

The influence of the substrate on chemical identification of dopant atoms in graphene with AFM

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Abstract

The capability to chemically identify single surface atoms with AFM becomes especially important in graphene, where substitutional dopant heteroatoms are used to control the electronic properties. However, dopant elements topologically similar to carbon (such as nitrogen or boron) cannot be identified in graphene by performing a standard AFM measurement. By combining force-distance spectroscopy [1] with a recent dispersion-corrected density functional theory approach (DFT-D3 w/ Becke-Johnson damping [2]) we demonstrate the possibility to fill this gap and enable the quantitative chemical identification of dopant atoms in graphene. Since, depending on the fabrication method, graphene may be placed on virtually any substrate, at the same time we address the question of the influence of the substrate on the chemical identification. We indeed focus on nitrogen-doped graphene grown on Ir(111) or Cu(111), where, due to the resulting large-scale moiré corrugated structure, the local interaction between graphene and the substrate is spatially modulated. The results of our theoretical AFM simulations will show that the influence of the substrate is only significant when probing the dopant site in graphene. Overall, we will present a first extensive van der Waals density functional study of the geometry and electronic structure of nitrogen-doped graphene on Ir(111).

References

[1] Y. Sugimoto et al., Nature, **446** (2007) 64.

[2] S. Grimme et al., Wiley Interdisciplinary Reviews: Computational Molecular Science, **1** (2011) 211.

Figures

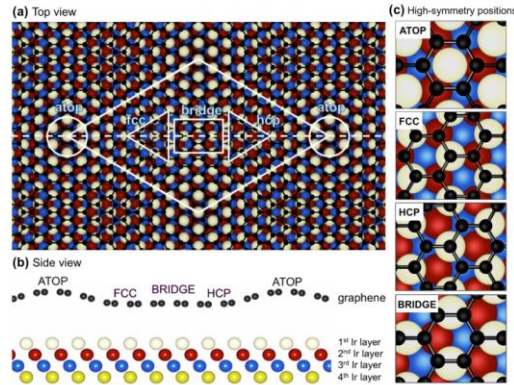


Figure 1. Moiré corrugated structure of graphene on Ir(111). The unit cell and the high-symmetry positions considered in the DFT calculations are shown.

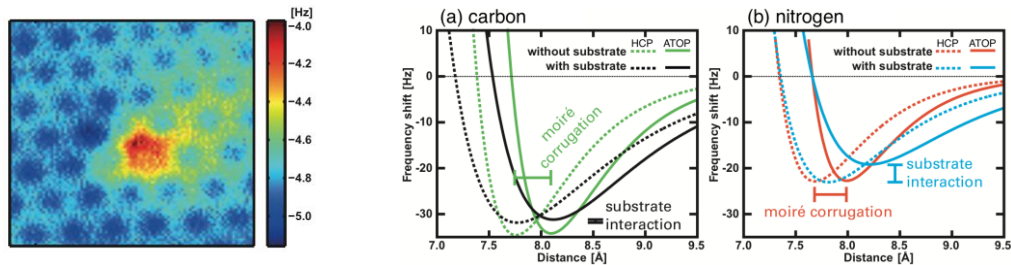


Figure 2. (Left) $\Delta f_{\min}$ map of CVD grown N-doped graphene/Cu(111), obtained from a stack of constant-height frequency-modulated AFM images at different heights with $V_{\text{gap}} = 0$ V. From this 3D Δf data cube a $\Delta f(z)$ spectrum can be obtained for each (x,y) lateral position. The fitted minimum $\Delta f_{\min}$ is then mapped. (Right) Calculated Δf as a function of the distance between a simple model of AFM tip and (N-doped) graphene/Ir(111). The curves obtained by probing (a) C and (b) N atoms located at ATOP or HCP high-symmetry positions are shown, either including or not including the Ir(111) substrate during the calculations.