Thesis for the Degree of Master of Science

Preparation and Chracterization of the Metal/Polymer Composite Film by Electroless Plating for EMI Shielding

by

Eun Sun Ji

Department of Chemistry

The Graduate School

Pukyong National University

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전자파 차폐를 위한 무전해 도금으로 제조된 금속/고분자 복합 필름의 연구 및 특성

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Approved as to style and content by :

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(Chairman) :

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(Member) : (Member) :

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Preparation and Characterization of the Metal/Polymer Composite Film by Electroless Plating for EMI Shielding

Eun Sun Ji

Department of Chemistry, Graduate School,
Pukyong National University

Abstract

This work is the electroless deposition of a copper layer onto the surface modified polyimide (PI) film. The surface modification was done by etching with the potassium hydroxide solution treatment. Ag particles were generated on Ag-doped polyimide film by ion exchange, followed by copper deposition using metallic silver particles as seeds. The copper layer was coated on the surface of polyimide film by electroless plating method. This metal/polymer composite film can be used as shielding film of electromagnetic wave. The thickness and surface morphology and composition of copper layer on the polyimide films were characterized with scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive X-ray (EDX). The optical properties of the prepared films were studied with FT-IR. Furthermore ability of shielding effect was studies with I-V curves.

Chapter 1.

Plating of Copper Layers on Polyimide Film Using Electroless Plating by Surface Modification

1. Introduction

Recently, plastics are now widely used to produce electronics housing and enclosure due to advantages such as design flexibility, light weight, low costs, good process ability and chemical stability. Specially, the metallization of polymer materials has attracted more and more attentions [1, 2]. Many polymer films, fibers and plastics are metallized for extensive applications in food packaging, microelectonics, computer technology and the automotive industry to provide an electromagnetic shielding property. With the increase of the use of metallized polymer films in the microelectronic industry, an understanding of the mechanism responsible for adhesion between metals and polymers has become of increasing importance. Among the polymers suitable for microelectronic application, polyimide has received a great attention due to their excellent thermal, chemical and mechanical stability, the easy of planarization and patterning by lithographic techniques and the low dielectric constant [3-7].

For all these reasons, polyimide (PI) film have been widely used in microelectronics and dielectric spacing layers, protective coatings and substrates for metal thin films, replacing traditional inorganic insulators such as SiO_2 in many applications. In these and other applications good adhesion between polyimide and metal substrate is required. Therefore, understanding the interfacial structure between metal and polyimide is an important topic to advance the technology. There are numerous methods for performing metallization on the PI film. For example, physical vapor deposition (PVD) approaches, water-borne process and electroless plating. They have found a niche for itself in industry mainly because it can be deposited as thicker metal film onto geometrically miniature surfaces [8-11]. Creating a pertinent surface roughness is a basic step to enhance adhesion strength for performing electroless plating on a PI surface. Various surface treatments and modification methods have been used to enhance the metal to polyimide adhesion. These include the uses of ion beam, photografting, plasma and sputtering. Most of these methods require high vacuum equipment and the productivity is low; thus they are not economically feasible. These methods introduce foreign materials and undesirable modified layers into the interfaces, resulting in possible reliability failure [12-15].

Interests in wet-process surface modifications of polyimide have increased due to simplicity and low cost. Polyimide films are resistant to most solvents and chemicals, but they react with oxidizing or reducing agents. However, if the concentration of the chemical reagents, reaction temperatures and reaction time are well controlled, the reactions can be confined to the surface.

Moreover, the seeding of the dielectric substrate is key to the subsequent successful electroless metal deposition. The traditional seeding process consists of either a two-step method using successively sensitization solution of $SnCl_2$ and then activation solution of $PdCl_2$. The solutions are expensive and could cause environmental problem [15-18]. So, new activation methods are more useful.

In this study, we prepared Ag^+-doped PI film to seed copper layer on the surface of the polyimide for electroless copper layer deposition. We found that Ag particles were generated and agglomerated in situ efficiently by annealing Ag^+-doped PI films. The surface structure and property of PI films, Ag seed layer, and Cu plated layer were examined by SEM, AFM and water contact angle measurement after each step of modification and plating.

2. Experimental Section

2.1. *Materials*

The chemicals used in this study are commercially available. Pyromellitic dianhydride-oxydianiline (PMDA-ODA) type polyimide film (50 ㎛ thick Kapton 200-H) was provided by Toray-Dupont as substrate. The PI films were cleaned with 2-propanol under ultra-sonication for 20 min at 50 ℃ and washed by deionized (DI) water (18 MΩ). Finally, they were dried in air before use.

Potassium hydroxide (KOH) is used as etching agent, silver nitrate ($AgNO_3$, 99+%) as activation agent and copper sulfate ($Cu_2SO_4 \cdot 5H_2O$), potassium sodium tartrate 4-hydrate ($KNaC_4H_4O_6 \cdot 4H_2O$), sodium hydroxide (NaOH), formaldehyde solution (CH_2O, 36.0% ~ 38.0%) were purchased from Junsei Chemical Co. and used without further purification.

2.2. *Surface modification*

The PI films were immersed in an aqueous 1.0 M KOH solution and 2.0 M KOH solution at 40 ℃ in the range of 0 to 40 min in order to obtain the corresponding potassium polymate. The excess of KOH was rinsed by deionized (DI) water. KOH solution was used to modify the PI film surface to form carboxylic acid group and amide group through cleavage of the imide rings. The modifications comprise the alkali catalyzed imide ring-opening

reaction.

The surface-modified PI films were immersed in an aqueous 0.1 M $AgNO_3$ solution at 50 ℃ for 30 min. The Ag^+ doping can be achieved by subsequent ion-exchanged with K^+ on surface–modified PI films. This results in the formation of Ag^+-doped PI surface. The chemical process of the above two steps is illustrated in Fig. 1.

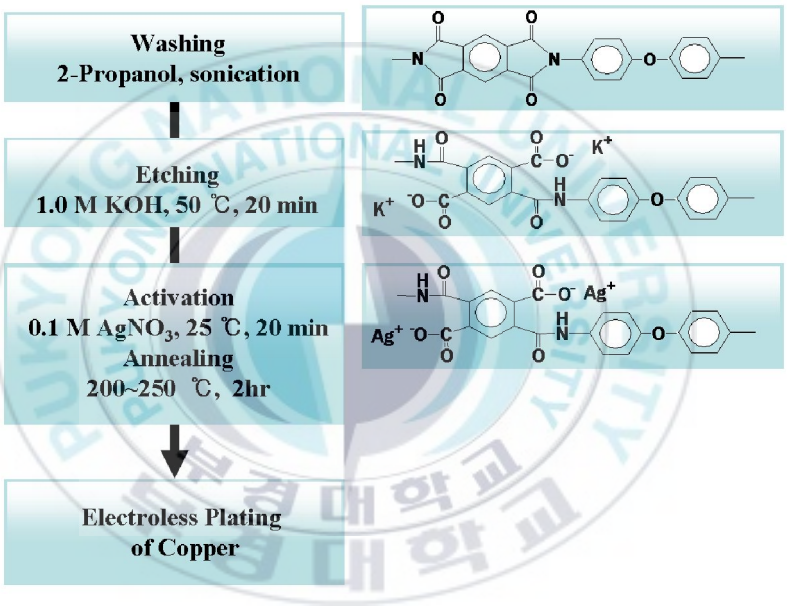

Fig. 1. The ring-opening reaction of the PI film.

The films were then annealed in a furnace at 200 ℃ for 2 hrs. Ag particles were generated and agglomerated in situ efficiently by annealing.

2.3. *Electroless plating*

The metallized film was immersed in the prepared copper solution. The copper solution bath for electroless plating containing 2.0 M $CuSO_4$, 2.0 M $KNaC_4H_4O_6$, 1.0 M NaOH, CH_2O 50 ml (37.2 wt%) was ultrasonicated for 20 min at 40~50 ℃. Copper in the copper solution was easily plated on the immersed film. The thickness of copper layer was controlled by immersing time. The cooper plated PI film was washed by DI water to remove by-products or residues and then dried in air condition.

2.4. *Characterization*

Atomic force microscopy (AFM, Nanoscope Ⅲa, Digital Instruments) in contact mode was used to investigate the topographic profiles and roughness of the films. The surface images of the modified surface of the PI film and layers of silver and copper were investigated by scanning electron microscopy (SEM, S-2150, Hitachi) and the samples were coated with gold for SEM analysis. Moreover, change of functional group on the surface was investigated by water contact angle measure measurement and the chemical structure of PI film was investigated by FT-IR (Perkin Elmer, FT-IR spectrometer, Spectrum 2000).

Adhesion strength was investigated by 3M scotch tape in order to cross-cut tape test (ASTM D 3359)

3. Results and Discussion

3.1. *Characterization of polyimide film surface – Increasing the hydrophilicity*

The point of the modification step was to increase the hydrophilicity of surface of PI film. As shown in Fig. 2, surface-modified PI film was derived from the imide ring opening reaction on the surface of the PI films. The mechanical modification plays a role in increasing the contact area of the PI by the alkaline solution, which was expected to boost the surface roughness and hydrophilicity of PI film. So, water contact angle of PI film was decreased. Fig. 1(a) shows the original PI film that has 63.5^{o} of water contact angle before etching. On the other hands, Fig. 1(b) shows the modified PI film that has 20^{o} of water contact angle after etching with 0.1 M KOH solution.

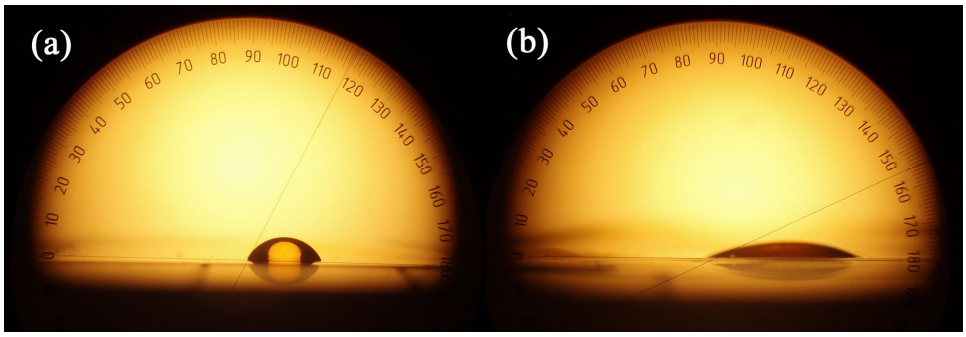

Fig 2. Water contact angle images of PI film (a) untreated, (b) treated with 0.1 M KOH.

Moreover hydrophilic properties of the films were searched by different concentrations of the base solution and reaction time for the modification on the surface of PI film.

The film was measured to determine water contact angle after treating with KOH of 1.0 M and 2.0 M according to the exposed times at 50℃. As time passes, water contact angle of the film was decreased to improve to hydrophilic property on the surface of the PI film. Furthermore increased mol concentration over 2.0 M KOH solution has the same effect with the reaction time. But excessive reaction time and mol concentration of KOH solution for the modification of the film resulted in the melted film by KOH solution.

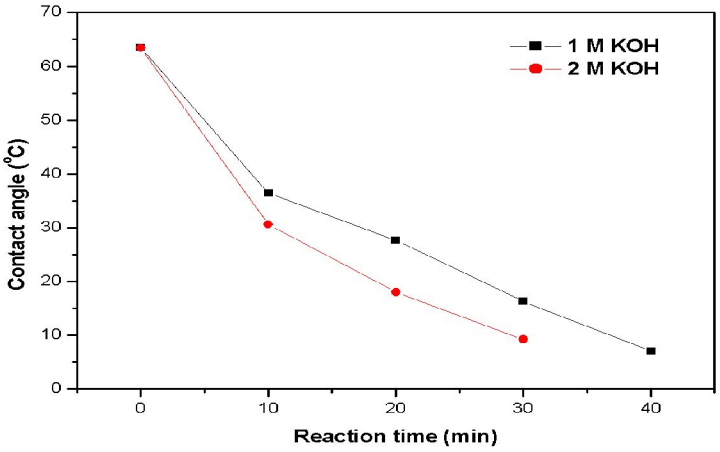

Fig. 3. Water contact angle changes with different the different concentrations of KOH and reaction times.

3.3. Morphology of polyimide film surface

When the PI films were immersed into a solution of KOH solution at 50 ℃ for 20 min, many reccesses appeared on the surface of the PI film. Figure 4 shows SEM images of the surface of PI film treated with pottsium hydroxide solution.

Fig. 4 (a) shows the SEM image of original PI film surface. The original PI film surface was relatively smooth. But (b), (c) and (d) show rough surface. The SEM image of the Fig 4 (b) was PI film surface treated with 1.0 M KOH at 50 ℃ for 20 min.

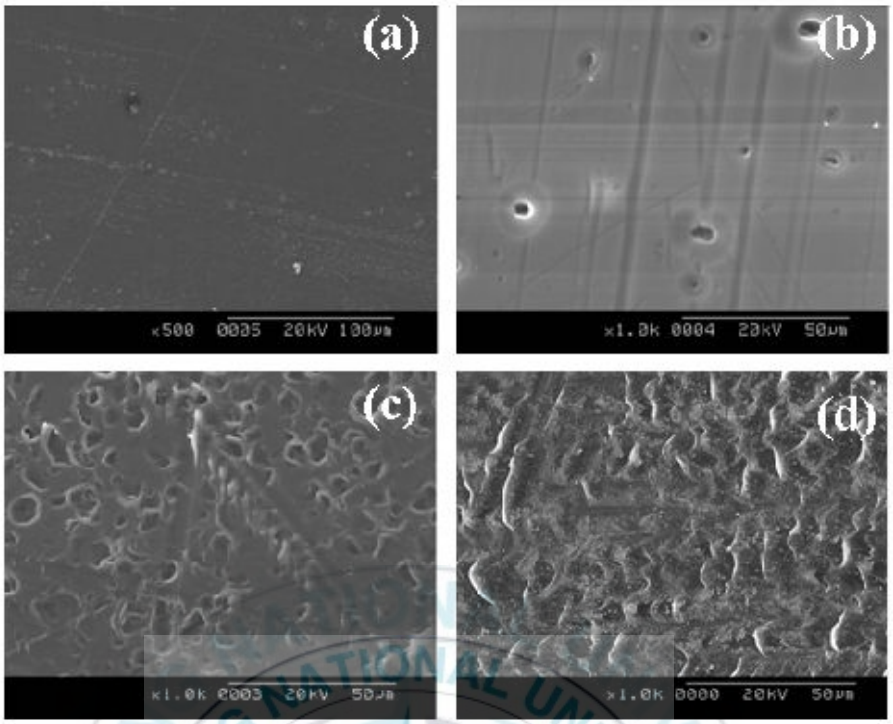

Fig. 4. SEM imges of etched surface of the PI film (a) original PI film, surface etched with (b) 1.0 M KOH 50 ℃, 20 min, (c) 1.0 M KOH 50 ℃, 40 min, (d) 2.0 M KOH 50 ℃, 20 min

The film in the Fig 4(b) shows etching step with creative hole on the surface. But the films in the Fig (c) and (d) that were treated by the excessive exposed reaction time and high mol concentration. The resulted in the PI film surface appered like wrinkles. Those films were not suitable for making metal/polymer complex film.

3.3. *Characterization on the composition of polyimide film surface*

The film after treatment with KOH solution progressed for activation step. The film has the roughness on the surface for the Ag activation step. The functional group of the opened ring structure by KOH gets bonded with K^+ ion. Then, the film of the bonded K ion on the surface immersed into silver nitrate solution for ion exchange between K^+ ion and Ag^+ ion. The Ag^+ ion gets reduced by reducing agent and it forms roughness on the surface of the PI film. Thus copper particles by electroless plating copper solution was plated on the heavy surface. Component of the surface of the PI film was measured by EDX.

As shown in Fig. 5, surface modified PI film was derived from the imide ring opening reaction the surface of the PI films. EDX survey spectra reflect the changes in chemical composition due to the hydrolysis reactions on the PI films. In the PI films of the virgin form, only C, O peaks were observed in the survey scan (Figure 5(a)). N peak was not due to similar position with C peak. After treatment with KOH solution, one additional peak of K was observed (Figure 5(b)). Etching of the film could not play a significant role because no distinct change was observed for the overall thickness of the films before and after surface modification.

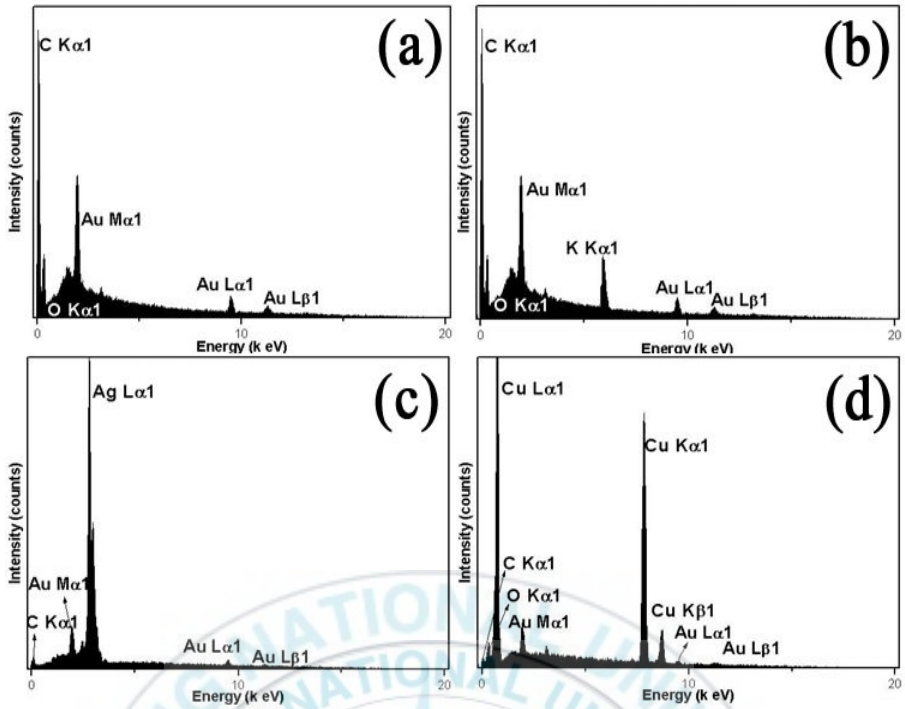

Fig. 5. EDX data of the PI film surface after each step: (a) original PI film, (b) after etching of the PI surface with KOH solution, (c) ion-exchanged with Ag^+ on the surface of PI film, and then annealed for the reduction from Ag^+ to Ag^0, (d) after electroless copper plating on the activated surface of PI films.

But the KOH solution provided modification of surface for the metallization with $AgNO_3$. KOH solution opened the imide ring on the surface of the PI film, and then K^+ was loaded with carboxylate functional group at the modified surface of PI. So, K peak was disappeared after metallization with $AgNO_3$ (Figure 5(c)). Instead, Ag peak was observed to be ion-exchanged with potassium ion on the surface of PI films. Ag^+ ion at the surface of PI film was

reduced to Ag^0 by annealing. This resulted in the formation of silver layer. This layer provides roughness on the surface for the electroless plated copper layer. The rough surface of PI film was immersed in the copper solution for the deposition of copper (Figure 5(d)).

3.4. *AFM image of the surface of polyimide film*

The original PI film surface in Figure 6(a) was relatively smooth.

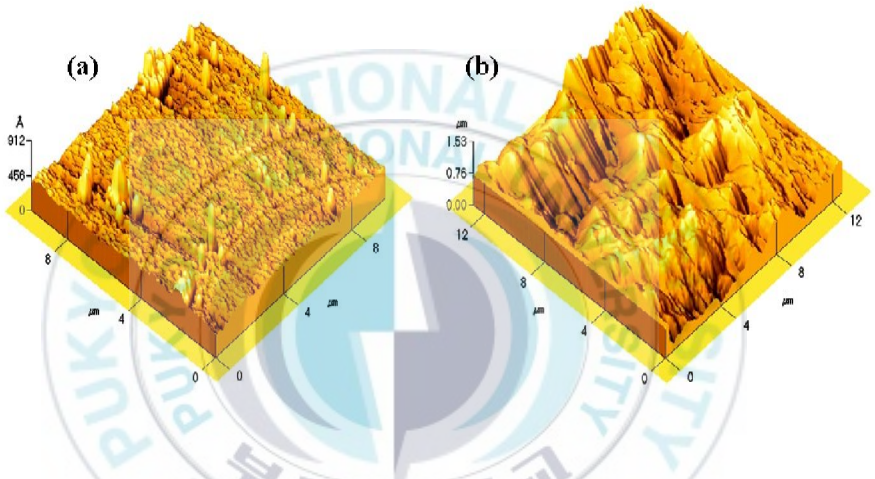

Fig. 6 AFM images of (a) untreated PI films, (b) after $AgNO_3$ solution treatment and annealing of PI films.

The surface became rougher after the films were treated with KOH and $AgNO_3$. Silver particle appeared on the PI film after annealing (Figure 6b). That is obvious difference in topography between the films after washing with 2-propanol and the annealed films after treatment with $AgNO_3$. In summary,

annealing caused both chemical and physical changes on the PI film surface: the Ag^{+} ions were reduced to Ag^{0} particles as well as the silver particles agglomerated to bigger ones in the ordered arrangement.

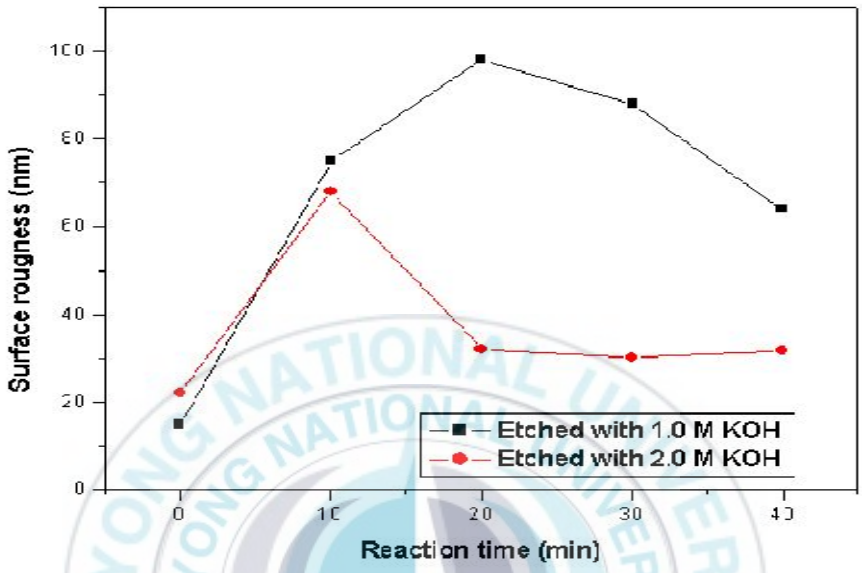

Fig. 7. Surface roughness PI films treated with KOH solution with different reaction times and concentrations of KOH solution

Roughness was measured with AFM. The film was treated with different reaction time and mol concentration for etching KOH solution.

It is shown is Fig. 4 and Fig. 7. The SEM images show the PI film surface treated with the excess reaction time and mol concentration KOH solution. It shows the pushed mark on the surface of the film. The mark is concerned to make the activation layer. The part of the mark was not easily bonded with Ag. So, the roughness was not higher.

Fig. 7. shows the surface roughness after activation step. The film which was treated by 1.0 M KOH solution at 50 ℃ for 20 min has the highest roughness. This film forms the grip/hold on the surface and stably bonded with Ag. As a result, it forms the highest roughness to the numerable silver ions reduced by annealing.

3.6. *SEM image of the copper layer*

The silver activated film was plated with electroless copper solution. The surface images of the PI films were measured with SEM. Fig. 8 shows the surface of the copper layer on the activated PI film. Fig. 8(a) shows the uniformity of copper layer. It shows holes on the surface and high roughness. But copper layers were not uniform of the Fig. 8(b), (c) and (d). Because, those films have pushed mark on the surface inserted the hole.

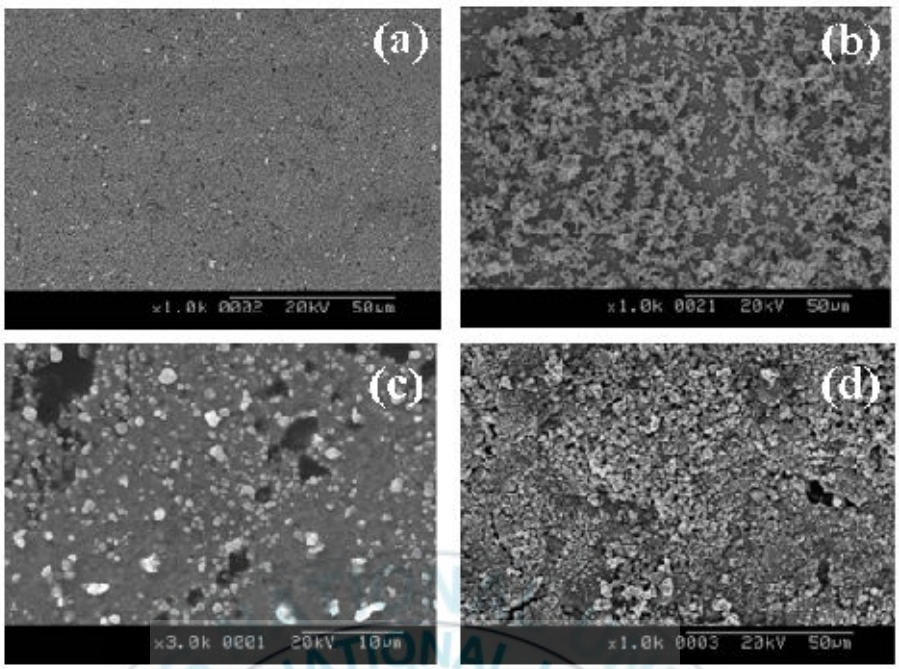

Fig. 8. SEM imge of the copper layer on the surface of the PI film, treated with etching solutions; (a) 1.0 M KOH 50 ℃, 20 min, (b) 1.0 M KOH 50 ℃, 40 min, (c) 2.0 M KOH 50 ℃, 20 min, (d) 2.0 M KOH 50 ℃, 40 min

3.7. *Adhesion strength between polyimide film and copper layer*

These various steps create hole on the surface and activation layer by silver due to pretreatement for electroless plating of copper. This work helps to increase adhesion strengh between polyimide film and copper layer. We measured adhesion strengh of the film. The method is cross cut tape test which is referred in ASTM D 3359.

The cross cut tape test is very simple method for adhesion strengh. At first,

the plated film was cut by knife and cut length was 20 mm and space 1 mm between each line. The edge of the knife has 15° or 30°. Then 3M scotch tape attatched on the surface of the cutted PI film. The tape was pushed by rubber and removed quickly from the surface. The adhesion strengh was determined by separated copper layer from the film. Fig. 9. show the standad level of desired adhesion strengh.

Classification	Percent area removed	Surface of cross-cut area from which flaking has occurred for six parallel cuts and adhesion range by percent
5B	0%	
4B	Less than 5%	
3B	5~15%	
2B	15~35%	
1B	35~65%	
0B	Greater than 65%	

Table. 1.ASTM –D3359 classification of adhesion test results

Table 1. shows the adhesion strengh and roughness. The adhesion strengh increases with increasing surface roughness. Especially, the film of the formated hole has very high adhesion strengh. It shows relation between formated hole on the surface by etching step and activation layer. Pushed mark was not highly

rough, as a result it was not formated by silver layer and the adhesion between PI film and copper layer was not good.

Mol concentration / reaction time	Morphology of the surface	Roughness (Ra)	Adhesion strength
1.0 M / 0 min	Smooth	15.11	0B
1.0 M / 10 min	Hold creation	75.28	4B
1.0 M / 20 min	Hold creation	98.44	4B
1.0 M / 30 min	Under the 20%	88.65	4B
1.0 M / 40 min	Been pushed surface	64.18	3B
2.0 M / 10 min	Hold creation	68.05	4B
2.0 M / 20 min	Been pushed surface	32.22	2B
2.0 M / 30 min	Been pushed surface	30.12	2B
2.0 M / 40 min	Been pushed surface	31.83	2B

Table 2. Results of the adhesion strengh between polyimide film and copper layer.

4. Conclusions

In this study, PI film coated with copper particles was fabricated by electroless plating technique. In order to increase the adhesion of copper particles on the PI film, the surface of PI films was treated with KOH solution. Thus, modified-surface of PI film was derived from the imide ring opening reaction on the surface of the PI films. K^+ ion was bonded at carboxylate functional group on the modified surface of PI. The holes were created on the

surface of the film after etching step. The holes create mark on the surface and this plays a role of activation. PI film having modified-surface was immersed into $AgNO_3$ solution. It was annealed for reduction of Ag^+ to metallized silver layer to improve the adhesion between copper particles and PI film. As the film with holes on the surface gets stably bonded with silver and results in the highest roughness. Copper was stably deposited on the surface of the PI films through the activation of silver layer by electroless plating of copper layer. Homogenous copper layer fabricated on the surface of PI film was deposited by electroless copper plating method.

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Chapter 2.

Electroless Copper Plating on the Polyimide Film Assisted by Nickel Presence and Its Effect on the Electromagnetic Interference Shielding

1. Introduction

Nowadays, electromagnetic interference (EMI) shielding materials is attracting public attention because of wide application of electronic devices are widely used, especially the mobile phone, the more electronic waves are emitted to interfere the surrounding nearby. Due to the increase in demand for faster, lighter, and more cost-efficient airborne vehicles (aircrafts, spacecrafts, etc) have forced designers to integrate individual avionics boxes into a compact electronic system. The radiated electromagnetic disturbance from these electronic systems may affect other sensitive avionic devices. Densely packed systems in a variety of industry fields also need to be protected from the electromagnetic waves [1-5]. Thus, research on shielding enclosures is essential for protecting electronic equipment that is vulnerable to EMI phenomena. Generally, in the past, electronic shielding enclosures were made up of metals. However, polymer composites and fiber-reinforced composites containing

conductive fillers such as carbon particles, carbon fibers and dielectric of magnetic loss materials have been extensively used for EMI shielding in recent years. Most polymeric materials are transparent to EM radiation and provide no shielding against EMI. In electronic components serious problems such as noise enhancement and malfunction of electronic instruments have been raised. Several research works have reported the shielding materials made by various techniques, namely conductive coating, conductive papers, conductive composites and zinc spraying. Therefore, it is interesting in preparing a light and flexible EMI shielding materials by electroless plating.

Polyimide (PI) is a low-*k* material with high thermal stability and has been widely used in the microelectronics industry. Various efforts have been made to produce metallization on PI film surfaces. Copper electroless metal deposition is a primary choice because it is a relatively low-cost and low-temperature technology [6-8].

Previously, we described the characteristics of the copper plated PI film such as roughness of surface, hydrophilic and adhesion strength between PI and copper layer. In this chapter, electronic properties of the other type of shielding film which was prepared by different electroless plating solution such as copper or copper/nickel molar ratio.

2. Experimental Section

2.1. *Materials*

The chemicals used in this study are commercially available. Pyromellitic dianhydride-oxydianiline (PMDA-ODA) type polyimide film (50 ㎛ thick Kapton 200-H) was provided by Toray-Dupont as substrate. The PI films were cleaned with 2-propanol under ultra-sonication for 20 min at 50 ℃ and washed with deionized (DI) water (18 MΩ). Finally, they were dried in air before use.

Potassium hydroxide (KOH) is used as etching agent, silver nitrate ($AgNO_3$, 99+%) as activation agent and copper sulfate ($Cu_2SO_4 \cdot 5H_2O$), nickel sulface ($NiSO_4$), potassium sodium tartrate 4-hydrate ($KNaC_4H_4O_6 \cdot 4H_2O$), sodium hydroxide (NaOH), formaldehyde solution (CH_2O, 36.0% ~ 38.0%) were purchased from Junsei Chemical Co. and used without further purification.

2.2. *Surface modification*

The PI films were immersed in an aqueous 1.0 M KOH solution at 50 ℃ for 15 min to obtain the corresponding potassium polymate. The excess of KOH was rinsed by deionized (DI) water. KOH solution was used to modify the PI film surface to form carboxylic acid group and amide group through cleavage of

the imide rings. The modifications comprise the alkali catalyzed imide ring-opening reaction.

The surface-modified PI films were immersed in an aqueous 0.1 M $AgNO_3$ solution at 50 ℃ for 30 min. The Ag^+ doping can be achieved by subsequent ion-exchanged with K^+ on surface–modified PI films. This result in the formation of Ag^+-layer PI surface. The films were then annealed in a furnace at 200 ℃ for 2 hrs. Ag particles were generated and agglomerated in situ efficiently by annealing.

2.3. *Electroless plating*

The home-made electroless copper plating solution with the bath composition given in Table 1 was used in this research. Electroless copper plating was carried out at room temperature for up to 5 min in a sufficiently stirred plating bath. The plated PI film was washed by DI water and dried by nitrogen blowing, and stored under the nitrogen atmosphere.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
$CuSO_4$	10 g/L	8 g/L	7 g/L	5 g/L	3 g/L
$NiSO_4$	0 g/L	2 g/L	3 g/L	5 g/L	7 g/L
Na_2CO_3	10 g/L				
NaOH	10 g/L				
$KNaC_4H_6O_6$	50 g/L				
HCHO	50 mL/L				
pH	8 ~ 9				
Temperature (℃)	60 ℃ ~ 70 ℃				

Table 1. The composition of electroless copper solution

3. Results and Discussion

3.1. *Structure on the surface of etched PI film*

Fig. 1 shows FT-IR ATR spectra of the PI film. Fig. 1 (a) was spectra of the original PI film. As shows in Fig. 1, symmetric and asymmetric stretching peaks of carbonyl groups appeared at 1780 cm^{-1} and 1720 cm^{-1}. Stretching peak of C-N appeared at 1370 cm^{-1} and bending peak of imide C=O appeared at 720 cm^{-1}, respectively. Fig. 1 (b) was spectrum of modified PI film by KOH. It showed the stretching C=O of amide at 1650 cm^{-1} as the peak intensities at 1780 cm^{-1} and 1720 cm^{-1} were decreased. Asymmetric stretching peak intensity of COO^- at 1595 cm^{-1} increased. Meanwhile peak intensity of C-N at 1370 cm^{-1} decreased.

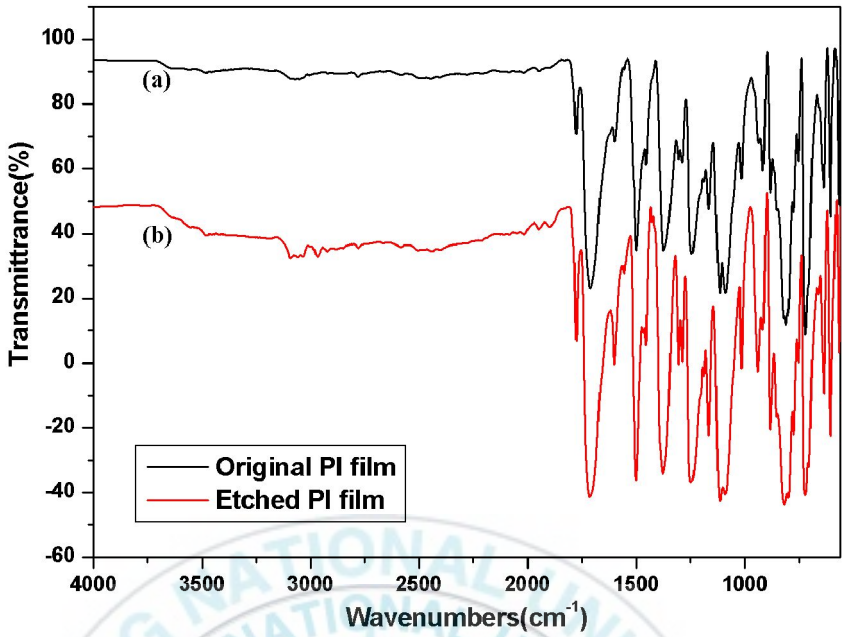

Fig. 1 FT-IR ATR spectra of PI films; (a) original PI film, (b) modified PI film by KOH solution (50 ℃, 15 min)

3.2. *Surface image and composition of the plated PI film surface*

The film was plated by electroless copper solution which has different molar ratio of nickel. Size of copper particle on the surface of PI film decreased due to the increased molar ratio of nickel.

EDX spectra of all samples didn't show nickel peak. But size of copper particles decreased. Because the nickel sulfate accelerated velocity to plate on the surface of PI film copper particles formatted as layer on the surface for short time.

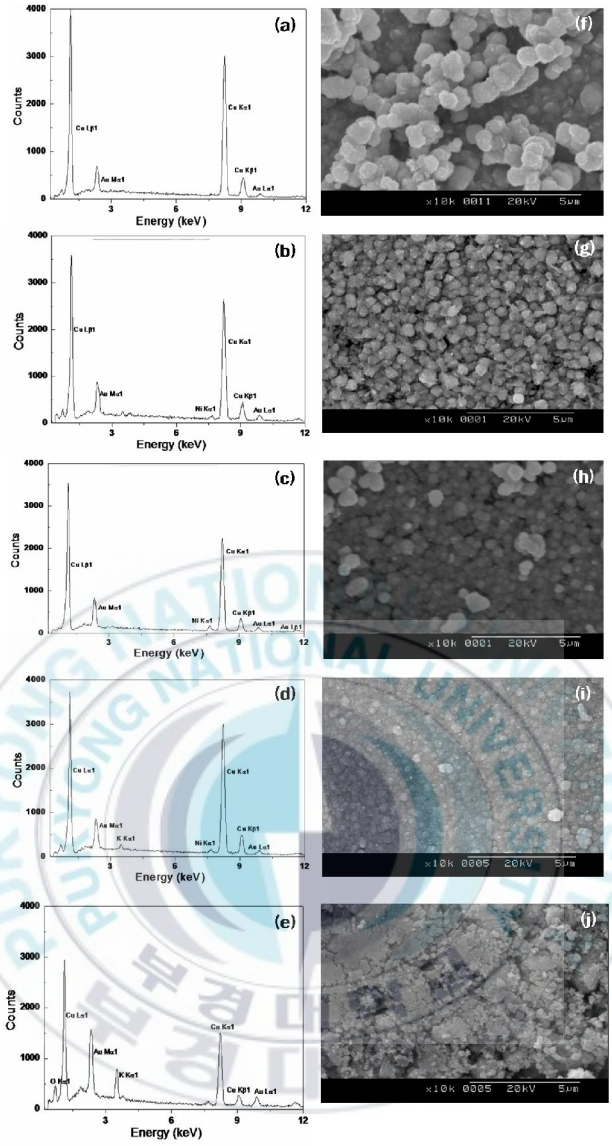

Fig. 2 EDX spectra and SEM images of each sample.

3.2. *Morphology of plated PI film surface*

The result of AFM image is same with SEM image. The roughness on the surface of PI film was decreased similar due to molar ratio of nickel.

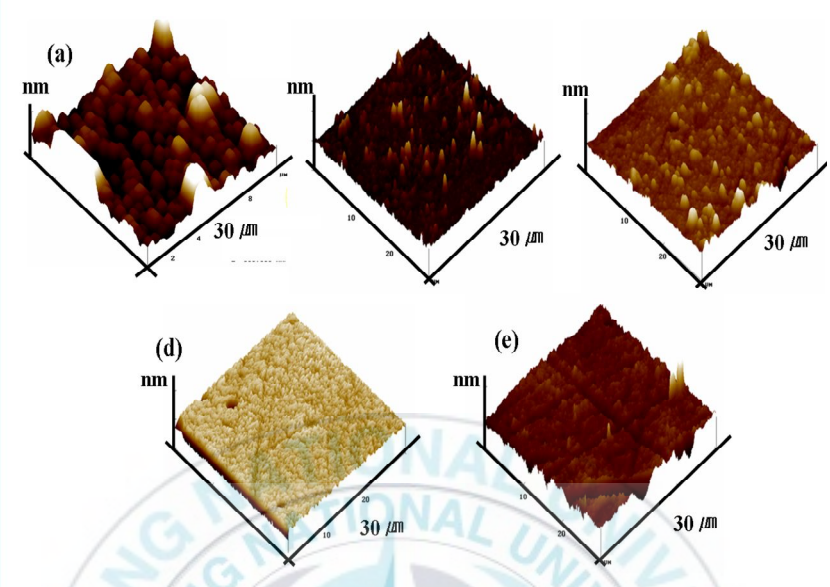

Fig. 3 AFM images of each sample.

Fig 3 (a), the size of particles is big on the other samples. Fig 3 (d) shows the copper layer by copper/nickel electroless solution which has 1 to 1 molar ration between copper and nickel. The layer was uniform.

3.3. *Adhesion strength and hardness*

We measured adhesion strengh and hardness of the film. The method is cross cut tape test and hardness test by pencil which is referred in ASTM D 3359. The hardness test used pencil by Mistubishi Co.. Pressure of pencil is 700gf. Usally, mark of “B” to pencil is soft and make of “H” to pencil is hard. Forthermore

number with of pencil making mean the increase of hardness like as “B” or “H”.

The adhesion strenth was measured by cros –cut test.

Number of samples	Molar ration (Cu : Ni)	Hardness	Adhesion strength
Sample 1	10 : 0	5H	1B
Sample 2	8 : 2	6H	4B
Sample 3	7 : 3	6H	4B
Sample 4	5 : 5	7H	4B
Sample 5	3 : 7	7H	4B

Table 2. Results of the adhesion strengh and hardness between polyimide film and copper layer

The result increased dut to molar ratio increse of nickel. Sample 4 and 5 showed a very higher hardness. All result of the adhesion strength between polyimide film and cooper layer is good except sample 1. The sample 1 showed a bad peeling phenomena. As the result, nickel in the electroless copper solution plays a role accelerator and help to the formation of copper particle.

3.4. *Electromagnetic interference*

The shielding effectiveness (SE) is given by:

$$SE = 10 \log (P_{in} / P_{out}) = 10 \log (E_{in} / E_{out}) = 20 \log (H_{in} / H_{out}) \quad (1)$$

where P is the energy field, E is the electrical field, H is the magnetic field strength.

Fig. 4 shows the result of EMI shielding effectiveness (SE) of copper coated PI films. According to the Schelkunoff theory [9], the EMI shielding effectiveness can be expressed by:

$$SE = A + R + B \tag{2}$$

Where A, R and B denote the absorbed wastage, reflected wastage and internal reflected wastage, respectively. At the low frequencies, the EMI shielding effectiveness attribute to the reverberation wastage, and at the high frequencies, the EMI shielding effectiveness lie on the absorption wastage [9-11]. We can get the relationship between shielding effectiveness and frequency according to the formula [12]:

$$SE(dB) = 50 - 10 \log (\rho \cdot f) + 1.7 t (f / \rho)^{1/2} \tag{3}$$

Where ρ, f and t are volume resistivity, frequency of transmitted wave, and thickness of composites, respectively.

Shielding effectiveness	Classification
0 ~ 10 dB	Ineffective
10 ~30 dB	The smallest effect
30 ~ 60 dB	Average
60 ~ 90 dB	More over average
More over 90 dB	The best effect

Table 3. Classification of the shielding effectiveness

Usually, EMI shielding film has shielding effectiveness from 30 to 60 dB. We conformed SE of the etch sample by equation according to the Schelkunoff theory. The volume resistivities of etch sample was 13 Ω · cm, 8.4 Ω · cm, 6.4 Ω · cm, 1.8 Ω · cm and 1.2 Ω · cm, respectively. For a 20 μm thick test sample, the EMI shielding effectivenesses was calculated by equation 3.

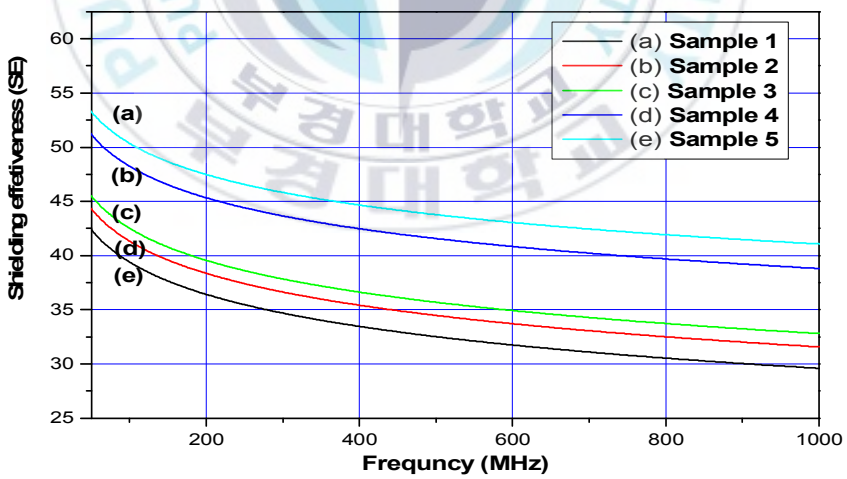

Fig. 4 Calculated SE values of etches sample.

The SE value of samples has over 30 dB at 1000 MHz. Specially; the sample 5 has the highest SE value among the samples. As a result, uniform layer from small particles has optimized SE value.

4. Conclusions

A novel copper coated PI film was manufactured by electroless plating techniques. The plated layer was formed by electroless copper solution which has different molar concentrations of nickel. The presence of nickel in the electroless copper solution accelerated the copper plating. Furthermore, the film has very high SE by copper layer.

In this study, PI film coated with copper particles was fabricated by electroless plating technique. The film was made for EMI shielding effectiveness. The surface of the film was treated by KOH solution. That solution opened the ring structure of the imide structure of the film. Due to the recesses formed on the surface of the film and that increases the adhesion strength between PI film and copper layer. Modified PI film treated by $AgNO_3$ solution. That was made as activation layer on the etched PI film. Finally, the activated film was immersed electroless copper solution which has different molar ratio of Ni. We prepared five different solutions and were used for plating of copper on the modified

surface of the PI film. The plated film has different morphology of the copper layer and EMI shielding effectiveness. The solution of the 70 wt% nickel of the metal source resulted in the uniformity copper layer and higher hardness strength and optimized EMI shielding effectiveness. But solution of the 0 wt% nickels of the metal source resulted in the rough copper layer and showed a decreased strength less than sample 5. Furthermore, rough surface with high volume resistance due to EMI shielding effectiveness has very low ability. It is necessary to prepare the uniform copper layer on the surface of the PI film for using EMI shielding film and uniform copper layer need the optimized molar ratio of the nickel in the electroless copper solution.

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전자파 차폐를 위한 무전해 도금으로 제조된 금속/고분자 복합 필름의 연구 및 특성

본 연구는 금속/고분자 복합 필름을 무전해 도금을 통해 제조하였다. 고분자 필름에 금속을 도금하기 위한 전처리로 염기성 용액을 사용하였고 이를 다양한 시간과 농도를 통해서 필름의 표면 변화를 유도하였다. 이러한 필름의 변화는 주사전자현미경 (SEM)과 적외선 분광기 (FT-IR)그리고 접촉각을 통해 알아보고 에너지 분산형 분광기 (EDS)는 조성원소의 분석에 사용되었다. 이러한 변화를 통해 개질된 필름은 질산은을 통해 활성화 표면을 가지게 되고 이 윗층에 금속이 도금될 수있도록 하였다. 개질정도와 활성화에 따른 필름과 금속의 접착력은 ASTM에 기인해 측정하였다. 기본적인 도금의 적정조건을 찾아낸 필름은 활용도 높은 금속의 도금을 위해 금속 도금욕의 조성 변화에 따른 도금막에 대한 연구가 진행 되었고 이는 도금욕의 니켈함량에 따른 도금막의 균일도로 확인해 보았다. 이러한 실험을 통해 고분자 필름의 최적의 개질조건과 무전해 도금에 있어서의 최적의 펠링타입의 구리 도금욕을 제조할 수 있는 조건을 밝혔다. 또한 본 실험을 통해 제조된 필름은 전자기파 차폐에 높은 효율을 보이는 기초 재료로 간접적 측정으로 본 필름의 전자기파 차폐 효능을 제시하고 있다.

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