CHAPTER III

EXPERIMENTAL

3.1 Materials

The specifications of chemical agents and materials for used in this research are shown in Table 3.1.

Table 3.1 Chemical agents and material list.

Chemical agent and Material	Manufacture / Grade
Commercialized polyimide film (PMDA-ODA)	Kapton Dupont / Kapton 100-HN
Potassium hydroxide (KOH)	Ajax Finechem / analytical grade
Silver nitrate ($AgNO_3$)	Ajax Finechem / analytical grade
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	Ajax Finechem / analytical grade
Potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$)	Ajax Finechem / analytical grade
Formaldehyde (HCOH)	Ajax Finechem / (38 wt %)

3.2 Experiment procedure

3.2.1 Surface modification

The polyimide film (2.5 x 2.5 cm) was immersed in 2 M an aqueous solution KOH at 60°C for 1 min in order to cleave imide ring in PI surface to form carboxylic

acid groups (PAA) (see in Figure 3.1). Then it was rinsed with deionized (DI) water to remove the remaining KOH solution from PI surface.

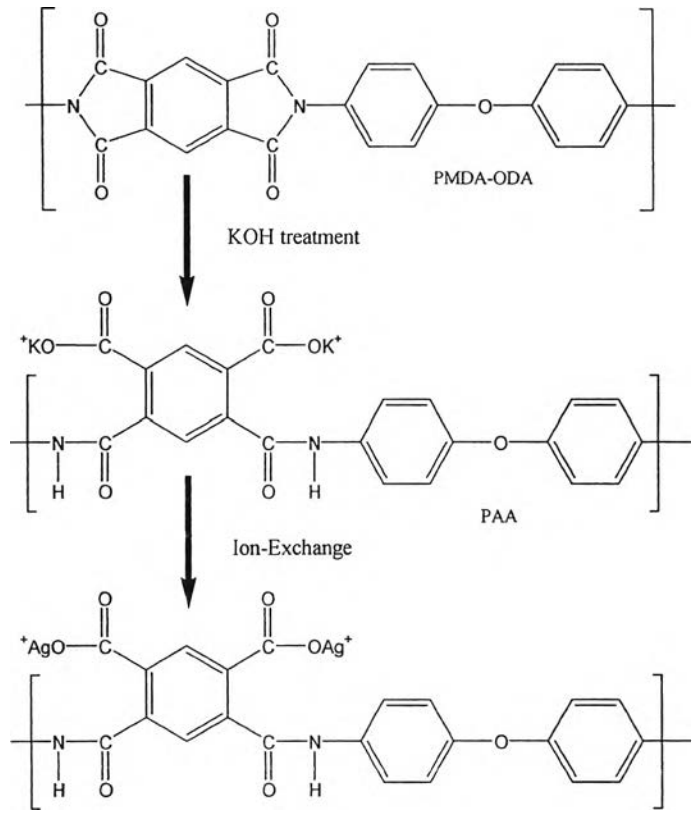

Figure 3.1 Surface modification of PI with KOH and $AgNO_3$.

The modified PI films were immersed in an 0.01 M aqueous solution of $AgNO_3$ at room temperature for 5 min. The Ag^+ doping into polyimide film could be achieved by ion-exchange with K^+ on the modified PI surface (see in Figure 3.1). Then, it was rinsed with deionized (DI) water to remove excess amount of Ag^+.

3.2.2 UV irradiation

After the surface of PI films was modified to dope with Ag^+, metallic silver (Ag^0) was formed by irradiation with ultraviolet light for various periods of times in air at room temperature, using 2 of ultraviolet lamps (main wavelength of 215 nm). The ultraviolet lamps were put approximately at a distance of 3 cm above the film surface (see in Figure 3.2). In this study 3 procedures of ultraviolet irradiation were investigated, i.e. (i) conventional irradiation. (ii) water-assisted irradiation and (iii) cycle irradiation.

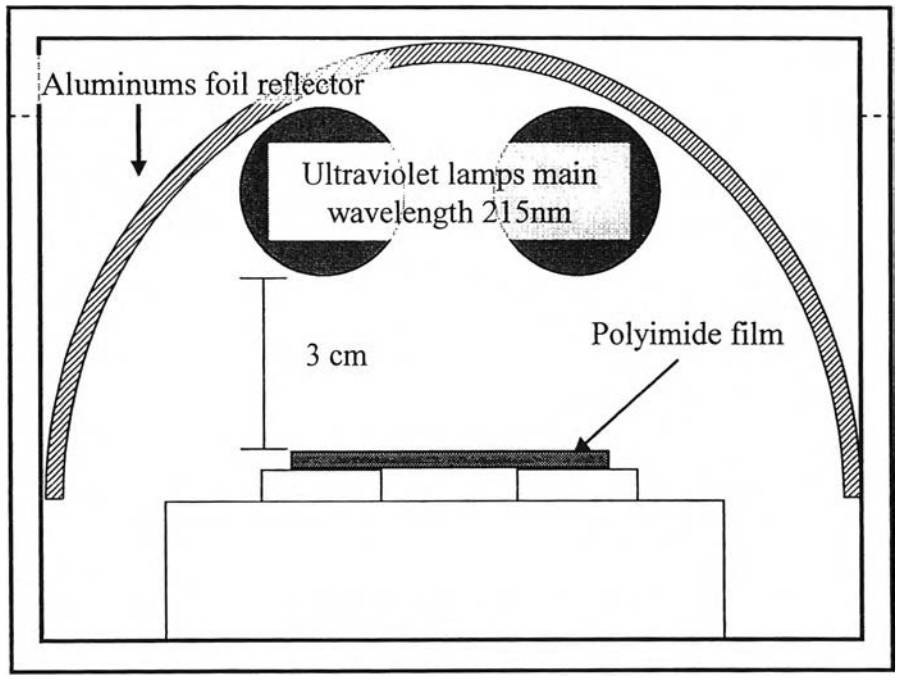

Figure 3.2 Ultraviolet irradiation chamber.

3.2.2.1 Conventional irradiation

The modified polyimide film was reduced by ultraviolet irradiation in a straight forward fashion for 30, 60, 90, 120, 180, 360 and 900 minutes, respectively.

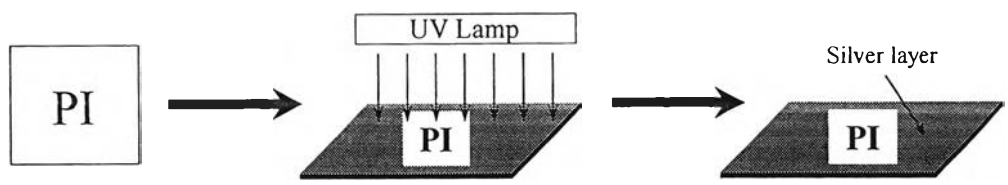

Figure 3.3 Process scheme of conventional irradiation.

3.2.2.2 Water-assisted irradiation

Modified PI films was reduced by ultraviolet irradiation, while 0.1 ml of distilled water was dropped onto polyimide film surface or sprayed to cover the whole area of PI surface after irradiation for 30, 60 and 90 minutes and brought back to irradiation to complete 3 hours (see in Figure 3.4).

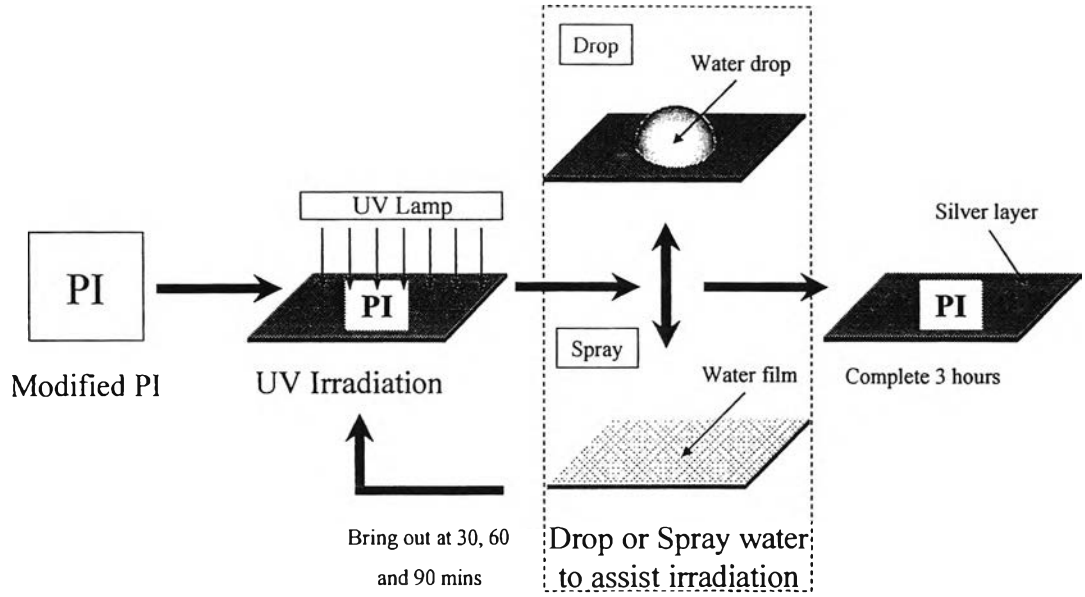

Figure 3.4 Process scheme of water-assisted irradiation.

3.2.2.3 Cycle Irradiation

The modified polyimide film was reduced by ultraviolet irradiation in step-wised fashion. After the normal irradiation process for certain period of time, the irradiated polyimide film was brought out of the ultraviolet light and immersed in an aqueous solution of KOH (2 M) for 1 minute, followed by rinsing with deionized (DI) water. After that, the modified polyimide film was immersed in an aqueous solution of $AgNO_3$ (0.01 M) at room temperature for 5 min. The ion-exchange between Ag^+ and K^+ on the modified PI surface will take place according to Figure 3.1. Then, the polyimide film was rinsed with deionized water and brought back to ultraviolet irradiation again (see Figure 3.5). In this section, 3 cycles was used. However, the total irradiation time was kept at 3 hours.

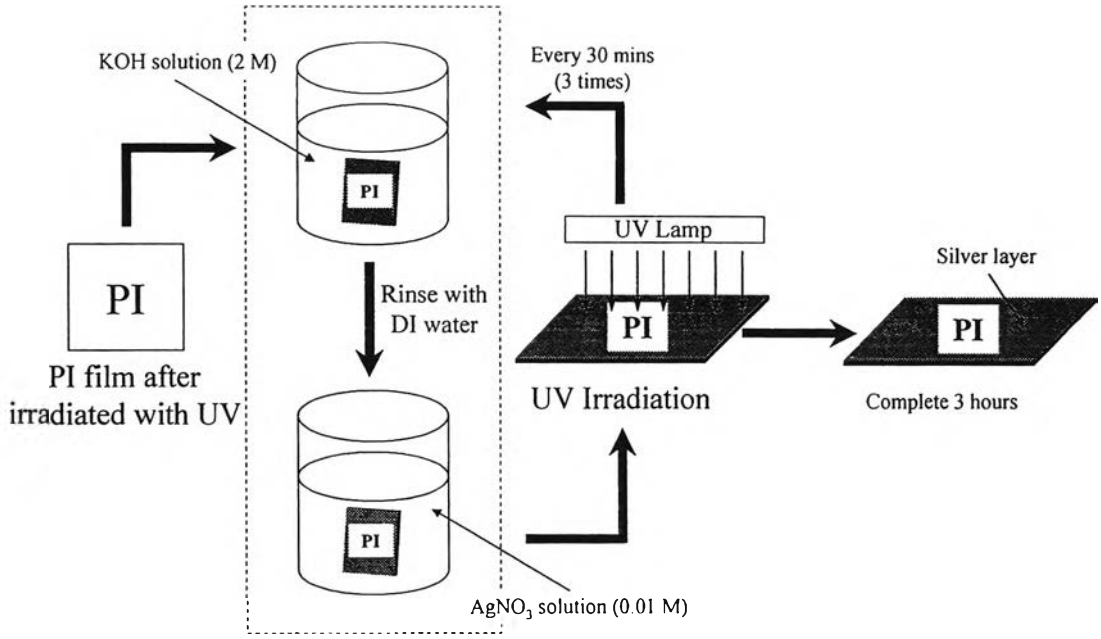

Figure 3.5 Process scheme of cycle irradiation.

3.2.3 Heat treatment

After ultraviolet irradiation, silver layer was formed on polyimide film surface. In order to increase thickness of the silver layer, the polyimide film was subsequently annealed at 200 °C for 2 hours using hotplate (see Figure 3.6). The temperature was hold at 100 °C for an hour before rising to 200 °C.

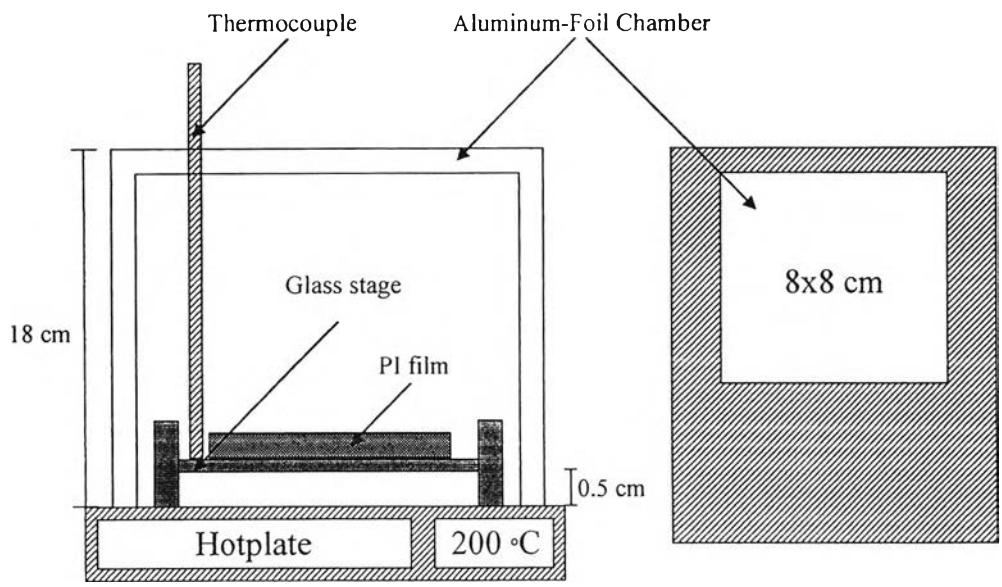

Figure 3.6 Heating chamber.

3.3 Reduction with sodiumborohydride ($NaBH_4$)

After the surface of PI films was modified and doped with Ag^+, metallic silver (Ag^0) was formed by immersed in an aqueous solution of $NaBH_4$ (0.01 M) for 20 seconds.

3.4 Copper electroless plating

A solution for copper electroless plating bath is consisted of components shown in Table 3.2.

Table 3.2 Chemical agent for electroless plating bath solution.

Chemical agent	Amount
Potassium hydroxide (KOH)	11.22 g/L
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	12.484 g/L
Potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$)	6 g/L
Formaldehyde (HCOH)	12.8 ml/L

The electroless solution was ultra-sonicated for 20 minutes. The metalized polyimide film was then immersed in the electroless plating bath at 60°C for 1 hours. After that, it was rinsed with deionized water and dried at 100 °C for 1 hour in air.

3.5 Characterizations

3.5.1 X-ray Diffraction Analysis (XRD)

Crystalline phases of the product were determined from X-ray diffraction analysis, using a SIEMENS D5000 diffractometer with CuKα radiation. Each sample was scanned in the range of 2θ = 10-50° with a step size of 2θ = 0.02°.

3.5.2 Attenuated Total Reflection Fourier transform Infrared Spectroscopy (ATR-FTIR)

The functional groups in the samples were determined by using a Nicolet 6700 infrared spectrometer. The spectra were recorded at wavenumber between 400 and 4000 cm^{-1} with resolution of 4 cm^{-1}. The number of scan for the measurement was set at 64.

3.5.3 Scanning Electron Microscopy (SEM)

Morphology of the coated film was examined by using a scanning electron microscope (Hitachi S3400), operating in SE mode with aperture number 3 and acceleration voltage of 15 kV.

3.5.4 Transmission Electron Microscopy (TEM)

Thickness of metallic silver layer was observed on a JEOL JEM-2100 Analytical Transmission Electron Microscope, operated at 80-200 keV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The crystallographic information was also obtained from the selected area electron diffraction (SAED) analysis performed in the same instrument.

3.5.5 UV/Visible Light Spectroscopy (UV/VIS)

Absorption and transmission of light through the polyimide film were monitored by UV/VIS (PerkinElmer Lambda 650). The spectra were recorded at wavenumber in the range of 400-800 cm^{-1}, a mask with 1x1 cm opening was used to cover the polyimide film sample.