CHAPTER III

EXPERIMENTAL

3.1 Materials, Equipments and Instruments

3.1.1 Materials

1. Stainless steel grad 316L
2. Palladium (II) chloride ($PdCl_2$), 99.9% from Alfa Aesar
3. Tetra ammine palladium (II) chloride monohydrate ($Pd(NH_3)_4Cl_2 \cdot H2O$, 98%) from Alfa Aesar
4. Tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$), 98% from Carlo Erba
5. Hydrazine anhydrous (N_2H_4), 99.5% from Aldrich
6. Hydrazine hydrate ($N_2H_4.H_2O$), 99.5% from BDH chemical
7. Disodium ethylenediaminetetraacetrate (Na_2EDTA), 99.5% from Carlo Erba
8. Sodium carbonate, Na_2CO_3
9. Sodium hydroxide NaOH
10. Trichloroethylene, C_2HCl_3
11. Iso-propanol, C_3H_7OH
12. acetone
13. Quartz wool from Alltech
14. Argon gas, 99.999% from Thailand Industrial Gas Co., Ltd
15. Nitrogen gas
16. Cr-Target for sputtering technique.

3.1.2 Equipments

1. Furnace reactor
2. Digital flow meter from Altech
3. Flow meter
4. Plasma sputtering chamber

3.1.3 Instruments

1. Scanning electron microscope (SEM), JEOL model JSM-5800LV with Energy Dispersive Spectrometer (EDS)
2. X-ray photoelectron spectroscopy, XPS

3.2 Experimental Procedures

The experimental procedures were divided into 5 parts:

1. Preparation of stainless steel supports
2. Preparations of intermetallic diffusion barriers
3. Electroless plating of palladium membranes
4. Evaluations of the efficiencies in reducing intermetallic diffusion of the barriers
5. Surface characterizations of the palladium membrane

3.2.1 Preparation of stainless steel supports

100-cm^2 sheets of stainless steel were cut into 1-cm^2 specimen and drilled at one corner. The general procedure for metal plating was shown in Figure 3.1.

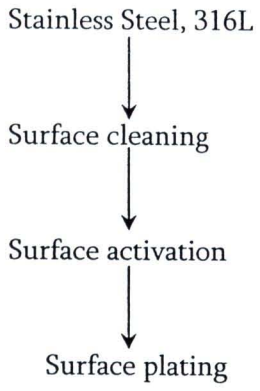

Figure 3.1 General procedure for preparation of the stainless steel supports.

The surface of the stainless steel supports was cleaned prior to activation to remove contaminants such as oil, grease and dirt. The supports were washed either with an alkaline solution if electroplating deposition was subsequently performed or with commercial solvents if plasma sputtering was subsequently performed.

a) Surface cleaning with an alkaline solution.
The supports were immersed in an ultrasonic bath of the solution at ~60°C for one hour and then washed thoroughly three times with deionized water in an ultrasonic bath. Finally, the supports were soaked in iso-propanol to remove any trace amount of water and dried at 100°C for 3 hours. The chemical composition of the alkaline solution is given in Table 3.1.

Table 3.1 Composition of the alkaline solution for cleaning the stainless steel supports.

Compound	Concentration
Sodium phosphate, $Na_3PO_4 \cdot 12H_2O$	45 g/l
Sodium carbonate, Na_2CO_3	65 g/l
Sodium hydroxide, NaOH	45 g/l
Detergent	5 ml/l

b) Surface cleaning with commercial solvents.

Cleaning with commercial solvents was a successive immersion of the supports in three different commercial solvents followed by a rinse in deionized water as given in Figure 3.2. The support was soaked for 5 minutes in each bath containing ~25 ml of solvent. A thoroughly cleaning requires the steps to be repeated four times.

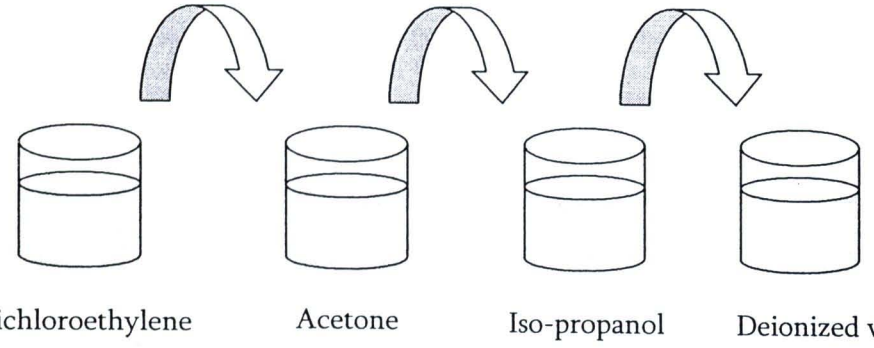

Figure 3.2 One loop of stainless steel cleaning with commercial solvent.

3.2.2 Preparations of intermetallic diffusion barriers

Three techniques were employed in preparing the diffusion barrier:

3.2.2.1 Thermal oxidation,

3.2.2.2 Electroplating followed by thermal oxidation, and

3.2.2.3 Plasma sputtering with or without thermal oxidation.

3.2.2.1 Thermal oxidation [22]

The cleaned support was oxidized at 600°C for 6 hours with heating rate 4°C/min in air in muffle furnace. (Appropriate temperature and time were determined by preliminary XPS study.) The oxidized stainless steel was then weighed and activated.

3.2.2.2 Electroplating/oxidation

The electroplating device setting is depicted in Figure 3.3. The chromium plating solution consisted of 250 g/l chromic acid and 1.25 g/l sulfuric acid as a catalyst in 200:1 ratio. The chromium plating was performed at room temperature with current density ~100-150 A/ft^2.

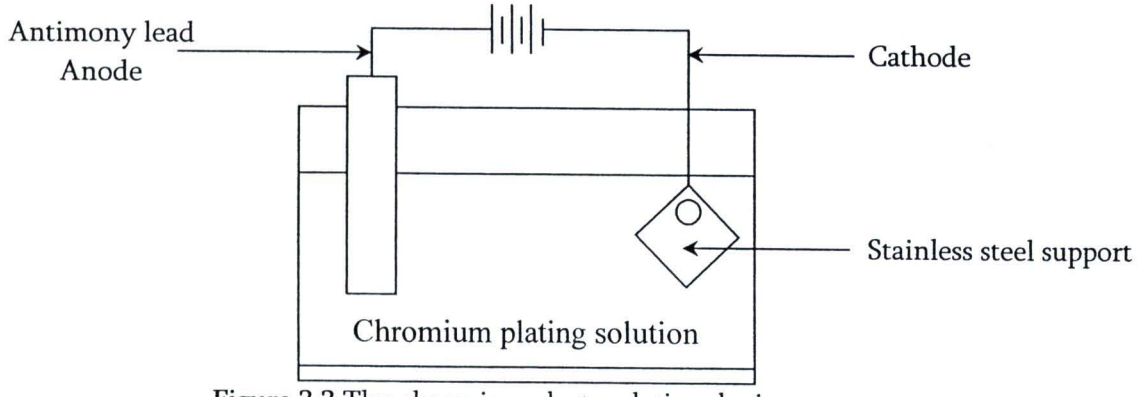

Figure 3.3 The chromium electroplating device.

3.2.2.3 Sputtering

This technique involves bombarding a target with energetic particles that cause surface atoms to be ejected and then deposited on a substrate close to the target [23]. Substrates are placed into the vacuum chamber, and are pumped down to their process pressure. Sputtering starts when a negative charge is applied to the target material (material to be deposited), causing a plasma or glow discharge. The configuration of such an instrument is depicted in Figure 3.4.

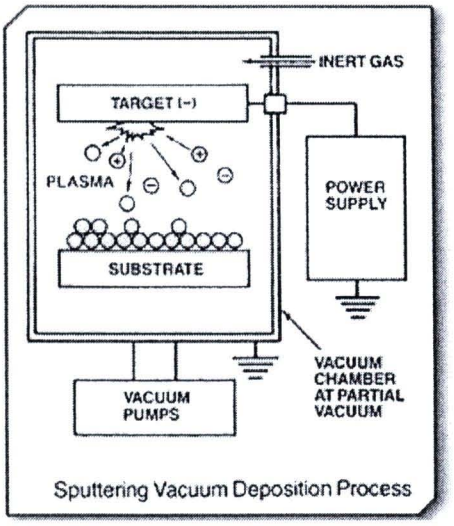

Figure 3.4 Sputtering instrument setting

Two Cr-based diffusion barriers were formed by sputtering as diagramed in Figure 3.5:

(a) sputtering of pure chromium metal in argon atmosphere followed by oxidation at 600°C for ~6 hours,

(b) sputtering of pure chromium metal in nitrogen atmosphere without oxidation.

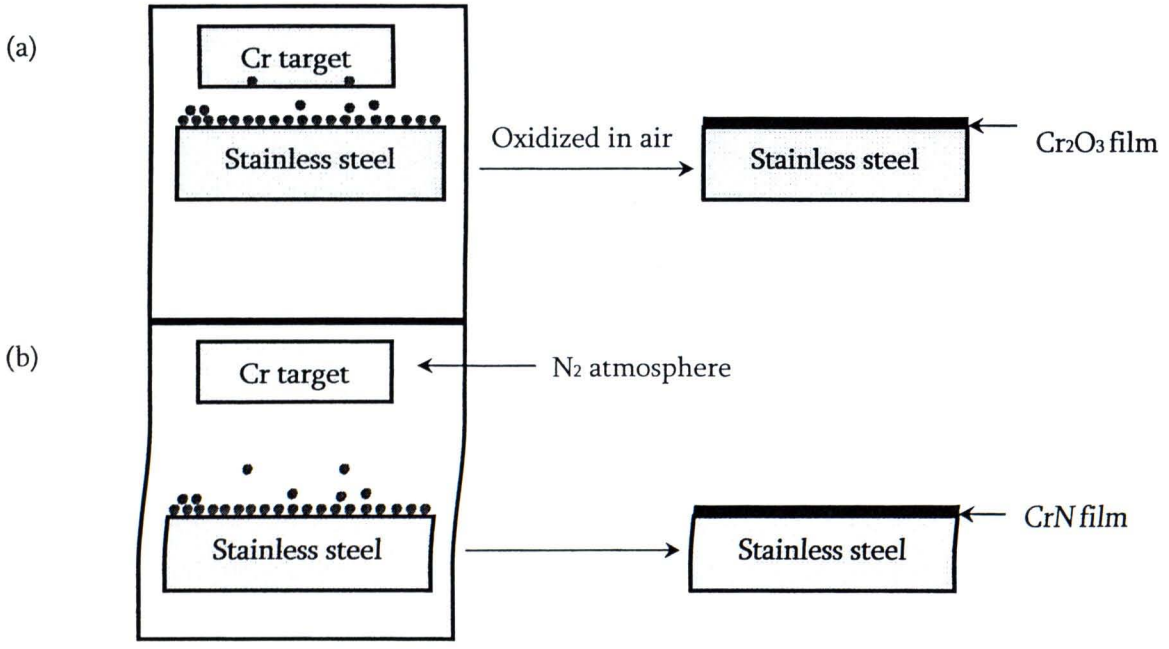

Figure 3.5 Two intermetallic diffusion barriers formed on stainless steel by sputtering.

All the sputtered filmed were prepared in DC high vacuum system, with the background pressure at 1.2 x 10^{-5} Torr. After the substrates were cleaned and introduced into the deposition chamber, the system was pumped down to evacuate the pressure until reached the background pressure. Then the sputter gas (and reactive gas for reactive sputtering for CrN were add to the working pressure of 6.3 x 10^{-3} Torr, before started the plasma glow discharge. The thin film synthesis was done at room temperature and the power of 245W (350V 700mA) was supplied to the magnetron. This gave the deposition rate of about 0.2 nm/sec.

3.2.3 Electroless plating of palladium membranes

The surface of the supports was first activated to initiate the deposition of Palladium atoms.

3.2.3.1 Surface activation

The activation process consisted of successive immersion at room temperature of the supports in 1 g/l $SnCl_2$ solution followed by 0.1 g/l $PdCl_2$ solution with two rinses in deionized water between these baths. After $PdCl_2$ immersion and prior to the first rinse, the supports were briefly dipped in 0.1 M HCl to remove any trace amount of tin compounds on the surface. The schematic diagram of one loop of the activation process is depicted in Figure 3.6. The surface activation in $SnCl_2$ and $PdCl_2$ solutions was generally repeated 6 times and a perfectly activated surface was smooth and grayish brown in color.

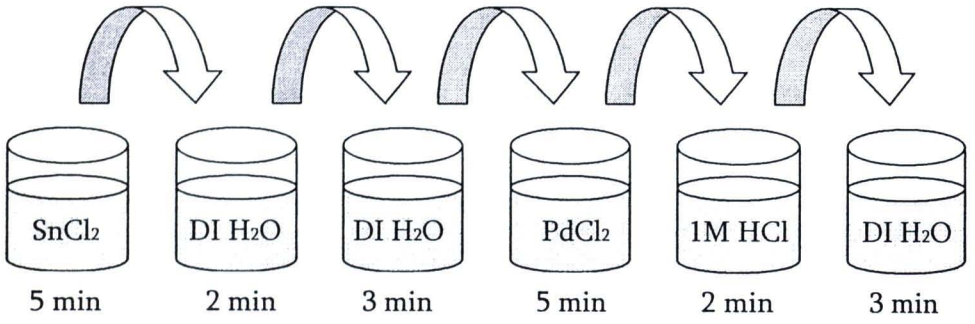

Figure 3.6 One loop of the activation process.

3.2.3.2 Electroless plating deposition of palladium

The plating solution was prepared by mixing the first three compounds given in Table 3.2 [24] at lease one day prior to plating to form stable metal complexes. The palladium plating bath as shown in Figure 3.7. The hydrazine reducing agent was added just prior to plating.

The activated supports were immersed in the plating solution which was renewed every 90 minutes. The supports were rinsed with hot deionized water between plating baths. After deposition was complete the membrane was allowed to cool down at room temperature in deionized water and dried at 100°C for 3 hours.

The layer thickness was measured using gravimetric method given in Equation 3.1.

Table 3.2 Chemical composition of electroless Pd plating solution.

Compound	Concentration
Tetraaminepalladium (II) chloride, $Pd(NH_3)_4Cl_2 \cdot H_2O$	4.0 g/l
Ammonia solution, NH4OH (28%)	198 mg/l
Disodium ethylenediamminetetraacetate, Na_2EDTA	40.1 g/l
Hydrazine hydrate, $N_2H_4 \cdot H_2O$	5.6 – 7.6 ml/l

$$\text{Thickness}\ (\mu m) = \frac{\Delta \text{Weight (mg)} \times 10}{\text{Plated Area (cm}^2) \times \text{Density of the plated metal (g/cm}^3)} \quad (3.1)$$

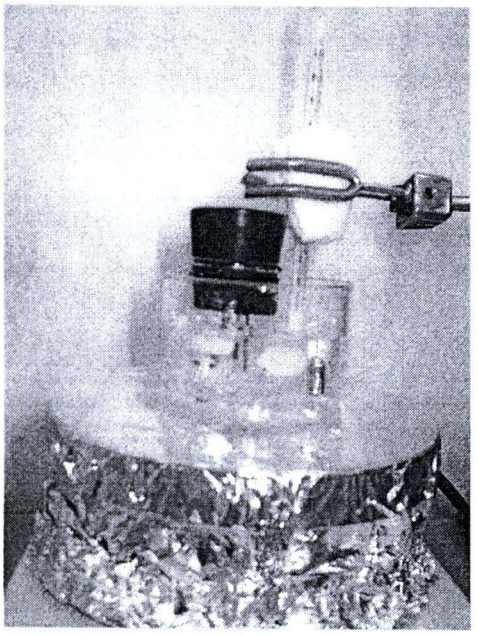

Figure 3.7 Palladium plating bath.

3.2.4 Evaluations of the efficiencies in reducing intermetallic diffusion of the barriers

The efficiencies in reducing intermetallic diffusion of the barriers were assessed as diagramed in Figure 3.8. The palladium membrane on the PPS supports with different forms of Cr-based diffusion barrier was heated in argon atmosphere in a muffle furnace at 450, 500 and 550°C for 24 hours and the metal composition of the membranes were quantitatively determined using SEM-EDS. Quantitative SEM-EDS analyses were performed as a part of the surface characterization of the Palladium membrane described below.

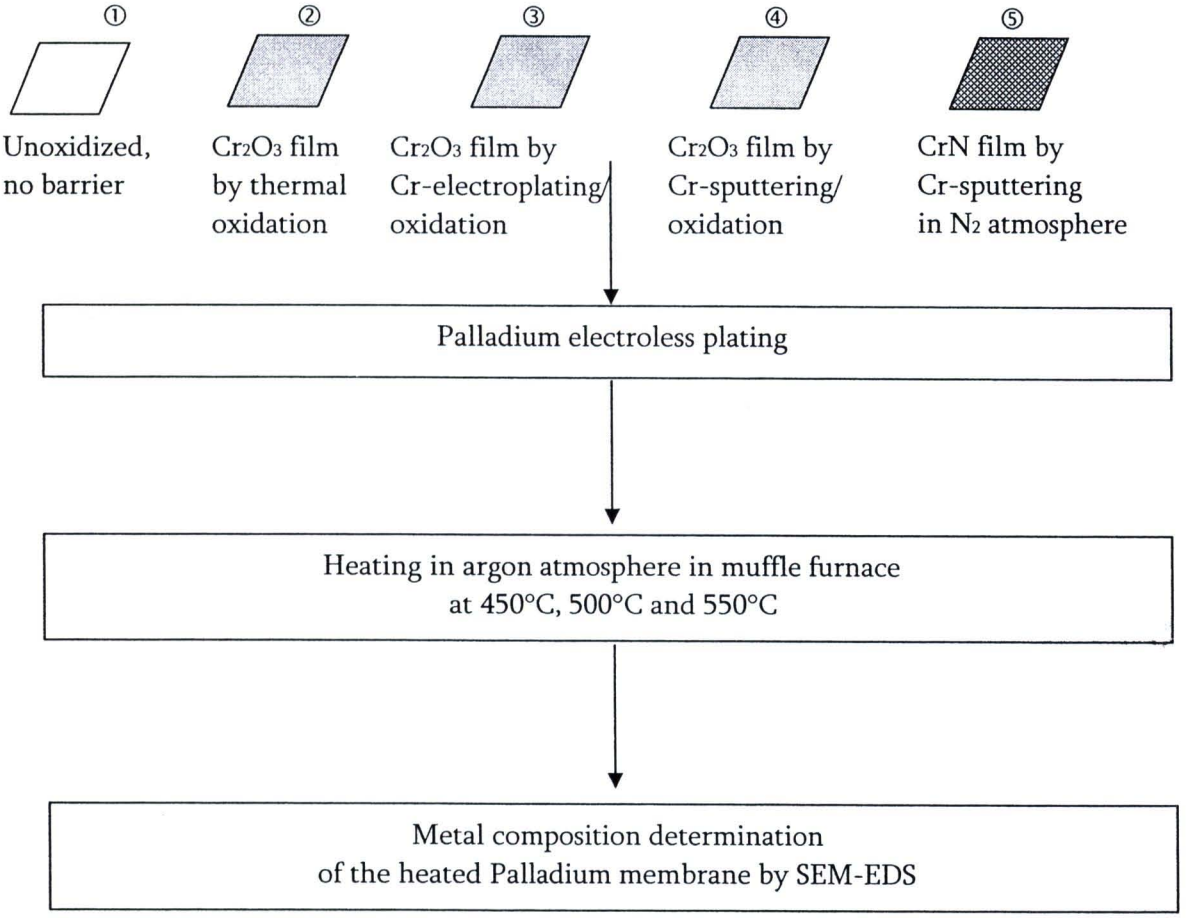

Figure 3.8 Assessment of the efficiencies in reducing intermetallic diffusion by the Cr-based barriers.

3.2.5 Surface characterizations of the palladium membrane

Surface characterizations were performed using scanning electron microscope equipped with electro dispersive spectrometer (SEM-EDS) for both qualitative and quantitative analyses. The spatial resolution for SEM-EDS lied between 0.8-1.2 μm. SEM specimens of the metal deposited stainless steel were cut using a SiC saw blade and ground with phenolic powder in a Smithells II mounting press. The resounding samples were ground with SiC papers with increasing grain fineness from 80 to 400 grits. Grinding was performed using Metaserv 2000 grinder-polisher. Vibromet I automatic polisher was employed to polish the sample to 1-μm thin overnight. Prior to SEM cross-section analyses sample was painted with carbon ink and gold-coated to avoid charging.