초임계 무전해 도금 기술을 사용한 PET기판위의 구리박막의 표면 형태학

강전언 · 김남기· 류정 · 이희대[1] · 김문선*
성균관대학교 화학공학과, [1]목원대학교 응용화학과
(moonsunkim@skku.edu*)

Surface Morphology of Copper Thin Layer Plated on Poly(Ethylene Terephthalate) Substrate by Supercritical Fluid Using Electroless Plating Technology

Jeon-Un Kang , Nam-Ki Kim , Jung Ryu, Hee-Dai Lee[1], Moon-Sun Kim *
Department of Chemical Engineering, Sungkyunkwan University ,
[1]Department of Applied Chemical Engineering, Mokwon University
(moonsunkim@skku.edu*)

Introduction

With industrial advances, current interests in the study on the surface property have stimulated the developments in the electrical and novel material industry. Plating is to apply a metallic coating to another material surface. The most common surfaces to be plated are metals and plastics and plating can be used for different reasons. Surface treatment technology is classified into the dry process and the wet process. It is a wet process that metal ion is reduced on the substance from aqueous solutions. The kinds of wet process are electroplating and electroless plating etc. Dry process is using the high reaction rate in vacuum condition. There are CVD (chemical vapor deposition) and PVD (physical vapor deposition) processes [1]. 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[2]. Metal foil and conductive paints and laquers, sputter-coating, vaccum plating are recently developed metal-coating techniques[3]. Some objects are plated to increase their sturdiness and to provide a hard shell for whatever it is plate on. Some are plated to avoid corrosion, and a few are plated just to give an attractive finish. Among them, supercritically electroless metal plating is preferred way to produce metal-coated materials[5]. Because supercritically electroless plating has advantages in terms of coherent metal deposition, excellent conductivity and applicability to complicated-shaped materials or nonconductors, it can be applied to most polymer substrates. Supercritical fluid is defined as 'a fluid above its critical temperature and critical pressure'. It has particular characteristics which are different from conventional solvent. Supercritical fluids have been studied extensively in attempts to gain accurate and detailed knowledge of their fundamental properties. The utilization of supercritical fluids is studied widely. Generally, plating is sustained by the catalytic nature of the plated metal surface itself, so the adhesion at the metal/polymer interface and the mechanical and electrical properties of the coating are important considering the use of such materials in technological applications[5]. Considering the difficulty to obtain adherent metal coatings by supercritically electroless plating on commonly used polymers and the lack of research describing the processing of flexible metallized polymer films by supercritical plating methods. Cabanas at al.[6] studied the deposition of Cu film from supercritical

fluids using Cu(I) β-diketonate precursors. The present work was focused on the supercritically 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.

Theory

Faraday's law

During 1833 - 1834, Faraday published the results of a series of investigations on the relationship between the quantity of electricity passing through a solution and the amount of metal, or other substances, liberated at the electrodes : The conclusions were expressed in the two following laws [7].

① The amount of chemical decomposition produced by a current is proportional to the quantity of electricity passing through the electrolytic solution

② The amounts of different substances liberated by the same quantity of electricity were proportional to their chemical equivalent weights.

The quantity of electricity required to liberate 1 equiv. of any substance according to the second of Faraday's law, should be independent of its nature; this quantity is called the faraday; it gives the symbol F and, and will be seen shortly, is equal to 96,485 coulombs. Therefore, from the first of Faraday's laws, that I amperes following for t seconds will cause the deposition of W grams, it follows that

$$W = \frac{I \cdot t \cdot e_q}{F} \tag{1}$$

where

W = the quantity of being deposited in the electrode, g

I = the current which passes between electrode, A

t = the time which the current flows, sec

e_q = equivalent weight of deposited substances

F = faraday coefficient

The characteristics of supercritical fluid

A supercritical fluid is defined as a substance above its critical temperature (T_c) and critical pressure (P_c). The critical point represents the highest temperature and pressure at which the substance can exist as vapor and liquid in equilibrium. Supercritical fluid technology offers tremendous advantages, such as the absence of any organic solvent residues, and selective extraction and fractionation of different compounds. All of these advantages are almost impossible to obtain easily from conventional processes at low operating costs. Therefore, supercritical fluid technology is an ideal tool for the processing of active compounds for use in food products and dietary supplements. Supercritical CO_2 is certainly one of the most popular fluid because of its physiological compatibility, non-toxicity, inflammability, convenient critical parameters (T_C = 31 °C, P_C = 7.38 MPa), inexpensiveness, and environmental friendliness.

Experimental

Sample preparation

Poly(ethylene trephthalate) films (100㎛, SKC), as a filler were rinsed with ethanol 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) supercritical 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, supercritical Cu plating was conducting that the speciments were immersed in the supercritical Cu metallization reactor 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 35-65℃ , pH 12.5, CO_2/electrolyte (volume ratio) = 9, Cu/Ni = 12.5, the pressure of 7-17 Mpa for 10min. 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℃.

Experimental apparatus

Variables to be considered in supercritical plating process are the pressure, temperature, reaction time, agitation condition, composition of the electrolyte, and methanol concentration. ssel(SUS316) in a temperature controlled air bath with a magnetic agitator.

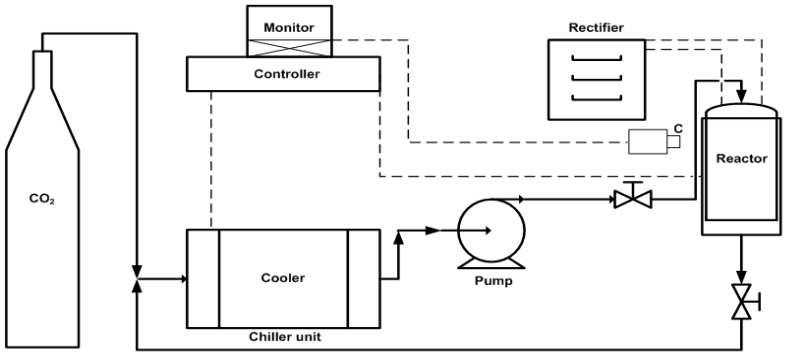

Fig. 1. Schematic diagram of supercritical plating system with supercritical CO_2

Fig. 1 shows that schematic diagram of supercritical electroplating system using supercritical CO_2. CO_2 is liquefied by chiller unit and poured into reactor by high pressure pump. The composition of nickel-electrolyte bath was given in Table 1

Table 1. Bath composition and plating condition of supercritical 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	12.5
	Temperature	35-65℃
	Time	10min
Post-treatment	Citric acid	0.01-0.1M
	NaH_2PO_2	0.01-0.5M

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 65℃, the optimum pH was 12.5, 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 supercritical 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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