Sublattice Localized Electronic States in
Atomically Resolved Graphene-Pt(111) Edge-Boundaries

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SUPPORTING INFORMATION:

1.- Materials and Methods.

2.- Details of the electronic structure of the G-Pt step boundary.

3.- An alternative configuration of the G-Pt step boundary found in the calculations.

4.- Crystalline borders and their relation with Moiré patterns.

5.- Possible design of an hypothetical dual channel nanoribbon.

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1. **Material and methods.**

*Experimental STM images*

Experiments were carried out in an ultrahigh vacuum (UHV) chamber with base pressure of $1 \times 10^{-10}$ mbar. The Pt(111) single crystal sample was cleaned by repeated cycles of Ar$^+$ sputtering and subsequent annealing at 1200K. After several cycles the sample purity was checked with low energy electron diffraction (LEED) and STM. Once the sample was free of contaminants we proceeded to graphene growth. For that purpose we exposed the clean Pt(111) to a partial pressure of propane ($C_3H_8$) of $1.1 \times 10^{-8}$ mbar during 15 min keeping the sample at 900K and subsequent annealing at 1050 during 20 min. Submonolayer coverage of graphene islands was observed in the STM sessions with an estimated coverage of $>0.1\text{ML}$.

STM images were acquired using a room temperature (RT) microscope. We used both topographic and quasi-constant height modes with typical biases of $-250\text{mV}$ to $250\text{mV}$ and currents between 0.1 nA and 4 nA. WSxM software was used for data acquisition and image analysis. The thermal drift was corrected with a home-made program, which resize the images for a given hexagonal unit cell by keeping the fast scan axis as the reference distance.

Quasi-constant height images were acquired tuning the scanning conditions to constant-height but with feedback parameters reacting more slowly than usual conditions while recording the current map. With these measurement conditions we were successful in simultaneously resolving the Pt atoms within the Pt(111) regions and the C atoms within the graphene islands. These exceptional resolving conditions could not be achieved under any other working mode explored by us. However, obtaining these high-resolution STM images is very demanding and tip crashes are relatively common. We would like to emphasize that the information obtained by topography and quasi-constant height images is exactly the same, and that the only difference between both modes is an increased atomic resolution, as the step jump is not followed properly by the scanning tip inducing poor imaging resolution in regular feedback loops. This is evidenced in Fig. S1, where the topographic and the quasi-constant height images are presented. We have also presented for the quasi-constant height the process of Fast Fourier Transform (FFT) filtering. This process eliminates noise coming from the experiment without altering the atomic features of the measurement.
Figure S1: STM images of the ZZ1 interface (2.5x2.5 nm²). A) Filtered image recorded in constant current mode. B) Unfiltered image recorded in quasi-constant height mode. C) FFT-Filtered image of B).

DFT calculations

We have calculated all the structural and electronic properties using DFT as implemented in the VASP code. For these calculations we employed the PBE functional empirically corrected to include van der Waals interactions (using the D2 Grimme approach) projector augmented wave (PAW) pseudopotentials, and a plane-wave cutoff of 400 eV. For the Pt we used the parameters C6(Pt) = 20 J·nm⁶/mol and R0(Pt) = 1.9 Å for the vdW-D2. We used the default values given in ref. 35 for the rest of the chemical species. The results shown on the paper are calculated without including spin polarization but we have also explored the possible magnetic solution of the system allowing it. We found that the interesting border was not magnetic while we recovered the expected magnetization in the H-terminated graphene end. As we focused our study in the G-Pt boundary edge we stuck to the non-polarized scheme.

We have exploited the intrinsic periodic nature of the calculations, considering a unit cell where we cut the Pt surface and enforce a shift in the z coordinate of the cell (see Fig. S2) to recover the periodicity (the ABC stacking of the metal). In this way, we have still a quite realistic description of the system without the need to include the other half of the Pt slab, reducing significantly the computational effort. Nevertheless, we keep the longer G ribbon (including a free standing region) to ensure that both G edges (the one in contact with the Pt and the one saturated with H atoms) are effectively decoupled. The cell includes a slab of 5 layers of Pt at which a single sheet of graphene (a 3x12 cell with 72 atoms) has been attached. The 4 lower Pt layers contain 28 atoms each, while the one on top has half the area of the others (14 atoms) and the graphene layer is bonded to its free edge. To make
the electronic properties of the flake more realistic, we have saturated the other border with 3 H atoms. This edge does not pretend to mimic any border of the simulated experiments. Calculations with a flake half the length of the one in Fig. S2, confirm that the structural properties of the G-Pt boundary are not significantly affected by the flake length. The lattice constant of the Pt crystal was optimized for both PBE (to have this value as a reference) and PBE-D2, obtaining a value of 3.98 Å for the first and 3.95 Å for the latter. However, the mismatch between the C and Pt lattices in the 3x3 Moiré of G/Pt(111) is small (0.6 %), and in our calculations we decided to fix the size of the supercell to match the relaxed graphene lattice (a₀ = 2.46 Å) calculated with PBE-D2.

We have constructed several different initial configurations with slightly different positions for the atoms in the Pt-G contact. All of them converged after the relaxation process to one of the two structures showed in Fig. 3 and Fig S6. For these structural relaxations, we have only fixed the positions of the Pt atoms of the three lowest layers and the z coordinate of the C atoms of the half sheet next to the free edge (H-terminated) as to simulate the Pt-G distance that we would expect in a G-flake over a Pt terrace 29. The final structures correspond to energies converged better than 10⁻⁴ eV/atom and forces smaller than 0.02 eV/Å. We have used a 2x6 Γ-centered Monkhorst-Pack grid to make the relaxation of the structures. For the DOS calculations, we first evaluated the electronic charge over a 2x21 Γ-centered Monkhorst-Pack grid, and then we calculated the DOS over a 4x75 Γ-centered Monkhorst-Pack. Together with this very fine k-points mesh we have chosen a small value for the broadening (σ=0.05 eV) which make us very confident about the convergence of the calculations.
Figure S2: Scheme of the theoretical simulation of the step. The unit cell, shown on top, is repeated to create the step, as illustrated below. The atoms that are highlighted in green were fixed in the z direction during the relaxation while the ones highlighted in yellow were fixed in all directions.

STM profiles

The experimental STM images can be deeper understood with the help of theory. In our approach, we use a nonequilibrium Green’s function formalism to evaluate the currents \(^{37}\), using the OPENMX code \(^{38}\) to map the Hamiltonian into a local orbital basis, and an idealized Pt apex with a single dz2 orbital to represent the microscope tip. Besides, all the simulations include the contribution to the current of multiple scattering processes, that are mandatory when exploring the short tip-sample distance range \(^{37}\). This model produces atomically resolved profiles (see Fig. 3E) and is important for the understanding of the experimental images.

2.- Details of the electronic structure of the G-Pt step boundary.

The boundary configuration showed in the Fig. 3, presents a clear electronic edge state at \(~0.8\) eV above the Fermi level. It derives from the graphene π-band. It is the main state of the G zigzag edge but broaden and shifted in energy due to the interaction with the Pt. The contribution to the DOS of each one of the C edge atoms (see Fig. S3A) is very similar as the chemical environment is mostly the same for the three atoms. This peak extends only
over one of the sublattices, A, and it rapidly decays going inside the flake but is uniform parallel to the edge (see Fig. S3A). This uniformity is in contrast to the results for the G/Ir system. The LDOS shows other peaks, like those at \( \sim +0.6 \) eV and \( \sim +1.1 \) eV, that can be explained by the finite size of our model graphene nanoribbon.

**Figure S3:** A), B) and C) LDOS of the atoms depicted in the ball-and-stick model corresponding to the atomic configuration shown in Fig. 3 in the main text. In A) we can see that the LDOS of the C atoms in sublattice A (the sublattice to which the C atoms bonded to the Pt atoms belong) decreases as we get away from the step. As the chemical environment of the 3 C atoms of the step edge (1A\(_1\), 1A\(_2\) and 1A\(_3\)) is very similar, the LDOS of each of them is almost the same. On the other hand we can see that in the opposite end of the graphene flake simulated (saturated with H atoms) is the other sublattice (B) the one that has a peak in the LDOS that decreases as we move away from this end. The C atoms of the sublattice A at that end (orange) have a very small LDOS. In C) we can see the LDOS of the Pt atoms bonded to the C atoms. As it happens in the case of the first row of C atoms the LDOS of the 3 Pt atoms (Pt\(_1\) in blue, Pt\(_2\) in green and Pt\(_3\) in yellow) are very similar. We can see the same localized electronic state at \( \sim +0.8 \) eV appearing in the LDOS of the entire row in our system (black solid line) compared to the LDOS of the system without the graphene flake (black dashed line) that does not show any peak at this voltage. D) The addition of the LDOS of all the Pt atoms (left scale) and all the C atoms (right scale).
Fig. S3B shows the LDOS associated with the H-terminated edge: the peak of the LDOS corresponds in this case to the contribution of the atoms of the sublattice B (the LDOS of the nearby atoms of the sublattice A is suppressed) and it decreases as you get away from the first row. The Pt is too far (in all directions) to have any influence on the LDOS of these atoms and thus the peak is centered at \( \sim 0 \) eV \(^3,4\). The peak is narrower than the other in which the interaction with Pt has result also in broadening \(^1\). We have also study how the edge state of the G-Pt boundary extends on the Pt due to strong C-Pt interaction. Fig. S3C show the LDOS projected on the Pt atoms bound to G. Clear traces of the G state at \( \sim 0.8 \) eV are observed on the three Pt atoms, indicating a good metal contact between Pt and G. For reference we also show in Fig. S3D the LDOS of the total Pt and the total C contributions. In the latter we can appreciate both peaks: the one of the step edge and the H-terminated one.

The presence of the G-edge has a profound influence not only for energies around the edge state at \( \sim +0.8 \) eV but also in a wider energy range including the Fermi level. Our calculated LDOS at zero energy shows the same spatial decay found for the main peak (see Fig. S4).

**Figure S4:** Zoom in the LDOS of the different rows of the A sublattice of the graphene flake as they are named in Fig. S3. The decay of the LDOS while you go away from the edge that can be seen in the main peak is also present at the surroundings of the Fermi level.

This spatial decay can also be observed in the STM profile simulations. The dependency with the voltage was analyzed in Fig. 3 where only the decay of the state localized in the sublattice A can be observed. On the other hand in Fig. S5 the decay of the state in the two sublattices can be compared. In this case the simulations are performed at 0.05V at different tip-sample distances, being one of them the same used in Fig. 3 (2.75 Å with Årespect to the uppermost atom in the cell). In this case the decay length of sublattice A is 5.9 Å while the value for the other sublattice is more than double (13.7 Å). Another feature can be observed in Fig. S5: the dependency of the relative height between Pt and C atoms.
with the tip-sample distance. In Fig. 1 can be clearly seen that in the experiments the Pt is brighter than the C. However in the theory this relative brightness totally depends on the tip-sample distance. The larger it is the brighter the Pt with respect to the C. For small distances the C atoms are even brighter than the Pt ones. Of course the first rows of C are always quite bright because of the localized state, but after the first rows the isolated-graphene like profile arises. After that the current starts increasing again even in the sublattice A atoms. That is not because the state is located there, but an effect of the presence of the tip in the calculation which is seeing the wider DOS peaks located in the sublattice B atoms. That is why the peaks in both profiles (red and green of Fig. S5) are in the same spatial position, the position of the sublattice B atoms, and not slightly shifted from each other as should be if the peaks coincide with the position of the atoms of each sublattice.

![Figure S5: STM constant height profile simulations at a bias voltage of 0.05V. Results for tip-surface distances (measured with respect to the uppermost atom in the cell) of 3.00 Å (A),...](image-url)
2.75 Å (B) and 2.50 Å (C) are shown. The different profiles are depicted in D) being in red the profile through the sublattice A atoms of the graphene, in green the profile through the sublattice B atoms and in blue the sublattice through the Pt atoms. The values of the blue profile are similar to the red profile in the Pt region even though the latter does not goes through top Pt sites. Decay lengths are calculated for the states localized in each of the sublattices. From A) to C) the decay lengths for the sublattice A are 5.9 Å, 5.9 Å and 6.1 Å while for sublattice B we have 12.6 Å, 13.7 Å and 16.2 Å.

3.- An alternative configuration of the G-Pt step boundary found in the calculations.

When relaxing the system from different initial configurations of the Pt-G interface, two stable structures were found in the calculations. The main difference between them is the position of the atoms in the edge: while in Fig. 3B the Pt atoms move towards the graphene flake and the C atoms are close to the typical graphene sheet ones, in Fig. S6B the Pt atoms remain almost in bulk positions and the C atoms are the ones moving towards the Pt. Besides, in the first case we have just three Pt atoms bounding with the three C atoms (see Fig. 3A), while, in the second one, we have one Pt-C bond and another Pt atom passivating the other two C atoms (see Fig. S6A). The match between this alternative theoretical structure and the STM experimental images for the ZZ1 and ZZ2 edges is clearly worse (see Fig. S6C) than for the structure proposed in the main text. The energy of the two models is very similar although the configuration that has a better agreement with the experiments has lower energy. The energy difference between both models is ~75 meV.
**Figure S6:** A) and B) Ball-and-stick model of another stable atomic configuration for the contact between graphene and a Pt(111) step edge calculated with DFT. Distance bonds, A), and out of plane displacement, B), of the carbon edge atoms are indicated (in this case the Pt atoms remain close to bulk positions). C1) and C2) Overlay of the relaxed structure with the best-fit STM images. It can be seen that the fit is worse than in the other configuration. Areas where there is a clear conflict between the image and the structure are highlighted. Circled in green there are some areas showing electronic density in the experimental STM image while regarding the theoretical model there should be no atoms or bonds there. The carbon rings bordered by the yellow dashed line show a considerable mismatch between the theory and the experimental data. D) Local density of states (LDOS) of the graphene atoms for the 1st (red), 2nd (blue), 3rd (green) and 4th (pink) row of carbon atoms belonging to the same sublattice and for the 1st (orange) one of the other sublattice. A localized electronic state at an energy of ~+0.8 eV (above $E_F$) can be observed only in one sublattice, although is not compared to the other step.
model. E) Local density of states (LDOS) of the Pt atoms at the edge of the step that are bond to the carbon atoms (solid red) versus the same atoms in a step without a graphene flake attached (dashed red). We can no longer see the localized electronic state in the Pt LDOS.

**Figure S7:** A), B) and C) LDOS of the atoms depicted in the ball-and-stick model corresponding to the alternative atomic configuration shown in Fig. S3. In A) we can see that the LDOS of the C atoms in sublattice A (the sublattice to which the C atoms bonded to the Pt atoms belong) decreases as we get away from the step. As the chemical environment of the 3 carbon atoms of the step edge (1A1, 1A2 and 1A3) is different, the LDOS of each atom varies. On the other hand we can see that in the opposite end of the graphene flake simulated (saturated with H atoms) is the other sublattice (B) the one that has a peak in the LDOS that decreases as we move away from this end. The C atoms of the other sublattice at that end (orange) have a very small LDOS. In C) we can see the LDOS of the 3 Pt atoms bonded to the C atoms (Pt1, Pt2 and Pt3) the LDOS of the full row (Pt1 + Pt2 + Pt3) in solid black and the comparison with the calculation of the same Pt configuration without the G flake. D) shows addition of the LDOS of all the Pt atoms (left scale) and all the carbon atoms (right scale) compared to the total DOS (left scale) of the system.

The structural differences reflect in changes in the electronic properties (Figs. S6D, S6E and S7). Due to the stronger C-Pt interaction in this alternative structure, the peak in the LDOS projected on the C atoms at the step edge (see Fig. S6D) is wider and lower in
energy. We can no longer see a clear trace of this state in the LDOS projected on the Pt edge atoms (Figs. S6E and S7C). Differences in the bonding configuration of the carbon atoms show up in the corresponding LDOS (Fig. S7A), at variance with the identical behavior found for the structure discussed in the main text (Fig. S3A). As expected, the behavior of the other border of the flake saturated with H atoms (see Fig. S7B) is very similar in both models. Fig. S7D compares the total LDOS of the Pt with the total C LDOS (in a different scale). In spite of the quantitative differences described above, the electronic states associated with the two structures for the G-Pt edge share the same spatial localization properties: they are confined in one of the graphene sublattices and decay very rapidly when moving away from the edge.

4.- Crystalline borders and their relation with Moiré patterns.

Analogously to the standard notation used for nanotubes, we can assign the crystallographic stable interfaces with a couple of chiral vectors (defining a chiral vector as for nanotubes: two integers, n and m, denoting the number of unit vectors along two directions in the surface crystal lattice) one for Pt and other for the graphene (edge). With this notation, the ZZ1 step can be denoted as \((1,2)_P (3,0)_G\) and ZZ2 as \((-2,3)_P (0,3)_G\). Every one of those pairs of vectors represent a possible Moiré, however only a few of all the possible combinations of these pairs will be stable. The phenomenological model presented in ref. 23 indicates that, in a first approximation, the existing Moirés are the those that minimize the strain. However, not only strain plays a role. In the case of border-like edges the energetic of the interface is also important.

The study of the crystallographic parameters of the Moiré superstructures by STM images is a difficult task, because simultaneous atomic resolution in both graphene and metal surface is required. It is important to notice that usually, STM images of graphene Moirés lack of any information about the commensurability of the superstructures. Thus, even though we could say that near the graphene-Pt border the structure is commensurate, nothing can be said about zones far apart from the edges, as the accumulation of mismatch will either disrupt the long range order of the Moiré superstructure or generate defects, such as ripples, vacancies, or domes. Fig. S8A shows a small epitaxial graphene island grown attached to a Pt step. As usual, it appears with part of its area inside the upper Pt terrace, indicating mass transport. Looking carefully to the lower left part of the image we see a 6x3nm² graphene nanobubble.
Figure S8: A) STM image showing a graphene island, a nanobubble can be seen in the lower part. 17x17 nm², 1.9nA, 100mV. B) Detail of a crystalline edge with a graphene zigzag termination (ZZ3), 10x10 nm², 3.94nA, 10mV. C) Detail of a crystalline edge with a graphene zigzag termination (ZZ4), 10x10 nm², 3.94nA, 10mV.

Fig. S8 shows STM images of 3 border-like atomically resolved crystalline edges giving rise to different Moiré superstructures. Figs. S8B and S8C correspond to Moiré patches of ξG/Pt(111) for ZZ3 and μG/Pt(111) for ZZ4. Using the vector notation, these edges correspond to these pairs of chiral vectors: (8,0)ₚ (9,0)ₔ for ZZ3 and (7,1)ₚ (8,1)ₔ for ZZ4. Both involve large number of atoms, and they escape the capabilities of regular DFT calculations. However, a visual inspection of these edges (and others not shown) provides us with some general ideas about their atomic structures. At first sight, it seems that in all crystallographic border-like edges, the graphene islands end up in a zigzag configuration. Hence, the Pt atoms at the edge absorb the largest part of the strain and reconstruct to adopt the structure that yields the maximum possible graphene ending in a zigzag arrangement.

Fig. S9 illustrates this point. In this figure we have schematically reproduced edges similar to ZZ3 and ZZ4 of Fig. S8, another hypothetical ZZ edge (called ZZX) and an amorphous edge. Graphene prefers to stabilize its edges by maximizing the number of the energetically favored- zigzag edges. The amount of the armchair regions needed in the interface (marked in the figure by red ovals) depends on the angle between G and Pt (and therefore the angle between the Moiré and the Pt). We observe that the more often found graphene edges are those which have maximized the number of zigzag unit cells versus the armchair ones, thus, in Fig. S9, ZZ4 will be preferred versus the A edge, although both are rotated of 6⁰. The A termination is exclusively observed in defective regions of the G-Pt edge, like A2 in Fig. 2.
**Figure S9:** Schematic model of the preferred graphene termination of border-like at the G-metal interface. The bluish side corresponds to the Pt region, with crystallographic direction, indicated by a blue arrow, along the horizontal (except for ZZ3, where it is along the vertical). The graphene tends to adopt zigzag configurations by minimizing the number of armchair unit cells for a given crystallographic angle with respect to the Pt surface. Armchair configurations are marked with red ovals.
The fact that the system tends to maximize the number of straight regions of zigzag termination intercalating single armchair unit cells leads to an interesting secondary effect. The Pt edge directions are normally parallel to the apparent angle of the Moiré (see Fig. S10). This means that if we ignore the local relaxation of individual Pt atoms, the G-Pt edge is not parallel to the crystallographic directions of the substrate, but to the direction of the Moiré superstructure. This can be very useful for determination and assignment of the structure of unknown rotational domains with large scale STM or AFM images, even when the periodicity of the Moiré is not resolved. However, one has to be very careful if using this method for Moiré determination, as there are normally more than one Moiré with a similar apparent angle, i.e. there are more than one rotational domains with different crystallographic angles yielding Moirés with different atomic structure but the same apparent angle.

The case of the edges between $(\sqrt{7}\times\sqrt{7})R19^\circ$ graphene and Pt described in the main text (ZZ1 and ZZ2) present the –rather rare- particularity that the crystallographic directions of Moiré and graphene are the same, i.e. $19^\circ$, and thus it wrongly seems that the edges are parallel to the crystallographic directions of graphene. The case of ZZ4 (Fig. S8C), or the island shown in Fig. S8A, are the rule. The edges run parallel to the Moiré crystallographic directions. In Fig. S10 we see more examples of these behavior: zigzag G-Pt edges in which the Pt crystallographic border runs parallel to the Moiré apparent angle.

ZZ3 seems to be different, as the Moiré runs perpendicular to the edge. However, this Moiré corresponds to the case where the angle between the graphene and the Pt is 0 degrees, and then the normal edge would be exclusively formed by armchair termination, which is energetically unfavorable. This edge adopts the structure shown in Fig. S9 ZZ3 diagram. It maximizes the zigzag graphene unit cells at the metal interface by creating the corner-like structures that can be observed in the experiments, see Fig. S8B.
Figure S10: STM images showing graphene edges running parallel to their Moiré apparent angles. Nanobubble or graphene folds can be seen in the islands A) 30x30nm², 2nA, -100mV. B) 30x25nm², 1nA, 50mV.

In conclusion, we have shown that it exists a relationship between the Moiré and the crystallographic border-like edges that may be an important factor in the determination of the orientations of graphene epitaxially grown on Pt(111). Although other kinetic effects, such as the formation of defects or folds due to the shrinking occurring during the cooling-down after the growth annealing (due to the difference between the thermal coefficients of graphene and the substrate) can also play a role.

We usually observe graphene domains embedded within the upper Pt terrace, indicating mass transport within the upper terraces, see for instance Fig. S8A. However we do not know which is the real growth mechanism as we only are able to study the final stage of the graphene CVD growth process. In principle, two possibilities can be envisaged. First, graphene nucleation on the upper terrace undergoes etching of some Pt atoms within this terrace. Thus, the graphene domains would grow "going into" the Pt step. The second possible explanation implies severe mass transport on the substrate surface due to the high temperatures needed during growth. The diffusion of Pt atoms might occur both along the step-edges and on within the terraces. In this case the graphene would nucleate into the described G-Pt edge boundaries and the diffusing Pt atoms would embrace the graphene seed, as can be seen in Fig. 1A.
We have never observed graphene growing on the terraces situated above the crystalline domains of the G-Pt(111) interface. This is contrary to what happens in G/Ir(111) where this mechanism has been observed \(^{23}\).

In some cases, when the size of the terraces is big enough, we see that large graphene domains can grow over the Pt step edges situated on the lower terrace. Thus, graphene grows as a sheath covering anything (in this case step edges) that it finds in its way. In these cases we do not normally observe any change of the Moiré parameters.

**5.- Possible design of an hypothetical dual channel nanoribbon.**

Taking into account that we have shown that there are electronic states confined in every one of the graphene sublattices, we can take advantage to transport independently current through out the edges without mixing both signals. If a graphene flake is contacted with two different border-like edges as indicated in Fig. S11, these atomically precise nano-leads will excite respectively every one of the two graphene sublattices. This proposal indicates the possibility of two-ways atomically controlled transport via localized electronic states in every one of the graphene sublattices.

![Figure S11: sketch showing a possible two-channel conductor. This proposal takes profit of the sublattice states that appear at the G-Pt interface through the contact of two independent electrodes exciting the different channels.](image)

The possibility of combining the spin, valley, and sublattice quantum numbers in the same device opens new paradigms in the electronic design of graphene-based nanoelectronics.
6.-COMPLETE LIST OF REFERENCES


