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PETASCALE SIMULATIONS OF GRAPHENE NANORIBBON DEVICE STRUCTURES

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EXECUTIVE SUMMARY

This project focuses on high-performance calculations for materials and devices of high current interest, as well as on development of petascale methods for such simulations. In FY'18, we concentrated on three applications: (1) metallic contacts to 1D graphene nanoribbons (GNRs), which were established by varying their widths. While 7-atom-wide armchair GNR (7-aGNR) is a semiconductor, 14-aGNR and 21-aGNR are metallic and form a seamless staircase contact to 7-aGNR. (2) We also worked on atomic-level stability of both zigzag and armchair edges of GNRs against oxidation. In a joint experimental–theoretical investigation, we showed that hydroxyl and epoxy species were produced by oxidization, leading to a significantly reduced bandgap of the 7-aGNR. We mapped out the evolution of edge structures and revealed the reaction path and the produced chemical species of both for the zigzag and the armchair edges. (3) We also investigated potential GNR-based devices and proposed a novel structure that can be manufactured with atomic precision and exhibits significant negative differential resistance.

RESEARCH CHALLENGE

Electrical contact to low-dimensional (low-D) materials is a key to their electronic applications. Traditional metal contacts to low-D semiconductors create gap states that can pin the Fermi level (E_F). However, low-D metals possessing limited density of states at E_F can enable gate-tunable work functions and contact barriers. Moreover, a seamless contact with native bonds at the interface that does not introduce in-gap states can act as an optimal contact electrode. Indeed, an ohmic contact has been achieved in 2D transition metal dichalcogenides at the interface of the metallic 1T'-phase and the semiconducting 2H-phase. We demonstrated an all-carbon staircase contact to ultra-narrow graphene nanoribbons (GNRs), a wide bandgap 1D semiconductor. A combined scanning tunneling microscopy and density functional theory study revealed the native covalent-bond nature and the quasi-metallic contact characteristics of the interfaces. The GNR staircase points constitute a promising route to high-performance graphene nanoelectronics.

The stability of graphene nanoribbons (GNRs) against oxidation is critical for their practical applications. We systematically studied the thermal stability and the oxidation process of ambient-exposed armchair GNRs with a width of seven carbon atoms (7-aGNR), grown on an Au(111) surface. The atomic scale evolution of the armchair edges and the zigzag ends of the aGNRs after annealing at different temperatures were revealed by using scanning tunneling microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and first-principles calculations. In the oxidation process, O_2 molecules first dissociate and then react with carbon atoms at the edges. Two different oxygen species were identified at the armchair edges, namely the hydroxyl pair and epoxy with one bridge oxygen bonded to two edge carbons. These oxidization species modify the electronic properties of pristine 7-aGNRs, with a bandgap reduction from 2.6 eV to 2.3 eV and 1.9 eV for the hydroxyl pair- and epoxy-terminated edges, respectively. These findings revealed that both the zigzag and armchair edges of GNRs can be oxidized after thermal annealing and that the oxidization can greatly affect the electronic properties of GNRs, which also opens an opportunity for using GNRs as high-temperature oxygen sensors.

The development of atomically precise synthesis of graphitic nanostructures promises a revolution in device design to deliver novel electronic functions. A prominent example is the negative differential resistance (NDR) device, for which many designs based on graphene nanoribbons (GNRs) were proposed. However, a controllable fabrication method of such devices with atomic precision has yet to emerge. We proposed a practical device structure, based on armchair GNRs, which exhibits strong NDR effect. Our computational evaluation of the traditional resonant tunneling diode uncovers important issues at the atomic scale concerning the need to minimize the direct tunneling current between the leads while achieving high peak current. The proposed device consists of a short semiconducting GNR and its lower-gap intermediate segments, which enables high current by the alignment of levels across the segments while enlarging the tunneling distance between the leads.

METHODS & CODES

The electronic structure calculations used the Real-space-MultiGrid (RMG) and Quantum Espresso codes. The quantum transport nonequilibrium Green's function calculations used the localized orbitals and nonequilibrium Green's function (NEGF) branches of the RMG code.

RESULTS & IMPACT

Our results indicate that GNRs with variable widths and seamless heterostructures can be realized by using only one molecular precursor. This is different from previous reports where type-I and type-II semiconducting heterojunctions were synthesized with several nanometers of GNRs by using two different precursors. The lack of strongly localized interfacial states is highly desirable for making a good electrical contact to the semiconductor material, as verified in 2D heterojunctions between the metallic 1T'-phase and the semiconducting 2H-phase transition metal dichalcogenides (MoS_2 and $MoTe_2$). The conjugated wide GNRs are either quasi-metallic or small-gap semiconductors with limited DOS at the E_F, similarly to the 2D metals. They can be used as electrical contacts to the ultra-narrow semi-conducting aGNRs, which would avoid Fermi-level pinning and a high Schottky barrier. Furthermore, a staircase with gradually diminishing bandgaps can potentially be used to direct charge transport, while the long and wide branches in the GNR heterojunctions (HJs) facilitate their integration with more conventional contact electrodes. The staircase HJs with atomically controlled interfaces thus provide a promising interconnect to the semiconductor gate material.

We found that GNR oxidization leads to the formation of hydroxyl- and epoxy-group-terminated edges, which lead to significantly reduced bandgaps of GNRs. The significant changes of electronic properties suggest that aGNRs can be used as high-temperature oxygen sensors. The finding that both zigzag ends and the armchair edges can be oxidized by thermal annealing may also help in understanding oxidization of other graphitic structures.

Utilizing the type-I band alignment between the 7-aGNR and the polymer-GNR intermediate, we designed an experimentally realizable nanoscale NDR device with a practical peak-to-valley current ratio and peak current. The computationally guided design uncovers new aspects important for atomic scale devices concerning the need to minimize direct tunneling between the leads while maintaining sufficient peak current and peak-to-valley current ratio. Starting from the concept of a resonant tunneling diode and controlling the confinement and interfacial levels energy matching, we discovered a new, broadly applicable design for atomic-scale ballistic NDR devices, based on multiple narrow segments of low and high bandgap atomic-scale constituents.

WHY BLUE WATERS

The applications described above require a very large parallel supercomputer with a high-speed interconnect among the nodes (due to frequent exchange of substantial amounts of data among nodes). Each project required many runs to explore its various scientific issues, with a substantial amount of analysis between the runs. High availability and quick turnaround are thus also very important for timely progress in our research.

PUBLICATIONS & DATA SETS

Ma, C., et al., Seamless Staircase Electrical Contact to Semiconducting Graphene Nanoribbons. *Nano Letters*, 17 (2017), DOI:10.1021/acs.nanolett.7b02938.

Ma, C., et al., Oxidization stability of atomically precise graphene nanoribbons. *Phys. Rev. Mat.*, 2 (2018), DOI:10.1103/PhysRevMaterials.2.014006.

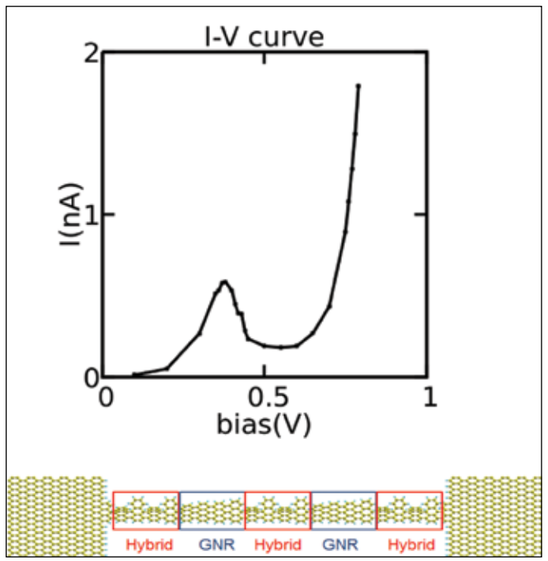

Figure 1: Calculated I-V curve and structure of a negative differential resistance device based on graphene nanoribbon and graphene nanoribbon precursors.