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Improvement of copper plating adhesion on silane modified PET film by ultrasonic-assisted electroless deposition

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ABSTRACT

Copper thin film on silane modified poly(ethylene terephthalate) (PET) substrate was fabricated by ultrasonic-assisted electroless deposition. The composition and topography of copper plating PET films were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. Peel adhesion strength, as high as 16.7 N/cm, was achieved for the planting copper layer to the modified PET substrate with ultrasonic-assisted deposition; however, a relative low value as 11.9 N/cm was obtained for the sample without ultrasonic vibration by the same measurement. The electrical conductivity of Cu film was changed from 7.9×10^4 to 2.1×10^5 S/cm by using ultrasonic technique. Ultrasonic operation has the significant merits of fast deposition and formation of good membranes for electroless deposition of Cu on PET film.

1. Introduction

Flexible circuit boards (FCBs) based on Cu on polymer substrates are used as flexible interconnections, such as the hinges of cellular phones or chips on flex packaging, and are expected to be used more in the upcoming flexible IT gadgets [1,2]. Flexural endurance and long-term reliability of FCB acting as an electrically connector fundamentally rely on the peel strength, which is inherently related to the adhesion between Cu and polymer substrates [3,4]. Non-adhesive flexible copper clad laminate (FCCL) has been adopted as the base substrate for FCB with high density pitch [5]. Good adhesion between Cu and polymer substrate is the primary concern and has been researched in many studies which are generally related to physical or chemical surface modification [6,7]. The Cu/polyphenyl ether (PPE) film chemically modified by plasma treatment was measured to have an adhesive strength of up to 16 N/cm, which is the highest value reported [8]. The Cu/polyimide (PI) film pretreated by ion beam irradiation was detected to have an adhesive strength of about 8 N/cm, and Cu/PI FCCL is the most popular raw material for FCB in industry [9–11]. Poly(ethylene terephthalate) (PET) has been widely used in membranes, microelectronics, photonics and optics, because of its outstanding thermal, mechanical, physicochemical and dielectric properties [12]. Nevertheless, knowledge of the adhesion properties of Cu/PET system remains insufficient.

In general, copper metallization can be achieved by various methods, such as physical vapor deposition, chemical vapor deposition, electroplating and electroless plating [13]. Electroless plating is one of the most frequently adopted industrial processes for metallization because of its low cost, inherent selectivity and simplicity of processing [14]. Normally, electroless metallization has to be preceded by $SnCl_2$ sensitization and $PdCl_2$ activation. From the economic and environmental point of view, as well as the simplicity in process operation, it is desirable to have an auto-catalyst process without $SnCl_2$ and $PdCl_2$ for the electronic industry. Ultrasonic assistant during electroless plating generates a specific agitation resulting from the cavitation phenomenon on the surface of the substrate and in the liquid, which leads to high quality metal coating [15].

In this study, the auto-catalyzed, ultrasonic-assisted electroless copper plating on PET film with modification of silane was reported. The composition and topography of copper films were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. The adhesion strength of the copper plating with the modified PET surfaces was evaluated by peel adhesion strength measurement. Effect of the ultrasonic assistance during the copper depositing process was also discussed.

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2. Experiment

2.1. Materials

The PET film used in this study was purchased from Shanghai SPC Chemical Co. in rolls. 3-Aminopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, $CuCl_2{\cdot}2H_2O$, H_3BO_3, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$ ($EDTANa_2{\cdot}2H_2O$) and $C_2H_{10}BN$ (DMAB) were purchased from Sinopharm Chemical Reagent Co. Deionized water was purchased from Shanghai FDQ Water Co. The solvents were of analytical grade and were used without further purification unless otherwise mentioned.

2.2. Pretreatment of PET films

PET films of 75 μm thickness were cut into 5 cm × 1 cm sections for treatment. Firstly, the films were washed ultrasonically in acetone and deionized water for 15 min, dried at 60 °C for an arbitrary length of time. Secondly, the cleaned films were dip-coated with the 2-butanone solution of 0.5 vol% 3-aminopropyltrimethoxysilane and heated at 125 °C for 1 h to form a silica-like layer. Then the films were irradiated in air by UV-light (wavelength: 185 and 254 nm, TUV PL-L, PHILIPS Lights Co.) for 1 h. Finally, the films with the silica-like surface layer were immersed in a xylene solution containing 0.5 vol% 3-mercaptopropyltriethoxysilane for 2 h, then rinsed with xylene, ethanol and deionized water, respectively. The resulting films were heated at 125 °C for 30 min in air to remove residual solvents.

2.3. Ultrasonic-assisted electroless plating

The ultrasonic-assisted electroless copper plating experiments were performed at a constant ultrasonic frequency of 40 kHz with 120 W power (Ultrasonic cleaner, DL-120A, China, Zhisun Co. Ltd.) in a cell filled with 200 mL bath. The pretreated PET films were put into the same neutral aqueous solution without catalyst. The composition of electroless bath and the operating conditions were listed in Table 1. Deionized water was used to prepare the solutions. The pH was adjusted using NaOH or HCl to a final value of 7.0. After plating, the samples were carefully rinsed with deionized water, ethanol and dried in an oven for 1 h at 50 °C.

2.4. Electroless plating without ultrasonic

The pretreated PET films were put into the solution as shown in Table 1 with a magnetic stirring. Deionized water was used to prepare the solutions. The pH was adjusted using NaOH or HCl to a final value of 7.0. After plating, the samples were carefully rinsed with deionized water, ethanol and dried in an oven for 1 h at 50 °C.

2.5. Characterization

Scanning electron micrographs (SEM) were obtained by a Philips XL 30 electron microscope. The samples were deposited on a sample holder with a piece of adhesive carbon tape. The topography of copper films was characterized by a Nanoscope AFM from Veeco Ins. An arithmetic mean of the surface roughness (R_{RMS}) (area: 10 μm × 10 μm) was calculated from the roughness profile determined by AFM. XRD patterns (2θ ranges from 30° to 95°) were recorded at room temperature with scanning speed of 0.15°/min using Cu Kα radiation (λ = 0.154 nm) from a 40 kV X-ray source (Rigaku D/max-γB) and diffracted beam monochromator, operated at 100 mA. Raman spectrums were characterized by a Raman spectrometer (LabRam-1B, France, JY Co. Ltd.). XPS measurement was performed on a PHI 5000C ESCA system with Mg Kα source at 14.0 KV and 25 mA. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The electrical conductivity of cooper films was measured by a four-point probe (BD-90). To evaluate the adhesion of the copper plating, a standard peel test (ASTM D 3330) was carried out at a rate of 12 cm/min at room temperature in air. For the above study, scotch tape with a width of 1 cm was stuck over a length of 4.0 cm on the copper film. Care was taken to see that there were no air gaps or wrinkles. Then the sample with the scotch tape was kept under a pressure of 10 N for 10 min. A 180° peel test was carried out after fixing one end of the sample in one jaw and the scotch tape end with the piece of paper adhered to it in another jaw. For adhesion strength reported here, at least 20 sample measurements were performed and averaged.

Table 1
Composition and operation conditions of electroless plating.

Chemical	Concentration (g/L)
$CuCl_2{\cdot}2H_2O$	10
H_3BO_3	8
$C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$ ($EDTANa_2{\cdot}2H_2O$)	20
$C_2H_{10}BN$ (DMAB)	8
pH	7
Temperature (°C)	50
Time (h)	2

3. Results

Raman spectra of untreated (a) and silane modified (b) PET films are indicated in Fig. 1. A peak at 1730 cm^{-1} is attributed to carbonyl (C=O) stretching vibration, and a peak at 1617 cm^{-1} is ascribed to phenyl ring stretching vibration. The C–H stretching vibration due to methylene group is observed at 1463 cm^{-1}, the aromatic C=C stretching vibration is observed at 1285 and 1362 cm^{-1}. A peak at 1189 cm^{-1} belongs to ester (C(O)–O) stretching vibration. Phenyl ring breathing vibration is revealed at 1003 cm^{-1}. Silane modified (b) PET films have additional peaks at 1096, 921 and 856 cm^{-1}, which contribute to –C(O)N and Si–O–Si stretching vibration. The adhesion strength for the silane layer with the PET film was measured to be more than 50 N/cm, which indicates that silane is firmly attached to the PET substrate.

Fig. 2 shows the SEM photographs of the copper coating on PET films with (a) and without (b) ultrasonic operation. The thin copper film on silane modified PET substrate (a) was more compact and smoother than sample (b). The color of the deposit of sample (a)

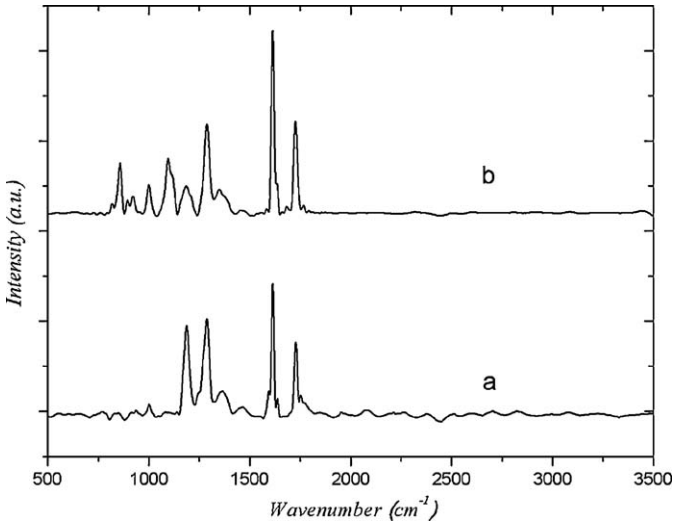

Fig. 1. Raman spectra of untreated (a) and silane modified (b) PET films.