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Electrodeposition Cu and roll transfer of graphene for large scale fabrication of Cu-graphene nanolayered composite

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Abstract
Nanolayered composites are reported to exhibit high strength due to the high density of interfaces. Previously, metal–graphene nanolayered composite had been fabricated by vacuum based deposition of metal layers and wet transfer of graphene layers, both of which are time consuming processes that limit the scalability of the nanolayered composite. In this study, the vacuum based deposition of metal and wet transfer of graphene have been replaced with electrodeposition of metal and roll-based dry transfer of graphene to greatly enhance the scalability of the nanolayered composite fabrication. Fabricated Cu-graphene nanolayered composites with layer spacing of 200 nm, 300 nm, and 400 nm were tested under compression, and the strengths are calculated to be 1.38 GPa, 1.15 GPa, and 1.06 GPa, respectively. The strengths are within the range reported previously for the case of wet transfer and sputter deposited metal, but the new fabrication method has greatly enhanced scalability.

1. Introduction
Nanolayered composite structures, composed of alternation of two different materials joined by 2D interfaces, are known to have unique and outstanding mechanical properties that far surpass those of the same two-phase systems with random orientations. For this reason, many researches with different combinations of nanolayered composites have studied the strengthening mechanism of such nanolayered composites and reported that the dislocation blockage at the interfaces is responsible for the strengthening that increases with reduction in repeat layer spacing down below sub-micron scale [2]. Graphene, which has ultra-high strength and modulus even though it is only an atomic layer in thickness, is being recognized as a promising strength enhancing material in such nanolayered structures [3–5]. As the techniques for synthesizing and transferring the graphene are developed, attempts to implement this material in various applications are made by many researchers. The enhanced mechanical properties of such carbon based materials in combination with metals and their potential applications in flexible electronics industries are reported in numerous studies [1, 6–10]. The strengthening mechanism of graphene in the metal–graphene nanolayered composite under compression or repeated bending has been studied in depth in previous studies [1, 6]. In the paper by Kim et al, nanopillar compression tests of metal–graphene nanolayered composite revealed for the first time that the dislocation motions are successfully blocked at the metal–graphene interface to enhance the mechanical properties of the whole structure [1].

The metal–graphene nanolayered composites with alternating layers of metal and graphene, however, possess a crucial limitation in terms of scalability [11]. The fabrication method used in the work by Kim et al involves vacuum based physical deposition of metal layers and wet transfer of the graphene layers, both of which are time-consuming processes. The wet transfer process of graphene layer involves CVD synthesis of graphene on a Cu foil, spin coating supporting polymer layer (PMMA) on one side of the graphene on Cu foil, etching the Cu foil on the other side by floating on etching solution, and then transferring on to desired
surface by scooping method [1]. This method of wet transfer [12] has been demonstrated in using graphene for applications such as solar cell [13], transparent electrode devices [14, 15], biosensor [16], and energy applications. However, this wet transfer process possesses inevitable limitations such as it takes extensive time to perform and that it can only be performed by hand, in laboratory scale. The wet transfer of graphene also has problems of the PMMA residue that remain on the surface of graphene even though PMMA is etched by acetone and rinsed with DI water to minimize any residue. The vacuum based metal transfer is also costly with limited scalability, which make it unsuitable for larger scale applications. As a highly scalable fabrication method of the metal-graphene composites, metal matrix composites (MMCs) with nanolaminated structures have been reported in the study by Li et al. [11] In this paper, Al-RGO nanolaminated composites have been fabricated by composite powder assembly method and have been shown to exhibit much higher strengths compared with random mixture composite. Although the fabrication of Al-RGO nanolaminated composite is proposed as a method for large scale production of metal-graphene nanolayered composites, it may be an inefficient method in terms amount of reinforcing material used, compared with the nanolaminated composite fabricated using monolayer graphene.

The fabrication process of large scale graphene has recently been greatly improved by rapid heating methods such as halogen and joule heating, compared to thermal CVD process [17]. In addition, various efficient methods for transferring the graphene onto desired surfaces such as direct deposition method [18], carrier film method [14], hot pressing method [19], bubble transfer method [20], and direct transfer method [21–23] are being studied for large scale transfer. Among these, the roll-based transfer is most suitable for large scale fabrication of graphene-based 2D composites. In this study, we propose to incorporate roll-based graphene transfer and electrodeposition of metal in order to enhance the scalability that can be adopted for industrial production of metal-graphene nanolayered composites for potential application as an electrode for flexible electronics.

2. Experimental

2.1. Fabrication of Cu-graphene nanolayered composite

In order to overcome the scalability limitations of wet transfer of graphene in fabrication of Cu-graphene nanolayered composite, electrodeposition of Cu layers and roll based dry transfer of graphene layers for nanolayered composite fabrication are developed. The schematic for the overall process is shown in the figure 1. Each of these processes are explained in detail below.

2.1.1. Roll-based transfer of graphene.

First, conventional thermal CVD is used to grow a graphene layer on the Cu foil (35 µm thickness, Alfa Aesar). CVD growth of graphene onto sacrificial Cu foil is known as the best method for synthesizing high quality single layer graphene [24]. An adhesive carrier film is then attached onto the CVD grown graphene surface using a roll laminator. Then, the carrier film/graphene/Cu foil composite is then floated on APS solution to etch out the sacrificial Cu foil, and the remaining carrier film/graphene is rinsed with DI water to wash away any remainder etching solution and any other residues. Then, the carrier film/graphene structure is completely dried out in air and is ready for roll transfer using the same roll laminator. The transfer process is carried out simply by placing the graphene side on top of the desired surface (i.e. electroplated Cu), applying adequate heat and pressure using the roll laminator heated to 110 °C, and lifting off the carrier film [25]. The silicone-based adhesive material in the carrier film used in this process is known to have extremely low work of adhesion with the graphene surface compared to other commonly used substrates [26]. This difference in the adhesion between the carrier film-graphene and the graphene-electrodeposited Cu allows for the graphene to detach from the carrier film completely and thus transferred onto the electrodeposited Cu surface [25].

2.1.2. Ozone UV irradiation of the graphene surface.

After the roll transfer of graphene onto the electrodeposited Cu layers, the surface of graphene is treated with ozone UV irradiation (UVO Cleaner, Jelight Company) in order for uniform electrodeposition of next Cu layer in sub-micron thickness range. The average intensity of the lamp is 30 mW/cm² at wavelength of 253.7 nm. Although electrodeposition of Cu is widely used for various applications [27], such process for uniform and thin (sub-micron) deposition on the graphene surface has not been reported. Initial electrodeposition attempts without any surface treatments of the graphene have been unsuccessful due to uneven Cu seed formations near the graphene defect areas. Other studies have shown that the proper surface wettability and maintaining uniform current paths are two important factors for uniform electrodeposition of metal on graphene surface [28–31]. As one of the methods for achieving such conditions, surface treatment of the graphene with ozone UV irradiation for 10 min duration is implemented in this study.

2.1.3. Electrodeposition of Cu layers.

First 100 nm of all samples are deposited on silicon substrate by sputtering (Magnetron sputtering system, SNTEK) for the deposition of uniform and conductive electroplating seed layer [32, 33]. The sputtering is conducted in chamber environment of 3 mTorr pressure, 12 sccm Ar flow under 50 W for 1250 s. For electrodeposition process, the electrolyte containing copper sulfate (25 g l⁻¹) (HanTech PMC) and sulfuric acid to maintain pH of 0.5 is used. Electrolytic copper
(99.99%) is used as the anode of the process. Pulse reverse current electrodeposition (PED) process [27] is utilized where the forward pulse deposited Cu ions at current of 5 mA cm\(^{-2}\) onto the substrate for 9 s and then the reverse pulse of \(-5 \text{ mA cm}^{-2}\) was imposed for 2 s to cleanse out extra Cu ions, impurities, and gases that may have been entrapped onto the surface during the forward pulse process. During the reverse pulse cycle, parts of the rough Cu surfaces are etched to further enhance the uniformity of the electrodeposited Cu layers. The deposition current, hence the rate, was maintained constant for all samples and only the number of forward/reverse cycles was varied accordingly to deposit desired thickness of Cu. The roll-based graphene transfer, UV treatment, followed by electrodeposition of Cu on graphene surface were repeated multiple times to fabricate Cu-graphene nanolayered composite with layer spacing of 200, 300, and 400 nm with the same total thickness around 1 \(\mu\text{m}\). Cu only reference of 1 \(\mu\text{m}\) thickness was also fabricated using electrodeposition of Cu, as shown in the figure 4.

2.2. Mechanical properties analysis via \emph{in situ} pillar compression test

Focused Ion Beam (Helios 450 F1) was used to fabricate nanopillars from Cu-graphene nanolayered composites with repeat layer spacing \(\lambda = 200 \text{ nm}, 300 \text{ nm}, 400 \text{ nm}\) and Cu only sample with 1 \(\mu\text{m}\) thickness. The operation voltage of the FIB was maintained at 30 kV and current range of 9.1 nA–0.23 nA was used. The dimensions of the pillars were fabricated to be diameter of \(\sim 350 \text{ nm}\) and height of 1 \(\mu\text{m}\) (~1:3 diameter to length ratio) to minimize end constraints while avoiding buckling. The compression tests of the nanopillars were performed using \emph{in situ} SEM with Hysitron PI-87 picoindenter system equipped with 1 \(\mu\text{m}\) flat punch tip. The resulting true stress-strain curves are calculated using the constant volume, homogeneous deformation model \((A_0L_0 = A_pL_p)\), where \(A_p\) and \(L_p\) are the final cross-sectional area and height of the pillar, respectively. Assuming that the volume of the pillar is constant and that the pillar deforms uniformly, the values of the pillar’s final cross-sectional area and the length can be calculated using the equations \(A_p = \frac{A_0L_0}{L_0 - \frac{\epsilon_\text{pillar}}{2}\frac{L_0}{A_0L_0}}\) and \(L_p = \frac{A_0L_0}{A_p} \left[ 1 - \sqrt{1 - 4\left(\frac{E_p}{E_p + \frac{1}{3}}\right)\left(L_0 - \epsilon_\text{pillar}\right)} \right] \), respectively. The \(\epsilon_\text{pillar}\) is corrected displacement of the nanopillar, which is total displacement of the indenter tip subtracted by the displacement that the material below nanopillar moved. Finally, the true stress and true strain are calculated using the values of \(A_p\) and \(L_p\) given by \(\sigma = \frac{P}{A_p}\) and \(\varepsilon = \epsilon_\text{el} + \epsilon_p = \frac{P}{E_pA_p} + \ln \frac{L_0}{L_p}\). More detailed derivations of the constant volume, homogeneous deformation model are presented in the work by Greer \etal [34].

Although nanopillar compression are conducted on limited cross-sectional area with diameter of several hundreds of nanometers, the strengthening phenomenon observed in this scale is also applicable in larger scale. Despite numerous studies showing the strengthening effect in pillar compression tests as the external dimension (i.e. diameter) of the pillar decreases [35–37], in Cu-graphene nanolayered composite structure, the external pillar dimension is not the limiting factor for the strengthening of the structure. Instead, the
thickness of the individual Cu layers and the number of the graphene interfaces determine the strength of the composite, as directly shown in detail in the section 3.2.

3. Results and discussion

3.1. Effect of UV-ozone treatment on graphene surface

Introduction of UV irradiation on the surface of graphene is to intentionally introduce defects throughout the graphene layer so that the electroplated Cu can grow uniformly to achieve a thin film with uniform thickness. Without the UV irradiation process, the Cu would grow highly inhomogeneously, where the Cu chooses to grow at few sites with existing defects on the surface of the graphene as shown in the figure 2(a). The cross-section images of the electrodeposited Cu on graphene surface as shown in the figure 2(b) clearly display the increase in uniformity of thickness as the UV irradiation time increased. The UV-ozone treatment affects the sp\(^3\) carbon bonds of the graphene, highly oxygenating the graphene surface [38]. The increased coverage of the oxygen atoms on the graphene surface will enhance the wettability of the electroplating solution on the graphene surface so that the uniformity of the electrodeposition increase significantly. Wettability, as a measure for potential uniformity of the electrodeposited Cu layers, was also analyzed by measuring the contact angle of the surface. UV irradiation times of 0 to 2, 5, 10, and 20 min resulted in H\(_2\)O contact angle to decrease from 90 to 90.7, 60.1, 29, and 17.5 degrees, respectively, as shown in figure 2(c). It can be seen that the inherent surface wettability of graphene is very low, which resulted in accumulation of the water based plating solution and island Cu growth around the initial graphene defects, as previously seen in the figures 2(a) and (b). As the UV irradiation time increased, the wettability has also increased, resulting in much more uniform electrodeposition of Cu layers.

Although the uniform Cu deposition can be achieved with UV irradiation, one of the disadvantage of the UV treatment is the damage on the graphene surface, which can in turn affect its effectiveness as a strength enhancer. The D peak disorder, at around 1350 cm\(^{-1}\), of the UV treated graphene surface is measured to study such a damage, by Raman spectroscopy as shown in the figure 3. From this result, it can be seen that UV irradiation for longer than 10 min can seriously damage the structure of the graphene via formation of atomic defects and transformation of the sp\(^2\) bonding to sp\(^3\) in the graphene structure [39]. Although longer UV irradiation will enable more uniform deposition of Cu layers, the accumulated damage on graphene layer may seriously affect the overall strength of the Cu-graphene nanolayered composite. Thus, UV irradiation time of 10 min has been determined as the optimal time for achieving both uniform electrodeposition of Cu layers while minimizing the defects on graphene to maintain its strengthening effects in the form of Cu-graphene nanolayered composite.

Figure 2. SEM (a) surface images of electroplated Cu on graphene surface and (b) cross-section images as the UV irradiation time varies from 0 min to 20 min. (c) The contact angles of graphene with different durations of UV irradiation in ambient environment.
3.2. Strengthening effect in EP Cu-graphene nanolayered composite

To analyze the mechanical properties of the Cu-graphene nanolayered composite made by electroplating of Cu and roll-based transfer of graphene in comparison to those of reference study [1] on vacuum deposited Cu and wet-transferred graphene nanolayered composite, nanopillar compression tests were conducted to obtain stress versus strain curves for repeat layer spacings of \( \lambda = 200, 300, 400 \) nm. The same constant volume homogeneous deformation model as in the reference study was used for stress-strain calculations for a meaningful comparison. As expected, the stress-strain curve revealed highest strength of the nanolayered composite at the smallest layer spacing as shown in the figure 5(a). The average flow stresses at 5% plastic strain points for \( \lambda = 200, 300, 400 \) nm Cu-graphene and 1 \( \mu \)m Cu only samples are determined to be 1.38 GPa, 1.15 GPa, 1.06 GPa, and 0.75 GPa, respectively.

The flow stresses at 5% plastic strain of Cu-graphene nanolayered composites fabricated by electrodeposition of Cu and roll transfer of graphene are plotted along with those from reference study fabricated by e-beam deposition of Cu and wet transfer of graphene in one plot for direct comparison of the two conditions, as shown in the figure 5(b). Two different phenomena can be observed here. First, the magnitude of flow stresses of the electroplated Cu-graphene nanolayered composite for all layer spacings is higher than that from reference study. As revealed by EBSD analysis as shown in the figure 4(a), the average grain size of electrodeposited Cu in this study is about 50 nm. The smaller grain sizes will result in additional restriction on the initial motion of dislocations that thus cause strength to increase.

Second, although the trend of increase in strength with reduction in the repeat layer spacing are similar, the rates of increase in strength with reduction in repeat layer spacing are different for the cases of electroplated Cu-roll transferred graphene and e-beam deposited Cu-wet transferred graphene. The slope of log stress versus log \( \lambda \) for the electroplated Cu-roll transferred graphene nanolayered composite is \(-0.380\), which is slightly less steep in comparison to that of the reference study with slope of \(-0.402\). As previously mentioned in above section 3.1, the roll-transferred graphene is subjected to UV irradiation for 10 min in order to allow for uniform electrodeposition of Cu layers, and this process causes inevitable damage to be accumulated on the graphene layers. It is possible that the damaged graphene would then be slightly less effective in blocking the dislocations across the Cu-graphene interfaces, which is the key strengthening mechanism of metal-graphene nanolayered composites in the reference study.

3.3. TEM analysis of the Cu-graphene pillars before and after compression

TEM images of the pillars before and after the compression tests on Cu-graphene nanolayered composite with \( \lambda = 200 \) nm are shown in the figure 6. Although the electroplated Cu grain size is too small for in depth analysis of the dislocation movement within the grains, several meaningful observations could be made. Because of the taper in the pillar, where the cross section is narrower at the top surface, the pillar starts to deform from the uppermost layer.
As dislocations are nucleated and propagated, the graphene interface effectively blocks the dislocation motion that then triggers more complex slip systems to result in bulging, as observed in the inset of figure 6(b). Higher magnification dark field TEM image taken at the interface shows dislocation pile-up at the graphene interface as shown in figure 6(b). At high enough stress, new dislocations will be nucleated and propagated in the 2nd Cu layer that then piled-up at the graphene interface and this cycle is repeated for general deformation of the pillar. It should also be noted that the metal and graphene layers remain intact without observable shearing of the interface after heavy deformations.

The nanolayered composite fabrication technique introduced in this study was demonstrated to successfully synthesize of metal-graphene nanolayered composite with much improved scalability. By replacing the vacuum based deposition of metal layers with electrodeposition and replacing the wet-transfer of graphene with roll-based transfer, the production cost and time can be greatly reduced and the overall process can also be systemized into continuous roll-to-roll process. Analysis of the Cu-graphene nanolayered composite with the new fabrication method demonstrated that similar strengthening effects were observed as in the work by Kim et al who used vacuum based metal deposition and wet transfer of graphene. Details of what was found in terms of...
mechanical properties. Thus, with the introduced novel fabrication technique, Cu-graphene nanolayered composite exhibiting high strength can be produced at much larger scales than previously reported.

4. Summary

Electrodeposition of Cu and roll-based dry transfer of graphene are used to fabricate the Cu-graphene nanolayered composite, which had been reported to have ultra-high strength with much enhanced scalability for larger production. The wettability of the electroplating solution on the graphene surface is enhanced by treating the graphene surface with ozone UV irradiation in order to uniformly deposit the Cu layers through electroplating even at submicron thickness. Roll-based transfer of CVD grown graphene, together with electrodeposition of Cu, was used to fabricate nanolayered composites with layer spacings of 200 nm, 300 nm, and 400 nm. Nanopillar compression revealed an increase in strength of the nanolayered composite as the layer spacing decrease was observed, as expected, where the 5% flow stress increased from 1.06 GPa to 1.38 GPa as the repeat layer spacing decreased from 400 nm to 200 nm. The slopes of the log plot of 5% flow stress versus repeat layer spacing are $-0.380$ for the electroplated Cu-roll transferred graphene nanolayered composite in this study and $-0.402$ for that in reference study. The overall strength of the electroplated Cu-graphene was higher because of the smaller grain sizes compared to those from evaporative deposited Cu. On the other hand, the more defects introduced on the graphene surface during the UV treatment resulted in reduced strengthening effect in the case of electroplated Cu-roll transferred graphene. The reported new methodology of large scale fabrication of Cu-graphene nanolayered composite with ultra-high strength is expected to have an impact on potential commercial production of this material system for applications in the areas requiring extreme mechanical properties such as the flexible, stretchable metal interconnects.

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