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Improvement of Adhesion between Copper Layer and Polyimide Films Modified with Alkaline Potassium Permanganate and/or Alkali Surface Treatments

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Summary: The adhesion strength of polyimide films were enhanced by treatment with alkali and/or alkaline potassium permanganate. No effect observered on the thermal decomposition as measured by TGA. The chemically modified PI film surface was then treated with a catalyst, coated with nickel by electroless plating, and a subsequent layer of electrolytically applied copper. Water contact angles on the treated PI surface were decreased. As surface roughness of treated PI films was increased, adhesion increased also. Even though the modified PI films had little decrease in their thermal properties, they demonstrated a maximum adhesion strength up to 837 g_f/cm.

Keywords: adhesion; alkaline potassiun permanganate; elctroless plating; modify; polyimide

Introduction

Polyimides have been widely used as protective overcoats and dielectric layers for semiconductor devices because of their good properties, e.g. low dielectric constant, excellent thermal and mechanical properties, and good planarizability.[1,2] Since polyimides are applied as an interlayer between substrates such as metals, ceramics, and other polymers, the adhesion between the polyimide and these materials is particularly important for the performance of semiconductor devices. Modification of PI film is used to improve adhesion between copper layer and polyimide. There are two methods of PI film modification; dry process and wet process.[3] Dry processes include irradiation of surface with generated plasma treatment, corona treatment, ammonia treatment[4,5] Wet processes include KOH treatment,[6] amine treatment.[7] In this study, in order to enhance adhesion strength, we performed chemical modification by a wet-process. Polyimide films were treated with alkaline $KMnO_4$, KOH, and ethylene diamine, or their mixtures. The chemically treated PI surface was then treated with a catalyst, coated with nickel by electroless plating, and a subsequent layer of electrolytically applied copper. Interaction between modified PI film and plated metal was investigated.

Experimental Part

PI film was used Kapton 200H(50 μm). $KMnO_4$, KOH and ethylene diamine manufactured by Junsei were used for the surface treatment of PI. Alkaline potassium permanganate was prepared by dissolving a 15 g of $KMnO_4$ into 1.2 N KOH aqueous solution. Electroless Ni plating solution manufactured by KMP tech.(Nimuden-SX, Korea) was used. Catalyst solution was prepared with $PdCl_2$(Kojima Chemicals), $SnCl_2$(Junsei). Treatment condition of PI films were listed in Table 1∼2. The chemically treated PI surface was then

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Table 1.
Treatment condition for surface treatment of polyimide; first step: EDA, and last step: alkaline $KMnO_4$.

Code	Reaction time(min)	
	60 °C EDA	75 °C alkaline $KMnO_4$
A-1	1	5
A-2	3	5
A-3	5	5

Table 2.
Treatment condition for surface treatment of polyimide: first step: KOH, second step: alkaline $KMnO_4$, and last step: EDA.

Code	Reaction time (min)		
	RT, 3 M KOH	75 °C alkaline $KMnO_4$	RT 30% EDA
B-1	1	5	1
B-2	1	5	3
B-3	1	5	5
B-4	3	5	1
B-5	3	5	3
B-6	3	5	5
B-7	5	5	1
B-8	5	5	3
B-9	5	5	5

treated with a catalyst solution, coated with nickel by electroless plating for, and a subsequent layer of electrolytically applied copper.

ATR (attenuated total reflection) FT-IR spectra of treated PI films were obtained using a Shimadzu FT-IR 8300. Morphology of surface treated PI films were analyzed with a AFM(atomic force microscopy, Veeco model MMAFM-2). Adhesion strength of PI/metal plate was measured by a 90° peel test at an peel rate of 10 mm/min using SPG model S8D25-90A. 10 mm

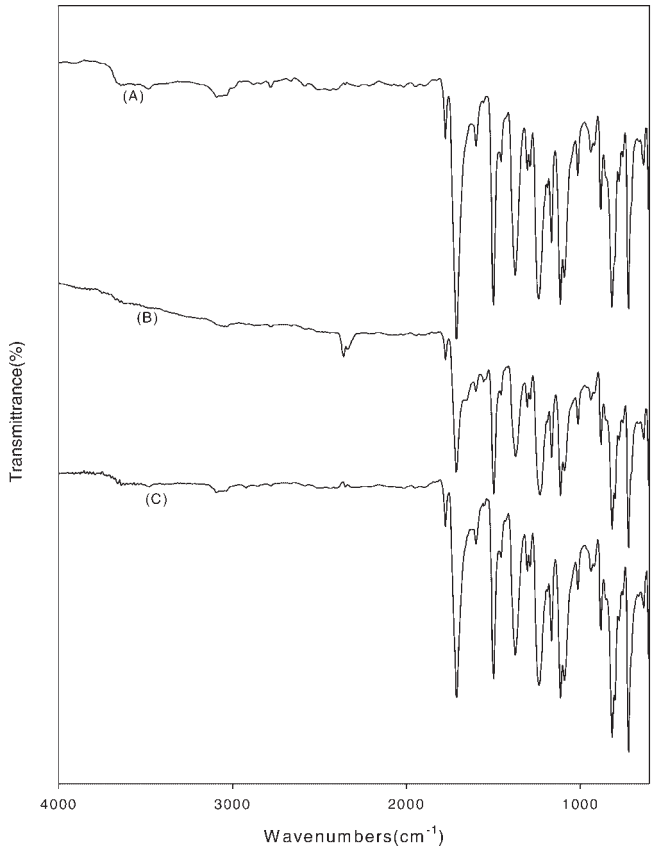

Figure 1.
FT-IR ATR spectra of PI films treated with various conditions; (A) untreated, (B) treated with 30% EDA (60 °C, 5 min), and (C) A-3.

wide copper layer strips cut with a razor blade were peeled from PI.

The thermal stability of treated PI films were measured using a 951 TGA thermogravimetric (TG) analyser supplied by TA Instruments. The TG analysis curves of the treated PI films were recorded at constant heating rate of 20 C/min under air. Receding and advancing water contact angles on the treated PI surface were measured in an automated contact angle goniometer, Model DSA-100 supplied by KRUSS.

FT-IR ATR Spectrum

Figure 1 shows FT-IR ATR spectra of modified PI films. (A) was spectrum of the virgin PI. As shown in Figure 1(A), 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. (B) was spectrum of PI film modified with EDA. It showed streching C=O of amide at 1650 cm^{-1} as the picks at 1780 cm^{-1} and 1720 cm^{-1} were decreased. Asymmetric stretching of COO^- at 1595 cm^{-1} increased its intensity; meanwhile peak of C–N at 1370 cm^{-1} decreased its intensity. However, no change occurred with treatment of alkaline $KMnO_4$ after treatment of EDA(C).

Thermal Property

Figure 2 shows TGA thermograms of untreated PI and A-1. The virgin sample showed strong heat stability up to 550°C, but it started to degrade when temperature reached at 600°C. When temperature reached at 700°C, it degraded completely. Modified PI film (A1) showed the similar thermal behavior as virgin sample, except slightly lower degradation temperature over 600°C.

Contact Angle

The contact angle of untreated PI showed 73.4°, EDA treated PI film showed 60.7°, however, the contact angle was decreased after treatment (Table 3). A-1 showed 49.2°, and B-4 showed 48.0°, respectively. A decreasing of contact angle attributed to increment of hydrophilicity of sample caused by the formation of acid and amide. It showed good adhesion when contact angle laid between 45 and 50°.

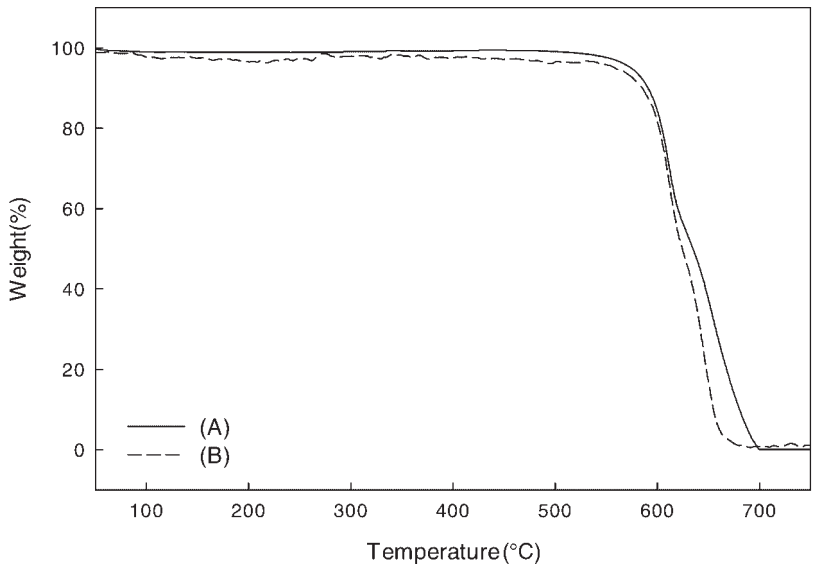

Figure 2.
TGA thermograms of untreated PI film (A) and A-1 (B).

Table 3.
Contact angle of PI films treated under various conditions.

Code	Contact angle (°)	Code	Contact angle (°)
A-1	49.2	B-4	48.0
A-2	47.2	B-5	48.5
A-3	44.4	B-6	47.2
B-1	53.1	B-7	47.1
B-2	50.1	B-8	45.1
B-3	46.3	B-9	44.8

Morphology

Figure 3 shows morphologies of modified PI films. Ra values of untreated PI film was 1.058 nm and EDA treated film (B) was 2.470 nm. In case of (C), its roughness increased up to 4.382 nm. PI film modified with 30% EDA (B) showed a little increase in surface roughness, but A-3 and B-4 showed a much larger increase in surface roughness.

Adhesion Strength

Metal plating was only performed on PI film with surface modification. Table 3 shows peel adhesion strength of modified PI films between electroplated Cu layer. It showed 402 g_f/cm of adhesion for EDA treated samples and increased its adhesion to 710∼837 g_f/cm with following alkaline $KMnO_4$ treatment. Type B showed lower values than type A. When KOH treatment time increased, adhesion strength of B1-3 increased. B4 showed the highest adhesion strength of 687 g_f/cm. Otherwise, 5-6

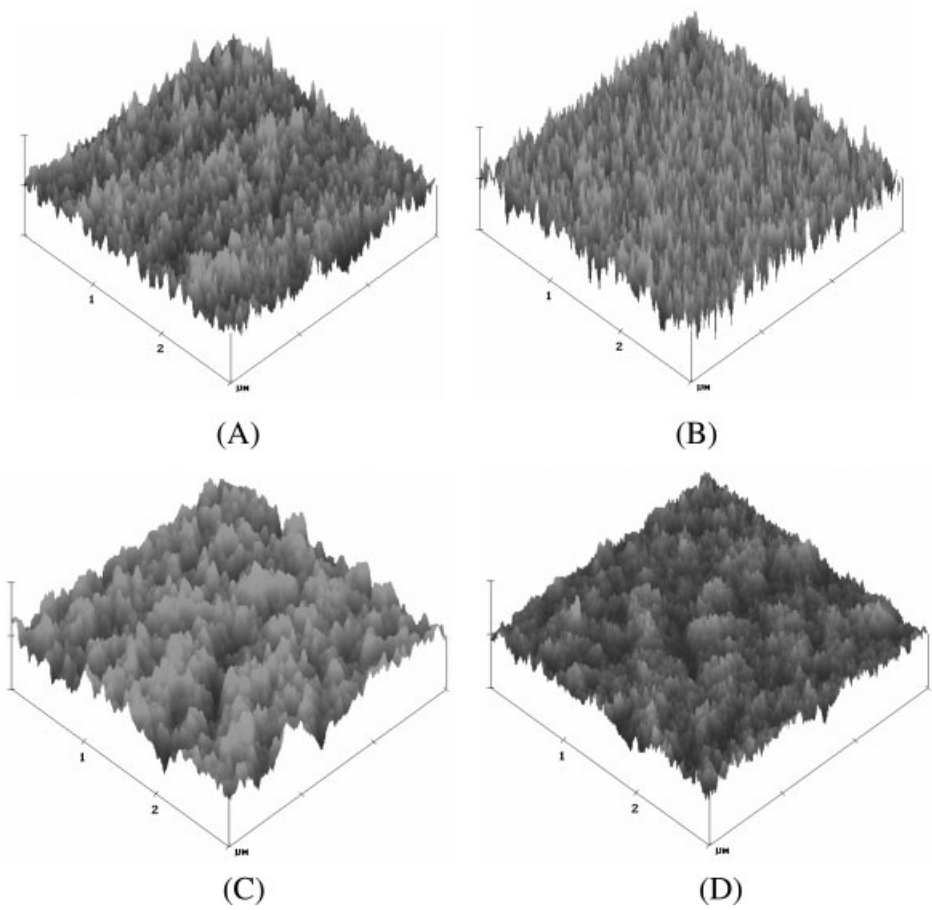

Figure 3.
3-Dimensional AFM photos of PI films; (A) virgin, (B) treated with 30% EDA (60 °C, 5 min), (C) A-3, and (D) B-4.

Table 4.
Peel adhesion strength between modified PI film and electroplated Cu layer.

Code	Adhesion strength (g_f/cm)	Code	Adhesion strength (g_f/cm)
A-1	837 ± 5	B-4	687 ± 2
A-2	730 ± 7	B-5	531 ± 5
A-3	710 ± 2	B-6	433 ± 3
B-1	490 ± 3	B-7	481 ± 6
B-2	547 ± 5	B-8	462 ± 3
B-3	544 ± 8	B-9	533 ± 8

showed decreasing tendency of adhesion strength, when KOH treatment time increased. As surface roughness increased, adhesion increased (Figure 3 and Table 4). The reduction of contact angle showed strongest adhesion strength at 45∼50°.

Conclusion

Metal plating was only performed on PI film with surface modification. Water contact angles on the treated PI surfaces were decreased. As roughness of treated PI films were increased, adhesion increased. Maximum adhesion strength was 837 ± 5 g_f/cm with EDA modification and then alkaline potassium permanganate.

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