CHAPTER 3

Experimental procedure

This chapter described all the experimental procedures employed in this work. It was pointed to synthesize vertically aligned ZnO nanowires by chemical vapor deposition technique using acetone to be oxygen source. Then, the obtained product was applied in gas sensor. Experimental process will be separated into 4 parts, as followed.

3.1 Preparation of seeding layer

Substrate will be prepared by glass slide in size of 0.5 cm x 1 cm. To clean and remove surface contamination on substrate, glass slide was sonicated by ultrasonic cleaner in detergent, acetone and DI water for 15 min, respectively. Next, seeding solution was prepared by 5 mM solution of zinc acetate dehydrate in acetone on hot plate stirrer at temperature of 50°C. After that seeding solution was applied by drop coating technique on substrate for 5 times to ensure complete coverage. All the mentioned above was shown in Figure 3.1.

3.2 Synthesis of vertically aligned ZnO nanowires by chemical vapor deposition

In this part, experiments will be divided into 2 groups according to interesting parameters; growth temperature and acetone flow rate. Acetone vapor and also argon gas were used to be oxygen sources and carrier gas, respectively as shown in Figure 3.2.

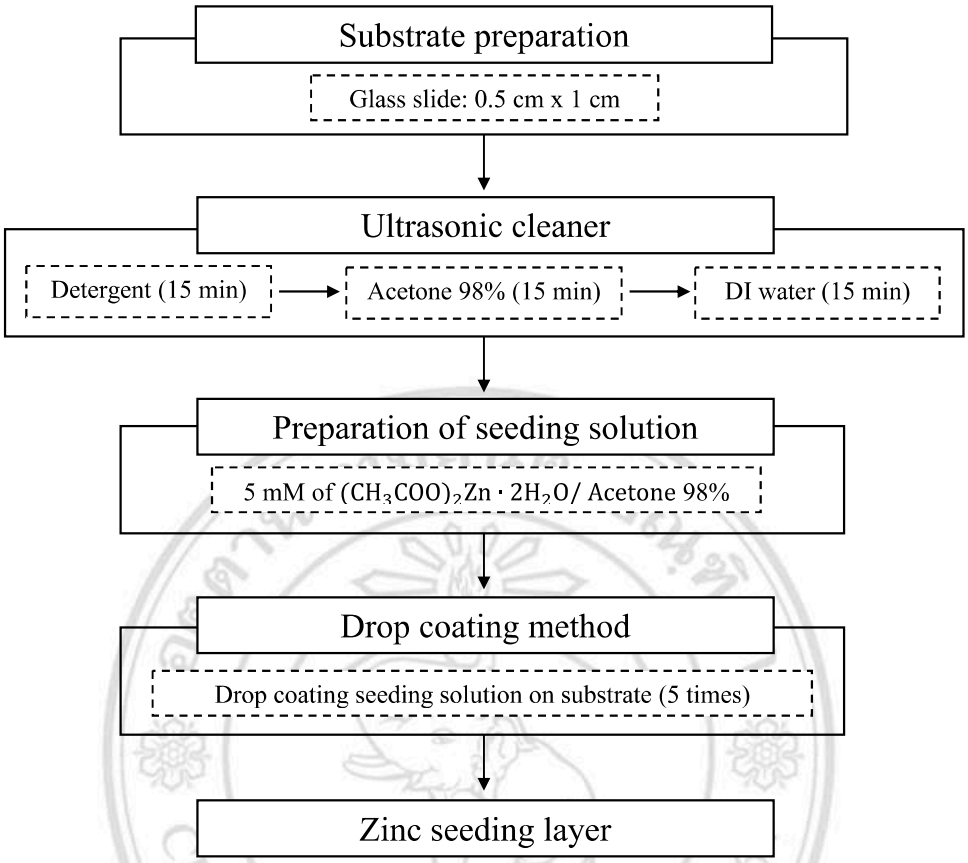

Figure 3.1: Illustration of seeding preparation

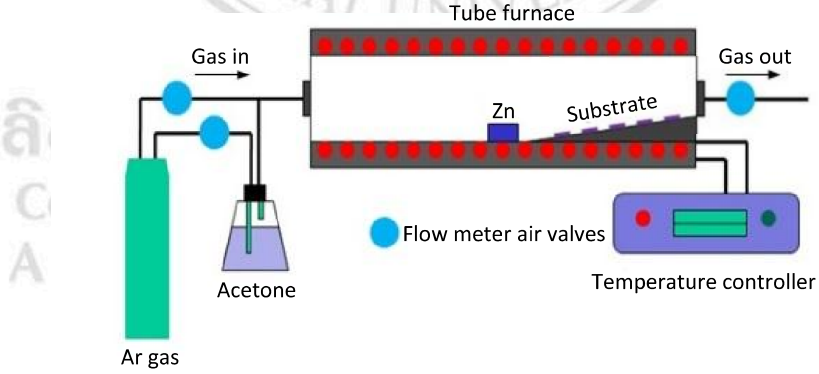

Figure 3.2: Schematic diagram of a typical tube-furnace CVD system

3.2.1 Growth temperature

The vertically aligned ZnO nanowires were grown in a tube furnace by chemical vapor deposition (CVD) technique. In the process, 0.25 g of Zn powder as a source was placed at the center of the tube furnace at $850°C$. The prepared substrate with Zn seeding layer was set at growth zone, in temperature range of $400°C - 550°C$ position under ambient argon gas with a flow rate of 1 L/min in the tube furnace for 7 minutes in order to get rid of remaining in the tube furnace. The valves of the CVD system were closed for preventing ZnO vapor leakage out of the system during ionizing. At the temperature heating up to $850°C$, acetone flow was fixed with a rate of 5 sccm mixed with Ar gas of 0.5 L/min for 15 min. After that, the valves were closed for the oxidation reaction of Zn for 30 min. Then, the valves were opened and Ar gas of 1 L/min was released for 15 min to push out gas in tube furnace before turning off system. A typical experimental system is shown in Figure 3.3.

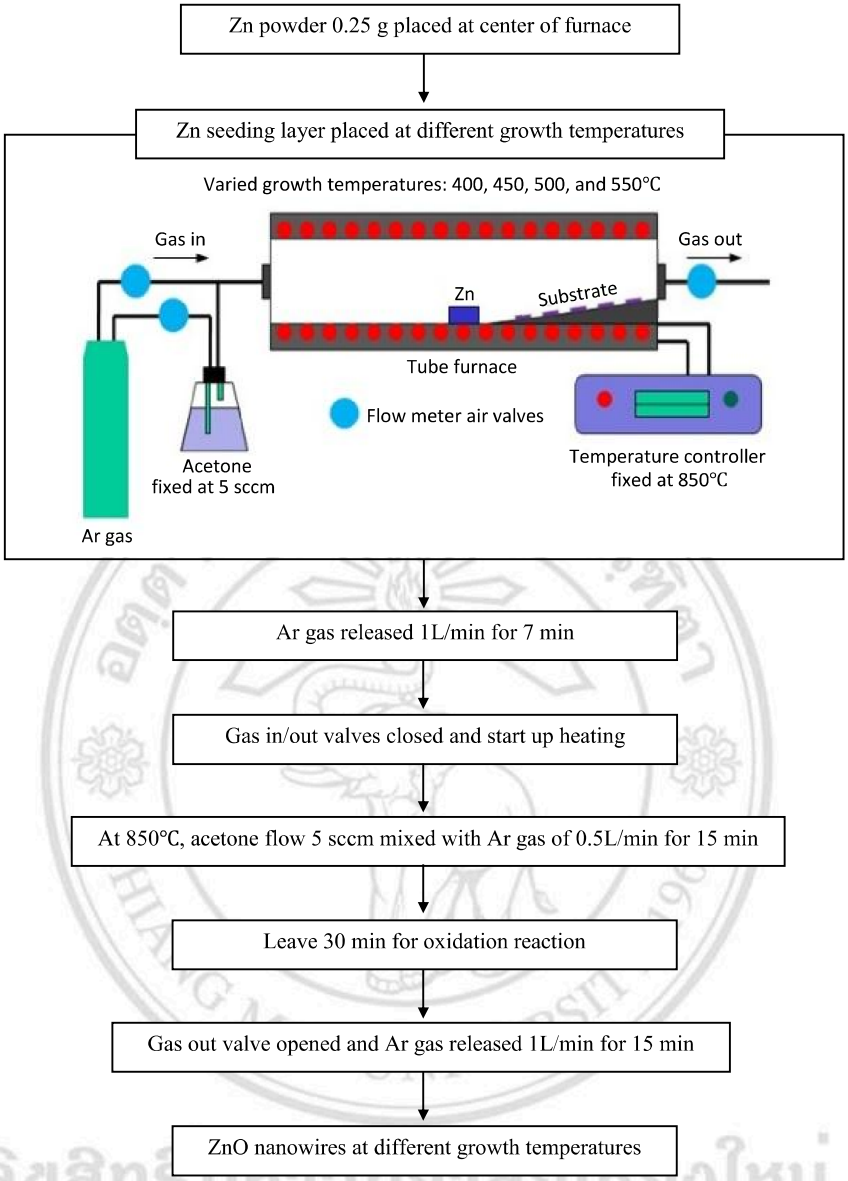

Figure 3.3: Schematic diagram of growth process at different growth temperatures.

3.2.2 Acetone flow rate

In this part, the acetone flow rate was varied in order of 5-45 sccm. The synthesis experiment was fixed at growth temperature of 500°C. The experimental process was shown in Figure 3.4.

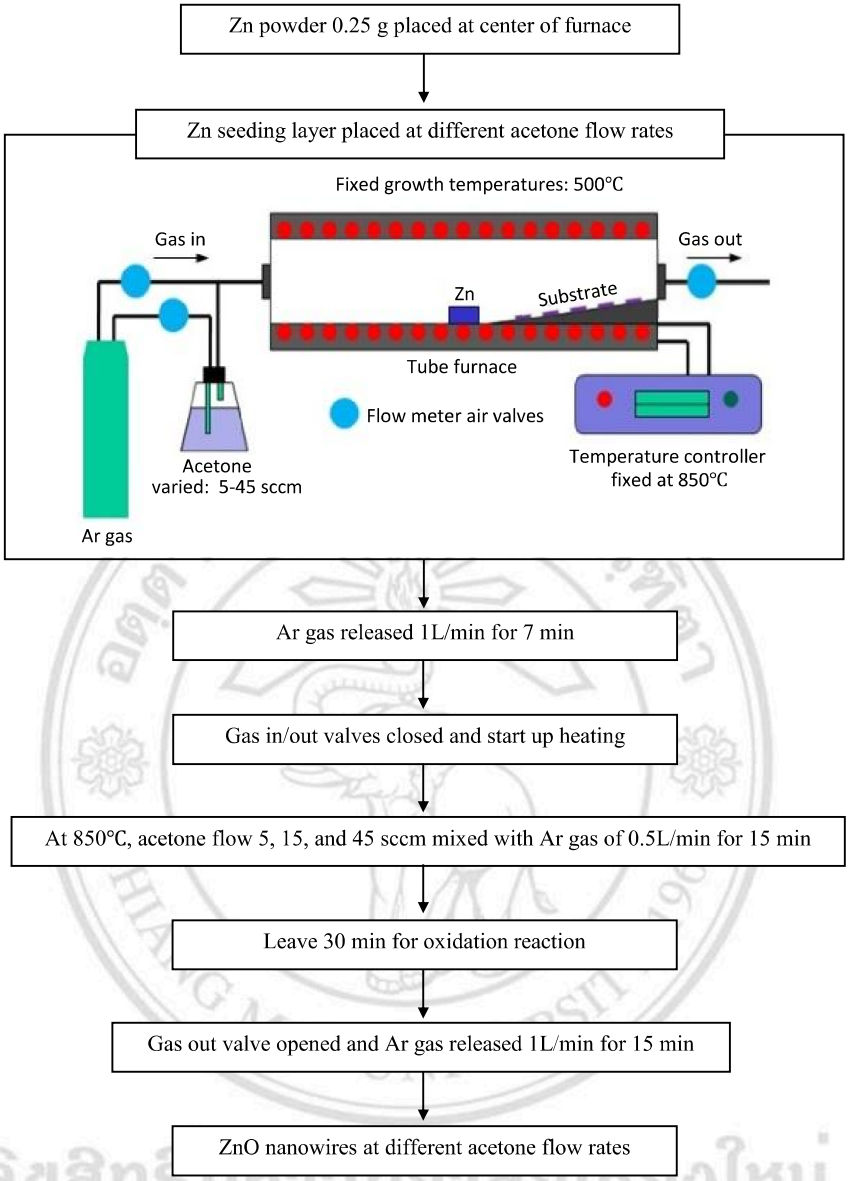

Figure 3.4: Schematic diagram of growth process at various acetone flow rates.

3.3 Characterization of morphology and crystal structure of vertically aligned ZnO nanowires

3.3.1 Characterization of morphology by scanning electron microscopy

The scanning electron microscopy instrument is made up of two main parts consisting of the electronic console and the electron column. The electronic console equips control system and switches which allow for instrument modifications such as filament current, accelerating voltage, focus, magnification, brightness and contrast. The electron column is where the electron beam is generated under vacuum, focused to a small diameter, and scanned across the surface of a specimen by electromagnetic deflection coils. The lower component of the column is called the specimen chamber. The secondary electron detector is placed above the sample stage inside the specimen chamber. Specimens are mounted and secured onto the stage which is controlled by a goniometer. The manual stage controls are found on the front side of the specimen chamber and allow for x-y-z movement, 360 rotation and 90 tilt. A diagram of the components of the electron column is shown in Figure 3.5.

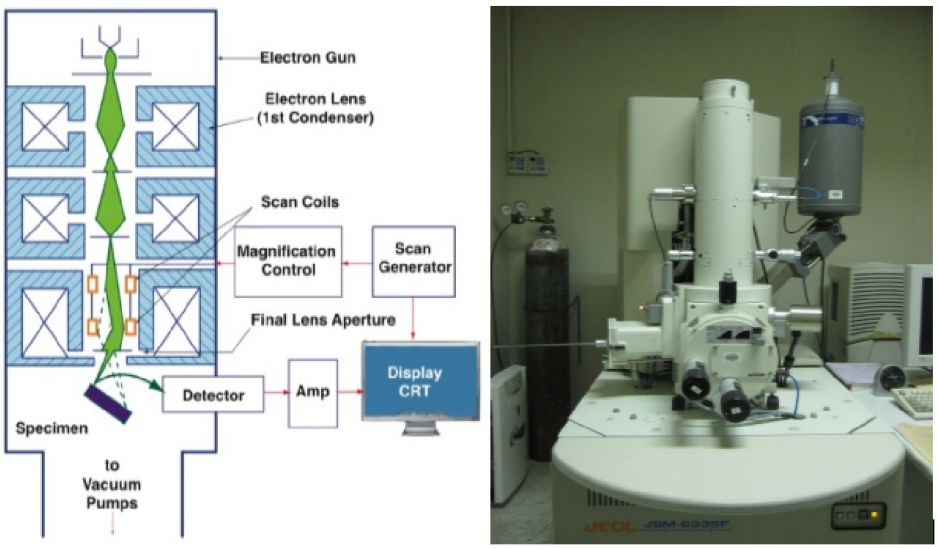

Figure 3.5: Illustration of scanning electron microscopy located at Chiang Mai university (http://micron.ucr.edu)

3.3.2 Characterization of crystal structure by x-ray diffractometry

Here, x-ray diffractometry (XRD) is used to characterize the crystal structure. The following will show how the XRD works. An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an x-ray beam crashs an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In nearly all directions, it will have a destructive interference, which is, the combining waves are out of phase and there is no derivable energy leaving the solid sample. However, the atoms in a crystal are arranged in a regular pattern, and in a very few directions. It will have constructive interference. The waves will be in phase and be well defined x-ray beams leaving the sample at various directions. Hence, a diffracted beam may be represented as a beam composed of a large number of scattered rays mutually reinforcing one another.

X-rays have wavelengths on the order of angstroms (1 Angstrom = 0.1 nm). This is the typical inter-atomic distance in crystalline solids, making x-rays the correct order of magnitude for diffraction of atoms in crystal materials. When x-rays reflect from a series of parallel planes inside the crystal. The orientation and inter planar spacing of these planes are defined by the three integers *h, k, l* called miller's indices. A given set of planes with indices *h, k , l* cut the *a* axis of the unit cell in *h* sections, the *b* axis in *k* sections and the *c* axis in *l* sections. A zero indicates that the planes are parallel to the corresponding axis.

Bragg's Law[41] was used to explain the interference pattern of x-rays scattered by crystals, as shown in Figure 3.6. The diffraction has been developed to study the structure of all states into matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest. The relationship describing the angle at which a beam of x-rays of expectional wavelength diffracts from a crystal surface can be written as

$$2d \sin\theta = n\lambda, \tag{3.1}$$

where λ is wavelength of the x-ray, θ is scattering angle, n is integer representing the order of the diffraction peak, and d is inter-plane distance of atoms.

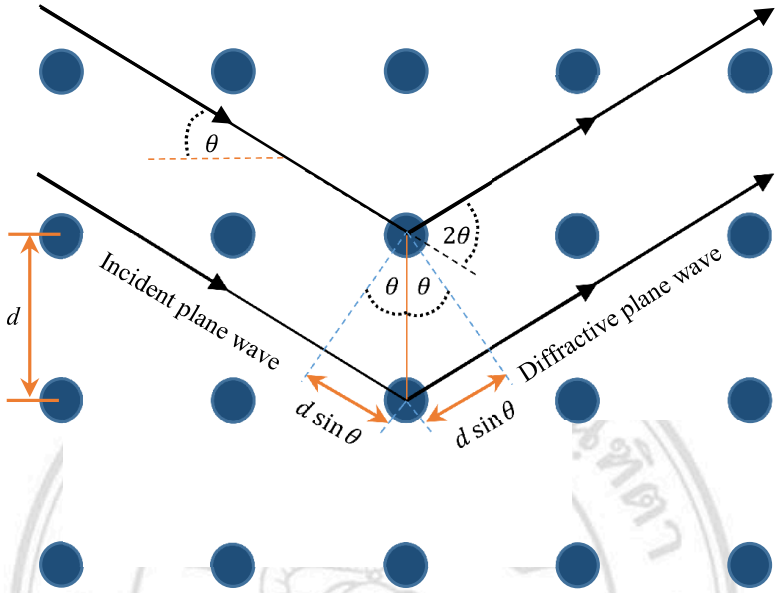

Figure 3.6: Schematic diagram of x-ray diffraction pattern

The experimental result is the relation between intensity of diffractive x-ray and refractive angle (2θ). As a result, it can be analyzed and identified plane direction (hkl) by Bragg's law. For example, in case of hexagonal phase[43], the relation of inter-plane distance of atoms (d) and miller's indies (hkl) or miller's indies for hexagonal crystal system $(h, k, -(h+k), l)$ is given as

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{3.2}$$

Moreover, XRD result can be used to approximate particle size of ZnO nanowires by Scherer's equation[36], given as

$$t = \frac{K\lambda}{\beta \cos\theta}, \tag{3.3}$$

where K is the shape factor, λ represents the x-ray wavelength used for the measurement, β is the line width (FWHM) in radians, θ is the Bragg angle, and t is the mean size of the crystalline domains. The formula yields a lower bound on the possible particle size.

The shape factor enables one to determine the average size of single crystal. Assuming a Gaussian function to fit the peak, the shape factor is 0.9, followed as

$$t = \frac{0.9\lambda}{\beta \cos\theta} \tag{3.4}$$

3.4 Fabrication and investigation of vertically aligned ZnO nanowires gas sensors using ethanol vapor

The gas sensors base on vertically aligned ZnO nanowires were simply fabricated as a resistor in electronic circuit. Sample is chosen one condition from main experiment fabricating sensor device. The sensors were manufactured by putting gold paste as electrodes on the top of surface above ZnO nanowires. Two electrodes were put on the top or at the end of sample before annealing under temperature of $50°C$. The heater for gas sensor was made from tube furnace which could be controlled the operating temperature in the range of $350°C - 550°C$. The operating temperature was observed by thermocouple which was placed at the same point of gas sensor. The resistance of sensor was evaluated by using a volt-amperometric technique under normal atmosphere and ethanol atmosphere.

The electrical determinations were performed with an applied voltage of 5 volts. The current and voltage across the load resistor were measured by ammeter and voltmeter, respectively. The ethanol sensing properties of sensor based on vertically aligned ZnO nanowires were tested in ethanol atmosphere at ethanol concentration of 500 ppm. The ethanol vapor with various operating temperature was originated from ethanol solution by using breathing human simulator (GUTH labolatories Inc., Harrisburg USA). The sensor response is evaluated as the ratio of the resistance of sensor in air and in the ethanol-air mixed gas. The overall set up experiment and investigation process for ethanol sensing properties were shown in Figure 3.7 and 3.8, respectively.

<table>
<tr><th colspan="7">MAIN EXPERIMENT</th></tr>
<tr><td colspan="7">Preparation of seeding layer</td></tr>
<tr><td colspan="7">Prepare zinc seeding layer on substrate by 5 mM solution of zinc acetate dehydrate</td></tr>
<tr><td colspan="7">Synthesis of vertically aligned ZnO nanowires by chemical vapor deposition (CVD) technique</td></tr>
<tr><td colspan="4"><u>Group 1 : varied growth temperature</u>
Fixed acetone flow rate constant at 5 sccm</td><td colspan="3"><u>Group 2 : varied acetone flow rate</u>
Fixed growth temperature constant at 500°C</td></tr>
<tr><td>400°C</td><td>450°C</td><td>500°C</td><td>550°C</td><td>5 sccm</td><td>15 sccm</td><td>45 sccm</td></tr>
<tr><td colspan="7">Characterization of morphology and crystal structure of vertically aligned ZnO nanowires</td></tr>
<tr><td colspan="7">Characterization of morphology by Scanning Electron Microscopy (SEM)
Characterization of crystal structure by X-Ray Diffractometry (XRD)</td></tr>
<tr><td colspan="7">ADDITIONAL EXPERIMENT</td></tr>
<tr><td colspan="7">Investigation of vertically aligned ZnO nanowires gas sensors by using ethanol vapor</td></tr>
<tr><td colspan="7">Choose one condition (500°C of growth temperature and 5 sccm acetone flow rate) from main experiment fabricating sensor device and testing at 500 ppm ethanol vapor under various operating temperature in ranges of 350°C to 550°C</td></tr>
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Figure 3.7: Illustration of overall set up experiment

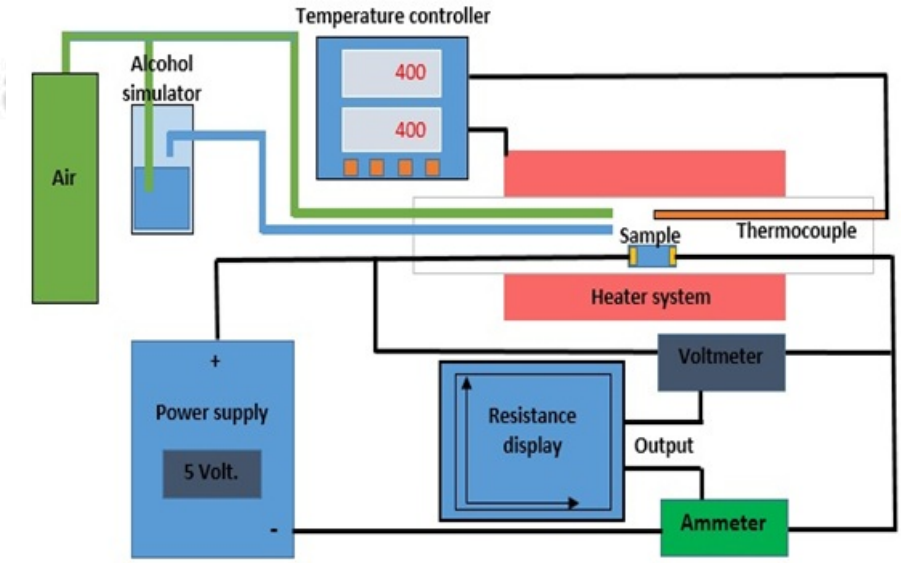

Figure 3.8: Schematic diagram of ethanol sensing characteristic measurement