CHAPTER II

THEORY & LITERATURE SURVEY

2.1 Principle of polyelectrolyte film construction

2.1.1 Polyelectrolyte film (PET film)

Polyelectrolyte multilayer films offer new coating opportunities [16]. This technique has been described as being theoretically able to cover many kinds of surfaces. The mechanisms allowing film coating involve essentially electrostatic interactions, but the assembly of such multilayer structures has also been shown on non-ionic or non-polar substrates. Film is constructed by the alternate adsorption of oppositely charged polyelectrolytes at the surface of material, easily obtained when the material is dipped in polyelectrolyte solutions. The driving force for film construction is the charge excess (alternatively positive and negative) that appears after each new polyelectrolyte adsorption. A deposition cycle creates a bilayer, and this cycle can be repeated as often as necessary. The number of deposition cycles and the types of polyelectrolyte used in the construction control the thickness and roughness of the multilayered film. Recently, Callewaert et al. have employed surface morphology and wetting properties of surface coated with an amphilic diblock copolymer that were polystyrene-*b* -poly(acrylic acid) (PS-PAA) for modulatating hydrophobicity-hydrophilicity switching [17]. They reported that the surface roughness decreases with increasing the PAA/PS block length ratio and it was larger for dip-coated than for spin-coated layers. Moreover, dynamic wetting reveals that the reorganization of coated layer depends on the pH of the solutions due to the deprotonation and swelling of the PAA chains. A hydrophilic surface was obtained for the large PAA block after immersion at pH 11. Self-assembled polyelectrolyte film was studied on the effect of layer number and charge of the external layer using variety of electrochemical techniques such as cyclic voltammetry and linear sweep voltammetry with rotating disc electrode [18]. The research work demonstrated that the electrochemical property of films relies on the deposition condition. It was also found that the increased number of layer films lowed to the film permeability. In application of superhydrophobic surface, a polyelectrolyte multilayer surface was used for construction of the lotus leaf structure as like the honeycomb [19]. And then, the polyelectrolyte was coated by SiO_2 nanoparticles. The surface of SiO_2 film has been hydrophobic character after modifying the surface by semifluorosilane. Moreover, the polyelectrolyte film formation plays role on the pH of polyelectrolyte solution when using ISA technique [20]. The ISA can be used to generate robust thin films in the large pH range. The 16 bilayers film exhibits transmittance of 51% at 643 nm. Zhu et al. developed smart surface using PS-PAA and characterized the film by AFM, FE-SEM and contact angle measurements to investigate the physiochemical features of the copolymer brushes [21]. The results show the surface wettability depends on PS/PAA mole ratio and the external solvent properties. Capability of hydrophilic surface can be maintained by basic solution treatment, as well as, polar solvent such as ethanol. However the surface can be reversed to hydrophobic by acidic solution or toluene because of the rearrangement or reorganization of polymer chain. In addition, surface roughness was improved by enhancing the tunable range of wettability which was done by coating with micro textured ZnO nanorods. During the past decade, the noionic and polymer type surfactant PEG has been used as templates to prepare several porous materials (TiO_2, SiO_2 and so on) due to its high chemical stability [22]. Especially, porous ZnO thin films on glass substrate was prepared by sol-gel method with PEG (Polyethylene glycol) as an organic template, zinc acetate as a precursor, ethanol as a solvent and diethnolamine as a chelating agent. Result reveals that structure of ZnO thin film exhibits hexagonal wurtzite structure. The transmittance in the visible region of the thin film was 80%. Consequently, it is interesting in both of scientific and technological standpoint for superhydrophobic surfaces and superhydrophilic surfaces. They would be applied to self-cleaning coatings. Latterly, the multilayer polymer films by LbL method (layer-by-layer self-assembly technique) was used to prepare ZnO nanoparticles embedded in multilayer polymer films [10]. The film was absorbed into zinc nitrate solutionwas absorbed and then, precipitated using ammonium hydroxide. Transmission electron microscopy study reveals that the morphologies and growth of ZnO nanoparticles were restricted by number of precipitation cycle.

2.1.2 Layer-by-layer (LbL) coating technique

Based on a simple and environmentally friendly layer-by-layer (LbL) coating technique, it affords nanoscale control over the internal architecture and extends three-dimensional molecular in a direction perpendicular to the solid support [10]. To date, various semiconductors, metallic and magnetic nanoparticles have been directly incorporated with polyelectrolyte multilayer films. Especially, the in situ synthetic method based on LbL technique can achieve particle size control and good dispersion homogeneity over the entire matrix [18-19, 23-24]. It is well known that the LbL process of polyelectrolyte multilayers can be utilized to fabricate conformal thin film coatings with controlling molecular level over film thickness and chemistry. A coating of this type is capable of any surface amenable to the water-based LbL. The adsorption process is mainly used to assemble these polyelectrolyte multilayer, including to the inside surfaces of complex object.

2.1.3 Chemical etching (or wet etching) [25]

The roughness of generated surface can be an important issue for the wet polishing and deep wet etching of channels. Improving the etching surface quality can be performed by adding HCl to the HF solution. The role of HCl is to transform the insoluble products, such as CaF_2, MgF_2 and AlF_3, into soluble ones:

$$CaF_2 \rightarrow CaCl_2,\ MgF_2 \rightarrow MgCl_2,\ AlF_3 \rightarrow AlCl_3$$

More experimental data are presented. The optimal HF (49%)/HCl (37%) ratio was found to be 10/1 for Corning 7740 as well as soda lime. Moreover, the etch rate was not much affected by the modification of the composition (a decrease of 5%). The discoveries were used for the fabrication of dielectrophoretic devices packaged at wafer level, which are presented. In many case mentioned applications, a glass wafer, which was previously bonded on a silicon structure, was chemically thinned using a wet etching process in HF/HCl (10/1) from 500 to 100 μm. In this way, mechanical lapping and polishing were replaced by wet etching. The uniformity of the etching process was under 5% while the measured roughness of the surface was 10 nm. Moreover, via-holes for metallization were performed in the 100 μm-thick glass layer with a right selection of the material and good process design. Hydrophilicity or hydrophobicity of the surface, as we previously mentioned, also plays an important role. A small defect (micro-creep) on a hydrophobic surface will be very difficult to be filled with the etching solution. Silicon surface presents a hydrophobic characteristic, and for this reason, amorphous silicon or polysilicon masks, which generally give better results, are preferred over Cr/Au mask. The hydrophilicity of the surface can be changed by retaining and hard baking the photoresist mask.

2.2 Photoinduced hydrophilic property

2.2.1 Physicochemical property of Zinc oxide (ZnO)

Zinc oxide (ZnO), a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, has high transmittance and importance semiconductor material with excellent chemical and thermal stability [2, 6, 8, 13-14]. ZnO thin film is extensively used for various applications such as pH sensors, varistors, surface acoustic wave devices, optical waveguides, solar cells, biosensors and photoinduced hydrophilic glass [26-29]. Therefore many researchers in different fields have been all interested in ZnO thin film. The wetting properties of metal oxides thin films, mainly TiO_2 and ZnO, have been widely studied, since irradiation with UV light may significantly modify their wettability. This photoinduced transition can be reversed after storage in the dark place, indicating self-cleaning characteristics [29].

Several research works demonstrated that the ZnO films were polycrystalline with hexagonal wurtzite structure. The physicochemical property of ZnO was presented in Table 2.1

Table 2.1 Physicochemical property of ZnO [15, 30]

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	-
***a,c* Lattice constants**	3.249Å, 5.201Å
Refractive index	2.0

2.2.2 Principle of photoinduced hydrophilic property

The photoinduced hydrophilic property of semiconductor metals is obtained under irradiation with a certain wavelength. A semiconductor, which is theoretically described by valance band and conduction band, includes ZnO, TiO_2, ZrO_2, Fe_2O_3, WO_3 and so on. Band gap of a semiconductor is defined as a difference between its valence band and conduction band which could be related to the wavelength of photon. A photon having higher energy than or equal to the band gap is absorbed by the semiconductor, leading to the transition of electron from valence band to conduction band. Such irradiation excites electrons ($\bar{e}$) and holes (h^+) on the surface as shown in equation 2.1-2.2.

$$ZnO + 2h\nu \rightarrow ZnO^{*}(2\bar{e} + 2h^{+}) \tag{2.1}$$

$$O^{2-} + h^{+} \rightarrow \tfrac{1}{2}\,O_{l}^{-} \tag{2.2}$$

$$O_{l}^{-} + h^{+} \rightarrow 1/2O_{2} + \text{oxygen vacancy} \tag{2.3}$$

$$Zn^{2+} + \bar{e} \rightarrow Zn^{+}\ (\text{defective site}) \tag{2.4}$$

The holes can react with lattice oxygen leading to the formation of surface oxygen vacancies that represent in the equation 2.3 while some electrons can react with lattice metal ions to form defective sites as shown in equation 2.4. Water molecules can replace these oxygen vacancies producing chemisorbed hydroxyl groups. The photoinduced hydrophilic property ZnO is known as a photosensitive semiconductor due to its photoinduced hydrophilic property.

The scientists have been generally studied mainly of TiO_2 and ZnO, because their wettability may be significantly improved by the irradiation with UV light. This photoinduced transition can be reversed after storage in the dark, indicating self-cleaning characteristics [6]. Most recent, ZnO thin film was prepared by sol–gel dip coating method using zinc acetate as a precursor and then photoinduced hydrophilic property of the coated glass substrate was investigated [2]. It was reported the ZnO thin films, prepared using ethanol as the solvent, 0.10 M zinc acetate as a precursor, withdrawal speed of 3.0 cm/min, and calcination temperature of 500°C, can exhibit transmittance of above 90% in visible region and highly hydrophilic property with the water contact angle of 5 degree after 30 min UV irradiation. However, the pH value of sol-gel may affect the size of synthesized ZnO then, Rani et al. studied the influence of pH value of the sol on the crystallite size, morphology and structure of ZnO powder. The synthesized nanocrystalline ZnO powders were prepared via sol-gel route using zinc acetate and methanol as a precursor and then adjusting the pH value of the desired solution with sodium hydroxide for dye-sensitized solar cells [31]. The pH of sols was obtained in the range of 6 to 11 since the acidic nature of the solution (≤ 6) prevents the gradually crystalline of ZnO powder at room temperature. It was found that the largest size nanocrystallite about 14 nm of ZnO powder was obtained at pH value of sol 9. And, the

XRD pattern exhibit the poor crystal quality was observed at pH value more than 9. The synthesized ZnO powders were successfully applied to be an electrode material for dye-sensitized solar cells. Li et al. studied about preparation of superhydrophobic of 2D ZnO having ordered pore arrays using solution-dipping template [8]. The morphology of the film was controlled by concentration of precursor. Hydrophilicity of the film also depends on concentration of precursor. The highest contact angle (165°) was exhibited at high precursor (1.0 M) and small sliding angle (less than 5°). It was also found that the modification of the ordered pore array film using micro or nanodevice film improved the resistance and self-cleaning properties. The surface transition from hydrophilicity to superhydrophobicity was induced by single crystalline ZnO nanorod array films (ZnO-NAFs) [8]. ZnO-NAFs were characterized by X-ray diffraction and scanning electron microscopy (SEM). The hydrophilic surface exhibited small water contact angle (9.6±0.8°) while the superhydrophobicity showed high water contact angle (156.2±1.8°). Many researchers are interested in preparation of nanocrystalline ZnO for superhydrophilic applications. The nanocrystalline ZnO thin films were fabricated by using zinc acetate as a precursor and cathodic electrodeposition as a deposition method [29]. The ZnO thin films were characterized by scanning electron microscopic (SEM), X-ray diffraction (XRD). However, the film was exposed to UV-light irradiation and keeping it in the dark storage, it was found that the surface wettability of the electrodeposited ZnO thin film reversed from hydrophobicity to super-hydrophilicity transition.

2.2.2.1 Wettability and contact angle

The wetting of rough surfaces is composed of two distinct wetting states. In the first state, water remains are suspended on the top of roughness surface while, air is enclosed underneath [4, 6, 19, 32-33]. Water drops in this *Cassie or composite* state of wetting are often easily displaced by slightly tilting substrates (superhydrophobic behavior). In the second state, liquid penetrates the surface. The consequential “penetrating” drops are less mobile due to a high contact angle (CA) hysteresis and they remain strongly pinned to a specific position. The CA of drops in this state of wetting is described using Wenzel's equation (equation 2.5)

$$\cos\theta_r = r\cos\theta_s \qquad (2.5)$$

Where θ_s is the CA on the smooth material, θ_r is the CA on the rough surface, and r is the roughness factor, i.e., the factor by which the area of rough surface is enlarged compared to that of the smooth surface.

Wenzel's model is regarding only the behavior of drops in thermodynamic equilibrium; (equation 2.5) predicts the "most stable" (Marmur) equilibrium CA for a given surface. However, on rough surfaces, the actual CA may deviate from the value predicted by Wenzel wetting. As an outcome of CA hysteresis, it is often impossible to experimentally determine Wenzel's CA for a given surface. Qualitatively, Wenzel's model predicts the following trend: with an increasing roughness, a hydrophilic surface should become more hydrophilic.

Moreover, the contact angle can be related to Young's equation [34]. The Young's equation clarify that 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 control the contact angle of the droplet.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \qquad (2.6)$$

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)

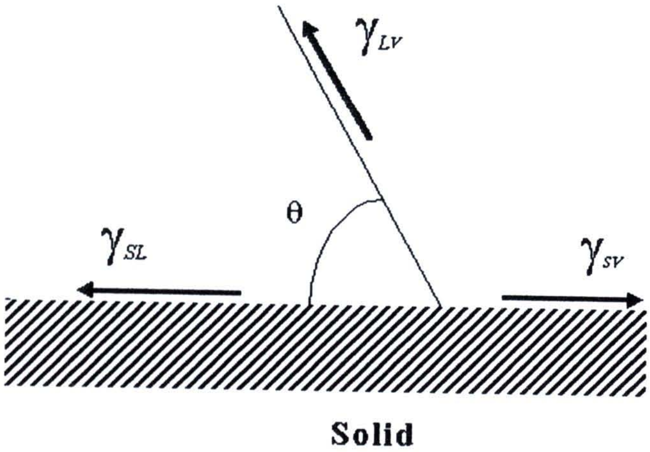


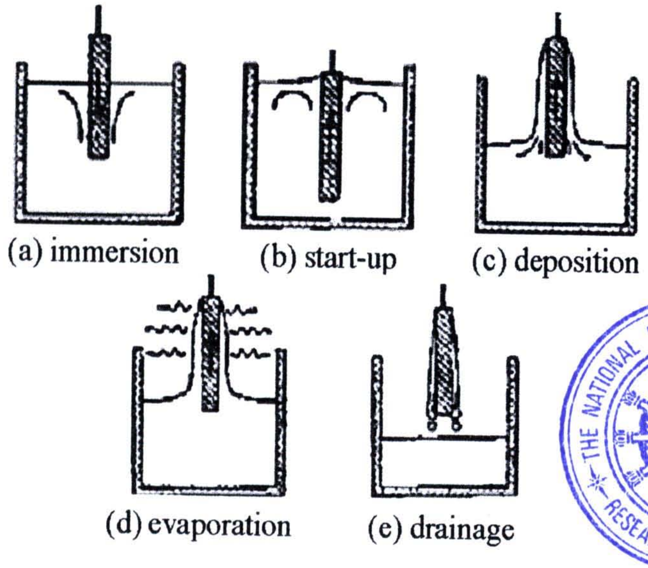
Figure 2.1 Schematic of a sessile drop on a surface [35].

2.2.2.2 Definition of hydrophilicity

In general, hydrophilic surface with a CA less than 5° can be realized through a three-dimensional or two-dimensional capillary effect on hydrophilic surface [33]. On the other hand, hydrophobic surfaces with a water contact angle (CA) greater than 150° can be obtained by controlling the topography of hydrophobic surface. In the Wenzel case, the liquid completely fills the grooves of the rough surface whereas they contact, the surface roughness dramatically enhances the CA on the hydrophobic surface but decrease the CA on the hydrophilic surface owing to the capillary effect.

2.3 Dip-coating technique for thin film fabrication

A batch dip coating process is generally divided into five steps: immersion, start-up, deposition, evaporation and drainage (See in figure 2.2) [36]. 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. After the solvent is evaporated, a uniform solid film is deposited upon the surface of the substrate. The liquid film formation is achieved by 2 major forces, i.e. gravity draining of liquid solution and evaporation of solvent.



(a) immersion (b) start-up (c) deposition

(d) evaporation (e) drainage

Figure 2.2 Fabrication stages of the dip coating process: (a) immersion,(b) start up, (c) deposition, (d) evaporation and (e) drainage [34]

A dip coating model was base purely on the hydrodynamics of a Newtonian fluid flow, ignoring solvent evaporation. This model considered a case of low viscosity of an infinite moving plate and relatively large liquid container. The liquid surface is divided into two independent regions.

(i) 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.

(ii) 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.

$$h_0 = 0.944\frac{(\eta u_0)^{(2/3)}}{\sigma^{(1/6)}(\rho g)^{(1/2)}} \tag{2.7}$$

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

Dip coating process is a simple method 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 to prepare non-planar substrate because the film thickness will not be homogeneous. And, it has to use a long time for processing and requirement of treatment of waste coating solution [34]. The process of dip coater involves immersing and withdrawal speed of substrates into a reservoir of solution (Figure 2.3).

In this thesis, an originally 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 = 3.0-9.0 cm/min, immersed time = 0.5-90.0 min, power supply = 12V.

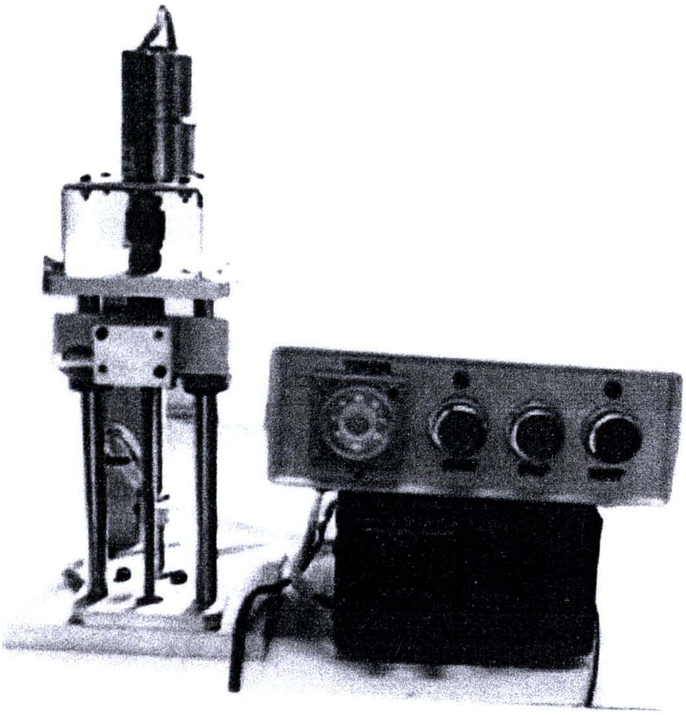


Figure 2.3 Dip coater machine (CEPT, CU)

2.4 Characterization of ZnO incorporated with PET films

PET films containing ZnO were characterized by UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU) using for optical transmittance of the films and investigation the element on the surface. The morphology of the films was also observed by Field Emission Scanning Electron Microscopy (FE-SEM; JSM7600F; JEOL). Atomic Force Microscopy (AFM; Veeco, Scanning Probe Microscopy Controller) was obtained grain size, morphology and surface roughness. And, the viscosity of polymer solutions for fabrication polyelectrolyte was measured by Rheometer (Rheostress 600; Haake). The reaction between polycation with polyanion and polymer with ZnO on the films by analyzing the chemical bonding and molecular structures were analyzed by Fourier transform infrared spectroscopy (FTIR; FT/IR6200 JASCO). In addition, Energy dispersive X-ray spectrometer (EDX-600HS; SHIMADZU) used for chemical characterization of the samples where as thickness and surface roughness were measured by confocal laser scanning microscope (CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS). To characterization the hydrophilicity of the films, they were irradiated by a certain wavelength light before obtaining by water contact angle measurement.

2.4.1 Rheometer [36]

The viscosity of polymer concentrations was measured by rheometer. It was used for those fluids having a great value of viscosity and requires more parameters to be set and measure. The samples were placed on horizontal plate and a shallow cone placed into it. The gap between the surface of the cone and the plate is 1 mm. The cone and plate rheometer were also operated in an oscillating mode in combined rotational mode to measure viscosity of polymers that represent to Eta in the unit of Pa·s. In the case of the polymer occur crosslinking, the analyzed data could show the value of G''. On the other hand, the G' would be found if the sample is not crosslinked.

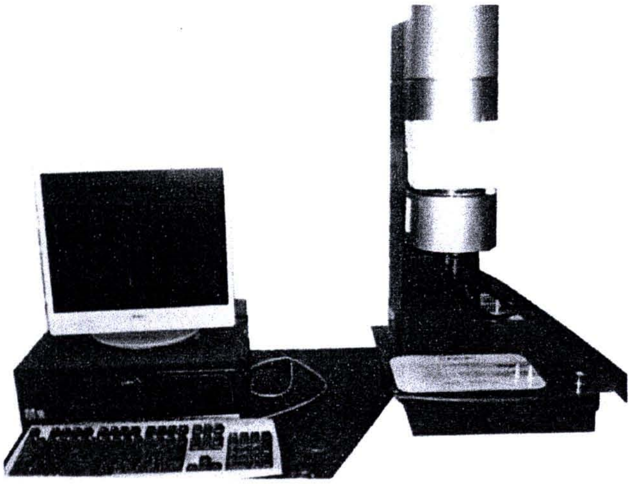


Figure 2.4 Rheometer (Rheostress 600; Haake)

2.4.2 UV - Vis spectrophotometer

The optical transmittance of PET films incorporated with ZnO was characterized by UV-Vis spectrophotometer which compared with the uncoated substrate that had already been cleaned. UV-Vis spectrophotometer measured the intensity of the light passing through a sample (I), and compared with the the incident light at a given wavelength (I_0) before it passed through the sample. The ratio of I/I0 is called the transmittance, and is usually expressed on % T. However, it relations with the absorbance that can be explained by the equation: $A = -\log(\frac{\%T}{100\%})$. The wavelengths of absorption peaks can be correlated with the optical band gap of element which is determined by the second derivative spectrum [37]. Therefore, the samples were also investigated the element on the surface by detecting the absorption band using UV-VIS spectrophotometer.

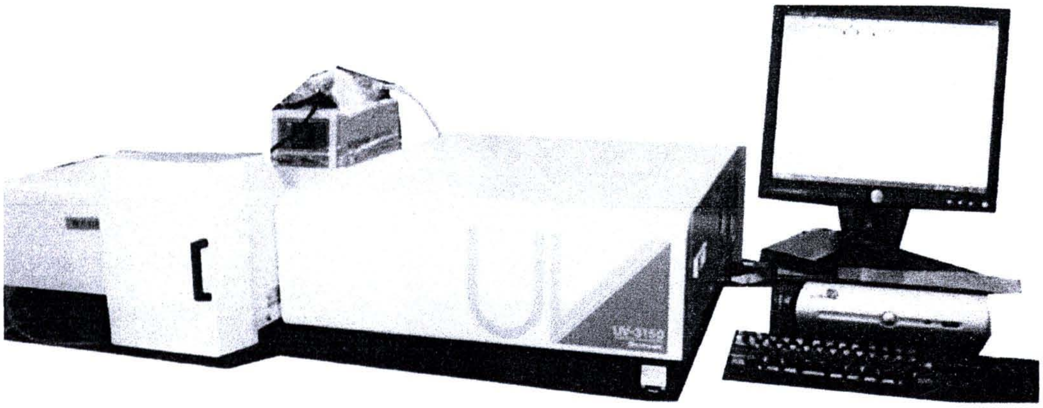


Figure 2.5 UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU)

2.4.3 Confocal Laser Scanning Microscope (CLSM or LSCM)

Film thicknesses were obtained by confocal laser scanning microscope with depth selectivity using the high resolution optical image [38]. The laser beam passed through a light source aperture and then was focused by an objective lens into a small area on the edge of film. Scattered and reflected laser light from the illuminated spot was then re-collected by the objective lens. After passing a pinhole, the light intensity was detected by a photodetection device, transforming the light signal into an electrical one that was recorded by a computer. The film thicknesses were evaluated by comparison between the light intensity of substrate and the coated area wherein, the surface roughness were considered the different of intensity of light in the each points on the surface of film.

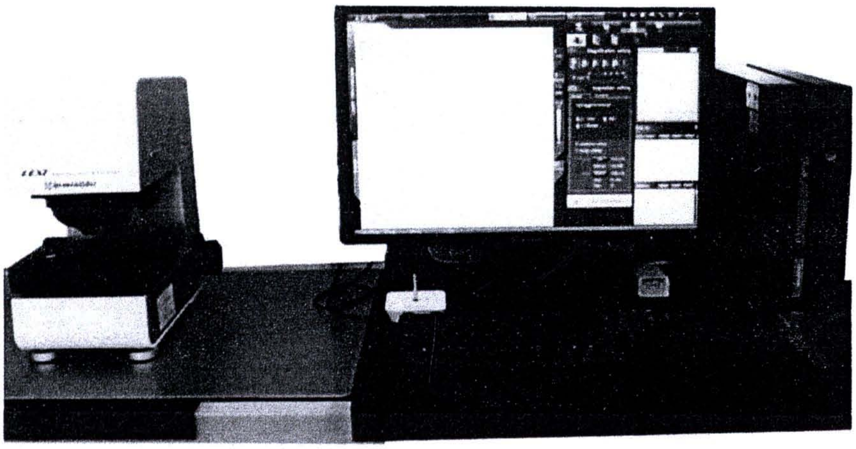


Figure 2.6 Confocal Laser Microscope
(CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS)

2.4.4 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to obtain the reaction between polycation with polyanion and polymer with ZnO on the films by analyzing the chemical bonding and molecular structures. The sample solutions were coated on the quartz SiO_2 as same as the condition to prepare the films on glass substrates. The coated samples were set on the sample holder in the nitrogen atmosphere. The samples were exposed to infrared radiation and then, they absorbed the radiation at frequencies that match their vibration modes [39]. The detector was measured the radiation absorption as a function of frequency produces a spectrum which can be considered to indentify functional groups and compounds.

Figure 2.7 Fourier transform infrared spectroscopy (FTIR; FT/IR6200 JASCO)

2.4.5 Field Emission Scanning Electron Microscope (FE-SEM)

Field Emission Scanning Electron Microscope was used for observation morphology of ZnO embedded in PET films. And, it was also used for analyzation the chemical compositions on the surface. The samples were prepared by scratching and breaking in the appropriate size to fit in the specimen chamber. They were dried in the oven at 60°C for 1 day. And then, the dried samples were coated with an ultrathin coating osmium for 10 nm that is electrically-conducting material. After that, they were placed into the sample stub and scanning by the electron beam. The signal output was observed in the standard detection mode such as secondary electron imaging or SEI and back-scattered electrons BSE or COMPO mode [40]. The SEI mode is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital conversion and saved as digital image. BSE or COMPO mode consists of high-energy electrons originating in the electron beam, which are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image. BSE were used to detect contrast between areas with different chemical compositions.

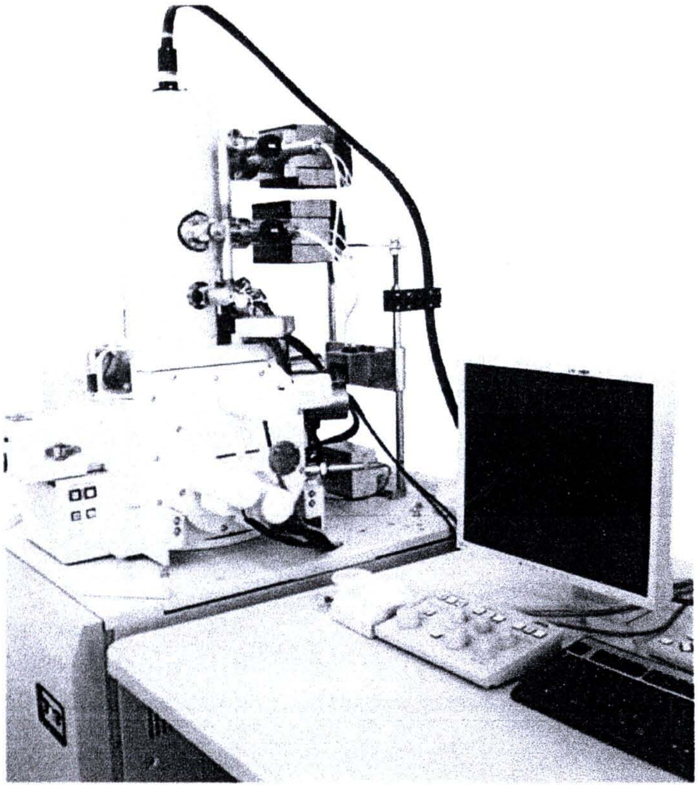


Figure 2.8 Field Emission Scanning Electron Microscope (FE-SEM; JSM7600F; JEOL)

2.4.6 Energy Dispersive X-ray spectroscopy (EDX) [41]

The elemental analysis or chemical characterization of the PET films containing ZnO was analyzed by energy dispersive X - ray spectrometer that connects with FE-SEM. The EDX systems are most typically observed on SEM image which exhibited characteristic of the particular element and indicated the element that presented under the electron probe. This is achieved by creative index of X-rays that collected from a particular spot on the specimen surface which is known as a spectrum.

2.4.7 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) was used for observation the morphology, grain size and roughness of the ZnO embedded in the PET films. The samples were scratched and broken at the suitable area and then, placed on the stub. And then, the microscale cantilever with a sharp tip (probe) at its end used to scan the surface of sample. A tip was used for closeness of the surface; forces between the tip and the sample keep on a deflection of the cantilever.

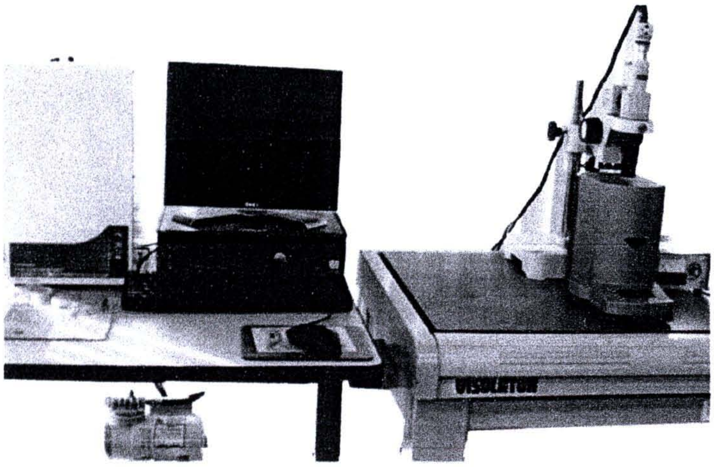


Figure 2.9 Atomic Force Microscopy
(AFM; Veeco, Scanning Probe Microscopy Controller)

2.4.8 Contact angle measurement

The hydrophilic property of PET films containing ZnO was analyzed by water contact angle using water drop 2 μL on the different five points underlying coated substrate sample. The samples were irradiated by using the UV-A lamp (SAPHIT A.J.L. Supplies, Thailand) with emission wavelength in a range of 300-460 nm and output of 20 watts for a different certain time before classification their property by water contact angle measurement.

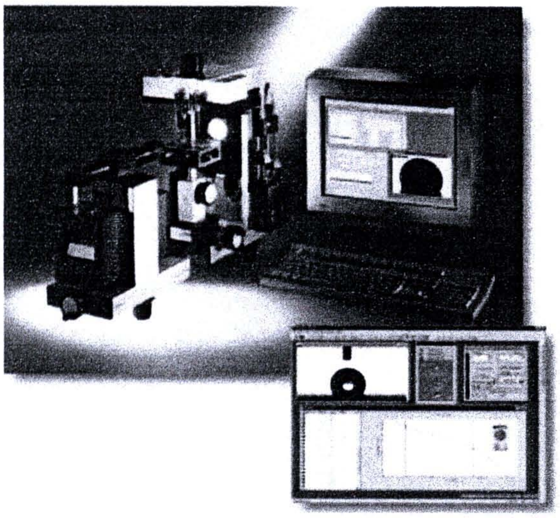


Figure 2.10 Contact angle measurement