



CHAPTER III

FUNDAMENTAL

3.1 Photoinduced hydrophilic property

3.1.1 Physiochemical property of Zinc oxide (ZnO)

ZnO is an *n*-type semiconductor with wide band gap energy of 3.3 eV. It is abundantly available in nature and exhibits various excellent properties such as optical, electrical and photocatalytic properties (Berber et al., 2005). From many researches presented that ZnO films were polycrystalline with a structure that belong to the ZnO hexagonal wurtzite which unit cell is composed of both three axis as *a*, *b* and *c* ($a = b \neq c$) and three angles as α , β and γ ($\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and the physiochemical as shown in Table 3.1.

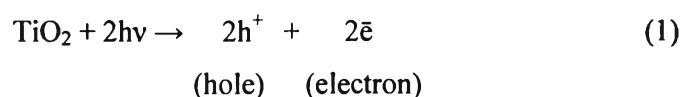
Table 3.1 Physiochemical property of ZnO

Other names	Zinc white
Molecular formula	ZnO
Molar mass	81.4084 g/mol
Crystal structure	Hexagonal wurtzite
Density and phase	5.606 g/cm ³ , solid
Solution in water	Insoluble
Melting point	1975°C (decompose)
Boiling point	-
<i>a,c</i> Lattice constants	3.249Å, 5.201Å
Refractive index	2.0

3.1.2 Principle of photoinduced hydrophilic property

The principle of photoinduced hydrophilic property occurs under irradiation of semiconductor metal. A semiconductor, which could be theoretically described by valance band and conduction band, includes ZnO, TiO₂, ZrO₂, Fe₂O₃, WO₃ and so on. Band gap of a semiconductor is defined as a difference between its valance band and conduction band which could be related to the wavelength of photon by irradiation. A photon with energy higher than or equal to the band gap is absorbed by the semiconductor, leading to transfer of electron from valance band to conduction band. Such irradiation could give rise to electrons (\bar{e}) and holes (h^+) on the surface.

The holes can react with lattice oxygen and leading to the formation of surface oxygen vacancies while some of electrons can react with lattice metal ions to form defective sites. Water molecules can replace these oxygen vacancies producing chemisorbed hydroxyl groups. For example, the photoinduced hydrophilic property mechanism of TiO₂ is known photosensitive semiconductor. The formation processes of oxygen vacancy on TiO₂ surface are presented in equations (1-4)



Meanwhile, water molecules may coordinate into the oxygen vacancy sites, which lead to adsorption and spreading of water molecules on the surface. Superhydrophilic property could be related to the water contact angle approaching zero (See figure 3.1).

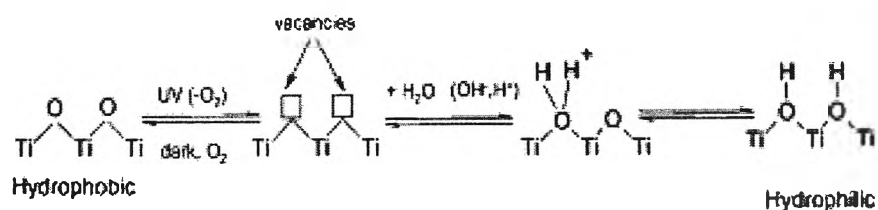


Figure 3.1 Mechanism of photoinduced superhydrophilicity of TiO₂

(Fujishima, Hashimoto and Watanabe, 1999)

Moreover, ZnO is the one of semiconductors which can provide hydrophilic property after irradiation. Sun, Nakajima, Hashimoto et al. (2001) studied the photoinduced surface wettability conversion of ZnO and TiO₂ thin films prepared by spray pyrolysis method. The water contact angles of ZnO and TiO₂ thin films are 109 and 54 degrees before UV irradiation. Upon irradiation, the contact angles of both films would decrease to 0 and 5 degrees, respectively.

Wettability and contact angle (John C. Berg, 1993)

Wetting phenomenon involves the interaction of a liquid with a solid. It can be spreading of a liquid over a surface, the penetration of a liquid into a porous material medium, or the displacement of one liquid by another. It can help to characterize surfaces and to determine solid/liquid interactions. Wettability is most often described by a sessile drop. A schematic diagram is shown in Figure 3.2. The contact angle (θ) is a measure of wettability. A low contact angle means high wettability and a high contact angle means poor wettability.

In the sessile drop method, a drop is placed on a horizontal surface and observed in cross section through a telescope. A goniometer in the eyepiece is used to measure the angle. The angle of vision is just slightly off horizontal so the edge of the drop and its reflected image are both visible. This allows the tangent to be determined precisely at the point of angle between the drop and the surface.

Moreover, the contact angle can be related to Young's equation. After a liquid droplet is applied on a solid surface, the balance between the cohesive force in the liquid and the adhesive force between the solid and the liquid would control the contact angle of the droplet.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

Where

- γ_{SV} = the surface tension of solid-vapor surface
- γ_{SL} = the surface tension of solid-liquid surface
- γ_{LV} = the surface tension of liquid-vapor surface
- θ = the contact angle (CA)

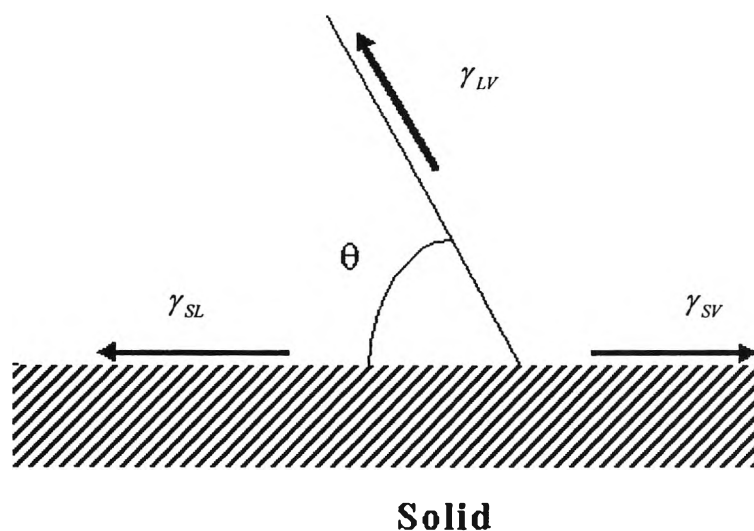


Figure 3.2 Schematic of a sessile drop on a surface

Definition hydrophilicity

The contact angle is value representing wettability of the surface. Such angle is determined by the interactions across of three interfaces which a liquid/vapor interfaces meet solid surface. The general concept is illustrated in Figure 3.2 which illustrates a small liquid droplet on a flat horizontal solid surface. Hydrophilic surface is the substrate that has the contact angle between 5° to 90° . But this angle is less than 5° , the substrate surface is called “superhydrophilic”. In addition, the surface has hydrophobic which the contact angle is more than 90° . If the contact angle is much more 150° , these surface is called “superhydrophobic” (Bico et al., 2002).

3.2 Dip coating technique for thin film fabrication

In general, a batch dip coating process could be divided into five steps: immersion, start-up, deposition, evaporation and drainage (See figure 3.3). The process involves immersing a substrate into a reservoir of solution for some time thereby ensuring that the substrate is completely wetted and then withdrawing the substrate from the solution bath (Landau and Levich, 1942). After the solvent is

evaporated, a uniform solid film is deposited upon the surface of the substrate. The major forces are viscous drag, gravitational force and surface tension.

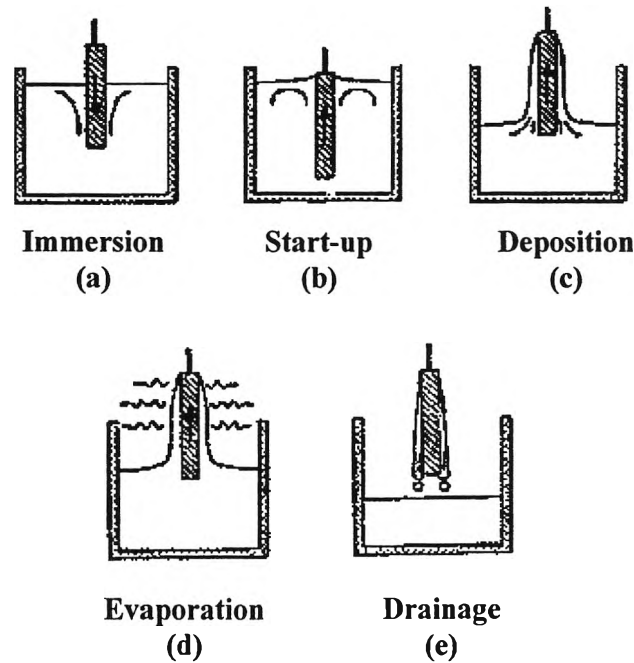


Figure 3.3 Fabrication stages of the dip coating process: (a) immersion, (b) start-up, (c) deposition, (d) evaporation and (e) drainage (Brinker et al., 1994)

A dip coating model was proposed based on the hydrodynamics of a Newtonian fluid flow, ignoring solvent evaporation. The model considered a case of low viscosity of an infinite moving plate and relatively large liquid container. The liquid surface is separated into two independent regions, i.e. (i) the region of the surface situated high above the meniscus and directly dragged by the plate, where the surface of liquid may be taken to be nearly parallel to the plate surface and (ii) the region of the meniscus of liquid, which is slightly deformed by the motion of the plate. By using the classical lubrication equations, a matching condition for the film entrainment and used to obtain an expression for the film thickness as shown in equation (Yimsiri and Mackley, 2006)

$$h_0 = 0.944 \frac{(\eta u_0)^{(2/3)}}{\sigma^{(1/6)} (\rho g)^{(1/2)}}$$

Where

- h_0 = the limiting film thickness
- u_0 = the withdrawal speed (WS)
- η = the solution viscosity
- ρ = the solution density
- σ = the solution surface tension

The advantages of dip coating are a simple process for depositing a thin film of solution onto a plate, cylinder, or irregular shaped object, easy to maintain, low cost and uncomplicated equipment. On the other hand, the disadvantages of the dip coating are the difficult handling of large panes, use a long time for processing and requirement of treatment of waste coating solution.

A dip coater is equipment that is generally employed in the controlled immersion and withdrawal of substrates into solutions for sol-gel coating (Figure 3.4).

In this thesis, a hand-made dip coating with adjustable withdrawal speed and immersed time is employed.

The technical data are as follow dimensions (W×L×H) = 15cm×15cm×25cm, withdrawal speed = 3.0-12.0 cm/min, immersed time = 0.5–60.0min, power supply = 12V.

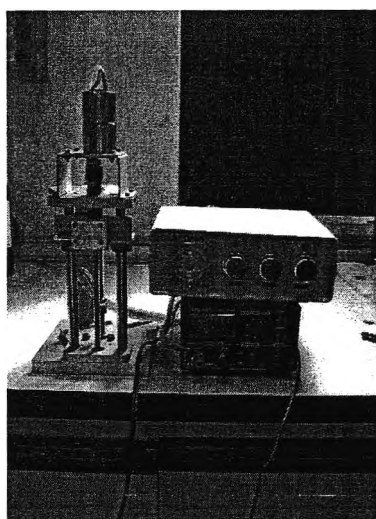
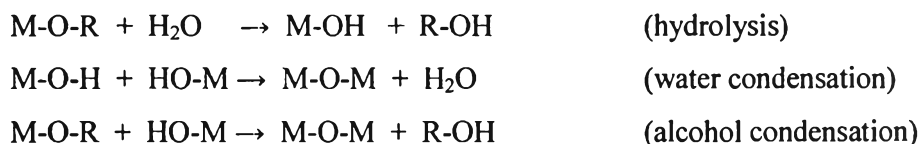


Figure 3.4 Dip coater

3.3 Sol-gel process for precursor preparation

3.3.1 Sol-gel synthesis

Sol gel synthesis occurs in liquid solution of metallic oxide precursor which microstructure is produced from two reactions consisting of hydrolysis and condensation reactions.



The productions from sol gel method are oxide colloidal suspension and metal oxide which is generated by hydrolysis reaction and condensation reaction, respectively.

The sol is made of solid particles with diameter of a few hundred nanometers. They are suspended in a liquid phase. Then, the particles condense in gel and become macrostructure will cross-link characteristics so the gel is dried at low temperature produced porous solid. When the gel is heated and decomposed anions, gel is given oxides to rearrange of the structure and occurred crystallization.

This process is applied with the preparation oxide materials thin films. They are usually deposited in two-step process. In the first step, a gel film is deposited from a wet precursor solution by deposition method such as dipping, spinning, spraying or aerosol deposition. And the last step, the gel film converts to an oxide film by using calcination or annealing technology. The calcination is a thermal treatment process applied to solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction and the annealing is a heat treatment that alters the microstructure of a material causing changes in properties such as strength and hardness.

Sol-gel process has many advantages such as easier composition control, better homogeneity, low processing temperature, lower cost, easier fabrication of large area films and possibility of using high purity starting materials (Maiti et al., 2007).

3.3.2 Characterization of precursor

The precursor concentrations are characterized by viscometer (Brookfield DV-E) because the viscosity is essentially Newtonian fluid and relationship with the film thickness. The viscosity is a measure of the resistant of a fluid. The viscometer ensures easy and accurate read out of test results for the measurement of viscosity, while also displaying rotational speed and spindle in use.



Figure 3.5 Viscometer

3.4 Characterization of thin films

The instruments used to characterize ZnO thin films are UV-Vis spectrophotometer (Perkin Elmer; Lambda 650), Scanning Electron Microscopy (SEM; JSM5410LV), Atomic Force Microscopy (AFM; Veeco, Scanning Probe Microscopy Controller), Energy dispersive X-ray spectrometer (EDX; ICA 300), surface profiler, X-ray diffraction and contact angle measurement for finding transparency, shape, grain size, roughness, thickness, phase and hydrophilic property, respectively.

3.4.1 UV-vis spectrophotometer

Optical transmittance of the ZnO thin films are characterized by comparison with uncoated substrate using UV-Vis spectrophotometer. 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 ratio I / I_0 is called the *transmittance* and usually expressed as a percentage (%T).

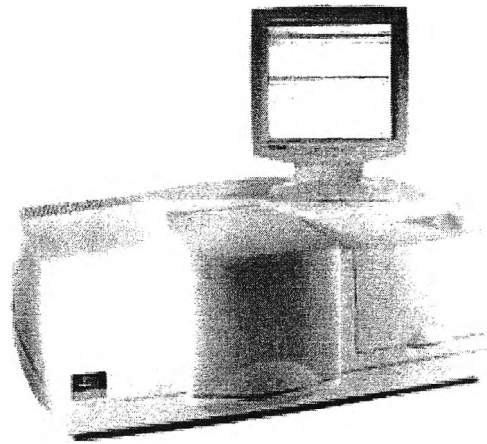


Figure 3.6 UV-Vis spectroscopy (UV-Vis)

3.4.2 Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscope (FESEM)

Scanning Electron Microscopy is used to study the morphology of ZnO thin films and Field Emission Scanning Electron Microscope is used to study the film thickness of the ZnO films with cross section view. The sample is prepared by scratching and breaking. The appropriate area of the prepared sample is placed on the stuff. The specimens are loaded into the sample chamber and then the observation was conducted immediately with using image catch scanner for taking the photos.

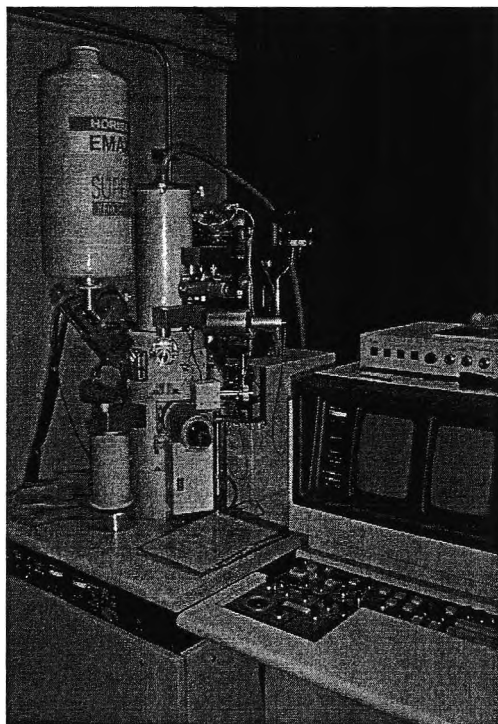


Figure 3.7 Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM)

3.4.3 Energy Dispersive X-ray spectrometer (EDX)

The energy dispersive x-ray spectrometer is employed for elemental analysis that the x-ray generated from any particular element characteristic and can be used to identify which the elements are presented under the electron probe. This is achieved by constructing an index of x-rays collected from a particular spot on the specimen surface which is known as a spectrum. EDX is usually used incorporating with scanning electron microscopy.

3.4.4 Atomic Force Microscopy (AFM)

The morphology, grain size and roughness are characterized by AFM. The sample is prepared by scratching and breaking. The appropriate area of the prepared sample is placed on the stuff. After that, a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according.

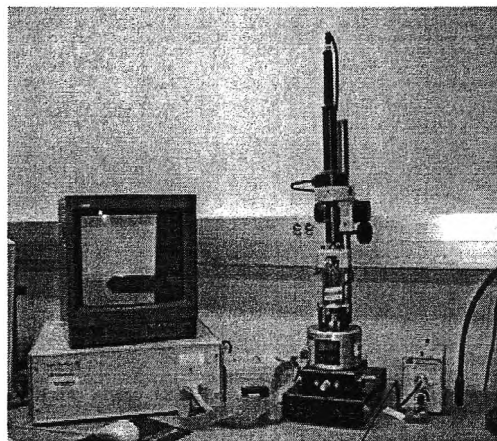


Figure 3.8 Atomic Force Microscopy (AFM)

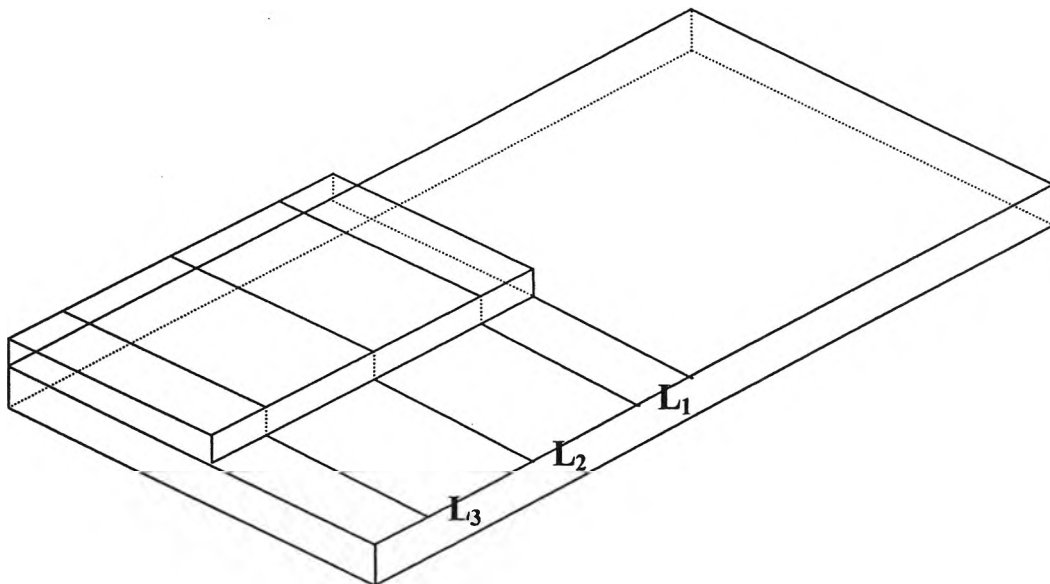
3.4.5 Surface profiler

The film thickness is measured by surface profiler as show in Figure 3.9. The samples are analyzed under a diamond tipped stylus on the scan length. The stylus can scan length of sample surface and surface variations. The data are recorded and the graphic screen display exhibits in video imaging. The film thickness is different of the glass surface and the film surface which the samples are prepared by level step of glass surface with tapping. Starting, the half of glass substrate is tapped using the plastic and coated in the solution by dip coating technique. Then the tap is stretched on the substrate and the film coated on the substrate is calcined.



Figure 3.9 Surface profiler

In the experiment, the film thickness is measured in the different positions such as top, middle and bottom that they call L_1 , L_2 and L_3 , respectively. Each position is measured in five points as shown in Figure 3.10. So the film thickness is average thickness.



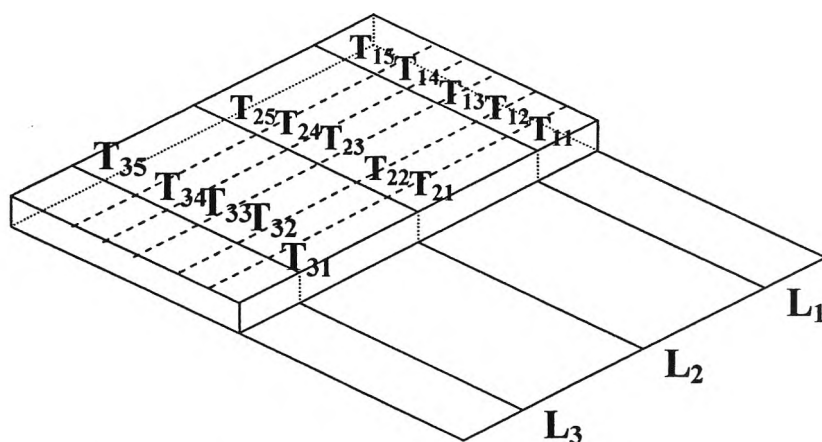


Figure 3.10 Schematic of the film thickness measurement

Average film thickness (positions):

$$T_1 = \sum_{i=1}^5 T_{1i}$$

$$T_2 = \sum_{i=1}^5 T_{2i}$$

$$T_3 = \sum_{i=1}^5 T_{3i}$$

- Where
- T_1 = average film thickness of top position
 - T_2 = average film thickness of middle position
 - T_3 = average film thickness of bottom position
 - T_{1i} = film thickness of top position ($i = 1, 2, 3, 4, 5$)
 - T_{2i} = film thickness of middle position ($i = 1, 2, 3, 4, 5$)
 - T_{3i} = film thickness of bottom position ($i = 1, 2, 3, 4, 5$)

Average film thickness (total positions):

$$T_{AVG} = \sum_{i=1}^3 \sum_{j=1}^5 T_{ij}$$

- Where
- T_{AVG} = average film thickness
 - T_{ij} = film thickness at different positions ($i=1$; top, $i=2$; middle, $i=3$; bottom) and ($j= 1, 2, 3, 4, 5$)

Standard deviation:

$$SD = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2}$$

Where x_i = film thickness at total positions
 \bar{x} = average film thickness at total positions
N = total number in experiment = 15

3.4.6 X-ray Diffraction (XRD)

The XRD is used to analyze phase of the investigated ZnO powder. Figure 3.11 shows the XRD analysis system used in this work. The ZnO powder is spread on the sample holder and then set in the equipment which provides x-ray beam for the analysis and α -Alumina is used as a standard sample to observe the instrumental broadening since its crystallite size is larger than 2000 Å.

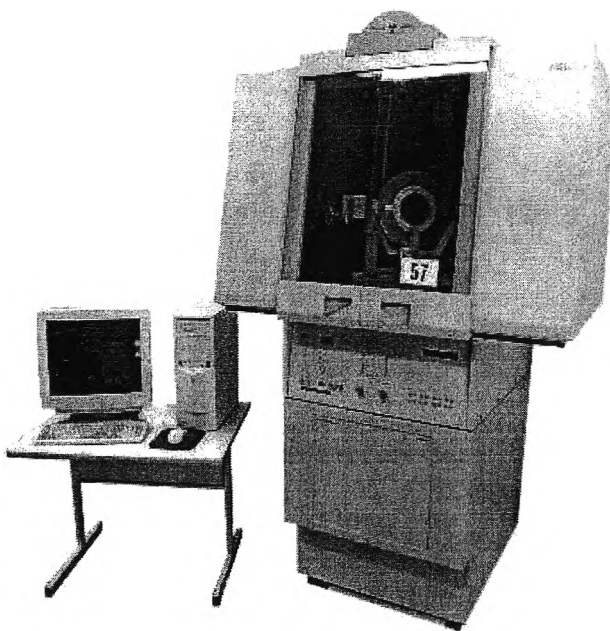


Figure 3.11 X-ray Diffraction (XRD)

3.4.7 Contact angle measurement

The hydrophilic property of the ZnO thin films is examined by measuring the contact angle of water droplets by a contact angle meter (See Figure 3.12). Water droplets with consistent volume of 12 μL are placed at five different positions on each coated substrate sample for measuring the contact angle. A UV-A lamp (SAPHIT A.J.L. Supplies, Thailand) with emission wavelength in a range of 300 – 460 nm and output of 20 watts is employed to irradiate each coated glass specimen in prior to water contact angle investigation.

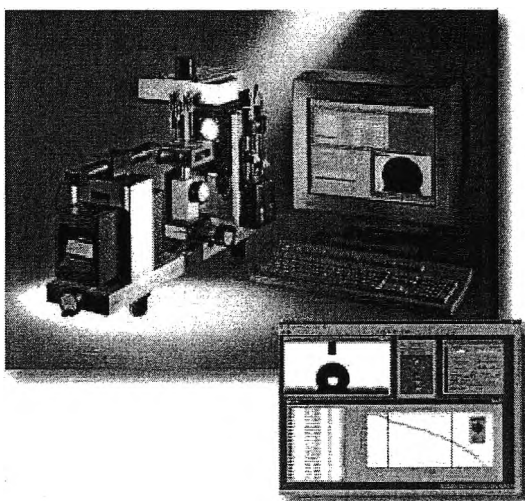


Figure 3.12 Contact angle measurement