All-Wet Metallization Process for Transparent Polyimide Films

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Abstract. Electrically conductive Ag thin films were successfully formed onto optically transparent polyimide films via all-wet chemical process. The process involves alkaline-induced surface modification of polyimide films, subsequent incorporation of Ag⁺ ions through ion exchange reaction followed by reduction of incorporated Ag⁺ ions. Initial alkaline treatment time determines thickness (depth) of surface-modified layer and amount of Ag⁺ ions loading consequently. Higher Ag⁺ ions loading result in forming electrically conductive Ag thin films and its granular interfacial structure. Cu electroplating is able to be conducted on the resulting Ag thin films directly, and adhesive strength between the Cu/(Ag) film and transparent polyimide substrate reached up to 2 kN m⁻¹.

1. Introduction

Optically transparent polyimide films have received much attention due to their thermal stability, flexibility, and chemical durability as an alternative to glass substrates used for various optoelectronic devices including solar cells, electronic papers and displays. For such applications, surface metallization technique is essential to fabricate electrodes and circuits onto film surfaces. Generally, dry process including physical vapor deposition (PVD) and chemical vapor deposition (CVD) is employed in order to fabricate metallic thin films onto polyimide film substrates [1-3]. However, dry process consumes larger energy and higher cost than wet process involving electroless and electroplating is applied for metallizing polyimide surfaces. To carry out successful electroless plating for polymer substrates, proper roughness yielding anchoring effect and consequent preferable adhesion and catalytic activity initiating electroless plating reaction have to be induced to the substrate surface through relatively tedious process consisting of a lot of steps, e.g., pre-cleaning, water rinsing, chemical etching, sensitizing, and activating [4].

On the other hand, direct metallization process has been developed as a facile technique for metallizing polyimide surfaces [5-14]. The direct metallization process for polyimide films mainly consists of alkaline-induced surface modification, metallic ions incorporation through ion exchange reaction, and reduction of incorporated metallic ions. In the previous report [14], Cu plating film fabricated onto the polyimide (Kapton) film through direct metallization process showed 1 kN m⁻¹ of...
90° peel strength, the value of which is sufficient to microelectronic uses. In this study, direct metallization process for transparent polyimide substrate (Figure 1) has been investigated and the adhesion between resulting Cu plating films and transparent polyimide substrates has been evaluated.

![Figure 1. Schematic illustration for direct metallization process for transparent polyimide films.](image)

2. Experimental

Optically transparent polyimide films are commercially received from Mitsubishi Gas Chemical Company, Inc. (Neopulim L-1000, 100 and 200 μm in thickness). All chemicals excepting for Cu electroplating additives were purchased from Nakalai Tesque Company, Inc. and used without any purification. A brightener (Top Lucina) added into Cu electroplating solution was kindly provided by Okuno Chemical Industries Co., Ltd.

Transparent polyimide films were immersed into 5 M KOH aqueous solution at 70 °C for 3 h. After KOH treatment, the films were rinsed with large amount of water and immersed into 50 mM AgNO₃ aqueous solution at ambient temperature for 5 min. After immersion into AgNO₃ aqueous solution, the films were rinsed with water and immersed into 1 mM KBH₄ aqueous solution at 30 °C for 5 min in order to reduce Ag⁺ ions incorporated into the film. After reduction of Ag⁺ ions, the films were washed with copious amount of water. Finally, Cu electroplating was conducted on Ag thin film formed on the polyimide film with plating bath composition and conditions expressed in Table 1.

| Table 1. Cu electroplating bath composition and conditions. |
|----------------------------------------------------------|
| CuSO₄•5H₂O               | 70 g dm⁻³                     |
| H₂SO₄                   | 200 g dm⁻³                    |
| Cl⁻                     | 50 mg dm⁻³                    |
| Brightener              | 5 ml dm⁻³                     |
| Temperature             | R.T.                           |
| Current density         | 2.0 A dm⁻²                     |

FT-IR spectra of the transparent polyimide film surfaces before and after KOH treatment were recorded on a Nicolet 4700 spectrometer with an ATR attachment. Amount of Ag⁺ ions incorporated in surface-modified polyimide films were quantified by using an ICP atomic emission spectrometer (Shimadzu ICPS-8100). UV-VIS absorption spectra of the films were collected with an UV-3150
spectrometer (Shimadzu). Sheet resistance of Ag thin films was measured with a low resistivity meter (Loresta EP MCP-T360, Mitsubishi Chemical Analytech) using a 4-pin probe method. Cross-sectional TEM observations were performed with JEM-2100, JEOL operating at 200 kV. Cross-sections of the films for TEM observations were prepared with a microtome (Ultracut UCT, Leica) using a diamond knife. Adhesive strength between Cu plating film and transparent polyimide substrate was evaluated by means of 90° peel test with using a bond tester (Dage 4000, Nordson DAGE) operating at 25 mm/min of peel rate.

3. Results and discussion

3.1. Surface modification of transparent polyimide films
Changes in molecular structure of the polyimide films before and after KOH treatment were characterized with ATR-FTIR spectroscopy and the obtained spectra were shown in Figure 2. The spectrum obtained from a bare transparent polyimide film shows typical absorption peak (i) assigned to imide C=O stretching modes at 1780 and 1710 cm⁻¹ (Figure 2A) [15-17]. On the other hand, after KOH treatment for 3 h, absorbance for these absorption bands are significantly decreased and new absorption bands attributed to (ii) amide I band (carbonyl stretching) and (iii) amide II band (coupling C-N stretch and N-H deformation) are appeared at 1680 and 1550 cm⁻¹, respectively (Figure 2B) [15-17]. In addition, absorption band (iv) corresponds to carboxylic acid groups is obviously appeared at 1410 cm⁻¹ with neutralizing the KOH-treated film with 1% HCl aqueous solution (Figure 2C) [15-17]. These results indicate that amide bonds and carboxyl groups are successfully formed via hydrolysis reaction of five-membered imide rings with KOH treatment in the present condition. According to the previous investigation, in the case of Kapton film, similar degree of surface modification had been achieved by treating with 5 M KOH aq. at 50 °C for 5 min [8,9]. In order to modify a Neopulim film surface similarly, it is found that a much stronger hydrolysis condition has to be required. These behaviors may be related to intrinsic water absorption properties of 2.9 and 1.6%, for Kapton and Neopulim films, respectively.

![Figure 2. ATR-FTIR spectra obtained from transparent polyimide films (A) before and (B) after KOH treatment for 3 h (C) followed by neutralization with using 1% HCl aqueous solution.](image)

3.2. Incorporation of Ag⁺ ions
As reported elsewhere [8,9], Ag⁺ ions will be incorporated into the surface-modified layer of transparent polyimide film via ion exchange reaction between K⁺ and Ag⁺ ions with immersing the surface-modified film into AgNO₃ aqueous solution. Figure 3 shows relationship between initial KOH treatment time and amount of incorporated Ag⁺ ions in the films after ion exchange step (2nd step in
Ag$^+$ ions loading is linearly increased with increasing initial KOH treatment time. From the previous studies [7], it has been found that thickness of surface-modified layer in depth direction is increased in proportional to initial KOH treatment time. Depth profiling revealed that incorporated metallic ions were homogeneously distributed in the surface-modified layers in macroscopic scale [11,14]. In other words, cation exchangeable site, i.e., carboxyl groups, would be homogeneously formed over entire surface-modified layer through initial KOH treatment. Therefore, Ag$^+$ ion loading can be readily controlled with initial KOH treatment time.

Influence of KOH treatment-induced surface modification and subsequent Ag$^+$ ions incorporation on optical transparency of the films was investigated with UV-VIS absorption spectra (Figure 4). There is no change in UV-VIS absorption spectra for before and after KOH treatment and following Ag$^+$ ions incorporation, which indicate those two steps (1st and 2nd step in figure 1) yield no deterioration in optical transparency of the present polyimide films.

![Figure 3. Effect of KOH treatment time on Ag$^+$ ion loading after ion exchange reaction in AgNO$_3$ aqueous solution.](image3)

![Figure 4. UV-VIS absorption spectra obtained from the films (A) before and (B) after KOH treatment for 3 h and (C) subsequent Ag$^+$ ions loading.](image4)

3.3. Formation of Ag thin films

Film appearance of the films after reduction of incorporated Ag$^+$ ions, which were fabricated with different initial KOH treatment time, is shown in Figure 5. Initial KOH treatment for 0.5 and 1 h gives rise to formation of the films colored light yellow and brown, respectively, and these colors can be attributed to surface plasmon resonance absorption of Ag nanoparticles. On the other hand, mirror-bright Ag films are successfully formed onto the surface of the transparent polyimide films which were initially KOH-treated for 2 and 3 h. While former two samples (corresponding to figure 5B and C) showed too high resistivity to measure, latter two samples (corresponding to figure 5D and E) showed relatively lower sheet resistance of 10.3 and 3.02 $\Omega$/sq, respectively, the values of which are acceptable to carry out direct electroplating.

Figure 6A–C show cross-sectional TEM images of the films after reduction treatment of incorporated Ag$^+$ ions and subsequent Cu electroplating. Ag particles of few tens of nanometers in diameter are deposited at the surface of transparent polyimide film and it seems that the particles coagulate with each other (Figure 6A). This film, which is corresponding to the sample in figure 5C, showed almost no electric conductivity. The cross-sections prepared for TEM observation had at least 100 nm in thickness, thus Ag thin film shown in figure 6A would be made of isolated Ag particles, in other words, that would be not continuous film. Initial KOH treatment for 3 h results in formation of thicker Ag film and granular interface consisting of Ag nanoparticles and surface-modified polyimide layer as shown in Figure 6B. After Cu electroplating, uniform Cu film is directly deposited onto the Ag thin film and the specific granular interfacial nanostructure is maintained. Such interfacial
microstructure would be an effective adhesion promoter between metallic films and polymer substrates [14].

Adhesive strength between Cu/Ag film and transparent polyimide substrate was evaluated by means of 90° peel test. Typical peel strength profiles against peeling distance are shown in Figure 6D. Extremely high peel strength (>1.5 kN m⁻¹) is demonstrated for the most part of the films, while there are a few poor adhesive regions. Interestingly, the peel strength value over 2 kN m⁻¹ is much higher than the value (1 kN m⁻¹) of Cu plating films on Kapton films which were fabricated in the same way reported in the reference [14]. The detailed mechanism for the difference in peel strength between Neopulim samples and Kapton samples is under the investigation. One of the probable reasons is assigned to difference in intrinsic mechanical properties for each type of polyimide film.

Figure 5. Changes in film appearance (A) before and (B–E) after reduction of incorporated Ag⁺ ions prepared with initial KOH treatment for (B) 0.5 h, (C) 1 h, (D) 2 h, and (E) 3 h.

Figure 6. Cross-sectional TEM images of the films (A, B) after reduction of incorporated Ag⁺ ions and (C) subsequent Cu electroplating and (D) representative three profiles of 90° peel strength of Cu plating film corresponding to the sample (C). Initial KOH treatment time; (A) 1 h, (B–D) 3 h.
4. Conclusion
We have successfully demonstrated that mirror-bright Ag thin films are readily deposited onto transparent polyimide films via direct metallization process with relatively stronger surface modification condition. Cu electroplating can be performed on electrically conductive Ag thin films having specific interfacial microstructure. Extremely high adhesive strength between Cu films and transparent polyimide substrates is suitable for optoelectronic applications.

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