking process is used to synthesis Cu_2O and Al doped ZnO film for p-n junction solar cell application.

1.4 Theory

Metal oxide exhibits in wide range of functional properties depending on their physical and chemical properties such as crystal structure, electrical and optical properties. From their fascinating properties, metal oxides have been used a base material for many applications such as light emitting diode, solar cell and many electronic devices. Among these metal oxides, ZnO and Cu_2O are an interesting semiconductor oxide due to they are earth abundant material, cost effective and non-toxic. Moreover, ZnO and Cu_2O have been suitable to innovate a heterojunction for solar cell application.

1.4.1 Structure and properties of semiconducting oxide materials

1) Copper (I) oxide or cuprous oxide

Copper oxide is the inorganic compound and has two stable phases, cuprous oxide (Cu_2O) and cupric oxide (CuO). The Cu_2O phase is naturally the reddish colored solid and can appear either yellow or red, depending on the size of the particle. The Cu_2O is a typical p-type semiconductor [19] material and has low toxicity, cheap and good environmental acceptability. It has normally direct band gap energy in the range of 1.96 eV to 2.38 eV.

Table 1.1 Fundamental properties of cuprous oxide.

Chemical formula	**Cu_2O**
Molar mass	143.09 g/mol
Appearance	brownish-red solid
Density	6.0 g/cm^3
Melting point	1,232 °C
Boiling point	1,800 °C

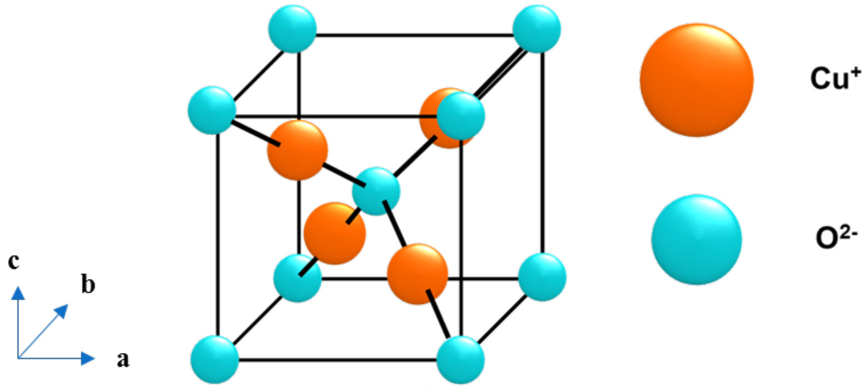

Figure 1.5 Cubic structure of Cu_2O.

The cuprous oxide crystalline appears basically in form of cubic lattice structure. A unit cell has two oxygen atoms that form body centered cubic (bcc) and four copper atoms that form face centered cubic (fcc), which is shown as Figure 1.5. The lattice parameter of the Cu_2O film was found to be a = 0.42696 nm with dominant lattice plane of Cu_2O (111) , (220), (110) and (200) by X-ray diffraction which is shown as figure 1.6. [4]

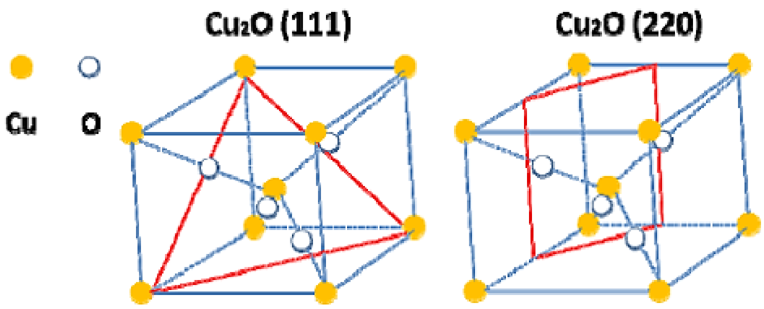

Figure 1.6 Cubic structure of Cu_2O with its dominant lattice plane of (111) and (220) [5].

2) Zinc oxide

Zinc oxide (ZnO) is the inorganic compound and white color in form of powder. There are three forms of ZnO crystals which includes hexagonal wurtzite, cubic zincblend, and cubic rocksalt. Among their crystals, the hexagonal wurtzite structure is most stable at normal condition. It is wide band gap semiconductor material and exhibits excellent properties in spectrum range of ultraviolet light.

Table 1.2 Fundamental properties of zinc oxide.

Chemical formula	**ZnO**
Molar mass	81.38 g/mol
Appearance	White solid
Odor	odorless
Density	5.606 g/cm^3
Melting point	1,975 °C
Boiling point	2,360 °C

ZnO is a natural n-type semiconductor with wide band gap energy of 3.2 eV to 3.4 eV as well as stability in the presence of Cu_2O and suitability as a window material in solar cell structure of Cu_2O/ZnO. It is a direct gap semiconductor and has the lattice structure of hexagonal with lattice constant of a= 0.32495 nm and c= 0.52069 nm which is shown as figure 1.7.

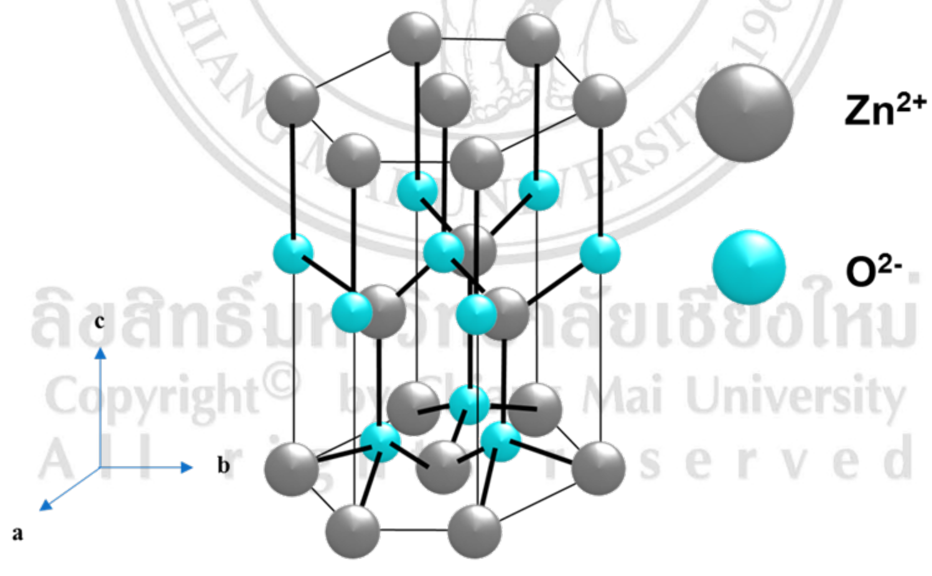

Figure 1.7 Hexagonal structure of ZnO.

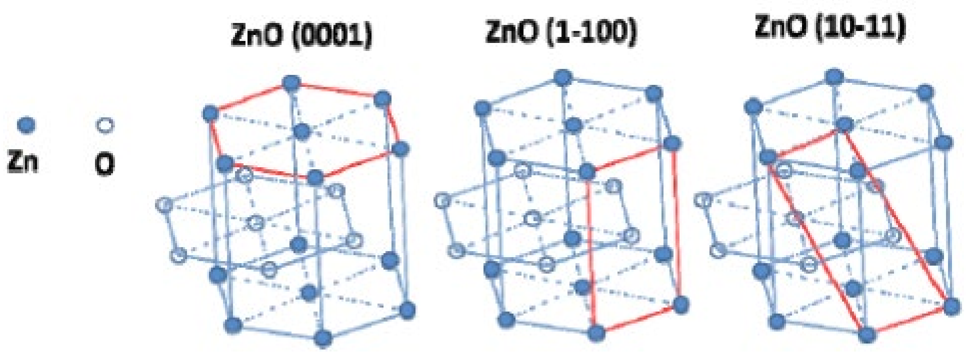

Figure 1.8 Hexagonal structure of ZnO with dominant lattice plane of ZnO (0001), (1-100) and (10-11) from XRD diffraction [5].

1.4.2 Effect of Aluminum doped ZnO

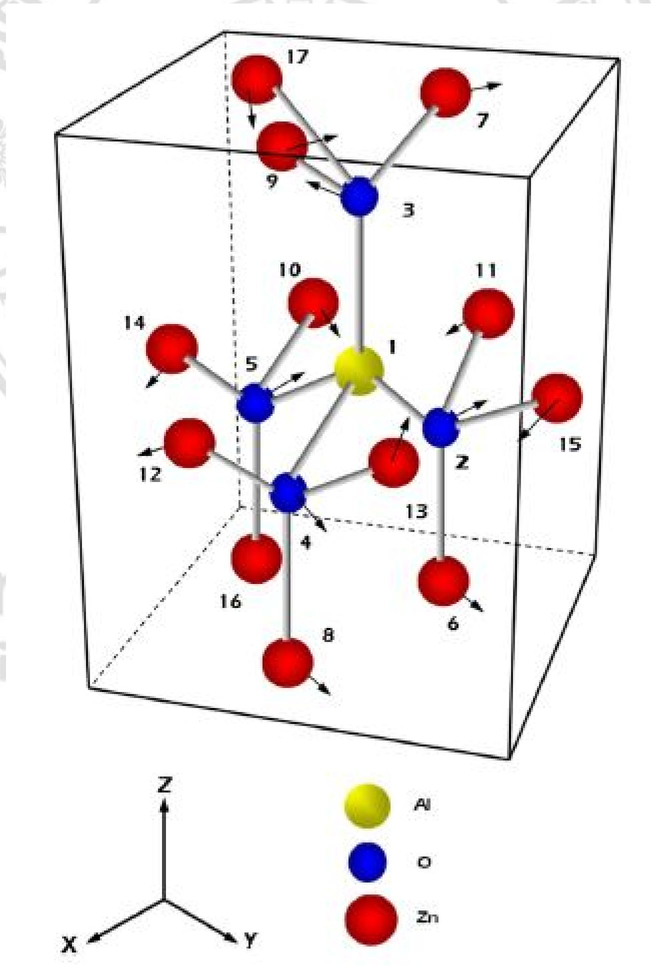

Figure 1.9 A schematic diagram showing the vicinity of Al impurity within the wurtzite-type structure of the ZnO crystal [11].

ZnO is typically performance in good properties, which has been used to be a candidate material for a lot of applications. Moreover, this material has been studied to improve a property for each application by using element impurity doping. Aluminum usually is used to dope in ZnO (AZO) in order to improve electrical property. The atomic substitution of Al to Zn present one extra valence electron into the system since Al atom possesses in three valence electron while Zn atom has only two valence electron. The consequence of this electron jump is the produce a free electron in the conduction band, which increases the n-type electrical conductivity in the Al doped ZnO material and consequently produces a reduction in its resistivity [11]. The structure to present the atomic substitution of Al to Zn in crystalline structure is shown in Figure 1.9. Effect of Al doped ZnO on electrical resistivity is illustrated in Figure 1.10.

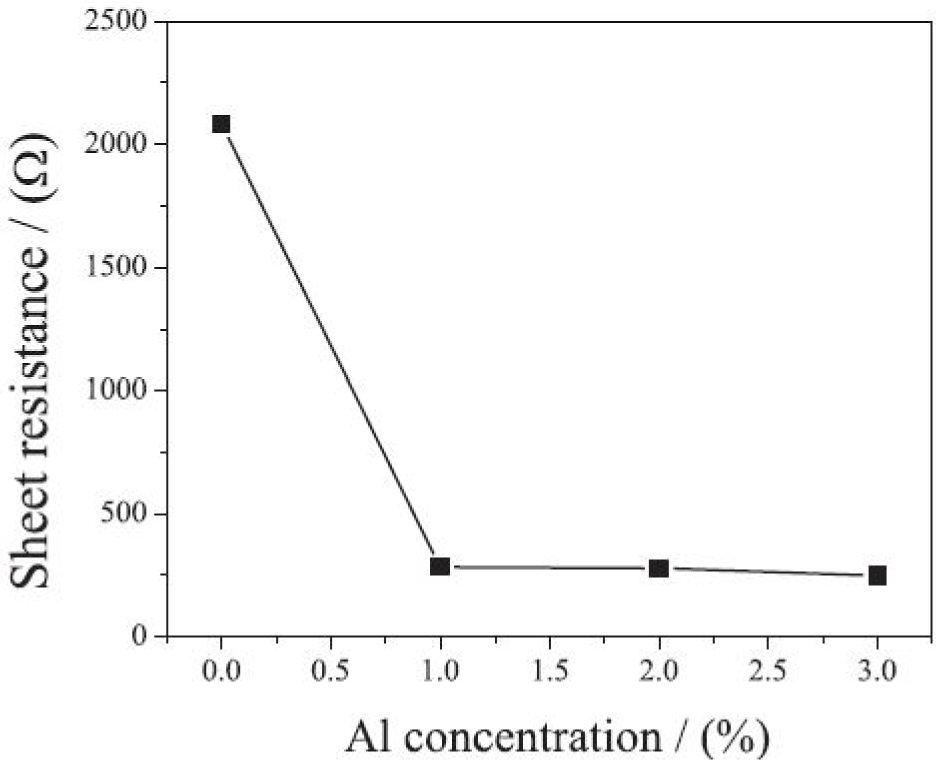

Figure 1.10 Sheet resistance of AZO thin films for different
Al dopant concentrations [12].

1.4.3 ZnO/Cu_2O heterojunction

Cuprous oxide and zinc oxide are semiconductor material which can innovate to be a p-Cu_2O / n-ZnO heterojunction solar cell. Cu_2O is used as the absorber layer for absorption the light and generate electrons. ZnO is used as the acceptor layer. The electron separation was done by inner electric field in depletion region or interface which is shown as figure 1.11.

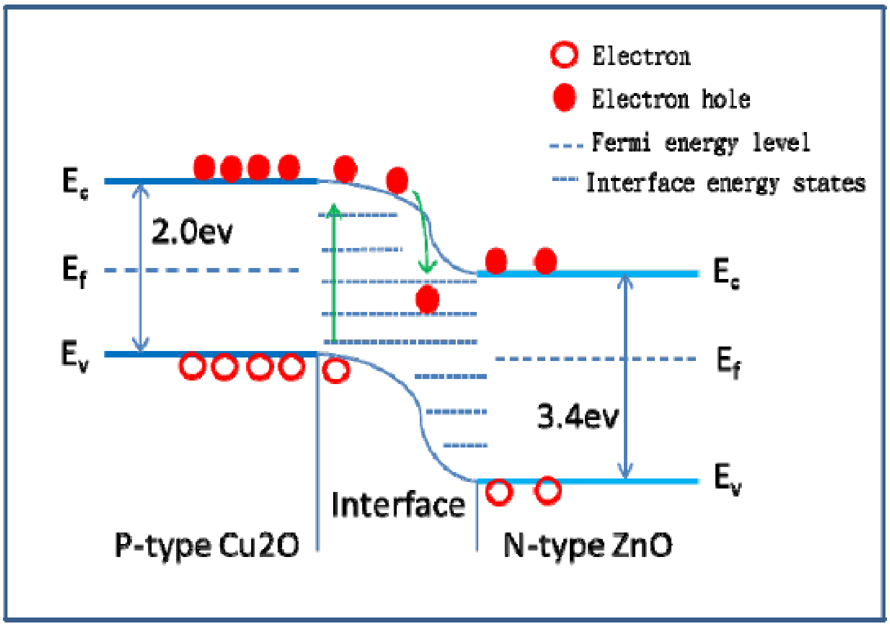

Figure 1.11 Schematic p-Cu_2O / n-ZnO heterojunction solar cell [5].

Basically, the absorber layer, Cu_2O, has the valence band level of -4.9 eV and the conduction band of -2.8 eV as well as they can absorb the range of visible light with energy of ~2.0 eV up. In contrustly, the ZnO layer consists of the valence band level of -7.6 eV and the conduction band of -4.4 eV [15] that is illustrated as figure 1.12.

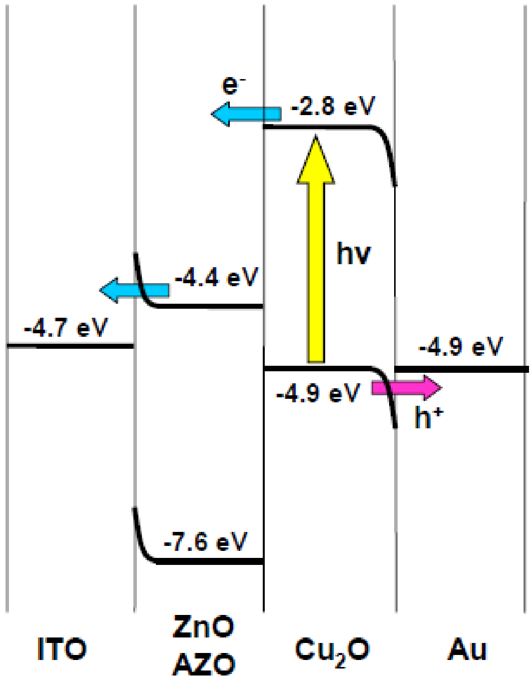

Figure 1.12 Energy level diagram of ZnO(AZO)/Cu_2O-based solar cells [15].

1.5 Research Plan, Methodology and Scope

5.1 Literature reviews of related research

5.2 Fabrication of ZnO and Cu_2O film prepared by sparking process

5.3 Find the condition of Al doping in ZnO film prepared by sparking process

5.4 Film characterizations by SEM, EDS, Raman spectroscope, UV-Visible spectroscope

5.5 Investigation and fabrication AZO/Cu_2O heterojunction prepared by sparking process

5.6 Data analysis, discussion and conclusion

Table 1.3 Research Plan.

	Research activities	12 months			
		1-3	4-6	7-9	10-12
1	Literature reviews of related research				
2	Fabrication of ZnO and Cu_2O film prepared by sparking process				
3	Find the condition of Al doping in ZnO film prepared by sparking process				
4	Film characterizations by SEM, EDS, Raman spectroscope, UV-Visible spectroscope				
5	Investigation and fabrication AZO/Cu_2O heterojunction prepared by sparking process				
6	Data analysis, discussion and conclusion				

1.6 Expecting Benefits

1.6.1 Know-how of fabrication for ZnO and Cu_2O film prepared by sparking process

1.6.2 Obtaining optimized condition for Al doped ZnO(AZO)/Cu_2O heterojunction prepared by sparking process for solar cell application