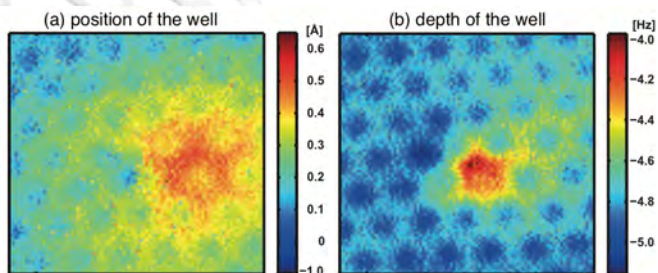


CONCLUSIONS

The results of our AFM simulations are in excellent qualitative agreement with the experiments on N-doped graphene/Cu(111) recently carried out by the Condensed Matter and Interfaces group at the Debye Institute for Nanomaterials Science in Utrecht.



The measurements on N-doped graphene/Ir(111) are in progress within the same group. We believe that, if the chemical identification capabilities demonstrated in this work will be actually reflected in that context, then a substantial contribution would be given on behalf of the emergence of this identification technique in the AFM field of research.

Important repercussions could affect not only the graphene domain, but also all those scientific and technological areas in which important functional properties are dictated by a short-range ordering and the chemical nature of defects, dopants, adsorbates or individual atoms.

ACKNOWLEDGEMENTS

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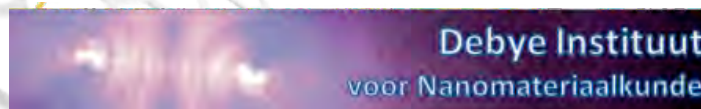
Co-funded by the
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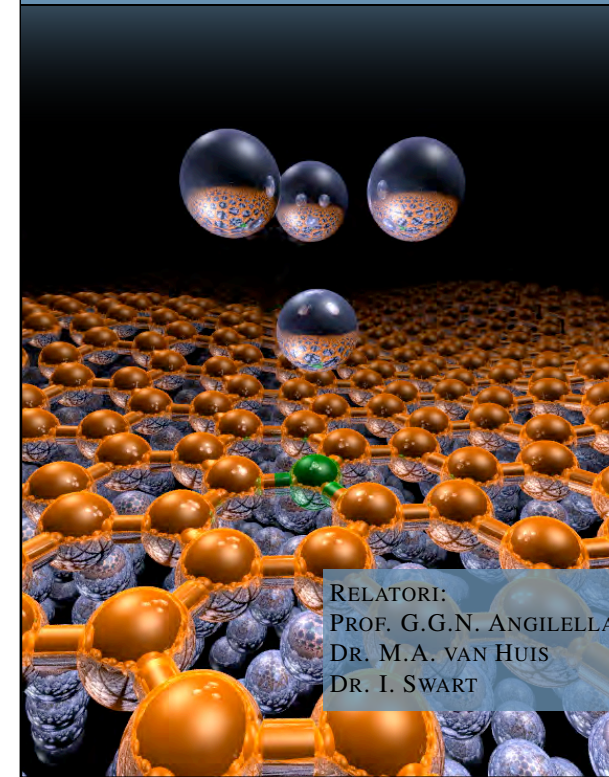


Universiteit Utrecht



GAETANO CALOGERO

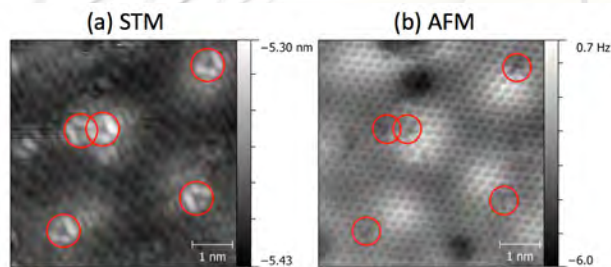
A VAN DER WAALS DENSITY FUNCTIONAL
STUDY OF N-DOPED GRAPHENE/IR(111)
FOR CHEMICAL IDENTIFICATION OF
INDIVIDUAL ATOMS WITH STM AND AFM



RELATORI:
PROF. G.G.N. ANGILELLA
DR. M.A. VAN HUIS
DR. I. SWART

INTRODUCTION

As emerges from the “*Science and technology roadmap*” for **graphene**, recently developed within the framework of the European Graphene Flagship, the stunning properties of this 2D carbon allotrope promise to impact and benefit several areas of society in the near future. Many of its brightest prospects depend on the ability to synthesize large high-quality samples with controllable electronic properties. At the state-of-the-art one of the most viable approaches is to grow doped graphene on a close-packed metal surface, such as Cu(111) or **Ir(111)**. The resulting graphene structure is often characterized using scanning tunneling microscopy (STM) and atomic force microscopy (AFM). However, **dopant** atoms such as nitrogen substituted in graphene **are not visible in a standard AFM measurement**.



PURPOSES

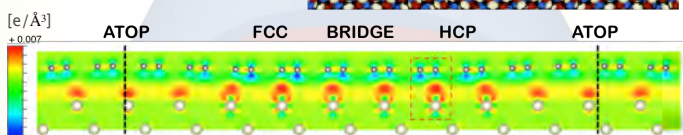
By performing an extensive DFT investigation of N-doped graphene on Ir(111), we demonstrate the possibility to fill this gap and enable the chemical identification of individual atoms using an AFM.

In particular, we use the recent DFT-D3(BJ) approach in order to accurately simulate the short- and long-range forces that govern: the geometric and electronic structure of graphene in this system, the interplay between N dopants and the metal substrate, the characteristic nitrogen signature in STM images and the interactions between this system and a model of an AFM tip.

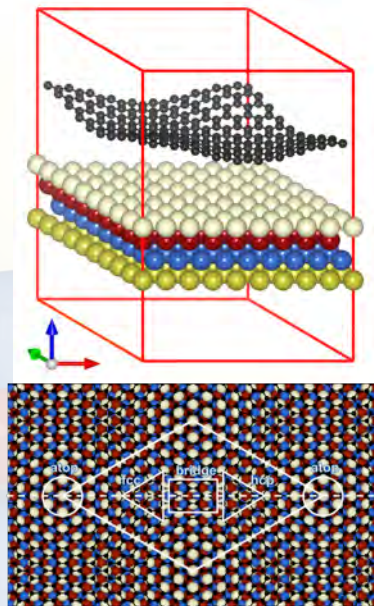
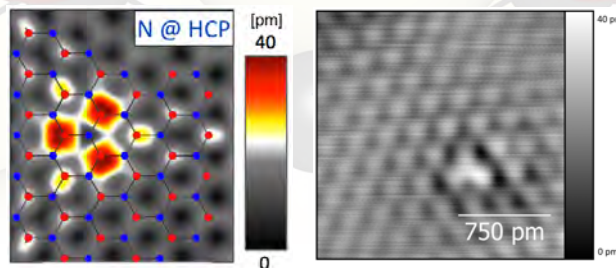
Our model is a supercell of $(9 \times 9 \times 4)$ iridium atoms and a single layer (10×10) graphene.

RESULTS

We first quantitatively reproduce the state-of-the-art model for graphene/Ir(111), recovering the typical moiré corrugated structure and the expected physisorption with chemical modulation.



Since only few authors have studied the effects of *simultaneously* doping and metal-supporting graphene, we study N-doped graphene/Ir(111) in terms of geometry, energetics, charge density distribution, local density of states (LDOS). We find that the electronic properties are substantially similar to those reported for a free-standing graphene (n-type doping, sp^2 -rehybridization involving the N's three nearest neighbors, triangular N-signature in STM). A LDOS analysis suggests that the optimal N-C imaging contrast in constant-current STM may be achieved by setting a bias voltage of ≈ 0.6 V, which provides a resonance with the most distinctive N electronic state.



By calculating the interaction energy between our system and a 4-Ir-atom tetrahedral model of an AFM tip at a range of distances z , we indirectly simulate the frequency-shift spectra $\Delta f(z)$ measurable with a non-contact AFM in frequency modulation. These curves turn out to have a single minimum at specific values z_{\min} and Δf_{\min} . The key point is that Δf_{\min} can be uniquely regarded as a specific chemical signature of the probed atom in the surface.

By probing N and C atoms located at top and valley sites in the graphene moiré structure we show that it is possible to chemically identify a N dopant in graphene using an AFM.

The chemical contrast is found to be site-independent, with a small influence of the metal substrate only observed when probing a N atom. We associate this effect to the hybridization occurring at the interface between the N p_z -orbital and the metal d-orbitals.

