Stability of Few Layer Graphene Films Doped with Gold (III) Chloride

Mir Abdullah-Al-Galib, Bo Hou, Tahmeed Shahriar, Sandra Zivanovic, and Adarsh D.

Radadia*

Institute for Micromanufacturing, Louisiana Tech University, 911 Hergot Avenue,
Ruston, LA 71272, U.S.A.

Corresponding Author: Adarsh D. Radadia, Institute for Micromanufacturing, 911 Hergot
Avenue, Ruston, LA 71272, U.S.A, Phone: +1 318 257-5112, E-mail:

radadia@latech.edu.

Abstract

In this paper we study the stability of few layer graphene (5-7 layers) doped with gold nanoparticles through spin coating of a gold (III) chloride solution. Specifically sheet resistance, optical transmittance and surface morphology were monitored over a period of four weeks. Through scanning electron microscopy we observed that the gold nanoparticles of 29.1 ± 1.3 nm diameters, which were formed on surfaces freshly doped with a 20 mM solution, agglomerate and fuse over the period of four weeks into larger particles of 50-110 nm diameters. At the end of four weeks of aging, regardless in air or vacuum, the optical transmittance at 550 nm for the doped samples resumed a value close to that of undoped samples. During these four weeks, the sheet resistances of the samples doped with 20 mM gold chloride also increased from 130 ohm/sq to 300 ohm/sq,

but stayed comparable to indium tin oxide. In summary, despite the instability of doped FLG surfaces obtained using gold (III) chloride solutions, this study warrants the use of doped FLG films for building the next generation photovoltaics.

Keywords:

Few layer graphene, gold chloride doping, gold nanoparticles, graphene photovoltaics

1. Introduction

Indium tin oxide (ITO) and its doped analogues have dominated the field of transparent anodes that are used for building solar cells [1-3]. The research to control deposition thickness, morphology, and surface termination has been pivotal in their practical implications [4-6]. The limited availability of indium and the resulting inflation in indium prices generates the need to find alternative materials that can also meet the needs of the next generation of optoelectronic devices such as lightweight, flexible, low-cost, and compatibility with large-scale manufacturing methods [7-9]. Graphene, which is a single sheet of hexagonally arranged sp^2 -hybridized carbon atoms, has become a promising candidate to form transparent anodes for solar cells [10-13]. The uniqueness of its electronic structures arises from delocalization of charge carriers over large areas, thus making an ideal plane of graphene a scattering-free platform for carrier transport [14, 15].

The first use of graphene as an electrode for solar cell was demonstrated by Eda *et al.* in 2008 [16]. A 14 nm thick film of reduced graphene oxide with a transparency of ~64% at 550 nm and a sheet resistance of $40 \text{ k}\Omega/\square$ was used to create a graphene/poly(3,4-ethylene dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS)/poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM)/Al solar cell with a device efficiency of 0.1%. The sheet resistance of graphene was lowered through thionyl chloride-mediated chlorine doping of the reduced graphene films that originally measured $100 \text{ k}\Omega/\square$. Shortly thereafter Wu *et al.* [17] also demonstrated an graphene/copper phthalocyanine/fullerene/bathocuproine/Ag solar with graphene anode deposited by spin coating an aqueous graphene solution on glass. Although the optical transmittance of

graphene used in their case was greater than 80%, the sheet resistance varied between 5 k $\Omega/\square$ to 1 M $\Omega/\square$. The short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (η) were found to be 2.1 mA/cm², 0.48 V, 0.34 and 0.4% respectively in the case of graphene as the anode compared to 2.8 mA/cm², 0.47 V, 0.54, and 0.84%, respectively in the case of ITO as the anode. Wang *et al.* [18] reported construction of a dye-sensitized solar cell (graphene/TiO₂/dye/spiro-OMeTAD/Au) using graphene with sheet resistance between 0.9 to 1.08 k $\Omega/\square$ and found a J_{SC} of 1.01 mA/cm², a V_{OC} of 0.7 V, a FF of 0.36, and an η =0.26% for graphene-based solar cell compared to a J_{SC} of 3.02 mA/cm², a V_{OC} of 0.76 V, FF of 0.36, and an η =0.84% for ITO-based solar cell.

While most of the earlier solar cells with graphene electrodes were fabricated using reduced graphene oxide and suffered from high sheet resistivity of the electrode, Kian Ping Loh and co-workers [19] reported the use of graphene grown by chemical vapor deposition (CVD) on nickel to create a graphene/PEDOT:PSS/P3HT:PCBM/LiF/Al solar cell with an η =1.71%, which was ~55% of that obtained from ITO devices (η =3.1%). For 6–30 nm thick graphene films, the average sheet resistance varied from 1350 to 210 $\Omega/\square$ with an optical transparency from 91% to 72% in the visible light wavelength range. CVD graphene films have grain boundaries that are formed *in situ* during synthesis and minimize the contact resistances with neighboring graphene domains in comparison to the relatively higher flake-to-flake contact resistances in case of reduced graphene oxide films. Another key to obtaining such η value according to the authors was the usage of 1-pyrenebutanoic acid succinimidyl ester for surface energy modification of graphene.

Later, De Arco *et al.* [20] also demonstrated the use of graphene synthesized by chemical vapor deposition (CVD) on nickel to construct a solar cell (graphene/PEDOT:PSS/copper phthalocyanine/fullerene/bathocuproine/Al). A high quality CVD graphene with sheet resistance of $500 \Omega/\square$ and 75% optical transmittance at 400 nm light wavelength were used. Graphene-based solar cells resulted in a J_{SC} of 4.73 mA/cm^2 , a V_{OC} of 0.48 V, a FF of 0.52, and an $\eta=1.18\%$ compared to a J_{SC} of 4.69 mA/cm^2 , a V_{OC} of 0.48 V, FF of 0.57, and an $\eta=1.27\%$ for ITO-based solar cells.

Although the optical transmittance through graphene can be well controlled through restriction of its thickness, the higher sheet resistance of graphene than ITO has been identified as the key-limiting factor in developing graphene-based photovoltaics [7, 13]. Jing Kong and co-workers [21] demonstrated the method of reducing the sheet resistance of CVD graphene as low as $150 \Omega/\square$ at 87% optical transmittance by doping it with gold nanoparticles (AuNPs). In the proposed process gold chloride (AuCl_3) was dissolved in nitromethane and spun coated onto transferred CVD graphene. It is proposed that Au^{3+} precursor spontaneously reduces to form Au nanoparticles on the surface of graphene. A doped graphene/PEDOT:PSS/copper phthalocyanine/fullerene/bathocuproine/Al solar cell produced an $\eta=1.63\%$, which was quite comparable to the $\eta=1.77\%$ obtained with solar cell made with ITO anodes [22]. Kong and co-workers [23] found that this method of doping also allows favorably adjusting the surface potential of graphene films by up to $\sim 0.5 \text{ eV}$ by controlling the immersion time. Photovoltaic devices fabricated based on *n*-type silicon interfacing with graphene films demonstrated a maximum power conversion

efficiency (PCE) of ~0.08%, which is more than 40 times larger than the graphene-silicon devices without doping.

While the data reported so far is collected from freshly doped single-layer and multi-layer graphene films, this paper further studies the temporal variations in optical transmittance and sheet resistance of such gold nanoparticle doped few-layer graphene (FLG) films up to four weeks. Special care was taken cleaning the FLG prior to doping and removing polymeric residues originating from the FLG transfer process. Scanning electron microscopy (SEM), and atomic force microscopy (AFM) were performed in addition to sheet resistance, optical transmittance, and reflection measurements to measure the evolution of FLG properties over time in air and vacuum.

2. Materials and methods

2.1 FLG synthesis and cleaning. FLG synthesized by CVD on 1 mil thick copper foil using methane and hydrogen was obtained from Graphene Laboratories, Inc. FLG was transferred to 10 mm square and 1 mm thick fused quartz chips using previously published PMMA based method. [24, 25]. To reduce the PMMA residue, the FLG was soaked in a 1:1 (v/v) solution of dichloromethane (DCM) and methanol for 1 h [26]. Further, the FLG was rinsed in excess methanol and dried under a gentle stream of nitrogen prior to annealing in 5% H₂/95% Ar at 400 °C for 1 h.

2.2 Doping with AuNPs. Doping of FLG with gold nanoparticles was carried out by spin coating gold (III) chloride (AuCl₃) solutions on the above-cleaned FLG chips. A 50 µl

solution of either 1, 5, 10, 15, or 20 mM AuCl_3 (Sigma) in nitromethane (Sigma) was spin coated on FLG at 2500 rpm for 60 s and then the chips were baked at 150°C for 10 minutes. Doping was performed in a 1000 class cleanroom under ambient environment (50% RH, 20°C). The doped samples were stored in a polystyrene petridish, either in air or in a vacuum desiccator as needed for the experimental observations.

2.3 Characterization. Scanning electron microscope (SEM) images were taken with a Hitachi S-4800 with 1 kV extraction voltage such that minimal charge damage is caused to the film while imaging with adequate resolution. Image analysis was carried out using ImageJ. Atomic force microscopy (AFM) images were taken with an Agilent 5420 in tapping mode with a silicon probe (Nanosensors PPP-NCHR) and the scan area was fixed to $0.5 \times 0.5 \mu\text{m}^2$. The AFM probe used had a $5 \mu\text{m}$ tall tip, and less than 10 nm tip radius. Image analysis was carried out using Gwyddion. Optical measurements were performed in air at $20 \pm 1^\circ\text{C}$ and ~50% relative humidity with a Filmetrics F10-RT reflectometer, which was calibrated using Al_2O_3 reflectance standards. Sheet resistance (R_s) measurements were made by van der Pauw method using a LakeShore 75013 SCSM Hall measurement system. The measurements of R_s were carried out ten times with an excitation bias of 10 mV and averaged. Stokes shifts of Raman scatterings were measured using a Horiba Jobin Yvon LabRAM Aramis spectrometer equipped with a 632 nm wavelength laser, a 1200 lines/mm grating, a $100 \mu\text{m}$ slit, a $50 \mu\text{m}$ pin hole, and a 50x objective.

3. Results and discussion

The proper removal of the residual PMMA from the surface of transferred FLG and annealing treatment were important to achieve surfaces with similar surface energy across all the samples used in our experiments. The presence of PMMA on graphene is known to create extrinsic scattering, which degrades its properties such as electrical conductivity and optical transparency [27]. Furthermore, the density of AuNP formation on graphene by spin coating AuCl_3 has been shown to be modulated by the surface energy of the graphene [28]. Fig. 1 shows the SEM images of the FLG before and after the cleaning routine that we adopted to remove the residual PMMA. After the cleaning routine, although not completely, a significant amount of PMMA was removed off of FLG. The cleaned FLG was further used for AuNP doping.

Fig. 2 shows results from a detailed AFM and SEM study on particle diameter and particle density. The results are calculated using 4-5 images of different positions on the sample. The sampling area was kept to $1\ \mu\text{m} \times 1\ \mu\text{m}$ (512x512) or $2\ \mu\text{m} \times 2\ \mu\text{m}$ (1048x1048). As shown in Fig. 2A, AFM studies show that the particle size increases with concentration of the AuCl_3 solution. AuNPs of $14 \pm 2.43\ \text{nm}$ (equivalent radii) are obtained with 1 mM and $29.1 \pm 1.3\ \text{nm}$ with 20 mM AuCl_3 . For accurate estimation of particle sizes, blind estimation of tip shape was carried out followed by reconstruction of the image using the estimated tip. The results showed that the height of the particles were similar to the equivalent particle diameter calculated on an average. The data in Fig. 2A was used to calculate the influence of AuCl_3 concentration on the AuNP volume. It was found that the AuNP volume followed a power law with an exponent of 0.69. The AFM images were also used to calculate the AuNP density as shown in Fig. 2B. The AFM

imaging was carried in a small area ($1\text{-}4\ \mu\text{m}^2$). SEM was carried out to investigate larger areas ($10\text{-}25\ \mu\text{m}^2$). The samples doped with 1 and 5 mM AuCl_3 showed too few particles to yield a high confidence (standard deviation $\geq$ average) on the results. Hence only data for 10, 15, and 20 mM AuCl_3 are presented in Fig. 2B. As can be seen, SEM results show lower AuNP density compared to AFM results for samples doped with 10 and 15 mM solutions, while a close agreement is found for samples doped with 20 mM solution. Nevertheless, the trend in the AuNP density was found the same. Samples doped with 10 and 15 mM did not show a statistically significant difference ($p > 0.05$, t-test) in AuNP density, while samples doped with 20 mM solution showed a statistically significant drop when compared to the samples doped with 10 and 15 mM solutions. Also we noted that none of the concentrations resulted in a continuous network of AuNPs (percolation). This can be evidenced in an AFM image for 15 mM solutions with highest AuNP density (see Fig. 2B). Our results on the size dependence of AuNP on AuCl_3 concentration clearly do not agree with that previously reported [21, 28]. Kim *et al.* [21] reported formation of AuNPs in the range of 10 to 100 nm independent of the AuCl_3 concentration. A more detailed study led by Lee *et al.* [28] also had found no correlation between the AuNP size and AuCl_3 concentration.

Fig. 3A shows the sheet resistance (R_s) of the FLG samples before and after doping. At AuCl_3 concentrations of 1 mM, 5 mM, 10 mM, 15 mM and 20 mM, the sheet resistance of each sample reduced by approximately 54%, 50%, 37%, 69%, and 99%, respectively, when compared to their individual sheet resistance prior to doping. The sample doped with 20 mM AuCl_3 concentration showed an R_s as low as $130\ \Omega/\square$, which is similar

magnitude to the $112 \Omega/\square$ reported for the FLG doped with 20 mM AuCl_3 by Kim *et al.* [21]. Furthermore, Fig. 3B shows the change in R_s of doped FLG samples with time. Measurement points with large error bars indicate the difficulty of making a solid contact to the FLG with the van der Pauw electrodes. Within measurement errors shown in Fig. 3B, the R_s values for FLG samples doped with 1 mM, 5 mM, and 10 mM solutions do not change regardless whether the samples were stored in air or vacuum. However, for FLG samples doped with 15 mM and 20 mM solutions, the R_s values were found to increase at the end of three weeks storage time to $\sim 145\%$ and $\sim 225\%$ of the original values respectively, even though the two samples were stored differently, one in air, while the other in vacuum. This is in somewhat congruent with a report by Gunes *et al.*, [29] where two-layer and three-layer graphene films on polyethylene terephthalate showed a 40% increase in R_s upon aging for 21 days under ambient conditions. However, in their case, changes were seen with a 10 mM solution, while in our case changes in R_s were not seen with the use of a 10 mM solution on a 285-nm thick oxide. Similarly, Kim *et al.* have also reported an increase in R_s for single- and double-layer graphene films (on 300-nm oxide) doped with 10 mM solutions and stored under ambient conditions.[21] However, the amount of increase in R_s was only 10% in 20 days. Further, the changes in R_s were higher when solutions with lower concentrations were used. This is quite contrary to what we observed in our studies.

Fig. 4A shows the percentage transmittance ($\%T$) obtained from the FLG films on quartz substrates before and after doping. FLG films prior to doping do not show significant difference in $\%T$ between the samples. Also, the $\%T$ values indicate presence of 5 to 8

layers in the FLG samples according to the nonlinear equation for transmittance $T = (1 + 1.13\pi\alpha N/2)^{-2}$ proposed by Zhu *et al* [30] where $\alpha = e^2/(c) \approx 1/137$ is the fine-structure constant and N is the number of layers. As the AuCl_3 concentration used during FLG doping was increased from 1 mM to 15 mM the transmittance of monochromatic light for 400-750 nm wavelengths was generally reduced. This was expected since the higher AuCl_3 concentrations led to higher seed density up to 10 mM as well as larger AuNPs, and thus lowering the light transmittance. However, at a doping concentration of 20 mM, the optical transmittance at wavelengths below 750 nm was better than for the 15 mM doped sample. This can be explained by the aggregation of AuNPs observed on the FLG samples doped with 20 mM AuCl_3 solution under SEM and AFM, but not observed with doping concentrations below 20 mM. For wavelengths above 750 nm, Fig. 4A shows the transmittance curves for 1, 5, 10, and 15 mM doping concentrations were starting to merge. For wavelengths above 950 nm, samples that were doped with 20 mM were found to be more transparent compared to the samples doped with lower concentrations. A further study is needed to understand the higher transparency with highly doped samples. Here we further report the calculated values of light absorbance, linear attenuation coefficient, and extinction coefficient. To the best of our knowledge such coefficients have not been reported for doped FLG films. These published values will allow simulating novel optical devices with doped FLG in the future. Fig. 4B shows the absorbance values ($A = 2 - \log_{10} \%T$) calculated using the transmittance data. From the Beer-Lambert's law, the transmittance data, and assuming the average thickness of the FLG was about 2 nm, the linear absorption coefficient ($\alpha = A/(0.4343 z)$) was calculated and shown in Fig. 4C as a function of wavelength. Linear absorption coefficient

quantifies the ease of penetrating the FLG by a beam of light. The absorption coefficient is large when the beam is quickly absorbed as it passes through the film, and the absorption coefficient is small when the medium is relatively transparent to the beam. Fig. 4D shows the extinction coefficient ($k = \alpha\lambda/4\pi$) of the doped FLG calculated from transmittance data plotted versus the wavelength of the light. The k determines the rate of decrease in optical transmittance through scattering and absorption.

Fig. 5 shows the effect of doping of the FLG films and aging of the doped FLG films. Fig. 5A shows that doping with 1 mM AuCl_3 solution created a minor difference in the optical transmittance before and after doping as well as there was relatively minor change past one week of storage in vacuum. Fig. 5B shows the optical transmittance of FLG on doping with 5 mM AuCl_3 improves, however the transmittance thereafter does not change relatively even with one week storage in air. Reductions in optical transmittance are expected with deposition of AuNPs, and hence we believe this improvement in optical transmittance has resulted from removal of polymeric residues on this sample. Such improvement was not seen on any other sample. Fig. 5C shows that the optical transmittance of FLG on doping with 10 mM AuCl_3 reduces as expected, however was found to improve up on storage in vacuum for one week. Fig. 5D shows that the optical transmittance of FLG on doping with 15 mM AuCl_3 reduces as expected, however the transmittance does not fully restore to that found before doping as in the case of 10 mM AuCl_3 . Fig. 5E shows that the optical transmittance of FLG on doping with 20 mM AuCl_3 significantly decreases compared to the samples with lower doping concentrations as expected and the optical transmittance does not change with storage for one week in

air. The Fig. 5A-E show that the morphological change happening on the surface of graphene is dependent on the AuNP density achieved by varying the AuCl_3 concentration. Thus a larger AuNP density implies it will take long time for the surface morphology to stabilize. Fig. 5F shows the changes in optical transmittance observed at 550 nm for FLG samples doped with different concentration of AuCl_3 . A generic trend describing the differences in optical transmittance from storage in air or vacuum was difficult to discern. Regardless of the storage condition, the optical transmittance seems to increase at the end of four weeks. This further points towards the surface mediated agglomeration of AuNPs on FLG that was observed through sheet resistivity changes on FLG films doped with 15 mM and 20 mM AuCl_3 concentration.

To confirm our hypothesis of graphene surface mediated AuNP aggregation, we examined the size and morphology of AuNPs on the FLG sample doped with 20 mM AuCl_3 after 4-week storage in vacuum. The AuNPs did not appear as agglomerates but instead as fused gold AuNPs of larger size as shown in Fig. 6. The size of the AuNPs ranged between 50 to 110 nm and averaged ~ 90 nm in diameter, which is almost four times the average size of AuNPs found on freshly doped FLG surface. In addition the aged FLG surface was found devoid of any AuNPs smaller than 10 nm, which were observed on FLG surfaces freshly doped with 20 mM AuCl_3 . Similar change in AuNPs was observed on the FLG samples doped with 15 mM and 10 mM but difficult to discern on FLG samples doped with 5 mM. We believe that during the surface-mediated reduction process of Au^{3+} to Au, the AuNPs are essentially AuNPs coated with dried AuCl_3 . Over the aging period of four weeks, the AuNPs that were formed initially aggregate due to the difference in surface energy between the AuNP and the underlying

graphitic plane. The AuCl_3 surrounding each AuNP gets reduced, the chlorine ion and atoms disappear leaving behind a fused AuNP. Kwon et al. have shown using X-ray photoemission spectroscopy that the chlorine anions and chlorine atoms disappeared after thermal annealing at 400 °C [31, 32]. Their SEM images revealed the capability of annealing to gather the unstable metal cations, thereby inducing the aggregation of metal particles. The degree of doping of the graphene sheets was strongly related to not only metal cations but also chlorine anions. Therefore, aggregation of the metal particles and adsorption of chlorine ions degraded the properties of graphene as a function of annealing temperature. In contrast we did not anneal the doped FLG past 150 °C. We see the degradation over time although not at similar scale as that obtained through annealing at 450 °C.

4. Conclusions

In summary, we have advanced the understanding on the stability of the FLG surfaces doped with AuCl_3 . Our freshly doped FLG surfaces show similar AuNPs as previously reported in the literature. The drop in sheet resistance and optical transparency upon doping was found to be also similar to that reported previously. However, we found that the doped FLG surfaces were unstable, forcing agglomeration and fusion of the AuNPs that were formed on freshly doped surfaces. This was directly observed through SEM imaging. Upon aging of the doped FLG for four weeks, we also found that the sheet resistance and optical transparency increased over a period of four weeks regardless in air or vacuum. Although the doped FLG samples after aging for four weeks attained an optical transparency close to that of undoped FLG at wavelengths at 550 nm, the sheet

resistances remained lower than those for undoped FLG. Despite the morphological instability of the doped FLG surfaces, this study shows the use of AuCl_3 -assisted doping of FLG will still be useful for enhancing the conductivity of FLG.

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FIGURES

Figure 1. Scanning electron microscopy images showing the impact of cleaning routine on the reduction of the PMMA residue over FLG.

Figure 2. (A) Equivalent AuNP size calculated from AFM images. (B) AuNP density calculated using AFM and SEM images. (C) AFM image of AuNPs on FLG doped with 15 mM AuCl_3 .

Atomic force microscopy images of three FLG samples doped with 5, 10 and 20 mM AuCl_3 solutions. (A) Topographical images, and (B) height profile along the dashed line in (A).

Figure 3. (A) Sheet resistance measurements of FLG samples made before and after doping with different AuCl_3 concentrations and (B) the change in the sheet resistance of the doped FLG samples as a function of storage time.

Figure 4. (A) Percentage transmittance measured and therefrom (B) calculated absorbance, (C) linear absorption coefficient α , and (D) extinction coefficient k for FLG samples. Data shown on the left and right side of the dashed line were obtained before and after doping respectively.

Figure 5. (A-E) Optical transmittance measured for doped FLG films over the optical range of 370 nm to 1050 nm before doping, after doping, and after 1 week of doping. During the 1-week post-doping period, the samples were stored in air or vacuum as indicated in the graphs. (F) Optical transmittance of doped FLG at a wavelength of 550 nm as a function of storage times up to four weeks.

Figure 6. SEM images of FLG sample doped with 20 mM AuCl_3 solution recorded (A) immediately after doping and (B) after 4-weeks storage in vacuum after doping and with zoomed inset.

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