Interaction of Metals with suspended Graphene observed by Transmission Electron Microscopy

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Graphene, the first two-dimensional material to be isolated, has become the focus of intense fundamental research due to its extraordinary properties, but even more so has spurred massive interest into studies regarding nanotechnology applications.[1, 2] An area of immense importance for the latter is the study of the metal-graphene interactions, because metals have to be used in every single application of graphene as functional material.[1, 3] The effects of metals on the transport, electronic, magnetic and structural properties of graphene have been investigated both experimentally[3] and theoretically by means of Density Functional Theory[4] with arguably more emphasis on theoretical than on experimental studies.

There is in particular a lack of high resolution transmission electron microscopy (TEM), thus limiting our understanding of this system as it is perhaps the only technique allowing direct imaging of the interactions between suspended graphene and metals. Here, various metal impurities have been introduced via evaporation onto graphene sheets obtained by CVD-growth. Au-, Cr-, Ti-, Ni-, Pd- and Al-deposited graphene sheets were then studied at atomic resolution in scanning TEM (STEM).

Gold atoms and clusters are mainly observed on hydrocarbon contamination as previously reported.[5, 6] The cluster sizes vary and are not equally distributed on the graphene surface (fig 1a). As a result of surface treatments, in our case by exposing pristine graphene samples to a cold hydrogen plasma,[7] the cluster distributions and sizes are affected, although they remain on the hydrocarbon contamination.[7] Gold cluster distributions become more uniform in hydrogenated samples (fig. 1b and c) and cluster sizes become similar.

Another way to study metal clusters on graphene is to anneal them either in a gas environment or in vacuum at elevated temperature to study their stability at high temperatures. As can be seen in fig. 1d, as the clean graphene areas widen during high vacuum annealing at 700 ^{o}C, the gold clusters, which reside on the hydrocarbon contamination, are forced to move towards each other (fig. 1e). When the annealing temperature is increased to 950 ^{o}C, we find that the gold clusters have agglomerated and almost melted, and as a result have flattened, while most of the contamination has disappeared (fig. 1f).

Gold has never been observed to introduce any damage into graphene. This conclusion can be drawn with high certainty from STEM studies,[6] where a 60kV acceleration voltage has been used for imaging, which is known to be well below the displacement threshold for graphene.[8] In contrast, damaging of graphene has been observed in the presence of Al, Ti, Cr, Pd and Ni, as is predicted by theory.[9] Except in a few circumstances clusters of all these metals are also found to reside on hydrocarbon chains. However, observation during repeated STEM scans shows that smaller clusters and individual atoms are drawn out of their initial positions, i.e. from the middle of contamination patches, to the edge of the contamination. As soon as metals reach the border between hydrocarbon and clean graphene, they interact with the clean graphene surface. Initially point defects (vacancies) are created, and this process repeats itself as long as new metal atoms are supplied from nearby metal clusters to the emerging holes. High angle annular dark field (HAADF)-STEM imaging has been

employed to study individual ad-atoms on graphene. The etching process is shown for Al in the HAADF images in fig. 2.

References

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Figures

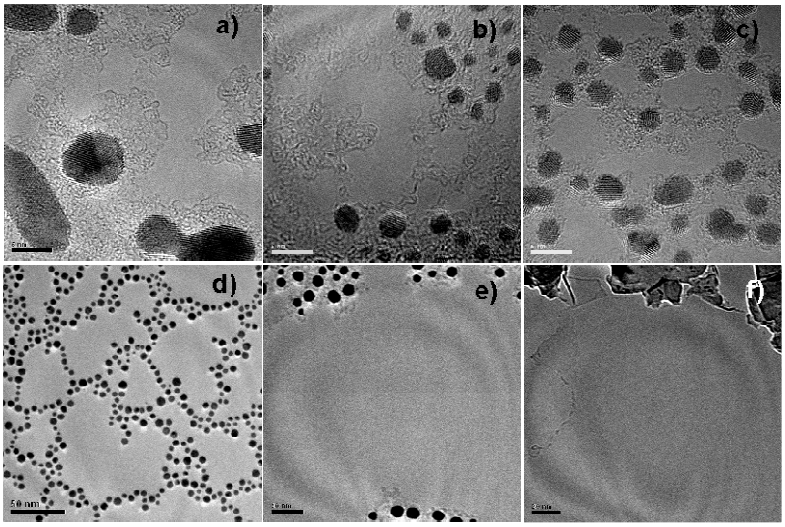

Figure 1. *Bright field (BF) image of 2Å gold evaporated a) on pristine, b) on 2-cycle hydrogenated, c) 4-cycle hydrogenated monolayer graphene. The scale (5nm) is chosen to be same in images a) to c) for accurate comparison. d) annealed at 700 ^{o}C, e) showing magnified image of (d), f) as (d) but annealed at 950 ^{o}C. The scale bar is 50nm in (d) and same in (e) and (f), 20nm.*

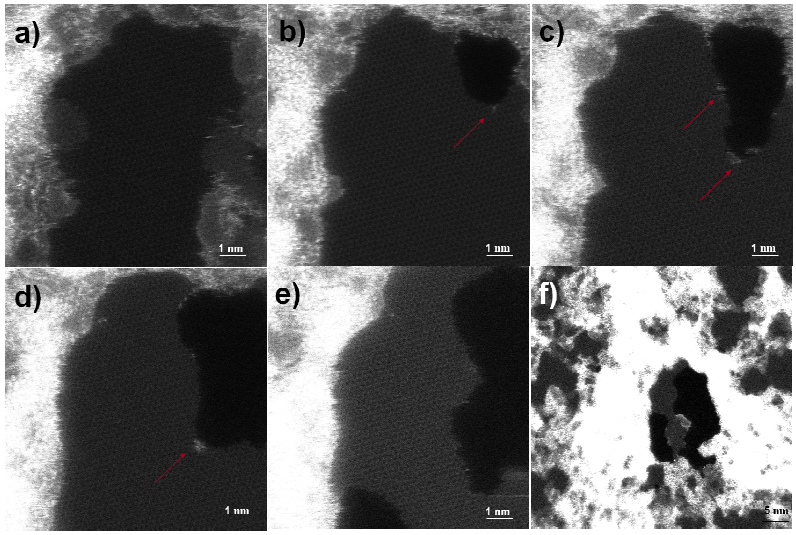

Figure 2. *HAADF images of graphene etching in the presence of an Al layer of 2Å nominal thickness a) before etching, b) after the start of hole formation, c) after hole enlargement in subsequent scans, d) after continued etching as result of sustained supply of Al atoms to the hole's edge (some Al-atoms are arrowed in red in (b), (c) and (d)), e) after etching has almost stopped because Al atom supply has ceased; f) presents lower magnification overview of the Al distribution and hole evolution. The scale bar is same in images a) to e), 1nm.*