An In-Situ TEM Study on the Formation of Gold Carbide

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In this study, a freestanding graphene membrane sheet serves as a quasi transparent substrate for aberration-corrected high-resolution transmission electron microscopy, as an in-situ heater, and as carbon supplier. The sheet has been previously decorated with gold nanoislands. During electron irradiation at 80 kV and at temperatures of approximately 1000 K, the accumulation of gold atoms has been observed on defective graphene sites or edges as well as at the facets of gold nanocrystals. Both resulted in clustering, forming unusual crystalline structures. Their lattice parameters and surface termination differ significantly from standard gold nanocrystals. We describe the stepwise formation of these little structures starting from irregular periodical arrangements of gold atoms into rectangularly shaped monolayers, then bilayers and entire cuboids of many atomic layers. Our experimental data, supported by electron energy loss spectroscopy and density-functional theory calculations, suggests that isolated gold and carbon atoms form — under conditions of heat and electron irradiation — a novel type of compound crystal, Au-C in zincblende structure.

1. Introduction

In 1900, Mathews & Watters reported about an very explosive gold acetylide Au_2C_2 [1]. The substance has been treated as a 'true' carbide and it was indeed the first time that the existence of gold carbide has been reported. Today, more than hundred years ago, the study of various compounds containing gold carbon bonds is covered by the field of organogold chemistry [2]. However, in comparison to many other pure metal carbides, there is no experimental evidence for a possible inorganic crystalline gold carbon compound and its structural properties [3]. This is not surprising, because bulk gold has almost no solubility for carbon under equilibrium conditions and the only (above mentioned) gold carbide supposed to be crystalline turned out to be extremely unstable [4]. Nowadays, there are several successful approaches in synthesizing carbide cluster ions for late transition metals such as gold [3]. Furthermore, several concepts have been developed in synthesizing, characterizing and understanding metastable carbide crystals regarding those transition metals [5, 6], but still with the exception of gold.

The structural analysis of new materials have undergone a tremendous improvement in the capabilities to explore the atomic configuration by aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) [7]. Our understanding of carbon systems such as graphene or carbon nanotubes has significantly benefitted from this development.

In-situ experiments enable the study of dynamic phenomena under direct observation of the atomic structure [8] within the range from room temperature up to ca. 2000 K [9]. Therewith, the potential of a free-standing graphene membrane as transparent and heatable substrate has been already demonstrated. Furthermore, this approach could be applied to investigate transformations of carbon adsorbates into graphene with atomic resolution [10]. In the present work, the approach of in-situ heating via electrical biasing the graphene has been applied with focus on gold nanoislands and their interaction with the graphene substrate driven by electron irradiation. The results have been interpreted with the help of density-functional theory (DFT) calculations and provide atomically resolved insights into an experimental (re)discovery of a surprisingly robust gold carbide phase.

2. Experiment

For this work, we prepared free-standing graphene layers with electric contacts in a TEM-compatible geometry. The graphene membrane is heated by Joule heating, and at the same time, electron irradiation during AC-HRTEM imaging drives structural changes and simultaneously allows atomic-level observation. Gold nanoparticles on the graphene sheet serve as a temperature reference, and are also involved in the reactions described below. The experimental concept of the electrically contacted sample cartridge and temperature estimates have been described in more detail previously [9]. In brief, a mechanically exfoliated graphene sheet is transferred onto a Si/SiN membrane structure with open windows and gold contacts, such that an electrically contacted and completely free-standing few-layer graphene substrate in a TEM-compatible geometry is formed. The gold nanoislands have been deposited ex-situ via thermal evaporation onto graphene. In-situ TEM has been performed applying AC-HRTEM combined with local electron energy loss spectroscopy (EELS). Further details are described in ref. [11].

3. Results and Discussion

The diffusion of Au adatoms on the nanoislands is already significant at RT and led to continuous shape changes of the particles upon heating [12]. After exceeding a certain temperature limit, the first almost spherically shaped particles form liquid drops and start to evaporate [13]. In accordance with theoretical predictions and similar experiments, the related melting temperature strongly depends on the particle size [14], and in our case is estimated to be in the range of 800 K to 1300 K for particle diameters in the range of 3 to 20 nm. The observations described in the following occurred at temperatures closely below the melting point of the gold particles (i.e., just before the particles melted upon increasing the heating current).

The diffusion barrier for gold adatoms on graphene is known to be fairly low — theoretically estimated to be 0.05 eV [15] — allowing the gold atoms to diffuse very easily along the surface. This movement is much faster than the average time used for a single frame exposure (0.5 to 1.0 s). For this reason we could only visualize single gold atoms, when they got trapped at grain boundaries, edge reconstructions or vacancies [16]. However, in

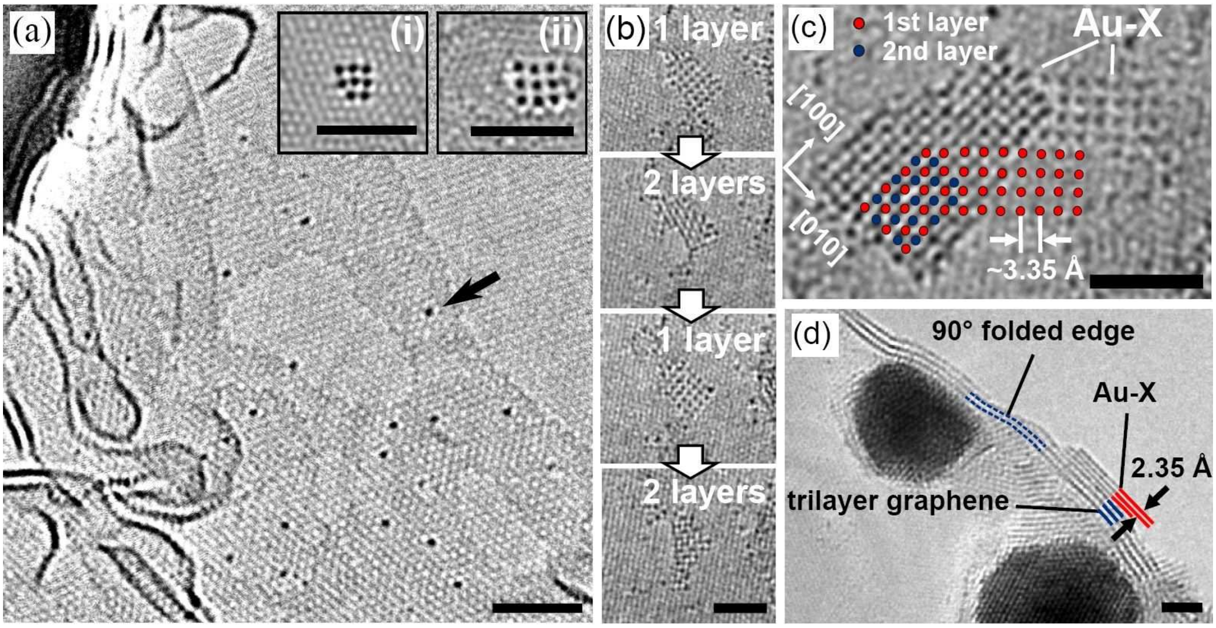

Fig. 1: AC-HRTEM images at 80 keV showing the atomic arrangements of gold atoms explored from tiny clusters towards small crystallites (scale bars are 2 nm). (a) Isolated heavy gold atoms trapped in carbon contamination on graphene, example indicated by an arrow. A larger gold particle is present in the upper left corner. Insets (i,ii) show small clusters that form under irradiation and heat within the carbon contamination layer on top of graphene. (i) Shows one very rare example found to be consistent with the interatomic distance of traditional gold clusters. Here, it has been determined to be 2.6 Å. (ii) Shows one of the frequently observed clusters having a larger spacing of 3.35 Å. (b) A repeated switching between a monolayer and bilayer structure in the same position. (c) A connected single- and double-layer region. The circles illustrate the atoms of the first and the second layer, respectively. (d) A few-layer graphene sheet with edges folded into a 90° angle. This side view enables also occasionally the side view on the Au-X structure (see marked region where 3 folded Au-X layers are found on top of folded 3-layer graphene).

these works there is no consideration of electron irradiation-induced diffusion mechanisms as discussed in Ref. [17, 18]. During the crystallization process of amorphous layers, we found plenty of gold atoms which were trapped at such lattice irregularities (Fig. 1a).

In many cases the adsorbed gold atoms within the carbon adsorbates form little clusters with squarish arrangements (insets of Fig. 1a). However, only one example could be identified with an interatomic spacing close to the bulk value for gold (2.88 Å) and expected for small clusters [19] (see Fig. 1a (i)). Typically, the clusters exhibit a surprisingly large nearest-neighbor atomic distance of 3.35 Å (see Fig. 1a (ii)). We assume that the larger spacing is due to the incorporation of low atomic number species into the 2-D gold lattice. However, those species will not be visible in-between gold atoms under the present imaging conditions, as supported by image simulations [11].

Several smaller regular clusters of Au-X with the 3.35 Å spacing have been observed, but only up to a size of about 30 Au-atoms, whereas larger Au-X clusters form multi-layer structures (Fig. 1b,c). In some cases, we could follow the transitions between single and

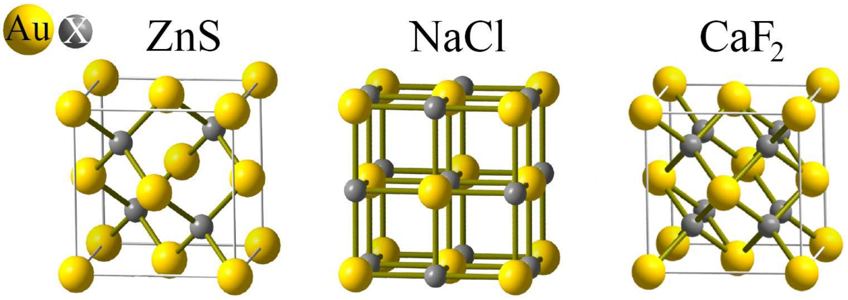

Fig. 2: Possible crystal structures with an unknown element X in the octahedral or in the tetrahedral voids of the gold fcc lattice.

double layers directly in real time (Fig. 1b). Fig. 1c shows a different example, where only a part of the structure is a single layer and the other part is a double or triple layer.

A side-view of the structure could be obtained for a cluster that had formed on the curved edge of a (partly broken) few-layer graphene substrate (Fig. 1d). Broken edges of freestanding graphene and few-layer graphene tend to curl up and show the typical van der Waals distance of 3.35 Å between the layers [20, 21]. A distance of 2.35 Å could be measured between the first and the second layer of our Au-X structure as marked in Fig. 1d. Considering that the atoms in the second layer are placed above the gaps of the first layer atoms (as shown in the plan-view in Fig. 1c), we obtain the same Au-Au spacing of 3.35 Å as between atoms inside a layer. Several times we observed tiny single-layers along with several larger, multi-layer structures [11]. Remarkably, the 3-D objects form precise cuboid shapes, as evidenced by their constant thickness (same contrast throughout the rectangle-shaped projection).

From these findings we can establish the structure of the Au-X lattice unambiguously. The gold atoms of these 3D nanocrystals exhibit a face-centered cubic (fcc) lattice structure with a corresponding lattice parameter of $\sqrt{2} \cdot (3.35 \pm 0.10)$ Å (a precise estimate was obtained from the fast Fourier transformation (FFT) taking the underlying graphene lattice as a calibration reference [11]). Bulk gold also has a fcc structure but with a smaller lattice parameter of $\sqrt{2} \cdot 2.88$ Å.

Considering the silicon nitride layer of the sample carrier, contamination induced during the graphene sheet transfer and/or adsorbed water from the surrounding regions of the sample carrier, several lighter elements like silicon, nitrogen or carbon could come into question. Finally, three different crystal structures are compatible to the observed fcc lattice for the incorporation of a second element: These are the zincblende (ZnS), the rock-salt (NaCl) and the fluorite structure (CaF$_2$) as illustrated in Fig. 2.

In order to determine the second element, local EELS was carried out in the TEM using a small beam diameter (5 nm). Multiple spectra with different energy ranges were acquired on a Au-X cube to consider the energy windows of the absorption edges of the above mentioned elements (Fig. 3). The presence of the elements carbon (Fig. 3a) and gold (Fig. 3b) is indicated by the clear signals of the carbon K absorption edge at 284 eV and the gold M$_5$ edge at 2206 eV. Silicon (Fig. 3c), nitrogen, and oxygen (Fig. 3d) as constituents can be excluded as the local EELS signals do not show any corresponding

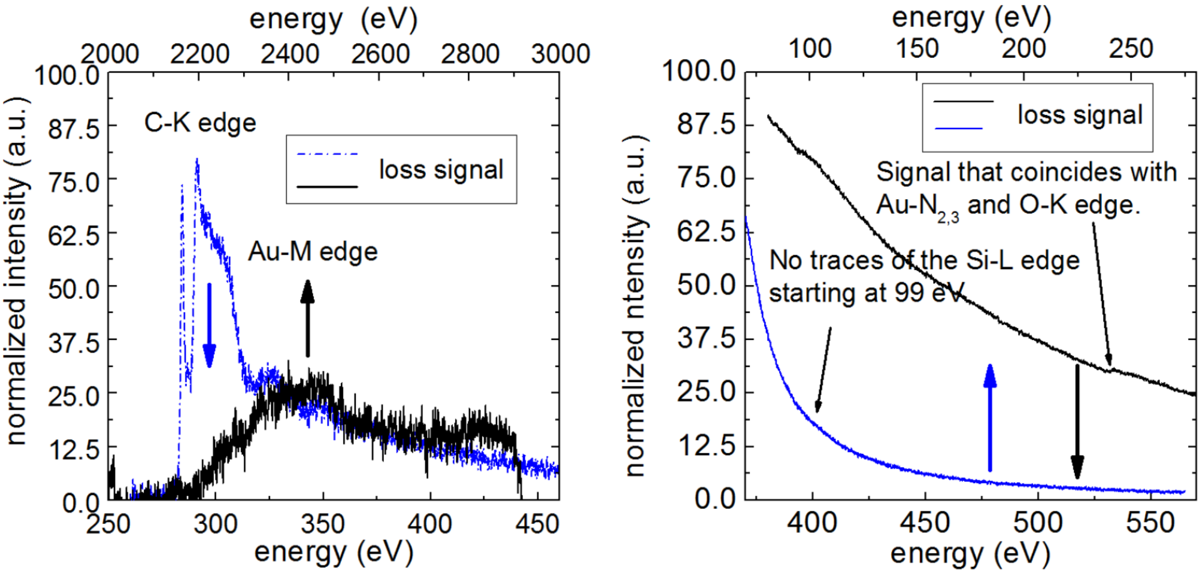

Fig. 3: Local EELS spectra acquired from Au-X on top of graphene. (a) Background-corrected energy loss of the carbon K edge at 284 eV and the gold M_5 edge at 2206 eV. (b) EELS spectrum obtained within energy range from 80 to 280 eV showing no signal of Si at 99 eV and within energy range from 370 to 570 eV. The signal at around 535 eV could caused by gold ($M_{4,5}$ edge) or oxygen (K edge).

absorption edges. The small signal at around 540 eV originates most probably from gold ($N_{2,3}$ edge). Energetically, it would also fit to the oxygen K edge. However, this signal is too weak (only 0.1 % above background) and therefore it would only correspond to a handful of atoms [22]. Although the detection of carbon appears to be trivial, because the Au-X cuboid is directly located on top of the multilayer graphene substrate, the exclusion of all other reasonable elements justifies the conclusion that carbon and must be the only constituent element in addition to gold.

In order to help identifying possible candidate compounds, we have performed DFT calculations. Clearly, only the small elements from the second row of the periodic table (C, N, O) provide a reasonable lattice match, while e.g. any theoretically considered silicon compound would result in a much larger lattice parameter than observed in the experiment. This also fits to the above mentioned EELS spectra showing silicon not to be locally present. Indeed, the smallest lattice parameter deviation Δ is achieved for the NaCl structures of AuC, AuN and AuO. However, DFT calculations combined with the generalized gradient approximation (GGA) tend to yield larger values compared to those observed in the experiments [23, 24], i.e. our calculated DFT-GGA value for gold is about 2.4% larger than the experimentally estimated one. If we treat this difference as a systematic error, we obtain the best agreement for the ZnS structure of AuC.

For all structures, we also determined the cohesive energies, i.e. the compound formation energies with respect to the most stable elemental structure. All calculated cohesive energies are positive. This means that the considered compounds are not thermodynamically stable. For gold carbide, the corresponding energies with respect to bulk gold and graphite indicate that it is most stable in the ZnS structure [11]. The endothermic character of its formation explains why there are so few reports on gold carbide. As already mentioned, it was identified a long time ago, and turned out to be explosive under rapid heating and ignites at temperatures above 180 ° [1]. Its structure has not been determined yet. Note, however, that here it is assumed that AuC is not formed from graphite but rather from the hydrocarbon deposits or defects on graphene. Under electron irradiation, both could be considered as permanent source of atomic carbon.

As a further experimental fact, we observed flat crystals and cuboids with a size not larger than 20 nm and an explicit (100) surface termination. For this reason we also compared the surface energies of thin AuC films with ZnS and NaCl structure. For all calculated surface orientations, we did not find any significant surface relaxation. In case of the ZnS structure, we obtained in agreement with the experiment that the formation of a (100) surface termination should be clearly favored versus the (110) and (111) surfaces. Furthermore, our calculation shows that surfaces terminated with gold should be energetically preferred. Moreover, the calculated electronic structure of a small AuC cluster adsorbed on graphene is only slightly modified compared to the one of the isolated AuC cluster. This indicates that AuC is weakly interacting with the graphene substrate and retains its properties upon adsorption on graphene. We find that AuC is metallic, similar as the stable compound tungsten carbide, WC, whose properties we determined as a reference [11].

4. Conclusion

In summary, we presented atomically resolved *in-situ* TEM studies of the heat- and irradiation induced formation of novel gold structures on graphene. We found periodic arrangements of individual gold atoms in form of rectangularly shaped atomic monolayers and bilayers as well as entire cuboids of many atomic layers. Both the DFT calculations and EELS analysis provide clear evidence for a crystalline compound formation between gold and carbon in a zincblende structure. On the theoretical side, they are predicted to be metallic and exhibit a bulk modulus of 141 GPa. Other properties of this exciting new material remain to be explored.

Acknowledgment

We thank our collaborators Jannik C. Meyer from the group of Physics of Nanostructured Materials at the University of Vienna, Axel Groß and Xiaohang Lin from the Institute of Theoretical Chemistry at the University of Ulm and Johannes Biskupek from the Electron Microscopy Group of Materials Science at the University of Ulm for their collaboration with respect to the scientific discussion, microscope operation and DFT calculations.

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