THz-STM of Atomically Precise Graphene Nanoribbons

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***Abstract*—Terahertz scanning tunneling microscopy (THzSTM) is applied to atomically precise graphene nanoribbons (GNRs) fabricated by bottom-up, on-surface synthesis. THz-STM images recorded in an ultrahigh vacuum, low temperature environment reveal rich, ångström-scale electronic detail within single GNRs, including aspects that are not visible with conventional STM imaging. Height-dependent THz-STM measurements further probe the GNR wavefunctions with sub-ångström vertical resolution, providing a new level of clarity.**

I. INTRODUCTION

On-surface synthesis of graphene nanoribbons (GNRs) from molecular precursors has introduced unprecedented precision into the design and fabrication of nanoelectronics [1]. By selecting an appropriate species of precursor molecule, GNRs with atomically defined widths, shapes, edges, junctions, topology, and functionalization can be created on an Au(111) surface [2,3]. However, since atomically precise GNRs are only a few atoms wide, steady-state STM and atomic force microscopy (AFM) have been the only techniques capable of addressing them individually so far, limiting applications. Here, we show that terahertz scanning tunneling microscopy (THz-STM) can capture the local electronic structure of single GNRs in finer detail than even STM thanks to its ability to operate at ultra-low tip heights.

II. GRAPHENE NANORIBBON GROWTH

We grow seven-atom wide (N=7) GNRs with armchair edges (7-AGNRs) *in situ* on a single-crystal Au(111) surface (Figure 1a), which acts as a catalyst [1]. 7-AGNR sample production begins with evaporation of 10,10′-dibromo-9,9′bianthryl (DBBA) precursor monomers from a Knudsen-type effusion cell at 180 ºC. The precursor monomers are deposited onto a room-temperature single-crystal Au(111) substrate. Initially, the gold surface facilitates dehalogenation of the DBBA molecules. Thermally activated diffusion is triggered at 200 ºC, mediating the formation of polymer chains (Figure 1b) through carbon-carbon coupling at halogen-free atomic sites. A final annealing step to 400 ºC reduces the linear polymer to a flat 7-AGNR with atomically precise widths and edges through a process of cyclodehydrogenation that produces carbon-carbon bonds along the boundary between neighboring anthracene monomers. A section of an example 7-AGNR resolved by constant-current STM is shown in Figure 1c.

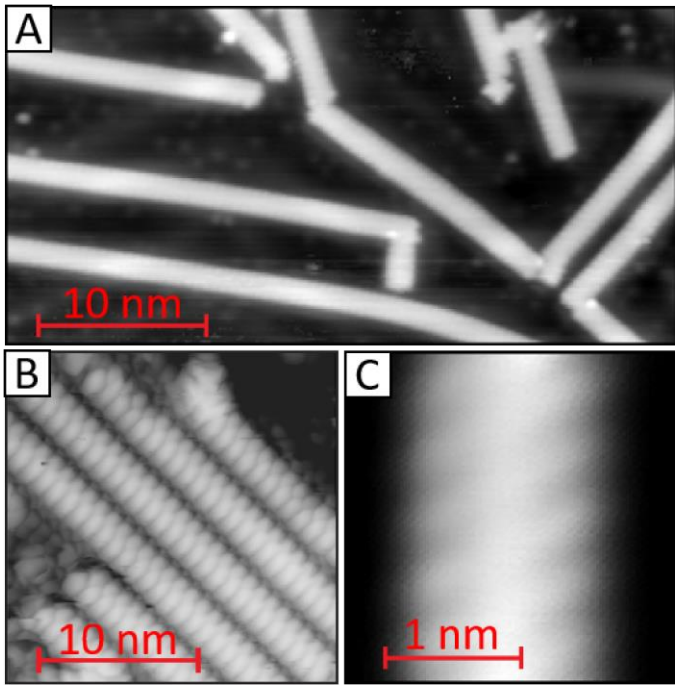

Figure 1. (a) Atomically precise 7-atom wide armchair graphene nanoribbons (7-AGNRs) grown via on-surface synthesis. (b) Linear polymer chains formed as an intermediate step during bottom-up growth of 7-AGNRs. (c) Pristine 7-AGNR grown in-situ on Au(111). All images are taken by STM under UHV conditions in constant-current mode with setpoint parameters, V_{dc} = -1 V and I_{dc} = -50 pA

III. THZ-STM SETUP

THz-STM uses a phase-stable, single-cycle THz pulse as an ultrafast voltage transient across an STM tunnel junction [4-8]. The voltage transient acts on the instantaneous STM current voltage characteristic, generating an ultrafast asymmetric current pulse with a rectified component that can be detected by time-integrating STM electronics. The femtosecond duration of the current pulse enables ultrafast measurements with atomic resolution [5,7] provided the rectified component can be detected with a duty cycle of 10^{-6} to 10^{-7}, defined by the ratio of the current pulse duration to the time between laser pulses. Our THz setup (based on a Light Conversion Carbide regenerative amplifier) operates at 1 MHz, so THz-induced rectification of one electron per THz pulse corresponds to an average current of 160 fA, which can be comfortably detected by our custom designed commercial STM (CreaTec).

IV. DFT SIMULATIONS

Real-space density function theory (DFT) simulations of the 7-AGNR wavefunction predict the existence of a rich electronic structure that evolves rapidly with tip height [9]. Example plane cuts through the calculated probability density of the valence band at 5 Å (Figure 2a, right) and 2 Å (Figure 2b, right) above the 7-AGNR atomic plane highlight the fact that far more detail is visible closer to the 7-AGNR. The effect is yet more pronounced for the conduction band (not shown). Conventional STM differential conductivity measurements (Figure 2a, left) are consistent with the DFT calculation at 5 Å, where little spatial detail is present. The tip height for such STM measurements is determined by the voltage and current setpoint (V_{dc} = -1V; I_{dc} = -50pA). The tip height can be decreased by increasing the current setpoint, but imaging becomes unstable before the more interesting spatial structure of the 7-AGNR electron density appears.

V. THZ-STM OF 7-AGNRS

The low duty cycle of the THz-induced tunnel current in THz-STM has necessitated THz-STM imaging with relatively low tip heights compared to conventional STM to increase tunneling probability [5]. However, the impact of the tip height on the resulting THz-STM images has been relatively unexplored. Here, we use this aspect of THz-STM to our advantage. Employing an ultrahigh vacuum, low-temperature THz-STM setup, we image a 7-AGNR (Figure 2b, left) at a tip height that is 3 Å closer than in conventional STM for the same voltage. This allows us to resolve the spatial structure of 7-AGNR electronic states in unprecedented detail, as the apex of the tip raster scans through the middle of the 7-AGNR wavefunctions rather than their extremities like it does in conventional STM. Further recording THz-STM images as a function of height, we observe changes to the image, and even an inversion of the rectified current polarity (not shown), implying different vertical decay rates for the valence and conduction bands. These measurements open the door to sub-ångström-scale tomography of the electron densities in atomically precise GNRs as well as ultrafast THz-STM imaging and spectroscopy of GNR transient electronic states.

VI. SUMMARY

THz-STM imaging of atomically precise graphene nanoribbons can be performed at ultra-low tip heights not accessible with conventional STM, revealing unprecedented detail in the spatial structure of their electronic states.

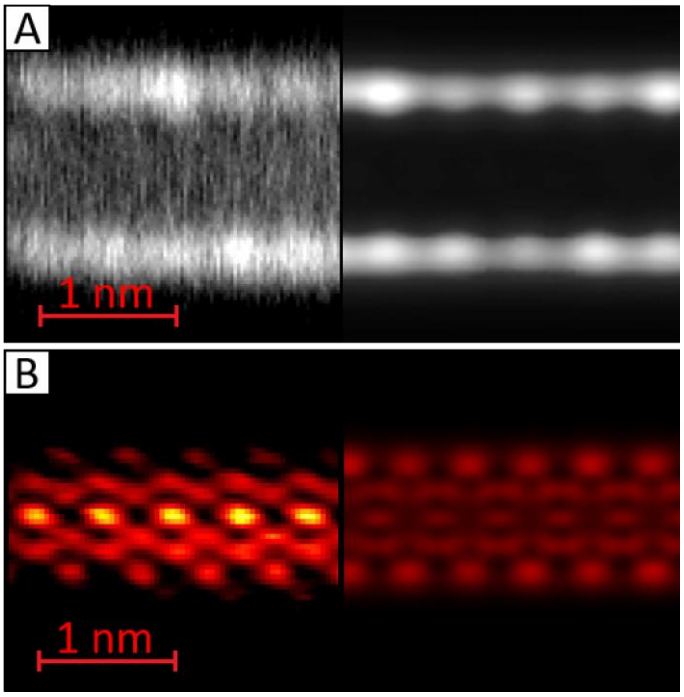

Figure 2. (a) Conventional constant-height differential conductivity image (left) taken at a tip height of Z_0, which is set over the center of the 7-AGNR with V_{dc} = -1 V and I_{dc} = -50 pA, along with the corresponding DFT simulation of $|\Psi|^2$ at a tip height of Z = 5 Å (right). (b) Constant-height THz-STM image of the valence band local density of states measured in rectified electrons per terahertz pulse at a tip height of $Z = Z_0$ - 3 Å (left) and corresponding DFT simulation at a tip height of Z = 2 Å (right).

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