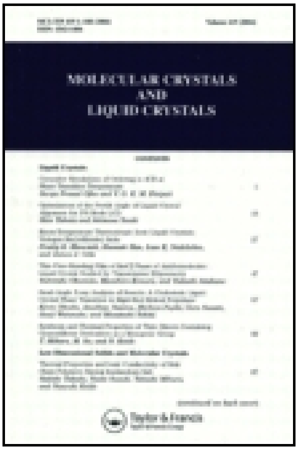

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Copper Metallization on the Surface-Modified Polyimide Films by Electroless Plating Method

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Copper Metallization on the Surface-Modified Polyimide Films by Electroless Plating Method

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This work researched the electroless deposition of copper layer onto the surface modified polyimide (PI) film. The surface modification was done using a base solution treatment and an activation layer of Ag. Finally metal copper layer was then deposited on this modified surface using the electroless plating technique. The thickness and surface morphology of copper layer on the polyimide films were characterized with atomic force microscopy (AFM), scanning electron microscopy (SEM). The chemical binding of the prepared films was studied with FT-IR.

Keywords: electroless plating; polyimide film

INTRODUCTION

Metallized dielectrics such as metal layer coated polyimides are extremely important in fabrication of microelectronics devices. Recently, as an alternative to conventional lithography-based vacuum metal deposition and chemical metallization strategies such as fabrication of metallic patterns on polymeric substrate using ion-doped precursors [1,2]. Had been investigated such approaches utilize simple solution chemistry and could provide low-cost fabrication of metallized polymers with chemical diversity allowing control of the degree of surface metallization.

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We prepared polyimide (PI) film using an ion-doped precursor for metallization. PI has been increasingly used in the microelectronic packaging industry. Polyimides are generally characterized by excellent thermal, chemical, and mechanical stability and low dielectricconstant [3,4]. These properties have motivated many efforts to develop advanced interconnection, particularly with copper, for metallization on PI surface. Copper deposition by electroless method is a primary choice because it is a relatively low-cost and low-temperature technology.

However, due to the somewhat inert surface of PIs, it is difficult to form adhesive bonds with these materials. If the desired bulk properties of PIs are to be retained, then an alternative to this problem is surface modification [5–7].

There are numerous methods for performing metallization on the PI films. In addition to the physical vapor deposition (PVD) approaches, water-borne process has been found as a niche for itself in this industry mainly because it can deposit thicker metal film onto geometrically miniature surfaces. For performing electroless plating on a PI surface, creating a pertinent surface roughness is a basic measure to enhance adhesion strength. The seeding of the dielectric substrate is the 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 $PdCl_2$ [8,9]. The solutions are expensive and could cause environmental problem, so new activation methods can be attractive.

In this study we prepared Ag^+-doped PI film to seed the polyimide for electroless copper deposition. The surface structure and composition of PI films and copper plated layer were examined with AFM, EDX and FT-IR after each step of modification or plating.

EXPERIMENTAL

Materials

The chemicals used in this study are commercially available. Pyromellitic dianhydride-oxydianiline (PMDA-ODA) type polyimide film (50 µm thick Kapton 200-H) was provided by Toray-Dupont as substrate. The PI films were cleaned with 2-propanol under ultrasonicaion for 20 min at 50°C and washed with deionized (DI) water (18 MΩ). Finally the film was dried in air before its use. Potassium hydroxide (KOH) used as etching agent, silver nitrate ($AgNO_3$, 99 + %) used as activation agent and copper sulfate ($CuSO_4 \cdot 5H_2O$), potassium sodium tartrate 4-hydrate ($KNaC_4H_40_6 \cdot 4H_2O$), sodium hydroxide (NaOH), formaldehyde solution (CH_2O, 36.0 ~ 38.0%) were purchased from Juncei Chemical Co. and used without further purification.

Polyimide Metallization

(1) *Surface modification*

The PI films were immersed in an aqueous 1.0 M KOH solution at 50°C for 20 min and 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. After the treatment, it was rinsed with copious amount of DI water to remove the remaining KOH solution from the surface of PI film.

The surface-modified PI films were immersed in an aqueous 0.1 M $AgNO_3$ solution at room temperature for 20 min. The Ag^+ doping could be achieved by subsequent ion-exchange with K^+ on surface-modified of PI films. This resulted in the formation of Ag^+-doped precursor layers. The chemical process of the above two steps is illustrated in Figure 1. After being rinsed with copious amount water, the silver ion-doped films were subjected to the irradiation with ultraviolet light irradiation for several time durations in air at room temperature to reduce the adsorbed Ag^+ ions to metallic silver. A fluorescent lamp (main wave length of 315 nm) with a heat ray cut filter was used for that purpose.

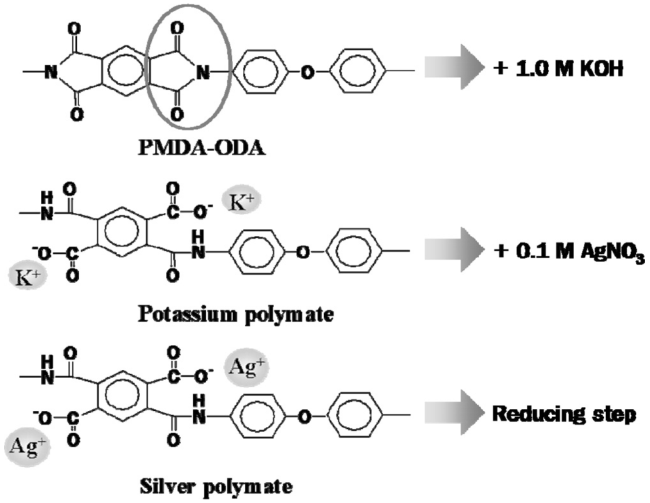


FIGURE 1 The ring-opening reaction of the PI film.

(2) *Electroless plating*

The copper solution bath for electroless plating contained 0.04 M copper sulfate, 0.035 M potassium sodium tartrate 4-hydrate, 0.25 M sodium hydroxide and 0.6 M aqueous solution of formaldehyde (37.2 wt%). The metallized film was immersed in the prepared copper solutions. The solution was ultra-sonicated for 20 min at 40 ~ 50°C. Copper in the copper solution were easily plated on to the immersed film surface. The thickness of plating layer was controlled by varying the immersing time. The plated PI film was washed with DI water to remove by-products or residues and then dried in air condition.

Characterization

The surface morphology of the layers of silver and copper were investigated by atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments) in contact mode. The chemical structure of PI film was investigated by FT-IR (Perkin Elmer, FT-IR spectrometer, Spectrum 2000). Composition of surface layer was investigated using as energy dispersive X-ray (EDX, S-2150, Hitachi) spectrometer.

RESULTS AND DISCUSSION

Characterization on the Composition of Polyimide Film Surface

As shown in Figure 2, modified-surface of PI film was derived from the imide ring opening reaction at the surface of the PI films. EDX survey spectra reflected the changes in chemical composition due to the hydrolysis reactions on the surface of PI films. In the surface of PI films of the virgin form, only C, O peaks were observed in the EDX spectra (Fig. 2(a)). N peak was not observed because of N peak has similar position with C peak. After treatment with 1.0 M KOH solution, one additional peak of K was observed (Fig. 2(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. But the treatment with 1.0 M KOH solution provided the surface modification. 1.0 M 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. K peak disappeared after metallization with 0.1 M $AgNO_3$ solution (Fig. 2(c)). Instead, Ag peak was observed since Ag^+ was ion-exchanged with potassium ion on the surface of PI films. Ag^+ on the surface of PI was reduced to Ag^0 by a reduction step. This resulted in the formation of

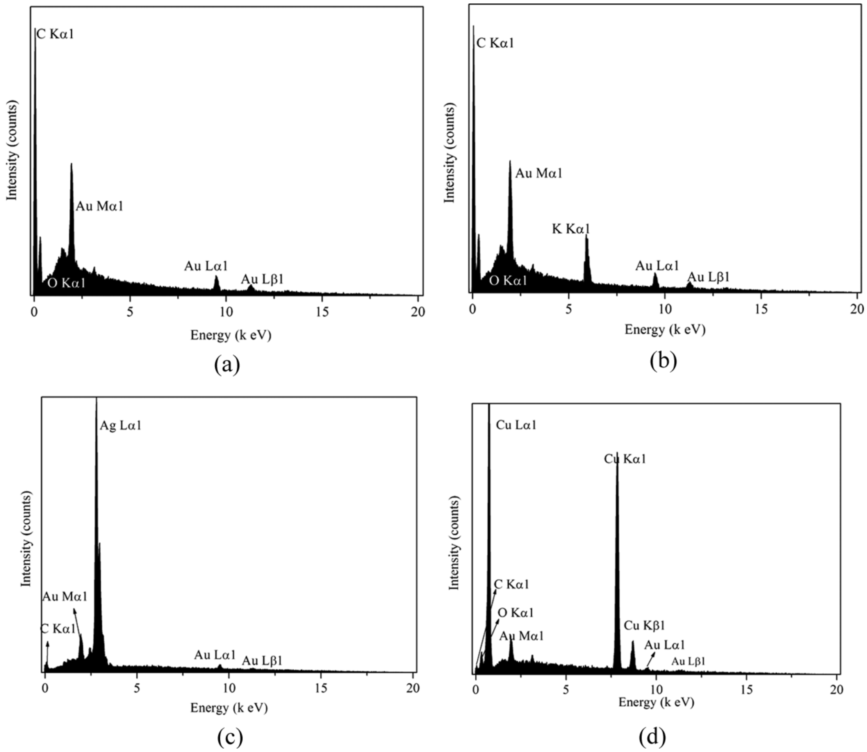
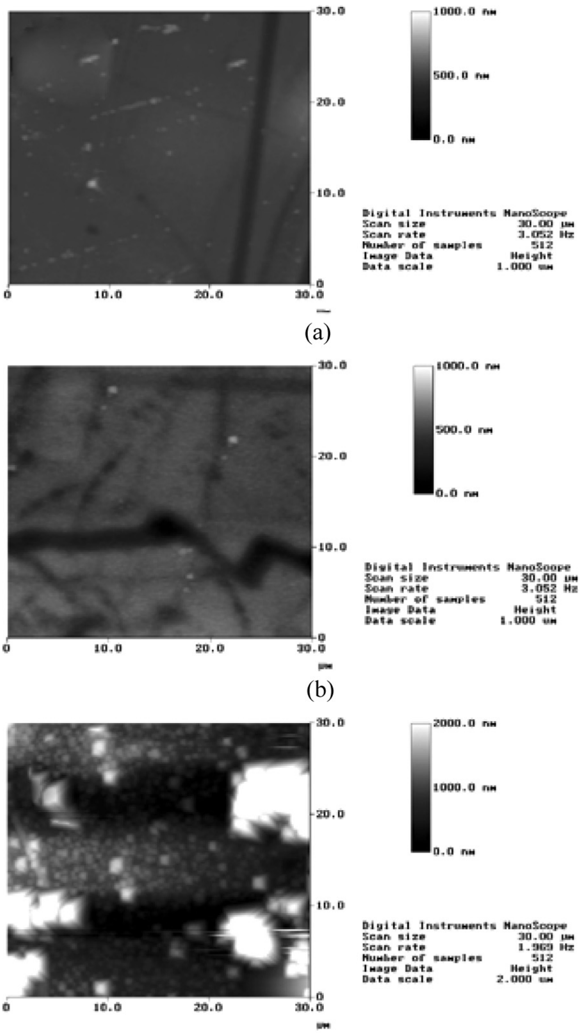


FIGURE 2 EDX data of the PI surface after each step: (a) PI film, (b) after etching of the PI surface with KOH solution, (c) ion-exchanged with Ag^+ on the surface of PI, (d) after electroless copper plating of PI films.

Ag layer. This Ag layer provided a roughened surface for the electroless plating of copper layer. The roughed surface of PI film was immersed in the copper solution for deposition of copper (Fig. 2(d)).

Surface Morphology of Polyimide Film

Surface morphology of PI surface was observed with an AFM and are shown in Figure 3. Figure 3 shows the changes in surface morphology during each step. Original PI film had the smooth surface. When the film was etched with 1.0 M KOH solution (Fig. 3(a)) the surface of PI film was modified to form carboxylic acid group and amide group through cleavage of the imide rings. This is shown in Figure 3(a). The modified-surface was immersed into the 0.1 M $AgNO_3$ solution for ion-exchange with K^+, and then silver ion on the surface of PI film



(a)

(b)

(c)

FIGURE 3 The AFM image of PI film surface: (a) after 1.0 M KOH solution treatment, (b) after ion-exchanged with Ag^{+}, (c) after plating with copper.

was reduced to silver layer (Fig. 3(b)). By illuminating with a fluorescence lamp at room temperature for 1 hr. Silver particles were successively produced and observed with AFM after reduction of Ag^{+}. The silver particles resulted in the uniform surface layer. This film was immersed into copper solution for 20 min at 40 ~ 50°C. Copper was

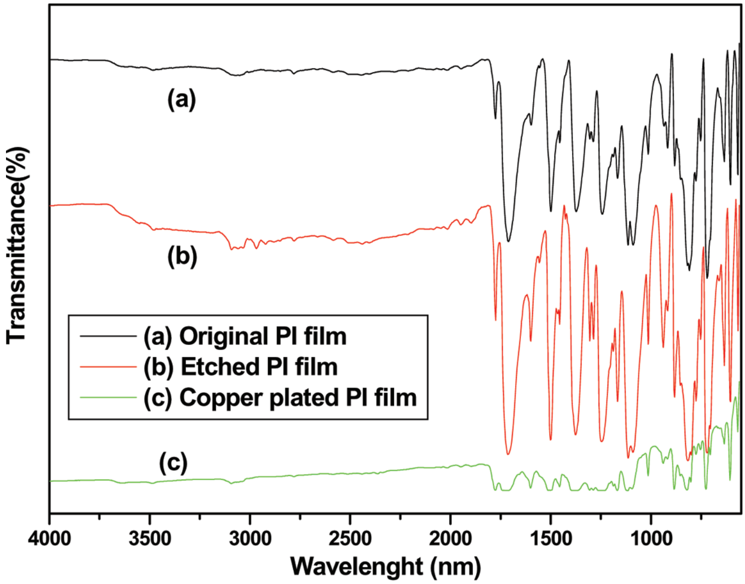


FIGURE 4 The FT-IR spectra of the surface of PI film at the different stages of modification: (a) the initial state, (b) after 1.0 M KOH solution treatment, (c) after plating with copper.

deposited on the surface of the Ag metallized PI film (Fig. 3(b)) and resulted in the copper plating (Fig. 3(c)).

FT-IR Study of the Polyimide

Figure 4 shows the FT-IR spectra of the PI films coated with metal layer by electroless plating method after each step. Figure 4(a) shows FT-IR spectrum of original PI film. Figure 4(b) shows FT-IR spectrum of PI film treated with KOH solution. Characteristic peaks observed at around 1650 cm^{-1} and 1370 cm^{-1} in Figures 4(a) and 4(b) are corresponding to the carbon and oxygen double bond and carbon and nitrogen single bond in imide of PI film. Figure 4(b) shows the other peak observed at around 3600 cm^{-1}. This corresponded to the carbon and oxygen single bond of modified surface of PI film. Through the result, it can be seen that the surface of PI film was modified by ring opening reaction. Figure 4(c) shows FT-IR spectrum of PI after copper plating. The peak intensities of PI at 1700 cm^{-1} and 1350 cm^{-1} in Figures 4(a) and 4(b) were gradually decreased as increasing the thickness of copper plating. The results indicated that activated surface of PI was gradually plated with copper.

CONCLUSION

In this study, PI film coated with copper particles was fabricated by electroless plating technique. In order to increase adhesive of PI film, the surface of PI films was treated with KOH solution. It was seen that modified-surface of PI films was result of the imide ring opening reaction at the surface of the PI films. K^+ bonded at carboxylate functional group on the modified surface of PI. PI film on the modified-surface when it was immersed into 0.1 M $AgNO_3$ solution and then dried with fluorescence lamp, Ag^+ ions to metallic silver layer that was used to improve the adhesion between copper plating and PI film. Copper was deposited very stability by surface of films through the activation on the silver layer by electroless copper plating. Uniform copper layer was deposited on the surface of PI film by electroless plating method. Although more work is needed to optimize a thickness of plating layer and the particle size on the PI films, there are promising applications of these processes to fabricate metal coated conducty film.

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