

## The Interaction of Graphene with Metals Studied by *In-situ* Electron Microscopy

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The interaction between graphene and metals is of high importance in the understanding of the growth of graphene from catalytically active metals but also from the viewpoint of doping graphene with foreign atoms. *In-situ* electron microscopy allows the atomic-scale observation of this interaction in a wide temperature range. Dissolution or precipitation phenomena, where carbon atoms are taken up by or extruded from metallic crystals, can be observed as well as the interaction between the graphenic lattice and individual metal atoms [1]. Of particular importance in this context are structural defects in graphene [2] due to the possibility of trapping dopant atoms and thus changing the electronic properties of graphene locally. Since the formation energy of single or multiple vacancies in graphene is above 7 eV, the replacement of carbon by other atoms needs an energetic process such as the ballistic atom displacement by electron beams [3]. Therefore, both defect formation and interaction of defective graphene with metal atoms can be observed in the same experiment in an electron microscope.

The mechanism of trapping metal atoms in graphene was studied by creating defects in the graphene lattice under electron irradiation while metal atoms were migrating on the surface of graphene [4, 5]. In a certain temperature range, tungsten atoms were seen to be trapped in localized defects but can also escape from the defects at sufficiently high temperature. A detailed analysis in a combination of experiments and computation shows that reconstructed divacancies (figure 1) such as the 555-777 type (3 pentagons and 3 heptagons) act as traps, binding the metal atom with an energy of 2 eV [4]. A direct replacement of carbon by metal atoms was excluded, showing the instability of single vacancies in graphene at elevated temperatures. The diffusive migration of trapped Au and Pt atoms was also studied by *in-situ* observation of the metal atoms. Activation energies of the order 2.5 eV were obtained [6].

Trapping of metal atoms at defects in graphene can also be induced selectively with atomic precision. In an electron microscope with aberration-corrected condenser, the electron beam spot with a diameter of 1 Å was focused on pre-selected positions of the graphene lattice, leading to subsequent trapping of metal atoms in these locations [5]. This was used to create a pattern of dots, decorated with foreign atoms, on a graphene sheet.

The interaction between graphene and catalytically active bulk crystals was studied by heating a bilayer system, consisting of an amorphous carbon film covered with a polycrystalline layer of Fe, Ni, or Co. Above approximately 600°C, the dissolution of carbon in the metal layer was observed, followed by the segregation of single- or multi-layer graphene on the metal surface (figure 2) [6]. Ostwald ripening of the metal crystals at increasing temperature allowed us to liberate the graphene areas and thus to observe the growth of graphene *in-situ*. This is a solid-state growth process (no gases are involved) which is induced by the lowering of the energy of the carbon system from the energetically higher amorphous phase to graphene by using a catalytically active metal. At the same time, the metal crystals act as a diffusion channel for carbon atoms.

## References

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## Figures

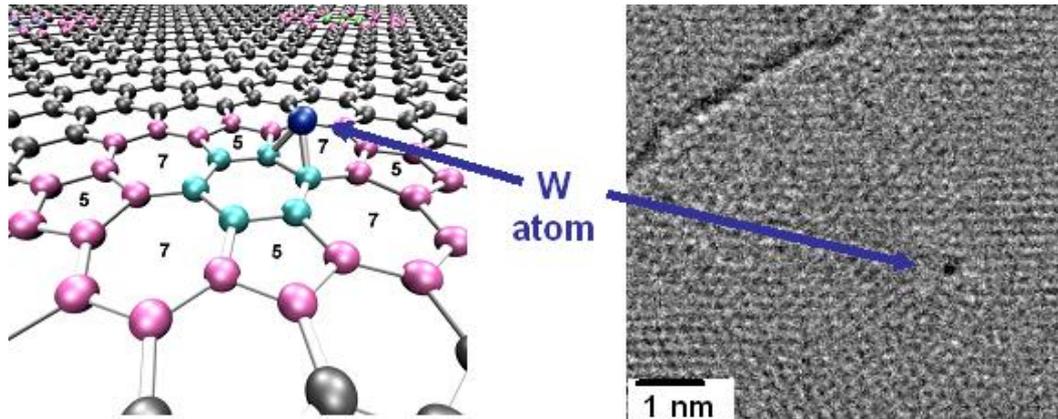


Figure 1: Trapping of a W atom on a reconstructed divacancy such as the (5555-6-7777)-defect as shown in the model on the left hand side. The Electron microscopy image shows a W atom trapped on such a defect in the uppermost layer of a multi-layer graphene sheet [4].

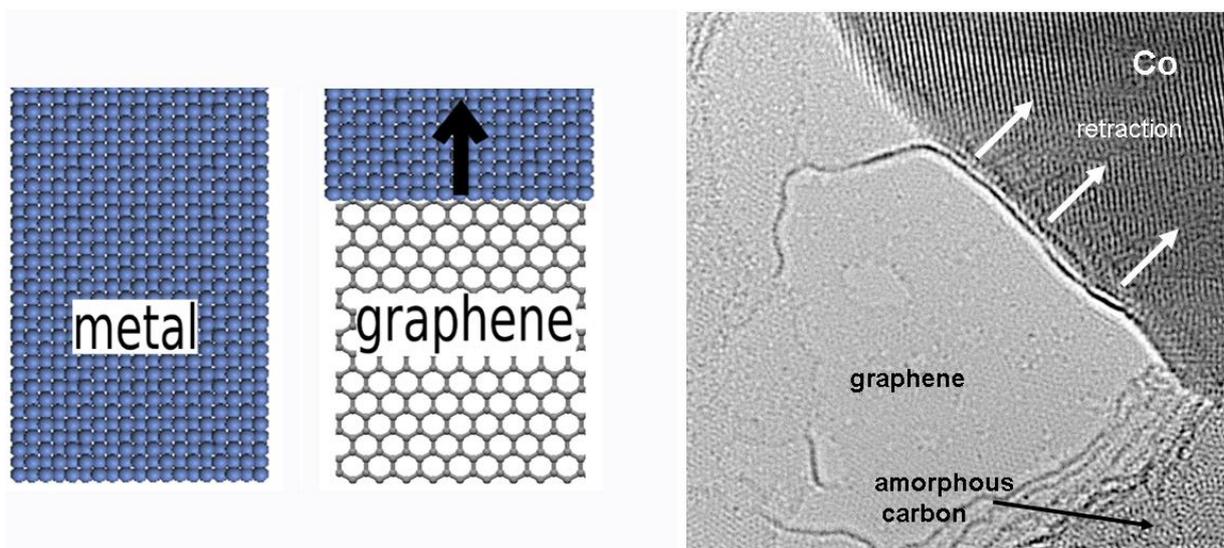


Figure 2: Solid-state transformation of amorphous carbon to graphene in the presence of a catalytically active transition metal. The metal initially covers the amorphous carbon film. After heating, the amorphous carbon is taken up by the metal. Subsequently, graphene nucleates on the metal surface which can be seen as the metal retracts by a ripening effect (model image on the left hand side). The TEM image shows a retracting Co crystal, leaving a graphene layer in its trace [7].