Application of Electroless Plating for Fabrication of Flexible and Integrated Piezoelectric Ultrasonic Sensors

by

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Abstract

Integrated (IUTs) and flexible ultrasonic transducers (FUTs) have been found to be of great interest for structural health monitoring (SHM) of graphite/epoxy (Gr/Ep) composite parts and structures. Because certain Gr/Ep composites do not have sufficient electrical conductivity, bottom electrodes are required for the IUT fabrication. Also FUTs using insulating polyimide (PI) membrane which offers high flexibility, bottom electrode is required as well. One main objective is to develop the electroless plating technique to deposit nickel (Ni) or silver (Ag) onto Gr/Ep composites and PI for IUT or FUT fabrication. The pre-treatments (cleaning, etching, sensibilization, activation and reduction) and reaction conditions (bath chemistry, temperature, time, agitation, etc.) have been investigated. Recipes of electroless nickel (EN) plating at room temperature (RT) and 90°C and RT electroless Ag plating have been developed. The interfacial adhesion of the Ni or Ag/substrate was also tested. The conductivity of the fabricated bottom electrodes was tested by ohmmeter. A 50~60µm piezoelectric film was fabricated by sol-gel spray technique. IUTs and FUTs consisting of these EN bottom electrodes, piezoelectric film and Ag paste top electrode perform well for SHM purposes.

Résumé

Les capteurs ultrasonores flexible (CUF) et intégré (CUI) sont très intéressants pour le suivi de la santé structurelle (SSS) des pièces de structures et de composites, composées à partir de carbone/époxyde (C/Ep). Parce que le C/Ep n'a pas suffisamment de conductivité électrique, une électrode de base est nécessaire pour la fabrication de CUIs. De plus, pour le CUF utilisant du polyimide (PI) comme membrane isolante nécessite aussi l'utilisation d'une électrode de base. Un des principaux objectifs de ce mémoire est de remédier à ce problème par le développement d'une technique de placage au tampon. Cette dernière déposera du nickel (Ni) ou de l'argent (Ag) sur le C/Ep et le PI pour obtenir des CUIs ou des CUFs. Les prétraitements (nettoyage, attaque chimique, sensibilisation, activation et réduction) et les conditions de réaction (bain chimique, température, temps, agitation, etc.) ont été étudiés. Les procédures pour le placage au tampon du nickel (PTN) à la température de la pièce (TP) et à 90°C ainsi que pour l'Ag à TP furent développées. Les adhésions de surface du Ni ou de l'Ag avec le substrat furent testées. Les conductivités électriques des électrodes de base furent testées avec un ohmmètre. Un film piézo-électrique de 50~60 µm fut fabriqué par une technique sol-gel. Les CUI et CUF fabriqués avec l'électrode de base faite à partir du PTN, du film piézo-électrique et une pâte d'Ag comme électrode de surface, excelle bien pour les besoins en SSS.

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Table of Contents

List of Figures

List of Tables

List of abbreviations

ACS...American Chemical Society
Ag...silver
Ag_3N...silver nitride
CH_3COONa..sodium acetate
$C_6H_{12}O_6$...glucose
CrO_3..chromic acid
dB..decibel
DI water..deionized water
EMI..electromagnetic interference
EN plating..electroless nickel plating
FUT..flexible ultrasonic transducer
Gr/Ep..graphite epoxy
HCHO...methanal
HCl...hydrochloric acid
H_2SO_4...sulfuric acid
IUT..integrated ultrasonic transducer
M...metal
MHz...Mega Hertz
mm..millimeter
$Na_3C_6H_5O_7 \cdot 2H_2O$...sodium citrate dihydrate
$NaH_2PO_2 \cdot H_2O$...sodium hypophosphate
NaOH..sodium hydroxide
NDT...non-destructive testing
NH_4OH...ammonium hydroxide
Ni..nickel
$NiSO_4 \cdot 6H_2O$...nickel sulphate hexahydrate
Pd...palladium
$PdCl_2$..palladium (II) chloride
PI...polyimide
PVDF..polyvinylidene fluoride
PZT..lead zirconate titanate
RT...room temperature
S...surface
SHM...structure health monitoring
Sn...tin
$SnCl_2$...tin (II) chloride
SNR...signal-to-noise ratio
SS...stainless steel
TEC...thermal expansion coefficient
UV...Ultraviolet
µm...micrometer

1. Introduction

Ultrasonic technology has commonly been used in industrial applications for flaw detection and evaluation, dimensional measurement, and material characterization. Ultrasonic transducers (UTs) have demonstrated excellent capacity to detect, identify and characterize defects or voids in the materials with good sensitivity, high accuracy, fast speed and simplicity to operate. Integrated UTs (IUTs) have been fabricated for such applications (Krautkramer, *et al.*, 1990; Birks, *et al.*, 1991; Ihn, *et al.*, 2004). The thickness mode longitudinal wave piezoelectric UTs are directly coated onto the objects to be diagnosed. Recently, due to the rapid development of industrial manufacturing processes, advanced applications of on-line process diagnosis and in-situ structure health monitoring (SHM) are also required. In certain applications such as to aerospace, nuclear and medical diagnosis and so on, conventional UTs showed difficulties or inconvenience in being used with curved surfaces. One of the merits of IUTs is that they can be directly deposited onto the curved surface of the objects to be inspected (Jen, *et al.,* 2006; Kobayashi, *et al.,* 2007; Kobayashi, *et al.*, 2008). Also flexible UTs (FUTs) are also desirable to be designed and fabricated to optimize the contact between FUTs and curved parts for improved ultrasonic inspection purposes. Due to its superior conformabilities, FUTs can align itself with the object surface to maximize the ultrasonic energy to be transmitted (Kobayashi, *et al.*, 2007). The desired features for IUTs and FUTs include strong signal strength, broad bandwidth and high signal-to-noise ratio (SNR). In addition, often the IUTs and FUTs are required to withstand high temperature for the use in the process diagnostics of industrial processes such as polymer extrusion, polymer injection molding, light weight metal casting, non-destructive testing (NDT) of nuclear power, chemical and petroleum plants, engines, etc. (Jen, *et al.,* 2006; Kobayashi, *et al,.* 2007; Ono, *et al.,* 2007; Kobayashi, *et al.,* 2008).

A typical thickness mode piezoelectric film UT consists of a substrate, a bottom electrode, a piezoelectric active layer and a top electrode. Sometimes a conductive substrate, such as metals, acts as the bottom electrode. An electric voltage will be applied onto the top and the bottom electrode to enable the piezoelectric ceramic film to generate the thickness longitudinal waves into the substrate. (Buchanan, 2004; Setter, 2005; Kobayashi, *et al.*, 2007).

Before the design and fabrication, the desired characteristics of the UT should be specified for desired application requirements and suitable for operation environment conditions. The design for a practical piezoelectric film UT needs to consider at least three aspects: microstructure, piezoelectric materials and film thickness. Also the material selection and development of application techniques should be considered in the four basic parts of the sensors: substrate, bottom electrode, piezoelectric ceramic material and top electrode (Kobayashi, *et al.*, 2007). The main objective of this thesis is to focus on the development of bottom and top electrodes for several IUT and FUT applications to be described throughout the thesis.

1.1 Piezoelectric materials

The piezoelectric materials can convert electric energy to mechanical energy (ultrasonic), and vice versa (Bradley, 1991). These materials are widely used not only because of their suitable piezoelectric properties but also due to their easiness of fabrication into a variety of shapes and sizes. The commonly used piezoelectric materials include two types: piezoelectric ceramics and piezoelectric polymers (piezoelectric ceramic / polymer composites) (Webster, 1999). These piezoelectric materials have been investigated for the fabrication of thickness mode piezoelectric sensors in past decades. Each of these two materials has its own advantages and disadvantages.

Piezoelectric polymers such as polyvinylidene fluoride (PVDF) and PVDF copolymers have been applied in commercial available flexible sensor market. They have acceptable piezoelectric activity and attractive flexibility (Rosen, *et al.*,

1992). However, they have lower electromechancial coupling coefficient than piezoelectric ceramics. Thus, sensitivity of sensors made of piezoelectric polymers may not be good enough to detect detailed features of physiological signals (Ono, *et al*., 2006). Also the existence of polymer usually prevents its application at elevated temperatures. For example, PVDF shows significant piezoelectric deterioration at only above 65ºC and some other piezoelectric polymers have relatively higher piezoelectric deterioration temperatures but still are limited to 90~100ºC (Chen, 2007; Kobayashi, *et al*., 2006). Thus researchers are still trying to find out new piezoelectric polymers that are capable of maintaining their properties at high temperatures. In addition, most of PVDF UTs are useful for applications in frequencies higher than 1MHz. They are not suitable to diagnose thick and high attenuation materials such as human flesh, graphite epoxy (Gr/Ep), etc. which require low frequency (< 1MHz) (Webster, 1999; Kobayashi, *et al.*, 2007).

Piezoelectric ceramic / polymer composites, in which piezoelectric ceramic powders or rods are mixed into polymer matrix host, may have higher electromechanical coupling coefficients than piezoelectric polymers and lower dielectric losses; but still the low glass transition temperature makes them easily become soft when the temperature is above 180ºC. Also piezoelectric ceramic / polymer composites sensors were reported to show good ultrasonic performance only below 80ºC due to the fact of decoupling of piezoelectric ceramic rods from polymer matrix (Kobayashi, *et al*., 2006).

Piezoelectric ceramics are the dominant piezoelectric UTs materials because of their high piezoelectricity and easiness to fabricate into various shapes and sizes. And the effectiveness of any piezoelectric UT heavily depends on the piezoelectric material chosen. Lead zirconate titanate (PZT) has become the most prominent and useful electroceramics since the 1960's because of its good ferroelectric and dielectric properties (Sze, 1994; Webster, 1999). To maximize the efficiency of piezoelectric film UT, the piezoelectric material should

preferably have high piezoelectric constant and be miniaturized. To satisfy these two requirements, a sol-gel spray method has been developed (Kobayashi, *et al.*, 2000). A new concept FUT has been developed. It comprises a metal foil (stainless steel or aluminum, brass, copper, etc.), a sol-gel sprayed PZT composite ceramic layer and a silver (Ag) paste as the top electrode (Ono, 2007). The metal substrate is conductive and works as both the substrate and bottom electrode. The PZT composite (PZT-C) film to be described in Chapter 2 can be fabricated by sol-gel spray technique and the thickness varies from 30 to 150 μm. The details of the fabrication procedures will be presented in the next chapter. The capability of these FUTs operated in the pulse-echo mode for NDT on flat and curved surfaces of different materials ranging from room temperature (RT) to 150ºC. The strength of the ultrasonic signals was comparable with that of commercial broadband UTs. In this research, we will use polyimide (PI) as the substrate for fabrication of FUTs and Gr/Ep for the fabrication of IUTs.

1.2 Bottom electrode

Nowadays, a thin layer of metals and alloys can be deposited by many electroless plating methods (Davis, 2000). There are several metallic candidates suitable to serve as bottom electrode for IUTs or FUTs. Some of them have been investigated and each has different merits and drawbacks. The Ag paste can be easily coated as the top or bottom electrode, but the adhesion may not be so strong during thermal cycling at temperatures above 250ºC. Platinum plate is an excellent candidate for high temperature use with good adhesion, but it needs a thermal treatment up to 800ºC, which is a limitation of use for many materials and structures. Also the platinum has wetting difficulty for soldering. Thin layer copper can be deposited on non-conductive substrates by an electroless plating technique, but it has corrosion and oxidation in the daily environment because copper oxide is a semiconductor which provides poor conductivity (Jost, 1960). Furthermore copper may easily be diffused into substrate surface (especially on PI) and causes poor adhesion (Rabilloud, 2000). Nickel (Ni) has traditionally been used as barrier layer in industrial applications (Davis, 2001). Based on all the above explanations, in this research, Ni has been selected as one ideal candidate as a

bottom electrode with good conductivity and interfacial adhesion. Electroless silver (Ag) plating has also been investigated due to its popular uses for metallization of substrates in industrial applications (Mallory, *et al.*, 2002).

1.3 Top electrode

In previous research, Ag paste has been applied as a top electrode (Kobayashi, *et al.*, 2006). In this research, we mainly continue using Ag paste as top electrode; Electroless nickel (EN) plating on top of PZT film as top electrode also was investigated.

1.4 Metallization of non-conductive substrates by electroless plating

Electroplating and electroless plating are two commonly used methods for metallization in industrial applications. In electroplating, metal deposition can be deposited via the electrochemistry method whereby electrons are provided by an exterior power supply to reduce metal ions to a metallic state. In the electrochemical process, metal (M) is deposited on the surface of the noncatalytic surface (S) by an electrochemical oxidation-reduction reaction. Thus, electroplating cannot be applied to non-conductive surfaces since electrons cannot flow (Kanani, 2005).

Electroless plating is a chemical oxidation-reduction reaction which is initiated by noble catalytic metal particles and then preceded by autocatalysis. In electroless plating, there are at least complex metallic ions and a reducing agent. A chemical reducing agent can provide the source for electrons, thus no outer current power is needed. Hence non-conductive surfaces can be metalized by deployment of electroless plating bath (Mallory, *et al.*, 2002). Electroless plating has been widely used in industry for obtaining metal layer on either metallic or non-metallic substrates (Datta, *et al.*, 2005). It is cost-effective, convenient to implement at low temperature, and can provide acceptable electrical and mechanical properties (Mallory, *et al.*, 2002). But electroless plating requires the employment of a catalytic metal to kick-start and aid sustainment of the reaction. Non-conductive

surfaces (e.g. polymers, plastics, glass, etc.) have to be activated prior to the electroless deposition, that is, catalytic nuclei on the surface of noncatalytic material should be generated during this activation process (Popov, *et al.*, 2002; Paunovic, *et al.*, 1998). Two ways may produce catalytic nuclei: electrochemical and photochemical. The electrochemical method is chosen here because it has relatively less complex reaction kinetics than the photochemical method. In the electrochemical process, M is deposited on noncatalytic S by an electrochemical oxidation-reduction reaction (Paunovic, *et al.*, 1998):

$$M^{2+} + Red \rightarrow M + O_x$$
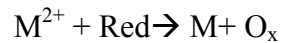
There are two kinds of EN plating: acid EN and base EN plating. Both bath chemistry and composition are important in the EN plating process (Davis, 2000). But there are other aspects that contribute to successful plating (Mallory, *et al.*, 2002). For best plating process design, the priorities are decided by the primary and secondary function of the Ni plating (Braunovic, 2006). To serve as bottom electrode in FUTs and IUTs, the Ni plating is required to have good conductivity and achieve good interfacial adhesion between plated Ni layer and substrate. Thus a plating sequence of pre-treatments, plating process and testing can be established. In our research, we applied an acid bath, and the reaction can be given in chemical equation as follows (Pauleau, 2002):

$$NiSO_4 + NaH_2PO_2 + H_2O \rightarrow Ni + NaH_2PO_3 + H_2SO_4$$
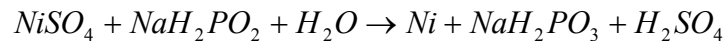
Acid bath was chosen because of several advantages over alkaline bath. They are higher deposition rate, increased stability, greater simplicity of bath control and improved properties of Ni-P (Phosphorus) deposition (Davis, 2000).

1.5 Metallization of PIs

A number of techniques have been utilized to realize the metallization of PI such as chemical vapor evaporation, physical vapor evaporation, sputtering, etc. However, specialized equipments are required for the above deposition process. And the introduction of high temperature may cause damages on the PI surface. Furthermore, the interfacial adhesion between PI and metal is poor in general. To improve the adhesion between metal and PI, traditional modification methods

include dry modification (ion beam, UV radiation and laser ablating) and wet modification (chemical etching). The wet process provides relatively homogeneous chemical solutions such as acids, bases, and so on; the reaction corresponding to this process can be easier to define. The solvent for wet process should not dissolve the PI (Sacher, *et al.*, 1990).

Proper etchant is chosen to eat away the PI surface to both increase the surface area and provide microscopic holes to achieve good adhesion between the interfaces of metal deposition and PI (Mittal, 1996). Chromium acid is a strong oxidizing solution and is an ideal candidate. After the etching process, the surface area of the PI is greatly enlarged and the PI turns from a hydrophobic material to a hydrophilic material; also microscopic holes left in the surface of the PI can provide the bonding sites for the deposited metal to increase the metal/PI adhesion. When a "chrome-sulphuric" etchant is used, the PI surface is attacked and the following reduction reaction can occur (Mallory, *et al.*, 2002):

$$Cr^{+6} + 3e^- \rightarrow Cr^{+3}$$
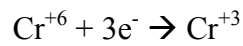
Proper etching time and temperature are crucial since the etchant is the most critical step to obtain successful Ni plating with good adhesion (Packham, 2005). Research results show that either underetching or overetching is harmful to plating. Underetched samples have troubles, such as poor adhesion and blistering; while overetched samples may result in degraded surface, thus causing both poor adhesion and skip plate. The temperature of the etching solution can range from 60ºC to 90ºC. After etching, the samples must be rinsed thoroughly with deionized water (DI water) to remove excess etchant on/in the surface, and then reduced by some chemical reduction solution, e.g. hydrochloric acid (HCl), because the existence of any hexavalent chromium is harmful to the following steps. Thus thorough rinsing must be applied to eliminate all the etchant trapped in blind holes to avoid *skip plate* that is due to the *bleed out* of the etchant in the following steps. A sensibilization solution and an activation solution are necessary since by applying them, the nuclei can be formed on the surface of the sample and trigger later electroless plating process on non-conductive surfaces. In

the sensibilization step, the sample is immersed in a stannous / chloride / hydrochloric acid solution to help the surface to absorb tin ions (Sn^{2+}); in the activation process, the sample is immersed in palladium chloride / hydrochloric acid solution, and the Pd^{2+} is to be reduced to Pd^0 (Charbonnier, *et al.*, 2004;Mallory, *et al.*, 2002):

$$Sn^{+2} + Pd^{+2} \rightarrow Sn^{+4} + Pd^0$$
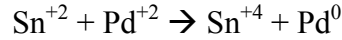
After the activation, metallic Pd exists on the surface of the sample and is surrounded by hydrolyzed stannous hydroxide. This excess stannous hydroxide should be removed to ensure the Pd particles work well enough as a catalyst. This accelerator can be organic or mineral acids and will remove the excess Sn but leave the Pd particles intact for later electroless plating. In fact, excess tin is harmful and prevents the occurrence of electroless plating. An accelerator might be needed but not always used. Rinsing with DI water can also help to remove the excess undesired ions on the sample surface. The following step is to immerse the sample into a reduction solution so as to help more $H_2PO_2^-$ absorbed on the surface of substrate. Absorbed ions and modules initiate next EN plating (Mallory, *et al.*, 2002).

1.6 Contents of the thesis

This thesis investigates the feasibility of applying an EN method for bottom electrode on PIs and Gr/Ep for several IUTs and FUTs application. The appropriate pre-treatment steps and reaction controls will be discussed and the objective is to find out optimized EN plating processes. The effects of pre-treatment steps (cleansing, etching, sensibilization, activation and reduction) and reaction conditions (chemical bath, reaction temperature, agitation and reaction time) will be investigated by analyzing the plating feasibility and metal/substrate interfacial adhesion (Charbonnier, *et al.*, 2004). The interfacial adhesion between plating and substrate surface will be tested by Scotch Tape Testing and the conductivity of the EN plating will be measured by ohmmeter (Dini, 1993; Kutz, M. 2002).

A PZT-C film will be fabricated by a sol-gel spray technique and Ag plating will be applied to coat a thin Ag film onto the PZT-C film as top electrode. Then the characteristics (center frequency, band width and SNR) of the fabricated FUTs and IUTs will be tested both at RT and/or at elevated temperature (150ºC) in a pulse-echo mode (Kobayashi, *et al*., 2006). Optimized pre-treatment steps and reaction controls during electroless plating of bottom electrodes will be extensively studied for the fabrication of IUTs and FUTs onto large size and/or complex shape samples (Kobayashi, *et al.*, 2008).

Other research tasks will also include: (1) applying Electroless Ag plating on PI at RT; (2) using the tap water and solution spray technique for the fabrication of EN plating as bottom electrode on PI and Gr/Ep; (3) applying RT EN plating on PI; (4) using EN plating at 90ºC onto the PZT-C film. All the results will be analyzed for the investigation of on-site fabrication of bottom and top electrode by electroless plating.

2. Fabrication and Evaluation of FUTs and IUTs Involving Electroless Plating Techniques and PIs

2.1 Introduction

PIs are high temperature engineering polymers with numerous outstanding electrical, chemical, thermal and mechanical properties, such as low dielectric constant, high thermal stability, good chemical resistance, low moisture absorption rate, etc. (Waris, *et al.*, 2005; Mittal, 2001). Because of above mentioned properties, PI has been chosen, in this thesis, to be the main substrate material for FUT and several other IUT devices. In particular, PI can sustain 350°C, which is crucial for the fabrication of PZT-C film of high piezoelectricity.

Its PI molecule structure can take two forms: aromatic heterocyclic structure shown in Figure 2.1 and linear structure shown in Figure 2.2. Both of them have the basic -imide functional group shown in Figure 2.3. The former type has unique properties that come from strong intermolecular forces between the polymer chains, thus it is more commonly commercially used (Mittal, 2001; Ohya, 1996).
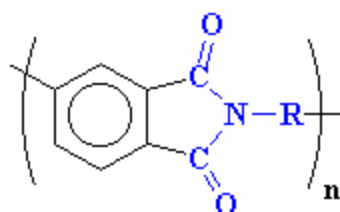

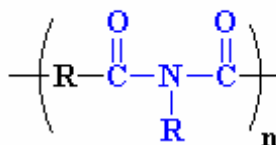**Figure 2.1 Primary structure of aromatic heterocyclic PI**

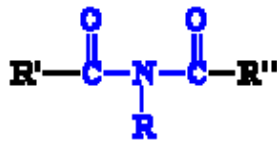**Figure 2.2 Primary structure of linear PI**

Figure 2.3 Primary structure of an -imide

Metalized PIs have been widely used in numerous electrical and electronics applications and have continuously attracted researchers' interests. Previous successful applications include printed circuit board, resistors, capacitors, flip chip devices, electronic connectors, EMI shielding, etc.(Suchentrunk, 1993). Being low stress level materials, PIs are inert to ambient fluctuations in conditions such as temperature and humidity (Wong, 1993). The metallization of PI is important in applications to provide desired properties such as optical reflectivity, electrical conductivity, etc. (Wu, *et al.*, 2005). The most commonly applied metals include silver (Ag), gold, copper, Ni and so on. Various methods have been developed to achieve these purposes. Electroless plating is one attractive approach to achieve metallization of PIs (Suchentrunk, 1993).

Recently our research focuses on applying PI material as substrate for the fabrication of FUT. PI is an ideal candidate because of its flexibility which benefits from its thin thickness (Ono, *et al.*, 2007). The material density, longitudinal and shear wave velocities of PI are 1.4kg/m^3, 2400m/s and 1400m/s, respectively. Also PI has high glass transition temperature, high Curie temperature and can sustain 350ºC and the sol-gel piezoelectric multilayer ceramic film fabrication process (Mittal, 1984). Because PI is non-conductive, a bottom electrode is required in the fabrication process of FUT. The metallization of the PI is necessary to provide electrical conductivity. The design consists of a PI film as base, a thin (several μms) metal layer as bottom electrode, a piezoelectric ceramic layer and a top electrode (Ono, *et al.*, 2007).

Despite its aforementioned attractive advantages, PI has an important issue related to its interfacial adhesion with metallization layer for successful applications (Sacher, *et al.*, 1990). Ni film was deposited on PI with an electroless plating

method (Ho, *et al.*, 2003); however, "Ni film/PI" interface adhesion is difficult to achieve due to the surface energy difference between these two materials (Suchentrunk, 1993). Complicated pre-treatment procedures are necessary to initialize the electroless plating reaction and enhance the adhesion of the EN plating on non-conductive substrates (Rabilloud, 2000). Numerous efforts have been used to improve interfacial adhesion between metal and PI, for example, cathodic sputtering, reactive ion etching, etc. (Ho, *et al.*, 2003). Therefore, the metallization of PIs includes complex process steps. One possible choice is that the PI films can be pre-treated by consecutive steps: cleaning, etching, sensibilization, activation and reduction. After these pre-treatment steps, the electroless plating process for Ni could be applied (Mallory, *et al.*, 2002). Based on all of the above, it is necessary to investigate pre-treatments steps, reaction time and their effects on both plating and adhesion.

Furthermore, for multilayer structure device, the reliability of these structures strongly depends on the interfacial adhesion of thin films. Extensive research over the past decades has led to the understanding that residual stress plays an important role, and can explain and prevent the failure of the multilayered structure. There are three types of stresses: intrinsic, stress and hygroscopic stress (Dumont, *et al.*, 2007). All of them contribute to the residual stress in EN plating on PI substrates. Intrinsic stress might be one result of non-equilibrium growth during the deposition process. Thermal stress mainly comes from the difference between two different thermal expansion coefficient (TEC) materials. Hygroscopic stress is caused by mismatched water absorption among various materials. Due to the existence of one or more stresses, the delamination between layers may occur (Dumont, *et al.*, 2007). It is desirable to decrease the stress as low as possible to enhance the adhesion. Therefore, it is important to evaluate the interfacial strength. Scotch Tape Testing has been widely applied in industrial applications as one of the simplest ways to estimate the interfacial adhesion (Chen , *et al.*, 1994).

The objective of the work in this Chapter is to fabricate and characterize FUT that consists of a membrane substrate (PI), a bottom electrode (electroless plated Ni film), a piezoelectric PZT-C film and an Ag top electrode (Kobayashi, *et al.*, 2006). Firstly we investigate methods to fabricate reliable Ni plating on flexible PI substrate as bottom electrode. The pre-treatment steps and reaction control will be studied and optimized for obtaining Ni plating on PI substrates. Then the conductivity will be measured by ohmmeter and the interfacial adhesion will be measured by Scotch Tape Testing. Effects of pre-treatment steps and reaction conditions will be investigated and processing conditions will be optimized as well. Next Ni plated PI will be used for fabrication of FUT with a PZT-C film and Ag bottom electrode. Finally, the characteristics of Ag/PZT-C /Ni/PI FUT will be tested in pulse-echo mode at RT and at 150ºC, respectively. All of these works will contribute towards understanding and evaluating the FUT fabrication method evaluation (Waris, *et al.*, 2005). EN plating is extended to be applied on large area PIs and PI lens to work as bottom electrode. Scotch Tape Testing is used to measure the interfacial adhesion between PI and EN plating. In the future work, EN plated PIs and PI lens will be used for fabrication of FUTs and IUTs with a PZT-C film and Ag bottom electrode.

2.2 Experimental procedures

2.2.1 Materials
PI membranes with a thickness of 50μm were obtained from NRC-IMI. This PI has a light brown color. All reagents were purchased from Sigma-Aldrich with ACS Reagent Grade or above and used as received without any purifying process.

2.2.2 Preparation of PI substrates
PI substrates were cut into different sizes according to the FUT design and for consideration of electroless plating. Firstly substrates were cleaned with dishwashing liquid for 10 min and rinsed by DI water; then they were further cleaned by the organic solvents such as methanol and acetone. After each cleaning, the substrates were rinsed well with DI water. The purposes of cleaning

include: 1) removing many residual contaminants, especially oil; 2) swelling the surface of the PI to enable chemical etchant to attack the surface.

2.2.3 Electroless deposition of Ni on PI substrates

The pre-treatment process is developed for PI on the basis of previous processing steps for non-conductive substrates. The flow chart of the metallization process is shown in Figure 2.4.

```
┌─────────────────┐
│   Substrates    │
└─────────────────┘
        ⇩
┌─────────────────┐
│    Cleaning     │
└─────────────────┘
        ⇩
┌─────────────────┐
│    Etching      │
└─────────────────┘
        ⇩
┌─────────────────┐
│ Sensibilization │
└─────────────────┘
        ⇩
┌─────────────────┐
│   Activation    │
└─────────────────┘
        ⇩
┌─────────────────┐
│   Reduction     │
└─────────────────┘
        ⇩
┌─────────────────┐
│Electroless Nickel│
└─────────────────┘
        ⇩
┌─────────────────┐
│     Drying      │
└─────────────────┘
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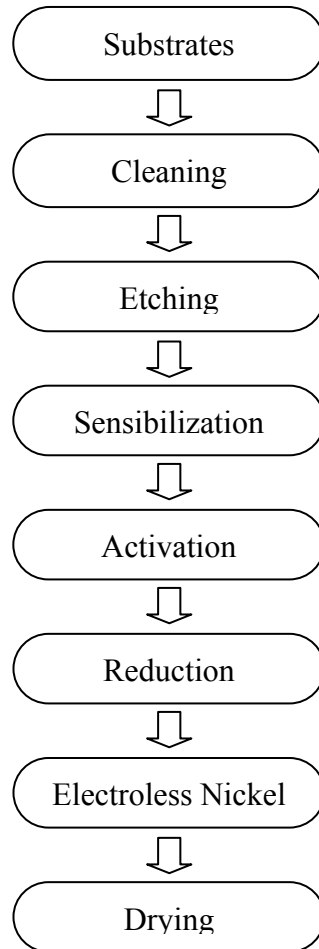
Figure 2.4 Flowchart of metallization process

In the first step, the PI substrates are etched by immersion of PI substrates in the chrome-sulphuric acid etchant at 60ºC and rinsed well by DI water; the next step involves the immersion of PI substrates into the sensibilization solution at RT for 10 min and rinsing the substrates well with DI water. After that, the activation is carried out by dipping the substrates into the activation solution at RT for 5 min and rinsing the substrates with DI water. Protective enamel coating is applied to

one side of each sample and dried in RT air for 10 min. Then the substrates are immersed into a reduction solution for 30 sec and rinsed well by DI water. Finally the substrates are immersed into a reducing solution at RT for 30 sec and rinsed by DI water. The compositions of pre-treatment solutions used are listed in Table 2.1

Table 2-1 Bath composition of pre-treatment solutions

Solution Name	Composition of the solution	Condition
Etching	Chromic Acid	400g/L
	Sulphuric Acid (98%)	370g/L
	Temperature	60°C
Sensibilization	Tin (II) Chloride	3.0g/L
	Hydrochloric Acid (37%)	3.567g/L
	Temperature	RT
Activation	Palladium Chloride	0.5g/L
	Hydrochloric Acid (37%)	11.89g/L
	Temperature	RT
	Immersion time	5 min
Reduction	Sodium Hypophosphite	20g/L
	Temperature	RT
	Immersion time	30 sec

* All solutions were diluted by DI water;
**Before the reduction step, the substrates were coated on one-side with nail color as a protecting layer;
*** After each step, the substrates were rinsed well by DI water

Upon completing all the pre-treatments above, the PI substrates are introduced in the EN plating bath. The composition of the bath is given in Table 2.2. In this bath, sodium hypophosphate serves as a reducing agent and nickel sulphate provides metal ions. Other composites include sodium acetate and sodium citrate dihydrate to work as a complexing agent and a buffering agent. The electroless solution is initially mixed well and the pH of the bath is adjusted to 5 by sulphuric acid. Then the solution is stirred by a magnetic stirrer and heated on a hot plate to maintain the temperature of the bath at 90ºC.

Table 2-2 Chemical composition of EN plating bath

Chemical	Formula	Concentration
Nickel sulphate hexahydrate	$NiSO_4 \cdot 6H_2O$	25g/L
Sodium hypophosphate	$NaH_2PO_2 \cdot H_2O$	20g/L
Sodium citrate dihydrate	$Na_3C_6H_5O_7 \cdot 2H_2O$	11.4g/L
Sodium acetate	CH_3COONa	10g/L
Sulphuric acid	H_2SO_4	As much as required

*DI water was used to dissolve the chemicals listed above.

The PI substrates are immersed in the plating solution shown in Figure 2.5 for various times (5, 10, 20, 30 min), and then immersed into 90ºC water for cooling down to RT. Then the plated substrates are rinsed by DI water to remove any residual chemicals for the prevention of further reaction. Lastly the plated substrates are dried in the RT air for 24 hr.
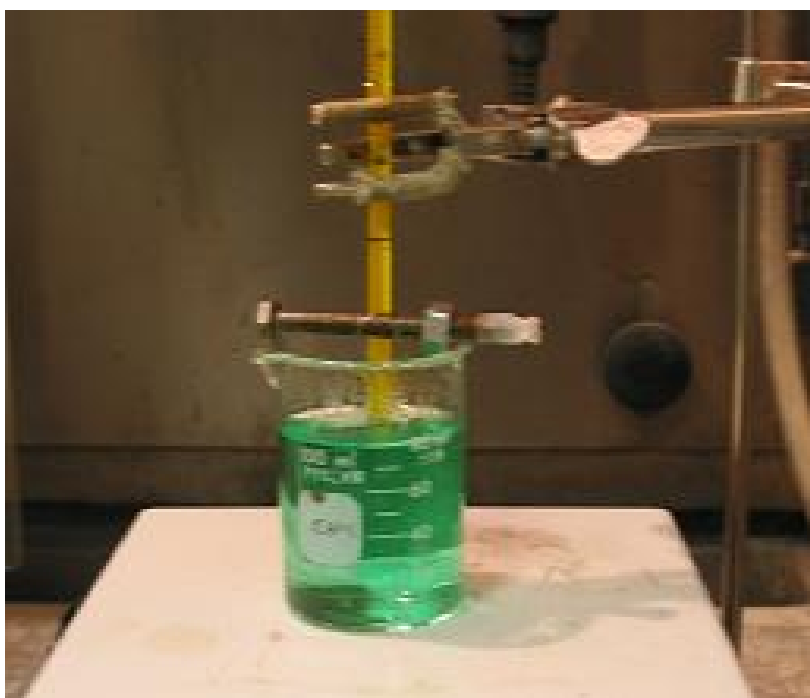

Figure 2.5 Arrangement of EN plating experiment (90ºC recipe)

2.2.4 Characteristics of EN plating on PI

The adhesion testing of the Ni plating is carried out by the Scotch Tape Testing method to each sample to test the interfacial adhesion between the metal/PI. The middle section of a 50mm long, 19mm wide tape was placed over the Ni film and

smoothed by fingers. Certain pressure by fingers is applied to ensure good contact between the tape and the plating. Sixty seconds after the application, the tape is removed by tearing one free end of the tape and pulling quickly at an angle of 90º. The method is illustrated in Figure 2.6.
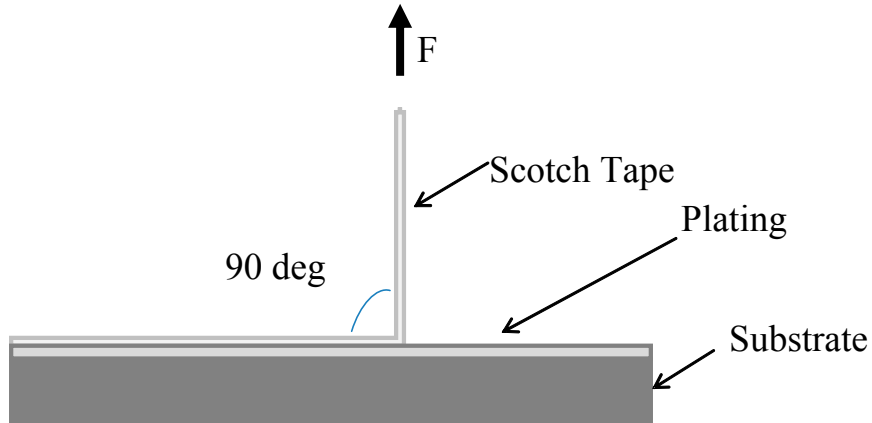

Figure 2.6 Illustration of Scotch Tape Testing for adhesion measurement

2.2.5 Fabrication of piezoelectric films

When the deposition of EN film is achieved with good adhesion and good conductivity, a PZT-C film described below is then fabricated on the surface of bottom electrode. The piezoelectric PZT powder were purchased with an averaged dimension of 50 μm and dispersed into PZT solution which has high dielectric constant by the ball milling method to achieve the gel (shown in Figure 2.7). The volume ratio between PZT powder and sol-gel solution is about 3:1.The final dimension of the PZT powder is estimated to be less than 1μm. An air brush is then used to spray the sol-gel composite directly onto the samples even with curved surfaces and odd shapes (shown in Figure 2.8). With this technique, the films PZT-C film can easily be produced at desired locations through a shadow mask made of even papers and plastic sheets. The spray coating was achieved manually and strong effort was used to achieve the uniformity of the PZT-C film. Since the IUT and FUT made of PZT-C film are desired to have broad bandwidth, the uniformity of the film thickness is not critical. After spray coating, thermal treatments such as drying, firing and annealing are carried out at proper temperatures with the optimal time duration depending on the substrate material

17

such as PI. Multiple layers were made in order to reach the desired thickness. Most often eight to twelve PZT-C layers were applied and each layer can have a thickness of 5~15µm. The PZT-C films are then electrically poled using the corona discharging technique (shown in Figure 2.9). During poling, the substrate was heated to proper temperature, depending on the substrate. Then a high positive voltage supplied from a high voltage DC power supply was fed into a needle that was located several centimeters above the film coated on the metal substrate which served as the ground electrode. The distance and voltage are optimized for different film thicknesses and geometries. The poling time was about 10 min. The corona poling method was chosen because it could pole the thick piezoelectric PZT-C film of a large area and on curved surfaces with ease.
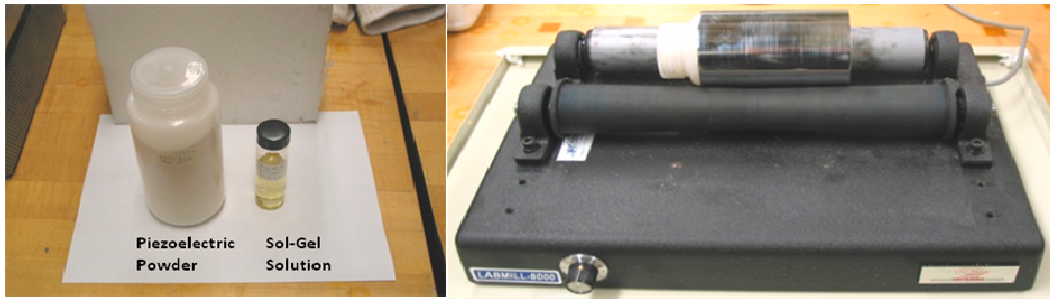

Figure 2.7 PZT powder, Sol-gel solution and ball milling
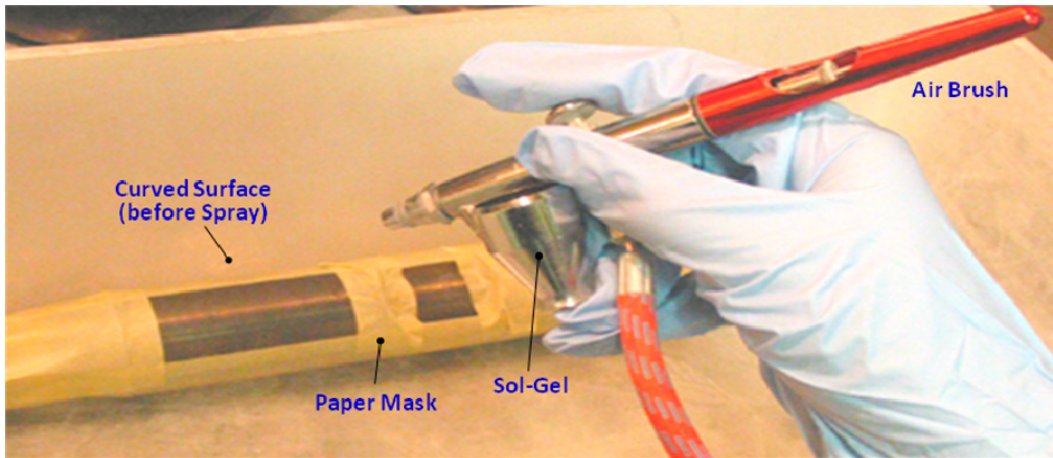
Figure 2.8 Sol-Gel spray with an air brush onto curved surface
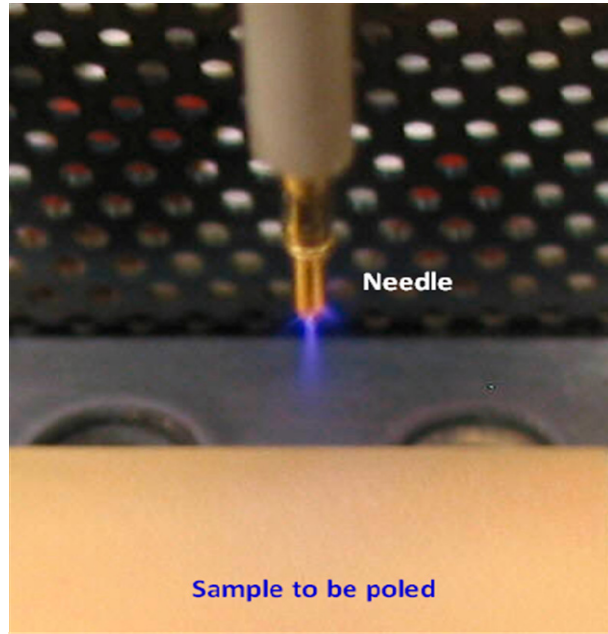
Figure 2.9 The experimental setup for poling

2.2.6 Fabrication of top electrode

Ag paste is applied to serve as top electrode. The top electrode is made at RT by Silver Kwik-Stik pen from SPI Supplied, PA. When the tip of the pen is being pressed, it allows the Ag colloid to flow through the opening. The thickness of the Ag layer is estimated at about 20μm with fairly good uniformity and the size of the top electrode can be selected easily by this convenient approach. In order to optimize the size of the top electrode, experiments were carried out and the result is discussed in Section 2.3.7. The Ag paste had been tested and its operating temperature could be up to at least 220°C. This FUT structure is demonstrated in Figure 2.10.
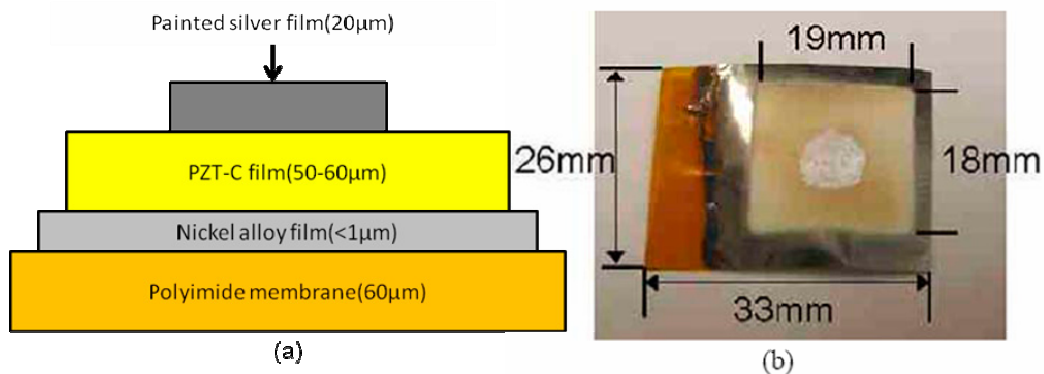
Figure 2.10 A FUT using PI membrane as the substrate with electroless coated Ni alloy film as bottom electrode (a) schematic diagram; (b) with top electrode

19

2.2.7 Testing of the Ag/PZT-C /Ni/PI FUT

The performances (center frequency, band width and SNR) of FUTs were tested both at RT and at elevated temperature (150ºC). The FUT shown in Figure 2.10 was pressed onto a 13.8mm thick SS plate at RT and 150°C. High temperature oil couplant was also placed between the probing side of the PI membrane and SS plate.

2.2.8 EN plating on large area PI as bottom electrode

Large area PI substrates with sizes of 75mm by 75mm were plated by EN. The complete processes are given in Tables 2.3 and 2.4. The adhesion between Ni and PI interfaces is tested by Scotch Tape Testing and proved to be good enough for use as bottom electrode (shown in Figure 2.11). This Ni plated large area PI as conductive flexible base material is preferable for fabrication IUT and FUT.

Figure 2.11 A 75mm by 75mm size PI sample with EN plating after Scotch Tape Testing

Table 2-3 Bath composition of pre-treatment solutions and processing conditions for large area PI

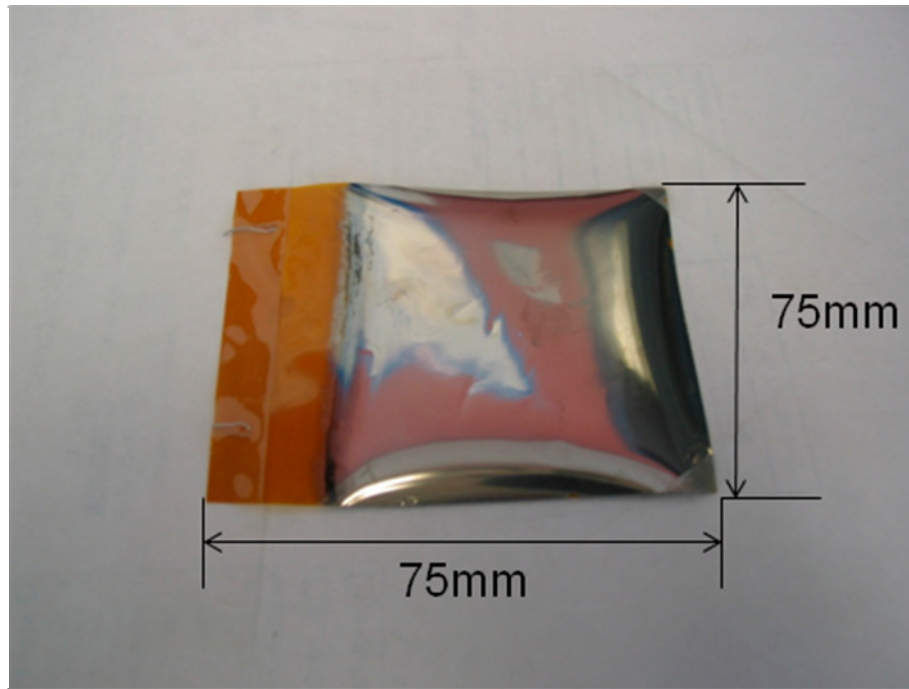| Bath	Composition		Condition
Etching Solution	CrO_3	400g/L	60ºC
	H_2SO_4 (98%)	370g/L	30 min
Sensibilization Solution	$SnCl_2$	3g/L	RT
	HCl (37%)	3.567g/L	10 min
Activation Solution	$PdCl_2$	0.5g/L	RT
	HCl (37%)	1.189g/L	5 min
Reduction Solution	NaH_2PO_2	2g/L	RT
			30 sec

Table 2-4 Bath composition of EN solution

Solution	Batch	Composition	Condition
EN Bath	$NiSO_4 \cdot 6H_2O$	25g/L	pH 5
	CH_3COONa	10g/L	(by 98% H_2SO_4)
	$Na_3C_6H_5O_7 \cdot 2H_2O$	11.4g/L	90ºC
	NaH_2PO_2	20g/L	10 min

2.2.9 Fabrication and characterization of PI lens

The etching time was decreased to 15 min and the plating time was shrunk to 7 min. All the other processing steps were used as the same described in Section 2.2.8. The adhesion between EN and PI lens was measured by Scotch Tape Testing.

2.3 Results and discussions

The reasons that might cause unacceptable plating can be categorized into four groups: improper substrate preparation, bath chemistry imbalance, solution contamination and equipment/mechanical problems. Any problem of the plating may be due to any one or more of the above reasons. Many factors may have effects on plating and adhesion such as etching, etching time, sensibilization and activation; rinsing and EN bath chemistry (Mallory, *et al.*, 2002).

2.3.1 Effects of etching and etching time

The etching temperature may range from 60ºC to 90º. In this experiment, the PI substrate is etched by a sulfochromic mixture at 60ºC for the reason of simplicities. Etching is the key step for EN plating on PI. The mechanism of

etching, which consists of PI surface modification of being oxidized by CrO_3/H_2SO_4, has been investigated. The PI shows an increased surface area and provides microscopic holes to achieve good adhesion between the interfaces of Ni deposition and PI. Chromium acid is a strong oxidizing solution and can turn the PI surface from a hydrophobic material to a hydrophilic material. Also by applying chromic acid treatment, precise modification control may be realized to obtain adequate cavities on the PI surface. In the following steps (sensibilization and activation), these cavities provide "traps" for ions (Mallory, *et al.*, 2002). Our experimental results have confirmed the importance of etching to achieve good adhesion of Ni plating on PI as shown in Figure 2.12 (a). And all the other pre-treatment steps and reaction conditions for these two PI samples are the same. Direct deposition of EN on pre-treated PI with sensibilization, activation and reduction, but without etching exhibited poor adhesion as shown in Figure 2.12 (b).

(a)   (b)
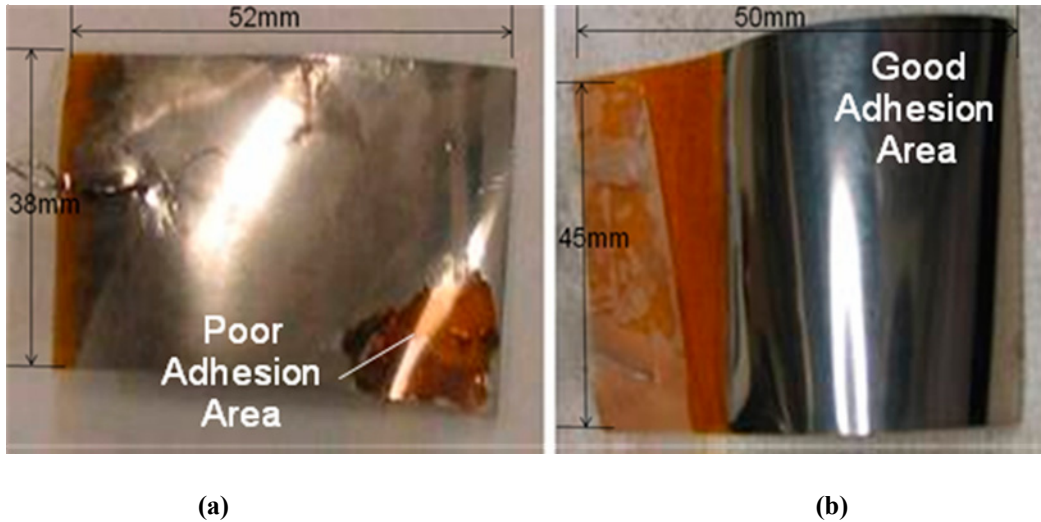
Figure 2.12 (a) PI sample with EN plating after Scotch Tape Testing (without etching); (b) PI sample with EN plating after Scotch Tape Testing (with etching time 30 min at 60ºC).

Etching time can affect the modified thickness. Excessive etching time will result in thinner thickness of the modified PI surface. Also to obtain good interfacial adhesion between Ni film and PI, PI surface must be etched to a proper state. A series of samples with five different etching times were prepared for investigating the effects of etching time on the plating and adhesion. The etching time in the etching solution increased in 10 min steps up to 50 min. The results of the etching

time and the adhesion are given in Table 2.5. According to experimental results, an etching time of 30 min can satisfy the modification requirements for PI membrane.

Table 2-5 Effect of etching time on adhesion

Etching Time (min)	10	20	30	40	50
Adhesion	Poor	Poor	Good	No Plating	No Plating

*all the other pre-treatment and reactions conditions were the same.

2.3.2 Effects of sensibilization and activation

As non-conductive substrate, the PI must be "planted" with noble metal particles as catalysts to initiate the electroless plating reaction. During the immersion into sensibilization solution, the cavities that have been generated in the etching step can absorb Sn^{2+} ions. Subsequently the Sn^{2+} ions can be replaced via ion exchange by immersing the pre-treated PI membrane into an activation solution that contains Pd^{2+} ions. Thus the Pd particles will initiate the EN plating reaction when the pre-treated PI membrane is immersed in ready-to-use chemical bath. The importance of the sensibilization and activation for EN plating on the non-conductive PI substrate was tested by experiments and the results are shown in Figure 2.13.
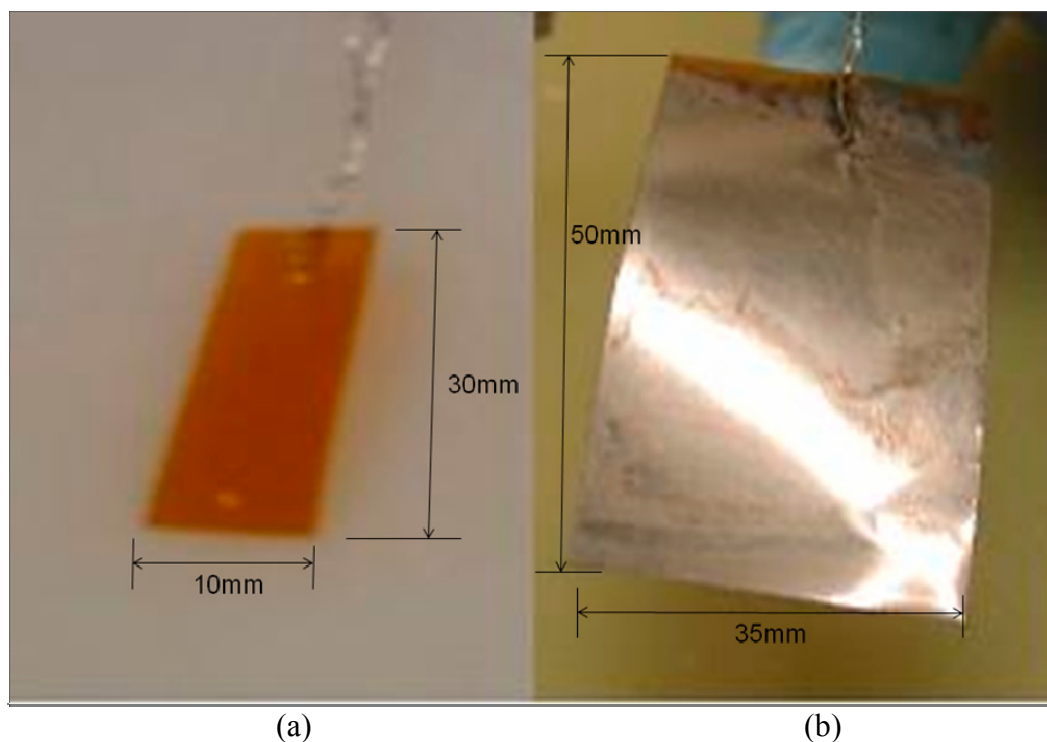
| (a) | (b) |

Figure 2.13 (a) PI sample after EN plating (without any pre-treatment except etching); (b) PI sample after EN plating (with pre-treatment)

Sensibilization, activation and reduction time were controlled at 10 min, 5 min and 30 sec, respectively, because appropriate treatment time for each step ensured absorption and replacement of metal ions in maximum content within the given time range.

2.3.3 Effect of rinsing

It is important to rinse the surface 60 sec after each pre-treatment step to avoid introducing any impurities or drag-in ions or particles which might be poisonous to the reaction and even result in instability of reaction solution. But overtime rinsing should be avoided; otherwise, the pre-treated substrate might become even non-catalysts when all ions or particles have been rinsed and dispelled with DI water.

2.3.4 Effects of EN bath chemistry

A typical EN solution contains the components as following: nickel sulphate hexahydrate (as oxidizing agent), sodium hypophosphate (as reducing agent), sodium acetate (as complexing agent), sodium citrate dehydrate (as buffering

agent) and sulphuric acid (as pH adjustor). The plating process must be taken care of well enough even with good pre-treatment guaranteed (Mallory, *et al.*, 2002).

1) pH value

The pH value of plating bath is adjusted at 5, although the reaction may occur between 4~6 (Mallory, *et al.*, 2002). If pH value exceeds 6, the solution will be unstable; however if pH value is below 4, low deposition rate or no deposition will happen.

2) Agitation

Continuous agitation is necessary (Mallory, *et al.*, 2002). The speed in this research is kept at 60r/m. EN film has a tendency to blister during the deposition process because of the evolution of hydrogen gas. Thus too slow agitation will cause Ni film with troubles such as blistering. Too heavy agitation inducing pitting, pattern or streaking of the plating should also be avoided.

3) Temperature

The plating rate generally increases with temperature. The reaction occurs only when the solution temperature is above 60ºC; but when the temperature of the solution exceeds 95ºC, the solution can be unstable and decomposed and plate-out on the reaction solution container. The temperature for the reaction process should be strictly controlled at 90ºC, but usually the solution temperature might fluctuate $\pm$ 1~2ºC.

2.3.5 Effect of reaction time

The thickness of the EN film has an effect on interfacial adhesion between Ni and PI. It is reported that too thin plating will lead to poor adhesion. The thickness of film increases when the reaction time extends. But the reaction will stop at a time limit since the reaction ions will be exhausted (Mallory, *et al.*, 2002). Due to the etching of the PI surface, it is difficult to precisely measure the thickness of Ni film. Thus in this experiment, we evaluated the effect of the reaction time on film adhesion to find out the proper reaction time. Scotch Tape Testing has been used to test the adhesion between deposited Ni and PI substrate. The result is listed in Table 2.6.

Table 2-6 Effect of reaction time on adhesion

Reaction Time (min)	5	10	20	30
Adhesion	Good	Good	Poor	Poor

*all the other pre-treatment and reactions conditions were the same.

The adhesion of the plated Ni film decreased when too thick Ni film is deposited. One possible reason is that when the Ni film is too thick, the water or moisture that has been absorbed during the electroless deposition process is more difficult to be evaporated; thus the Ni plated PI structure easily delaminates. From our experiment results, the optimized reaction time for EN plating on PI was 10 min.

2.3.6 Scotch Tape Testing

In the Scotch Tape Testing, the Ni coating showed poor adhesion if it could be peeled off by the tape. If the plating survives from the tape testing, it shows desirable good adhesion between the Ni and PI layers, and was good for use of following UT fabrication.

2.3.7 Optimization of size of top electrode

The result of signal amplitude versus the diameter of the top electrode is shown in Figure 2.14. The top electrode was made by Ag paste. The size increased from 2.5mm to 15mm in diameter and then the signal strength was measured after each increase. Figure 2.14 indicates that the optimal top electrode size for this FUT is 11mm in diameter.
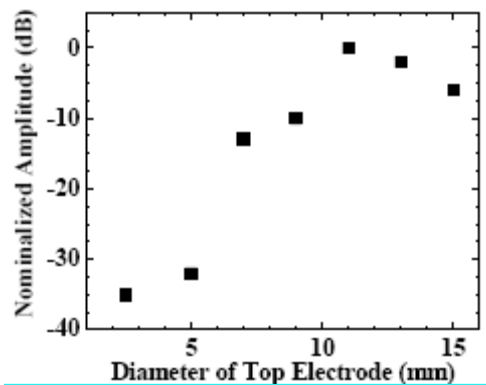

Figure 2.14 Signal amplitude versus the diameter of the top electrode of one FUT

2.3.8 Characterization of Ag/PZT-C/Ni/PI FUT

Figure 2.15 shows the FUT response, in time and frequency domains respectively, in pulse-echo mode at RT. L^2 and L^4 are the first and second round trip echoes through the 13.8mm thick SS plate. The center frequency, the 6dB band width and SNR of the L^2 echo are determined to be 13.8MHz, 5.5MHz and 17dB, respectively. The ultrasonic response of the FUT at 150°C is shown in Figure 2.16. The center frequency, the 6dB bandwidth and SNR of the L^2 echo at this operating temperature is 11.3MHz, 5.1MHz and 22dB respectively. It is observed that the signal strength of the L^2 echo at RT was decreased by about 6dB and the frequency bandwidth reduced by 0.4MHz as the FUT operated at 150°C because of the increased attenuation in the substrate couplant, and reduced strength in PZT layer.

(a)   (b)
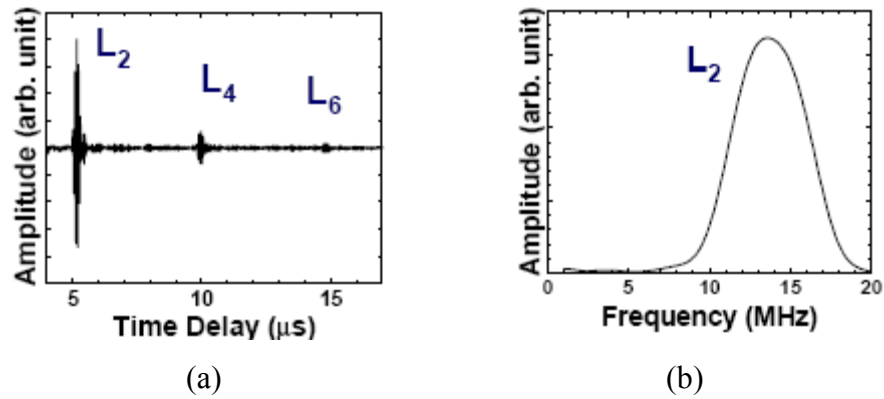
Figure 2.15 Ultrasonic performance of the FUT when being pressed onto a 13.8mm thick SS plate in (a) time and (b) frequency domain at RT under Pulse-echo mode

(a)   (b)
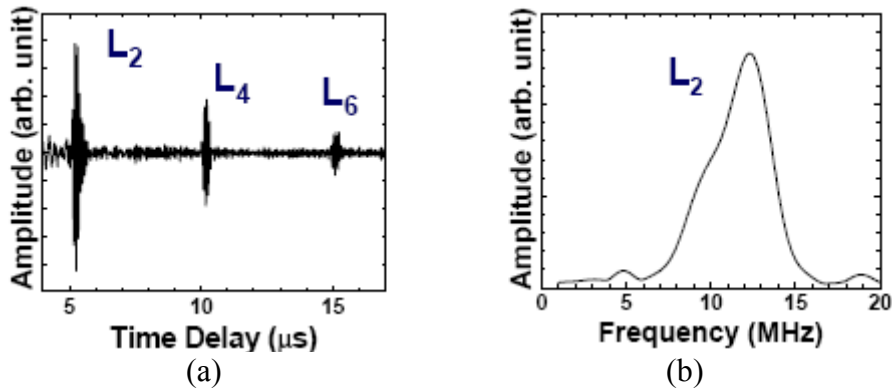
Figure 2.16 Ultrasonic performance of the FUT when being pressed onto a 13.8mm thick SS plate in (a) time and (b) frequency domain at 150°C under Pulse-echo mode

2.3.9 EN plating on large area PI and PI lens

The EN plating on PI membrane and PI rod showed good adhesion by Scotch Tape Testing (as shown in Figures 2.17 and 2.18).

Figure 2.17 An En plated PI after Scotch Tape Testing

Figure 2.18 An EN plated PI lens after Scotch Tape Testing

2.4. Conclusions
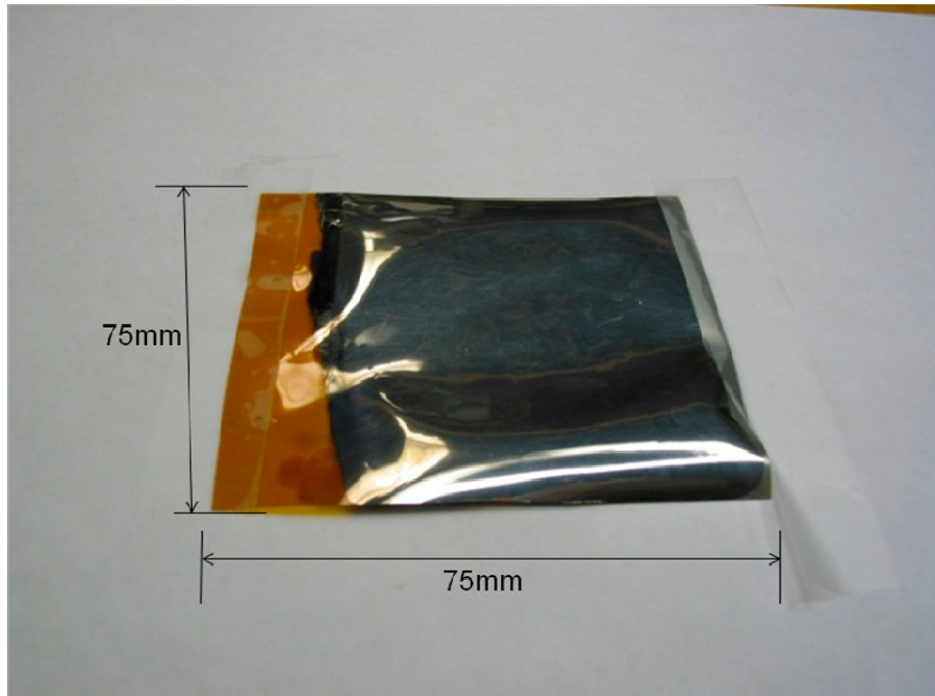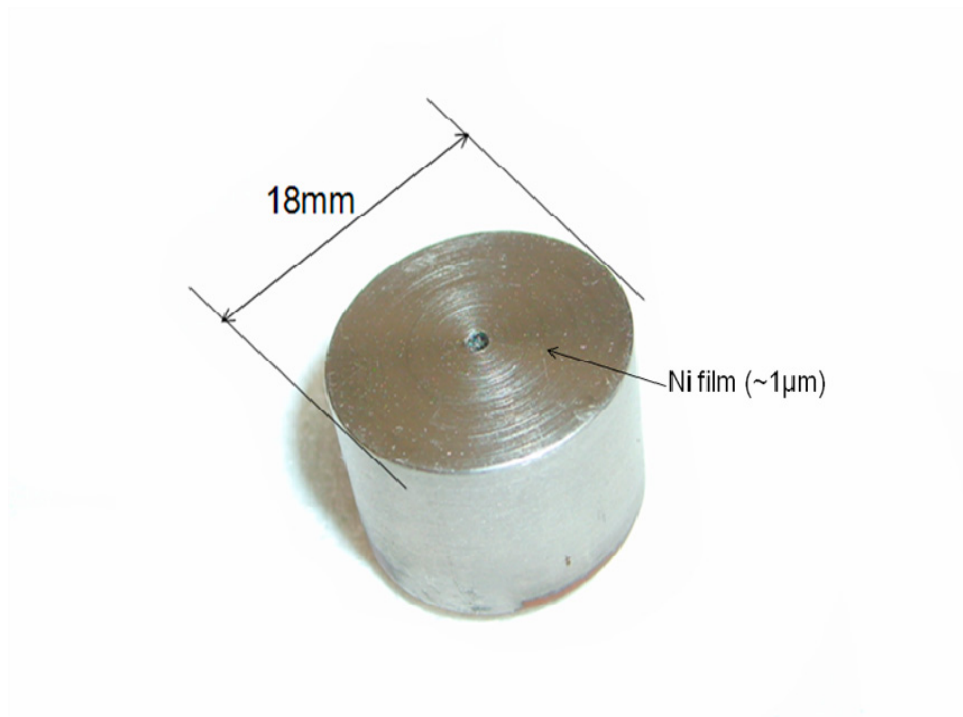
Various factors influencing the EN plating on PI were investigated. The properties such as interfacial adhesion between Ni and PI were strongly dependent on the pre-treatment (especially etching time) and the electroless plating time. A series of experiment results were analyzed to find out optimized methods to improve the adhesion of the Ni film on the PI surfaces. In terms of pre-treatment, etching was important to improve adhesion. When the etching time was less than 30 min, the plating showed poor adhesion and was easily peeled off in the Scotch Tape Testing; when the etching time was longer than 30 min, no plating could be deposited on the sample surface because the PI surface had been over-etched. Adhesive strength was the greatest when the PI was first etched in chromium acid at 60ºC for 30 min, next treated with sensibilization solution, activation solution and reduction solution for 10 min, 5 min and 30 sec, respectively. Adhesion was also improved when degreasing the PI surface well by dishwashing liquid and swelling the surface with organic solvent such as methanol and acetone. In terms of the reaction time, it was found that 10 min gave the best adhesion Ni plating on PI. Proper agitation and stable reaction temperature at 90ºC also have a positive effect on good Ni film with good adhesion. This method has been extended to deposit EN film on both 75mm by 75mm PI substrate and other PI material substrate in cylinder shape as bottom electrode. After the deposition of EN film on PI substrates, the samples were dried in the RT for 24 hr. The Scotch Tape Testing was carried out to each plated sample for qualitative evaluation of the adhesion achieved between Ni and PI interface. Due to the weight and thickness loss of the substrates in the etching step, it was not possible to determine the Ni film thickness. A thickness less than 1μm of Ni film with reaction time of 10 min was estimated. A PZT sol-gel spray technique was used to fabricate the piezoelectric film and Ag paste was applied as top electrode. The Ag/PZT-C/Ni/PI FUT was tested on a metal substrate of 12.7mm thick in a pulse-echo mode and showed 13.8MHz, 5.5MHz and 17dB for the center frequency, the 6dB band width and SNR of the L^2 echo respectively, in pulse-echo mode at RT; and

11.3MHz, 5.1MHz and 22dB for the center frequency, the 6dB bandwidth and SNR of the L^2 echo at 150°C respectively.

3. Fabrication and Evaluation of IUT Using the Electroless Plating Technique

3.1 Introduction

Composite materials such as Gr/Ep laminates are becoming the materials of choice for aerospace structures because of the high strength to weight ratio. Diagnostic structural health monitoring (SHM) and NDT technologies are increasingly being investigated by the aerospace industry to enable condition-based maintenance for cost-effective increased safety and eco-efficient designs (Birks, *et al.,* 1991; Gandhi, *et al.,* 1992; Giurgiutiu, *et al.,* 2002; Ihn, *et al.,* 2004). The IUTs and FUTs may provide real-time diagnostics (RTD) to detect defects for real-time SHM of Gr/Ep composites. With annual costs of maintenance of airframe structures at \$10.4 billion worldwide, SHM is a major objective of the aerospace community. The implementation of RTD IUT and FUT may reduce these costs by enabling condition-based maintenance based on RTD data for estimating the remaining life on a continuous basis. This approach will also enable modern aircraft designs with increased safety and cost reductions. In addition, RTD of Gr/Ep composites processing will help in the development of more efficient processes to significantly reduce production costs and increase composite use, resulting in energy savings, clean environment and life extension.

The PZT-C film based IUT can be designed with a structure of Ag/PZT-C/Ni/(Gr/Ep). The Gr/Ep composites may have high or low electrical conductivities. Their resitivities can be measured by using a standard four-point-probe. These composites may have dramatic different resistivities ranging from 0.2Ω-m to $22,000\Omega$-m at different locations. In general, its resistivity is higher than several hundred Ω-m. EN plating can be applied on Gr/Ep to serve as high conductivity bottom electrode. Chapter 2 has reported that EN plating has been successfully deposited on pre-treated PI substrates with good adhesion. It is expected that a similar method described in Chapter 2 may also be applied to

Gr/Ep composite samples with some modifications of electroless plating procedures. In this chapter, an optimized processing step will be investigated for successful EN plating on Gr/Ep substrates with good adhesion (Palaniappa, *et al.*, 2007). EN chemical bath and its process control have been intensively discussed. The successful EN plating on PI in Chapter 2 offers us a great of advantages in recipe choice and electroless plating process control. Here, only several factors are investigated in order to obtain Ni plating with good adhesion on Gr/Ep: (1) pre-treatment steps; (2) pre-treatment time; (3) reaction time.

In this chapter, we present our research studying the fabrication and evaluation of IUT coated on Gr/Ep composites. The bottom electrode of IUT is electroless plated Ni onto Gr/Ep composites. Firstly, we will study the effects of pre-treatment steps and optimized reaction conditions to ensure good interfacial adhesion EN plating on Gr/Ep. After applying EN plating method on Gr/Ep composite, the Ni plating properties such as adhesion will be evaluated. The piezoelectric PZT-C film and Ag top electrode fabrication technique and evaluation method will be the same as those mentioned in Chapter 2. Finally, the evaluation of IUT (Ag/PZT-C/Ni) on Gr/Ep composite will be carried out in pulse-echo mode.

3.2 Experimental procedures

3.2.1 Materials and sample preparation

All chemicals are the same as those used in Chapter 2, and used as received. Gr/Ep composites were obtained from NRC-IMI. A 1 mm thickness uni-directional Gr/Ep composite was cut into pieces for use. Also a honey cone structure Gr/Ep with dimensions of 370mm by 370mm has been used. The designed Ni plating area has a triangle area of 112 mm by 112mm at one edge. All of the composite samples are cleaned and rinsed in the same way as that for PI reported in Chapter 2.

Dishwashing liquid, RT, 10 min→rinsed by DI water→ methanol, RT, 2 min→rinsed by DI water→ acetone, RT, 2 min→ rinsed by DI water

3.2.2 EN plating on uni-directional Gr/Ep composite

Two uni-directional Gr/Ep composite samples are used to evaluate the effect of etching. Sample #1 with dimensions of 36mm by 52mm was etched by etching solution for 10 min and then rinsed well by DI water before the sensibilization step; for Sample #2 with dimensions of 32mm by 40mm, no etching step was applied. The pre-treatment solution and Ni bath composition are the same as described in Tables 2.1 and 2.2.

3.2.3 EN plating on large area honey cone structure

In order to verify that IUT can be deposited onto woven structure composites, a Gr/Ep sample with woven honey cone structure was selected. The resistivity measured for this sample was ~1.5Ω-m. The chemical solution composites are the same as the one for uni-directional Gr/Ep.

3.2.4 Fabrication of PZT-C piezoelectric layer and Ag top electrode

The fabrication of PZT-C composite film, the top electrode and poling technique were the same as those described for the PI substrate samples. For sample #2, a layer of 60μm thick PZT-C film was then deposited on top of this Ni layer and poled. A top electrode of 7mm diameter was made using Ag paste (shown in Figures 3.1 and 3.2). For IUT made on a honey cone structure Gr/Ep, after a ~1μm thick Ni layer as the bottom electrode of the IUT was coated at the corner (shown in Figure 3.6) of this sample, a layer of 60μm thick PZT-C composite film was then deposited at different places of this corner and poled. Ag paste was used to form the top electrodes of IUTs.
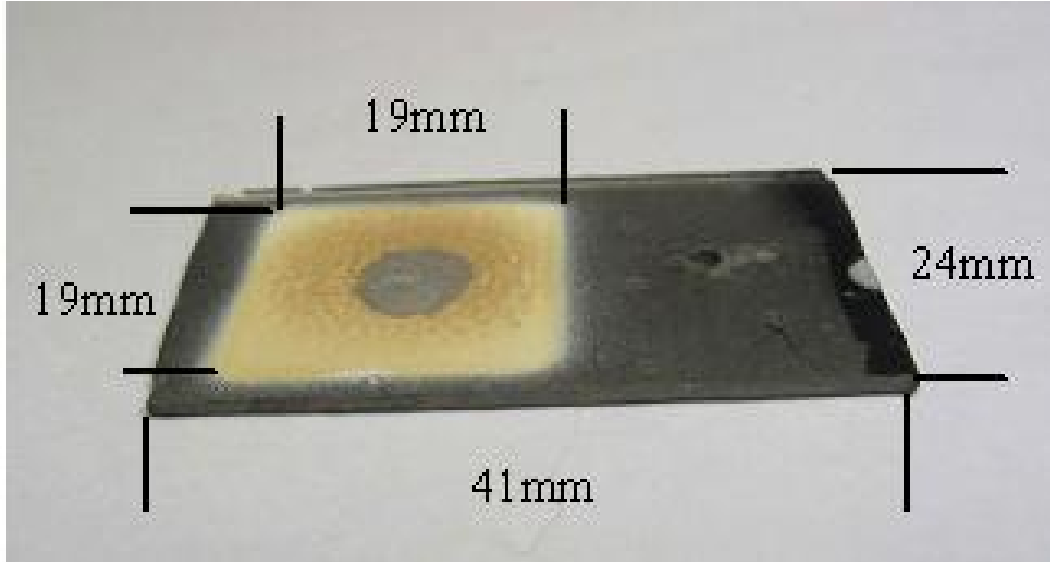
Figure 3.1 A UT using Gr/Ep as the substrate with electroless coated Ni alloy film as bottom electrode
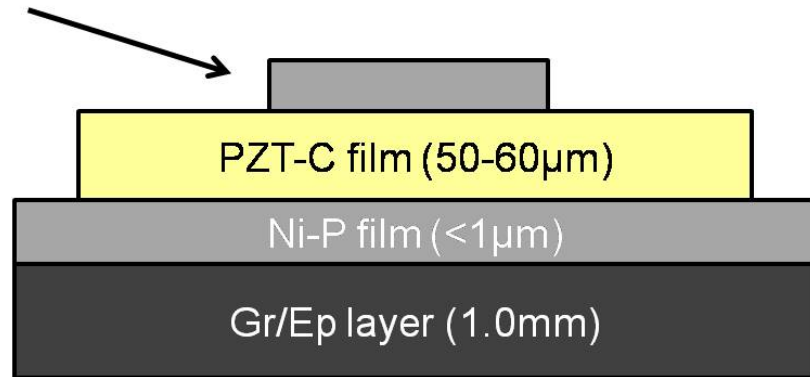
Figure 3.2 Schematic diagram of a UT using Gr/Ep as the substrate with electroless coated Ni alloy film as bottom electrode

3.2.5 Characterization of (Ag/PZT-C/Ni/ (Gr/Ep)) IUT

The ultrasonic performances of this IUT were tested at 23°C in a pulse-echo mode. The experimental results are shown and discussed in Section 3.3.3.

3.3 Results and discussion

3.3.1 Effect of etching on EN of Gr/Ep

For Gr/Ep substrate, the importance of the pre-treatment is exactly the same as for PI. But one difference is that no etching is required for Gr/Ep. From an experimental result, the Ni plating has been deposited and showed good adhesion

on the Gr/Ep without etching (see Figure 3.3). When etching was applied, the sample surface could be deposited with Ni but the surface of the sample became very coarse (see Figure 3.4). For EN plating on Gr/Ep, it was concluded that the etching step was unnecessary.
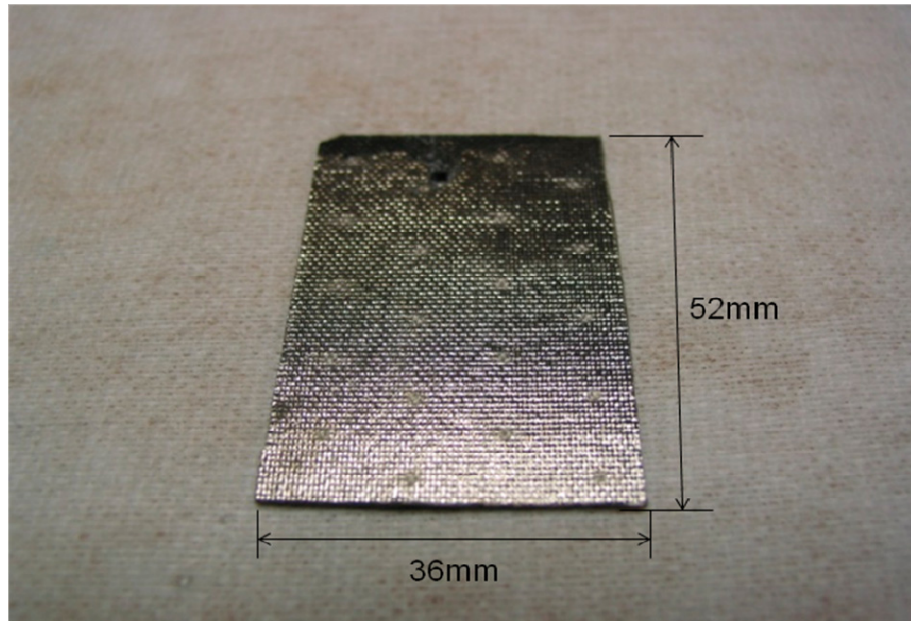

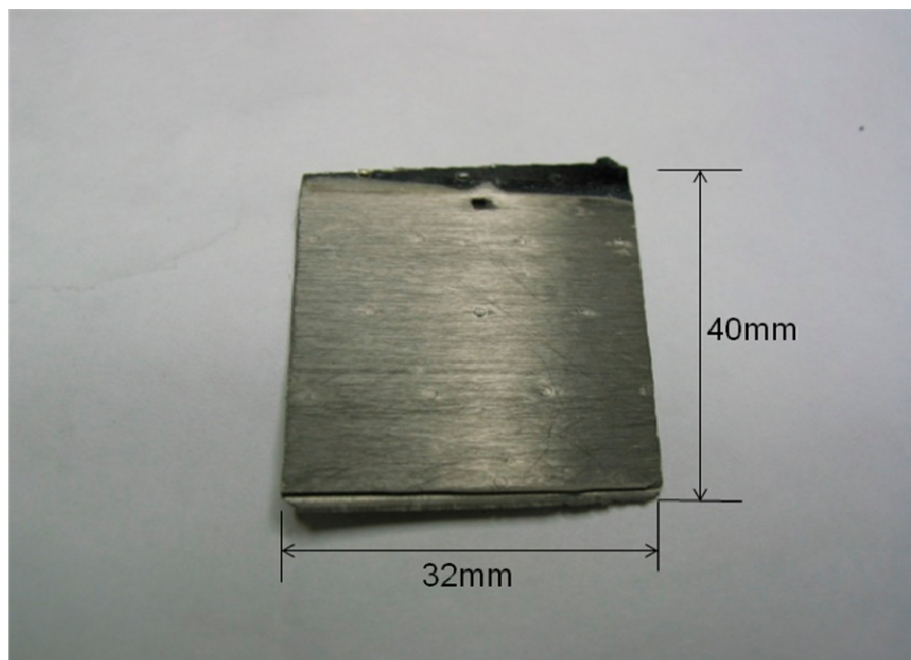**Figure 3.3 EN plated Gr/Ep without etching**

Figure 3.4 EN plated Gr/Ep with etching time of 10 min

For EN plating, Gr/Ep composite experienced pre-treatment and was immersed in a chemical bath for 10 min. In summary, a good pre-treatment flow for Gr/Ep composite is given in Table 3.1.

Table 3-1 Process parameters

Process	Condition	
Cleaning	Dishwashing liquid	5 min*
	Methanol	2 min
	Acetone	2 min
Sensibilization	Tin (II) Chloride	3g/L
	Hydrochloric Acid (37%)	3.567g/L
	Volume	80ml**
	Temperature	RT
	Immersion time	10 min
Activation	Palladium Chloride	0.5g/L
	Hydrochloric Acid (37%)	11.89g/L
	Volume	80ml
	Temperature	RT
	Immersion time	5 min
Reduction	Sodium Hypophosphite	2g/L
	Volume	80ml
	Temperature	RT
	Immersion time	30 sec
EN	EN Solution as Recipe***	10 min
Drying	RT	24 hr

* All solutions were diluted by DI Water to a certain volume;
** After each step, the substrate was rinsed well by DI water;
*** EN solution recipe is the same as given in Table 2.2.

3.3.2 EN plating on honey cone structure Gr/Ep

Based on the experimental obtained results from EN plating on uni-directional Gr/Ep, specified pre-treatment steps and reaction control are also suitable for honey cone structure Gr/Ep. The chemical composite for each solution was the same as the one used for former two uni-directional Gr/Ep samples. Only the volume of each solution (sensibilization, activation, reduction, and EN bath) was increased to 1200ml. The Scotch Tape Testing result showed good adhesion that has been achieved between Ni layer and Gr/Ep (in Figures 3.5 and 3.6).
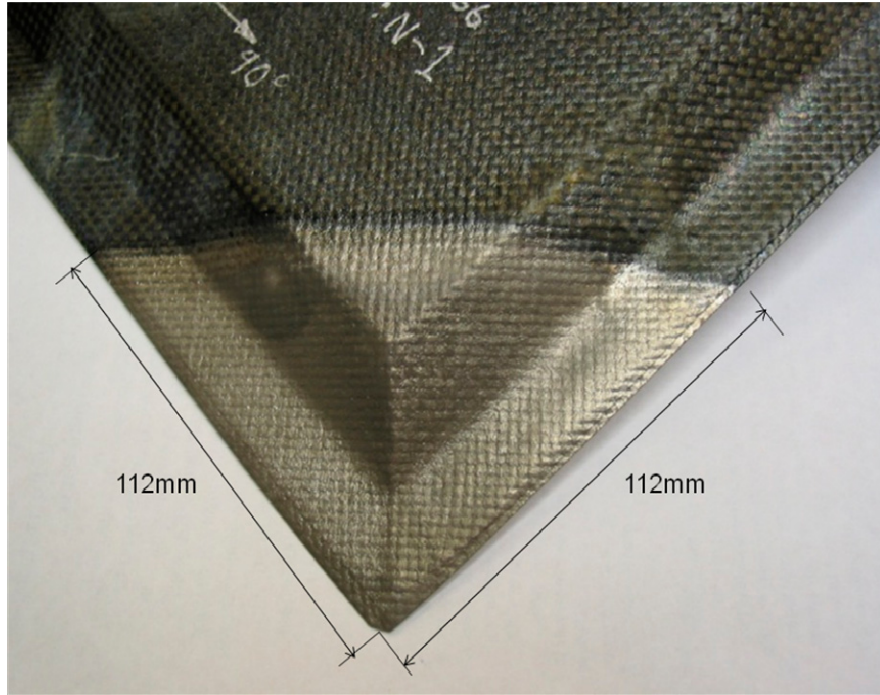
Figure 3.5 EN plating on honey cone structure Gr/Ep (before Scotch Tape Testing)
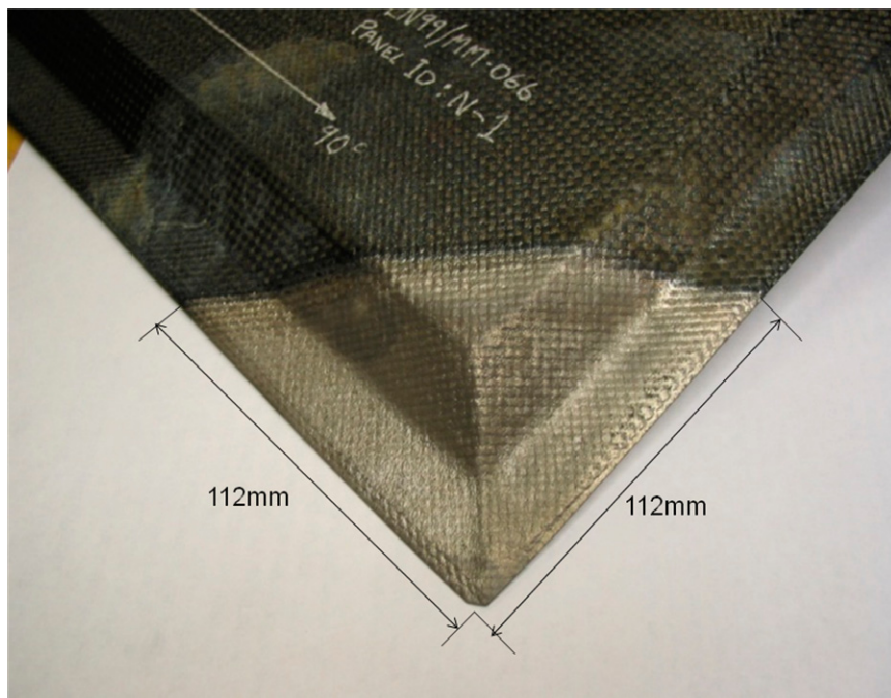

Figure 3.6 EN plating on honey cone structure Gr/Ep (after Scotch Tape Testing)

3.3.3 Characterization of IUT (Ag/PZT-C/Ni) onto Gr/Ep Composite

The performance of this IUT was tested at RT, and results are shown from the measurement results. The measured ultrasonic signals are given in Figure 3.7. The center frequency and 6dB bandwidth of the L^1 echo are 10.5MHz and 13.6MHz, respectively. The thickness of the Gr/Ep at the IUT site is 1mm.

(a)   (b)
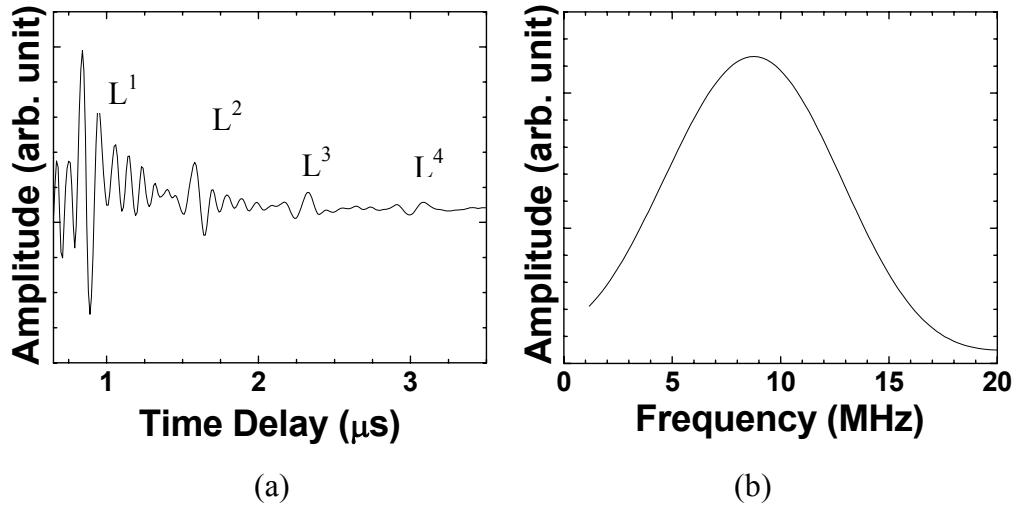
Figure 3.7 Ultrasonic performance of Ag TE / PZT-C / Ni / (Gr/Ep) shown in (a) time and (b) frequency domain at RT. Pulse-echo mode was used.

3.3.4 Fabrication and characterization of IUT(Ag/PZT-C/Ni) on honey cone structure Gr/Ep composite

Here only the measured ultrasonic signals using the IUT_1 indicated in Figure 3.8 are shown in Figure 3.9. The thickness of the Gr/Ep sample at the IUT_1 location is 1.58 mm. The center frequency and 6dB bandwidth of the L^1 echo were 7.6MHz and 7.7MHz, respectively. Figures 3.8 and 3.9 clearly show that IUT can be deposited and operated on such woven structure composite.

Figure 3.8 An IUT deposited onto a 1mm thick Gr/Ep composite plate.
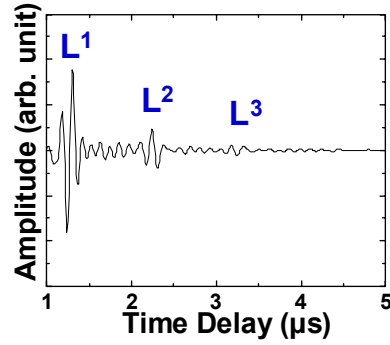
Figure 3.9 Measured ultrasonic signals in time domain at RT using the IUT$_1$ shown in Figure 3.8

3.4 Conclusions

The optimized processing conditions were obtained by analyzing preliminary studying results. The etching step was unnecessary for EN plating on Gr/Ep composite. All the other pre-treatment steps were similar to those for PIs. The pre-treatment time for sensibilization, activation and reduction were fixed at 10min, 5 min and 30 sec. The immersion time of any Gr/Ep sample in EN bath was 10 min. The reaction solution had a pH of 5 and the reaction temperature was 90ºC. Agitation was required to assist the release of hydrogen produced in the reaction and to keep solution homogeneous in the reaction process. The adhesion of the Ni layer on Gr/Ep was tested by Scotch Tape Testing. For both of Ni plated Gr/Ep samples, the piezoelectric film was a layer of 60μm thick PZT-C composite. Ag paste was applied as top electrode. The ultrasonic performances of these UT were tested at RT in a pulse-echo mode.

To characterize the IUT (Ag/PZT-C/Ni) deposited onto a 1mm thick uni-directional Gr/Ep composite, the center frequency and 6dB bandwidth of the L^1 echo were 10.5MHz and 13.6MHz, respectively. Several IUTs were deposited onto a honey cone structure Gr/Ep. The center frequency and 6dB bandwidth of the L^1 echo measured by IUT$_1$, shown in Figure 3.8, were 7.6MHz and 7.7MHz, respectively.

4. On-site EN Plating for Fabrication of IUT

4.1 Introduction

In Chapter 2 and 3, EN plating processes have been developed for Ni film on PI and Gr/Ep. Both PI and Gr/Ep substrates were immersed in a chemical bath. Pre-treatment steps were required to initiate EN plating and to ensure adequate adhesion (Charbonnier, *et al.*, 2004). EN plating has been deposited on both PI and Gr/Ep substrates by immersion in the chemical bath. During the processes, DI water was being applied for both dilution of solution and rinsing samples.

As mentioned in Chapter 1, on-site fabrication of IUTs is desirable for industrial applications. On-site fabrication means that for the IUT fabrication the large parts or substrates will remain not-moved, rather the fabrication kit, including electroless plating tools, should be portable and carried to the site of large parts or substrates. A portable fabrication kit is needed to satisfy such requirements. Based on the successful processes control for EN plating on PI and Gr/Ep, several modifications should be specified to accommodate changed situations from lab to on-site environment. Also for the fabrication of EN as bottom electrode for FUTs on PIs, it was considered to use tap water rather than DI water for rinsing samples. For on-site fabrication of EN as bottom electrode for IUTs on Gr/Ep, it was preferable to finish all the pre-treatment steps by the solution spray technique and deposit the EN film on Gr/Ep directly. Furthermore, a chemical bath for EN at RT can be more attractive and convenient for the on-site fabrication method. In addition, the 90ºC EN plating method was tried to fabricate top electrode on PZT-C film and the results prepared the preliminary work for further research.

In this chapter, we will present our research as follows: it begins with an experiment by applying tap water rather than DI water for rinsing the PI surface during the EN processes, but all other processing control will remain the same as described in Tables 2.1 and 2.2. Then the solution spraying technique will be carried out for each pre-treatment step and chemical reaction process for EN

plating on Gr/Ep. All pre-treatment steps and reaction conditions will be kept as described in Table 3.1 for Gr/Ep substrates. Then a new EN bath composition was taken for Ni deposition on PI at RT; followed by an investigation for the feasibility of EN plating on PZT-C film.

4.2 Experimental procedures, results and discussions

Unless specified, all materials and chemicals used in this chapter are the same as those used in previous experiments. Tetra sodium pyrophosphate and borane dimethylamine are purchased from Sigma-Aldrich with ACS grade. Both of them were used as received.

4.2.1 EN plating on PI by rinsing with tap water

The PI sample was prepared, cleansed, pre-treated and plated with the same procedures which were described in Tables 2.3 and 2.4. But one exception is that tap water was used, instead of DI water, for rinsing during all the processes. After 24 hours of drying in RT air, the adhesion between Ni and PI was tested by Scotch Tape Testing.

4.2.2 EN plating on Gr/Ep by solution spray technique

The Gr/Ep sample was cleaned and pre-treated in the order that was listed in Table 3.1. But each solution was sprayed by pipette directly on the sample surface. The deposited Gr/Ep sample was dried at RT air before Scotch Tape Testing.

4.2.3 Chemical bath for EN at RT

The PI sample was prepared, cleansed, pre-treated according to the same procedures described in Table 2.1. And the reaction solution is prepared according to the following steps:

1. Add 7.588g nickel sulphate hexahydrate into DI water 40 ml (solution A);
2. Mix well until nickel sulphate hexahydrate becomes completely melted;
3. Add tetra sodium pyrophosphate 16g into 40ml DI water and mix to help the crystal dissolve (solution B);
4. Add borane dimethylamine 0.48g to solution B and mix well (solution C);

5. Add solution C into solution A and add volume to 160ml;

6. Shake well to help all crystals dissolve;

7. Adjust pH to 5 using ammonium hydroxide (reaction solution).

Then the pre-treated PI sample is immersed into the RT solution (shown in Figure 4.1) and removed from the solution after 10 min. Afterwards the Ni plated sample is dried at RT air for 24 hours before observation and evaluation.

Figure 4.1 Arrangement of EN plating experiment (RT recipe)

4.2.4 EN plating on PZT-C film

The PZT-C/Ni/PI sample is pre-treated firstly by sensibilization solution for 10 min and rinsed well by DI water; it is then dipped in activation solution for 5 min and rinsed well by DI water. The chemical compositions of each solution are given in Tables 4.1 and 4.2.

Table 4-1 Chemical compositions of sensibilization solution

$SnCl_2 \cdot 2H_2O$	0.3g/100ml
HCl (37%)	0.3567g/100ml

Table 4-2 Chemical composition of activation solution

$PdCl_2$	0.05g/100ml
HCl (37%)	1.189g/100ml

The pre-treated sample is immersed into reaction solution for 60 min and removed out of the solution, then immersed into a new reaction solution for another 60 min. Then the sample is dried in air for 24 hours and for observation.

4.2.5 Effect of rinsing by tap water on EN of PI

The Ni plating showed good adhesion in the Scotch Tape Testing (as shown in Figure 4.2). This experiment proved that rinsing by tap water does not make much difference compared with rinsing by DI water on EN deposition on PI in terms of adhesion.
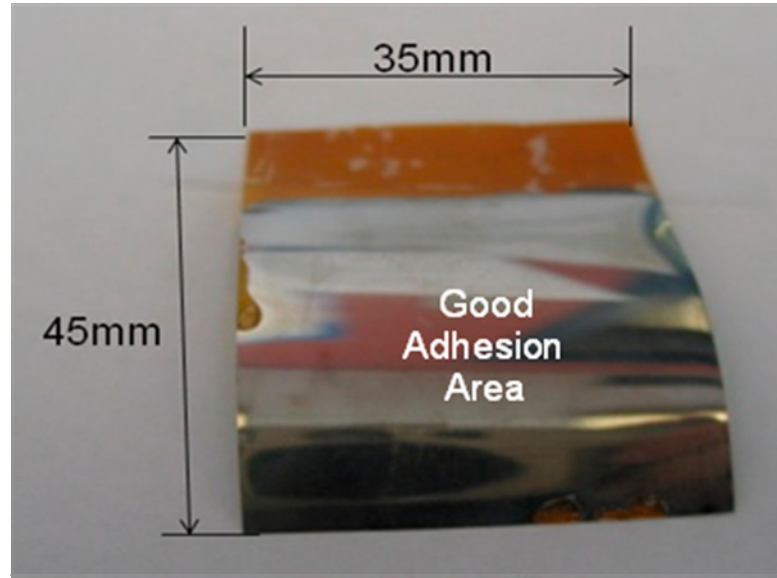

Figure 4.2 90ºC EN plated PI by rinsing with tap water (after the Scotch Tape Testing)

4.2.6 Effect of solution spray on EN of Gr/Ep

The Ni plating showed good adhesion in the Scotch Tape Testing (as shown in Figure 4.3). This experiment has proved that solution spray can be used as an alternate way of immersion for on-site fabrication of bottom electrode on Gr/Ep.
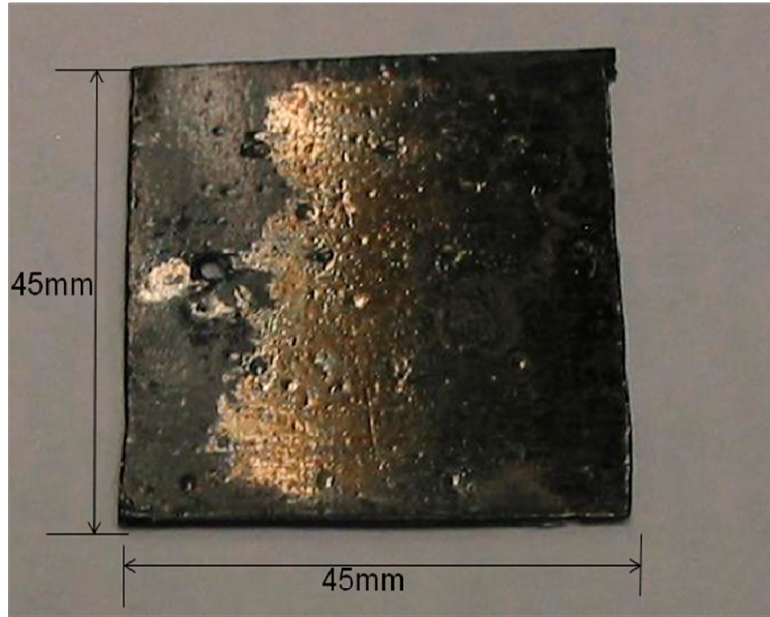
Figure 4.3 90ºC EN plated Gr/Ep with solution spray technique (after the Scotch Tape Testing)

4.2.7 Chemical bath for EN at RT

EN plating has been deposited at RT on pre-treated PI surface; but the surface of the plating is too coarse for its application as bottom electrode (as shown in Figure 4.4). Further research will focus on finding out a new bath composites recipe with reaction temperature at RT.
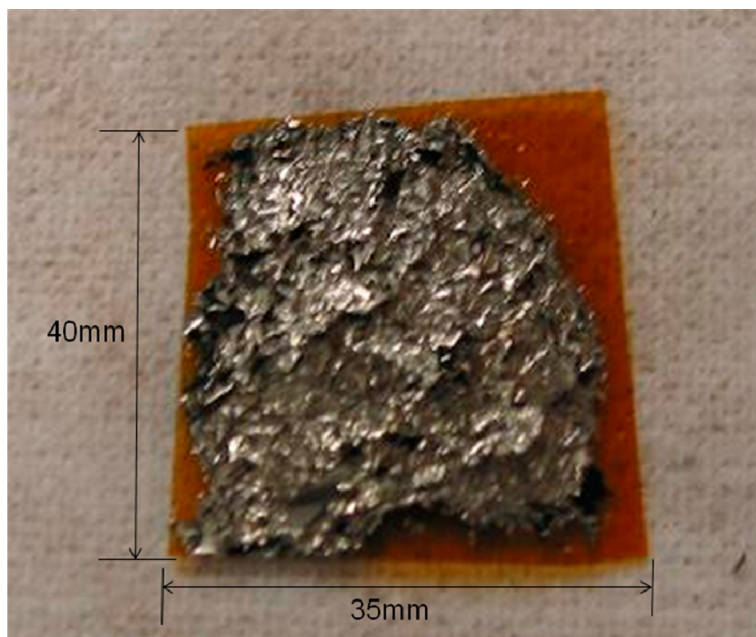
Figure 4.4 EN plated PI at RT

4.2.8 EN plating on PZT-C film

PZT-C film, as one kind of ceramics material, has numerous pores that may absorb ions and metal particles. But any chemical treatment might have caused damage to the PZT-C film itself. In the experiments, only sensibilization and activation solution were used to plant catalysts to initiate EN reaction. The same plating process had been repeated and applied to accumulate Ni film (as shown in Figure 4.5). The Ni film has many problems such as black deposit, dullness, skip plating and roughness which can not be used as bottom electrode.

Figure 4.5 90ºC EN plated PZT-C (a) after a turn over of 60 min; (b) after second turn over of 60 min (in same fresh solution)

4.3 Conclusions

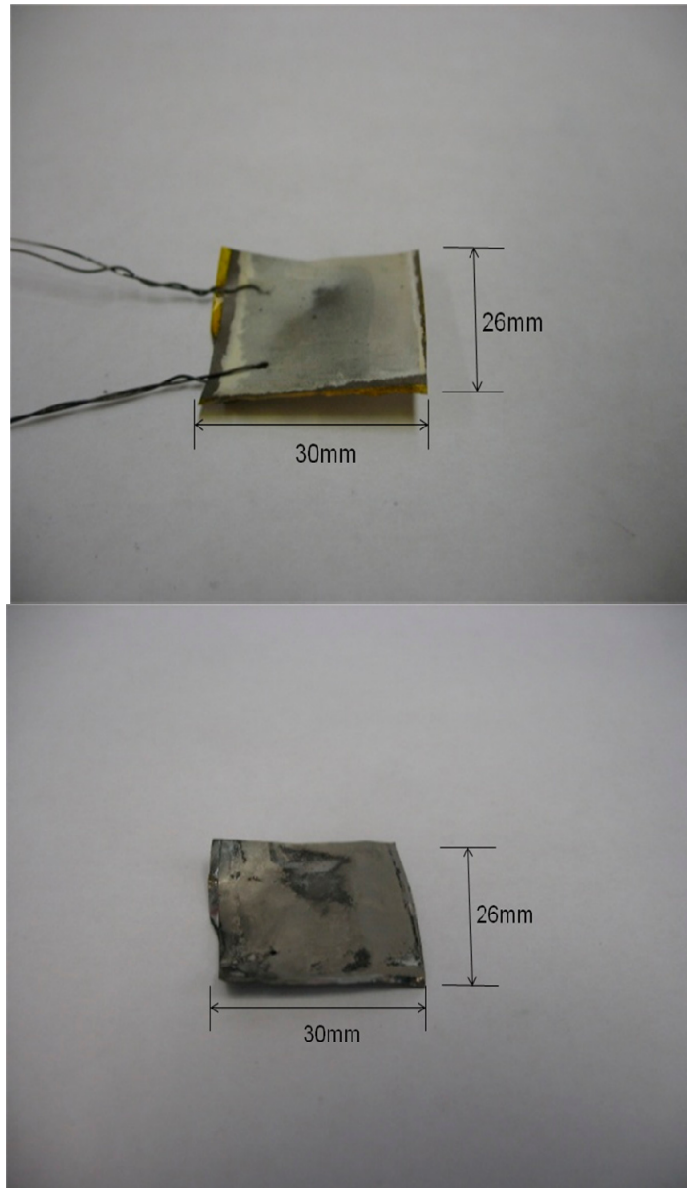The research in this chapter illustrates the feasibility of on-site fabrication of FUTs and IUTs. The applications of tap water rinsing and solution spray technology led to successful Ni plating with good adhesion on PI and Gr/Ep substrates. Further work will be continued with fabrication of PZT-C layer as piezoelectric film and metal as top electrode, and then these FUT and IUT characteristics will be tested and analyzed.

EN plating at RT was proved to be possible on PI substrate; but the composites did not satisfy the requirements for use as bottom electrode due to the roughness. A new chemical recipe must be found and carried out to achieve this goal.

EN plating has also been deposited on PZT-C film; but Ni film surface has problems such as black deposit, dullness, skip plating, roughness, etc. Also, RT EN plating processes might have caused damage on the PZT-C layer for its use as piezoelectric film. Also for integration of the IUT, the plating range should be limited within the designed area and a protecting layer is required. The choice of the protecting layer is difficult because it must not damage the PZT-C layer and must be easy to remove.

5. Fabrication and Evaluation of FUT Using Electroless Ag Plating Technique

5.1 Introduction

In the previous chapters, PI films have served as the substrate for the fabrication of FUTs. EN plating has been deposited on PI and acts as bottom electrode. Ag plating has been plated on modified PI (Buckley, *et al.*, 2006; Li, *et al.*, 2004). Also the colloidal Ag spraying technique has been directly applied on PI to achieve the purpose of metallization of PI and to provide low resistance and high conductivity bottom electrode (Kobayashi, *et al.,* 2007; Kobayashi, *et al.*, 2008). In this research, we applied electroless Ag plating on PI surface for obtaining bottom electrode and the following fabrication steps for the FUTs will be the same.

Electroless Ag plating on PI surface has been traditionally used to provide a conductive and reflective layer for applications which range from microelectronic to aerospace industry. Related work has been investigated in past years. A great number of substrates such as polymers, glass, metals and semiconductors can be coated in electroless Ag chemical bath (Buckley, *et al.*, 2006; Jiang, *et al.*, 2006). The key step for electroless deposition on dielectric materials is activation or seeding before metal plating (Chen, *et al.*, 2005). Various methods exist for making seeding layers before electroless plating. Previous efforts include chemical vapor deposition, and so on. Noble metals such as palladium can be chosen as seeding (Buckley, *et al.*, 2006; Jiang, *et al.*, 2006).

Traditionally, Ag mirrors can be deposited on glass in the Tollen's test which has been used to identify aldehyde and/or reducing sugar (Mitra, 2003). In the reaction, Ag ions react with an aldehyde or reducing sugar and are reduced to Ag particles which can be deposited on a glass surface. Generally Ag diamine solution can be called Tollen's reagent and works as a weak oxidant in the Ag

mirror reaction. Both glucose and methanal contain a function group of aldehyde. Reducing Ag salt with glucose and methanal can coat Ag mirror on substrate (Tracton, 2005). In this research, silver nitrate is chosen for its good solubility in water, so no organic solvent is required, and it is one compound that is available at high purity and at a low price (Dearden, 1976). In this reaction, the silver diamine complex is reduced by glucose and methanal to metallic Ag and forms deposition in situ. The reaction for electroless Ag plating is expressed in the following equation:

$$2Ag(NH_3)_2^+ + RC = O - H + 2OH^- \rightarrow 2A\overset{0}{g} + RCOOH + H_2O + 4NH_3$$
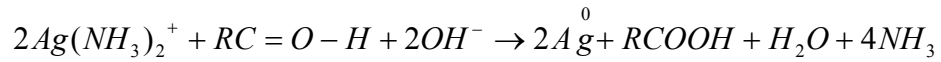
In this chapter, we present fabrication of bottom electrode on PI by the electroless Ag plating method and testing for characterization of the FUT using Ag as the bottom electrode. Firstly appropriate pre-treatment steps and reaction control will be specified by experimental investigation for electroless Ag plating on PI; secondly the peeling test will be applied to the adhesion between Ag plating and PI. PZT-C film and Ag top electrode will be fabricated in the same way as in Section 2.2.5 and 2.2.6. After fabrication of such FUT being finished, its ultrasonic characterization will be tested.

5.2 Experimental procedures

5.2.1 Materials
Silver nitrate, sodium hydroxide, glucose, methanal (37%), ammonium hydroxide (28%) are purchased from Sigma-Aldrich Co. and used as received.

PI substrates of 50μm thickness were cut into rectangular with dimensions of 33mm by 18mm. All samples are cleaned and rinsed in the same way as described in Chapter 2. This is done to remove contaminants on the samples' surfaces.

Cleaning steps are:

Dishwashing liquid, RT, 10 min→rinsed by DI water→ methanol, RT, 2 min→rinsed by DI water→ acetone, RT, 2 min→ rinsed by DI water

5.2.2 Electroless deposition of Ag on PI substrates

Proper pre-treatments for EN on PI have been discussed in Chapter 2; it is assumed that similar pre-treatment steps can be applied to PI before Electroless Ag deposition. The procedure is outlined in Figure 5.1.
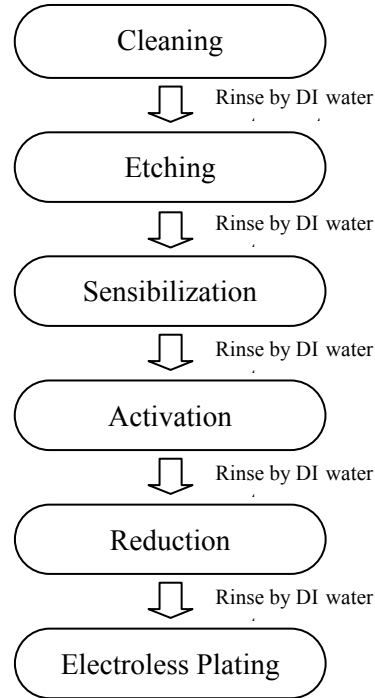
Figure 5.1 Flowchart of processing steps for electroless Ag on PI

To investigate the effects of pre-treatment steps on the electroless Ag plating, four samples are used by applying different choices of pre-treatment steps. The pre-treatment solution recipes are the same as in Chapter 2. After these pre-treatment steps, nail color is applied to one side of each sample and left to dry in the air for 10 min to obtain one-sided plating. The experimental design is shown in Table 5.1

Table 5-1 Pre-treatment step for PI 1~4

Step \ Sample No	Etching	Sensibilization	Activation	Reduction
PI-1	Yes	Yes	Yes	Yes
PI-2	No	Yes	Yes	Yes
PI-3	No	Yes	Yes	No
PI-4	No	No	No	No

The plating condition for electroless Ag plating, with glucose and methanal as the reducing agents, is shown in Table 5.2. For each sample, 40ml solution A and 40ml solution B are prepared before the reaction for safety reason and freshness. solution A is prepared according to the following steps:

1) add 28% ammonium hydroxide into a 10ml 7g/L silver nitrate solution and Ag^+ ions react with OH^- of aqueous ammonia to form a brown precipitate of AgOH;

2) add 28% ammonium hydroxide until the precipitate re-dissolves to give a clear, colorless solution;

3) dissolve 0.32g sodium hydroxide in 10ml DI water and add sodium hydroxide solution to previous clear and colorless solution until a dark brown precipitate forms;

4) add additional 1~2 drops 28% ammonium hydroxide solution;

5) dilute the solution A with DI water to 40ml; for solution B, dissolve 0.2g glucose and add 0.087g methanal (37%) solution in 20 ml DI water, and then adjust volume to 40ml.

The two solutions A and B are mixed by the volume ratio of 1:1 before the plating. To deposit Ag, the samples are immersed into the solution at RT for 1 hr. The plating process can be stopped by removing the sample from the chemical bath and rinsing it with DI water. Then all the samples are dried in RT air for 24 hr. After the experiment, the waste reaction solution should be diluted by nitric acid, because of an explosive precipitate formed in the experiment that is generally thought of as Ag_3N.

Table 5-2 Composition of plating solution used

	Components of Ag solution	Concentration
A	$AgNO_3$	7g/L
	NaOH	4g/L
	NH_4OH (25%)	desired
B	$C_6H_{12}O_6$	2.5g/L
	HCHO (38%)	1ml/L

*DI water was used to dissolve the chemicals listed above.

Scotch Tape Testing is carried out to qualitatively evaluate the PI/Ag interfacial adhesion. The conductivity of the Ag plating is measured by ohmmeter. These procedures are similar to those described earlier in Chapter 2. When the Ag plating shows good conductivity and good adhesion, it serves as bottom electrode. PZT-C film and Ag top electrode are then fabricated in the same way as described in Chapter 2. The characteristics of such FUT are tested in pulse-echo mode.

5.3 Results and discussion

5.3.1 Effect of pre-treatment on Electroless Ag plating

As shown from experimental results, Sample #1, #2 and #4 were plated slightly with Ag (as shown in Figures 5.2, 5.3 and 5.5), while the plating could not provide enough conductivity; Sample #3 was well plated with electroless Ag (as shown in Figure 5.4).

Figure 5.2 PI substrate after the electroless Ag plating experiment (Sample #1 -Side A)

Figure 5.3 Ag plated PI substrate after the Scotch Tape Testing (Sample #2-Side A)
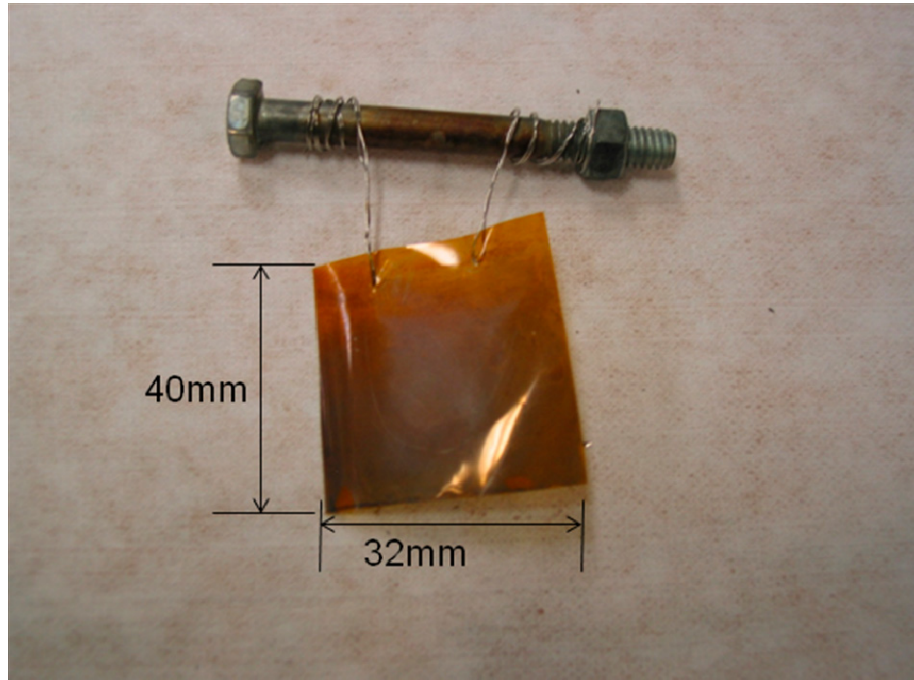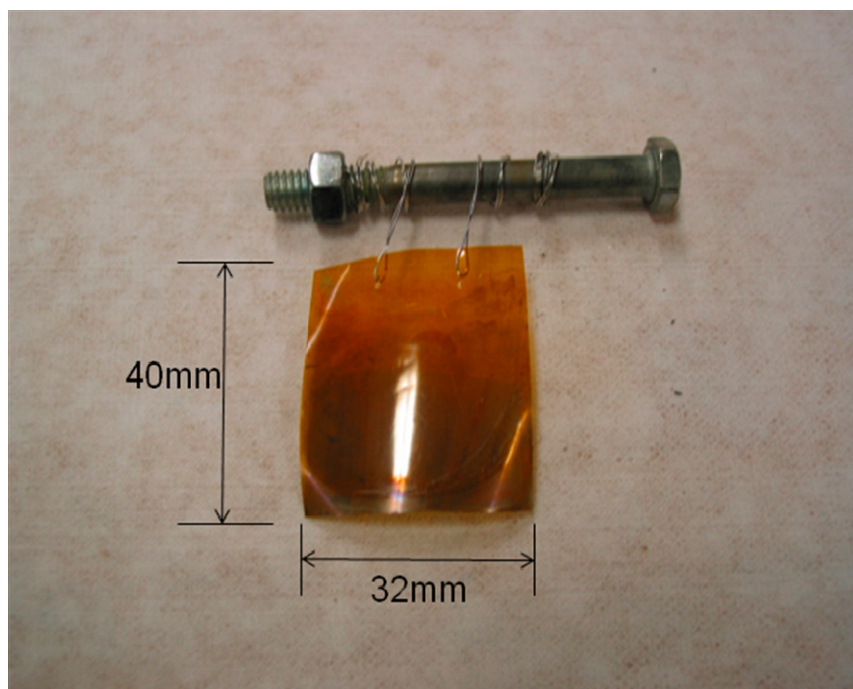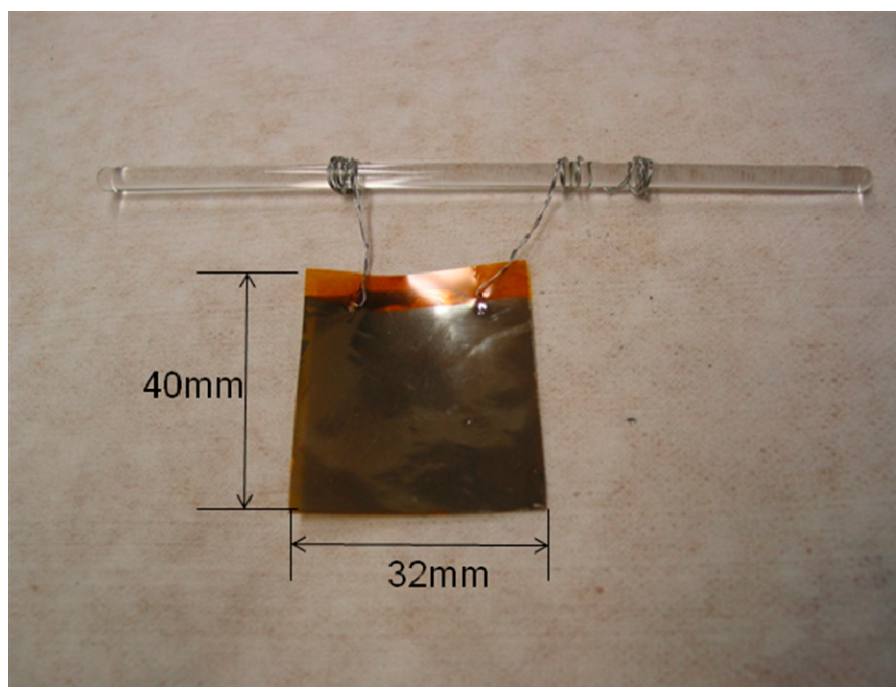

Figure 5.4 PI substrate after the electroless Ag plating experiment (Sample #3 -Side A)
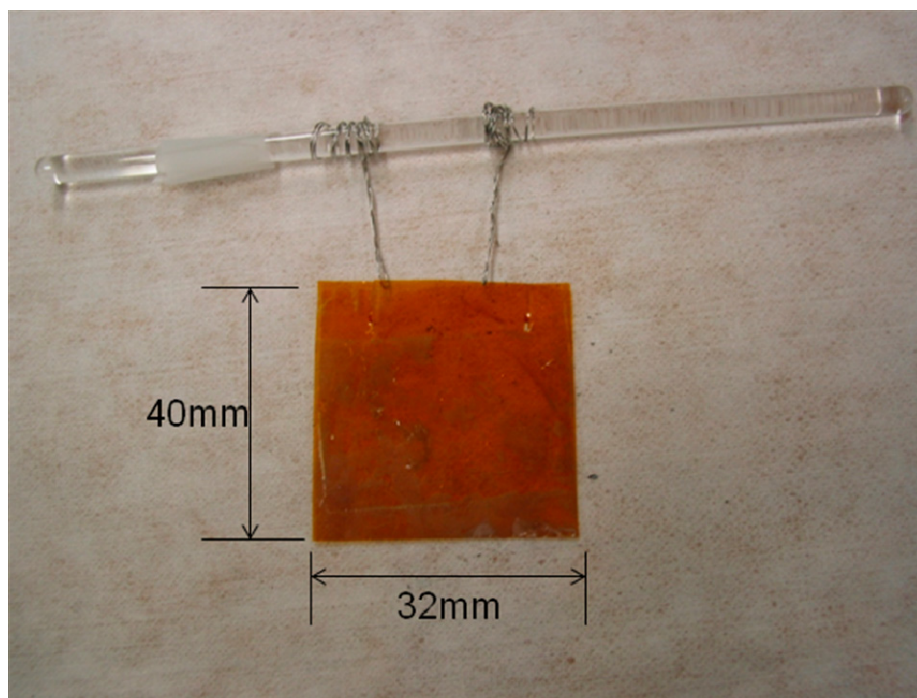
Figure 5.5 Ag plated PI substrate after the Scotch Tape Testing (Sample #4-Side A)

The Ag plating was successfully deposited on the sample which was pretreated with palladium nitrate and tin chloride solutions. This can be explained by its provision of sufficient nucleation sites to initiate electroless Ag plating and enhance adhesion of the Ag particles on the PI surface. Cleaned PI sample was immersed into a solution of $SnCl_2$/HCl at RT for 10 min, and rinsed by DI water; followed by immersing the sample into a solution of $PdCl_2$/HCl at RT for 5 min and rinsing by DI water. After completing the pre-treatment process of sensibilization and activation, the PI sample was immersed into electroless Ag plating chemical bath. It is concluded that three pre-treatment steps (sensibilization, activation and plating) of electroless Ag plating process of PI are necessary for Ag plating on PI with enough thickness. In the sensibilization step, Sn^{2+} ions were absorbed on the PI surface; then in the activation step, Pd^{2+} can be reduced to Pd by Sn^{2+} ions and can form a seeding layer to accelerate electroless Ag plating reaction on PI surface. The existence of Pd islands can help Ag particles to deposit on PI. Also from the result, the reduction step was proved to be unnecessary since it caused poor Ag deposition on PI.

5.3.2 Characterization of electroless Ag plating as bottom electrode

After finishing the deposition, electroless Ag plating showed good adhesion in Scotch Tape Testing (as shown in Figure 5.6)
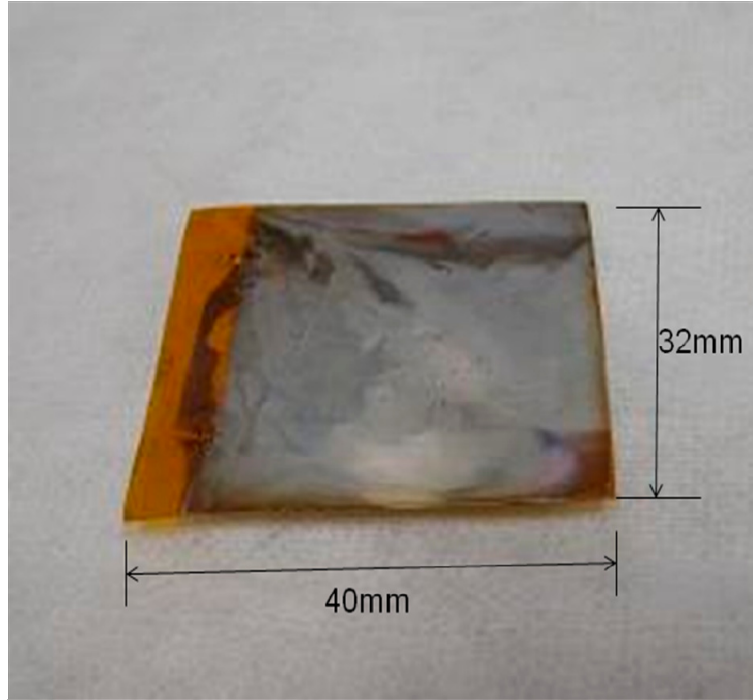
Figure 5.6 Electroless Ag plating on PI after Scotch Tape Testing

5.4 Conclusions

Electroless Ag plating was deposited on PI surface as bottom electrode. The surface had been pre-treated with palladium nitrate and tin chloride solutions for 10 min and 5 min, respectively. After each pre-treatment, DI water was used for rinsing the sample. Proper electroless Ag chemical composites and reaction control have been developed to ensure good adhesion plating. Scotch Tape Testing was used to test the adhesion between Ag plating and PI. In the future the fabrication of FUT using electroless plated Ag as the bottom electrode and its characteristics will be further studied and tested.

6. Conclusions

IUTs and FUTs have been found to be of great interest for ultrasonic NDT and SHM of metallic and Gr/Ep composite parts and structures. Due to the fact that certain Gr/Ep composites do not have sufficient electrical conductivity, they need bottom electrode for the IUT fabrication. Also FUTs using PI as substrate offer high flexibility. Because PI is an insulator, bottom electrode is required as well. Thus one main objective of this thesis is to develop the electroless plating technique to deposit Ni or Ag onto Gr/Ep composites of poor electrical conductivity for IUT fabrication and onto PI for FUT fabrication.

The electroless plating method consisting of two parts (pre-treatment steps and electroless deposition) has been developed to deposit Ni or Ag plating on PI and/or Gr/Ep substrates as bottom electrode for FUTs and IUTs. The interfacial adhesion between Ni or Ag plating and the PI or Gr/Ep substrates has been examined by Scotch Tape Testing, and the conductivity was measured by an ohmmeter. The investigation showed that the adhesion of Ni and Ag plating was strongly dependent on the pre-treatment steps (especially etching time) and the electroless plating time. And pre-treatment steps are necessary and important. For EN plating an etching time less than 30 min and a reaction time over 10 min led to poor adhesion; and an etching time more than 30 min resulted in no plating. Also proper cleaning, bath chemistry, reaction temperature and agitation helped to enhance the adhesion of such plating.

In this study, optimized pre-treatment steps and the EN plating at 90ºC on PI included: cleaning, etching (30 min), sensibilization (10 min), activation (5 min), reduction (30 sec) and reaction time (7~10 min). Also optimized pre-treatment steps and the EN plating (at 90ºC) on Gr/Ep consisted of cleaning, sensibilization (10 min), activation (5 min), reduction (30 sec) and reaction time (10 min). All Ni platings were tested with results of good conductivity and good adhesion. Electroless Ag plating at RT can be deposited under the following conditions:

cleaning, sensibilization (10 min), activation (5 min) and reaction time (60 min). The thickness of Ni plating with a reaction time of 10 min was estimated to be less than 1μm.

A sol-gel spray technique (Kobayashi, *et al.,* 2006) has been used to fabricate the piezoelectric PZT-C film on top of the Ni plating, which served as bottom electrode, on PI or Gr/Ep composites that had poor electrical conductivity. Ag paste was normally applied as top electrode. For characterization of IUT made of Ag/PZT-C/Ni/ (Gr/Ep), the center frequency and 6dB bandwidth of the first round-trip echo were 10.5MHz and 13.6MHz, respectively. The Gr/Ep composite was 1mm thick and uni-directional. As for the one similar IUT coated onto a 1.58mm thick honey cone Gr/Ep composite structure, the center frequency and 6dB bandwidth of the fist round-trip echo were 7.6MHz and 7.7MHz, respectively.

Electroless Ag plating has also been successfully deposited on PI surface as bottom electrode. The surface has been pre-treated with palladium nitrate and tin chloride solutions for 10 min and 5 min, respectively. However, the fabrication of FUT made of Ag/PZT-C/Ag/PI and its characteristics will be studied and tested in the future.

In this study there is an interest to see whether one can fabricate IUTs on-site. Since tap water is more convenient than DI water, the effects of rinsing by tap water and solution spray mentioned in Chapter 4 on substrates for EN plating were studied. The results showed that both of them have no obvious negative effects on the adhesion of EN plating. For the same reason, on-site fabrication EN plating at RT rather than 90°C with a different chemical bath composite has also been made and tested. The results showed that Ni platings obtained at RT EN were not suitable for use as bottom electrode due to their coarse surface. Finally an EN plating was deposited on PZT-C film surface after sensibilization (10 min), activation (5 min) and reaction time (two turns and each turn was 60 min); but the

Ni plating was not suitable for the use as top electrode for either IUT or FUT. Such a technique is still required to have further investigations. It is noted that Ag paste top electrode fabrication applied can be used on-site.

Therefore suggested further work remains to: (1) realize on-site fabrication with a portable fabrication kit; (2) further improve adhesion between multilayer structure by investigating surface structure after each step and microstructure for plating by scanning electron microscope (SEM) to find out more details and (3) investigate electroless plating of metals such as Ni or Ag or others as top electrode on top of PZT-C film.

The originalities of this thesis research may be revealed by the joint publications listed in references (Jen, *et al.*, 2006; Kobayashi, *et al.*, 2007; Kobayashi, *et al.*, 2008; Ono, *et al.*, 2007).

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