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Full Length Article

Highly adhesive and high fatigue-resistant copper/PET flexible electronic substrates

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ABSTRACT

A voidless Cu/PET substrate is fabricated by producing a superhydrophilic PET surface comprised of nanostructures with large width and height and then by Cu electroless plating. Effect of PET surface nanostructure size on the failure mechanism of the Cu/PET substrate is studied. The fabricated Cu/PET substrate exhibits a maximum peel strength of 1300 N m^{-1} without using an interlayer, and virtually no increase in electrical resistivity under the extreme cyclic bending condition of 1 mm curvature radius after 300 k cycles. The authors find that there is an optimum nanostructure size for the highest Cu/PET adhesion strength, and the failure mechanism of the Cu/PET flexible substrate depends on the PET surface nanostructure size. Thus, this work presents the possibility to produce flexible metal/polymer electronic substrates that have excellent interfacial adhesion between the metal and polymer and high fatigue resistance against repeated bending. Such metal/polymer substrates provides new design opportunities for wearable electronic devices that can withstand harsh environments and have extended lifetimes.

1. Introduction

Metal/polymer composite films simultaneously possess the individual advantages of both polymers and metals, including the flexibility and light weight of the polymer and the excellent electrical conductivity and electromagnetic wave shielding of the metal. Accordingly, these composite films have been widely applied in various industries from food packaging to microelectronics [1–4]. Among the various types of polymers, polyethylene terephthalate (PET) exhibits excellent transparency and low density compared to inorganic glass as well as outstanding thermal, mechanical, and physicochemical properties, and PET is extensively used in electronic devices and display panels [5–7].

Various metallization processes such as physical vapor deposition (PVD) [8], chemical vapor deposition (CVD) [9], atomic layer deposition (ALD) [10], electroless plating [11], inkjet printing [12], etc. have been used to fabricate metal/polymer composite films. With the recent growth in mobile phones and wearable electronics, there has been increasing demand for metal/polymer composite films with high functionality and increased product lifetime. The major factors determining electronic product lifetime in harsh environments are the interfacial adhesion between the metal and polymer, and fatigue resistance against failure from cyclic bending deformation. The need for improvements in these two aspects continues to increase [13–18]. However, when metal/polymer composite films are fabricated using the wet plating method (electroplating, electroless plating), the polymers have very low surface free energy ($\gamma_s < 100$ mJ m^{-2}) compared to the surface free energy of metals ($\gamma_s \sim 500$–5000 mJ m^{-2}) [19]. As a result, the plated metal film on the polymer is typically not dense due to the low wettability of the plating solution on the polymer substrates according to Young's equation ($\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta$) [20]. This results in low bending fatigue performance of the metal/polymer composite film as well as weak adhesion between the plated metal film and the polymer substrate. To address these limitations, the wettability of the plating solution on the polymer substrate should be improved preferentially, and various studies are currently being carried out [21–24].

Improving wettability of the plating solution has been generally reported to proportionally increase the interfacial adhesion

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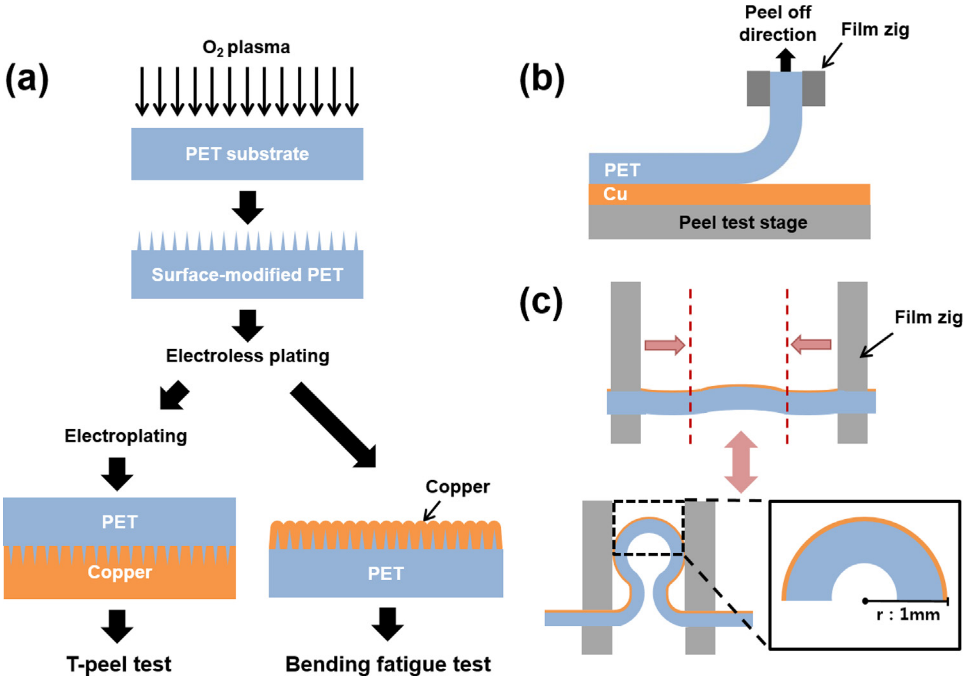

Fig. 1. Experiment flow chart showing the procedure to fabricate the Cu/PET flexible substrate (a) used for T-peel test (b) and bending fatigue test (c). Because the Cu layer fabricated by electroless plating is not thick enough to peel off, electroplating was performed additionally to increase the thickness of the Cu layer on PET.

of the plated metal film to the polymer substrate [25,26]. Polymer surface modification methods which have been carried out recently to resolve the poor adhesion between the metal and polymer in metal/polymer composite films include laser etching [27], plasma etching [28–30], ion beam etching [31,32], or chemical etching [33,34]. These methods increase the roughness of the polymer surface and consequently increase mechanical interlocking, or increase chemical bonding by generating chemical functional groups [35–38]. There are also methods which insert an inorganic adhesion layer such as Ni [39], Cr [40], Ti [41], Ni-Cr [42], or Ni-Cr-Mo [43] between the metal film and polymer substrate, or an organic adhesion layer such as amine [44,45] or silane [46,47].

Among the above methods being employed to resolve the poor adhesion, increasing the roughness of the polymer surface by etching is most widely used. However, most studies have simply reported that increased surface roughness contributes to the increase in interfacial adhesion [13,34]. Essentially no studies have been conducted on how the shape and size of the polymer surface nanostructures produced by etching influence the interfacial adhesion. Also, prior studies have mainly been conducted on ways of improving the interfacial adhesion between the metal and polymer, and there is a shortage of research on fatigue performance.

In this study, we overcome the poor wetting of the copper electroless plating solution on the PET surface and the poor adhesion between the Cu and PET by performing PET surface modification using oxygen plasma. To simultaneously maximize the Cu/PET interfacial adhesion strength and bending fatigue performance without using a tie layer between the Cu and PET, the size and shape of the anisotropic nanostructures of the PET surface were controlled by significantly varying the oxygen plasma etching time. The effect of sizes and shapes of superhydrophilic anisotropic nanostructures on the Cu/PET interfacial adhesion and fatigue properties was analyzed, and the failure mechanism of the Cu/PET flexible substrate depending on the shape and size of the nanostructures was first studied. In addition, by comparing the changes in wettability and interfacial adhesion according to the oxygen plasma treatment time, the relationship between wettability and interfacial adhesion was investigated.

2. Experimental procedures

2.1. Oxygen plasma treatment

Flexible PET films with dimensions of 100 mm (l) × 40 mm (w) × 100 μm (t) were cleaned ultrasonically in ethanol and deionized water for 5 min each at 25 °C, and dried with N_2 gas. The cleaned films were placed on a stainless steel cathode in a vacuum chamber. The chamber was evacuated to a pressure less than 1 mTorr. The oxygen flow rate, oxygen gas pressure, and bias voltage for the plasma treatment were 20 sccm, 10 mTorr, and −400 V, respectively.

2.2. Fabrication of Cu/PET flexible substrates

Fig. 1(a) shows the experiment flow chart showing the procedure to fabricate the Cu/PET flexible substrates used for T-peel test and bending fatigue test. The plasma-treated surfaces of the PET films were coated with copper layers by electroless plating. The composition of the electroless copper plating solution was $CuSO_4{\cdot}5H_2O$ (10.0 g L^{-1}) as a copper ion source, HCHO (5 mL L^{-1}) as a reducing agent, $NaKC_4H_4O_6{\cdot}4H_2O$ (28.25 g L^{-1}) as a complexing agent, 2,6-diaminopyridine (1 mg L^{-1}) as an accelerator, 2,2′-dipyridyl as a stabilizer (1 mg L^{-1}), $NiSO_4{\cdot}6H_2O$ (1 mL L^{-1}) as a stress-relief agent, sodium dodecyl sulfate (SDS, 1 mL L^{-1}) as a surfactant, and de-ionized water (remainder). The pH and temperature of the plating solution were maintained at 12.5 using NaOH and 33 °C, respectively. The thickness of the Cu films after electroless plating for 10 min was 200 nm. After electroless plating, the PET films coated with Cu were washed with de-ionized water to remove the remaining plating solution and then dried in a vacuum oven.

2.3. Adhesion test (3M tape test and 90° T-peel test)

To measure the adhesion strength between the Cu coating layer and PET substrate film, peel-off-tests were carried out using a universal testing machine (MTS Insight 1) with an attached 90° T-peel