Multiple Use of High Purity Copper Foils as Catalyst Substrates for Graphene Growth

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Abstract

Graphene is a new material with unique properties, discovered in 2004 by Nobel Prize for Physics A. Geim and K. Novoselov, that has a high potential for high-tech applications. However, the use of the material on an industrial scale requires its manufacture over large areas without loss of its superlative electronic properties, like those observed in graphene obtained by exfoliation of graphite at a small scale. One of the most promising techniques for large area fabrication (hundreds of square centimeters or even square meters) of graphene is by hot wall chemical vapor deposition assisted by a metal catalyst [1,2].

Among the possible CVD catalysts copper has distinct advantages over other transition metals because it is abundant and, not least, carbon is practically insoluble in it, which makes the growth of atomic monolayer graphene (SLG) on a copper surface self-limited [3]. In the case of transition metal catalysts with high solubility of carbon, severe segregation of C atoms to the inner surface of the metal occurs during cooling, originating multiple layers of graphene (MLG) [1] instead of SLG that readily forms on copper.

In order to lower costs, large-area deposition of graphene on copper foil would gain a lot if it were possible to recover and reuse the copper sheet in successive depositions. One way to meet this goal is the use of an electrolytic technique for separating the graphene sheet (covered by a temporary polymeric substrate, PMMA) from its native Cu substrate [4]. Using the graphene covered Cu sheet as a cathode in an electrolytic bath containing a dilute solution of potassium sulfate or persulfate, leads to the release of the graphene sheet / PMMA from the Cu surface due to hydrogen bubbling at the Cu / graphene interface as a result of water electrolysis.

Before being reusable, however, it is necessary to recover the copper surface since Cu oxides that form during electrolysis have a melting temperature above the graphene growth temperature on Cu catalyst. Two processes for cleaning the Cu surface were studied: a microwave oxygen plasma step for removing any residual PMMA, followed by removal of oxides, nitrides and other copper compounds possibly formed during the growth and transfer steps, by the use of an aqueous bath of hydrochloric acid or acetic acid; or direct immersion of the used Cu substrates in one of these acids. Cu is finally annealed at ≈ 1000 °C in a reducing atmosphere of hydrogen and argon before it can be reused as catalyst in a new CVD process run of graphene.

This work studies the chemical surface contamination of pure copper (fresh Cu sheets with purity of 99.999 %) after growth and removal of graphene and its evolution after each cleaning and/or annealing step. The results of the chemical analysis are interpreted taking into account the observations obtained by SEM images of the sample surface after each step of the treatment. The structure of the subsequent graphene layers deposited on the recovered Cu substrates is then compared, using Raman spectroscopy.

For each of the above mentioned cleaning routes samples were collected after successive immersion times, were studied and compared. Figure 1 shows the evolution of surface morphology after 7, 20 and 30 min of immersion in HCl (2%wt). In this series, samples were not exposed to O_2 plasma before entering the acidic bath. It can be seen that Cu compounds are progressively dissolved with immersion time in HCl. The insert suggests the presence of cubic Cu(I) oxide.

Figure 2 shows the evolution of the Cu surface during cleaning in AcOH for 1, 6 and 18.5 hours. The insert shows that, after 6 hours of immersion, there were still cubic crystallites present on the surface although they disappeared after 18.5 hours of annealing. The evolution of the Cu surface took place in a much longer time scale using AcOH cleaning than using HCl.

Figure 3 shows the Raman spectra of two samples immediately after transfer from native Cu recycled foils using PMMA temporary substrates. The CVD process was done at 1020 °C using methane and hydrogen for graphene growth. The recycled substrates were placed side by side in the reactor center zone. It can be seen that in a) the graphene 2D peak (Raman shift = 2695 cm^{-1}) is absent while in b) it is prominent and fitted to a single Gaussian with FWHM = 35 cm^{-1} which is proof of the presence of single-layer graphene (SLG) [5]. Most of other prominent peaks in the figure are attributable to the PMMA that covers the surface. Fig.3-a) corresponds to the cleaning procedure shown in Fig.1 whereas fig.3-b) corresponds to the cleaning procedure using AcOH shown in Fig.2. In order to reach a definite conclusion about the quality of the cleaning procedures statistics is needed for all cleaning routes. This will be the next step in this work.

References

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Figures
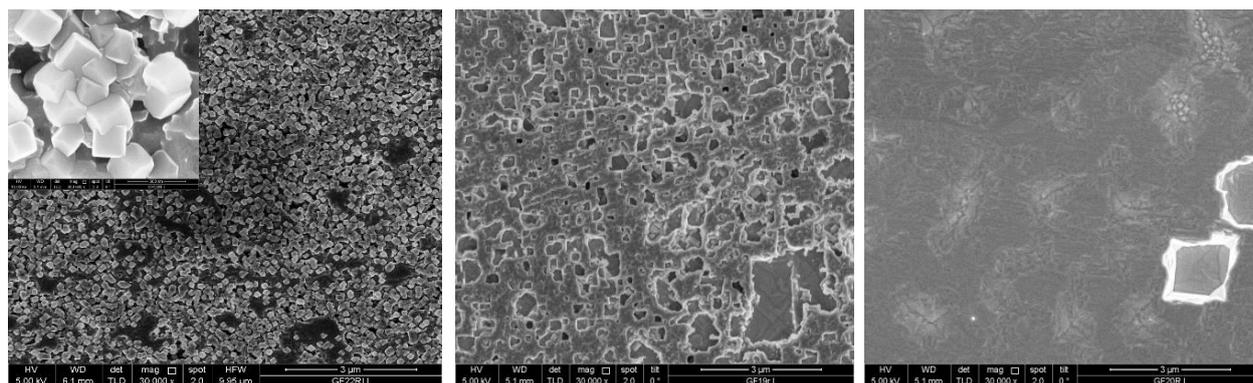
Fig.1 – Cu surface morphology after 7, 20 and 30 min of immersion in HCl. Insert is a high magnification (300k x) micrograph of the first image, showing the cubic symmetry of the crystallites covering the surface.
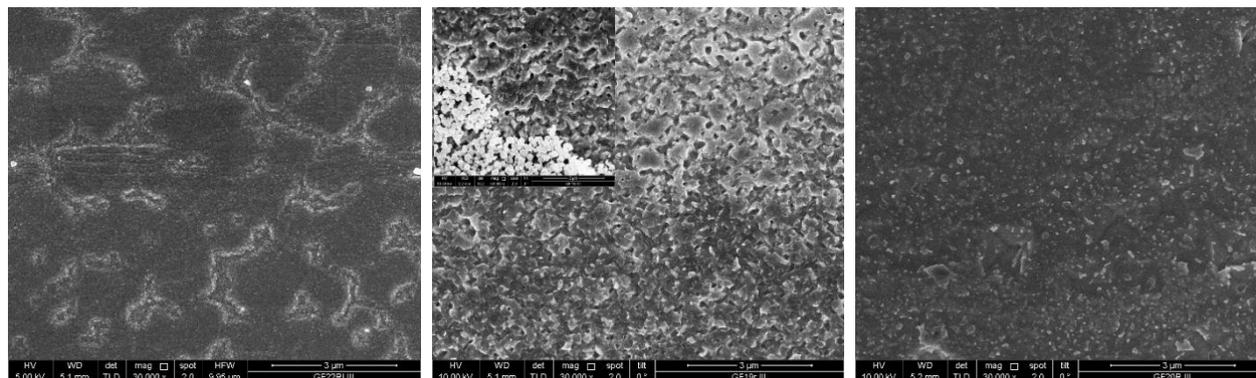
Fig.2 – Cu surface morphology after 1, 6 and 18.5 hours of immersion in acetic acid. Insert is a high magnification (50k x) micrograph of the second image, showing the cubic symmetry of the crystallites covering the surface.
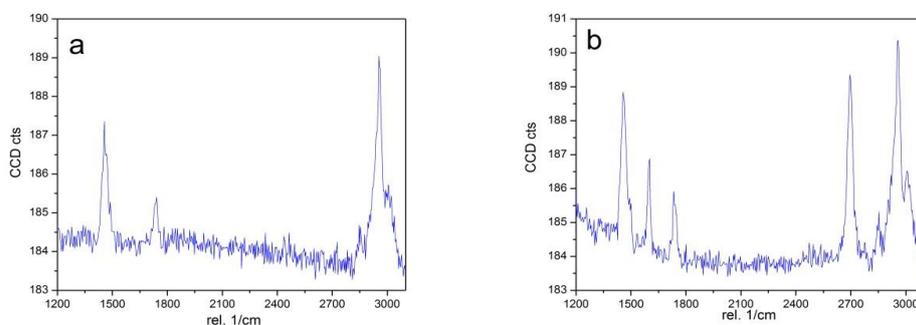
Fig.3 – Raman spectra of samples after transfer from native Cu recycled catalyst onto Si/SiO$_2$ substrate. a) corresponds to the cleaning procedure shown in Fig.1 whereas b) corresponds to the cleaning procedure using AcOH shown in Fig.2. In a) the graphene 2D peak (at 2695 cm^{-1}) is absent while in b) it is prominent and fitted to a single Gaussian with FWHM = 35 cm^{-1}.