CHAPTER FOUR

EXPERIMENT METHODOLOGY

4.1 Materials

4.1.1 Diamines

2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (BAO) obtained from Fluka and 4,4'-diaminodiphenylether (ODA, 98%) obtained from Aldrich Chemical Co. are vacuum-dried for 3 hours at 110℃ prior to use.

4.1.2 Dianhydrides

4,4´-oxydiphthalic anhydride (ODPA) and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) from TCI are purified by recrystallization from a high purity acetic anhydride and then dried in a vacuum oven at 120℃ for at least 14 hours. Pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) are obtained from TCI and Lancaster, respectively and used as received.

4.1.3 Solvents

N,N-dimethylformamide (DMF) from TCI is dried over molecular sieves. Dimethyl sulfoxide (DMSO) and 1-methyl-2-pyrrolidinone (NMP) are obtained from Aldrich Chemical Co. and stored over molecular sieves prior to use.

4.1.4 Additives

The titania additive is tetraethyl orthotitanate or named titanium ethoxide ($Ti(OEt)_4$), obtained from TCI. Other additive includes acetylacetone (acac) is available from Fluka.

4.2 Synthesis Procedures

The synthesis of the PI/TiO_2 hybrid films is carried out according to the Figure 4.1. Poly(amic acid) (PAA) solutions are made by reacting equal molar amounts of diamine and dianhydride in solution (15% solid content (w/w) for ODPA/BAO in DMF; 15% s.c. for PMDA/ODA in DMSO; 15% s.c. for BPDA/ODA in NMP; 22% s.c. for BTDA/ODA in NMP) under a nitrogen atmosphere. Dianhydride is added into the solution by five portions and it is better to ensure the complete dissolution of the prior portion before adding a fresh portion. After the dissolution of dianhydride, the PAA solution is further stirred for 2 hours at ambient temperature. After this period, the desired amounts of $Ti(OEt)_4$ and acac are completely mixed and added dropwise into the PAA solution with vigorously stirring to avoid local inhomogeneity. The mixing is proceeded with continuous stirring for another 12 hours.

The theoretically calculated content of TiO_2 in the hybrid films is under an assumption that all the $Ti(OEt)_4$ and PAA precursors are converted to TiO_2 and PI completely and there is no residual solvent after imidization process. The molar ratio of $Ti(OEt)_4$ to acac is fixed at 1 : 4. The theoretically calculated content of TiO_2 in the hybrid films is ranging from 1 wt% to 40 wt% in this study.

The freestanding hybrid films are made by casting the precursor sol onto a dust free glass plate with a doctor blade. The gel films are then cured in an air-circulating oven at the curing steps of 100℃ (1 h), 150℃ (1 h), 200℃ (1 h) and 300℃ (10 h). Upon cooling, the hybrid films are removed from the glass plate using a razor blade to lift off the hybrid films. Consequently, the PI/TiO_2 hybrid films have an average final thickness of 35 ~ 40 μm.

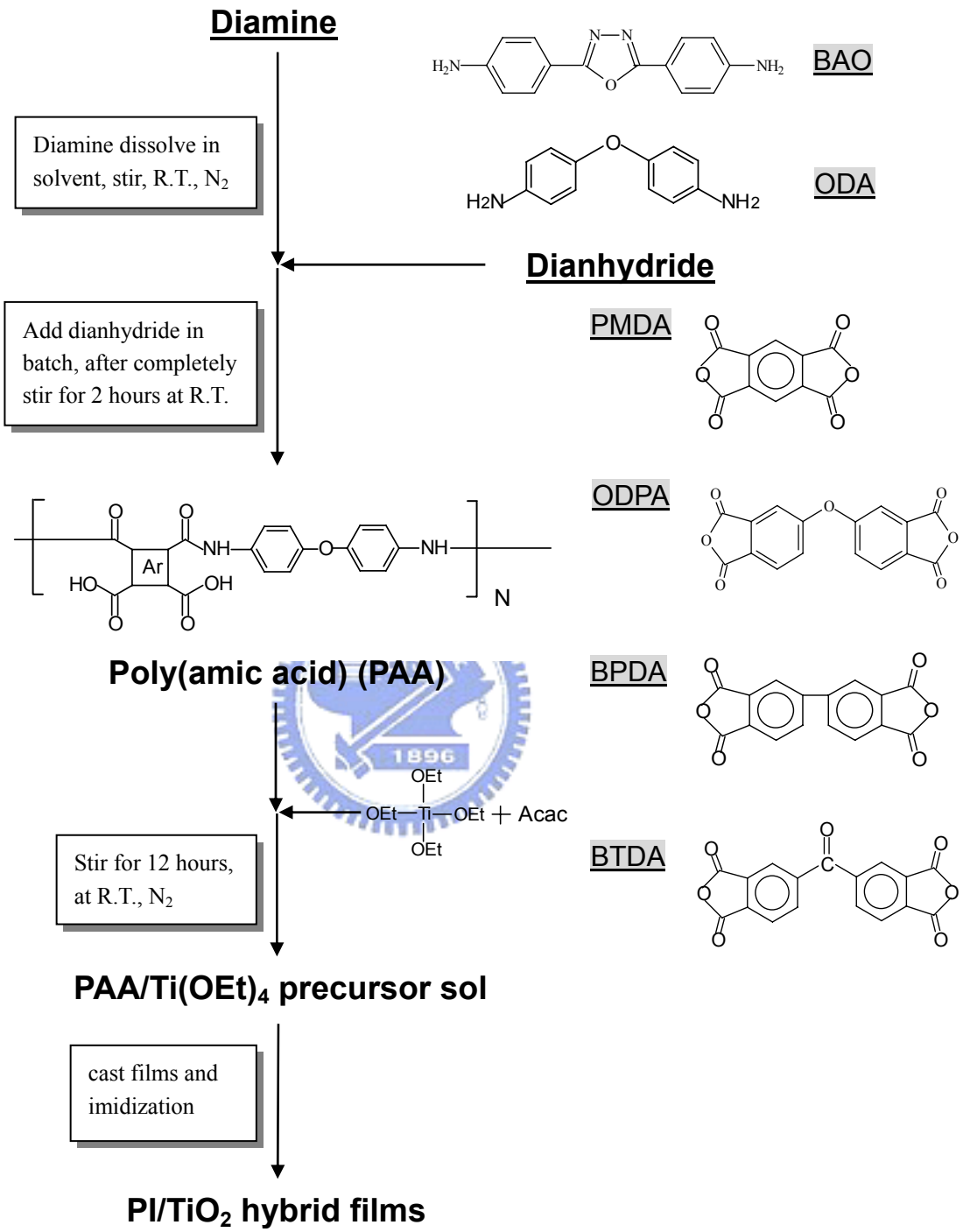

Figure 4.1 The flow chart of the procedures to prepare the PI/TiO_2 hybrid films.

4.3 Metallization Process

Metallization processes are sequentially proceeded with the following steps (Figure 4.2). First, the PI/TiO_2 hybrid film is dried in an oven at 250℃ for 2 hours to remove water absorbed by the film. Second, four conditions of plasma treatments by radio-frequency (RF) generator are used to pre-activate the PI/TiO_2 hybrid films surface before deposition of copper. They are:

1. No plasma treatment.
2. Only Ar plasma treatment.
3. N_2 plasma treatment is followed after Ar plasma-treated
4. O_2 plasma treatment is followed after Ar plasma-treated.

For the sake of brief notation, the Ar, Ar/N_2 and Ar/O_2 represent each condition of the plasma treatments used in this paper. The plasma is controlled by three parameters: a power of RF generator at 250 W, a system pressure of 20 mTorr and a treatment time of 180 sec in each step of plasma treatment. The flow rates of Ar, N_2 and O_2 are 50, 80, and 80 sccm/min, respectively.

After plasma treatment, 400 nm thickness of copper is deposited by Ar in sputtering system with a DC power of 1600 W for 600 sec without breaking the vacuum. The base pressure is below 10^{-6} Torr and the pressure during Cu sputtering is maintained at 20 mTorr. In this study, Ar is employed in the sputtering system due to its inertness, larger ion mass and high sputtering yield. Finally, in order to measure the adhesion of the samples by using a 90° peel test method (Model HT-8116 Hung TA), 30 μm thick copper is electroplated and strips of 10 × 80 mm^2 are made.

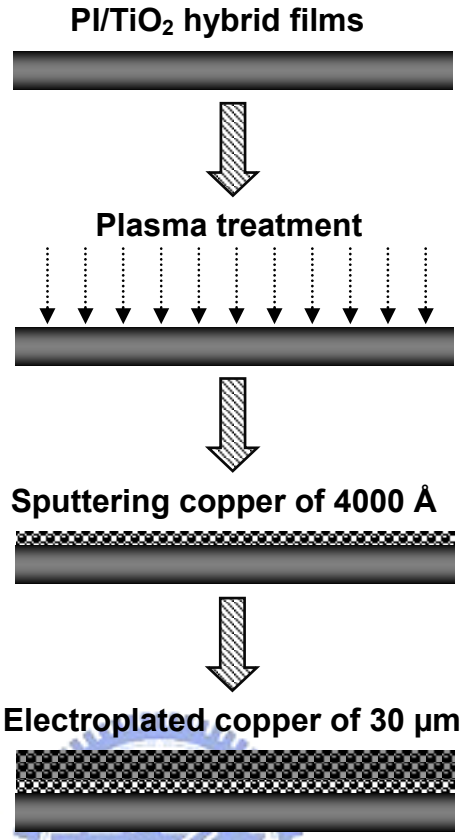

Figure 4.2 The metallization processes of PI/TiO_2 hybrid films.

4.4 Measurements

4.4.1 FT-IR and UV Analyses

FT-IR absorption spectra are recorded between 4000 and 400 cm^{-1} by Nicolet PROTÉGÉ-460. UV-visible absorbance spectra are collected on an Agilent 8453 spectrometer. For UV-visible analysis, the samples are spin-coated on quartz glass and heated. The thickness of PI/TiO_2 hybrid films are about 1000 Å.

4.4.2 X-ray Analysis

X-ray diffraction analysis is done by using a MacScience MXP model X-ray diffractometer. The equipment is operated with Cu-Kα radiation, operating at 50 KV, 100 mA, and a scanning speed of 4 degree min^{-1} at step of 0.02 °.

4.4.3 X-ray Photoelectron Spectroscopy (XPS/ESCA) Analysis

XPS spectra are obtained by using a ESCA PHI 1600 spectrometer working in the constant analyzer energy mode with a pass energy of 50 eV and Mg Kα (1253.6 eV) radiation as the excitation source. XPS analysis is done at room temperature and pressures below 10^{-10} torr. The take-off angle used in the XPS measurements is 90º.

4.4.4 Transmission Electron Microscope (TEM) Analysis

TEM is performed by employing a JEOL-200 FX transmission electron microscope. The samples for TEM study are first prepared by putting PI/TiO_2 hybrid films into epoxy capsules and curing the epoxy at 70 ℃ for 24 hours in vacuum. The samples are then microtomed with Leica Ultracut Uct into 90nm thick slices on which a 3 nm thick carbon layer is deposited after the slices are moved to a TEM copper grid.

4.4.5 Atomic Force Microscope (AFM) Analysis

The surface morphology change of PI/TiO_2 hybrid film after plasma treatment is analyzed by atomic force microscope (AFM) of Digital Instrument NS3a controller with D3100 stage. In each case, a certain area of 1 μm × 1μm is scanned by tapping mode.

4.4.6 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscope (SEM) is used to observe the peeled-off surface of polymer side. The apparatus used is JEOL JSM-6500F and specimens are pre-coated with a thin layer of gold (Au) to eliminate electron charging effect.

4.4.7 Mechanical Properties Analysis

The dynamic mechanical analysis (DMA) is carried out from 50℃ to 450℃ with a Du Pont DMA 2980 at a frequency of 1 Hz and heating rate of 2 ℃/min.

4.4.8 Thermal Expansion Analysis

The coefficients of thermal expansion (CTE) measurement of the hybrid films are carried out by using a Du Pont TMA 2940 at a heating rate of 10 ℃/min from 30 ℃ to 450℃. The CTE of PI/TiO_2 hybrid films are determined over a range of 50-200℃.

4.4.9 Thermal Stability Analysis

Thermal analyses of the PI/TiO_2 hybrid films are performed by a TA TGA 2950. The measurements are carried out under nitrogen with a heating rate of 20℃/min from 30℃ to 800℃. The polymer decomposition temperature (T_d) is determined at the temperature of 5 % weight loss.

4.4.10 Electrical Properties Analyses

The dielectric constants are measured by the Agilent 4294A at 1 MHz frequency after coating gold on both hybrid film surfaces with 300 Å thick and 5.5 mm diameter. The dielectric constant (k) can be calculated from the following formula $k = Cd/A\varepsilon_0$, where C, d, A, and ε_0 represent the observed capacitance; film thickness; gold area and free permittivity, respectively. Surface and volume resistivities are measured by employing an Agilent 4339B at voltage of 500 V.

4.4.11 Surface Energy Analysis

Surface energy is measured and calculated by Dynamic Contact Angle Analyzer FTA-200 from a contact angle test using two standard liquids: H_2O and CH_2I_2.

4.4.12 Measurement of Peel Strength

The peel strength between the PI/TiO_2 hybrid film and copper is measured by using 90° peel test method (Model HT-8116 Hung TA). The equipment of peel test is shown in Figure 3.3. The peel rate is 50.8 cm/min and the experimental value is obtained from the average of at least four measurements are performed.

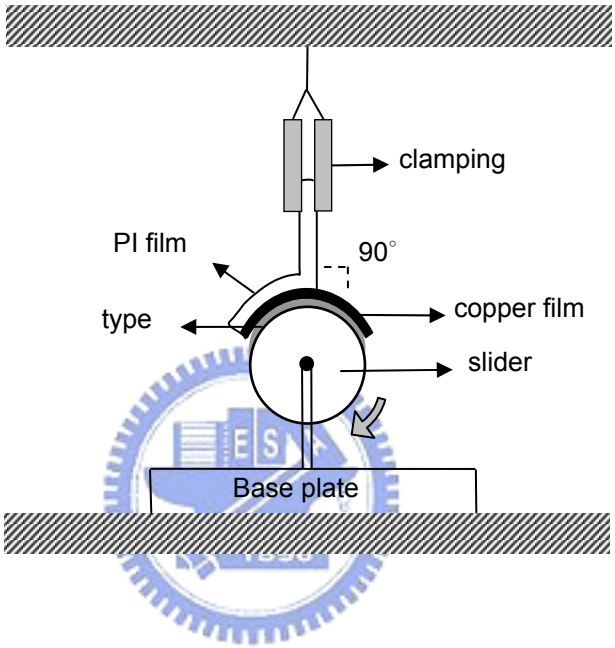

Figure 4.3 Schematic diagram of peel test.