CHAPTER 2

Experimental detail

Chapter 2 presents details of sparking method and the process of synthesis of ZnO, Al-doped ZnO, Cu_2O and AZO/Cu_2O heterojunction thin films by using sparking method. Characterization of these thin films are included Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Raman spectroscopy, X-ray Diffraction (XRD) and Ultraviolet-visible spectroscopy. Moreover, experimental measuring setup to study electrical property for thin films and to investigate current-voltage curve for AZO/Cu_2O heterojunction are included in this chapter.

2.1 Details of Sparking Process

Sparking process is a method to generate metallic particle in size of nanometer (nanoparticle). The equivalent circuit of the sparking process includes a high voltage power supply, a capacitor paralleled with metallic tips and metallic wires. When the high voltage source is provided to the circuit, sparking is occurred between a gap of metallic wire and produce nanoparticles that are deposited on a substrate below. The sparking equivalent circuit is shown as Figure 2.1. The sparking mechanism is shown in Figure 2.2.

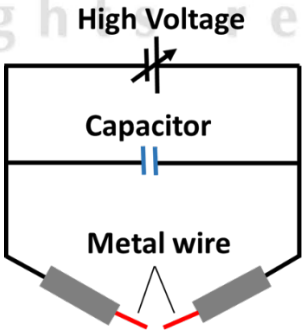

Figure 2.1 Equivalent circuit of sparking process.

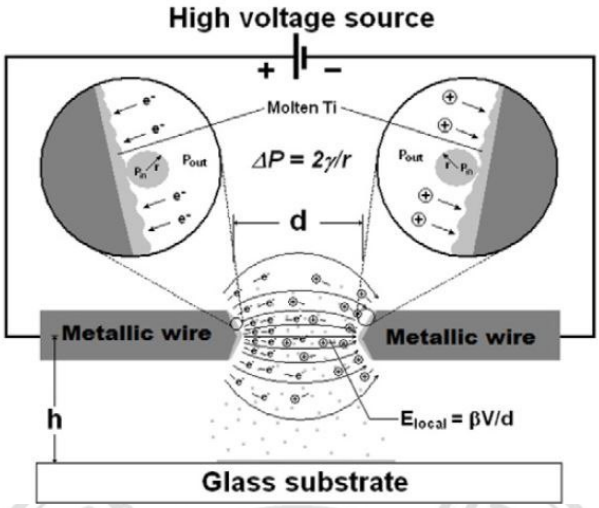

Figure 2.2 Schematic diagram of the mechanism [20].

This thesis, a semiconductor oxide thin film was deposited on the substrate by double tips sparking process. This double tips sparking process is a modified system in order to synthesize two metal oxides by using two different metal wires in a single step. These double tips includes main tips and doping tips. This sparking system is advantage for doping and composite material.

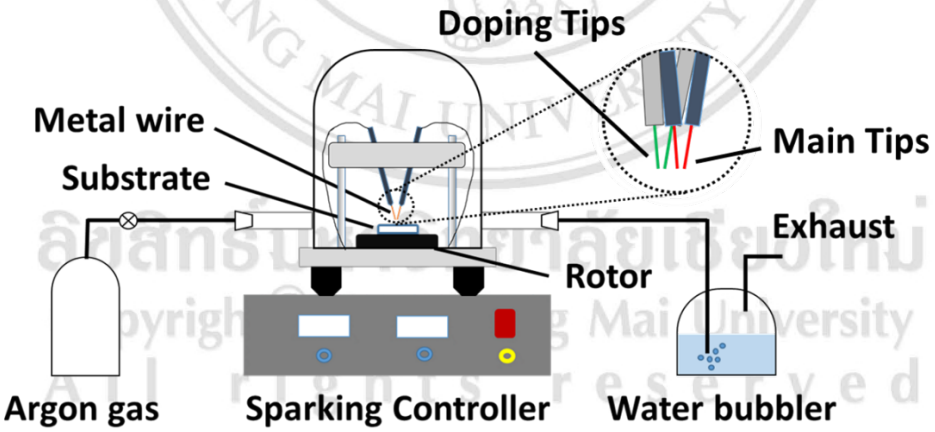

Figure 2.3 Schematic diagram of the double tips sparking process under flowing argon atmosphere for this thesis.

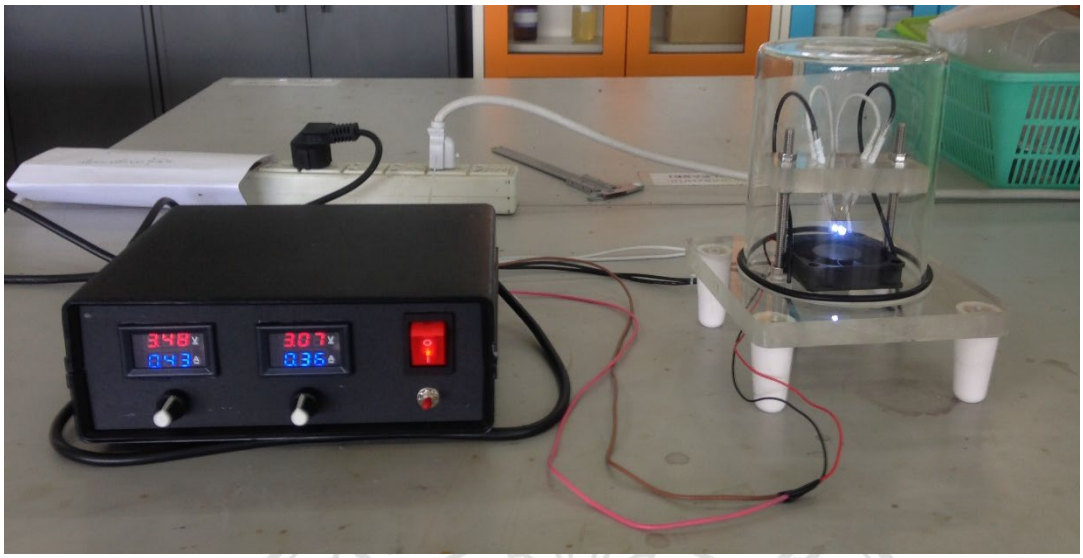

Figure 2.4 The double tips sparking machine.

2.2 Synthesis of nanoparticle films by sparking process

All of ZnO, AZO, Cu_2O and AZO/Cu_2O heterojunction were synthesized by double tips sparking process. The process was done under flowing Ar atmosphere. All nanoparticle metal were annealed in air for phase transition to metal oxide.

2.2.1 Synthesis of ZnO and AZO films

Both ZnO and AZO films were deposited on a rotating glass substrate by double tip sparking process. Zn (purity 99.99%, diameter 0.38 mm) and Al (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips and the doping tips, respectively. The gap between tips and the height of the tips above glass substrate were fixed at 1 nm. The sparking process was done for 5 min under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The doping ratio of Al to Zn was controlled by sparking energy using a different capacitor (C) paralleled Al doping tips. The capacitances paralleled Zn was fixed at 40 nF while those of Al were varied by 0.5, 1.1, 1.5, 3.1, and 4.7 nF. The as-samples were annealed at 400 ℃ for 60 min.

Table 2.1 Conditions of study for synthesis ZnO and AZO films.

Conditions	Capacitance paralleled Zn (nF)	Capacitance paralleled Al (nF)
1	40	-
2	40	0.5
3	40	1.1
4	40	1.5
5	40	3.1
6	40	4.7

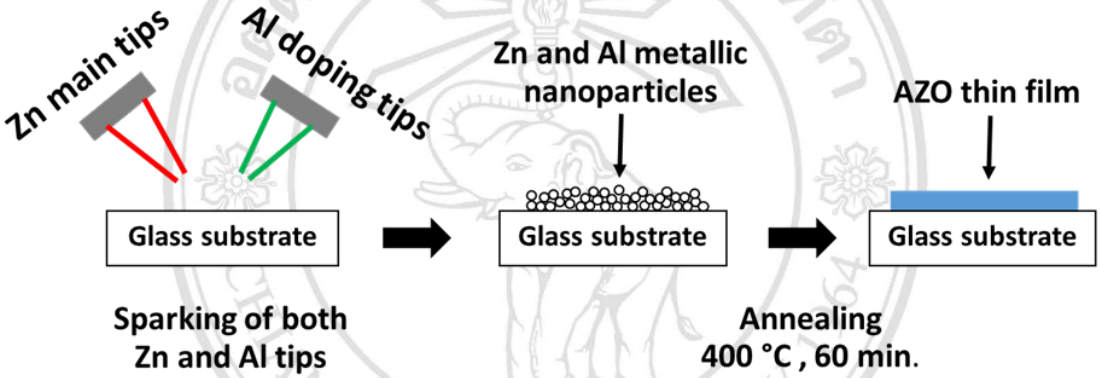

Figure 2.5 Schematic diagram for process of synthesis of AZO films.

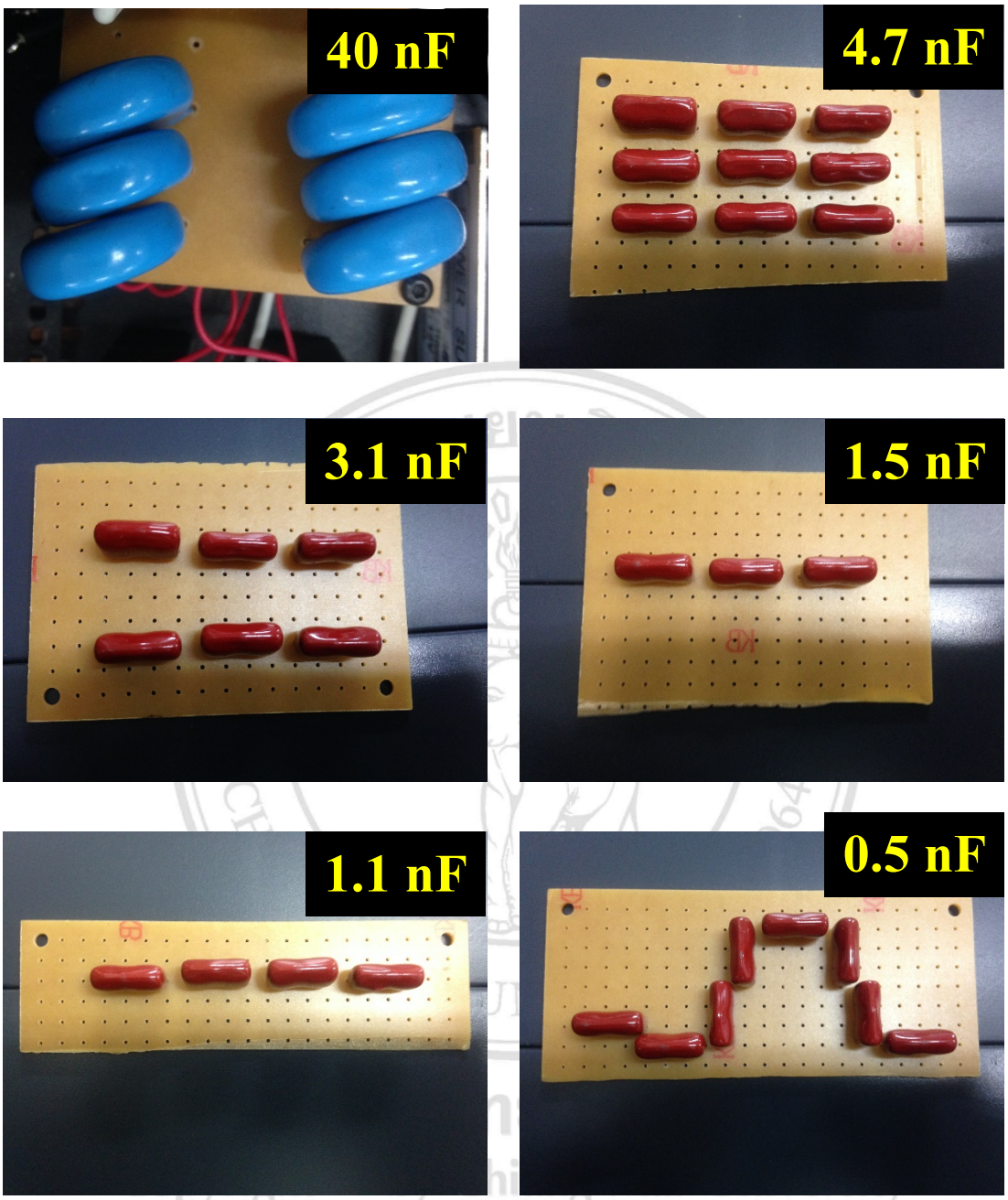

Figure 2.6 Different capacitor paralleled Al doping tips.

2.2.2 Synthesis of Cu_2O film

Cu_2O films were deposited on a rotating glass substrate by a tip sparking process. Cu (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips. The capacitances paralleled Cu tips was fixed at 40 nF. The gap between tips and the height of the tips above glass substrate were fixed at 1 nm. The sparking process was done under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The samples were annealed at 200 °C [21] in different annealing time. The soaking time of annealing treatment was varied by 10, 30, 60, 120 and 180 minutes, in order to provide optimize condition to form Cu_2O phase.

Table 2.2 Conditions of study for synthesis Cu_2O film.

Condition	Annealing time (min)
1	10
2	30
3	60
4	120
5	180

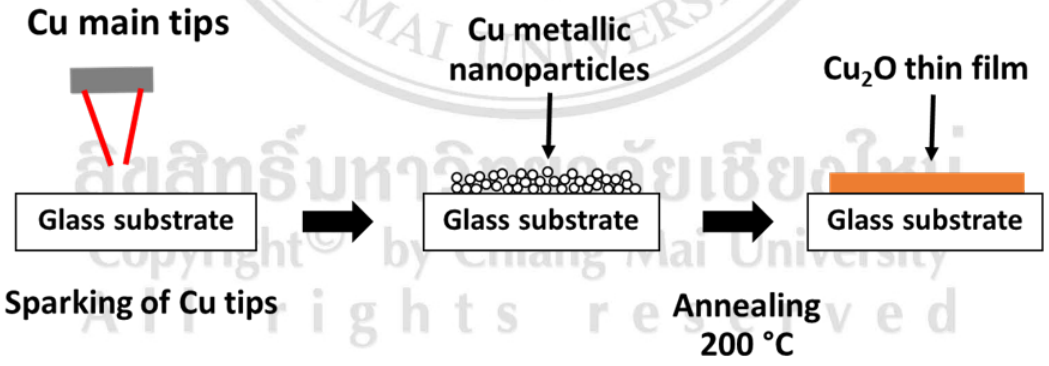

Figure 2.7 Schematic diagram for process of synthesis of Cu2O films.

2.2.3 Fabrication of AZO/Cu_2O heterojunction

A thin layer of AZO films were deposited on the FTO substrate by double tips sparking process. Zn (purity 99.99%, diameter 0.38 mm) and Al (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips and the doping tips, respectively. The sparking process was done for 5 min under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The sample was annealed at 400 °C for 60 minutes.

Cu_2O film was deposited on AZO film as a second layer by sparking process. Cu (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips. The capacitances paralleled Cu tips was fixed at 40 nF. The sparking process was done under flowing Ar atmosphere with a flow rate of 0.5 L/min at room temperature. The samples were annealed at 200 °C.

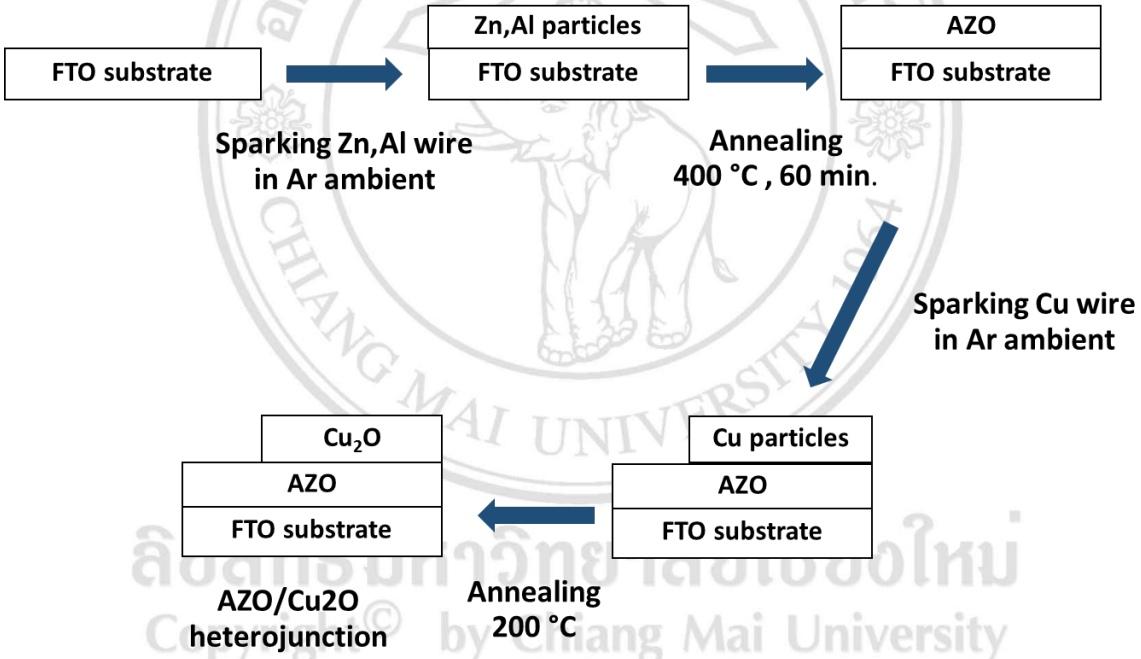

Figure 2.8 Device fabrication process AZO/Cu_2O heterojunction.

2.3 Characterization

The AZO, Cu_2O and AZO/Cu_2O heterojunction prepared by sparking process in this thesis were characterized in details of their morphologies and cross-section images, element composition, chemical structure, crystal structure, optical properties. The morphologies properties and cross-section images of the synthesized thin films were characterized by Scanning electron microscopy (SEM). The element and chemical composition of AZO thin films was investigated by Energy Dispersive X-ray spectroscopy (EDS). The chemical structure properties were examined by Raman spectroscopy in wavelength of 300-800 nm. The crystal structure of the films was investigated by X-ray diffraction (XRD) in the range of 10-60°. The optical properties were observed by using ultraviolet-visible (UV-vis) spectroscopy in wavelength of 300-800 nm.

2.3.1 Scanning electron microscopy (SEM)

The SEM is an electron microscope which has their expansion in 10 nm.it is a tool to picture a surface in micro and nano dimension. In generally, a microscope use a series of lens to bend light wave and create a magnified image. In contrast, the SEM uses electron beams instead of light to create the magnified image.

The internal arrangement of SEM is shown as figure 2.9. It includes as following components;

1) Electron gun

2) Condenser lens

3) Vacuum pipe

4) Aperture

5) Scanning coils

6) Specimen state

7) Objective lens

8) Chamber

9) Detector

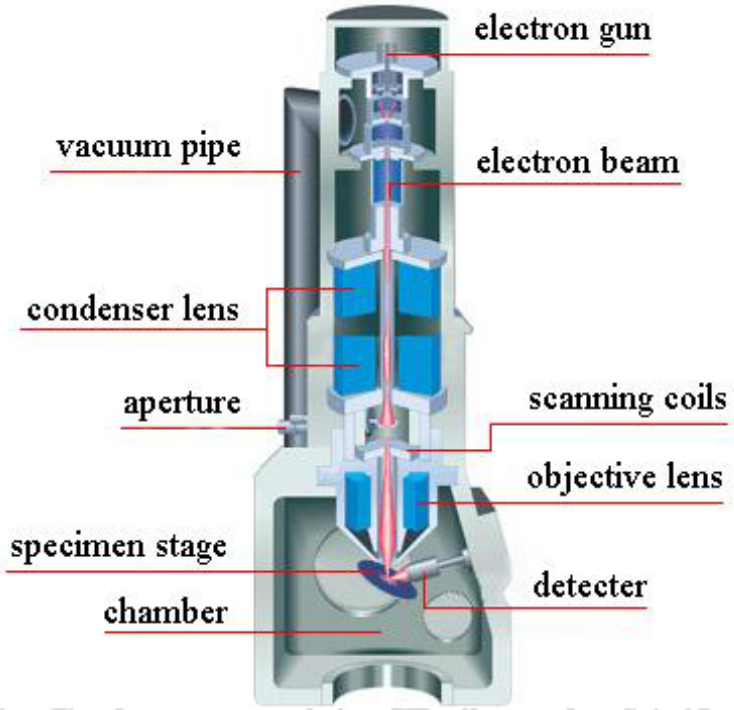

Figure 2.9 Internal arrangement of SEM [22].

Electron beams are produced from a field emission source and accelerated by a high electrical field. The Electron beam lines are focused by condenser lens and deflected by objective lens to produce a narrow scan beam. This scan beam bombards the objects prepared on the specimen stage. As a result secondary electrons are emitted from any surface on the object. A detector detects the secondary electrons and transform it to an electronic signal. All process as mention above is done in a high vacuum chamber. The signal is amplified and transformed to scan-image as shown on a digital image.

Figure 2.10 SEM at Chiang Mai University.

The SEM micrograph can adjust magnification range of 100X to 50000X for LV-scanning electron microscope at Chiang Mai University as shown in figure 2.10. In high resolution image normally was used to scan particle size and grain size of solid samples. Generally, SEM is used to analyze the surface morphologies and cross-section images.

2.3.2 Energy Dispersive X-ray Spectroscopy (EDS)

The EDS is an analytical method used for the elemental analysis or chemical characterization of a sample. It is a function that operates in SEM. It is one of the variant of X-ray fluorescence spectroscopy which relies on investigation of interactions between electromagnetic radiation and matter, analyzing X-ray emitted by the matter. The emitted X-ray relates to energy level of excited electron from matter which is different by each element. Therefore, EDS is a technique to analyze element composition in matter by energy dispersive.

In this thesis, EDS was used to investigate Al doping ratio in ZnO prepared by sparking process with using different capacitance paralleled at Al doping tips.

2.3.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique to analyze chemical structure of a sample that relates to vibrational, rotational and other low-frequency modes observed in a system. Raman spectroscopy uses a monochromatic light in different electromagnetic region to analyze in different sample by a laser in the visible, near infrared and near ultraviolet range are used to delineate the sample of semiconductor, biological cells and ceramic, respectively.

Figure 2.11 Raman spectrometer at Chuang Mai University.

In this thesis, AZO and Cu_2O thin films were characterized the chemical structure by using Raman spectrometer at Chiang Mai University. The samples were analyzed using monothematic light in visible region by 532 nm solid state laser. The samples were observed in wavelength of 300-800 nm.

2.3.4 X-ray Diffraction (XRD)

XRD relies on the deal wave or particle nature of X-rays to obtain information about a structure of crystalline materials. It is a technique to use identification and characterization of compounds based on their diffraction pattern. When as incident beam

of monochromatic X-ray interacts with a target material and then scatter of those X-ray from atoms within the target material. For regular structure such as crystalline, the scatted X-rays get by constructive and destructive interference, so called the diffraction process. The diffraction of X-rays by crystals is described by Bragg's law;

Consider the two parallel planes of atoms in Figure 1, which have the same h, k and l Miller indices and are separated by the interlunar spacing d or d_{hkl}

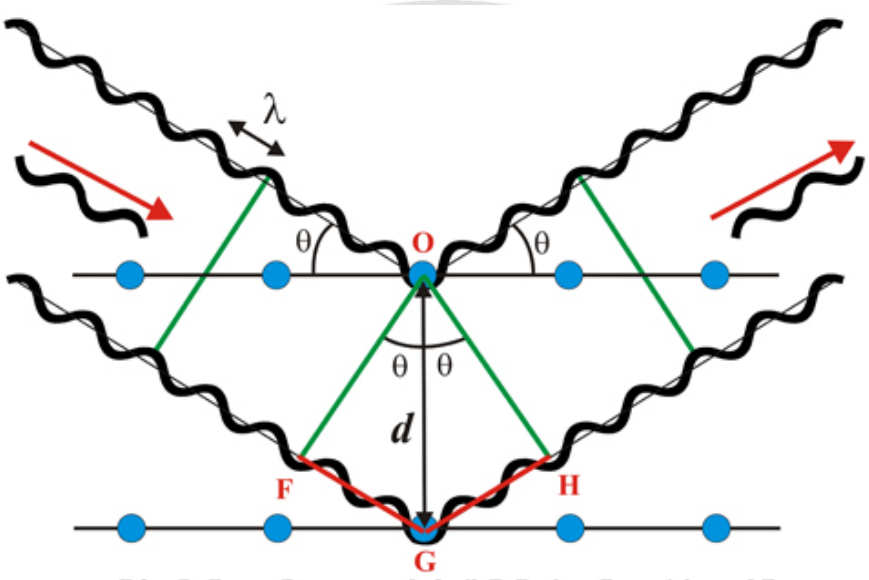

Figure 2.12 Diagram shows two planes with incident light and reflected light [23].

Form Figure 2.12, the two X – ray beams of wavelength λ, go in phase onto the respective planes, with an incident angle θ, form a wave front (first green line on the left). Cooperation effect will be happened. After reflection both X –ray beams must still be in phase, the path difference of the wave fronts **OF** and wave after reflection is equal to an integer number of wavelengths

This condition is equivalent, the sum of the **FG** and **GH** segments corresponds to an integer (**n**) times the wavelength (**λ**):

$$FG + GH = n\lambda \tag{2.1}$$

But $FG = GH$ and $\sin\theta = \frac{FG}{d}$ (2.2)

Therefore, we got

$$2d \sin\theta = n\lambda \tag{2.3}$$

The d – spacing value of each crystal is different. It depends on the structure of the material which is shown as Table 2.3.

In this thesis, AZO and Cu_2O thin films and AZO/Cu_2O heterojunction were characterized the crystalline structure by using XRD spectrometer at Chiang Mai University. The XRD patterns of samples were recorded in angle range of 10-60°. This XRD patterns were analyzed to determine crystalline planes and lattice parameters

Table 2.3 D-spacing value and constrains for crystal system.

Crystal system	**Constrains**	$1/d_{hkl}^2$
Cubic	a = b = c α = β = γ = 90°	$\frac{h^2+k^2+l^2}{a^2}$
Tetragonal	a = b ≠ c α = β = γ = 90°	$\frac{h^2+k^2}{a^2}+\frac{i^2}{c^2}$
Orthorhombic	a ≠ b ≠ c α = β = γ = 90°	$\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}$
Hexagonal	a = b ≠ c α = β = 90°, γ = 120°	$\frac{3}{4}\frac{h^2+hk+k^2}{a^2}+\frac{l^2}{c^2}$
Trigonal/Rhombohedral	a = b = c α = β = γ	$\frac{(h^2+k^2+l^2)\sin^2\alpha+2(hk+hl+kl)(\cos^2\alpha-\cos\alpha)}{a^2(1-3\cos^2\alpha+2\cos^3\alpha)}$
Monoclinic	a ≠ b ≠ c α = γ = 90°	$\frac{h^2}{a^2\sin^2\beta}+\frac{k^2}{b^2}+\frac{l^2}{c^2\sin^2\beta}-\frac{2hl\cos\beta}{ac\sin^2\beta}$
Triclinic	None	

.

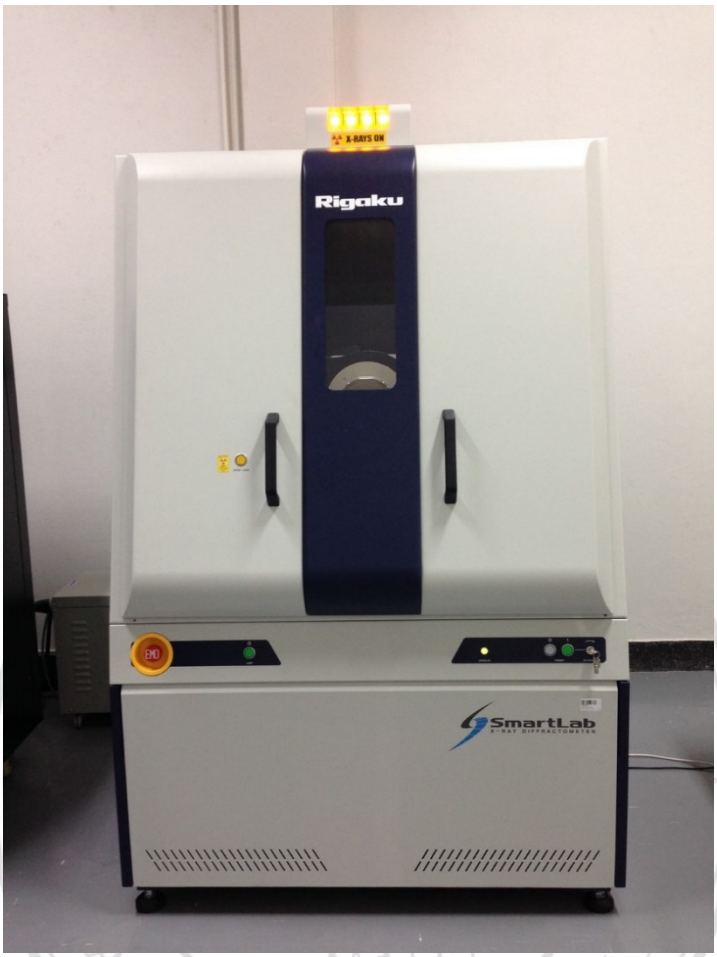

Figure 2.13 XRD instrument at Chiang Mai University.

2.3.5 Ultraviolet-visible (UV-vis) spectroscopy

The UV-Vis spectrophotometer is an instrument that used to investigate optical properties of a material such as transmittance, absorbance and reflectance by using UV-vis spectroscopy. This technique uses light in the visible and near UV range to activate a material and investigate effect the perceived color of the chemicals involved of the materials. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_0). The samples that are used for investigation can be a solid and a liquid. The ratio of I/I_0 is called the transmittance, and is usually expressed as a percent (%T). The absorbance is based on the transmittance, and is form of opposite log scale of transmittance.

The basic parts of a UV-vis spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths

of light, and a detector. The light source is often a Tungsten filament, which can produce the light in the wavelengths of 300 – 2500 nm, and a deuterium lamp, which is continuous over the ultraviolet region of 190 – 400 nm. The detector is typically a photomultiplier tube (PMT).

In this thesis, the optical properties of AZO and Cu_2O thin films were measured by UV-vis spectrometer at Chiang Mai University. The transmittance and absorbance of the samples were recorded in wavelength of 300-800 nm at room temperature.

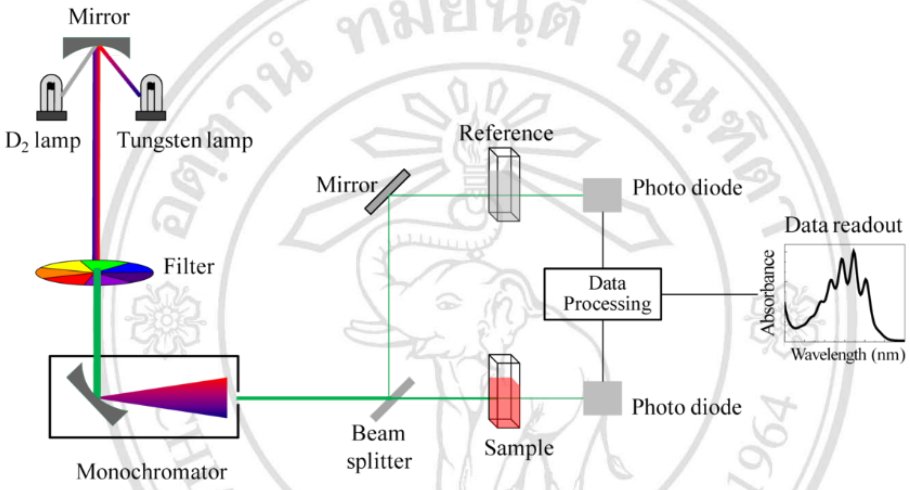

Figure 2.14 Diagram shows measuring process inside the UV-vis spectrometer [24].

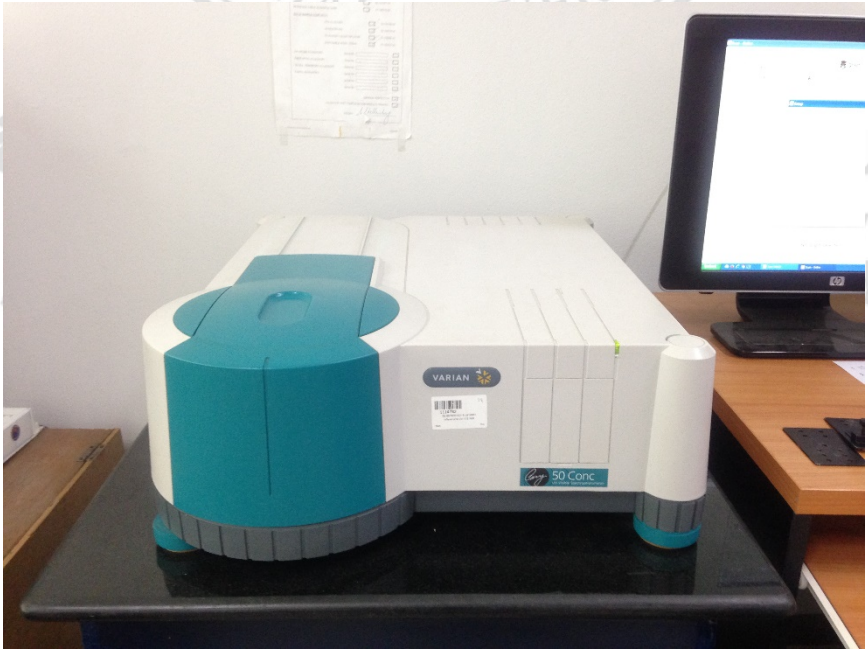

Figure 2.15 UV-vis spectrometer at Chiang Mai University.

2.4 Electrical property measurement

For electrical property, the resistivity is an important physics property. The film was fabricated in FTO substrate by sparking process. Their film's resistivity was measured by standard technique with a standard four probe technique with silver paste contact at room temperature. The resistivity was calculated the equation as follows:

$$\rho = R\frac{A}{h}(\Omega.cm) \tag{2.4}$$

where ρ = the volume resistivity

A = the effective area of measuring electrode

h = the film thickness

R = the resistance, which can determine from slope of V-I curve

For determine the V-I curve, their measuring setup includes a current constant source and voltmeter. The film resistivity measuring setup is illustrated in Figure 2.16.

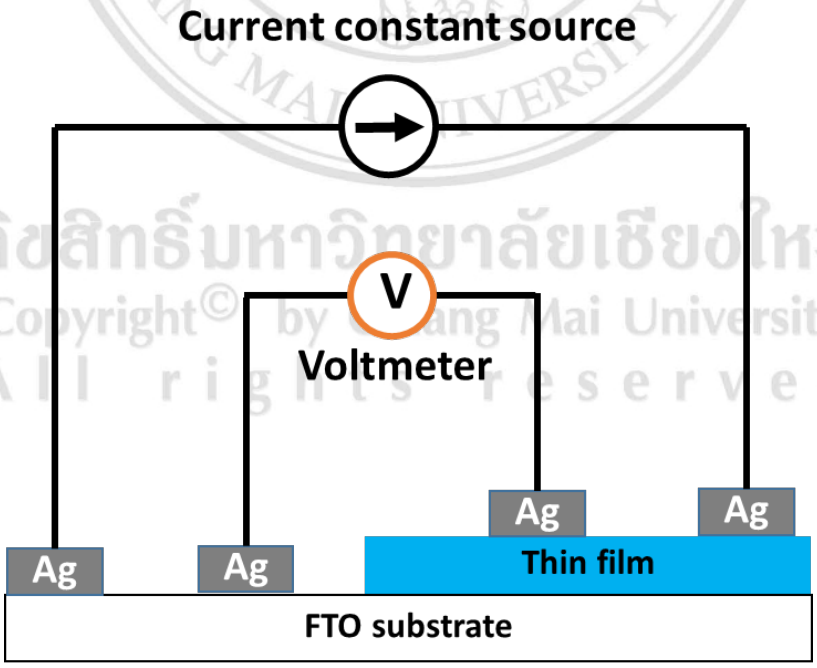

Figure 2.16 Film resistivity measuring setup.

2.5 Current-Voltage (I-V curve) measurement

Current-Voltage (I-V) curve has been used to study a p-n junction characteristic. The junction includes a-type and n-type semiconductor. Moreover, the I-V curve is used to study transportation mechanisms of the carrier between the junctions.

In this thesis, AZO/Cu_2O heterojunction was fabricated on FTO substrate by two step sparking process. The I-V curve was observed by I-V measurement setup with silver paste contact. The setup consists of a function generator that was set as a triangle function, ammeter and voltmeter. The triangle signal was sent to the circuit while ammeter and voltmeter was measuring at the same time.

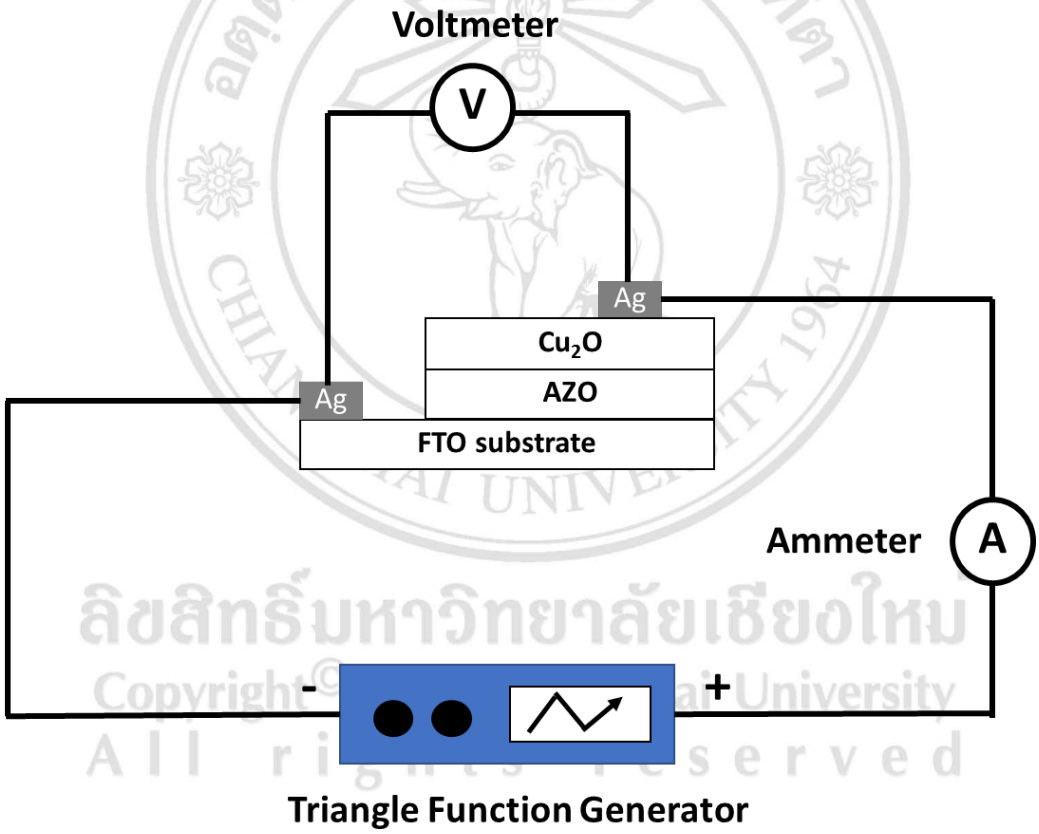

Figure 2.17 I-V curve measuring setup.