Scanning Transmission Electron Microscopy of Metal-Graphene Interaction

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Scanning Transmission Electron Microscopy of Metal-Graphene Interaction

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Abstract. Metal impurities, gold, chromium and titanium, have been deliberately introduced into graphene. The structural and topographic properties of doped graphene have then been studied by using conventional transmission electron and aberration corrected scanning transmission electron microscopy. Analysis revealed that metal atoms cluster preferentially in/on contaminated areas. Contrarily to observations that gold atoms do not adhere to clean patches of monolayer graphene, chromium and titanium were found to be more reactive with clean monolayer graphene, and the coverage was higher than for gold for the same evaporated amount.

1. Introduction

Graphene has spurred an intense research activity since 2004 [1]. The interaction between metal atoms and graphene is of great interest because metals, in particular gold, are used for a range of graphene applications, including making contacts to circuits [1] electrochemical catalysis [2] and biosensors [3].

This interaction has been studied theoretically by means of Density Functional Theory (DFT) [4], however, it has not been experimentally confirmed yet, since transmission electron microscopy observations are practically none existent [5]. So it would be important to observe, in particular via TEM, metal behavior on graphene to be able to understand the nature of the interaction, the effect of contacts (contact improvement) on electrical transport measurement, and to prove the theoretically predicted positions of metal atoms in the hexagonal graphene structure.

Here we present a (S)TEM study of metal-graphene interactions.

2. Experimental

We employ two different techniques for graphene preparation, exfoliation from HOPG graphite [1] and the CVD method, in which graphene is grown on copper [6]. Graphene layer numbers have been identified from electron diffraction patterns by comparing the first and second ring intensities, and by high angle annular dark field (HAADF) imaging in conjunction with electron energy loss spectroscopy (EELS). Metal impurities have been introduced onto mono- and few- layer graphene using electron

beam and thermal evaporators. For accurate comparison, the same amount of all three metals (2Å) has been evaporated on pristine graphene sample at room temperature.

High resolution imaging of metal atoms and clusters on the graphene surface has been carried out in stationary transmission electron microscopy mode (TEM) as well as in scanning mode (STEM), the former in a Tecnai F30, the latter in an aberration corrected dedicated STEM (Daresbury SuperSTEM). Atomic sites of singular metal atoms and clusters on graphene have been directly revealed in HAADF imaging mode by their approximate Z^2 dependence, and by relating HAADF with simultaneously obtained BF images.

3. Results and Discussion

Figure 1 shows results of 2 Å gold deposited on mono-layer graphene. We never observed gold atoms on single or de-coupled (turbostratic) layers, however, gold clusters and nano-crystals form in the hydrocarbon contamination, which indicates the extreme mobility of gold on the pristine (clean) graphene surface (figs 1a), b) and c)). Single gold atoms can only be observed on few-layer graphene films, where the bonding contribution from sub-surface layers appears to prohibit their diffusion and enhance the sticking probability to the graphene surface. The gold atoms, which have appeared on few-layer graphene (fig. 1d: some of them are numbered), were dissociated from the bigger gold cluster (left, fig. 1d) as a result of repeated scanning in the STEM. The atoms stay for a few scans in their positions. By comparing locations of gold atoms in the HAADF image (fig, 1d) with identical positions in the BF image, (fig. 1e), the sites can be identified as on top of carbon atoms (T-sites) in the graphene honeycomb structure. The position of metal impurities with respect to the hexagon structure depends on the metal's electron affinity to, and the electron density on the hexagon structure, e.g., on top of carbon atoms, bridging on top of between two carbon atoms or centered at the middle of the hexagon.
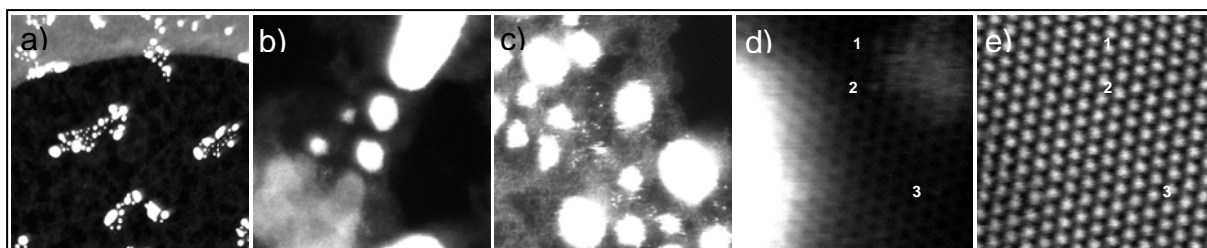
Figure 1. a)-c) HAADF images of 2Å Au doped mono-layer graphene shown at different magnifications and obtained at 60kV. d) and e) 5Å Au doped few-layer graphene: HAADF and corresponding BF image (the gold atoms are right of the numbers). Frame widths are 150, 25, 15, 3 nm in a), b), c), d) and e), respectively.

Chromium, similar to gold, was found mainly on hydrocarbon deposits (fig. 2a). However, the fractional coverage was larger (fig. 2a); this indicates that the Cr-clusters are flatter or less dense than the Au clusters. The crystallinity of the Cr clusters is lower than that of the Au clusters, suggesting that the Cr deposits in molecular form, possibly partially as Cr-oxide (fig. 2b); indeed EEL spectrum images have proven that high Cr levels coincide with oxygen signals. Interestingly, single Cr atoms do appear in some images on mono-layer graphene. These atoms stay in place over several image scans and then disappear, leaving di-vacancies behind. In subsequent scans further impurity atoms move to the edge of the vacancies, disappear upon scanning whilst enlarging the vacancy clusters: hole-drilling in graphene, as shown in fig. 2c), takes place. The hole keeps increasing upon repeated scanning. This is strong indication for the fact that Cr is more reactive with graphene than Au, and that Cr-mediated

C-C dissociation and vacancy formation takes place. This mechanism has been derived from observations of many image scans in different areas. Figure 2c) shows Cr-atoms decorating the edges of a hole in graphene (indicated by white arrow).
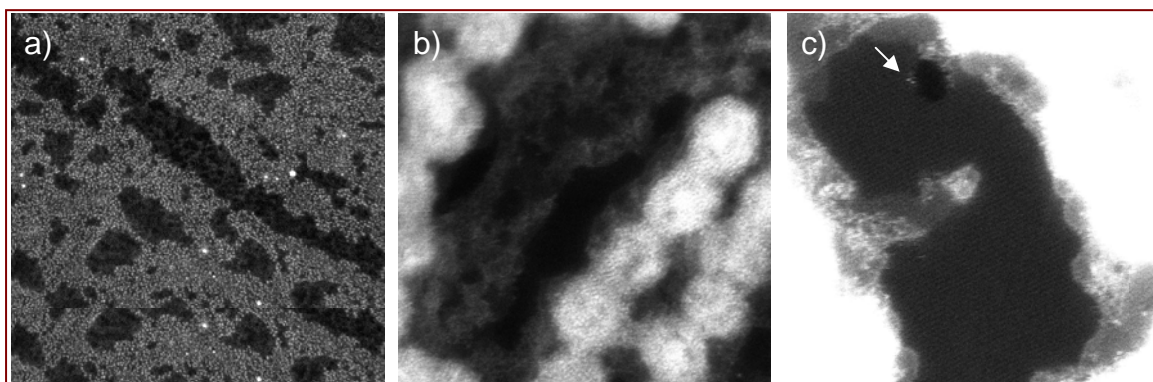
Figure 2. HAADF images of 2Å Chromium doped mono-layer graphene at different magnification, taken at 60kV. Frame widths are 200, 50, 20 nm in a), b), and c), respectively.

Titanium, in terms of coverage, is similar to Cr, and like Au and Cr it does not sit on the clean pristine graphene surface, as shown in low magnification images in fig. 3. Similar to Cr, Ti mediates vacancy formation in graphene at 60 kV, which is much lower than the threshold for carbon atom (as well as for Au, Cr and Ti atom) displacements by the electron beam [7]. This means that both, Cr and Ti have lowered the damage threshold for graphene as theoretically predicted [8]. Figure 3b) shows drilling of graphene: as soon as a hole appears it gets bigger after each repeat scan. Again the process is mediated by impurity atoms, which decorate and move along the hole's edge (fig. 3c). Observation of relatively strong Ti-graphene interaction has been predicted in recent DFT calculations [9]. The Ti binding energy on graphene is calculated to be much higher than the gold, which also explain the reason for weak interaction between gold and graphene and thus why gold is mobile on clean graphene [10]. Furthermore, energy transferred to Au ad-atom from the beam is the lowest among the studied metals [11].
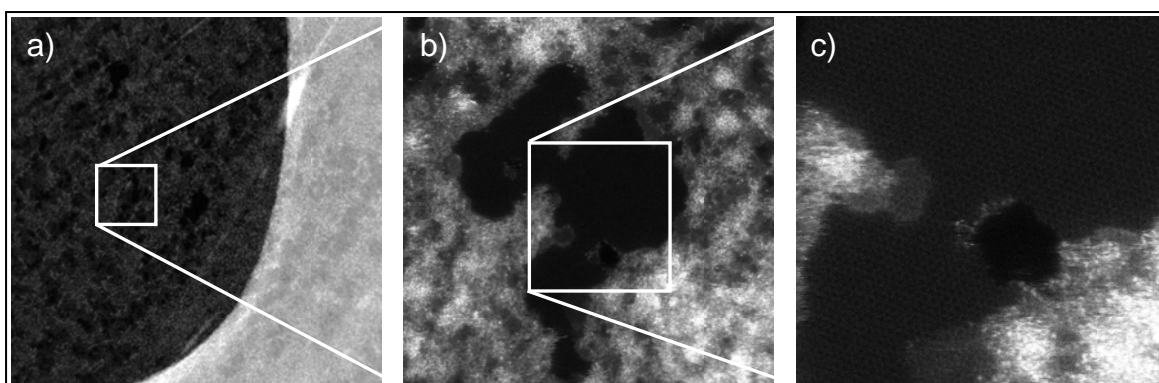
Figure 3. HAADF images of 2Å Titanium doped mono-layer graphene at different magnification, taken at 60kV. Frame widths are 250, 25, 10 nm in a), b), and c), respectively.

4. Conclusions

In conclusion, it appears that individual gold atoms do not adhere to clean single-layer graphene, whereas they are found to reside on top of carbon atoms on few-layer graphene. Cr and Ti appear to interact more strongly with mono-layer graphene and were observed to catalyse the dissociation of C-C and bonds under the electron beam, even at 60kV acceleration voltage. Bonding of occasional, singular Cr and Ti atoms to graphene is believed to initiate this process; it could also be a precursor for the frequent nucleation of clusters, which provide more continuous contact throughout the membrane (in contrast to Au). Thus the importance of Cr and Ti, which are used as sublayer underneath Au for improving electrical contacts on graphene, can be understood.

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