할셀 도금조에서 무전해 도금에 의해 PET에 도금된 구리층 특성에 관한 연구

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Study on Characteristics of Copper Film Immobilized on PET Substrate by Electroless-Plating Method in Hull Cell Plating System

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Introduction

The metallization of polymer materials has attracted attention in recent years due to its wide range of technological applications. Many polymer films, fibers and plastics are metallized for food packing, microelectronics, computer technology and automative industry to provide an electro-magnetic shielding property[1]. Metal foil and conductive paints and laquers, sputter-coating, vaccum plating are recently developed metal-coating techniques[2]. Among them, eletroless metal plating is preferred way to produce metal-coated materials[3]. Because electroless plating has advantages in terms of coherent metal deposition, exellent conductivity and applicability to complicated- shaped materials or nonconductors, it can be applied to most polymer substrates. The electroless process has been reported to occur due to a combination of partial electrode oxidation and reduction processes. The driving force for these reactions arises from the potential difference that exists between the metal solution interface and the equilibrium electrode potential for these (cathod and anode) half-reactions[2]. Generally, plating is sustained by the catalytic nature of the plated matal surface itself, so the adhesion at the metal/polymer interface and the mechenical and electrical properties of the coating are important considering the use of such materials in technological applications[4]. Considering the difficulty to optain adherent metal coatings by electroless plating on commonly used polymers and the lack of reseach describing the processing of flexible metallized polymer films by electroless methods, the present work was focused on the electroless metallization of poly(ethylene terephthalate) PET films with copper. The excellent adherence and flexibility obtained with the metallized films makes this simple and low-cost method viable for the fabrication of flexible circuits.

Experimental

Sample preparation

Poly(ethylene trephthalate) films (100㎛, SKC), as a filler were rinsed with ethanol (DEA JUNG, extra pure reagent) sonication bath for 30min, distilled water and dried in air. The metallization process of the polymer films consisted of the following steps: (ⅰ) cleaning (ii) etching (iii) activation (iv) acceleration (v) electroless Cu plating (vi) post treatment (vii) drying. Etching was carried out by immersion of the PET film in a solution containing 35% HCl (35%, DUKSAN, Korea) at 65℃. The time of acid etching was controlled from 30 to 90min in order to observe its influence on the hydrophilicity and surface roughness. after, samples were rinsed with distilled water and dried in air. Activation was conducted by immersion of the samples in an aqueous solution containing HCl (35%, DUKSAN, Korea), $PdCl_2$ (1g, Kojima. Co.) and $SnCl_2$ (98%, SIGMA-ALDRICH) at 25℃ for 10 min. The specimens were then rinsed with distilled water and immersed in a solution containing the accelerator (HCl 35%, DUKSAN, Korea) at 25℃ for 3min. Afterwards, Electroless Cu plating was conducting that the speciments were immersed in the electroless Cu metallization bath containing: $CuSO_4 \cdot 5H_2O$ (Exter pure, DUKSAN), $NiSO_4 \cdot 6H_2O$ (Fist grade, SHINYO), NaOH, Roselle salt (99%, ACS, SIGMA-ALDRICH) HCOH (37wt%, ACS, SIGMA-ALDRICH) mixed sol. at 40-80℃ , pH 7-12, Cu/Ni = 12.5 for 3-30min. Post treatment was carried out by citric acid (99.5%+, ACS, SIGMA-ALDRICH) and sodium hypophosphite (99%, ACS, SIGMA-ALDRICH) mixed sol. at 25℃ for 10min. Finally, the samples were rinsed with distilled water, ethanol and dried in an oven at 50℃.

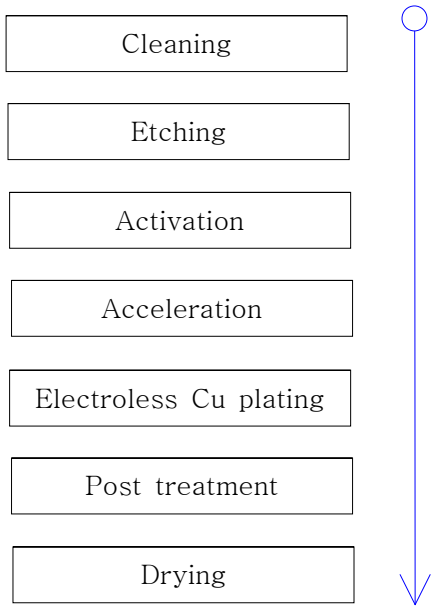

Figure 1. Flow chart electroless copper plating on PET film.

Table 1. Bath composition and plating condition of electroless copper plating

Process	Reagent	Concentration
Activation	HCl	0.1-1M
	$PdCl_2$	0.005-0.02M
	$SnCl_2$	0.08-0.32M
Acceration	HCl	0.1-2M
Bath	$CuSO_4$	0.01-0.1M
	$NiSO_4$	0.001-0.01M
	Roselle salt	10-60g/l
	HCOH	30-150ml
	pH	7-12
	Temperature	40-80℃
	Time	3-30min
Post-treatment	Citric acid	0.01-0.1M
	NaH_2PO_2	0.01-0.5M

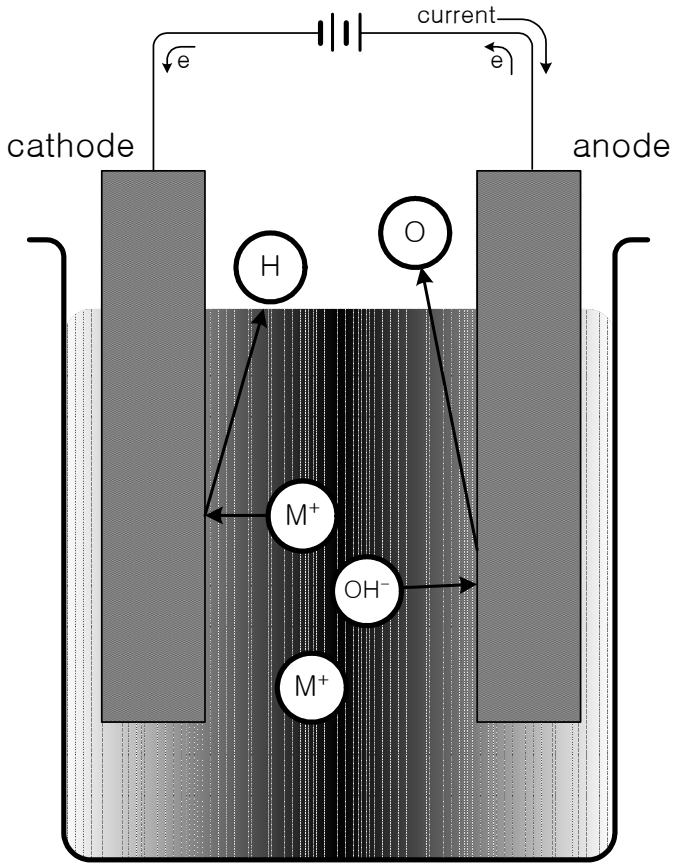

Figure 2. Schematics of electroplating system

Results and discussion

Copper plating was performed on the copper film immobilized by an electroless plating method to obtain the copper/PET film for the electronic parts. Through the experiments by copper plating method, the optimum temperature was 60℃, the optimum pH was 9, the optimum bath composition was Cu^{2+}/Ni^{2+} = 12.5 and the optimum plating time was 10 min. The characteristics of a plated copper film was analyzed with surface roughness, hardness, thickness deviation, and crystal structure and so on.

Conclusions

The methods of surface treatment and copper plating considered in this work, allow the production of copper coatings on PET films with appropriate structures for the fabrication of flexible plastic circuits. A detailed study on the thermal and chemical degradation mechanism of the PET substrates is still under study.

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