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Published in:
Journal of the Electrochemical Society

Link to article, DOI:
10.1149/2.0571506jes

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Selective Electroless Silver Deposition on Graphene Edges

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We demonstrate a method of electroless selective silver deposition on graphene edges or between graphene islands without covering the surface of graphene. Modifications of the deposition recipe allow for decoration of graphene edges with silver nanoparticles or filling holes in damaged graphene on silica substrate and thus potentially restoring electric connectivity with minimal influence on the overall graphene electrical and optical properties. The presented technique could find applications in graphene based transparent conductors as well as selective edge functionalization and can be extended to other metals than silver.

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Manuscript submitted December 8, 2014; revised manuscript received February 4, 2015. Published March 10, 2015.

Graphene is a material with unprecedented physical properties, and the understanding of these properties has tremendously improved in recent years. Graphene is highly flexible, mechanically very strong material with a charge carrier mobility higher than 200000 cm²/V-s and an electrical conductivity twice that of copper. For electronic and infrared photonic applications a great advantage of graphene is its linear dispersion relation and tunable conductivity. At the same time a single sheet of graphene absorbs 2.3% of visible light intensity, which is considerable taking into account its single atomic layer thickness, but small compared to other conducting films, which are invariably thicker. These properties contribute to make graphene suitable for optoelectronic and photovoltaic applications requiring transparent electrodes such as light-emitting diodes, solar cells and touchscreens thus replacing scarce, brittle and relatively expensive indium tin oxide that is extensively used nowadays. Moreover, large-area graphene and graphene-based materials are promising for nonlinear optical applications, sensing and catalysis.

Various methods for graphene production exist: liquid exfoliation, reduction from graphene oxide (high throughput but low-quality), mechanical exfoliation (high-quality in small areas), thermal decomposition of silicon carbide (high quality, large-area and expensive), or chemical vapor deposition (CVD) (medium-high quality). For the CVD processes, graphene is generally grown on copper and then transferred to an insulting substrate. During various micro- and macro-damages such as cracks and holes are commonly introduced in the graphene, breaking electrical connections within the graphene film and thus impairing the overall electrical properties.

To repair these defects and thus to recover the combination of high optical and electrical quality of the film it was suggested to connect graphene islands or graphene oxide flakes with percolated carbon nanotubes or silver nanowires. Such conductive films have been applied as electrodes in stretchable light-emitting diodes, ultraviolet light-emitting diodes, and for detection of hydrogen peroxide. The randomly placed nanowires form a percolating network, so the resulting composite material is transparent and conductive, but not tunable anymore, as variation of the electrochemical potential of graphene does not influence the conductivity of the silver nanowires.

Another research direction in graphene-metal composites is to combine graphene with metal nanoparticles. The nanoparticles can in principle be drop-casted or formed with electron beam evaporation under the metal percolation limit, but a more efficient and versatile process used here is to modify the procedure to achieve selective deposition on the edge of graphene flakes and on a SiO₂ substrate.

Methods

Graphene fabrication and transfer.— Graphene is grown in the Aixtron Black Magic vertical CVD system with a recipe similar to the previously reported ones. We use commercial copper foil (Alpha Aesar 99.9999% Cu) as catalysts for graphene growth. Before the growth the foils are annealed at 1050 °C in Ar/H₂ atmosphere. The growth occurs at the same temperature for 10–30 minutes after the addition of CH₄ flow in the chamber. The varying growth time results in different coverages of graphene on copper. All graphene growths were investigated by Raman spectroscopy, confirming single- or few-layer graphene with I(D)/I(G) ratio of order 0.1–0.2.

The transfer is done by etching the copper foil with ammonium persulfate, with the graphene supported by a poly(methyl metacrylate) (PMMA) layer. The adhesion of the graphene/PMMA onto an oxidized Si surface (100 nm of SiO₂) is promoted by baking at 180 °C. The target substrate is pre-treated in oxygen plasma to promote graphene adhesion. Finally, the PMMA is removed in acetone.
Silver is deposited onto graphene on SiO\(_2\) samples, through reduction of aqueous silver nitrate solution with formaldehyde. The chemical compounds used are listed in Table I (all reagents from Sigma-Aldrich\(^{24}\)). We used deionized millipore (MilliQ) filtered water at all steps. The important reaction steps in the silver deposition process are as follows: The sample is placed in the acidic tin(II)chloride solution for 5 minutes at room temperature. The acidic tin(II)chloride solution is used for surface treatment of the sample. This process binds Sn\(^{2+}\)-ions to the surface (to hydroxyl groups on the surface) as illustrated in Fig. 1a. These particles act as seeds from which the silver crystals grow. The sample is then rinsed for 15 minutes with deionized water to remove excess SnCl\(_2\) solution.

(ii) Afterwards the sample is immersed for 1 minute in ammoniacal silver nitrate solution that is prepared with the following reaction:

\[
2\text{AgNO}_3(aq) + 2\text{NH}_3(aq) \rightarrow \text{Ag}_2\text{O(s)} + 2\text{NH}_4\text{NO}_3(aq) + \text{H}_2\text{O},
\]

resulting in a cloudy solution. Adding more ammonium hydroxide shifts the equilibrium, creating silver ammonium nitrate,

\[
\text{Ag}_2\text{O(s)} + 2\text{NH}_3(aq) + 2\text{H}_2\text{O} \rightarrow 2\text{Ag(NH}_3)_2\text{NO}_3(aq) + 2\text{NH}_4\text{OH}(aq),
\]

which exist as ions in the solution:

\[
\text{Ag(NH}_3)_2\text{NO}_3(aq) + \text{NH}_4\text{OH}(aq) \rightarrow \text{Ag(NH}_3)_2\text{NO}_3(aq) + \text{NH}_4\text{+} + \text{NO}_3\text{+} + \text{NH}_2\text{+} + \text{H}_2\text{O}. \tag{3}
\]

When the pretreated sample is immersed into this solution the silver atoms bond to the Sn\(^{2+}\) groups on the surface of the sample. This step is illustrated in Fig. 1b.

### Table I. Solutions used for electroless silver deposition.

<table>
<thead>
<tr>
<th>Acidic tin(II)chloride solution</th>
<th>Ammoniactical silver nitrate solution</th>
<th>Formaldehyde solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ( \mu \text{L} \left( 15% \text{ SnCl}_2; 7.5% \text{ HCl}; 22% \text{ CH}_3\text{COOH} \right) )</td>
<td>1.25 ml ( \left( 2.0% \text{ AgNO}_3; 5.0% \text{ NH}_3 \right) )</td>
<td>250 ( \mu \text{L} \text{ CHOH} )</td>
</tr>
<tr>
<td>25.0 ml H(_2)O</td>
<td>57 ( \mu \text{L} \geq 25% \text{ NH}_3\text{OH} )</td>
<td>8.0 ml H(_2)O</td>
</tr>
</tbody>
</table>

**Standard electroless silver deposition.**— (i) Silver is deposited onto graphene on SiO\(_2\) samples, through reduction of aqueous silver nitrate solution with formaldehyde. The chemical compounds used are listed in Table I (all reagents from Sigma-Aldrich\(^{24}\)). We used deionized millipore (MilliQ) filtered water at all steps. The important reaction steps in the silver deposition process are as follows: The sample is placed in the acidic tin(II)chloride solution for 5 minutes at room temperature. The acidic tin(II)chloride solution is used for surface treatment of the sample. This process binds Sn\(^{2+}\)-ions to the surface (to hydroxyl groups on the surface) as illustrated in Fig. 1a. These particles act as seeds from which the silver crystals grow. The sample is then rinsed for 15 minutes with deionized water to remove excess SnCl\(_2\) solution.

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When the pretreated sample is immersed into this solution the silver atoms bond to the Sn\(^{2+}\) groups on the surface of the sample. This step is illustrated in Fig. 1b.

The samples were characterized using the scanning electron microscope Zeiss Supra VP 40 (SEM). Areas of transferred CVD graphene on SiO\(_2\) intentionally contain defects and cracks, as it can be seen from SEM microphotos in Fig. 2a. A Raman spectrum of transferred graphene is shown in the inset of Fig. 2a. Standard electroless silver deposition on these areas produced particles spread all over the surface of the sample, with the highest density (nearly a continuous layer) on graphene (Fig. 2b). A similar procedure applied on graphite has been reported to produce a continuous layer of silver.\(^{25}\) As this selectivity is exactly opposite to the requirements stated in the Introduction, several modifications of the procedure were investigated to reverse the selectivity.

**Exclusion of tin (II) chloride treatment.**— To avoid deposition of silver or graphene, we excluded the Sn\(^{2+}\) pretreatment of the sample (acidic tin(II)chloride solution). In this way the Sn\(^{2+}\) seeds are not created on silica or on the graphene surface, and thereby the silver growth is hindered. The rest of the process steps remain unchanged except timing. The sample is left in ammoniacal silver nitrate solution for 1 min and after the addition of formaldehyde another 2 min. In this way we were able to deposit silver exclusively on the SiO\(_2\) areas (Fig. 3a). Nevertheless, the silver layer on SiO\(_2\) is not continuous, and the deposited silver particles do not appear to bind neither to edges nor to surface of graphene flakes (dark areas in Fig. 3). Increasing the time the sample is left in ammoniacal silver nitrate solution to 3 min and 4 min after adding formaldehyde has the consequence of starting deposition of the silver particles on graphene (Fig. 3b).

**Hydrochloric acid treatment.**— Since we found that absence of Sn\(^{2+}\)-ions prevents silver deposition on graphene and taking into account that Sn\(^{2+}\) is predominantly attached to OH-groups,\(^{26}\) the number of hydroxyl groups was decreased by using concentrated hydrochloric acid treatment. The samples were characterized using the scanning electron microscope Zeiss Supra VP 40 (SEM). Areas of transferred CVD graphene on SiO\(_2\) intentionally contain defects and cracks, as it can be seen from SEM microphotos in Fig. 2a. A Raman spectrum of transferred graphene is shown in the inset of Fig. 2a. Standard electroless silver deposition on these areas produced particles spread all over the surface of the sample, with the highest density (nearly a continuous layer) on graphene (Fig. 2b). A similar procedure applied on graphite has been reported to produce a continuous layer of silver.\(^{25}\) As this selectivity is exactly opposite to the requirements stated in the Introduction, several modifications of the procedure were investigated to reverse the selectivity.
hydrochloric acid immediately before silver deposition. The binding energy of OH-groups is 0.8–3 eV\(^4\) and 0.54 eV\(^4\) respectively for SiO\(_2\) and graphene pristine surfaces, while it is larger for defects (1.8 eV for defected graphene with Stones-Wales and vacancy defects\(^4\)).

Therefore, we expect HCl to remove the majority of OH-groups from the graphene surface and leave silver on SiO\(_2\) and along the graphene edges.

We pre-treated the sample with concentrated (37%) HCl for 2 min, then rinsed it in DI water and immediately proceeded with the normal electroless silver deposition. This results in higher selectivity of silver toward the graphene edges, as reported in Fig. 4. During deposition the left side of the sample in Fig. 4a is covered by a sample holder, thus no silver is deposited in this area. Nevertheless, to the right from the sample holder edge, the reactants can access the sample surface leading to a complete silver coverage of the sample. In the transition region between these two areas, within approximately 10 \(\mu\)m from the continuous silver layer edge, silver grows more actively on the graphene edges. This leads to formation of nanoparticles and even short nanowires, shown in the inset of Fig. 4a. We suggest that this effect can occur due to the reduced concentration of formaldehyde in the area.

We replicated the experiment using a diluted formaldehyde solution (10 \(\mu\)L CHOH and 8.0 ml H\(_2\)O). The result, shown in Fig. 4b, is a higher selectivity of silver to the edges of graphene, not only near the sample holder, but everywhere on the sample. The size of the particles was 70 \(\pm\) 19 nm and their linear density was 5.2 particles per \(\mu\)m of the edge length. Even though small silver particles are seen to bind to the graphene surface or more likely near defects in the graphene sheet, the majority of the larger particles is formed on the edges leaving far less amount on silica.

**Figure 2.** (a) Graphene (dark areas) on SiO\(_2\) (bright areas). Damages, such as holes, are seen in graphene. The inset shows Raman spectrum of transferred graphene. (b) When silver is deposited by the standard procedure, the continuous layer of silver on graphene is formed (bright area). There is less silver on the silica substrate (discontinuous layer, dark area).

**Figure 3.** Silver deposited excluding step 1 (SnCl\(_2\) treatment) and using different timing in steps 3 and 4 (a) 1 and 2 minutes and (b) 3 and 4 minutes, respectively. The result of excluding step 1 is silver deposition predominantly on silica. The dark areas with no deposited silver are the graphene flakes.

**Treating SiO\(_2\) with SnCl\(_2\) before graphene transfer.**—The SiO\(_2\) substrate was treated with Sn\(^{2+}\) before graphene transfer with the aim of controlling the density of Sn\(^{2+}\) seeds. In particular, our goal was to make sure that no Sn\(^{2+}\) seeds were created on graphene, while depositing a continuous layer of silver on SiO\(_2\).

The samples pretreated with SnCl\(_2\) and then exposed to oxygen plasma (see Fig. 5a) show smaller density of the silver particles on SiO\(_2\) compared to the sample treated with the standard method (Fig. 2b). We can thus conclude that the Sn\(^{2+}\)-seed layer is removed by the oxygen plasma treatment. Therefore we performed the transfer without the oxygen plasma treatment of the SiO\(_2\) surface. This resulted in silver formation only on the exposed SiO\(_2\) areas, yet without forming a continuous layer (Fig. 5b). Moreover, silver deposition is more extensive on no plasma treated silica, as seen comparing Fig. 5a and 5b. The formation of a continuous layer of silver was obtained by increasing the deposition time to 8 min. In this way, silver forms a nearly continuous layer in most of the SiO\(_2\) areas (Fig. 5c). Silver clusters are observed on the graphene surface.

**Discussion**

Using the standard electroless formaldehyde-based procedure\(^4\) of silver deposition, we observe higher density of silver particles on graphene than on the SiO\(_2\) substrate (Fig. 2). This undesired selectivity can be explained by larger density of hydroxyl groups on graphene\(^5\) and consequently that Sn\(^{2+}\) seeds bond to them. Avoiding the Sn\(^{2+}\)-pretreatment, the desired selectivity with silver on silica is obtained, however, but not on graphene (Fig. 3). Although the silver layer on silica is discontinuous, even with a longer deposition time, this indicates that the silica surface contains other nucleation points in the
absence of SnCl₂ pre-treatment. In order to fill gaps, cracks and holes in graphene with silver, and to deposit silver exclusively on silica, there are two options: to remove seed points from the graphene surface, but leave them on the edge, or to avoid treating graphene with SnCl₂, while treating silica with it before graphene transfer. We have investigated both possibilities and demonstrated silver growth selectively on graphene edges after HCl treatment (Fig. 4) and continuous silver layer growth on silica, but not on graphene with SnCl₂ treatment before the graphene transfer (Fig. 5).

Except graphene edges, preferential silver deposition places can be introduced on graphene surface intentionally by, for example, tuning graphene growth conditions, introducing defects lithographically or drop-casting specific nanoparticles. One aspect not covered in this work, is the possibility and prevalence of silver deposition near vacancy defects inside the graphene, i.e. between edges. In contrast to the edges, the positions of individual vacancies are difficult to assess, which makes such a study significantly more challenging, as there is no simple way to tell if a silver particle located away from an edge was formed there due to a vacancy or other type of structural defect. A study of metal deposition near line defects in graphene has recently been published, however, the metal particles were deposited with atomic layer deposition.47

The possibility of growing silver nanowires from the graphene edges is also demonstrated (inset in Fig. 4a), but these results require further investigation. The growth of silver nanowires between graphene edges would be advantageous with respect to random nanowires drop-casting, since the latter leads to current conductivity mainly through the silver nanowires network, so the resulting composite material loses advantages of graphene’s tunability.

When pretreating the SiO₂ substrate with Sn²⁺ before the graphene transfer, we observed that graphene is surprisingly well transferred without use of oxygen plasma for adhesion promotion. This effect can be due to the OH groups on graphene interacting with the Sn²⁺-particles on SiO₂.

Conclusions

In conclusion, we have demonstrated electroless silver nanoparticle decoration of graphene edges. We have also shown selective silver deposition on the SiO₂ substrate between but not on top of graphene.
flakes. The nanoparticle decoration can be useful for repairing broken electrical connections in defect graphene for transparent conductive coatings or deterministic graphene nanopatterning, as well as for catalysis, disinfection, sensing, and nonlinear optical applications. The advantage of the electroless method is its scalability for mass production, cost efficiency, no need of high vacuum or a conductive substrate, contrary to the electrodeposition. Thus, the suggested method can be applied to silver deposition on graphene on virtually any substrate (for example, on polymer) and can be employed for effective graphene processing and development of the graphene-based devices. Moreover, the edge selective electroless deposition can be extended to other metals and, potentially, to other two-dimensional materials.

Acknowledgments

The authors acknowledge Mikkel Dysseholm Mar for SEM training and Tim Booth for useful discussion. A.A. acknowledges financial support from EC Graphene FET Flagship (604391), and the Center for Nanostructured Graphene funded by the Danish National Research Foundation (CNG, DNRF58). D.D. and M.V.L. contributed equally to this article.

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