GRAPHENE ON Ni(100): COEXISTENCE OF DIFFERENT MOIRÉ PATTERNS AT A SYMMETRY-MISMATCHED INTERFACE

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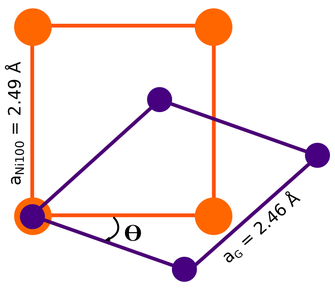
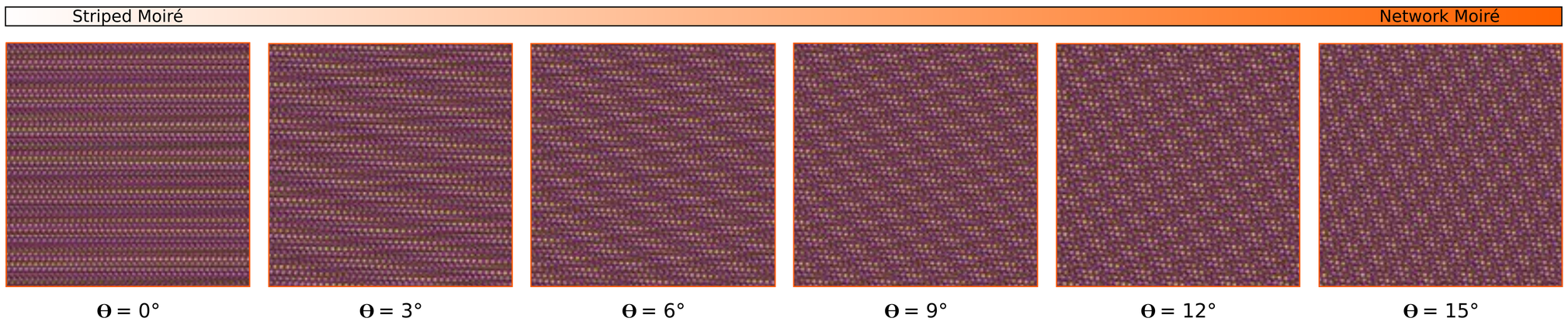
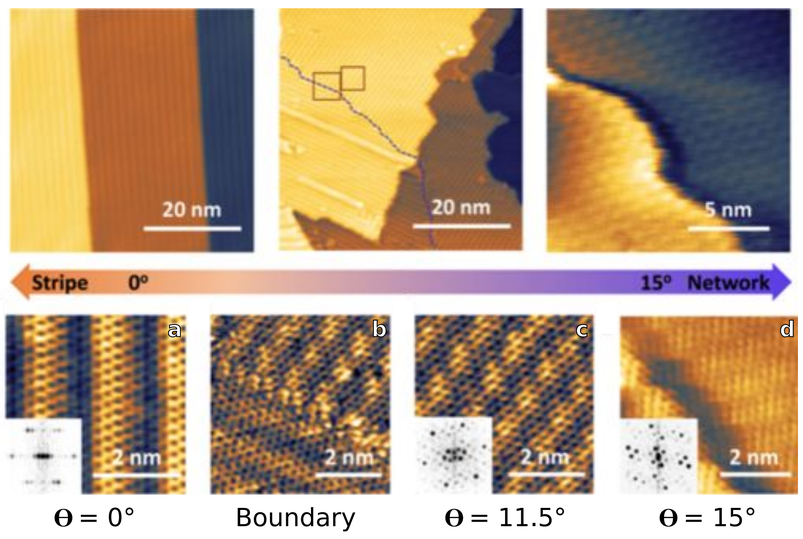
Graphene on Ni(100) forms a variety of Moire' patterns which can be well explained in atomistic models by the mismatch with the substrate, with periodicity depending on the relative angle between the hexagonal graphene and the square surface lattices. Evidence of the different Moire' structures is given by high resolution scanning tunneling microscopy images, that are well reproduced by ab-initio simulations. Beyond providing the detailed atomic-scale structures, the numerical simulationsallow a deep local characterization of the chemical bonding between thegraphene layer and the support. We also discuss the possible formationbeneath the graphene of a surface-confined nickel-carbide in specificregions of the Moire', whose presence is suggested by experimental STMimages.



Schematic rappresentation of Ni_{100} (orange) and graphene (violet) lattices. In evidence the convention for the angle rotation between the two lattices.





STM topographic images of representative graphene moirés exhibiting different periodicity and morphology (stripe & rhombic network). The graphene rotation angles (θ) are: (a) θ = 0° [V_b = 0.02 V, I_t = 5 nA]. (b) Zoom-in at the left square in the second top image [V_b = 0.15 V, I_t = 20 nA]. (f) Zoom-in at the right square in the second top image. θ = 11.5° [V_b = 0.15 V, I_t = 20 nA]. (d) θ = 15° [V_b = 0.005 V, I_t = 5 nA]. The insets of (d,f,g) are Fourier transforms of the corresponding graphene moirés.

Experimental evidences

- It has been found experimentally that graphene can grows with several kind of misorientation angles w.r.t. Ni(100) substrate, originating different moiré superstructures.
- The local thermodynamics and kinetics determine the graphene growth and, consequently, the particular moiré superstructure.
- Furthermore, it possible to have different moiré domains in the same nickel surface (picture (b) the figure).

Method and simulations

- QuantumESPRESSO package
- Density Functional Theory & GGA & VdW corrections
- Plane wave basis set with US PP

Slab geometry with 3 Ni layers: keping fixed the first Ni layer, we let the Ni slab free to relax along the z direction. Than we kept fixed all the Ni slab and we let graphene free to relax.

The planar "supercell" is linked to the particular moiré
Angle 0°: 1x12 with 12 Ni and 28 C
Angle 12°: √3x√3R33°41' with 13 Ni and 30 C

Simulated STM images: costant current method simulated using isosurface of energy intagrated on the local density of state (ILDoS).

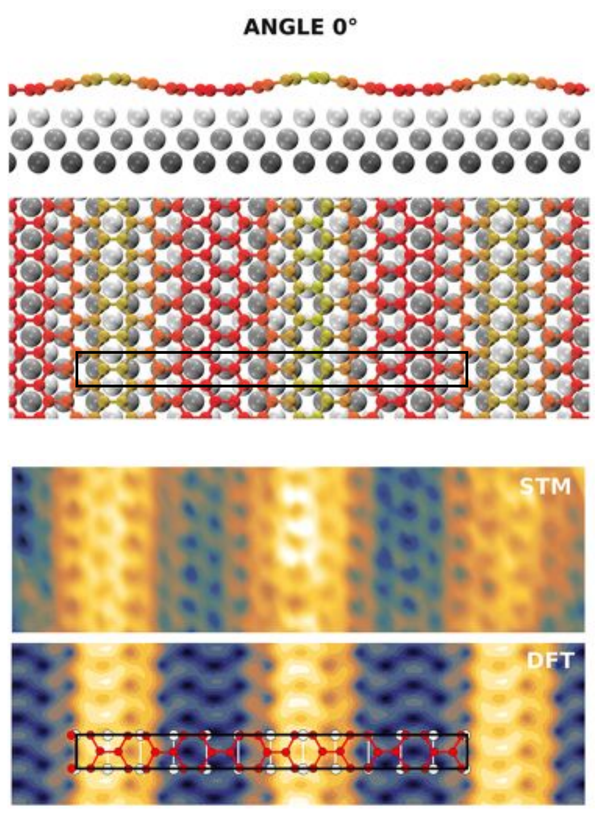
θ = 0° — *Striped Moiré* — *Network Moiré* — θ = 12°

In the configuration θ=0° the graphene sheet shows a very strong corrugation (1 Å) along the Ni(100) 100 direction, forming a striped moiré pattern that is clear visible from the STM measurements and also very well reproduced by the STM simulations.

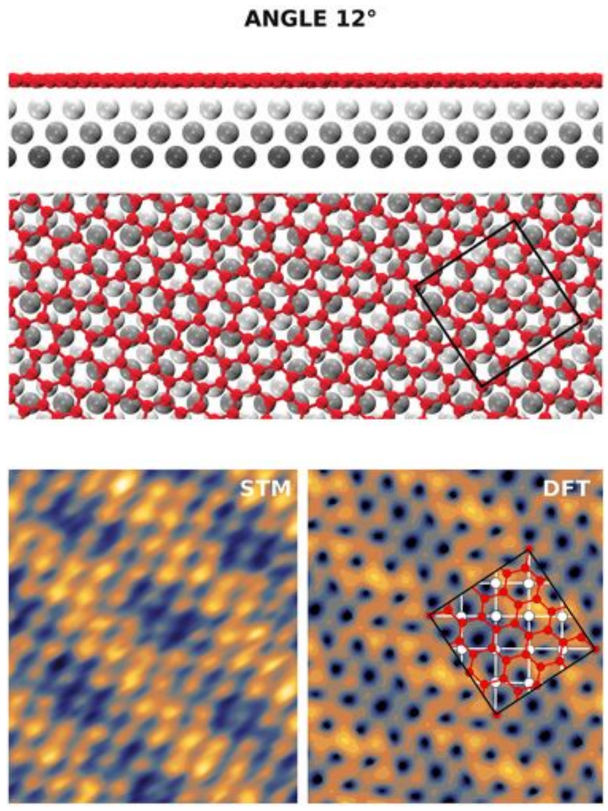
This strong corrugation is due to the alternation of chemisorption (dark) and physisorption (bright) regions, that are also characterized by a peculiar graphene electronic charge rearrangement.

Graphene Adsorption	
E_{ads}/C	0.17 eV
$d^*_{C\text{-}Ni}$ (Chem)	1.95 Å
$d^*_{C\text{-}Ni}$ (Phys)	2.95 Å

*for the chemisorption it was chosen the closest C w.r.t. Ni100, while for the physisorption the furthest.



G/Ni100 angle 0°. Top: atomistic model of the system. Middle: STM simulation. Bottom: STM measurement [Z. Zou, C. Afirch et al.].



G/Ni100 angle 12°. Top: atomistic model of the system. Middle: STM simulation. Bottom: STM measurement [Z. Zou, C. Afirch et al.].

In the configuration θ=12° the graphene sheet shows a very small corrugation (0.2 Å) w.r.t. the θ=0° configuration, forming a network moiré pattern that is clear visible from the STM measurements and also very well reproduced by the STM simulations.

Due to the low corrugation, we do not distinguish between chemisorbed and physisorbed regions, but it is possible to appreciate a peculiar graphene electronic charge rearrangement.

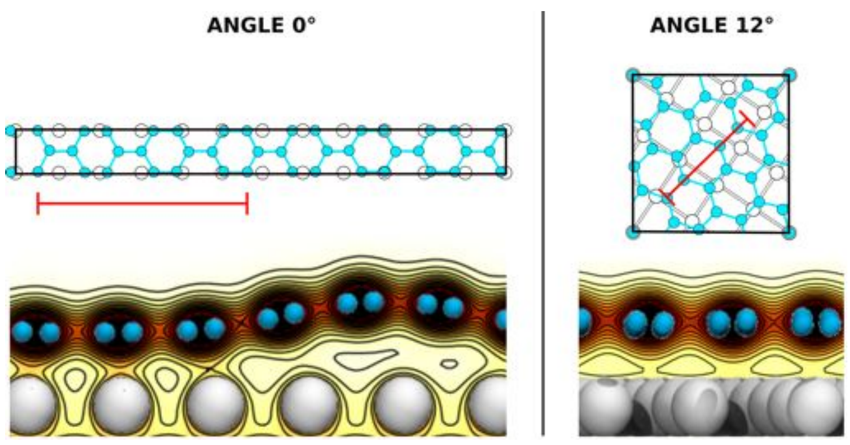
Graphene Adsorption	
E_{ads}/C	0.20 eV
$d_{C\text{-}Ni}$ (min)	1.95 Å
$d_{C\text{-}Ni}$ (max)	2.15 Å

Total charge density

Total charge density plots give an indication of chemisorbed and physisorbed regions, being characterized by presence or absence of electronic charge between graphene and substrate.

- Angle 0°: alternation of chemisorbed (blue in the STM image) and physisorbed (yellow in the STM image) regions*.
- Angle 12°: all the graphene layer is chemisorbed*.

*the coluor contrast in the STM images (experimental & simulated) is tuned in order to highlight the moiré pattern for each angle. Consequently, the STM coluor scale indicates different height ranges for angle 0° and 12°.



Bottom:Total charge density plots for striped (angle 0°) and network (angle 12°) moiré structures. Top: simulation cells for angle 0° and 12°. The red line indicates the section of the cell ortogonal to the total charge plot rappresented in the bottom. Charge density color scale: from white (absence of charge) to black (maximum of the charge).

Conclusions

- With ab-initio simulations we are able to identify the ground-state structures of the several moiré patterns of the G/Ni100 system.
- Simulated STM images were found in excellent agreement with the experimental measurements.
- The total charge analysis allow us to identify the chemisorbed and physisorbed regions of the moirés.

Support from the Italian Ministry of Foreign Affairs and International Cooperation (MAECI) and the University of Trieste (Finanziamento di Ateneo per progetti di ricerca scientifica - FRA2015) is acknowledged.