Trapping of metal atoms by reconstructed defects in graphene

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We present an in-depth investigation of the interaction between various types of metal atoms and defective graphene. Many of the current growth techniques for graphene produce material that is defective. These defects change the properties of graphene [1], which is why their effects need to be understood but also to take advantage of them in practical applications. Our graphene samples are prepared from HOPG or natural graphite by micromechanical cleavage with regular scotch-tape, which is then dissolved in acetone. The resulting suspension is dropped on standard TEM grids. These are subsequently cleaned by annealing at high temperature (1000-2000°C) under high vacuum, in a furnace. Metal nanoparticles are deposited on top of the sample during or after the annealing process. After these preparation steps, the sample is transferred into the TEM using a special holder, which allows for *in-situ* heating. We correlate our experimental observations with theoretical calculations to obtain a complete image of the observed phenomena.

1. Structuring at the atomic scale with a focused electron beam. The experiments show the possibility of creating sub-nanometer damage in graphene sheets, in a controlled manner, by electron irradiation [2]. We operate our microscope in STEM mode, which focuses the electron beam in a spot of about 1A in diameter. This is made possible by an aberration corrector fitted to the condenser lens system. Placing the beam in a fixed position on the sample yields multiple vacancies whose size varies between less than one and several nanometers and is controlled by the irradiation time. These evolve differently as a function of sample temperature and of the presence of atoms nearby. At lower temperatures, we find that these vacancies have a tendency to either close partially by the trapping of mobile carbon atoms and restructuring of the edges, or remain open. At higher temperatures, these vacancies anneal immediately by trapping atoms diffusing on the surface. We see this for carbon (given for instance by surface contamination) or, more interestingly, for several types of metal atoms. Metal atoms tend to replace carbon atoms in the lattice and lead to new structures which, provided the temperature is lowered and the irradiation stops, are stable. The technique can be extended by programming the beam control software of the microscope to create vacancies in the sample in a pre-defined pattern. Figure 1a shows a region of the graphene sample before irradiation. The large black area in the upper part represents a Mo nanoparticle while smaller black dots throughout the image are individual Mo atoms or small clusters. Figure 1b shows the same area after patterning. A triangular arrangement of Mo clusters is visible below the particle. Subsequent imaging and analysis show that, despite the temperature of 475°C and continued irradiation, some Mo atoms still remain trapped 40 minutes later.

2. Creation of vacancies on a larger area. The second set of experiments provides deeper insight into the trapping of metal atoms by reconstructed defects and the diffusion of metal atoms on the defective graphene surface [3]. We used W atoms, which provide good contrast in the electron microscope because of their high atomic number, and we subjected the sample to uniform and constant electron irradiation. We then acquired videos of the motion of these atoms on the graphitic surface. The atoms did not move as expected – by a standard random walk between adjacent lattice positions – but performed long-distance (1nm) jumps between certain lattice sites. Figure 2 shows the trajectory of an atom during such an experiment. Furthermore, multiple back-and-forth jumping between two defective sites appeared. At temperatures where this type of motion was observed (300-500°C), an interaction energy of about 2 eV between the atom and the lattice site is necessary for the trapping/detrapping behavior and the diffusion with a jump rate that matches the one we see in our experiment. The two extreme cases would be an atom on a perfect surface, which would diffuse too fast for in-situ observation (activation energy 0.5 eV) and an atom trapped in a single vacancy by replacing a carbon atom, making the metal atom immobile (7 eV). By simulating how surface defects reconstruct at these temperatures, we found that the most likely candidates for the structures that trap the W atom are reconstructed 555-777 or 5555-6-7777 defects. These complex structures start as double vacancies (created by the electron beam) and reconstruct at high temperatures. This scenario is further supported by the experimental observation of smaller (0.2 nm) jumps while the atom is trapped at a defective site, between two large jumps. These observations show a long-distance interaction between the metal atom and the defect. We can hence identify the unusual motion of the metal atom as jumps between reconstructed lattice defects in graphene.

References

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[3] O Cretu, A V Krasheninnikov, J A Rodríguez-Manzo, L Sun, R M Nieminen, and F Banhart, Phys. Rev. Lett. **105** (2010) 196102.

Figures

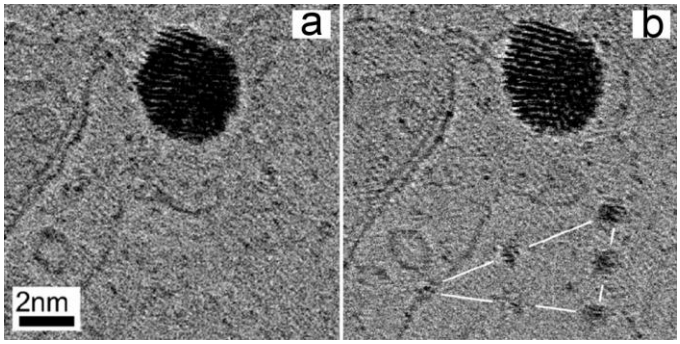

Figure1. Patterning of graphene by trapping Mo atoms at selected locations. The same sample area is shown before (a) and after (b) the patterning with a triangular arrangement of dots. Sample temperature 475°C; patterning time about 5 minutes.

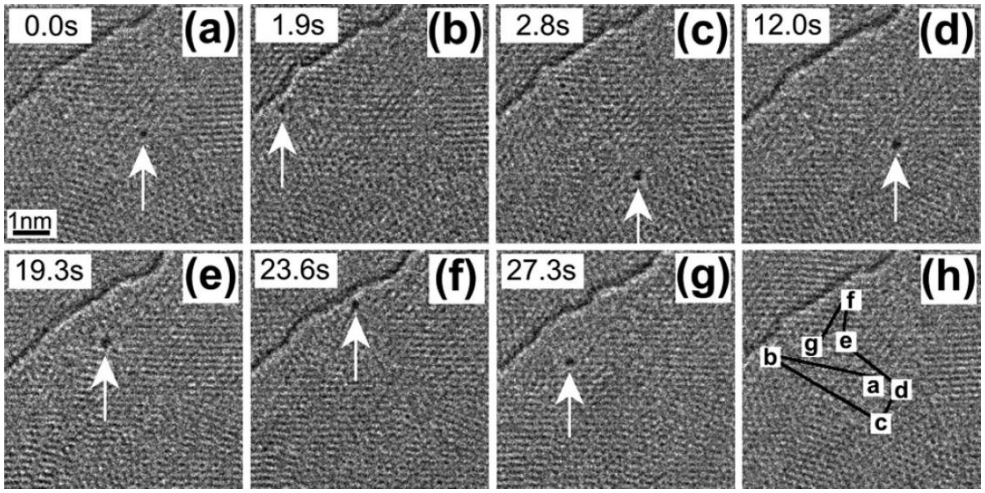

Figure2. Trajectory of a W atom diffusing on a graphene surface. The atom is shown in each of its stable positions on the lattice, marked by a white arrow (a-g); the total trajectory is represented in (h). Sample temperature 470°C; experiment time about 30s.