Heat Induced Dynamics of Gold Nanoparticles on Atomically Clean Graphene

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We designed a graphene based TEM sample carrier to enable atomically resolved studies of the heat-induced evolution of deposits on graphene. By in-situ application of electric current to a freestanding sheet of graphene, we obtain local temperatures exceeding 1000 K. We investigated various heat induced phenomena of gold particles on an atomically clean graphene surface. Initially, the gold nanoislands decrease their surface-area-to-volume ratio with increasing temperature by assuming a more spherical shape. At higher temperatures, we observe their migration and a self-organization into parallel straight lines.

1. Introduction

The utilization of the unique properties of graphene as a quasi transparent sample support [1–5] in conjunction with the progressive development of transmission electron microscopy [6] allowed high-contrast imaging of light atoms and molecules and their dynamics for the first time. Furthermore, the remarkable material properties of freely suspended graphene, such as superior electrical conductivity [7], highest mechanical stability [8, 9] as well as enormous thermal stability [10], provide a controlled generation of extreme temperatures by Joule heating [10–13].

In this way one important aspect of in situ sample manipulation can valuably be combined with the aspect of high-contrast imaging. For the in-situ Joule heating of a freely suspended sheet of graphene, we employ a microfabricated, in-situ applicable TEM sample carrier that was developed recently [14]. A graphene flake together with predeposited gold nanoparticles has been positioned directly above the electrode fingers of that carrier (Fig. 1). Its special design allows to obtain reliably temperatures in excess of 1000 K in atomically thin, crystalline and electron transparent single- and few-layer graphene membranes [14]. In this letter, we report on the results from observations of heat-induced dynamics of deposits on an electrically biased graphene membrane. The adsorbates described here are gold nanoislands predeposited by thermal evaporation onto the membranes.

2. Experiment

The investigations have been performed in an aberration-corrected (CEOS type corrector) FEI 80-300 Titan transmission electron microscope. This system was operated at an accelerating voltage of 80 kV in order to stay below the threshold for knock-on damage of graphene [15]. Sample carriers were mounted in a Fischione 2510 biasing TEM holder, and

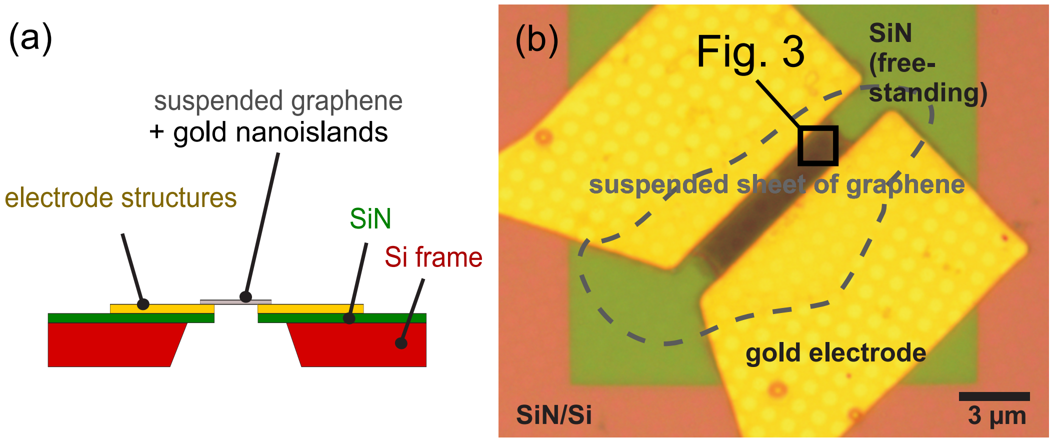

Fig. 1: (a) Cross-sectional schematic illustration of the sample carrier design. (b) Optical micrograph of the electrode support structure on which a graphene sheet is suspended. A small region is marked by a black square. In the following, we will have a closer look at this place, which corresponds to the TEM image in Fig. 3.

an electrical current was passed through the graphene sample by applying a bias voltage between the electrodes. We observed first significant transformations of gold nanoislands for an estimated current-density in the range of $2 \cdot 10^7\,\mathrm{Acm}^{-2}$ with an applied bias of about 2 V.

3. Heat Induced Phenomena

3.1 The dynamics of pre-deposited nanoislands

The initial observations under gentle heating correspond to previously described transformations and help to estimate the temperature distribution in our sample geometry. It is well known, that the diffusion of Au adatoms on the surface of gold nanoparticles is already significant at room temperature [16, 17], leading to continuous shape changes of the particles upon heating [18]. In case of our deposited gold nanoislands, we could nicely confirm the decrease of the particle surface-area-to-volume ratio, i.e. a transformation to more spherical shapes, with increasing temperature (Fig. 2a). After exceeding a certain temperature limit, the first of the almost spherically shaped particles form liquid drops and start to evaporate (Fig. 2b) [14, 19]. According to the theoretical predictions and similar experiments, the temperature related to this phase transition strongly depends on the particle size [20], and in our case was estimated to be in the range of 800 °C to 1300 °C. As the gold particles evaporate during TEM observation, a carbon shell with the shape of the original gold particle becomes visible (Fig. 2c). It appears that the carbon layer is formed on the gold particles under electron irradiation and then remains in shape even after the gold particle is removed. In previous in situ experiments with gold nanoparticles deposited on ultrathin amorphous carbon, it has been found that temperatures above 425 °C in conjunction with intense electron beam irradiation drive such a particle encapsulation [18]. Similar to our observations, these shells consist typically of

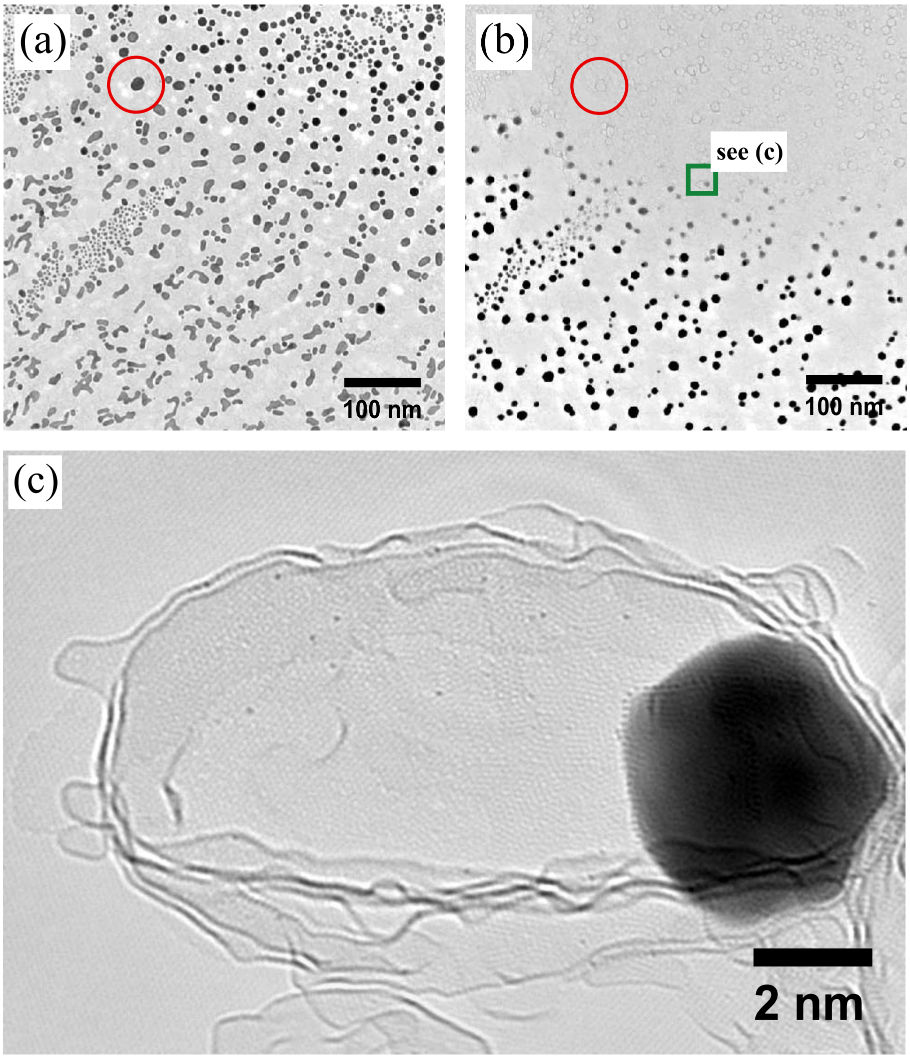

Fig. 2: (a) TEM image of gold nanoislands deposited on graphene. A temperature gradient from the lower left corner to the upper right corner corresponds to the variation of the gold particle shape. (b) The same area (the same position is indicated by an open circle) after further increasing the applied electrical current through the graphene sheet. The particles get encapsulated with carbon shells and finally evaporate. (c) A liquefied particle evaporates inside a shell of amorphous carbon (see also little square in (b)) at atomic resolution.

2–5 atomic carbon layers. Although the shells appear similar to closed graphene sheets, our atomically resolved images clearly suggest a large extent of imperfections. In particular, these atomic carbon layers don't exhibit a strict crystalline structure, but show a high degree of amorphization (Fig. 2c).

The phase transformations described above have been observed under permanent electron irradiation. Obviously this radiation is essentially accompanied with an electron beam induced demobilization and enrichment of hydrocarbons [21]. Therefore we repeated the same experiment without initial irradiation. Again we applied a current density of $2 \cdot 10^7\,\mathrm{Acm}^{-2}$, but kept wide areas of the graphene supported nanoparticles unexposed to the e-beam for several minutes. Then, we started recording images of these regions. Two very clear differences are found in this case: First, atomically clean graphene is obtained on large areas (Fig. 3), only if heat is applied before intense electron irradiation. This confirms that, initially, we have mobile hydrocarbon deposits on our samples that can be driven off by modest heating. However, after exposure to the electron beam, the contamination is fixed and transforms under heat (as described below) but does not evaporate. Second, the gold particles do not become encapsulated and do not leave behind a carbonaceous shell. Surprisingly, instead of liquidation or evaporation, we now observe that the particles as a whole become mobile and migrate to form linear clusters at elevated temperatures.

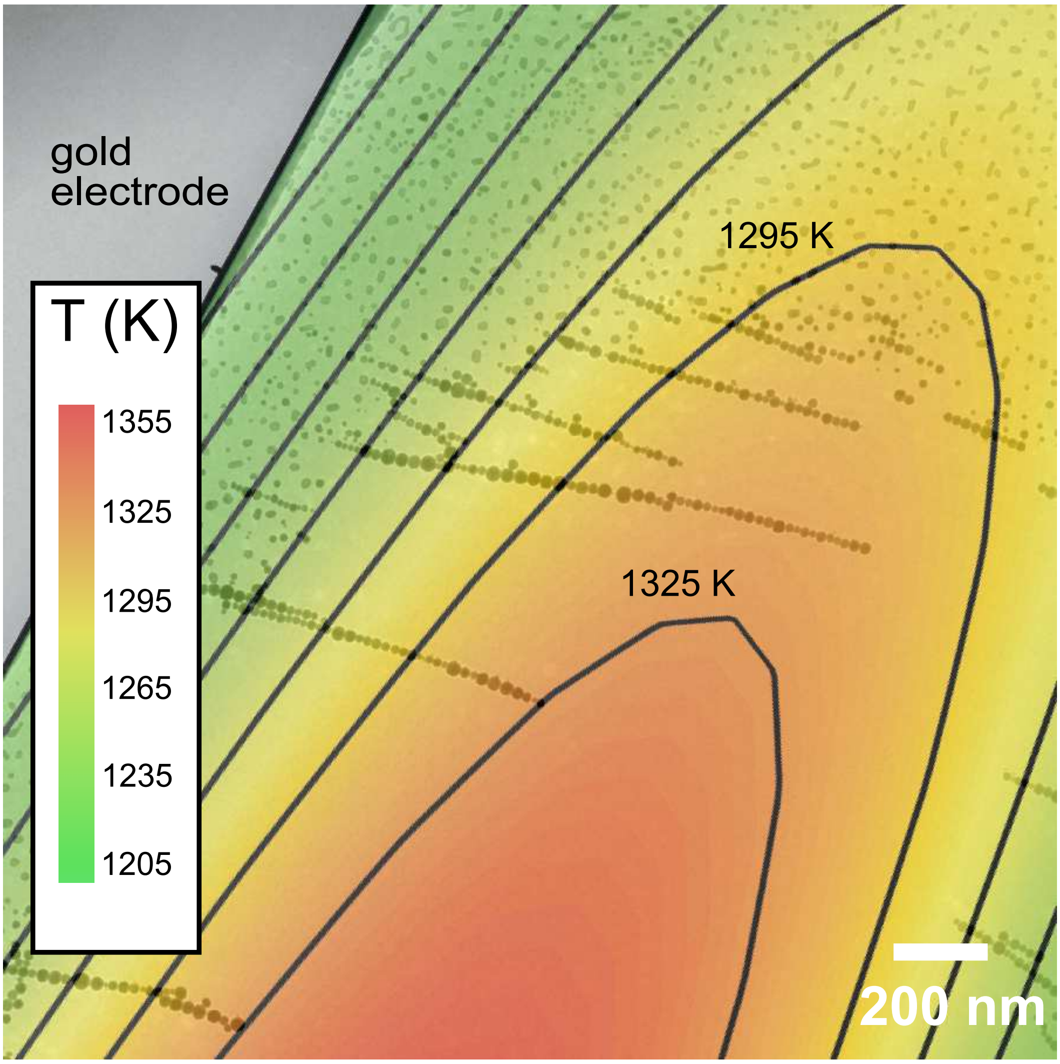

Fig. 3: TEM image of a sample area corresponding to the little empty square in Fig. 1b. In addition to the visible gold particle distribution we overlaid the corresponding temperature profile according to our FEM calculations.

This migration can be confirmed by molecular dynamic studies in conjunction with kinetic Monte Carlo simulations [22]. The migration or the so-called thermophoretic motion has been already investigated for gold nanoparticles in conjunctions with carbon nanotubes [23–25], but not on a graphene substrate. We believe that the driving force of the thermophoresis-like behavior corresponds to a preference of the particles to stay in the same aggregate state. If a certain gold particle is almost reaching its melting point, then the particle simply migrates into a direction of the negative temperature gradient. This interpretation would be consistent with our observation that initially, comparatively flat nanoislands do not show this significant movement (they are still far away from their melting point), whereas the hot, spherical particles do migrate.

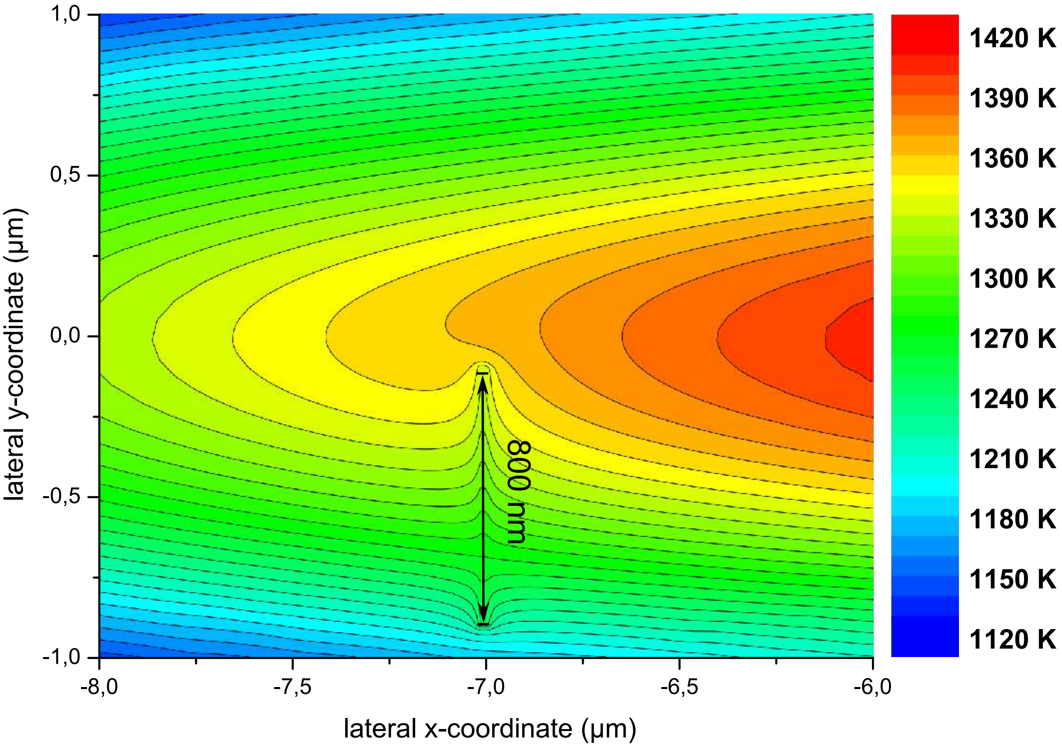

Fig. 4: FEM simulated temperature profile taking the presence of one gold particle chain into account. The gold chain perturbs the temperature profile such that gold particles which drift along the thermal gradient arrive at the end of the chain, indicating a possible mechanism for its self-organization.

Quite remarkably, the gold particles cluster into linear chains (Fig. 3). Towards a deeper understanding of this effect, we performed finite-element (FEM) simulations in order to obtain a temperature distribution for our sample geometry. In a first step, we include only the sample carrier geometry and the graphene membrane into the simulation. A resulting temperature profile is overlaid onto the image in Fig. 3. In the next step, we include a gold particle chain as a thermally conducting element into the simulation (Fig. 4). For a rough approximation we assumed a gold wire of 15 nm diameter and a length of 800 nm deposited on the graphene sheet. Furthermore, we neglected quantum size effects as well as an electrical conductance along the wire axis. For the result it was indeed important to assume the wire would rather conduct heat than electrical current perpendicular to the carbon shells (that encapsulate the gold particles). Otherwise an additional contribution of the electrical current flow through the gold wire compensates the local effect of increased heat dissipation. Now, the obtained temperature profile indicates that the gold particle chains create a ”short circuit” in the temperature profile, i.e. a nearly constant temperature along the chain and steep temperature gradients in the graphene membrane near their ends. This suggests a possible mechanism for the chain formation: Individual gold particles that migrate along the temperature gradient will most likely end up at the end of an already existing gold particle chain, thereby extending it by one element.

4. Conclusions

In summary, we presented atomically resolved in situ TEM studies of the heat-induced evolution of gold nanoislands on graphene. In case of an atomically clean graphene surface and at high temperatures, we found that the gold particles develop a surprising dynamic behavior. In particular, we investigated their migration along the negative temperature gradient that is apparently accompanied by an related self-organization effect aligning the particles into parallel straight lines.

5. Acknowledgement

Special thanks go to Jannik C. Meyer from the Electron Microscopy Group of Materials Science for his great support with respect to the microscope operation and scientific questions.

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