DEPOSITION OF FEW LAYER GRAPHENE ON PLASTIC SUBSTRATE FOR USING CONDUCTIVE LAYER AT METAL ELECTROPLATING

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1 Introduction

Graphene, a monolayer of carbon atoms packed into a two-dimensional honeycomb lattice, has attracted much attention in the scientific community, because of its ultrahigh mechanical strength, electrical conductivity [1,2], high electron mobility, and optical transparency [3,4]. Few layer graphene (FLG), which is composed of several individual graphene layers, is now under intensive investigation as the number of graphene layers plays an important role in adjusting their electronic and other properties [5]. Graphene sheets have the ability to strongly adhere to various substrates due to their high van der Waals attraction and large surface area. A chemically derived graphene solution was deposited on a flexible substrate for the preparation of a large area transparent flexible electrode [6]. It has been reported that graphene oxide (GO) sheets could be deposited well on a plastic substrate by the transfer process through the strong cohesive van der Waals forces between the GO sheets and the substrate [7].

Several methods have been reported for the production of graphene sheets including the micromechanical cleavage and thermal expansion of graphite [8-10], epitaxial growth on SiC surfaces [11,12] and chemical reduction of exfoliated GO [13,14]. Although GO is easy to fabricate, chemical reduction is necessary to recover its conductivity, and the reduced GO usually has lower conductivity than the pristine graphene [14]. It was reported that graphite could be exfoliated in specific solvents to give a defect-free monolayer of graphene [15,16]. This phenomenon relies on the use of particular solvents to provide exfoliation, such as N-methylpyrrolidone (NMP), whose surface energy is well matched to that of graphene. [16].

The surface metallization or metal plating of polymer-based substrates is widely used today in a large variety of technological applications ranging from the fabrication of printed circuits in optoelectronic devices to decorative coatings in consumer products [17,18]. Through the metallization of plastic substrates, which are lightweight, design-flexible, and low-cost materials, value can be added to them by inducing reflectivity, abrasion resistance, electrical conductivity, and a variety of decorative effects [19,20]. In the electrochemical metallization of plastics, however, the non-conductive plastic surface must be made conductive first, which is usually achieved through an electroless plating technique. Prior to the electroless plating, an etching process is usually employed to modify the non-conductive surface in order to improve the adhesion and surface seeding of the electroless catalysts, most commonly using chromic acid etchants [21]. However, this process needs to be replaced in the near future, because of the upcoming European ban on chromium waste [22,23]. Numerous chromium-free etching procedures using different solutions [24], or ion-assisted laser treatment [25], plasma modification [26], and excimer UV lasers [27] have been developed, but they are neither as efficient as chromic acid etching for achieving sufficient adhesion, nor available on an industrial scale.

In this sense, the metallization of a polymer using an intermediate layer of FLG is an efficient chromium-free process without the toxic pretreatment associated with the electroless plating process. In this study, natural graphite was expanded using microwave irradiation [28] and, then, the dispersion of FLG sheets was prepared from expanded graphite (EG) which was exfoliation by ultra sonication in NMP (N-Methylpyrrolidone). The dispersion of FLG sheets was vacuum filtered to make thin conductive films desirably aligned in the in-plane direction and,
subsequently, deposited on a polyethylene terephthalate (PET) substrate by a transfer method [29]. Then, nickel was electroplated on a FLG coated PET film (GCF) by one step electroplating without any pretreatment or electroless plating steps. The feasibility of forming of a metallic layer was investigated in detail by identifying the stages of metal seeding and growth to form a uniform layer of metal on the GCF.

2 Experimental

2.1 Materials

Natural graphite powder was purchased from Sigma-Aldrich (Product Number 332461). Nitric acid (68%), potassium permanganate (KMnO₄) and NMP (C₆H₄NO) were purchased from Sigma-Aldrich. Aluminium oxide membrane filters (Whatman Inc. UK) were used in the vacuum filtration process. The PET film (250 µm in thicknesses) was purchased from SK Corporation. Nickel sulfate hexahydrate (NiSO₄ • 6H₂O), nickel chloride hexahydrate (NiCl₂ • 6H₂O), and boric acid were purchased from Sigma-Aldrich.

2.2 Preparation and exfoliation of EG, preparation of dispersed FLG, transfer coating on the PET film, and nickel metallization on the GCF

For expanding graphite, natural graphite, nitric acid (68%) and potassium permanganate were mixed by a glass bar at a weight ratio of 1 : 1 : 2 in a porcelain dish at room temperature. Then, the porcelain dish was placed in a domestic microwave oven (X2-20MS, Whirlpool) and irradiated at 700 W for 60 seconds. EG was exfoliated in 100 ml of NMP by sonication (VC 505, Sonics) for 1 hour. The resultant dispersion was then centrifuged (Combi-514R, Hanil) for 2 min at 4,000 rpm. After centrifugation, decantation was carried out by pipetting off the top 15 ml of the dispersion and then the residual EG was sonicated and centrifuged five times. The preparation of FLG film was carried out immediately after centrifugation by the vacuum filtration of FLG dispersion through an aluminum oxide membrane filter (pore size of 200 nm) and the resulting FLG film were dried overnight at room temperature. The vacuum filtered FLG film was transferred onto the PET film and dried 24 h at 80 °C in vacuum. The sheet resistance of the GCF was measured by four-point probe technique (Universal Probe, Jandel) with a source meter. The light transmittance for the evaluation of the optical transparency was measured with an ultraviolet visual (UV-Vis) spectrometer (2120 UV plus, Optizen) in the wavelength range of 300 ~ 800 nm. The morphology of the GCF was examined by atomic force microscopy (AFM) (Innova, Veeco) in non tapping mode. Scanning electron microscopy (SEM) was used to observe the surface of the nickel metalized GCF.

Table 1. Specific electroplating conditions and thicknesses of the continuous layer on the GCFs.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>NG1</th>
<th>NG2</th>
<th>NG3</th>
<th>NG5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating time (min)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Voltage (V)</td>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Current (A)</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Size of Ni seed (µm)</td>
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<td>0.15</td>
<td>~ 0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Thickness of continuous layer (µm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

3 Results and discussion

Natural graphite and expanded graphite is shown in Fig 1(A and B). Untreated natural graphite has over 1 µm of size (Fig. 1A). Under microwave irradiation, a marked expansion of the natural graphite is accompanied by fuming and lightening. The worm-like structure of sample is clearly observed by SEM, as shown in Fig. 1B. The surface morphology of sample exhibits well expanded structure to prove full and regular expansion in direction of c-axis. Thus, natural graphite easily expanded by micro irradiation with electroplating bridge (copper sheets and clamp) for the purpose of enhancing the electroplating efficiency, and a nickel electrode was installed at the anode in a nickel electroplating bath. The nickel electroplating solution was composed of 350 g/L of NiSO₄ • 6H₂O, 45 g/L of NiCl₂ • 6H₂O, 45 g/L of boric acid. The nickel electroplating was performed for 1 ~ 40 min at 50 °C under bubble treatment. After rinsing with deionized water, the nickel electroplated GCF was dried for 24 hours at room temperature. Table 1 shows the specific conditions of the electroplating procedure used for the preparation of the nickel metalized GCF.
without consumption of time and extremely high temperature.

Fig. 1. SEM image of natural graphite and EG prepared by microwave irradiation (60 seconds)

The vacuum filtration process can be seen in Fig. 2A, where FLG dispersion is poured over the filter with a vacuum applied underneath. In this process, FLG sheets are oriented in the in-plane direction due to the vertical vacuum direction. The resulting layer of FLG sheets attached to the membrane (Fig. 2B) can easily be separated in DI water (Fig. 2C), where the layer of FLG sheets float on the surface of water. The layer of FLG sheets floating on the water surface can be transferred to the PET substrate film by slowly dragging the layer of FLG sheets and the PET film upward (Fig. 2D). Finally, the GCF prepared by the transfer coating process is easily bendable as well as transparent (Fig. 2E).

Fig. 2. (A) The process of vacuum filtration, (B) The vacuum filtered FLG, (C) Separating filter from vacuum filtered FLG in the DI water, (D) The PET substrate increase slowly toward the layer of FLG in the water bath, (E) Layer of FLG on the PET substrate.

Fig. 3 shows the 2D AFM images of the layer of FLG sheets transferred onto the glass substrate. A typical 10 µm × 10 µm square showing large numbers of FLG. The size of FLG is over 1 µm, approximately and image show well-deposited FLG without any voids or dimples by transfer coating method.

Fig. 3. A 10 × 10 µm square 2D AFM image of the GCF.

Fig. 4 shows transparency and sheet resistance of GCF by repeating de-taping process. The initial transparency and sheet resistance are 36.5 % and 0.4 KΩ/sq, respectively. Increasing the number of times of de-taping, weakly bonded FLG is removed from GCF. Although transparency of the GCF is improved by removed weakly bonded FLG, the sheet resistance is increased. It seems that the number of FLGs on the GCF is decreased by de-taping process. As a result, the contacted points between remaining FLGs on the GCF are reduced. The final transparency and sheet resistance are measured 64.4 % and 12 KΩ/sq.

Fig. 4. Transition of transparency and sheet resistance of GCF by de-taping process.
Fig. 5 (A-E) show the progress of electroplating over the FLG. Fig. 5A shows FLG sheets are well-deposited on the PET substrate with a size of a few micrometers in the in-plane direction. When the electroplating starts, the metal seeds that appear on FLG are seemingly more concentrated at the edges of FLG (Fig. 5B). The sizes of the metal seeds appear to be 30 ~ 100 nm after 2 min of electroplating in our experiment. As the electroplating proceeds, the metal seeds grow larger (Fig. 5C) and then become connected to each other (Fig. 5D). Finally, they form a continuous layer of metal (Fig. 5E). It is interesting to note that the metal particle seeds are formed favorably at the edges of FLG or in the space between the folded sheets in the early stage of electroplating (see Fig. 5B). The high surface energy at the edges of FLG is expected to be effective catalytic sites for the formation of the metal seeds. Overall, the metal seeds are formed in a discontinuous manner in the early state of electroplating, and then form a thin layer of metal after 5 min of electroplating under our experimental conditions.

4 Conclusions

In conclusion, EG materials had been rapidly and efficiently prepared by microwave irradiation in a short time with less consuming energy. Also, we described the feasibility of a new and powerful technique for the metallization of non electrical conducted plastic substrates without the use of an etching agent or a catalyst for the growth of the metallic layer.

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References


