CHAPTER 3

MATERIALS AND METHODS

As discussed in the previous chapter, one of the simplest processes for thin film deposition is the magnetron sputtering of the material on the desired substrate. This chapter presents the process of preparing Ag-Sb-Te films. Furthermore, various measurement and characterization techniques for studying deposited thermoelectric thin are explained in details.

PREPARATION Ag-Sb-Te THIN FILMS

The Ag-Sb-Te thin films were deposited on flexible polyimide substrates by DC magnetron sputtering system using the Ag : Sb : Te; 33.33% : 33.33% : 33.33% target (99.99% purity) (UlVAC (Thailand) Ltd.). Firstly, both substrates after cleaning processing were cleaned by ultrasonic washer within acetone, methanol and deionized water for 30 min each. Then, the substrates have been loaded onto a substrate holder in the vacuum chamber with a substrate distance and target approximately of 6.0 cm. Secondly, the deposition processing and condition settings used were a base pressure below 3.0×10^{-5} Torr, an Ar flow rate of 30 sccm, a working pressure about of 20 mTorr, sputtering power for a target of 50 W and the deposition time fixed at 1 min to a control the film thickness about of 100 nm. After the thin film deposition, as-deposited thin films were annealed at temperatures of 300°C, 350°C, 400°C, 450°C and $500\,^{\circ}$C under vaccum atmosphere for 30 min. A schematic representation of the research methodology is presented in Figure 16.

Table 1 Deposition condition of Ag-Sb-Te film.

Base pressure (Torr)	3.4×10^{-5}
Work pressure (Torr)	2.5×10^{-3}
Sputtering power (W)	50
Argon gas flow (sccm)	30
Deposition time (min)	1
Substrates	Polyimide
Annealing temperature (^{o}C)	300, 350, 400, 450 and 500

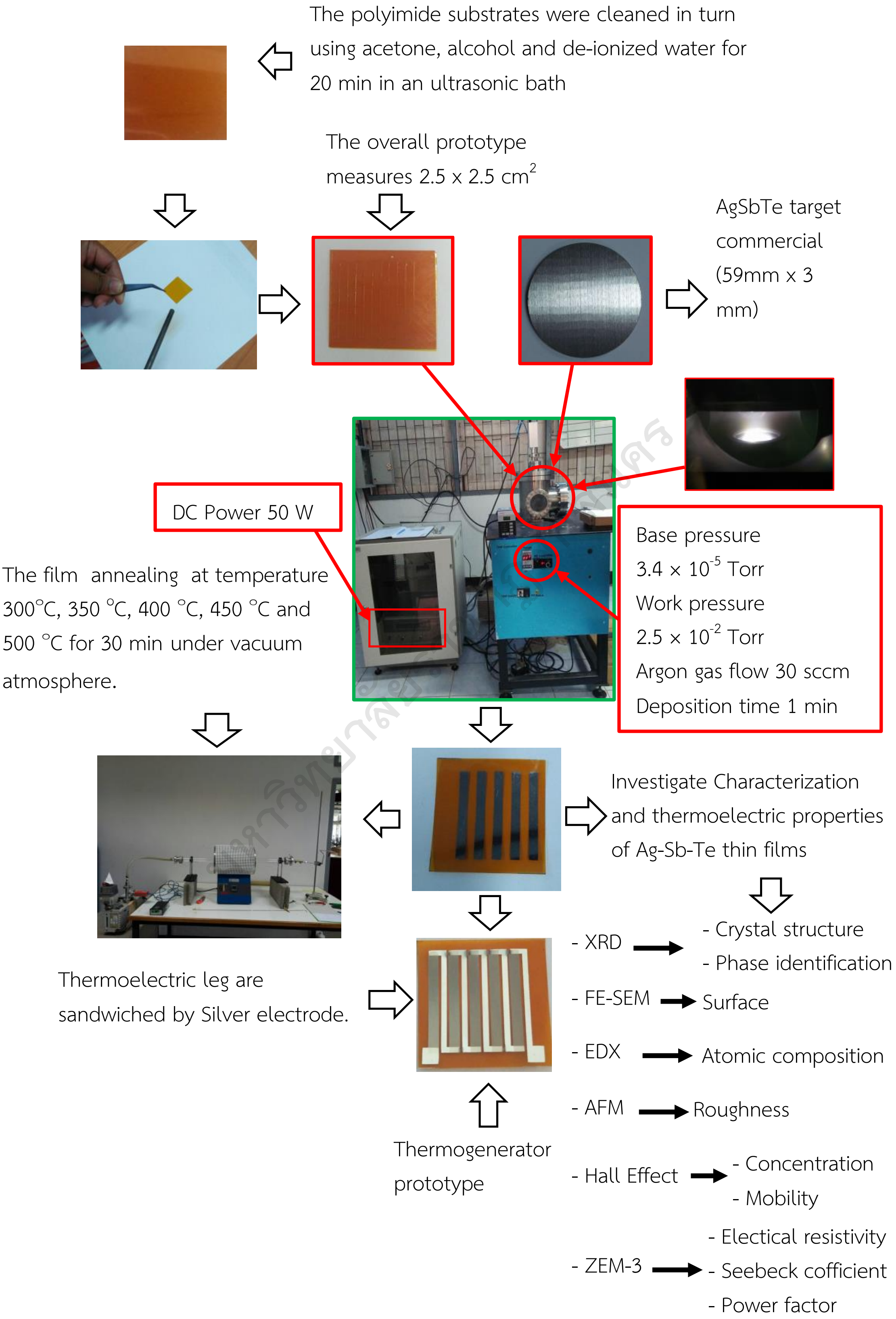

Figure 16 Diagram of research methodology

INVESTIGATE CHARACTERIZATION OF Ag-Sb-Te THIN FILMS

1. The crystal structure and phase identification were measured using grazing-incidence X-ray diffraction (GIXRD; TTRAX III, Rigaku) technique with Cu-K α_1 radiation (λ = 0.154060 nm) and the sample were $\theta - 2\theta$ scan from 20°–55°. This technique used the operation voltage at 40 kV, the current maintained at 30 mA, showed in Figure 17 (a).

2. The surface morphology and compositions of thin film were investigated using field-emission scanning electron microscopy (FE-SEM : SU8030) and energy dispersive X-ray spectroscope (EDX). Quantitative analysis of the different element was performed by standard-less analysis with 3% accuracy, showed in Figure 17 (b).

3. Atomic force microscopy

Atomic force microscopy (AFM, Park systems, XE-120) or scanning force microscopy (SFM) is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The information is gathered by "feeling" or "touching" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable precise scanning.

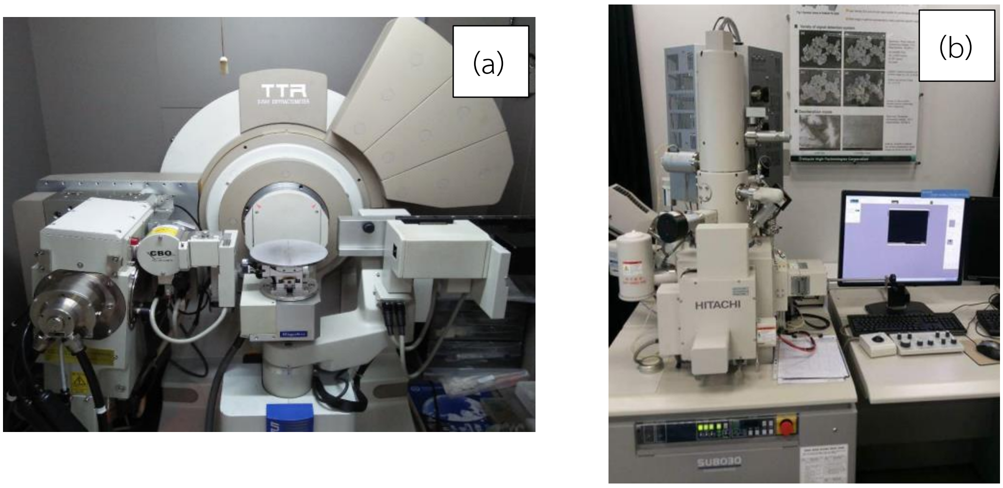

Figure 17 (a) Grazing-incidence X-ray diffractrometer (b) field-emission scanning electron microscopy.

Figure 18 Atomic force microscopy

INVESTIGATE THERMOELECTRIC PROPERTIES Ag-Sb-Te THIN FILMS

1. Carrier concentration and mobility of film were measured at the room temperature under a magnetic field of 0.55 by Hall measurement system (Ecopia, HMS3000).

2. The electrical resistivity and Seebeck coefficient were concurrently measured at room temperature using a ZEM-3 instrument (ULVAC-RIKO).

3. The calculation to power factor as following equation : $P = \frac{S^2}{\rho}$.

Figure 19 ZEM-3 instrument

FABRICATION AND INVESTIGATING THERMOELECTRIC GENERATOR PROTOTYPE OF Ag-Sb-Te THIN FILMS

1. Fabrication thermoelectric generator prototype

The below thermoelectric modular design created by Solid Work program was printed on heat-resistant material. Thermoelectric modular of in-plane configuration was designed as 5 pairs which the leg in 2.0 mm (w) × 20 mm (l) and the spacing between both legs was 2.0 mm, the overall prototype measures 25.40 x 25.40 mm^2. These thermoelectric leg are sandwiched by silver electrode, details as seen the Figure 20 (a) - (b).

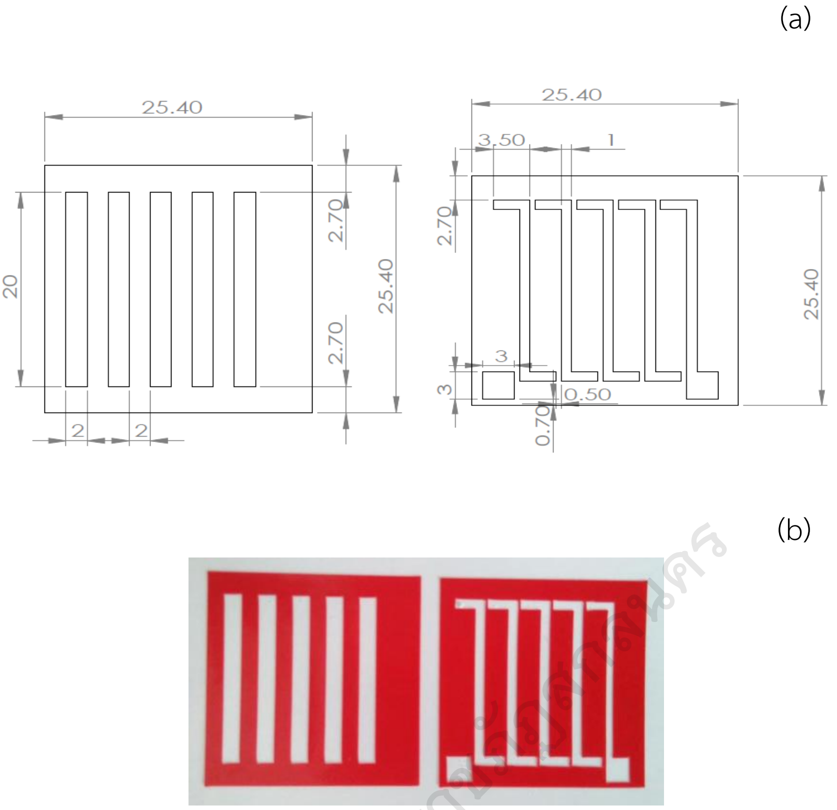

Figure 20 (a) The schematic design of the thin films thermoelectric generator (b) for deposition thermoelectric thin films and for deposition silver electrode thin films.

2. Investigating thermoelectric generator prototype

Investigating thermoelectric generator of thin films at room temperature, as shown in Figure 20. By heating and cooling the reservoirs, an absolute constant temperature difference of 50°C is maintained between T_C and T_H. The absolute temperature of the hot reservoir (T_H. The thermal gradients were also measured in increments at both ends using two separate thermocouples, that were in direct contact with the films (Figure 21).

The output voltage (V_{output}) of the thermoelectric generators was initially measured, while assigning a temperature gradient of $\Delta T = T_H - T_C$ and setting the temperature difference ΔT to ~ 20 °C. The V_{output} is directly proportional to the temperature gradient for a material pair p - p with temperature difference induced between the cold and hot side of thermoelectric generator which can be expressed as :

$$V_{output} = S\Delta T \tag{42}$$

Where S is the Seebeck coefficient (V K^{-1}) of the thermoelectric (TE) materials and ΔT is temperature difference between two surfaces of the generator in °C. The V_{output} was measured at the Ag electrodes pad connected to the thermoelectric legs by multimeter.

The power output (p) of film thermoelectric generators can be calculated as :

$$P = VI_L = \frac{V^2}{\left(R_L + R_{in}\right)} \times R_L = \frac{V^2}{4R_{in}} = \frac{1}{4R_{1n}} \times \left(nS\Delta T\right)^2 \tag{43}$$

Where, R_{in} is the internal resistance of generator including material, R_L is the external electrical load resistance, I_L is the electrical load current output. The voltage output of thermoelectric generator depends on the temperature gradient, thermoelectric materials properties and the geometric design of the legs.

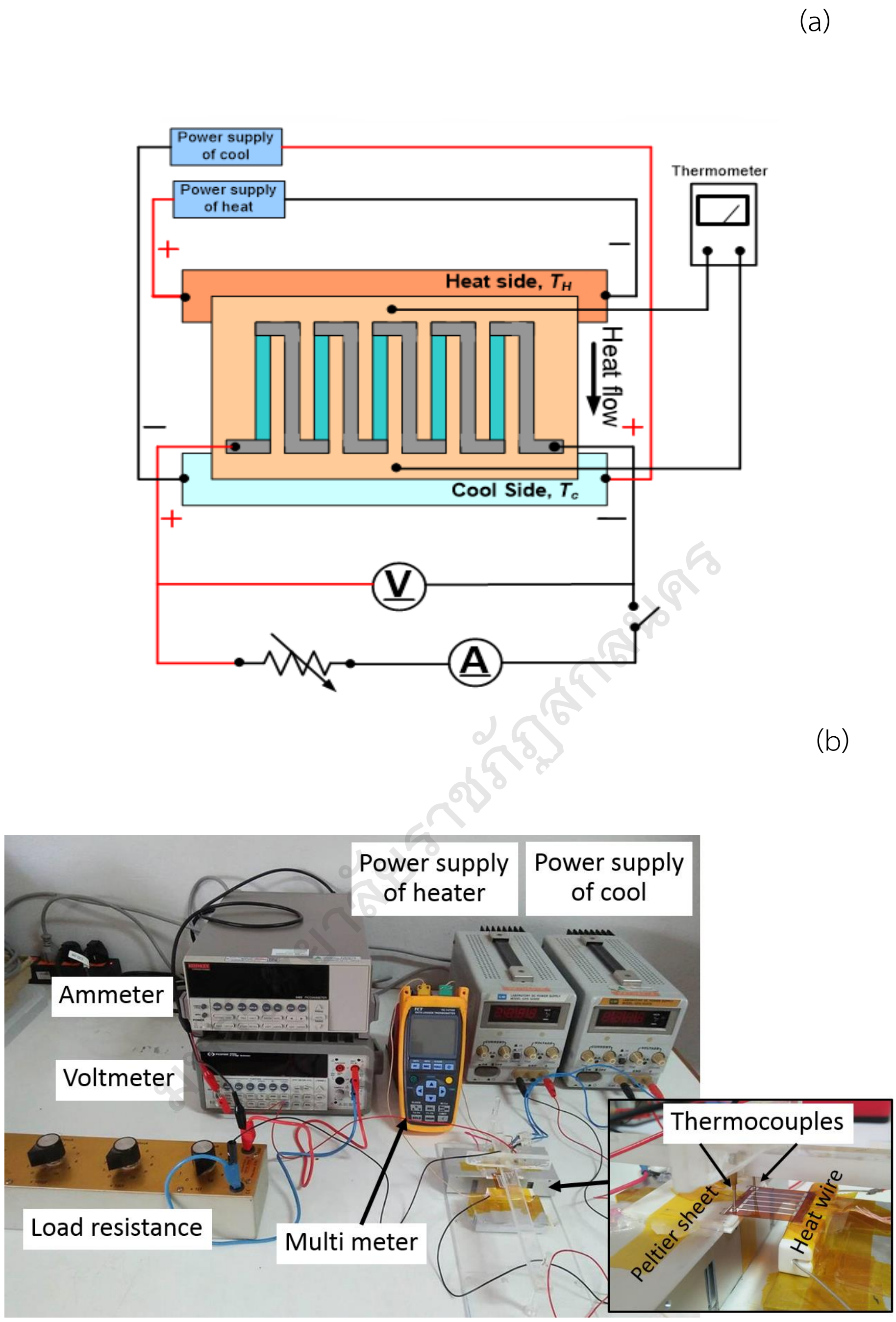

Figure 21 (a) Schematic of thin film thermoelectric generators measured as functions of the temperature difference (ΔT) between the hot and cool junction and (b) experimental setup of the measurement of the output voltage (V_{out}) of film thermoelectric generators.