Published in final edited form as:

ACS Nano. 2016 December 27; 10(12): 10698–10705. doi:10.1021/acsnano.6b05823.

Tomography of a Probe Potential Using Atomic Sensors on Graphene

Jonathan Wyrick^{1,*}, Fabian D. Natterer¹, Yue Zhao^{1,2,3}, Kenji Watanabe⁴, Takashi Taniguchi⁴, William G. Cullen¹, Nikolai B. Zhitenev¹, and Joseph A. Stroscio^{1,*}

¹Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

²Maryland NanoCenter, University of Maryland, College Park, MD 20742, USA

³Department of Physics, South University of Science and Technology of China, Shenzhen, China

⁴Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044 JAPAN

Abstract

Our ability to access and explore the quantum world has been greatly advanced by the power of atomic manipulation and local spectroscopy with scanning tunneling and atomic force microscopes, where the key technique is the use of atomically sharp probe tips to interact with an underlying substrate. Here we employ atomic manipulation to modify and to quantify the interaction between the probe and the system under study that can strongly affect any measurement in low charge density systems, such as graphene. We transfer Co atoms from a graphene surface onto a probe tip to change and control the probe's physical structure, enabling us to modify the induced potential at a graphene surface. We utilize single Co atoms on a graphene field-effect device as atomic scale sensors to quantitatively map the modified potential exerted by the scanning probe over the whole relevant spatial and energy range.

Graphical abstract

*Corresponding Authors: jonathan.wyrick@nist.gov, joseph.stroscio@nist.gov.

The authors declare no competing financial interests.

Keywords

STM; Graphene; Cobalt; Atomic Manipulation; Defect Charging; Probe Potential; Tip-induced Band Bending; Screening

Atomic manipulation and direct *in situ* measurement by scanning probes has enabled the design of artificial nanostructures and led to a wealth of scientific discoveries.^{1–16} The long-range electrostatic interaction between a scanning probe and a sample has significant consequences and can provide unique measurement and manipulation capabilities. For example, the potential of a scanning tunneling microscope (STM) probe tip locally top gates graphene and other low carrier density materials, due to insufficient screening of the electric field in the STM junction at low carrier densities; this phenomenon is often referred to as tip-induced band bending because of its effect on the local electronic structure of a material. As a result, the local doping under the tip can be inverted with respect to the background doping to create a ring-like pn junction that supports whispering gallery mode resonances.¹⁷ The probe potential can also modulate the charge state of an adsorbate or impurity, as demonstrated in semiconductors and graphene.^{18–23} Conversely, we can use an impurity, *e.g.* an adatom interacting with the low-density two-dimensional graphene carriers, as an atomic sensor of the probe action. In the present work, we demonstrate the use of such an atomic sensor to map the induced charge in the material and the potential landscape of the probe tip on the atomic scale.

RESULTS AND DISCUSSION

Clustering of Co atoms on the Graphene Surface

Our experiment utilizes Co atoms deposited on a back gated field-effect graphene device in ultra-high vacuum (UHV) and an electro-polished Ir probe tip (see methods). Co atoms are easily manipulated on the graphene surface by an STM probe and can be brought together to form larger clusters (Figure 1). Scanning tunneling microscopy (STM) topography images taken at various locations on the sample show protrusions with different apparent heights and suggest the presence of single Co atoms and clusters on the graphene surface. The Co structures can be characterized by their measured heights, widths, and by their interaction with the probe tip (some atoms were easily disturbed by the scanning conditions used while others were not).

The graph of Figure 1a illustrates the variety of observed adatom widths and heights as measured in topography (Figure 1b) under the fixed conditions: back gate voltage, $V_g = 40$ V, sample bias, $V_g = 300$ mV, setpoint current, $I = 500$ fA. Taking the cluster of points around 0.3 nm to 0.4 nm to correspond to single Co atoms in Figure 1a, suggests that most of the species on the surface are monomers, dimers, and trimers of Co. We attribute the aggregation of Co atoms into larger clusters to their movement in the presence of the tip-induced electric field, *i.e.*, we frequently encountered cluster formation between consecutive images (one atom disappeared while another increased in apparent height). Figure 1c-d shows a case where this occurred during a lateral manipulation event. The STM tip was positioned above the central atom while the current, sample bias, and back gate were ramped

to ($I=400\text{pA}$, $V_b=50\text{mV}$, $V_g=-40\text{V}$) before the tip was moved along the path indicated by the red arrow. The resultant topography scan in Figure 1d shows that while the central atom was moved, a nearby cluster also changed in the process. The inadvertently formed cluster indicated by the green arrow of Figure 1d is larger and wider than the two species that were combined, but otherwise appears as a single unit. Based on frequent observations of this behavior, even during regular topography scans, we suggest that the different cluster sizes are primarily due to cluster formation while scanning the surface. Using minimal scanning conditions (*e.g.* 900fA , or 500fA setpoint currents) was therefore necessary to avoid moving the Co atoms unintentionally. While lateral manipulation was facile, we found that precise manipulation parameters varied from attempt to attempt and therefore proved non-viable. Additionally, unintentional vertical manipulation, where atoms can be picked up off of the surface, could also occur if low setpoints were not used; however, in contrast to lateral manipulation, controlled vertical manipulation was highly repeatable and used to modify the tip structure, as described in this study.

Using Co Atoms and Clusters as Sensors of the Probe-Potential

The charge state of the Co atoms and clusters can also be manipulated by the probe tip and back gate potentials, as demonstrated in previous studies.^{20,21} Figure 2 shows how we control the charge occupation of Co atoms (Figure 2a) by the probe tip potential and outlines the basic physics involved in the process. The three main variables influencing the atom charge state are the tip position, sample tunneling bias V_b , and the graphene device back gate potential V_g . The signature of the change in impurity charge state is a ring of peaked intensity in a spatial image of the differential tunneling conductance, dI/dV_b , as shown in Figure 2b. At large distances from the impurity, in region *I*, the tip potential is too weak to ionize the impurity. In region *II*, however, the impurity is ionized by the strength of the tip potential (Figure 2c). The lateral position of the ring thus coincides with the boundary between region *I* and *II* with the tip at position, r_T , producing a potential at the adatom location, r_a , sufficient enough to move the hybridized Co energy level through the Fermi level. At this spatial position, the electron occupancy is suddenly changed, as illustrated in Figure 2d. The change in the impurity charge state also modifies the local potential landscape around the impurity. In the present case, this shifts the local electronic structure relative to the Fermi level, producing a rapid increase in the total integrated local density of states (LDOS) underneath the tip, yielding a subsequent increase in tunneling current, and consequently a peak in the derivative spectra. Accordingly, the charging ring contours are a measure of the extent of the induced potential and screening charge in graphene.

The appearance of the charging ring for a given (V_b , V_g) can be deduced from a map of dI/dV_b as a function of (V_b , V_g), a so-called gate map.^{24,25} Figure 2e,f show a gate map recorded on and off a Co cluster, respectively. The Co resonant level, E_0 , disperses following the Dirac point, E_D , since it is tied to the graphene band structure. In contrast, the charging peak corresponding to the rings in Figure 2b, occurs at the *I/II* boundary and appears as a line in the “perpendicular” direction, as seen in previous work,²⁰ following the dispersion expected from a simple capacitive gating by the probe tip. We can follow the charging process if we focus on a given tunneling bias, for example, $V_b = 50\text{ mV}$. At large gate voltages, the tip potential is given by the conditions in region *I*, where the tunneling bias is

insufficient to raise the impurity level to E_F (e.g. the first scenario illustrated in Figure 2d). As the gate voltage is reduced, the charging line at the boundary III will be reached (the second scenario illustrated in Figure 2d) where the impurity will be charged. For even smaller gate voltages the impurity will remain charged at $V_b = 50$ mV (the third scenario illustrated in Figure 2d). Therefore, leaving the probe tip at a fixed position in space while reducing the gate voltage causes the system to change in such a way the tip goes from being in region I to being in region II; this means that the radius of the ring must have increased to encompass the tip position during this process. The ring radius will also increase with an increase in sample bias, as the tip does not have to be as close to the impurity to ionize it at a larger bias. These general trends in ring size and shape become more complex in the case of a multi-faceted tip potential, as shown below.

Modification of the Probe Tip

Figure 3 illustrates the modification of the probe tip using vertical atom manipulation. Figure 3a shows an initial image of a distribution of Co atoms on graphene using a probe tip with multiple apices, resulting in a complex image of the tip structure at each atom on the surface. In this case the Co adatoms are “sharper” than the tip and are imaging the tip structure. A point inversion of one of the Co cluster images yields an approximate shape of the actual tip termination, as shown in Figure 3b. We modify the structure of the probe tip by attaching Co atoms from the surface onto the tip to sharpen the tunneling apex, as illustrated by the red arrow in Figure 3a,c indicating where a Co cluster has been removed from the substrate by such a procedure. The thereby constructed tip is atomically sharp and can image individual Co atoms and clusters without artifacts, as seen by the image recorded at the same location with the modified tip. An interesting question arises as to what extent does the transferred Co atom modify the probe tip potential. Our results show that while the transferred Co atom makes the tip sharp for imaging, it still retains the initial structure of Figure 3b, producing an asymmetric potential profile. The additional Co atom also lowers the effective potential seen by graphene, producing a modulation in the potential landscape, as schematically indicated in Figure 3d. This effect is determined both by density functional theory modeling as well as by direct measurement, as detailed in the following two subsections.

Density Functional Theory Modeling

In order to investigate what effect a Co atom adsorbed onto an Ir tip should have on the potential that it presents to the graphene substrate, we performed a spin-polarized density functional theory (DFT) calculation for two slab models: one consisting of a Co atom on an Ir slab, and the other consisting of an Ir atom on an Ir slab (Figure 4).

Both systems show a lowering of the work function of the Ir slab due to the under-coordination of the adsorbed species; however, the adsorbed Co atom lowers the work function 1.57 eV more than its Ir counterpart. A lowering of the work function would also appear for a bulk Co tip, since it has a lower work function than Ir.²⁶ This means that regardless of the precise shape of the tip, the addition of a Co atom will locally reduce the work function, resulting in a locally weaker induced potential felt by graphene below the tip.

Experimental Measurement of Modified Tip-Potential

To measure the graphene screening charge induced by the modified tip potential, we record spatial dI/dV_b images as a function of gate voltage, as shown in Figure 5b–f, corresponding to the topographic image in Figure 5a. Only the central cluster (red) is changing its charge state for the particular range of gate voltage shown. The charging rings associated with this cluster appear at two locations in Figure 5b: surrounding the region I label, and as a contracted ring indicated by the black arrow. We observe a series of complex charging rings when we lower V_g in steps of 1.5 V in Figure 5b to Figure 5f. Two features stand out; one is the “U” shape of the charging contour in Figure 5d, which does not completely encompass the charged atom, and the second feature is the appearance of two rings in Figure 5e, *i.e.* the small ring around the central cluster and the large one, which is only partially observed. We show that these charging contours correspond to the induced potential from the multiple tip structure in Figure 3b.

In the analysis of the tip-induced potential it is convenient to use two coordinate systems: one for positions on the sample where coordinates are labeled with subscripted $\mathbf{r}$ position vectors, and one for the tip where coordinates are labeled with subscripted $\mathbf{x}$ position vectors ($\mathbf{x}_0$ being the location of the tunneling apex and chosen to be the origin of the tip system). These labels are included in Figures 2, 3, and 5. The transformation from a sample coordinate, $\mathbf{r}$, to a tip coordinate, $\mathbf{x}$, is given by $\mathbf{x} = \mathbf{r} - \mathbf{r}_T$.

In the following we present a model that allows us to fit the collection of charging contour data as a function of gate voltage. Assuming a tip shape with multiple adatom locations as deduced from Figure 3b, we modify a Thomas-Fermi screening model for the probe tip interacting with graphene described previously¹⁷ in order to include the effects of atoms adsorbed on the tip. The modified model gives the total induced potential $U'(\mathbf{r})$ as (see methods for the full derivation):

$$\frac{e(V_b - V_b^0) - U'}{4\pi e d_T} - \epsilon \frac{V_g - V_g^0}{4\pi d_g} + \Delta\rho_{Co} = \frac{e \operatorname{sgn}(U') U'^2}{\pi (\hbar v_F)^2}, \quad (1)$$

where intrinsic doping of the sample is taken into account by inclusion of the V_g^0 term, the work-function difference between tip and sample ($\phi_{tip} - \phi_{sample}$) at infinite separation) is accounted for by the V_b^0 term, and the dielectric constant is taken as $\epsilon = 5$. Here e is the elementary charge (taken to be positive), $\hbar$ is the reduced Plank constant, and $v_F = 10^6$ m/s is the Fermi velocity in graphene. The plate separation for the back gate is $d_g = 300$ nm. The Ir probe tip is approximated by an elliptic paraboloid and is incorporated into the model as a capacitor plate with separation, d_T at each point along the paraboloid, which is a function of the distance to the Ir apex at $\mathbf{x}_{Ir}$.

We introduce a term to account for the charge densities associated with adatoms on the tip at positions $\mathbf{x}_i$ as,

$$\Delta\rho_{Co} = \sum_i A_i \exp\left(-\frac{|\mathbf{x}-\mathbf{x}_i|^2}{2\sigma_i^2}\right). \quad (2)$$

That is, each of the features identified in the probe tip structure of Figure 3b is assumed to induce an additive charge of a simple Gaussian form. The index, i , runs over the three tip features while the coordinate $\mathbf{x} = \mathbf{r} - \mathbf{r}_T$ is the sample coordinate converted into the tip coordinate system.

The elliptic paraboloid of the original Ir tip is specified by a height of z_0 above the graphene, radius of curvature along the major axis of $R_{\parallel}$, and radius of curvature perpendicular to the major axis of $R_{\perp}$:

$$d_T = z_0 + \Delta z(\mathbf{r}_T) + \frac{|\mathbf{x}-\mathbf{x}_{Ir}|_{\parallel}^2}{2R_{\parallel}} + \frac{|\mathbf{x}-\mathbf{x}_{Ir}|_{\perp}^2}{2R_{\perp}}. \quad (3)$$

Since the tip-induced potential depends on the tip-sample distance, it can be affected by passing over an atom while the tunneling feedback loop is kept on during the dI/dV_b closed-loop maps. For this reason, the tip-sample separation of eq 3 includes an additional term, $z(\mathbf{r}_T)$, which is the topography of the sample underneath the tunneling apex so that when the tip passes over an atom, it is considered to be farther away from the graphene.

The condition that a given point, $\mathbf{r}_t$, in a dI/dV_b map lies on a charging ring is that the tip-induced potential at the location of the charging cluster must shift E_0 to E_F . The condition is then: $U'(\mathbf{r}_a) + E_0 = 0$, where $U'(\mathbf{r}_a)$ is found by algebraically rearranging eq 1 to solve for U' . We use this condition to perform a least-squares fit of the model to the charging ring contours in the dI/dV_b maps of Figure 5, shown collectively as a contour map in Figure 6a. The resulting tip-induced potential landscape is shown on a $15 \text{ nm} \times 15 \text{ nm}$ contour map in Figure 6b centered at the tunneling apex for the case of $V_g = 10 \text{ V}$. The green, blue, and violet rings show the respective Gaussian widths, $\sigma = (1.2 \pm 0.3, 2.1 \pm 0.1, 2.1 \pm 0.3) \text{ nm}$, applied to the positions $\mathbf{x}_0, \mathbf{x}_1$, and $\mathbf{x}_2$, indicated by the same colors in Figure 3b, while the Gaussian amplitudes are, $A = (-0.7 \pm 0.3, -3.3 \pm 0.7, 2.3 \pm 0.3) \times 10^{-9} \text{ C nm}^{-2}$, respectively.²⁷ The first two amplitudes lead to a decrease in potential from the adsorption of Co onto the tip, in agreement with the density functional theory calculations, while the last value increases the local potential. This could be due to native Ir atoms or adsorbed H_2 onto the tip, which can increase the local potential.¹⁷ The Ir probe tip is centered at $\mathbf{x}_{Ir} = (1.4 \pm 0.3, 1.9 \pm 0.2) \text{ nm}$ and separated from the graphene by a height of $z_0 = (0.65 \pm 0.08) \text{ nm}$, a contour of which is represented by the gray ellipse.²⁷ This fit results in a value of the Co resonance level $E_0 = (122 \pm 3) \text{ meV}$,²⁷ which agrees favorably with the gate map in Figure 2e.

As a check of the model we simulate the charging threshold contours, using the parameters found above. The charging rings of each V_g from Figure 6a are reproduced as a contour map in Figure 6c. Figure 6c is generated by setting V_g to each experimental value and extracting

the contour of $U'(\mathbf{r}_a) = -E_0$ in each case (with $\mathbf{r}_T$ spanning a $15 \text{ nm} \times 15 \text{ nm}$ scan region centered on the charging cluster). The model compares favorably to the experiment and reproduces all of the qualitative features of the experimental data. We can therefore extract the probe tip structure depicted in Figure 6b in which Co atoms and clusters adsorbed onto the tip create local variations in the tip-induced potential landscape. In particular the model reproduces the complex multiple charging ring contours, including the small charging ring in Figure 5e,f, which decreases in size as we decrease gate voltage, as opposed to the larger ring which increases in size, as seen for the larger charging contour in Figure 5e,f. This directly results from multiple potential minima of the probe tip, and is captured by the simulation results.

Dependence of Potential on Back Gate and Tip Height

Figure 7 shows the calculated tip-induced potentials shifted by the constant E_0 for each of the back gate voltages used experimentally. For a fixed tip position (Figure 7a–e) the shifted potential is given by $U'(\mathbf{r}, \mathbf{r}_T = \mathbf{r}_T^0, V_b = 300 \text{ mV}, V_g) + E_0$, and for a scanning tip (Figure 7f–j) the shifted potential is given by $U'(\mathbf{r} = \mathbf{r}_a, \mathbf{r}_T, V_b = 300 \text{ mV}, V_g) + E_0$. Here, $\mathbf{r}_T^0$ is defined to be the center of each potential depicted in Figure 7a–e, a fixed position on a clean region of the graphene surface (*i.e.* there are no Co atoms nearby). The measured tip-induced potential contours from Figure 6a are also included for comparison (Figure 7k).

The contour maps of Figure 7a–e show that there is variation in the tip-induced potential, for a fixed tip position, as the back gate is adjusted. For example, the two maxima appear sharper at a back gate voltage of $V_g = 4 \text{ V}$ than they do at $V_g = 10 \text{ V}$. The intersection of the potential energy surface with the blue plane indicates the contour that can be experimentally measured by imaging a charging ring (*i.e.* $U' + E_0 = 0$). Regions I and II are distinguished as regions of the tip-induced potential that lie above the blue plane and below it respectively (these regions are explicitly marked in Figure 7f). The model fit allows the full potential profile to be obtained for a particular gate voltage (Figure 7a–e), which cannot be obtained by simply measuring the charging ring contours at a particular V_g since only one contour is experimentally accessible at fixed V_g .

Figure 7f–j shows the potential induced in graphene at the location of the central cluster as the tip is scanned over the surface. The results demonstrate that the topography due to the presence of adatoms also plays a role in determining the measured contours. In particular, secondary charging rings appear around adatoms, and have the opposite V_g dependence compared to the outer primary charging ring during closed-loop spatial dI/dV_b maps (*e.g.* the shrinking circle that appears around the central Co cluster in Figure 5e–f).

Reproducibility

The multi-apex configurations of the tip are common and reproducible. We repeatedly changed the tip configurations on the nearby gold electrode -- used to supply the sample bias to the graphene -- by voltage pulses that modified the tip apex and subsequently examined different locations on graphene. The series of dI/dV_b maps in Figure 8 after such a tip treatment on the Au electrode now show charging rings associated with the three circled clusters in the topography scan of Figure 8a. As we vary the gate voltage, only the charging

ring associated with the top-most indicated cluster is visible in Figure 8b,c, then in Figure 8d the ring associated with the left-most cluster appears. Finally, in Figure 8g the ring associated with the right-most cluster is visible at the lowest gate voltage. As was the case for the tip configuration of Figure 5, the charging rings begin off-center from their associated charging species. However, in the present case the Ir apex lies above (in the y -direction, indicated in Figure 8b) the tunneling Co apex (*i.e.* the charging rings start below each cluster), rather than to the right, indicating that the tip configuration has been changed. This basic modification procedure was repeated multiple times, and in each case charging rings could be seen to originate off-center from the charging cluster, with accompanying variations in the orientation and geometry of the ring itself.

CONCLUSION

In summary, we have shown that the charge state of single atomic sensors can be used to perform tomography of the graphene screening charge density and the potential structure of a scanning probe tip on an atomic scale. Utilizing such atomic sensors opens up the possibility of engineering tip-induced potentials by attaching selected atoms, and subsequently using tomography of charging rings to map out modifications to the probe and induced potential: just as a sufficiently sharp feature on the sample can be used to generate an inverted image of tip topography, a charging feature on the sample can be used to generate a contour image of the tip potential. The resulting measurement of the screening of this potential can be used to determine the physics of electron interactions in low carrier density materials.

METHODS

Experimental

The experiments were performed on a graphene/hexagonal boron nitride device with a doped Si back gate, as described previously¹⁷. Measurements were carried out at 4.3 K with a custom-built low temperature STM, operating at a base pressure better than $5 \times \text{hPa}$ ¹⁵. The Ir probe tip was prepared by electrochemical polishing, and then heating and electron field evaporation in a field-ion microscope in the UHV chamber. Cobalt adatoms were deposited from a high-purity Co rod with an electron-beam evaporator onto the sample held at 6.7 K, and then cooled to 4.3 K for measurements. Spectroscopic measurements employed closed-loop differential conductance (dI/dV_b) mapping at a fixed sample bias of $V_b = 300 \text{ mV}$ by adding a sinusoidal voltage with root-mean-square amplitude in the range of 3 mV to 10 mV at 356 Hz, while varying the back gate (V_g) between scans. The dI/dV_b signals were measured with a lock-in amplifier using a time constant of 200 ms. Due to the ease with which Co atoms could be transferred onto the tip, we performed all topography scans with a low current setpoint of $I = 500 \text{ fA}$ (when not simultaneously recording dI/dV_b), and all scanning dI/dV_b measurements with a setpoint current of $I = 900 \text{ fA}$. During measurements where the tip was fixed in position we found that it was possible to use higher setpoint values at a lower sample bias of $V_b = 100 \text{ mV}$: $I = 50 \text{ pA}$ for fixed point spectroscopy above a cluster, and $I = 70 \text{ pA}$ away from the cluster.

Derivation of Thomas-Fermi Screening Model for Tip-induced Potential

We use the Thomas-Fermi screening model to relate the induced charge density, $\rho(\mathbf{r})$, in the presence of an external potential, as a function of the number density, $n_0(\mu)$, by applying appropriate shifts of the chemical potential, μ as,²⁸

$$\begin{aligned}\Delta\rho(\mathbf{r}) &= -e [n_0(\mu - U(\mathbf{r})) - n_0(\mu)] \\ &= -e \frac{\text{sgn}(\mu - U(\mathbf{r})) (\mu - U(\mathbf{r}))^2}{\pi(\hbar v_F)^2} + e \frac{\text{sgn}(\mu) \mu^2}{\pi(\hbar v_F)^2},\end{aligned}\quad (4)$$

where $U(\mathbf{r})$ is the total resulting potential, and $n_0(\mu)$ for graphene has been substituted on the second line of eq 4.

To model the effect of the back gate, we first consider the graphene sheet as a plate in a parallel plate capacitor with an applied voltage of V_g while ignoring the presence of the tip (*i.e.* solving for the behavior far away from the tip). In this case, charging of the capacitor plates causes the chemical potential to shift; the chemical potential is the induced potential, $\mu = U$. Substituting this into the right-hand side of eq 4 along with the expression for the induced charge on the capacitor plates on the left-hand side yields:

$$\varepsilon \frac{V_g - V_g^0}{4\pi d_g} = e \frac{\text{sgn}(\mu) \mu^2}{\pi(\hbar v_F)^2}, \quad (5)$$

where, as noted for eq 1, the plate separation is given by d_g .

In the present experiment, as is often the case in STM studies, it is most convenient to consider the induced potential relative to the chemical potential, so we define the quantity $U' = U - \mu$. The top-gating effect of the tip (due to the bias V_b) is also assumed to take the form of a charged parallel plate capacitor whose plate separation, d_T , varies as a function of position on the sample relative to the tip. Because the tip has been modified by attaching Co atoms, we consider the induced charge density to additionally depend on a non-capacitor term, ρ_{Co} . Substituting the induced charge density terms into the left-hand side of eq. 4 and using the relationship of eq 5 yields eq 1.

DFT Modeling

Calculations were performed on a real space grid^{29–31} with a grid spacing of 12.5 pm and a k -point mesh of $8 \times 8 \times 1$ centered about Γ , using the Perdew-Burke-Ernzerhof generalized gradient approximation³² for the exchange-correlation functional. The model system consisted of 3 layers of Ir atoms with 2×2 surface unit cells and a supercell height of 2.25 nm. The top two layers of the slab and the adsorbed Co atom were allowed to relax to within a tolerance of 0.5 eV/nm. Dipole corrections along the z -direction were employed in order to extract the work function on either side of the slab.

Acknowledgments

J.W. acknowledges support from the National Research Council Fellowship. F. D. N. greatly appreciates support from the Swiss National Science Foundation under project numbers 158468. Y. Z. acknowledges support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Grant No. 70NANB10H193, through the University of Maryland. J.W., K.W., T.T., W.C., N.Z., and J.S. are supported through their respective institutions. We would like to thank Steve Blankenship, Glen Holland, and Alan Band for technical assistance and Mark Stiles for valuable comments.

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Figure 1.

(a) Survey of apparent heights and widths of adsorbed Co atoms and clusters from STM topography measurements. (b) A subset of the images used to generate the graph in (a). (c) Topography scan before performing lateral manipulation (red arrow) on the central atom/cluster. (d) Topography scan after manipulation showing that multiple atoms (red, green and yellow arrows) moved during the procedure and subsequent post imaging. Manipulation parameters were 400 pA and 50 mV, corresponding to a junction resistance of 125 M Ω .

Figure 2. Controlling of Co adatom and cluster charge state

(a) STM topography images of a larger Co cluster (left) and a smaller Co cluster (right). (b) closed-loop dI/dV_b spatial image of the Co clusters in (a) showing charging rings (sharp peaks in the dI/dV_b signal) surrounding the Co clusters. Tunneling setpoints: closed-loop map at $I = 900$ fA, $V_b = 300$ mV, $V_g = -0.75$ V. (c,d) Schematics for the charge state control by the tip potential. The tip-induced charging rings occur when an adsorbed atom (red circle in (c)) experiences a tip potential large enough to pull a Co resonance energy level through the Fermi level, thereby changing its electron occupation, as indicated in (d). (e,f) dI/dV_b gate maps obtained on a single Co cluster, (e), and off the cluster, (f). The charging ring appears at the appropriate combination of (V_b, V_g) , which is seen as a line marked I/II in these maps. The Co resonance level is labeled E_0 , and the Dirac point E_D is marked by the dashed red curve in (e). The tip of the red arrow shows the bias voltage in region I needed to empty the Co level and to charge the Co atom, while the tip of white arrow indicates the bias voltage in region II required to pull the resonance level below E_F and fill the Co level to its neutral state. The gate map in (f) shows the charging line in the (V_b, V_g) plane responsible for the rings in spectroscopic maps as the tip approaches the Co atoms, as shown in (b). Tunneling setpoints: (e), $I = 50$ pA, $V_b = 100$ mV, (f), $I = 70$ pA, $V_b = 100$ mV.

Figure 3. Modifying the potential profile of the probe tip with vertical manipulation of Co atoms
(a) STM topographic image of Co atoms and clusters displaying repeated imaging artifacts due to the atomic structure of the probe tip. **(b)** Schematic of the tip shape estimated from the inversion of one group of the repeated patterns in **(a)** shown as a contour plot. **(c)** STM topographic image of the same area as in **(a)** after transferring Co atoms from the surface onto the tip apex. The objects seen in **(a)** now appear as distinct single atoms and clusters, reflecting a single atom tunneling center. The red arrow indicates one of the Co clusters which was placed onto the tip to achieve this result. Tunneling setpoints for **(a)** and **(c)**, $I=500$ fA, $V_b=300$ mV, $V_g=40$ V. **(d)** Simplified schematic of the resultant tip-induced potential profile after reshaping of the probe tip (solid line). With the tunneling apex (x_0 in the tip's coordinate system) offset from the original Ir tip apex (x_{Ir}) combined with a weakening of the potential at the tunneling apex due to transferred Co, charging rings will first appear off of the Co atoms and clusters rather than centered on them. Tomography of the charging rings vs gate voltage confirms this expectation, as demonstrated in the sections that follow.

Figure 4. Lowering of the tip work function by an adsorbed Co
 Slab model used in DFT calculations, and resulting potential energy curve (averaged in the x- and y-directions). A Co adatom on an Ir slab lowers the work function more than an equivalently placed Ir atom. The orange, dashed circle indicates the adsorbate which was varied from Co to Ir

Figure 5. Manipulation of Co cluster charge state with a modified probe tip potential
 (a) STM topographic image of Co clusters after tip modification, as described in Figure 3. Tunneling parameters, $I = 500$ fA, $V_b = 300$ mV. The central cluster changes charge state within the gate voltage range surveyed in (b–f), and is used to map the contours of the resultant tip-induced potential profile. (b–f) Closed-loop dI/dV_b spatial maps progressing from $V_g = 10$ V in (b) to $V_g = 4$ V in (f) showing the distorted charging rings developing as the tip laterally approaches the central Co cluster. The charging cluster is indicated by a red circle, while non-charging clusters are indicated by blue circles. dI/dV_b spatial map tunneling parameters, $I = 900$ fA, $V_b = 300$ mV.

Figure 6. Tomography of the graphene screening charge for a modified tip potential using an atomic impurity sensor

(a) 3D contour plot of the spatial charging rings obtained from the dI/dV_b maps in Figure 5. (b) Schematic of the modified tip and the potential it generates (orange contour map) in the context of the capacitor model described in eqs 1–3. The highest contour energy shown is located at 3 meV above E_F , contour spacing is 4.5 meV. The gray capacitor plate represents the graphene plane while the white plate is the back gate electrode. Co atoms on the tip are colored blue, while the third unidentified feature (x_2) in Figure 3b is colored pink. Dashed lines indicate the centers on the potential that correspond to each species adsorbed on the tip; the associated colored ellipses indicate the relative Gaussian widths (σ_i) used in eq 2. The Gaussian widths and amplitudes, the position of x_{T_i} relative to x_0 , and the resonance level E_0 are determined by a least squares fit to the data in (a). The orange contour map depicts the tip-induced potential for $V_g = 10$ V with the tip centered in the image, and with the parameters obtained from the fit to the data in (a). Additional contour maps at various gate voltages are shown in Figure 7. (c) 3D contour plot of the simulated spatial charging ring profiles reproduces the features of the data in (a). The simulated contour plot is solved for the condition $U'(\mathbf{r} = \mathbf{r}_a, \mathbf{r}_T, V_b = 300$ mV, $V_g) + E_0 = 0$, using the parameters determined by the fit.

Figure 7. Dependence of the tip-induced potential on back gate and tip height
(a–e) Tip-induced potential in graphene as measured in the sample coordinate system for a fixed centered tip, as a function of varying back gate voltage. **(f–j)** Tip-induced potential as measured at a fixed position on the sample while the tip (r_T) is raster scanned over the topography of Figure 5a. The blue plane represents the energy $E_F = 0$, where potentials have the constant E_0 added on to them. Contour spacing for each potential in **(a–j)** is 4.5 meV, with the highest lying contour being located above E_F by the following amounts: 3, 11.5, 20.5, 30, and 40.6 meV for V_g of 10, 8.5, 5.5, 7, and 4V respectively. **(k)** Reproduction of the experimental contours from Figure 6a for comparison.

Figure 8.

(a) Topography scan of the region appearing in the spatial dI/dV_b maps of (b–g). Charging species are indicated by the red circles. (b–g) spatial dI/dV_b maps as a function of decreasing V_g with the same three charging species indicated by filled red circles when their associated charging rings are apparent.