Growth of graphene on cylindrical copper conductors as anticorrosion coating: a microscopic study

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ABSTRACT

We have successfully grown graphene film on the surface of cylindrical copper conductors by Chemical Vapour Deposition (CVD). The quality and number of graphene layers have been investigated using Raman spectroscopy, Raman mapping and Scanning Electron Microscopy (SEM), as a function of methane gas flow rate and of the growth temperature. Transmission Electron Microscopy (TEM) analysis have been performed to verify the number of graphene layers confirming the results obtained by Raman. The results open up the possibility of using graphene as anticorrosion coating for copper cables and earth grids.

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1. Introduction

Graphene sparked intense studies in material science and condensed-matter physics after the publication of a method to isolate a single layer from graphite in 2004 [1]. Graphene is a single layer of carbon atoms in a honeycomb lattice arrangement [1-5], with exceptional electronic properties due to its unique band structure, which makes the electrons behave as Dirac massless particles. It is also one of the strongest and elastic materials, with a Young modulus above 1TPa and intrinsic strength of 130 GPa [6]. Moreover, its sp² bond structure makes it non-reactive, and the tight lattice structure is impermeable to all gas and liquids, showing a noteworthy performance as electrochemical protective barrier in comparison to other thin film materials, ideal characteristic for the use as anticorrosion coating.

An important application of this coating would be in protecting copper cables, and especially earth grids. A large copper mesh is usually installed at 0.5 metres depth in the ground to dissipate the electrical power system faults and the lightning strikes in the ground to
safeguard the people in the vicinity. Over the time, the earth grid conductivity and corrosion susceptibility decreases. Chen et al [7] reported that graphene coating on Cu foil clearly acts as a diffusion barrier and protects the underlying copper from oxidation. He has examined the chemical composition of both graphene coated and uncoated copper by X-ray photoelectron spectroscopy (XPS) where he shows uncoated Cu peaks are broader than the coated ones because of the presence of Cu₂O, CuO, Cu(OH)₂.

The present study aims at evaluating the potentiality of replacing conventional copper earth grid with graphene coated copper earth grid. For many other applications where corrosion and conductivity degradation is an issue, graphene coated copper could also be potentially used to improve the manufacturing stability and the longevity.

Chemical vapour deposition (CVD) is the most common method used to produce large area uniform graphene films. This method is produces graphene on catalytic metal surfaces (e.g. copper, aluminium, steel etc.) from carbon containing gases [8, 9]. The dominant growth process or the co-existence of CVD and surface segregation depends on solubility of carbon in the metal [9]. The process is very difficult to control in all polycrystalline metals where the grain boundaries act as nucleation sites for multilayer growth [10]. That is why single crystal and atomically smooth metals are usually preferred for growing high quality graphene. Also, the choice of the metal catalytic substrate is very important to avoid the diffusion of the carbon atoms into the bulk [11-13]. Cu surface is the best choice to produce graphene layers from a pure CVD process because the diffusion of carbon atoms in Cu is very low (0.001% at 1000°C) [14, 15]. All studies so far are using commercially available high purity Cu foils or very thin wires [16-20], polished initially by electrochemical methods [21]. To reduce the defects, the foil is then placed in the CVD tube at high temperature and 1500 Torr of H₂ for 7 h[16]. Yan et al [16] report that large crystals of ~ 2.3 mm in diameter of monolayer graphene with a mobility of approximately 11,000 cm² V⁻¹ s⁻¹ can be synthesized on these prepared Cu foils, by using a mixture of CH₄ and H₂. The effect of the electro-polishing techniques has been also evaluated to achieve a single crystal monolayer graphene with low D-band intensity [21, 22].

To replace the conventional copper earth grid with graphene-coated copper, a low cost, scalable graphene growth method on bulk Cu is required. The starting point for developing the graphene deposition technique on bulk cylindrical Cu conductors is the procedure described by Yao et al. [23].
In this article, we report about the successful CVD growth of graphene layers on sections of commercial Cu wires used as conductors in power lines and in earth grids. We analyse the quality and number of graphene layers by Raman spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX).

2. Experimental Section

To characterize the graphene growth on a full scale real Cu conductor and to evaluate their grounding performance, the graphene thin films growth was originally planned on bulk Cu cylinders (14 mm long and 6.25 mm radius), but it was difficult to focus both the Raman and SEM microscope because of the size. So, commercial Cu earth grid wires with 12.5 mm diameter were cut into 10 mm long half cylinders of 6.25 mm radius. The samples were cleaned by 2 min ultrasonication in iso-propanol and distilled water.

After finding the proper recipe of growing graphene on hemispherical Cu substrates, the experiments were run on 14 cm long samples.

The samples were inserted into a tube furnace (LABEC, 2-zone horizontal split tube furnace), raising the temperature up to 975°C under 100 SCCM Ar gas flow over a period of 1 h. After the set temperature was achieved, H_2 was introduced into the tube at 500 SCCM for 20 min in order to recover a pure metal surface [23]. Afterwards, CH_4 gas with flow rate of 6 SCCM was added to the H_2 flowing for 3 min. The experiment was concluded by switching off the CH_4 flow and cooling down the samples in a mixture of Ar (200 SCCM) and H_2 (100 SCCM) with a cooling rate of 10°C/min, following the procedure described by Yao et al. [23]. It took 3 h to cool down the system to room temperature. As the first deposition did not result in any graphene film on the substrate, the duration of H_2 and CH_4 flow was increased to 5 and then to 10 mins.

As the growth of graphene films on Cu surface with the above recipe was still unsuccessful, electro-polished samples were used as surface roughness is expected to play a role in the deposition process [17][21]. The electro-polished substrates were cleaned in an ultrasonic bath as explained above, and then placed in the tube furnace to undergo a process similar to the rough samples. In this case, the gas exposure for graphene growth was 10 mins, with 30 SCCM of CH_4 and 500 SCCM of H_2 at 975°C. In the last experiment, the temperature was increased to 1000°C to verify the effect of temperature on the quality of graphene film.
The samples for TEM analysis were coated with a thin layer of gold by a Leica EM SCD005 gold coater, to protect the graphene layers during the preparation. Cross-sections of the samples were prepared using a FEI Quanta 3D Dual-beam Focused Ion Beam (FIB), adding an extra layer of Pt to further protect the samples from the Ga ions. Raman spectroscopy measurements were performed at room temperature with a Renishaw spectrometer, by using a 785 nm laser and a 50X objective. The Raman signal was acquired at different points of the curved and of the flat surface of the conductors. A Raman mapping scan was done with an excitation laser of 532 nm wavelength. Image scanning properties were 150 points per line and 150 lines per image. The scan was run for a surface area of 150 μm × 150 μm.

3. Results and Discussion

A. Raman Analysis
Raman spectroscopy allows high-throughput, non-destructive and unambiguous identification and characterization of graphene layers. G peak at 1580 cm\(^{-1}\) and G’ peak (often called 2D) at 2700 cm\(^{-1}\) have been identified as a signature of graphene existence by several authors [24, 25]. These peaks are present also in graphite, but in a good quality graphene, the 2D peak is the most prominent one [25]. In addition to these two major peaks, a D peak is also observed at 1350 cm\(^{-1}\), linked to the presence of disorder or defects, like edges, point defects, and sub-domain boundaries [23]. The existence of D peak in our sample indicates that the grown graphene on the Cu substrate is not continuous or not uniform throughout the surface (Figure 1).
Figure 1: (a) Sketch of the hemi-cylindrical Cu substrate and (b-e) Raman spectra (785 nm excitation laser) acquired on samples grown in different conditions and on different sides of the Cu substrate: (b) 20 SCCM CH₄: 10 min gas flow at 975°C, (c) 30 SCCM CH₄: 10 min gas flow at 1000°C, (d) 30 SCCM CH₄: 10 min gas flow at 975°C, (e) 30 SCCM CH₄: 10 min gas flow at 975°C on the flat surface.

A low intensity of the D band relative to the G-band should be observed for a uniform and defect-free graphene deposition. Peak intensity ratios of I_D to I_G is in the range 0.05 < I_D/I_G < 0.3 for the graphene monolayer sample grown by CVD [24]. It has been reported [26] that the G to 2D peak intensity ratio (I_G/I_2D) provides a good indication of the number of graphene layers in the CVD-derived graphene samples. Both the shape and the G to 2G peak intensity ratio shown in Figure 1 and 2 indicate multiple layers of graphene on the samples. This estimate is supported by several authors [15, 26]. In Table I we present a summary of the Raman microscopy results for three characteristic growths in different conditions.
From these data we conclude that the deposition with 30 SCCM, 10 min at 1000 °C on flat surface show no evidence of good quality graphene (we found a very prominent D peak around 1160 cm\(^{-1}\) and a very small G peak at 1744 cm\(^{-1}\)). For depositions at 975 °C with 30 SCCM, on flat surface the D peak at 1315 is the highest peak observed indicating a large presence of defects, but a clear evidence of graphene with a G peak at 1595 and a 2D at 2633. The best results are obtained on the curved surface at 975 °C with 30 SCCM, with a small D peak and a large 2D peak, indicating high quality graphene [24, 25].

Table I: Location and intensity of D, G and 2D peak (for successful depositions) calculated from Raman spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity of D peak (arb Un)</th>
<th>Location of D peak (cm(^{-1}))</th>
<th>Intensity of G peak (arb Un)</th>
<th>Location of G peak (cm(^{-1}))</th>
<th>Intensity of 2D peak (arb un)</th>
<th>Location of 2D peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 SCCM CH(_4), 10 min 1000°C on curved surface</td>
<td>6000</td>
<td>1160</td>
<td>800</td>
<td>1744</td>
<td></td>
<td></td>
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<tr>
<td>30 SCCM CH(_4), 10 min 975°C on flat surface</td>
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<td>1315</td>
<td>5100</td>
<td>1595</td>
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<tr>
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<td>1371</td>
<td>6250</td>
<td>1631</td>
<td>3225</td>
<td>2648</td>
</tr>
</tbody>
</table>

B. Raman Mapping Analysis

In general, a Raman mapping instrument is equipped with point or line laser excitation. This instrument runs several Raman microscopic analyses across a user defined area facilitated by an automated shift of the instrument stage. The acquired Raman spectra then can be translated to chemical images providing information about the uniformity of any specific material (characterized by its unique wave number). This method allows to produce chemical images for each wavelength relevant to the material being studied[27]. Raman microspectroscopy is applied to record complete spectral maps of any surface of any object. It provides information on the position and the concentration of a given element on the surface of the object.

Raman mapping analysis of the curved surface by selecting the G peak (1580 cm\(^{-1}\)) is presented in Figure 2. The bright yellow area in the inset of Figure 2 indicates clearly the presence of a layer of good quality graphene, as the average Raman spectrum in the same picture, show a small D peak and \(I_{2D}/I_G < 1\) [24]. However, The broad 2D peak suggests the presence of multilayer graphene [25].
Figure 2: Full spectra of the point on Cu curved surface where Raman microscopy was used with increased exposure time and accumulations to determine the number of layers by studying the shape of 2D peak. In the inset we show the Raman mapping obtained by selecting 1580 cm\(^{-1}\) peak of the curved surface of a sample grown at 975° C exposing for 10’ at 30 SCCM CH\(_4\).

**C. TEM Analysis**

In order to characterize the thickness and the microscopic quality of the graphene layer, we performed a cross section TEM analysis.
Figure 3: TEM characterization of as-grown graphene layers. Left: TEM images and right: line profile for measuring the thickness of the graphene layers (L).

In Figure 3, TEM images of the cross section close to the surface in different points of the sample grown for 10' at 975˚C show the evidence of multilayer graphene. From a line profile measurement across the interface, we found an average interlayer spacing of 0.359 nm, 0.361 nm and 0.368 nm from Figure 3(a), (b) and (c), respectively which is very close to the value reported by Malard et al. [24] (0.342 nm). EDX mapping acquired during the TEM analysis (not shown) indicated four subsequent layers: the first containing mostly Pt deposited by the Focused Ion Beam to protect the surface and manipulate the cross section, the second containing Au, sputtered to protect the surface before exposing the sample to the FIB, the third containing carbon (C), and the last containing Cu. The C was also found on the other layers as an impurity, a contamination due to the preparation procedure, as the samples were rinsed in organic solvents. To reduce this effect and burn off the contaminants, the sample was cleaned by plasma etching. This process greatly reduced the level of C contaminants as shown in Figure 4. EDX analysis was repeated after plasma cleaning to
confirm that the graphene layers were intact. Figures 4 and 5 show the existence of a layer of C between the Cu and the Au, confirming the presence of graphene. In Figure 4, the graphene layer (red coloured map) can be seen on top of the Cu substrate (green coloured map). The gold plating (violet) and the platinum coating (turquoise) from FIB are also visible. The line profile (Figure 5) of the EDX SEM image shows clearly the presence of C (red line) between the Au and the Cu peak.

Figure 4: EDX mapping after plasma cleaning; Top left figure is the TEM image acquired in EDX and the others are the EDX mapping of specific elements.
Figure 5: EDX line profile of SEM across the interface after plasma cleaning showing the presence of C between Au and Cu, as a signature of the graphene.

4. Conclusion

In this paper we demonstrate that graphene layers can be easily grown on bulk cylindrical copper conductors by CVD, a simple process, which could be adopted to protect the power transmission lines from corrosion. The best results were obtained on electro-polished samples at 975°C under a flux of 30 SCCM CH₄. By combining TEM, SEM, EDX and Raman analysis, we were able to determine the quality and number of graphene layers grown on different regions of the conductors. A small D peak and broad G’ peak confirmed the presence of a good quality multilayer graphene film. Further studies, required to gain control over the number of graphene layers, are in progress.

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References


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