The Line Speed Effect in Roll-to-Roll Dry Transfer of Chemical Vapor Deposition Graphene

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ABSTRACT

A roll-to-roll (R2R) technique is especially desirable for transfer of chemical vapor deposition (CVD) graphene towards high-speed, low-cost, renewable, and environmentally friendly manufacturing of graphene-based electronic devices, such as flexible touchscreens, field effect transistors and organic solar cells. A R2R graphene dry transfer system is recently developed. Monolayer graphene is transferred from a copper growth substrate to a polymer backing layer by mechanical peeling. In this work, we present an experimental study to examine the effects of line speed of the mechanical peeling process on the transferred graphene quality. It is shown that the effect of line speed is not monotonic, and an optimal speed exists to yield the highest and most consistent electrical conductivity of transferred graphene among the process conditions studied. This study provides understanding of process parameter effects and demonstrates the potential of the R2R dry transfer process for large-scale CVD graphene toward industrial applications.

Keywords: Graphene, Roll-to-roll, Dry Transfer, High-throughput, Mechanical Peeling

1. INTRODUCTION

Graphene has been widely studied in recent years due to its extraordinary properties in electrical conductivity, thermal conductivity, biocompatibility, and mechanical flexibility [1]–[5], which make graphene a promising material for extensive applications in the electronics industry [6]–[8]. To utilize graphene in industrial applications, the most important steps are large-area graphene growth and transfer. Large-area and high quality graphene growth has been realized with the development of the roll-to-roll (R2R) chemical vapor deposition (CVD) process [9], [10]. After the graphene growth, the following process for device application is to transfer the as-grown graphene from the metal substrate to a specific target substrate with high-throughput production. However, this key step is still a challenge. Typically, wet chemical etching or hot water delamination were involved during graphene transfer, resulting in an inefficient, costly, unscalable, and non-environmentally friendly process [11]–[14]. Wet chemical etching requires dissolution of the metal substrate, which usually leaves chemical contaminants that are almost impossible to be fully removed from the transferred graphene films. Hot water delamination needs extra setup for liquid handing and graphene drying, introduce more time and cost to the process.

To overcome the drawbacks of wet transfer of CVD growth graphene, an etching-free dry transfer method using mechanical peeling was developed by utilizing the high adhesive energy of graphene/polymer compared with graphene/metal [15]–[19]. However, most of the studies on graphene dry transfer are either manually or with a double-cantilever beam (DCB) setup, making the transfer process unscalable. The R2R technique is not only desirable for graphene growth but also specifically suitable for graphene dry transfer towards a high-speed, low-cost, renewable, and environmentally friendly manufacturing process [19]–[21].

It was found from recent studies that the separation rate plays an important role in the mechanical peeling process of graphene transfer [16], [19], [22]. Sumin et al. [22] analyzed a multilayer graphene delamination process from nickel surface to a viscoelastic adhesive layer on a DCB setup. By investigating the crack deflection, the experimental results showed that transfer yield of multilayer graphene increased as a higher loading rate was applied. Similar results were reported by Hao et al. [19] from a R2R dry transfer study of graphene grown on copper. It was found that certain peeling process parameters such as the line speed and guiding roller diameter have a significant effect on the transferred graphene quality. The experimental data in the Hao et al. study showed a positive correlation between the linear film speed and the graphene coverage. Chaochen et al. [16] measured the adhesion energy of a graphene/polyethylene terephthalate (PET) interface by a standard DCB test. It was found that the adhesion energy of this interface is highly rate dependent. However, the graphene is found to be fractured with high separation rates in this study, suggesting that the effect of loading rate is not monotonic.

In this study, we investigate the film speed effect in a R2R graphene dry transfer process. An experimental study was conducted on a newly developed R2R mechanical peeling system [23] with simultaneous speed and tension control to transfer graphene from its copper growth substrate to a polymer target substrate. Electric resistance measurements and scanning electron microscopy (SEM) were used to evaluate the transferred graphene quality. The results show that there is an optimal film speed to achieve the lowest electrical resistance for the R2R dry transferred graphene. This work provides understanding for process parameter selection for future R2R dry transfer of graphene studies.

2. EXPERIMENT SETUP

2.1 R2R Graphene Dry Transfer Machine

The R2R graphene transfer machine developed in this study is shown in Fig 1. A stepper motor (1-DM542S-23HS45) was used to drive the unwinding roller and set the linear film speed of the system. Two brushless servomotors (Aerotech BM130) were used in the torque model to drive the rewinding rollers with gearboxes (PGCN23-5025) to provide the needed driving forces for continuous peeling. To measure the peeling tensions and maintain stable peeling during the R2R graphene transfer process, three load cells (MAGPOWR CL-1-50) were instrumented on the three tension rollers separately. In the previous study [21], we have verified that the linear film speed and the peeling tension on both sides (graphene/Cu film and graphene/polymer film) could be reliably controlled. After the laminated Graphene/copper/polymer film went through the two guiding rollers R_1 and R_2, graphene was transferred from the copper film onto the PET/EVA layer. This happens because the adhesive force between graphene and EVA/PET is larger than that between graphene and copper. To protect the transferred graphene film, a non-adhesive PET film was used as a protective layer right after the graphene delamination.

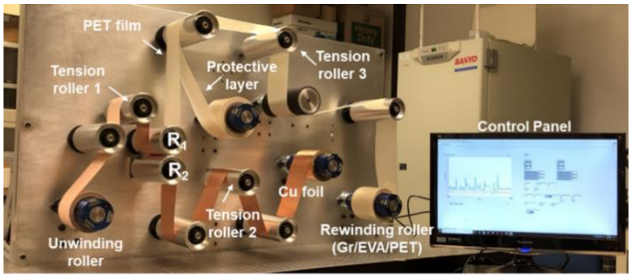

Figure 1. The roll-to-roll graphene transfer system using in this study.

2.2 Graphene Sample Preparation

The graphene samples used in this work are CVD-grown monolayer graphene on copper foil provided by Grolltex (San Diego, CA). The graphene coverage is uniform, with greater than 95% of monolayer and occasional bilayer islands. Figure 2 illustrates a simplified sample preparation procedure for the roll-to-roll dry transfer process in this study. The first step is to place the copper foil with as-grown monolayer graphene in DI water at room temperature overnight [18]. Then the copper foil with as-grown graphene was dried in room temperature with nitrogen flow. After that commercial PET/EVA (Ethyl Vinyl Acetate) films (Scotch Thermal Laminating Pouches TP3854-100, 3M) were laminated on both sides of the graphene-Cu-graphene foil at 150 °C using a commercial hot laminator (GBC HeatSeal H425). By this step a five-layer sandwiched foil PET/EVA-graphene-Cu-graphene-EVA/PET was obtained.

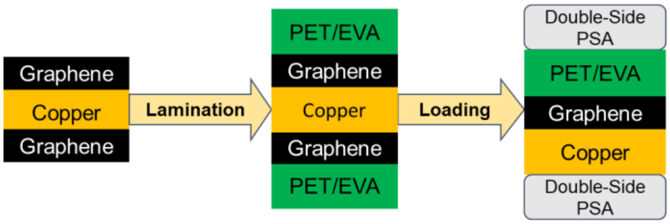

Figure 2. Sample preparation procedure.

In a process study of graphene dry transfer, it is better to use specimens instead of a long roll to avoid prohibitive cost. In addition, it would be much easier to adjust the discrete samples in a R2R machine. The sandwiched foil was cut into pieces. The size of the graphene specimen was 3 cm by 1 cm. These small, laminated specimens were baked under a vacuum oven at 150 °C for 30 min to improve the bonding between the PET/EVA and graphene layers. After baking, the PET/EVA layer on one side of the sample was manually removed. The final step of the sample preparation procedure was to sandwich the PET/EVA-graphene-copper sample between a PET carrier film (MYLAR® A, 254 µm thick) and a copper carrier film (Grainger 4UGU3, 76.2 µm thick). Double-sided pressure-sensitive adhesive tape (Double-side PSA, Scotch Tape 6137H) was used to attach the sample to the films on both sides. Then the laminated roll with PET/EVA-graphene-copper sample inside was loaded onto the R2R system for graphene dry transfer experiment, as shown in Fig 3.

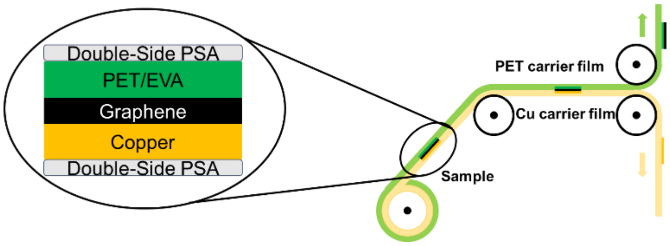

Figure 3. Loading graphene samples onto R2R machine.

2.3 Surface Electrical Resistance Measurements

To evaluate the electrical property without damaging the transferred graphene, an array of gold pads (90 nm Au and 19 nm Ni) was evaporated on top of the graphene as electrodes for resistance measurements, as shown in Fig. 4. The four-probe measurement technique was used to eliminate the contact resistance between graphene and the gold pads. With the array of electrodes, transferred graphene resistances at different locations of the sample could be characterized, such that the uniformity of dry transferred graphene could be analyzed. All resistance measurements in the study were performed with a nanovolt meter (Agilent 34420A).

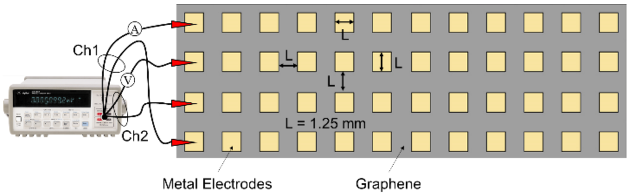

Figure 4. A schematic of the four-probe resistance measurement method used in this study with sample dimensions.

However, even if the quality of transferred graphene was uniform, the resistance measurements at different locations of the sample would not be the same due to the edge effect of the electric field distribution during the resistance measurements. A correction factor was needed before the electrical resistance of the dry-peeled graphene could be used to analyze the peeling process effects.

In this study, wet chemical etched graphene samples were used to obtain correction factors at different locations of the sample. The same gold pad array was made on wet transfer samples of the same size as the dry transferred samples. The resistance measurement at the center of the sample was used as a basis, and the measurements at all other locations were normalized against this value to yield correction factors as shown in Fig. 5. Since the quality of wet transferred graphene samples can be assumed uniform, these correction factors can be used to eliminate the edge effect in the surface resistance measurements and reveal the quality uniformity of dry transferred graphene due to various process conditions. The measured resistance value shown in the next sections are all corrected resistance values. As seen in Fig. 5, the surface resistance measurements could be 70% higher than the true values due to the edge effect in the resistance measurements.

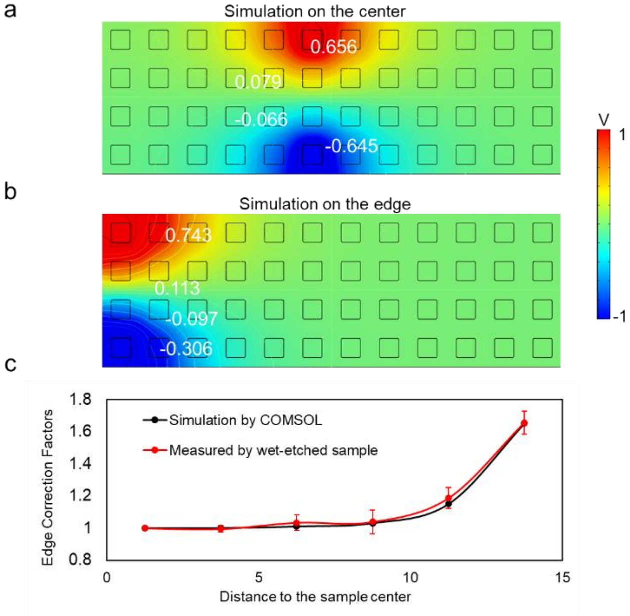

Figure 5. Correction factors for the edge effect. (a) COMSOL simulation of electric field when probes are applied on the sample center and (b) when probes are applied on the sample edge. (c) Comparison of correction factors for the edge effect between COMSOL simulation and measurements results. Three measurements were taken under each condition. Error bars show the standard deviations.

A finite element simulation model was built in COMSOL to verify the correction factors at different locations on the sample. Figure 5(a) and (b) show the simulation results at different locations, and it is seen that the measurements closer to the edge are affected more by the edge effect than those at the center. In addition, the simulation results match well with the measurements.

3. RESULTS AND DISCUSSION

3.1 Electrical Resistance Measurement Results

The edge-effect corrected sheet resistance measurements of transferred graphene are used to analyze the effect of peeling speed. To study the effects of film speed, peeling tensions were fixed at 10 N on both the PET carrier film and the copper carrier film. The strains on the carrier films are less than 0.1% under this condition. Figure 6 shows the resistance variation among the transferred graphene sample.

When peeling speed is low (0.5 m/min), there was large variation among the surface resistance measurements along the peing direction of the graphene sample. In addition, the resistance of the peeling front in this case was significantly higher than the rest of the sample, indicating an inconsistent peeling start with damaged transferred graphene. As the speed increased to 2 m/min, the transferred sample became more uniform. However, if the peeling speed kept increasing, the uniformity of the sample tended to decrease as shown in the figure.

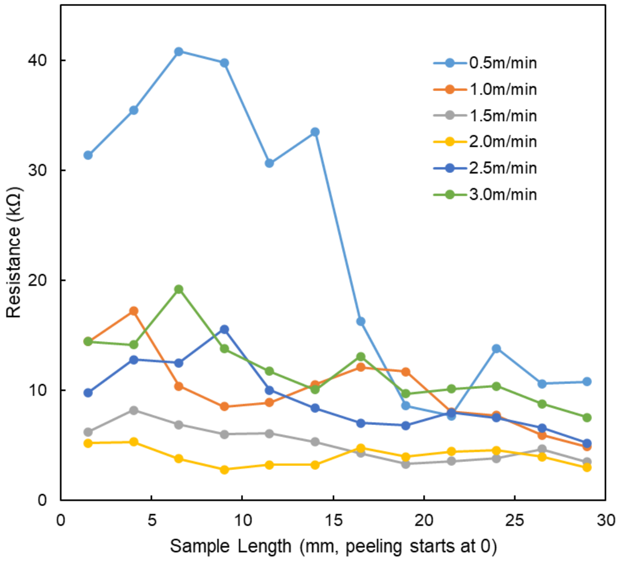

Figure 6. Surface resistance variation of transferred graphene samples.

Taking the sample average of all resistance measurements under each speed condition, the overall effects of speed can be examined, as shown in Fig 7. The average resistance value of a peeling condition is defined at the average of all the sample resistance values under that peeling condition. With the peeling tension set at 10 N on both films, the average sample resistance reached a minimum value when the speed was at 2 m/min. When the peeling speed was low, the standard deviation among samples was dramatically higher than the rest of the conditions. This indicates an unstable and uncompleted graphene transfer. Both the standard deviation and average resistance decreased when peeling speed increased from 0.5 /min. However, as shown in Fig 6, the transferred graphene quality will decrease when the peeling speed is higher than 2 m/min.

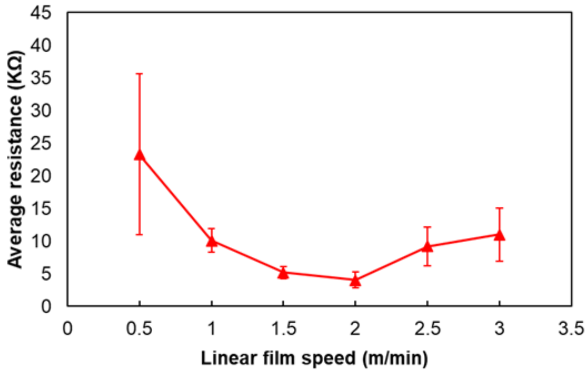

Figure 7. Average resistance of transferred graphene under different linear film speeds. Three measurements were taken under each condition. Error bar shows the standard deviation.

3.2 Discussion

Scanning electron microscopy (FEI Quanta 650 ESEM) (SEM) under the low vacuum mode was used to identify the coverage of graphene after R2R dry transfer. Under the 2 m/min peeling speed condition, the graphene coverage is identified to be over 99%. When the peeling speed increased to 2.5 m/min, the graphene coverage of the transferred sample reduced significantly, which matches the electrical resistance measurement result. Several areas of exposed EVA can be clearly identified in an SEM image of the 2.5 m/min sample, as shown in Fig. 8. The white areas represent exposed PET/EVA without graphene coverage, while the dark areas show the graphene coverage on the polymer. The white areas were due to that graphene was not peeled off or was damaged during peeling. The graphene coverage calculation was done with image processing software ImageJ [24].

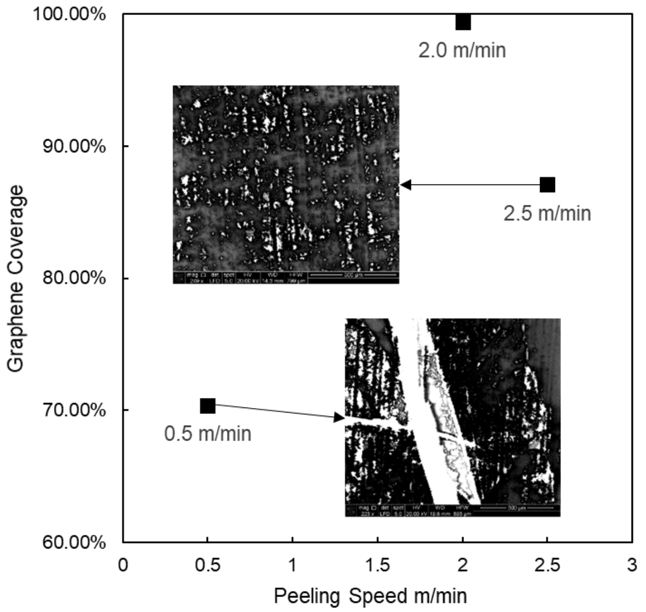

Figure 8. Graphene coverage measurements with an inserted SEM image of the transferred graphene under the peeling speed at 2.5 m/min.

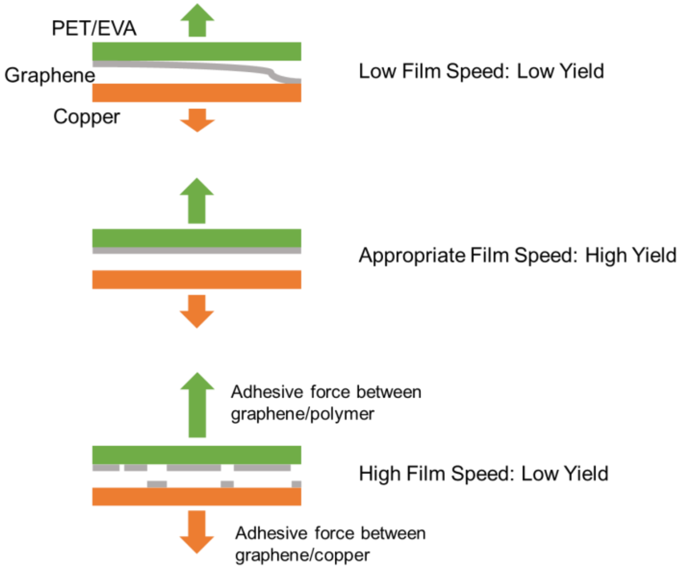

Figure 9. Schematic of line speed effect in R2R graphene dry transfer process.

The line speed effect in the R2R graphene dry peeling process can be explained with a schematic shown in Fig. 9. The up and down arrows are used to show the adhesion forces between PET/EVA and graphene and between graphene and the copper substrate. The size the arrow represents the magnitude of the adhesion force. When the film speed is low, the resistance in the peeling start area is significantly higher than that in other areas of the sample. The average resistance of entire sample at this speed is also higher than that at other speeds, indicating that large areas of crack were generated, and the transfer process was unsuccessful. Similar observations were also found by Sumin et al. [22] with a DCB setup for peeling multilayer graphene from a nickel substrate. The rate effect was investigated by analyzing the deflection of cracks. It was reported that a large deflection of crack occurred at a low loading rate due to highly mismatched elastic moduli between the Ni and the adhesive layer, while this mismatch will be mitigated when a higher loading rate is applied due to the viscoelastic property of the adhesive layer. The property of PET/EVA film is highly rate-dependent [25], resulting in a low bonding force between graphene and PET/EVA at a low speed.

When the film speed is too high, the transferred graphene film is teared into pieces. Previous study by Chaochen et al. [16] has found that the adhesion energy at the graphene and polymer interface and that at the graphene and copper interface will both increase with increasing separation speed. When the peeling speed is high, the adhesive force at the graphene/EVA/PET and the graphene/copper interfaces are both high, which means the two competing forces could generate more defects and fractures in the graphene film during mechanical peeling. Overall, both low peeling speed and high peeling speed will introduce additional damage during the mechanical peeling process of graphene transfer, indicating an appropriate film speed should be selected for R2R graphene dry transfer.

4. CONCLUSION

A R2R mechanical peeling system is developed for dry transfer of large-scale CVD graphene. Experiments were conducted to investigate the line speed effect of the graphene peeling process. The quality of transferred graphene was studied by electrical resistance measurements. When peeling speed is low, the graphene transfer process was unsuccessful due to highly mismatched elastic moduli between the copper and adhesive layer and the low bonding force between graphene and the adhesive layer. When peeling speed is high, the adhesive force at the graphene/EVA/PET and the graphene/copper interfaces are both high, causing more defects and fractures in the weak areas of the graphene film. An optimal film speed should be used for R2R graphene dry transfer to enable high-quality graphene for large-scale industry applications.

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