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Full Length Article

Electromagnetic shielding effectiveness of a thin silver layer deposited onto PET film via atmospheric pressure plasma reduction

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ABSTRACT

This study presents the first use of a plasma reduction reaction under atmospheric pressure to fabricate a thin silver layer on polyethylene terephthalate (PET) film without the use of toxic chemicals, high voltages, or an expensive vacuum apparatus. The developed film is applied to electromagnetic interference (EMI) shielding. After repeatedly depositing a silver layer through a plasma reduction reaction on PET, we can successfully fabricate a uniformly deposited thin silver layer. It was found that both the particle size and film thickness of thin silver layers fabricated at different $AgNO_3$ concentrations increase with an increase in the concentration of $AgNO_3$. However, the roughness of the thin silver layer decreases when increasing the concentration of $AgNO_3$ from 100 to 500 mM, and the roughness increases with a further increase in the concentration of $AgNO_3$. The EMI shielding effectiveness (SE) of the film is measured in the frequency range of 0.045 to 1 GHz. As a result of optimizing the electrical conductivity by measuring sheet resistance of the thin silver layer, the film fabricated from 500 mM $AgNO_3$ exhibits the highest EMI SE among all fabricated films. The maximum values of the EMI SE are 60.490 dB at 0.1 GHz and 54.721 dB at 1.0 GHz with minimum sheet resistance of 0.244 Ω/□. Given that the proposed strategy is simple and effective, it is promising for fabricating various low-cost metal films with high EMI SE.

1. Introduction

At present, mobile communications and electric vehicles are popular. Owing to the use of electrical energy for transmitting and signal distribution, electronic devices such as radio receivers, telephone communications, car electronics and electric cables can generate electromagnetic interference (EMI) [1]. Electromagnetic emissions can come from several sources, such as lightning, relays, DC electric motors, and fluorescent lights, and the creation of EMI has had detrimental impacts on the performance capabilities of devices and the surrounding environment [12]. Furthermore, the generation of electromagnetic waves at a high frequency can present potential health hazards to mankind [2]. Hence, reducing electromagnetic emissions and protecting components are major issues for circuit designers which are likely to become even more important in the future [3].

An effective EMI shielding material must reduce undesirable emissions and protect components from stray external signals [1]. In general, there are three functions of EMI shielding [1]. The first is to reduce radiation using charge carriers, resulting in the requirement of electrical conductivity of the shielding materials. The second function of EMI shielding is the absorption of EMI radiation due to the electric properties and/or magnetic dipoles interacting with the radiation. Both the reflectivity and absorption characteristics are related to the electrical conductivity of the shielding materials. The third function of EMI shielding is to address multiple internal reflections which arise from scattering centers and interfaces or defect sites within the shielding materials.

It is well known that the material used for EMI shielding requires a light weight, high conductivity and excellent adhesion. In order to meet these requirements, the shielding materials used are concentrated on the metal shrouds, composites of polymer-matrix and conductive fillers, and carbon-based fillers [4–9]. Among shielding materials, silver is the best material for the fabrication of highly conductive composite materials, including thin films, sandwich structures, foams, and fibers due to its high conductivity (6.8×10^5 S/cm) as well as its low production cost compared to those of other metals [10–14].

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Thus far, the deposition of shielding materials has been done through sputtering, electrodeposition, electron beam irradiation, screen printing and chemical reduction, and plasma spraying [15–20]. These applications, however, are not convenient due to requirements such as special facilities, inconvenient vacuum chambers, or high voltages and the small cells used for deposition. In order to overcome these restrictions, atmospheric plasma recently becomes a great tool for synthesizing metal nanoparticles (NPs) and treatment materials [16,21–28]. For examples, Deng's group synthesized Ag NPs on non-woven polyethylene terephthalate (PET) fabric by using an atmospheric pressure plasma system [21]. Mohan Sankaran and his co-workers used microplasma to fabricate electrically conductive metal patterns at the surface of polymer films [16]. We recently developed a new process of efficiently synthesizing and immobilizing metal nanoparticles (NPs) on the surfaces of indium tin oxide (ITO)-coated PET film, polymers, and carbon materials [23]. This process, termed dry plasma reduction (DPR), can be conducted at atmospheric pressure and near room temperature without toxic reducing agents.

Here, we present the first report of the fabrication of a thin silver layer directly onto the surface of PET film through DPR with argon at atmospheric pressure and at a low temperature without the use of any toxic chemicals. The developed film is applied to EMI shielding and further optimized to improve the EMI shielding effectiveness (SE). It was expected that the thin silver layers would show excellent electrical conductivity and EMI SE performance. The proposed strategy is not only simple and efficient but also innovative; thus, it is promising for efficiently fabricating metal or alloy layers on the surfaces of materials with low melting points, such as plastics for EMI shielding applications, at a relatively low cost.

2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$, Assay 99.8 %) was purchased from Daejung Chemicals & Metals Co., Ltd. Ultrapure water was obtained from Human Science (Ultrapure 900, Capacity 15 L/h). Ethanol (Assay 99.8%) was bought from Sigma-Aldrich. The PET films used here were obtained from SKC Co., Korea. Note that these films are covered with a blue layer and coated with nano-silica/polyurethane film as a protective top-coat layer. The atmospheric-pressure plasma used in this study is AC plasma generated at a radio frequency of 13.56 MHz (Model ATMOS, Changjo Eng. Inc., Korea). The detailed plasma system is given in our previous studies [29,30]. Ultra-pure (purity 99.999 %) argon gas was used as the carrying gas. The argon gas was purchased from Special Gas of Korea.

2.2. Fabrication of silver thin films

A homogenous solution of ethanol and water at a volume ratio of 3:1 was initially prepared. Next, silver precursor solutions containing 100, 300, 500, 700, and 900 mM $AgNO_3$ in mixture solution were prepared. The PET film was cut into 5 x 5 cm squares and pretreated with plasma before use, as in our previous study [24]. Subsequently, 50 μl of the $AgNO_3$ solution was dropped on the plasma-treated PET substrate and allowed to dry at 70 °C for 150 sec. Note that the sample was kept in a petri dish at room temperature for 15 min before drying. Finally, the dried samples were treated by Ar atmospheric pressure plasma at a power of 150 W, a substrate movement speed of 5 mm/s, and a plasma treatment time of 8 min. The deposition procedure was repeated give times for each sample.

2.3. Characterization and measurements

The morphology of the Ag/PET was characterized using field-emission scanning electron microscopy (FESEM; Jeol JSM 7000F, JEOL, Japan). The structure of the thin silver layer on the PET substrate was analyzed using X-ray diffraction (Cu Kα, λ= 1.5406 Å; Bruker AXS, Germany) and transmission electron microscopy (TEM; JEM-2100F, JEOL, Japan). The chemical state of the thin silver layer was analyzed using X-ray photoelectron spectroscopy (XPS) with a spectrometer (Sigma Probe, Thermo Fisher VG Scientific, USA) equipped with an Al Kα X-ray source. The binding energy scale was calibrated using the binding energy position of 83.98 eV for the Au $4f_{7/2}$ *Core* level. Sheet resistances were measured using a four-point probe setup (CMT-SR 1000 N, Advanced Instrument Technology, Inc.). The root mean square (RMS) roughness of the thin silver layer on PET was characterized by means of a scanning probe microscope (SPM; XE-100, Park Systems, Korea). The energy dispersive X-ray spectrometry (EDS) mapping of the thin silver layer on the PET was characterized using field-emission scanning electron microscopy (FESEM; SU8230, Hitachi, Japan).

The EMI SE assessments of the thin silver layers were carried out in the frequency range of 0.045 to 1.0 GHz using the coaxial transmission line method (Anritsu, VNA Master, MS 2024B). Note that a disc-shaped sample with a diameter of 49 mm was prepared for this purpose.

3. Results and discussion

3.1. Synthesis and characterization of the thin silver layer

The entire fabrication process of the thin silver layer using a plasma reduction reaction under atmospheric pressure is sketched in Fig. 1. The process starts with the preparation of the metal precursor solution and the pretreatment of the PET surface using plasma. Note that the pretreatment of the PET substrate was conducted in the same manner used in our previous study [24]. Thus, the surface of the PET film becomes solvophilic. As the first step, a drop of the precursor solution is loaded onto the plasma-treated PET substrate and then uniformly spread on the surface of the film. The second step is a drying process of the solvent, which takes place at 70 °C and lasts 150 sec. Finally, the third step is the plasma reduction reaction. The remaining salts on the dried substrate are reduced to silver metal through plasma reduction (power of 150W, gas flow rate of 5 lpm, substrate moving speed of 5 mm/sec, and plasma reduction time of 8 min) under near room temperature and at atmospheric pressure. Note that this procedure was repeated five times. The products were then used for further analysis and application to enhance the EMI SE.

As shown in Fig. 2(a–f), the thin silver layer formed on the PET substrate becomes uniform after the five-fold deposition process. Furthermore, the deposited thin silver layers change from dark to bright from the first to the fifth depositions. This stems from the change in the thickness of the film, the number density of the Ag clusters, and the roughness of the film. For a closer examination of the micro-morphology of thin silver layer, we conducted SEM measurements, as presented in Fig. 2(g–k). As observed in the SEM images (Fig. 2(g and h)), the thin silver layer appears to have a smooth surface at a low resolution. However, a highly porous structure was observed in the enlarged SEM images (Fig. 2(i and j)). The porous structure was further clarified through a high-magnification SEM image, as shown in Fig. 2(k). Clearly, the particle sizes of the Ag clusters range from 100 to 200 nm. Furthermore, inter-connections between the Ag clusters on the surface of the thin layer were noted. Mackus et al. reported that such inter-connected Ag clusters are due to particle coalescence [31]. Owing to formation of the inter-