Electrophoretic deposition of high quality transparent conductive graphene films on insulating glass substrates

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Abstract. Graphene is a promising material for transparent conductive films (TCFs) because of its high electrical conductivity and excellent optical transparency over a wide spectral range. We have previously reported on an inexpensive means of producing graphene-based TCFs using chemically derived graphene flakes. However, the deposition of chemically derived graphene can yield poor stacking of graphene flakes, which degrades the electrical conductivity of the resulting films. Here, we describe an alternative approach for producing large areas of TCFs based on electrophoretic deposition of graphene onto glass substrates using charged graphene oxide flakes. This method enabled the deposition of highly stacked graphene films onto insulating glass substrates with potential for TCFs.

1. Introduction

Transparent conductive films (TCFs) have a wide range of important applications, including flat displays, light emitting diodes, and solar cells \cite{1}. Graphene is one of the most attractive alternative materials for TCFs because of its high electrical conductivity and optical transparency over a wide range of wavelengths. Graphene is an atomically thin layer of carbon with superior electronic properties that has been a subject of intense study since its discovery in 2004 \cite{2}. A major hurdle in the incorporation of graphene into electronics is the exfoliation of graphite into individual sheets on a large-scale and in a controllable way. Recently, the epitaxial growth of wafer-scale graphene on silicon carbide and copper substrates by chemical vapor deposition has been demonstrated \cite{3, 4}. However, these methods require complicated and time consuming processes to transfer the graphene onto more desirable substrates, and uniform deposition over large-areas is proving to be challenging.

Electrophoretic deposition (EPD) is an economical and versatile deposition technique that is used for deposition of coatings and films, such as phosphors for displays \cite{5}. EPD has many attractive features for the preparation of thin films from suspensions, such as high deposition rates and throughput, good uniformity, large-area deposition, and precisely controllable thickness of the resulting films. For example, EPD has been used to produce highly packed microstructural carbon nanotube (CNT) films exhibiting excellent electron-field-emission characteristics from colloidal CNT
suspensions [6]. Furthermore, Hasan et al have used EPD for the deposition of large-area graphene oxide (GO) films on stainless steel [7].

A governing principle of EPD indicates that it should not be possible to deposit films on nonconductive materials, such as insulating glass. Here, we describe an innovative EPD-based method for depositing graphene films on insulating glass and other non-conductive surfaces. Our method enabled the deposition of highly stacked graphene films onto insulating glass substrates without the need for sophisticated transfer processes. We successfully deposited graphene films showing lower sheet resistance compared with conventional deposition methods.

2. Experimental

2.1. Preparation of graphene oxide dispersed in solution

Chemically derived graphene was synthesized by the modified Hummer’s method [8], a well-known approach for producing monolayered graphene via liquid-phase exfoliation of graphite oxide. Natural graphite powder (SEC Carbon SNO-30) was washed in \( H_2SO_4 \) and \( K_2S_2O_8 \), and oxidized in \( KMnO_4 \) and \( H_2SO_4 \). After centrifugation, the resulting graphite oxide was exfoliated into graphene oxide (GO) by ultra-sonication (100 W, 30 min, 60 °C). Next, a GO aqueous dispersion was produced by centrifugation and dialysis to neutralize the pH of the solution. The surface charge (zeta potential) of obtained GO flakes in neutral water dispersion was examined with an OTSUKA ELECTRONICS ELSZ-1. Zeta potential measurement revealed that GO indicated highly negative charge \( \zeta_{GO} = -32 \) mV at pH7) due to ionization of the carboxylic acid and phenolic hydroxyl groups that are known to exist on the GO flakes. This negative characteristic plays an important role in electrophoretic deposition and leads to a stable dispersion without any aggregation for a few months.

The presence of monolayer GO flakes in the resulting GO aqueous solution was verified by atomic force microscopy, Raman spectroscopy, where peak shifts and the shape of the peak of the second-order two phonons at 2700 cm\(^{-1}\), referred to as the 2D band. The size of the reduced graphene flakes was up to 50 x 50 \( \mu \)m\(^2\)[9].

2.2. Setup of the electrophoretic deposition (EPD) system

The target substrate faced the Pt plate counter electrode to form a parallel-plate geometry with a separation of 3 to 20 mm. The entire electrode assembly was placed on a custom-built dip-coater (Oriental Motor Co. Ltd., DRS42SA2G-04KA). The set of electrodes were slowly submerged into the GO aqueous solution for concentrations of 0.1, 1.0, and 10 wt%). Electrophoretic deposition was carried out in constant voltage mode at voltages in the range 1 to 30 V using a programmable voltage source (ADVANTEST R6144) at room temperature and atmosphere. After electrophoretic deposition for 1 to 30 min, the graphene-deposited substrates were withdrawn from the solutions at a rate of 1 mm min\(^{-1}\) using the dip-coater.

2.3. Electrophoretic deposition on \( SiO_2/\) Si substrates

We used our EPD equipment deposit graphene films on insulating \( SiO_2 \) (90 nm) grown on highly doped, degenerate Si substrates. The substrates were first cleaned by sonication in acetone and distilled water, and \( O_2 \) plasma treatment immediately before being submerged into GO aqueous solution. Insulating \( SiO_2 \) faced the Pt plate counter electrode and a conductive lead was attached to the backside of the Si substrate. After electrophoretic deposition, the substrates were dried by a nitrogen \( N_2 \) gun and baked at 100 °C for 5 minutes. The variation of the morphology of the resulting graphene films by due to changes in deposition parameters was monitored by scanning electron microscope (JEOL JSM-7001F).
2.4. Electrophoretic deposited graphene films on glass substrates

To directly deposit graphene-based TCFs on insulating glass substrates, we tested the possibility of using a new EPD procedure as shown in figure 1. In this procedure, we attached conductive Cu tape (or other metallic films) onto the backside of glass substrates (Corning 7059) and then the front sides of substrates were exposed to O\textsubscript{2} plasma. A constant voltage was applied between backside Cu tape and Pt plate electrode during electrochemical deposition. Finally, the substrate was removed from the solution and the Cu tape peeled off (or etched off) and the substrates were dried and baked at 100 °C.

![Figure 1. A schematic diagram of our innovative EPD procedure.](image)

Chemical analysis of the resulting graphene films was carried out using X-ray photoelectron spectroscopy (XPS, ULVAC PHI5000, Al K\textsubscript{α}). The optical and electrical properties of graphene films were characterized by UV-visible spectrophotometer and van der Pauw measurements.

3. Results and Discussion

3.1. Optimization of deposition parameters

We optimized the electrophoretic deposition parameters (distance between electrodes, applied voltage, concentration of GO solution, and deposition time) by monitoring the morphology of graphene films deposited on SiO\textsubscript{2}/Si substrates. Under an applied voltage, the negatively charged graphene oxide sheets migrated toward the positive Si electrode, and were subsequently orderly deposited onto the surface of the positive electrode. The electrophoretic mobility was estimated 2.5 μm V\textsuperscript{-1} s\textsuperscript{-1} from following Helmholtz-Smoluchowski formula;

\[ u = \frac{\varepsilon_0 \varepsilon_{H_2O} \zeta_{GO}}{\eta_{H_2O}}, \]  

where \( \zeta_{GO} = -32 \) mV in water dispersion at room temperature. Although other parameters also affect the deposition rate, this estimation supports the high deposition rate (around 2 nm min\textsuperscript{-1}) of EPD method.

Notably, graphene films were deposited on the counter electrode under an opposite applied voltage. The GO flakes easily aggregated in solution when the electric field between electrodes – determined by the distance between the electrodes and the applied voltage – was sufficiently strong. Figure 2 shows the SEM images of graphene films when concentration of GO and deposition time were varied.
We found that the graphene films had a high GO density and uniform morphology. Moreover, we did not observe wrinkles in the deposited GO flakes (see an inset in figure 2a), which are observed in other deposition methods such as filtration and spin-coating [10, 11]. The wrinkle structures are considered to act as scattering centers in graphene-based TCFs as reported in studies on chemical vapour deposition graphene [12-14].

The optimized deposition parameters for producing uniform films of a few layers graphene are summarized in table 1. In the case of deposition on glass, it was required to apply higher voltage around 20 V because the thickness of glass substrate was much thicker than 90 nm.

**Table 1.** Optimized electrophoretic deposition parameters.

| Distance between electrodes | Applied voltage | Concentration of GO | Deposition time |
|-----------------------------|-----------------|---------------------|----------------|
| 5 mm                        | 10 V            | 1 wt%               | 5 min          |

3.2. Reduction of GO via electrophoretic deposition

The reduction of GO is a critical step for the fabrication of graphene-based TCFs from GO flakes. Therefore, high temperature annealing [15, 16] or chemical reduction by strong reducing agents such as hydrazine [17], and hydroiodic acid [18] is necessary after deposition of GO films. We used XPS measurements to determine the chemical state of graphene films produced by our EPD method. As shown in figure 3, the C1s XPS spectra clearly showed EPD-graphene films to be significantly reduced after deposition without any reduction process. From the semi-quantitative analysis of the XPS results, we estimated the relative amount of oxygen contained in the functional groups for each sample. Peak separation was carried out for all samples after Shirley background was subtracted. The relative ratios of each component consisted of aromatic rings (284.6 eV), C-OH (286.5 eV), C-O-C (287.0 eV), and O=C-OH (288.3 eV) as summarized in table 2. Surprisingly, the relative ratios of oxygen containing functional groups of EPD-graphene films were less than that of GO films reduced by gaseous $\text{N}_2\text{H}_4$ and annealing. Thus we conclude that the EPD-graphene films were electrochemically reduced during deposition, but further investigation is necessary to understand the mechanism of reduction process [19, 20].
Figure 3. C1s XPS spectra of GO, and EPD-graphene films deposited on SiO$_2$/Si and glass, and GO films reduced by gaseous N$_2$H$_4$ and annealing.

Table 2. Chemical composition of the samples.

|        | C-C     | C-OH    | C-O-C   | O-C-OH  |
|--------|---------|---------|---------|---------|
| GO     | 49.10 % | 25.64 % | 22.07 % | 3.18 %  |
| EPD on SiO$_2$/Si | 81.05 % | 6.41 %  | 5.00 %  | 7.55 %  |
| EPD on glass | 81.60 % | 13.52 % | 0.26 %  | 4.61 %  |
| RGO by N$_2$H$_4$ | 73.65 % | 19.08 % | 0.00 %  | 7.26 %  |

3.3. Optical and electrical properties of EPD-graphene films deposited on glass

The optical properties of graphene films deposited by EPD onto glass substrates were characterized by measuring the optical transmittance of the films. They films exhibited a flat optical transmittance spectrum in the visible to infrared region as shown in figure 4. The sheet resistance of the films was approximately $4.59 \times 10^4 \ \Omega \ \text{sq}^{-1}$ at a transmittance of 83.8 %. Chemically and thermally reduced GO film showed a sheet resistance of $1.13 \times 10^6 \ \Omega \ \text{sq}^{-1}$ at transmittance of 83.7 %. The lower relative ratios of oxygen containing functional groups of EPD-graphene films might be one of reasons for the lower sheet resistance of the EPD-graphene films. Moreover, high uniformity and an absence of wrinkles may also have resulted in the lower sheet resistance of the EPD-graphene films.
Figure 4. Optical transmittance spectrum of an EPD-graphene film. 
The inset shows a photograph of EPD-graphene film.

4. Summary
We described an innovative electrophoretic deposition (EPD) based method for depositing graphene films on insulating substrates. Our method enabled the deposition of highly stacked graphene films without requiring a reduction process or sophisticated transfer processes. The graphene films had a lower sheet resistance than that of chemically and thermally reduced GO films because of significant chemical reduction, higher uniformity, and higher stacking. Our EPD method shows promise for the production of large area graphene-based TCFs.

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