Electronic Devices Based on Graphene Nanoribbons: an ab initio study

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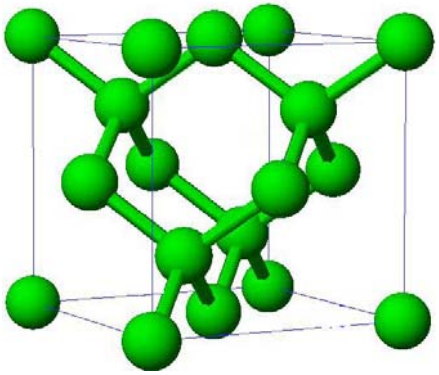
OUTLINE

- Recent progress on ultrathin graphite
- Basic electronic properties of graphene nanoribbons (GNR)
- GNR-based Field Effect Transistor
- Effect of edge defects on the spin-polarization of GNRs: Implication to Spintronics
- Conclusion and Summary

Motivation and Background

Carbon based materials

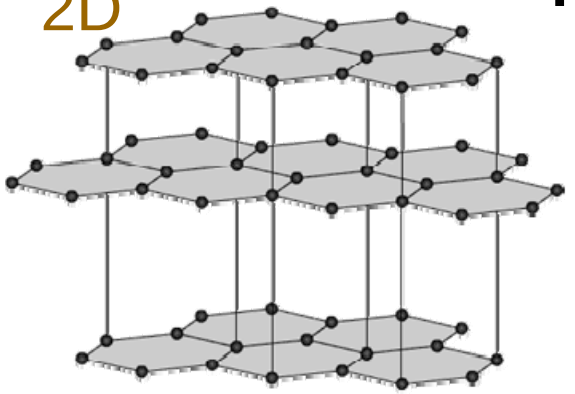
3D



Diamond

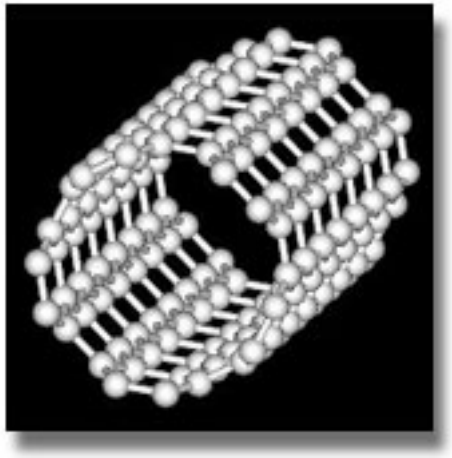
Graphite

2D

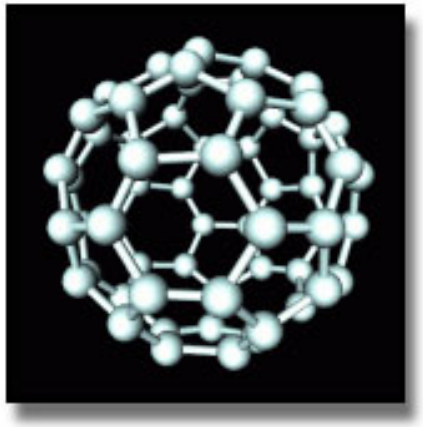


1D

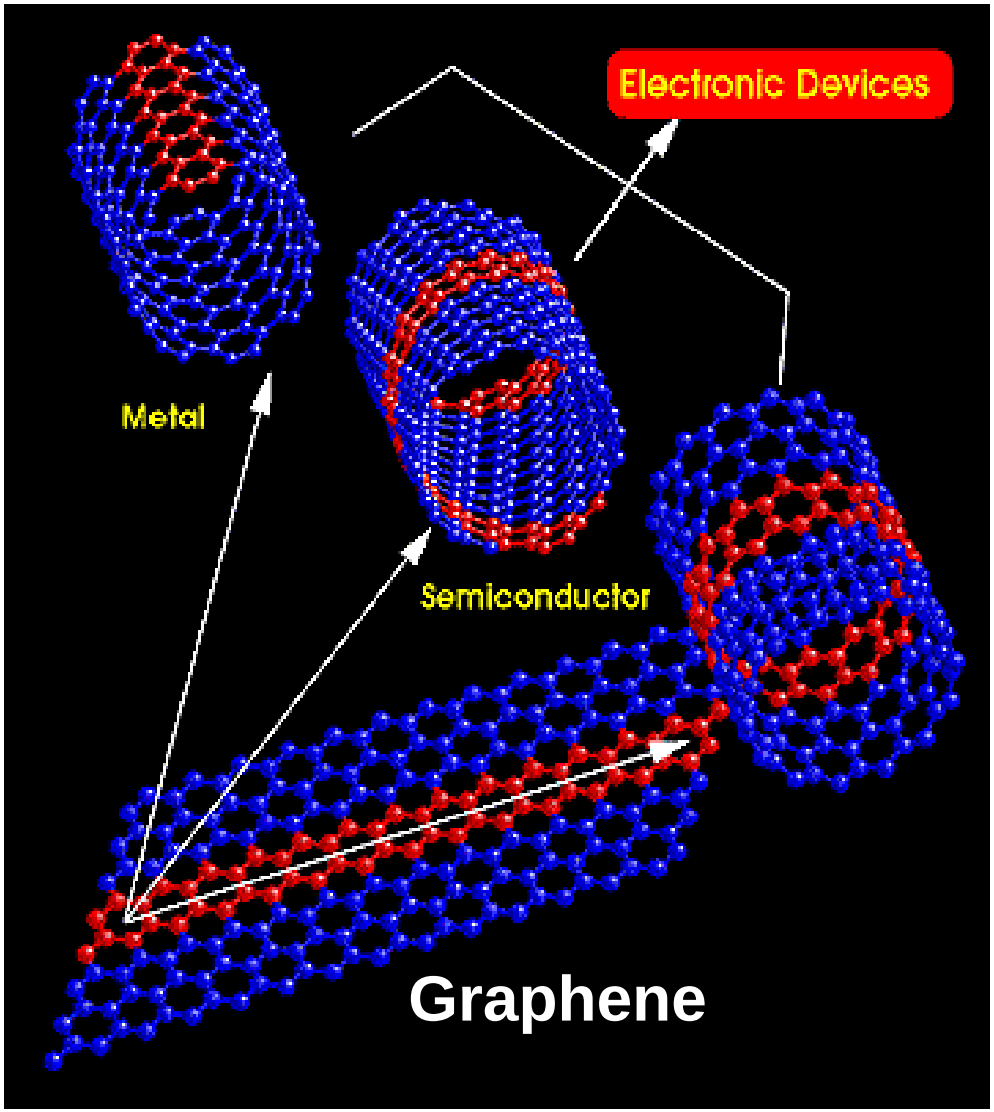
Carbon nanotube



C_{60} (Buckyball)



0D



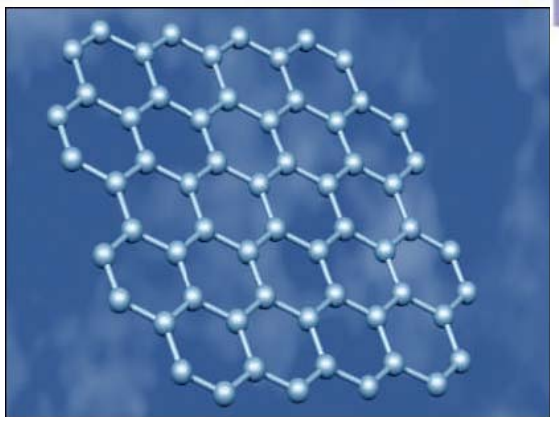
Unique electronic properties of CNTs come from unusual band structure of a single ***Graphene*** layer !

Carbon layer just one atom thick

Graphene

- Zero gap semiconductor with only two bands crossing at the Fermi level.

  Dirac particle with linear dispersion relation.



- High thermal conductivity and mechanical stiffness

  ~ the remarkable in-plane values for graphite (3,000 $Wm^{-1}K^{-1}$ and 1,060 GPa, respectively).

- High fracture strength

  comparable to that of carbon nanotubes for similar types of defects.

Last three years of graphene electronics

- 2004
  Successful fabrication of ultra-thin graphite sheet (UTGS)
- 2004
  Single layer graphene was fabricated on SiC surface
- 2004 & 2005
  Field Effect Transistor based on UTGS
- 2006 & 2007
  The ribbon width ~ 20 nm.
  One critical problem of graphene based electronics is to decrease the width of nanoribbon.

Fabrication of patterned graphene

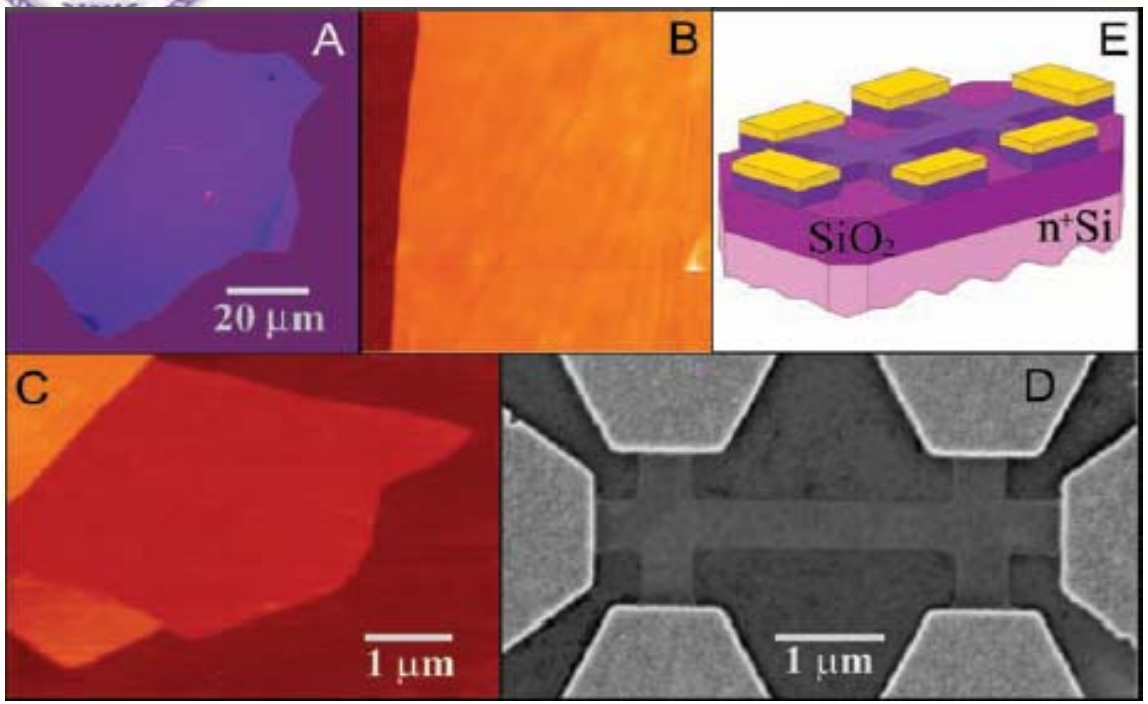
1. Graphite layer was scratched by **scotch tape** from 1 mm thickness highly-oriented pyrolytic graphite

2. Patterned structure is fabricated by **Electron-Beam Lithography**

K. S. Novoselov et al., *Electric Field Effect in Atomically Thin Carbon Films*, SCIENCE 306, 666 (2004).

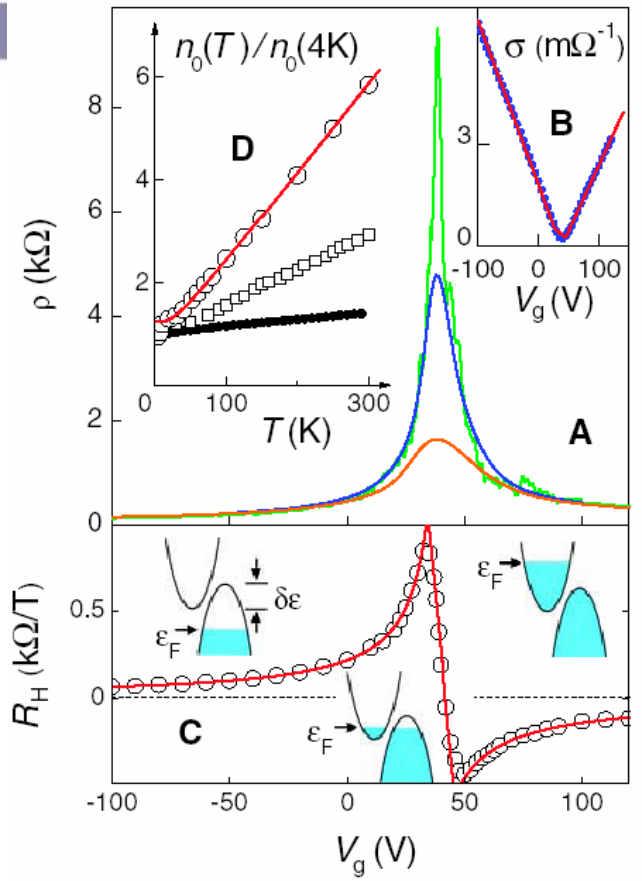
André Geim, University of Manchester

Graphene Field-Effect transistor



It becomes possible to prepare graphitic sheets of thicknesses down to a few atomic layers, to fabricate devices from them, and to study their electronic properties.

SCIENCE 306, 666 (2004)

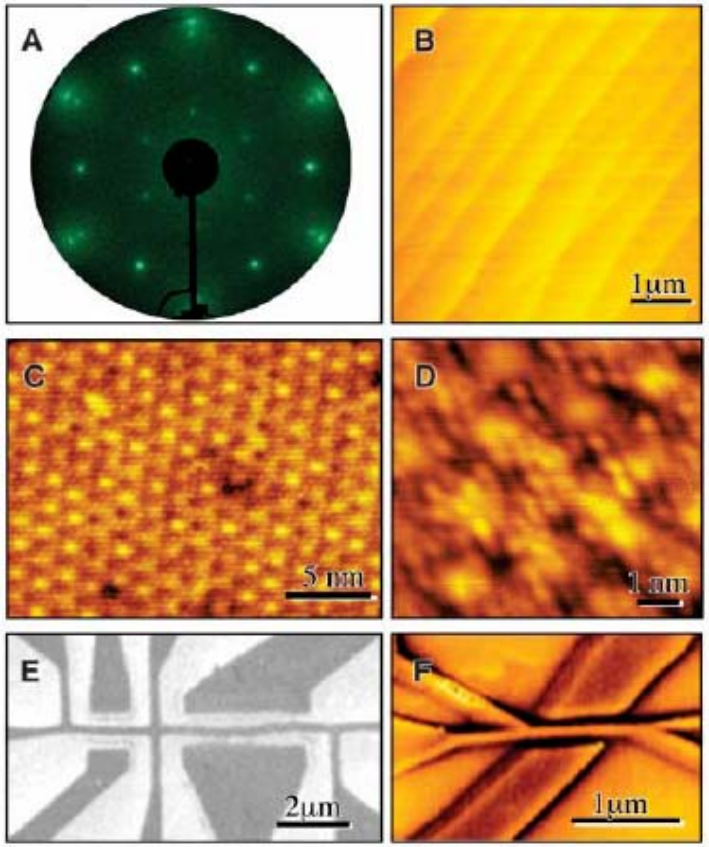


FET based on few-layer graphene

Conducting channel can be switched between 2D electron and hole gases by changing the gate voltage.

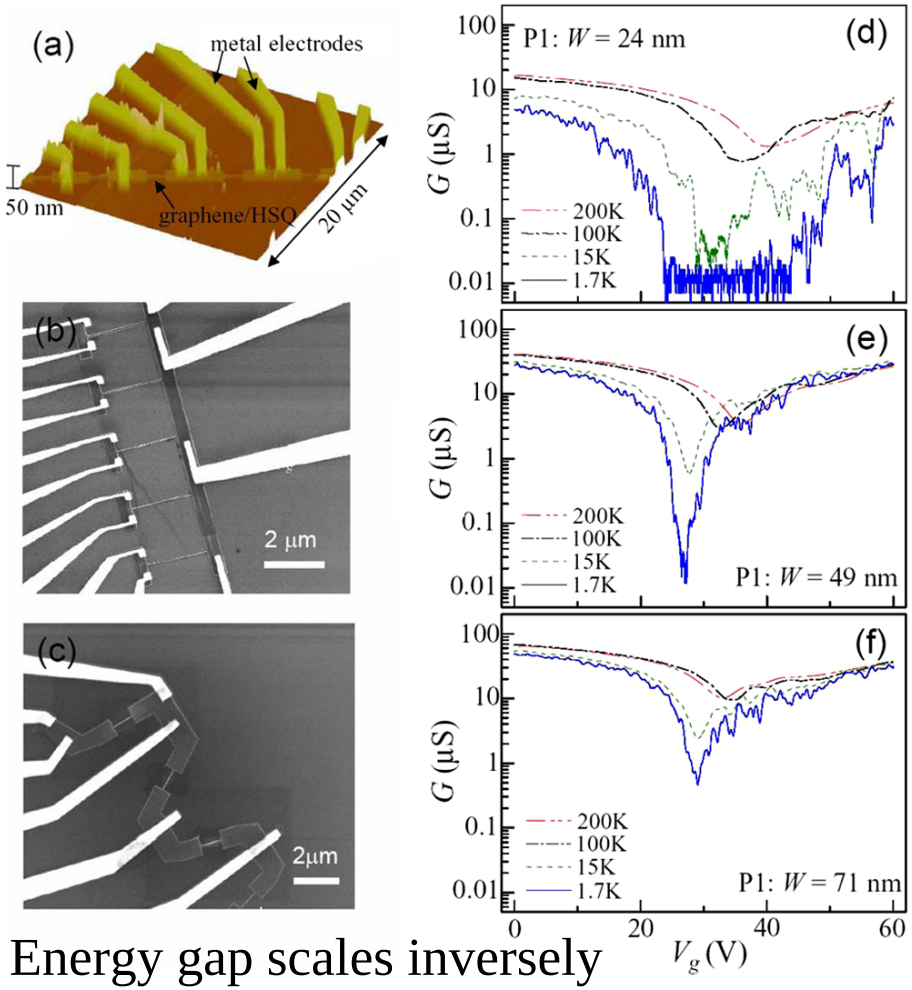
NanoPatterned Epitaxial Graphene

Single layer graphite achieved on SiC surface



Phase coherence length: 1 μm at 4K

W. A. de Heer, Science 312, 1191, 2006

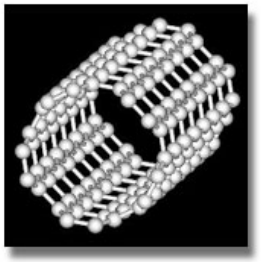


Energy gap scales inversely with the ribbon width

Philip Kim, PRL 98, 206805 (2007)

All the progresses in the area suggest a completely new possibility of graphene electronics (**Electronic circuits made up of continuous graphene sheets)** :

to fabricate junction devices using the inherent quantum confinement effect of quasi-one-dimensional Graphene nanoribbon. (GNRs).



Nanotube

- Proper control of nanotube growth with certain chirality;
- Hard for the mass integration and incorporation in circuits;
- Contact between nanotube and metallic electrodes.

Nanoribbon

- Easy to be fabricated using traditional lithography technique；
- Reliable “flat electronics” by constructing all devices in a continuous plane.
- Easy to realize typical contact, such as metal-semiconductor contact, with small contact resistance.

- Functional devices based on GNRs.

  --- Architectural designs
  --- Device performance
  --- Effect of edge defects

Novel architectural designs of molecular devices built on patterned GNRs.

Various device junctions can be constructed by connecting GNRs of different width and orientation with perfect atomic interface, and more importantly, device units can be selectively doped by manipulating the edge terminations of GNRs.

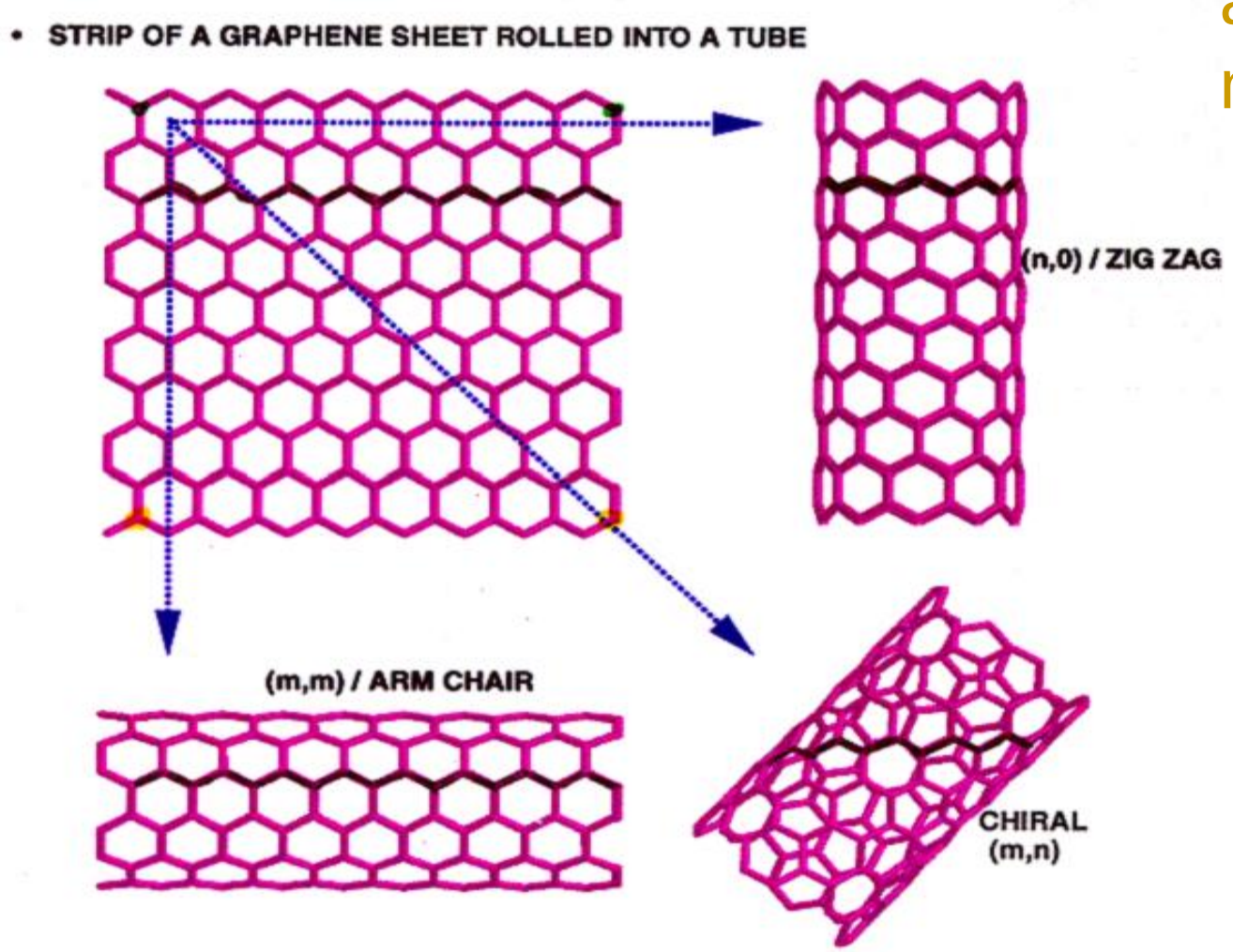
Theoretical Method

- VASP package within Density Functional Theory
- First-Principles non-equilibrium Green's Function based transport simulation (Atomistix ToolKit 2.0 package)

Electronic and transport properties of GNRs

Structure: Labeling a GNR

A nanotube is often viewed as a rolled-up piece of graphene



A nanoribbon is an unrolled nanotube !

Label a GNR following the way of naming a nanotube

Tube

Two ways to unfold single-walled nanotubes (SWNTs):

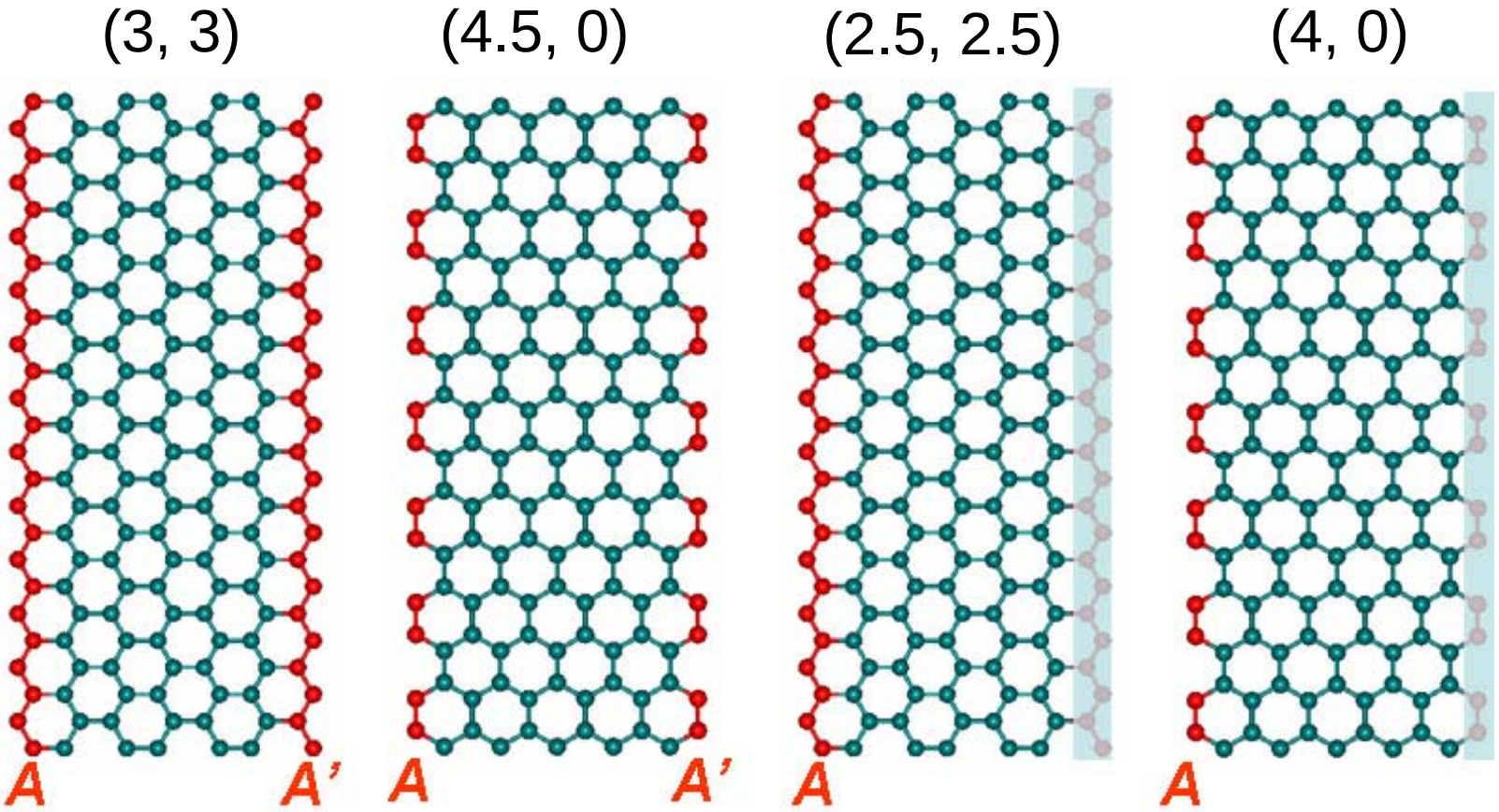
1) To cut open the SWNT along the axial direction through a row of atoms and then split the atom row onto both edges of the resulting GNR.

2) To cut open the SWNT through a row of C-C bonds and then a row of atoms will be missing on one edge of the resulting GNR.

In analogy to naming (*m*, *n*) SWNT, the GNRs are labeled in a unified sequence of **(*m*/2, *n*/2)** with uniquely defined ribbon orientation and width $(m/2)\ \ a_1 + (n/2)\ \ a_2$.

m and *n* are integers.

Any given (*m*, *n*) SWNT can unfold into either a (*m*, *n*) or (*m*-1/2, *n*-1/2) GNR.



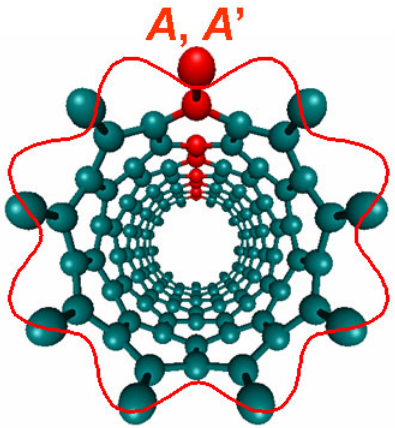
Armchair (asymmetric)

Zigzag (symmetric)

Armchair (symmetric)

Zigzag (asymmetric)

nanotube

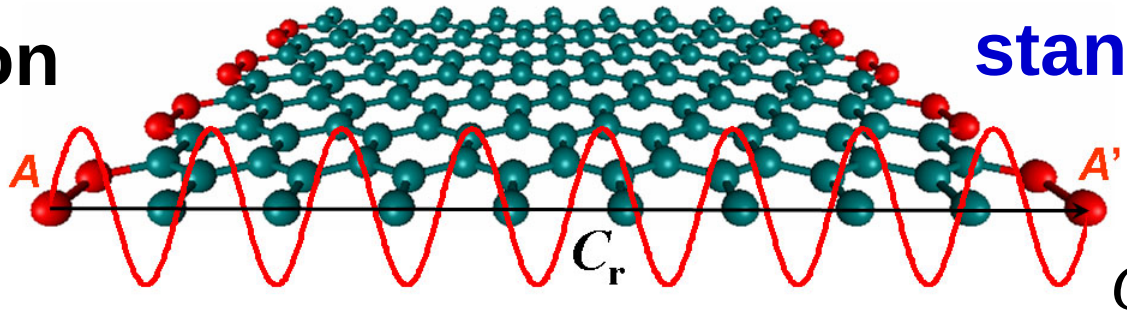


periodic boundary

vs

standing wave

nanoribbon



$$C_r = m\,a_1 + n\,a_2$$

- The electron confinement, the physical origin that gives rise to the differentiation of semiconducting and metallic behavior, is equivalent in the tube and ribbon configurations.

Similar quantum confinement for electrons

↓ nanotube and nanoribbon

Similar electronic structure-geometry dependence

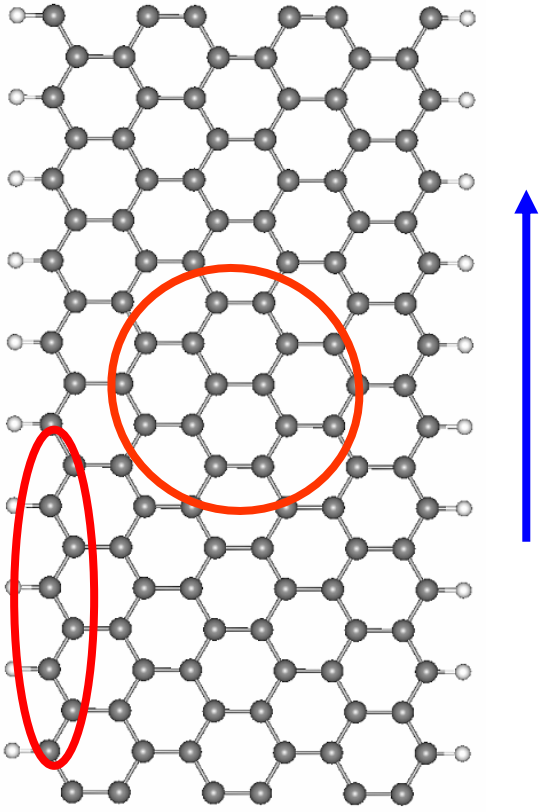
Different boundary conditions

↓ nanotube and nanoribbon

Different specific characteristics of electronic structure

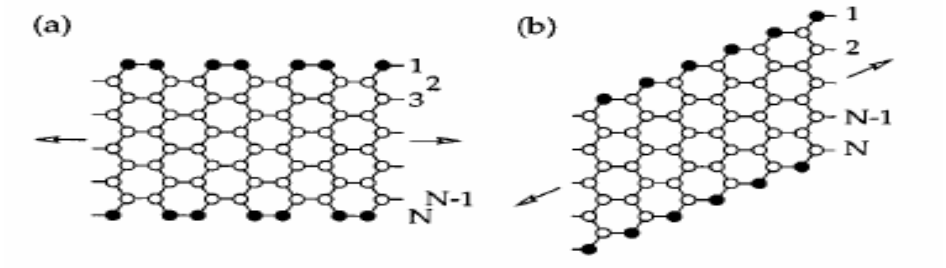
Some aspects in GNRs

- **Edge**
  - ➔ **Edge states**
  - ➔ **Edge doping & functionalization**
- **Body**
  - ➔ **strong sp^2 bonding**
- **Width and Chirality**
  - ➔ **armchair/zigzag**
  - ➔ **metallic/semiconducting**

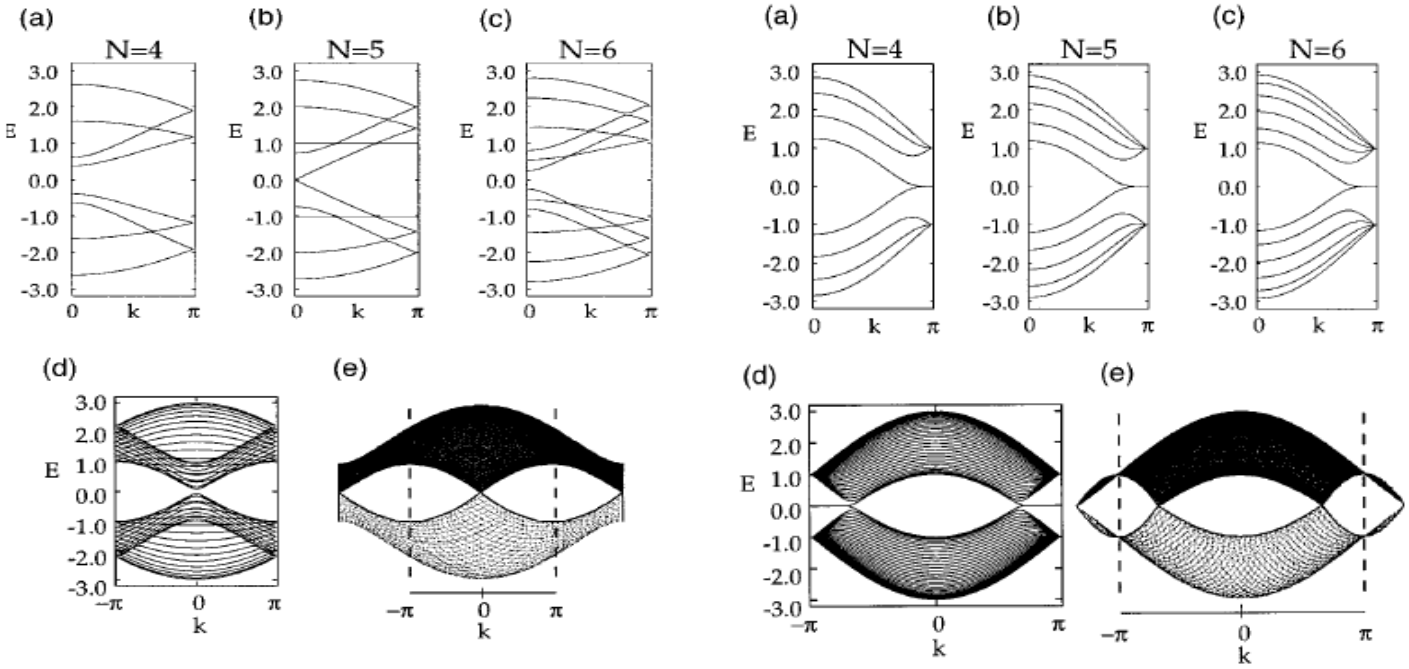


Electronic and transport properties

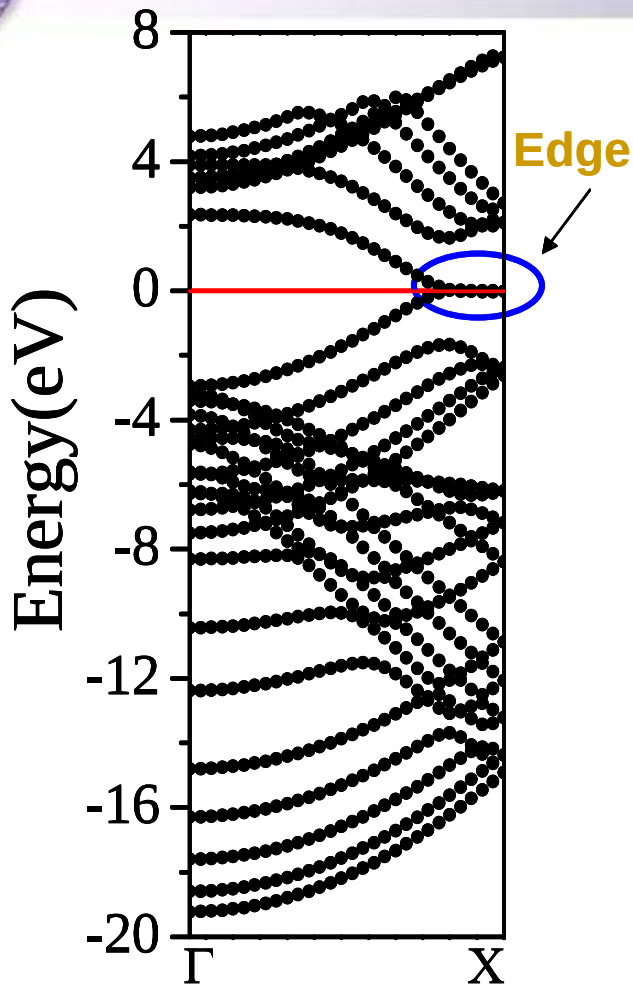
Many theoretical studies show that graphene ribbons may be either *metallic* or *semiconducting* depending on the crystallographic direction of the ribbon axis.



K. Nakada, et al, 1996



Our Calculations



(2, 2) armchair GNR

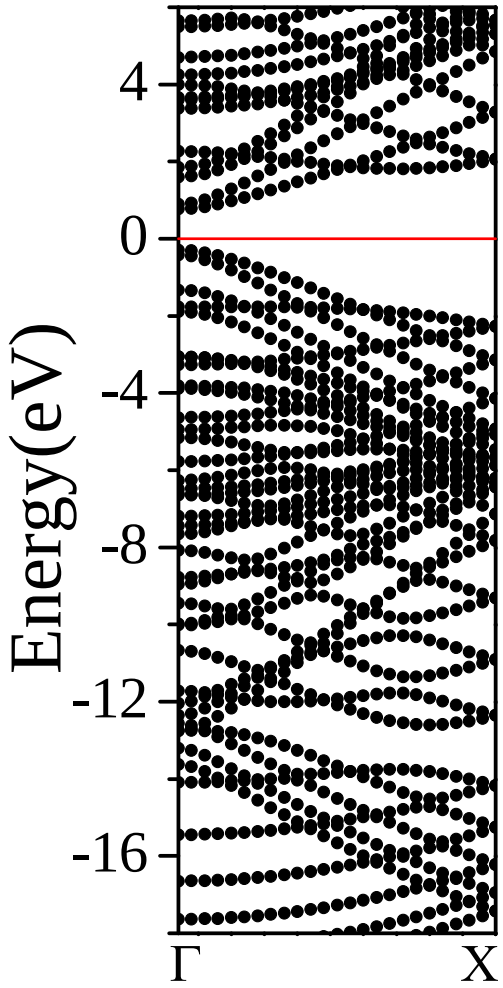
- All armchair (n/2, n/2) GNRs are metallic with edge states at the Fermi level
- The zero-temperature ground state of armchair GNRs is found to be spin-polarized, as predicted by previous calculations [Y. Son, M. L.Cohen, S. G. Louie, *Nature* **444, 347** (2006)].

- Energy difference between the spin-polarized and non-spin-polarized states is only ~20 meV per edge atom.

- Magnetization is strictly forbidden in 1D and 2D systems at finite temperatures within the Heisenberg model

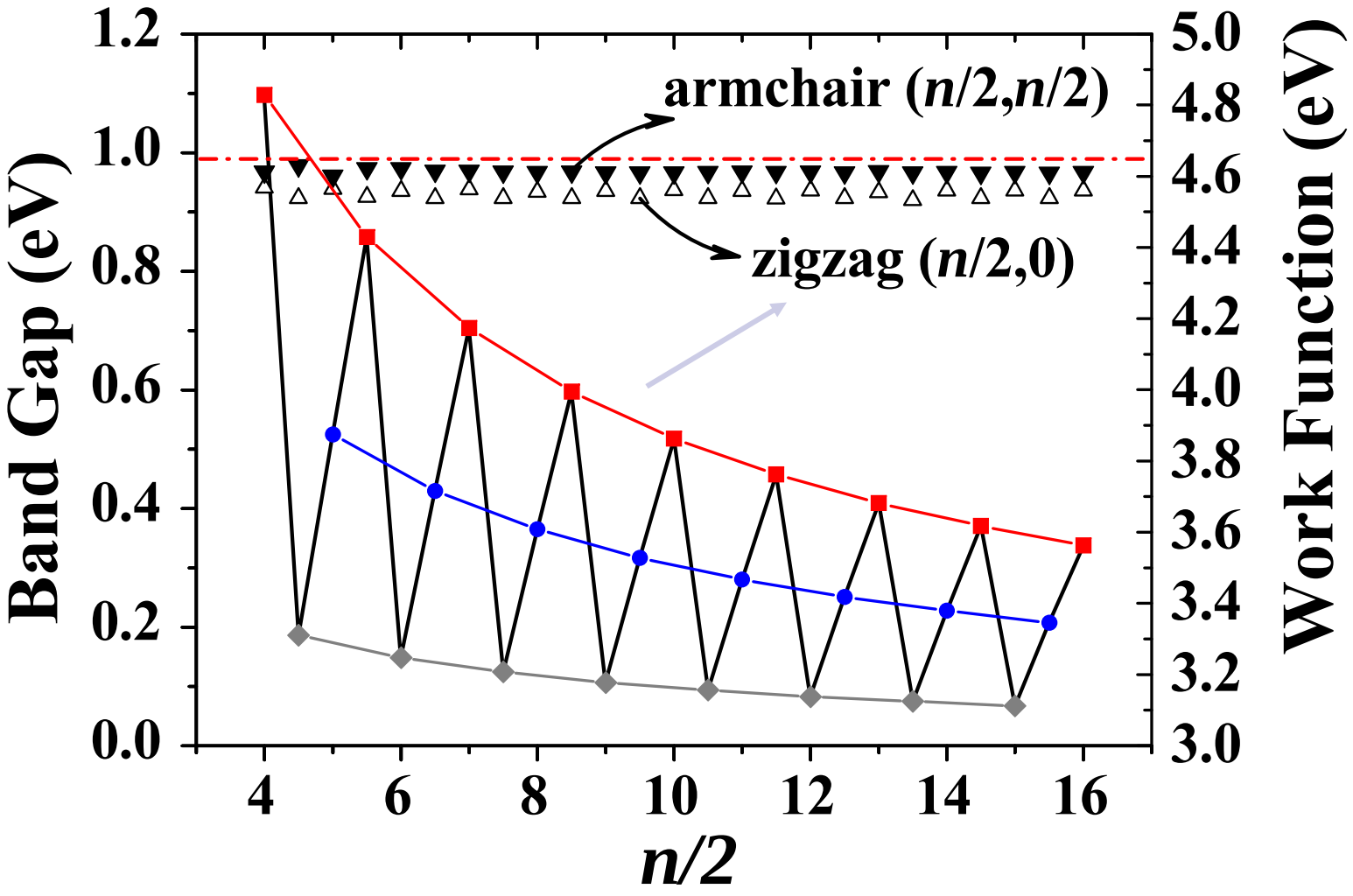
  [see N. D. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966)].

For our investigation of GNR-FETs, only the non-spin-polarized metallic state of armchair GNRs will be considered.

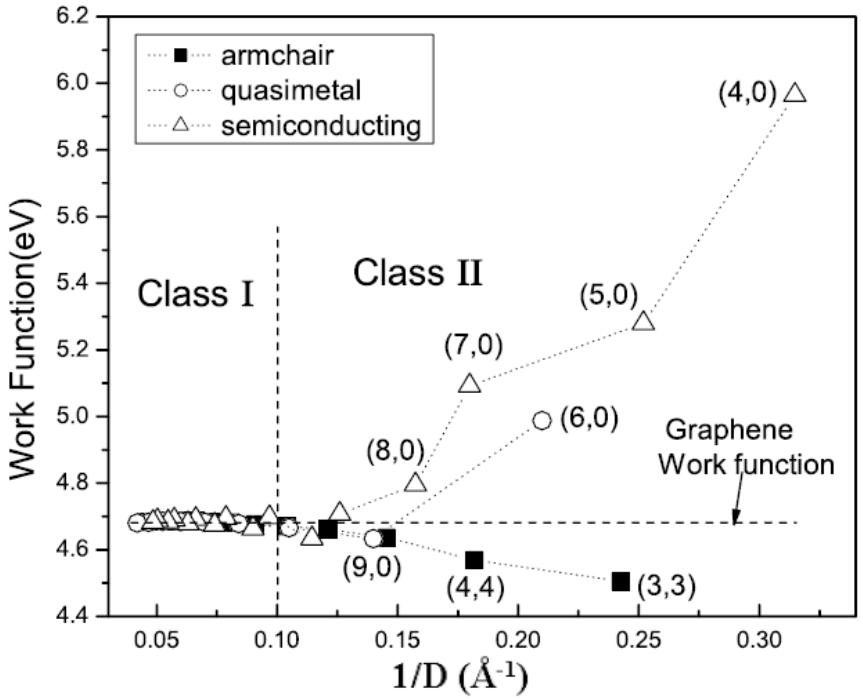


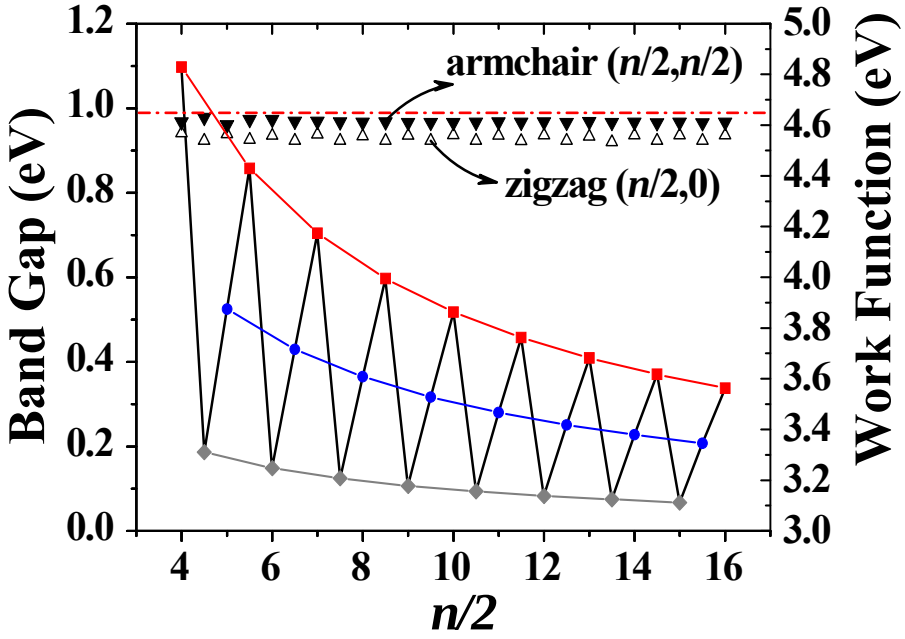
(4, 0) zigzag GNR

- All the (n/2,0) zigzag GNRs are semiconducting
- The dependence of the band gap of zigzag GNRs on the ribbon width is similar to that of zigzag nanotubes.


armchair (n/2,n/2)
zigzag (n/2,0)
Band Gap (eV)
Work Function (eV)
n/2
1.2
1.0
0.8
0.6
0.4
0.2
0.0
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
4
6
8
10
12
14
16

Work Function



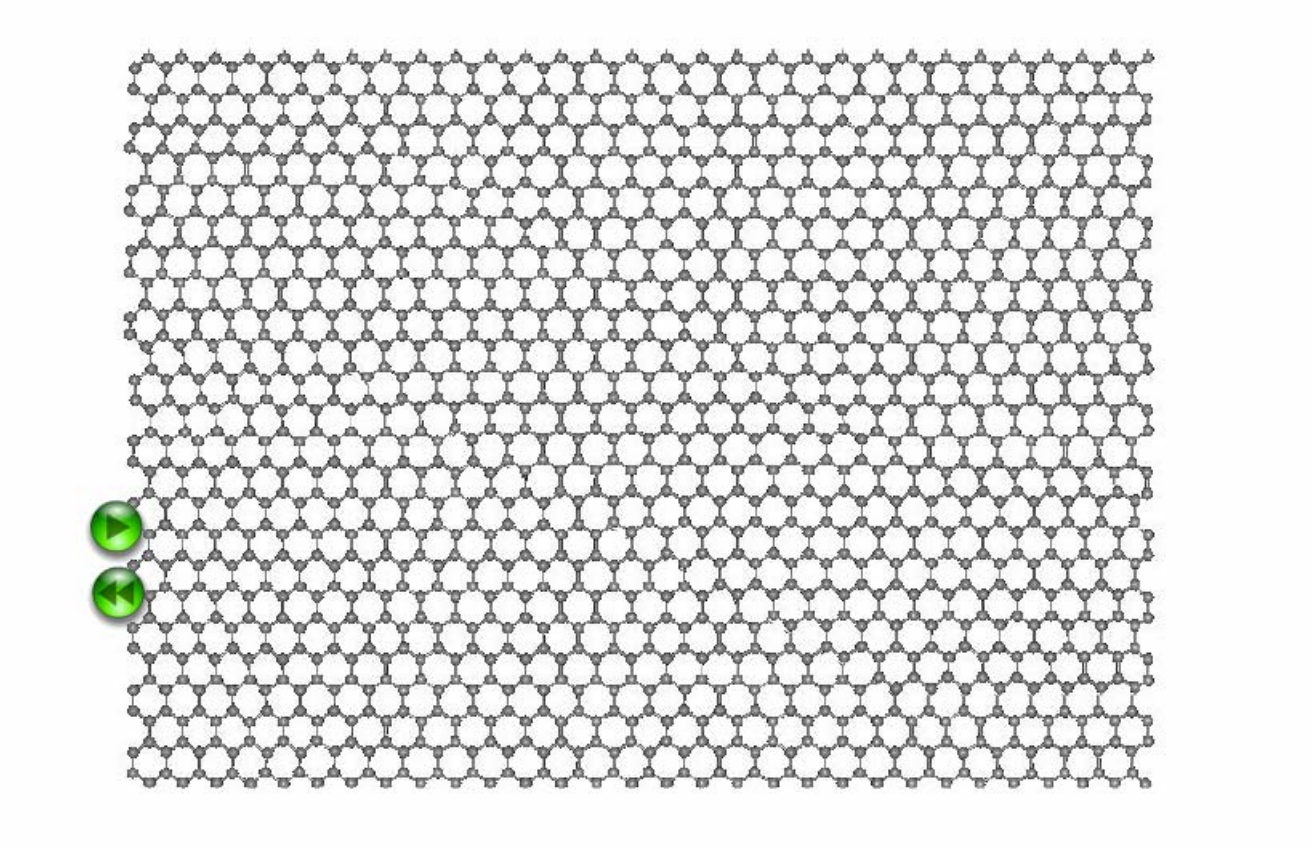


Without curvature effect in nanoribbons, the work functions of nanoribbons with different widths and orientation almost keep the same.

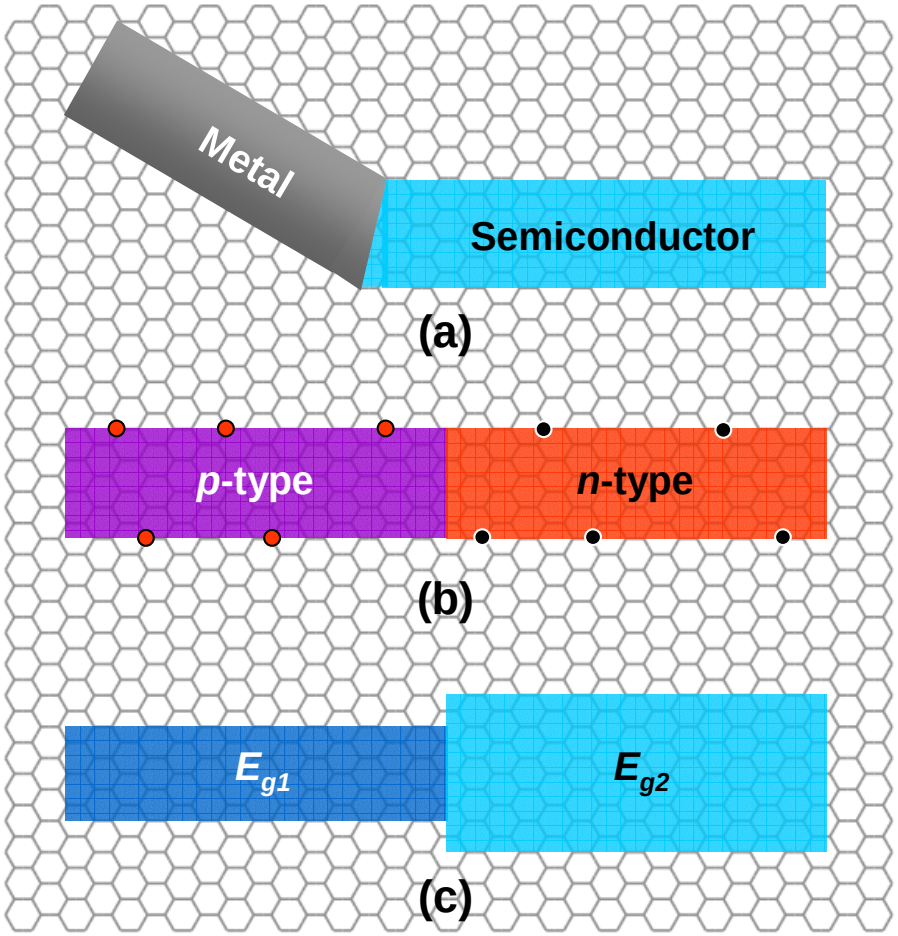
This characteristic is very important for device design!

GNR junctions based devices

- GNRs can be fabricated directly into device structures and even integrated circuits by a single process of patterning a graphene sheet.



Three basic device building blocks

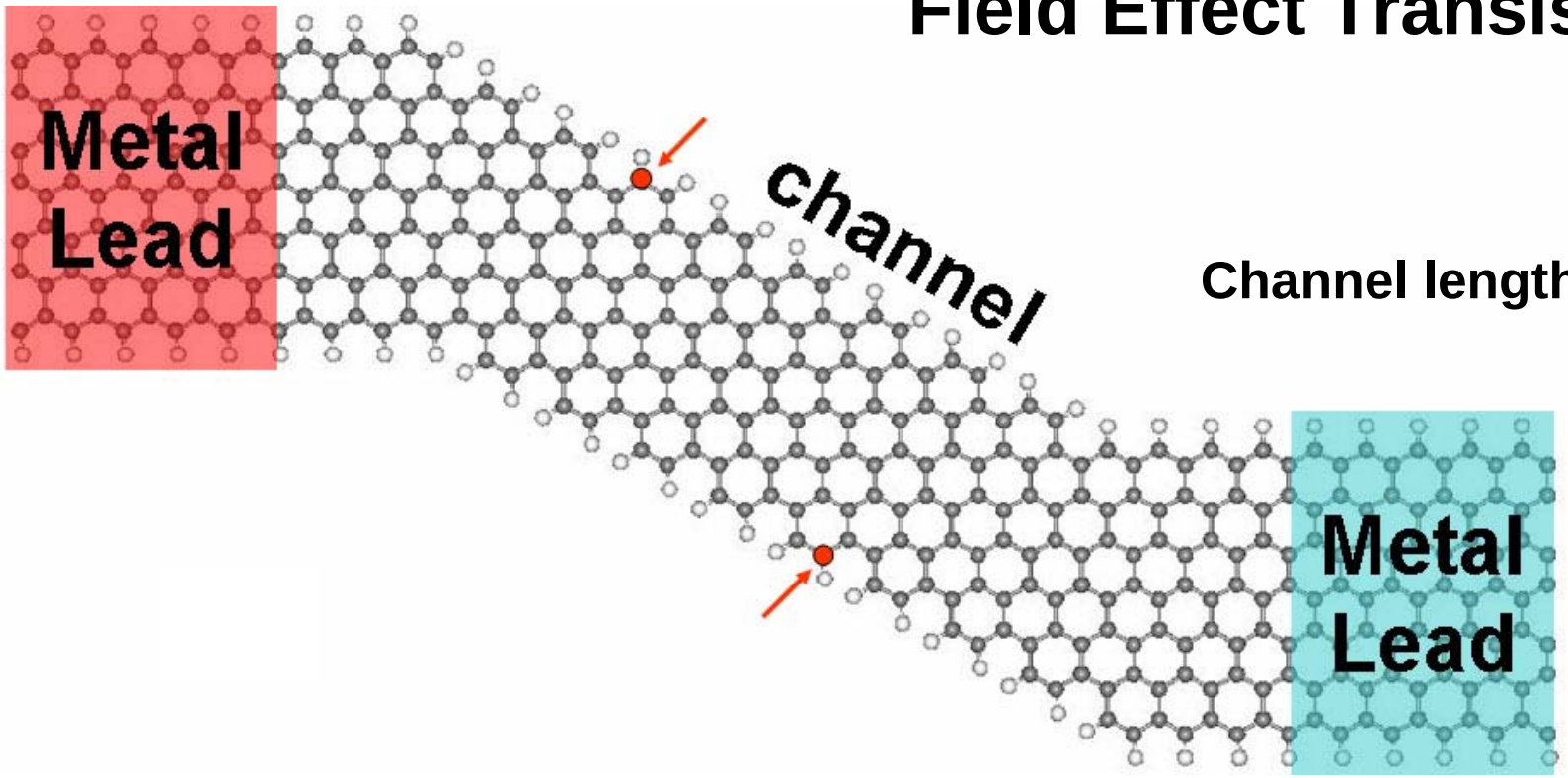


- Metal-semiconductor contact
- p-n contact
- Semiconductor-semiconductor heterojunction

Key advantages in designing and constructing device based on GNRs

- All the junctions between GNRs of different width and directionality have *perfect atomic interface*.
- Good connectivity: the GNR-based devices can be connected to the outside circuits exclusively via metallic GNRs
- *Edge doping* is easy for GNRs with two free edges.

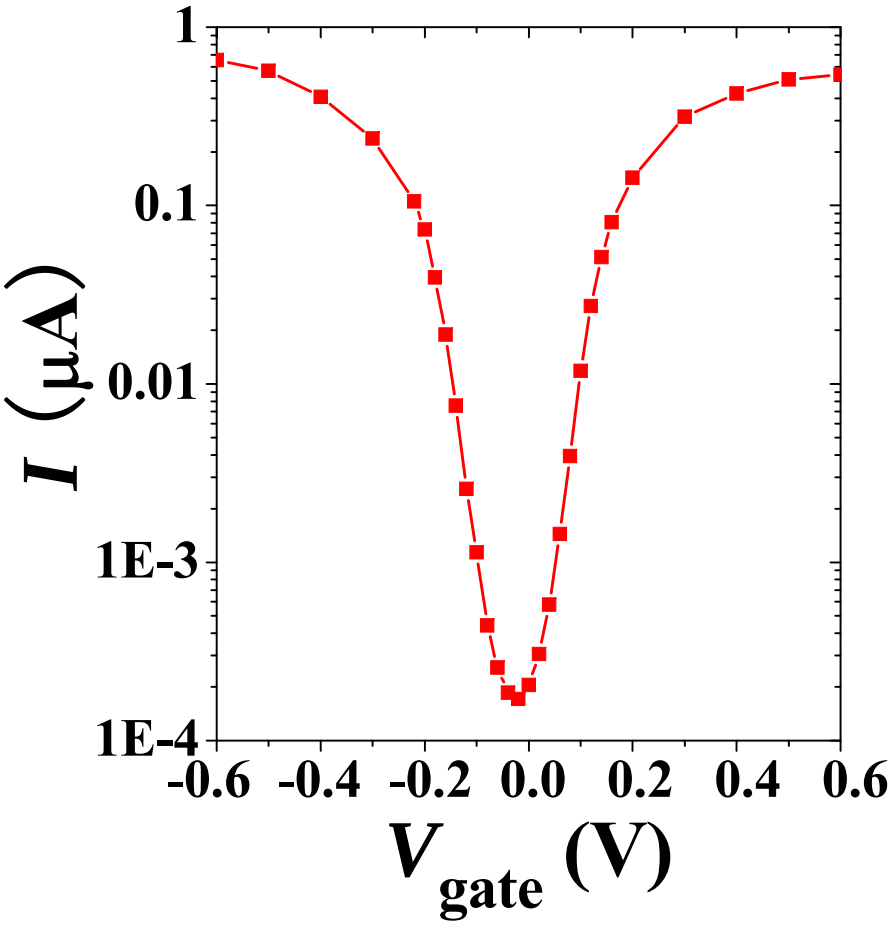
Nanoribbon based Field Effect Transistor



Channel length ~ 6 nm

(3,3) armchair GNR / (4.5,0) zigzag GNR / (3,3) armchair GNR

I-V characteristic of GNR-FET



Ambipolar transistor

Near-symmetric I-V_{gate} curve

On-current ~ 0.7 μA.

Minimum leakage current ~10^{-4} μA

Threshold Gate Voltage ~ 200 mV

On-Off ratio ~ 2000

Perfect atomic interface between the metal and semiconductor GNRs with minimum contact resistance.

I-V characteristic

Transconductance: $G_T = dI / dV_{\text{gate}}\Big|_{V_{\text{bias}}=1.0\text{eV}} / W$

$\sim 9500\ \text{S/m}$

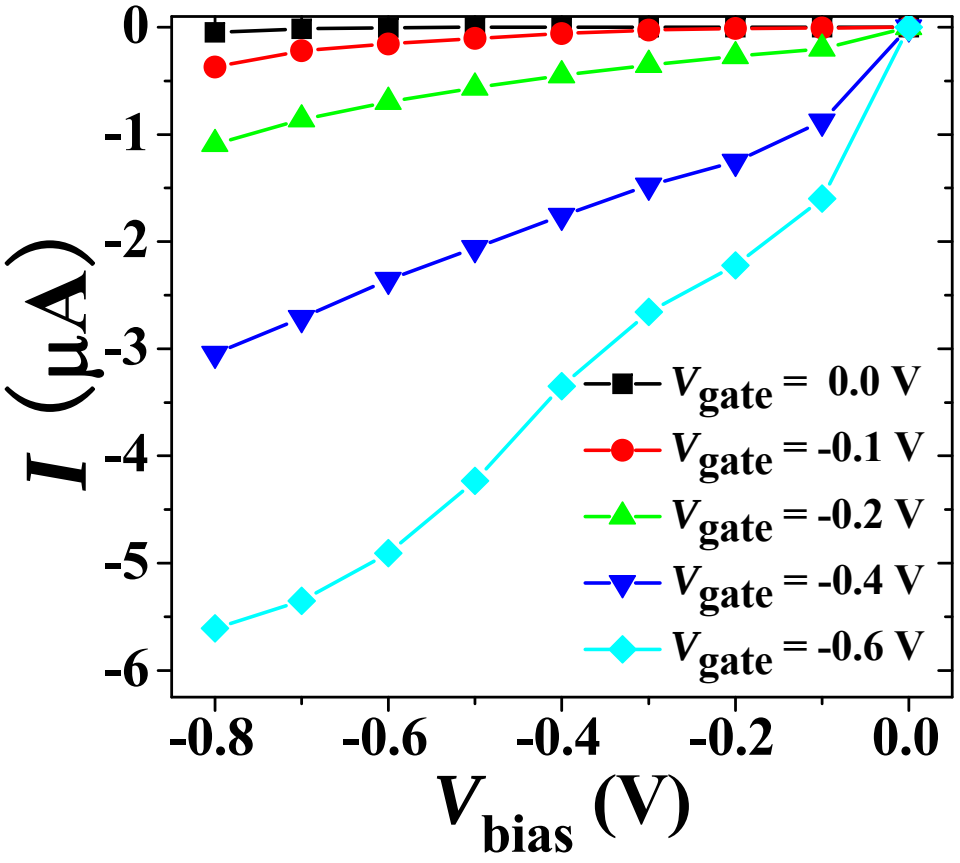
(10.5 mS without width normalization)

Comparable to the best value of 5000-7000 S/m achieved experimentally with SWNT-FETs **!**

Subthreshold swing: $S = dV_{\text{gate}} / d\log_{10} I \sim 60$ mV/decade

~ the value for the best SWNT-FETs, and the theoretical limit of conventional Si-based FETs

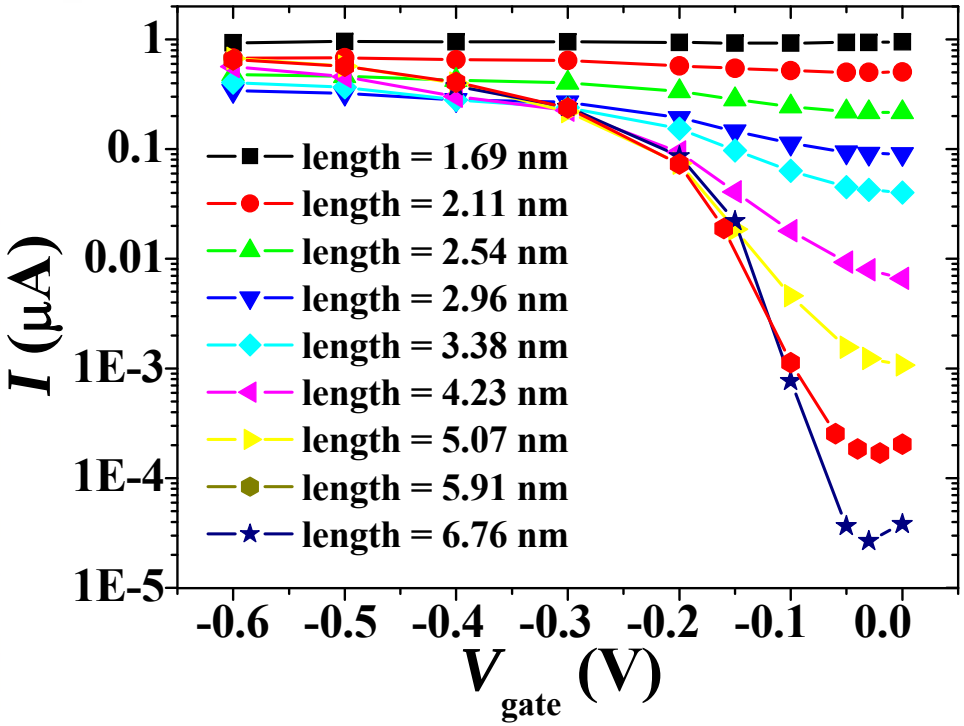
I-V characteristic

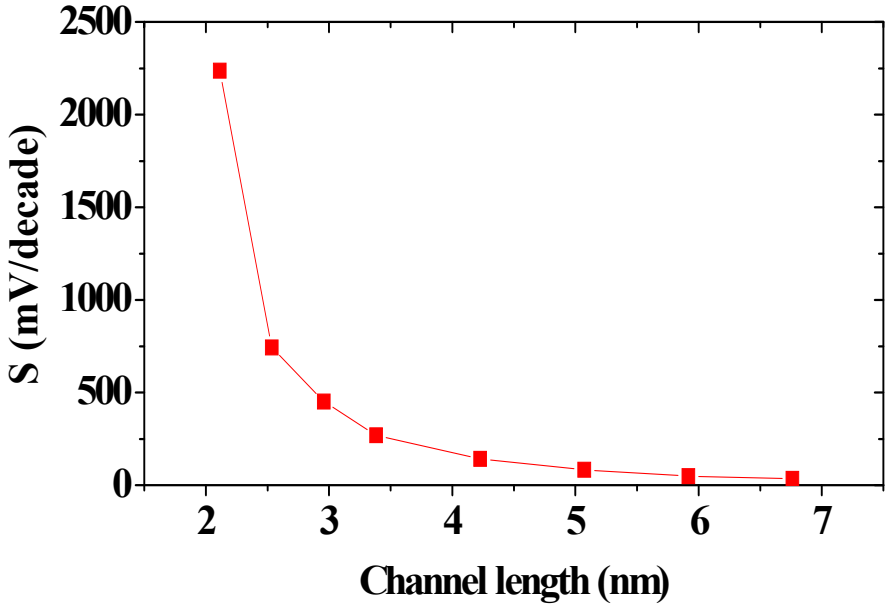


- A typical power-law behavior of semiconductor transport at low gate voltages
- An Ohmic behavior at large negative V_{gate}

Transport properties of the GNR-FETs can be effectively modulated by the gate voltage.

Dependence on Channel Length

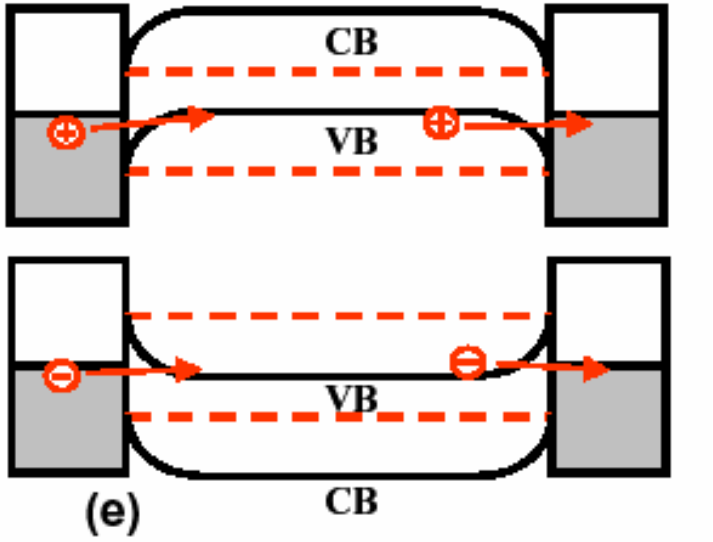




- S decreases with increasing channel length l_c.
- The on-current stays the same, independent of l_c, but the minimum leakage current at the OFF state increases rapidly with decreasing l_c, which gives rise to a large S.

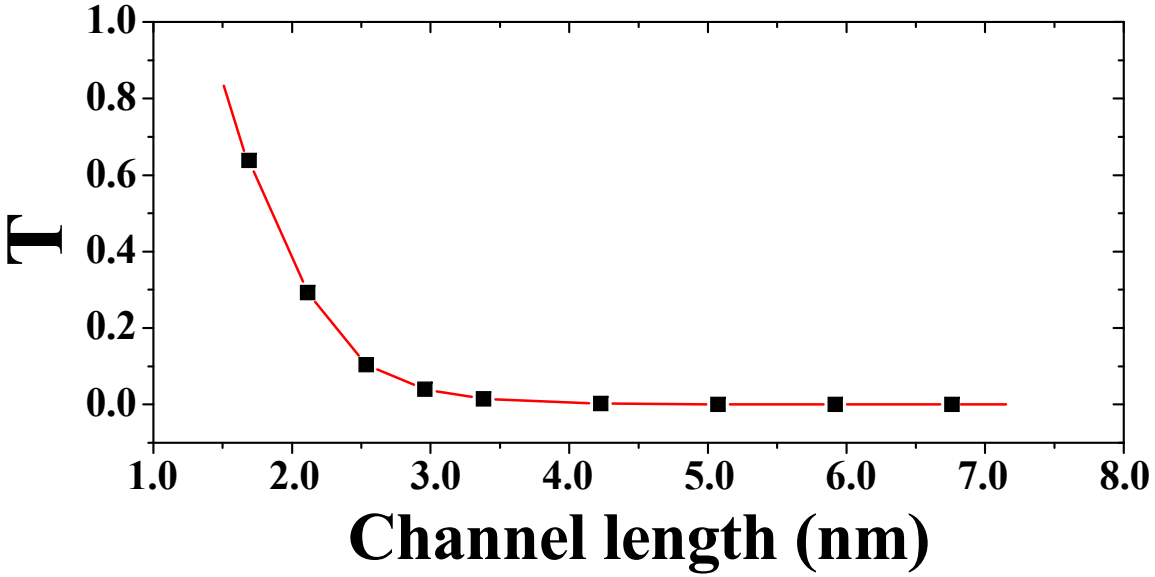
Physical Mechanism

Band-bending model:



- OFF state of zero gate voltage: the Fermi level is located at the midgap of the semiconducting channel, and the carriers can't transport through the channel.
- When a gate voltage is applied, the electrostatic potential in the channel is raised or lowered, and holes or electrons may tunnel from lead into channel.

Effective carrier mass



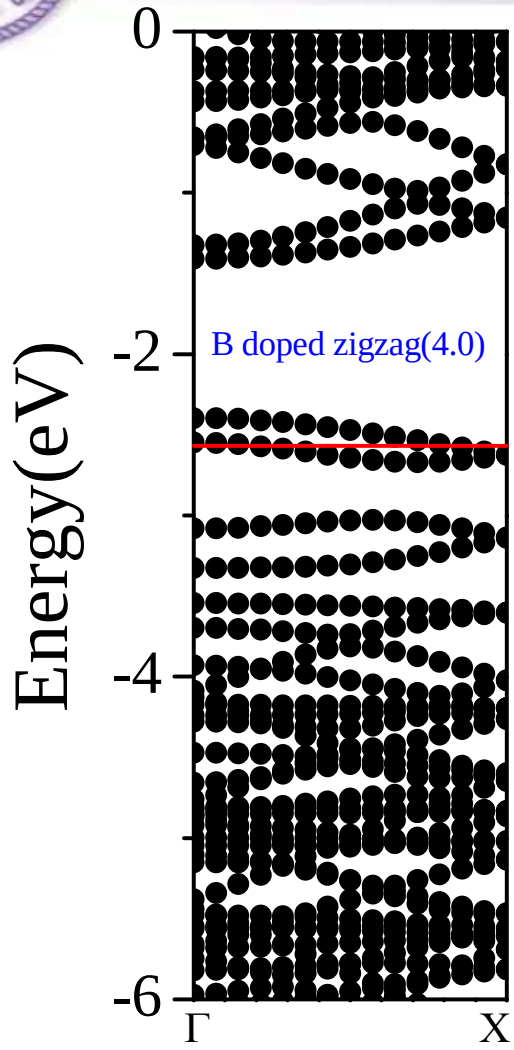
Using the semiclassical theory of tunneling through a finite square potential barrier, we have

$$T_m = 1/[1 + C\sinh^2(\kappa x)]$$

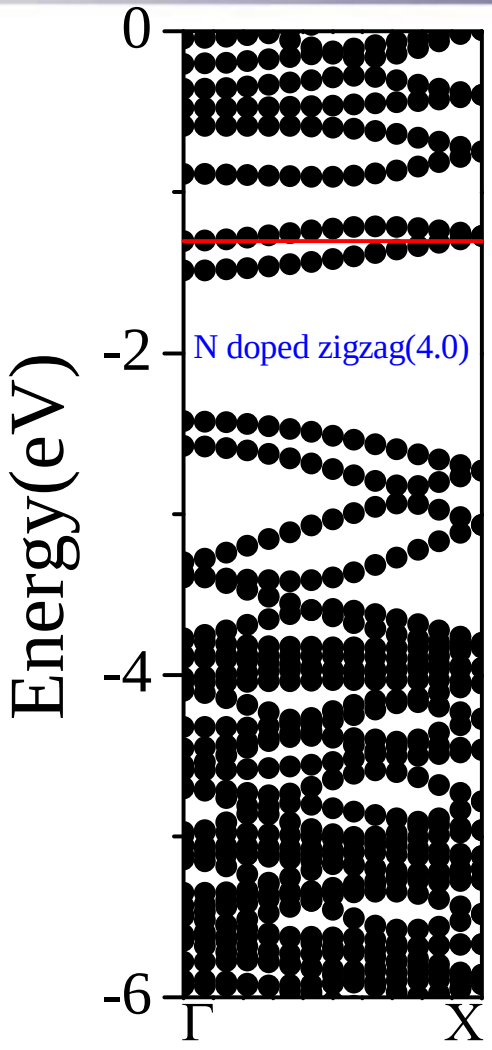
$$\kappa = \sqrt{2m^*\Delta}/\hbar$$

→ $m^* \sim 0.08\, m_e$

Edge doping



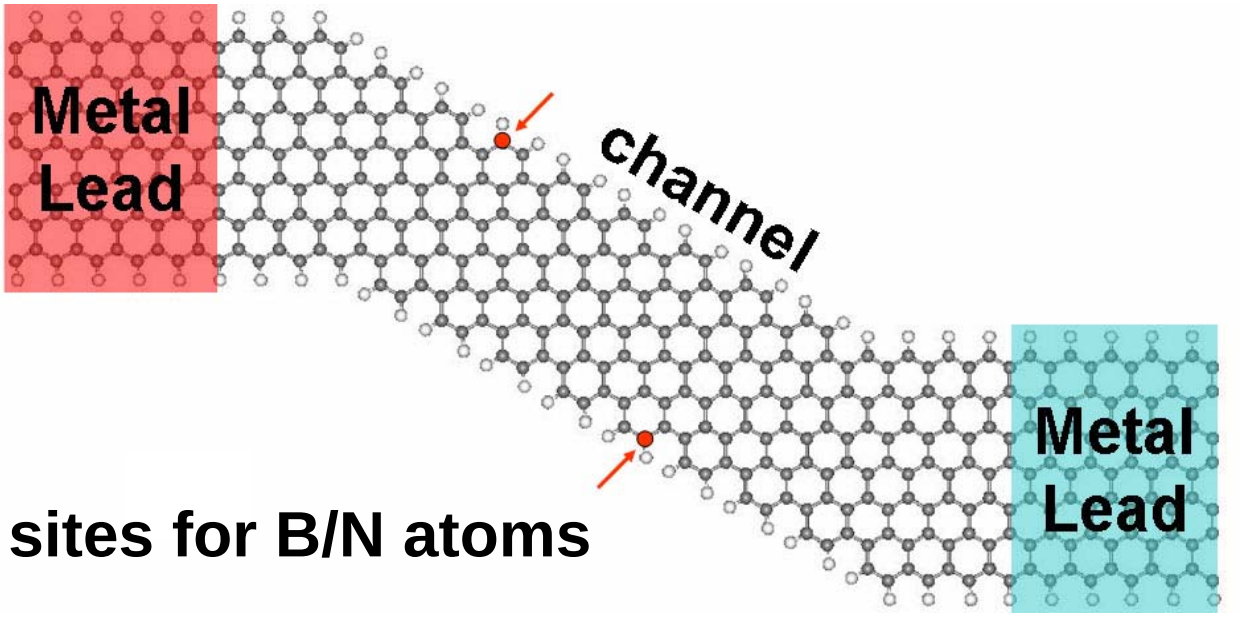
B-doping



N-doping

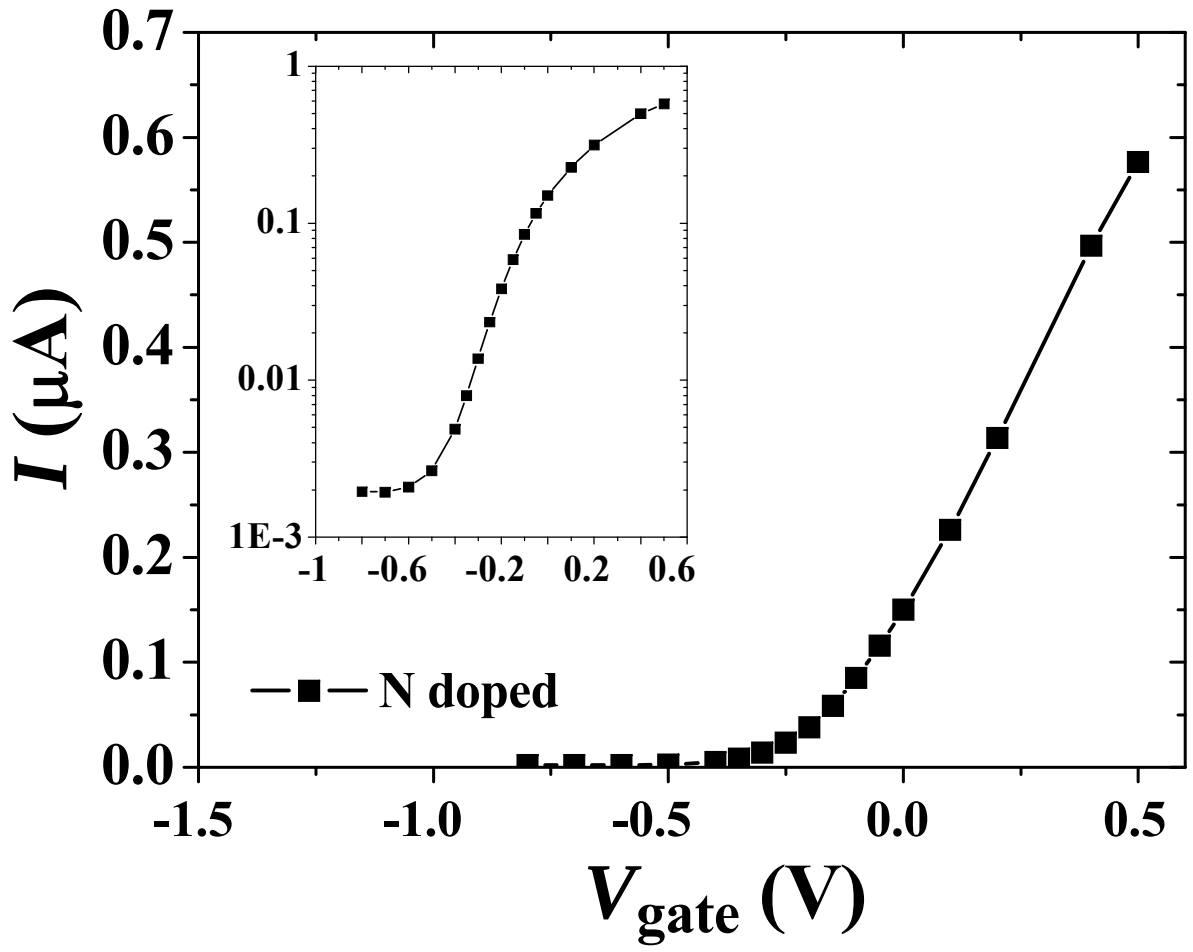
Edge doping of B/N atoms will lead to a shift of the Fermi level into the valence band/conduction band.

n/p-type FET



Doping sites for B/N atoms

I-V Characteristic



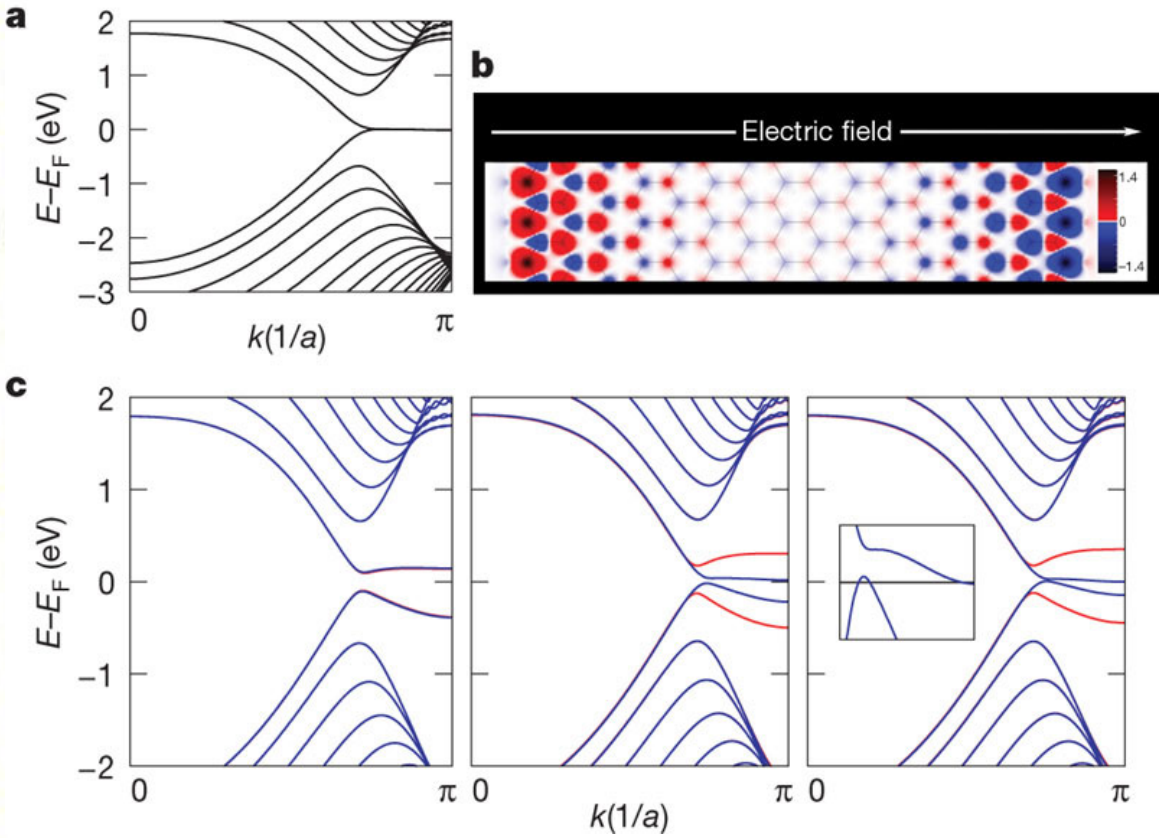
***n*-type GNR-FET**

On-Off ratio ~ 300

S ~ 200 mV/decade

Dopant concentration ~$2.4 \times 10^{13}/cm^2$

Suppression of spin-polarization by edge defect and impurity



ground state 0.05 V/Å 0.1 V/Å

GNRs was predicted to exhibit half-metallicity under in-plane homogeneous electric fields.

Young-Woo Son, et al., Nature 444, 347 (2006)

- The magnetism in GNRs is resulted from highly degenerate edge states:

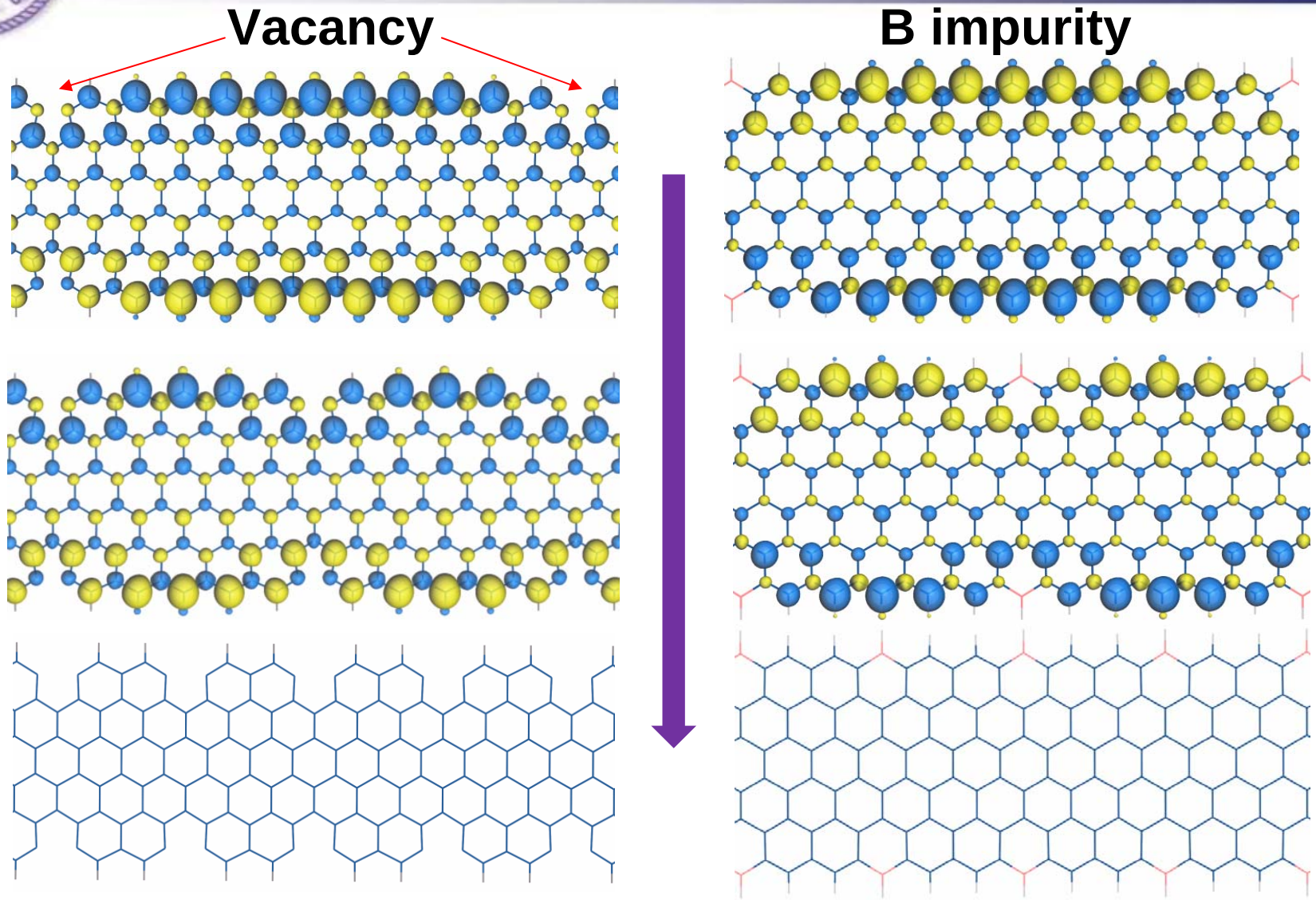
  Does it require a prefect edge structure ?

- Real sample of GNRs are unlikely to have prefect edges but contain structural defects and impurities of foreign atomic species…..

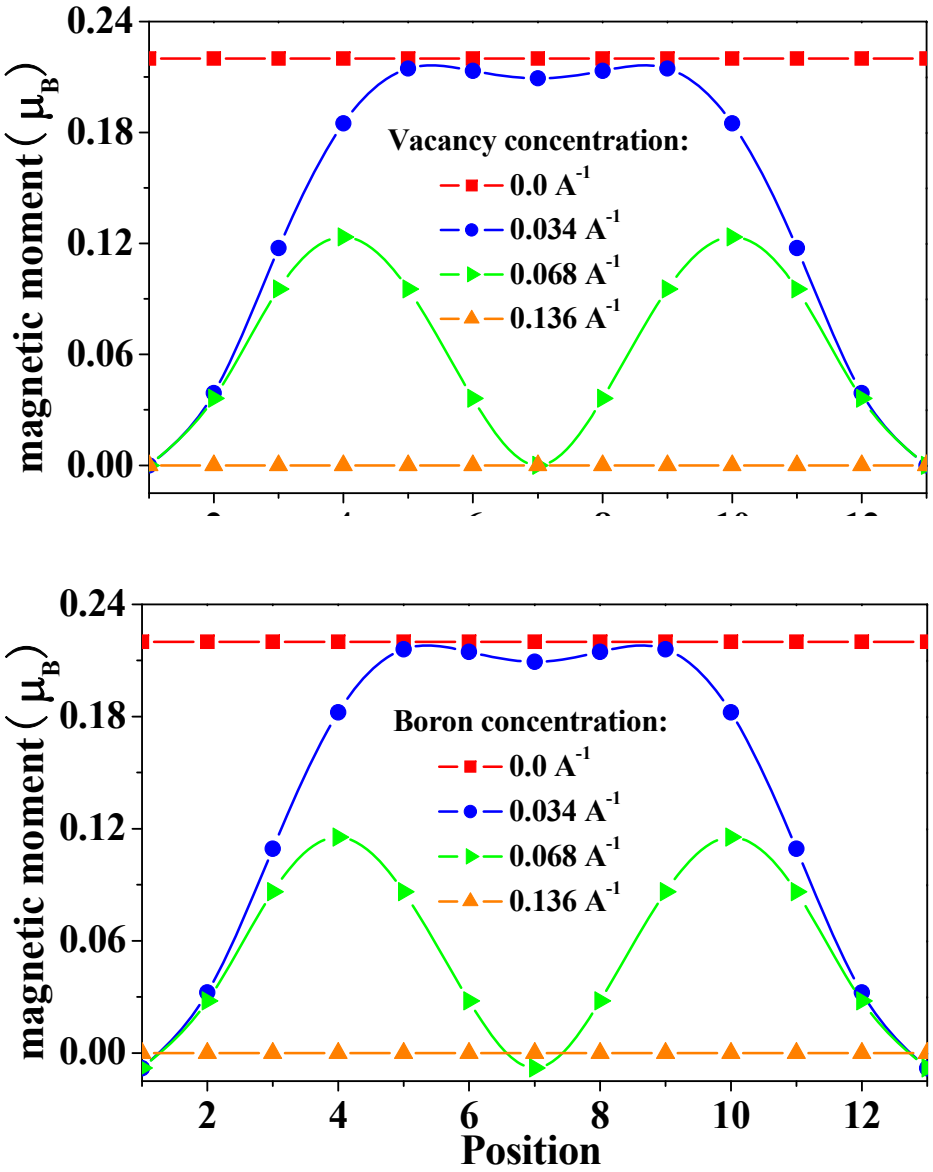
- How robust is the spin state in presence of edge defects and impurities ?

Vacancy and the substitutional boron (B) atom

Spin density



(3,3) GNRs with different defects concentration



Magnetic moment on the top edge

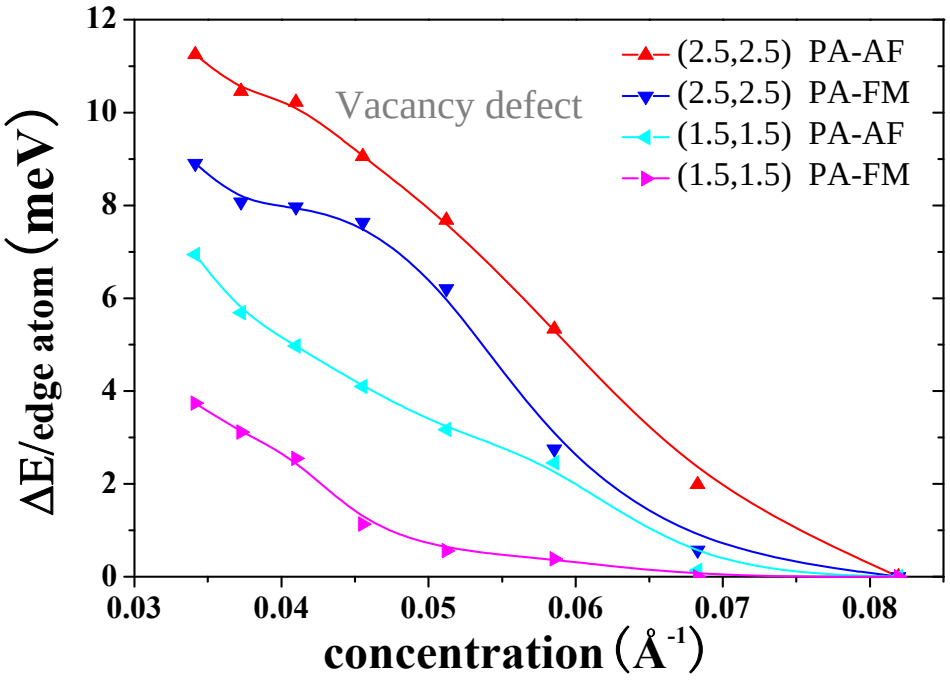
Spin-density wave!

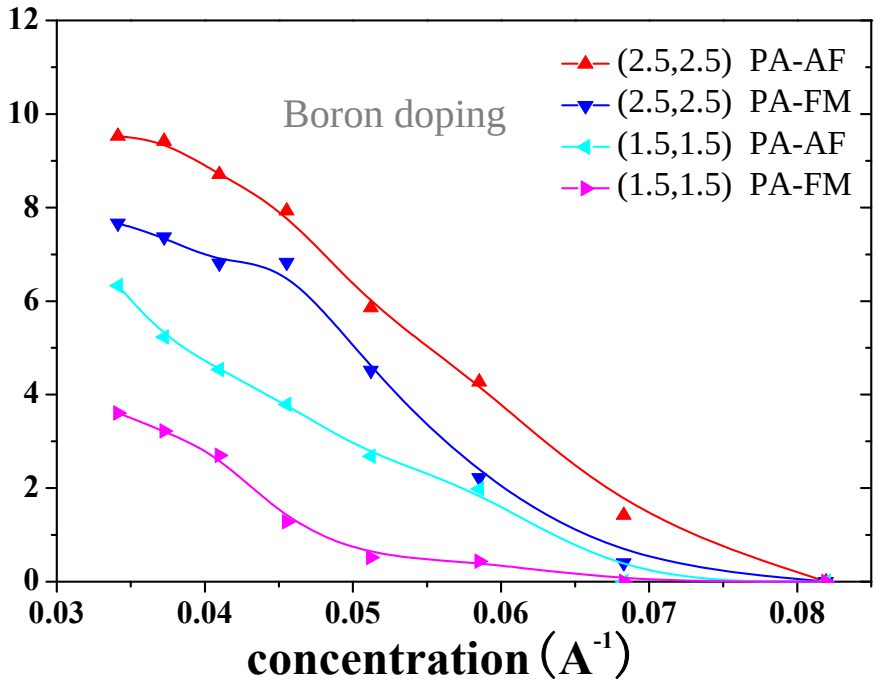
along the ribbon edge

Spin-polarization decreases with increasing edge defect concentration and eventually vanishes!

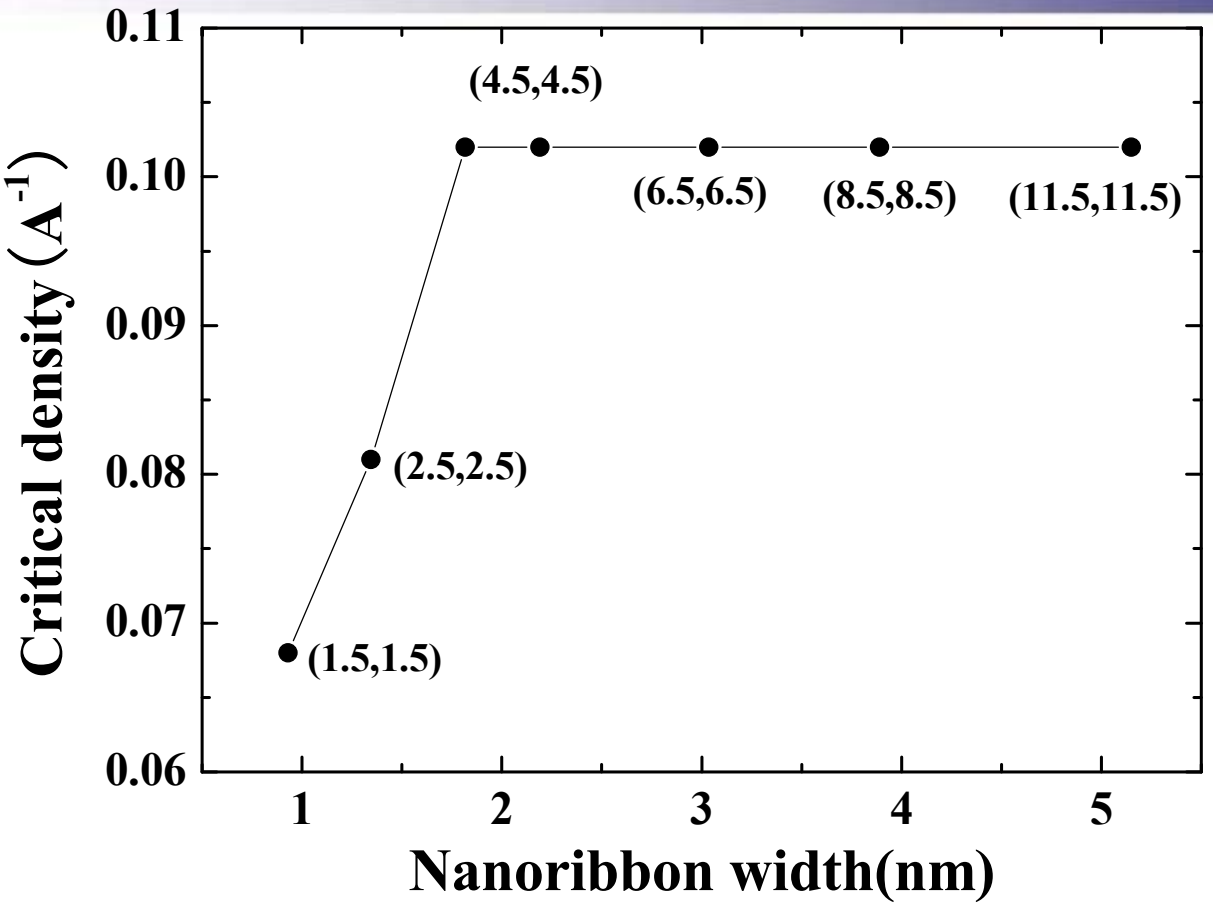
Relative stability of spin-polarized states

Energy difference per edge atom





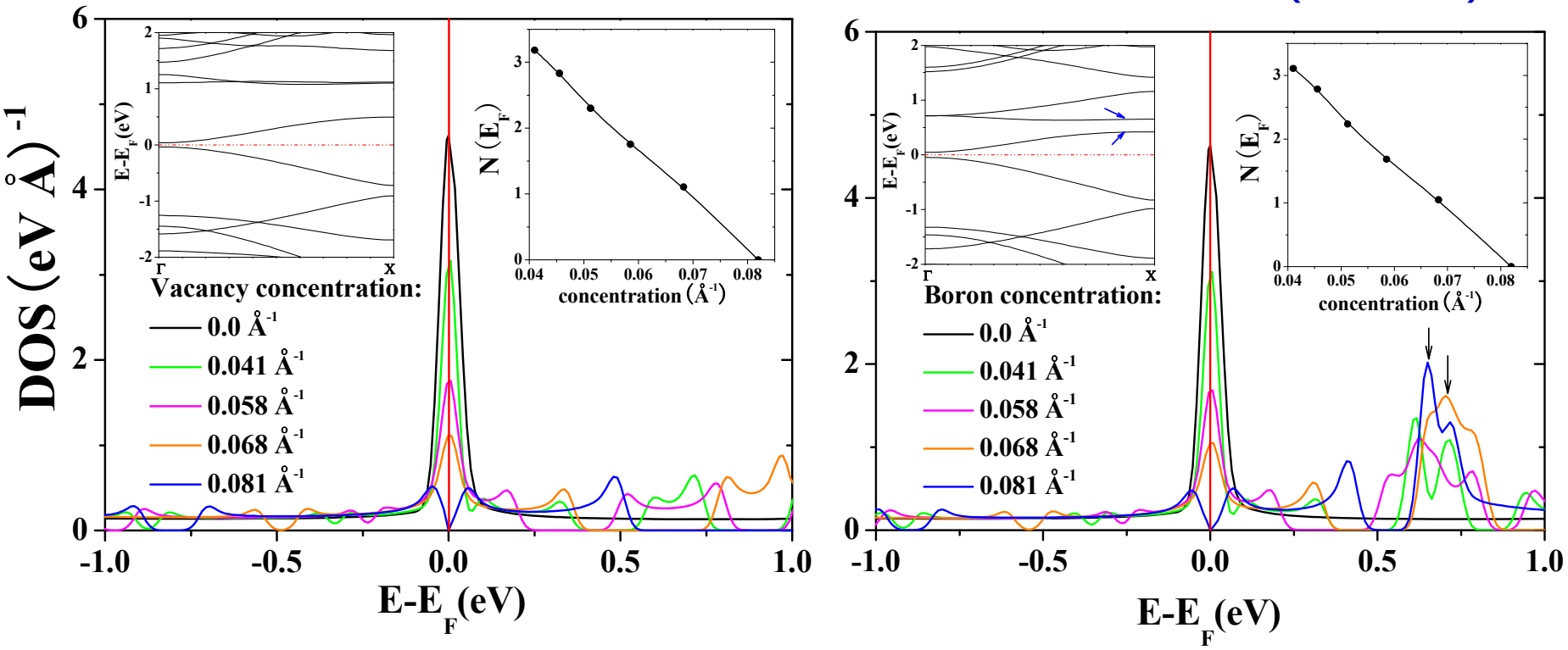
The energy difference between the magnetic state and nonmagnetic state decreases rapidly with increasing defect concentration.



Critical transition concentration (~0.1Å^{-1}) corresponds to an average defect-defect separation at the fourth NN positions on the edge.

Physical mechanism

DOS of the paramagnetic state (2.5,2.5) ribbon



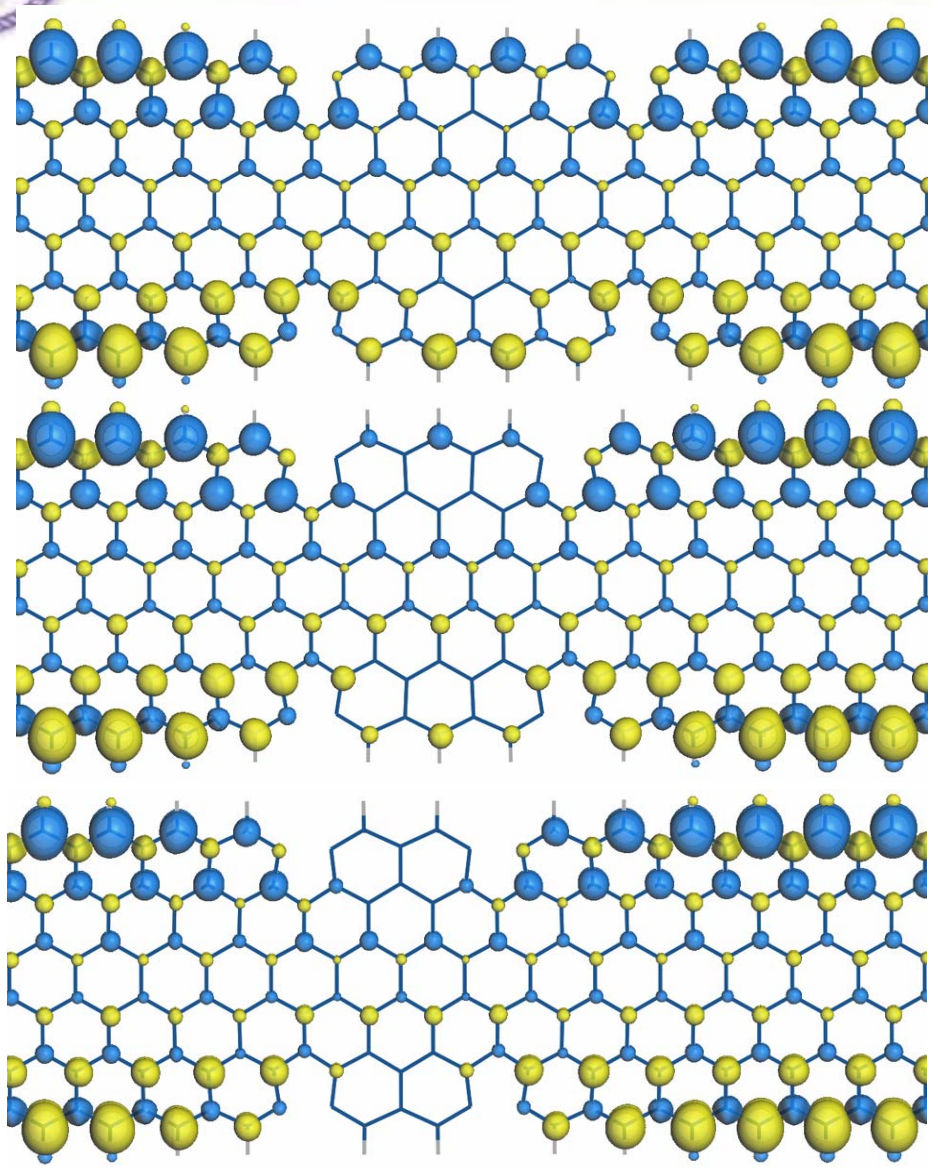
The spin suppression is caused by reduction (by vacancy) and removal of (by Boron) edge states at the Fermi energy.

The spin suppression by edge defect (impurity) can be understood in the context of itinerant ferromagnetism and local order. Magnetic moment in an itinerant magnetic material depends strongly on local coordination.

When a magnetic atom is introduced in a nonmagnetic medium, its moment is quenched at low concentration but can be redeveloped at high concentration and there is strong correlation between the magnetic dopants.

Conversely, when a nonmagnetic “impurity” is introduced in the magnetic medium, the moment is greatly suppressed at the impurity site and its vicinity.

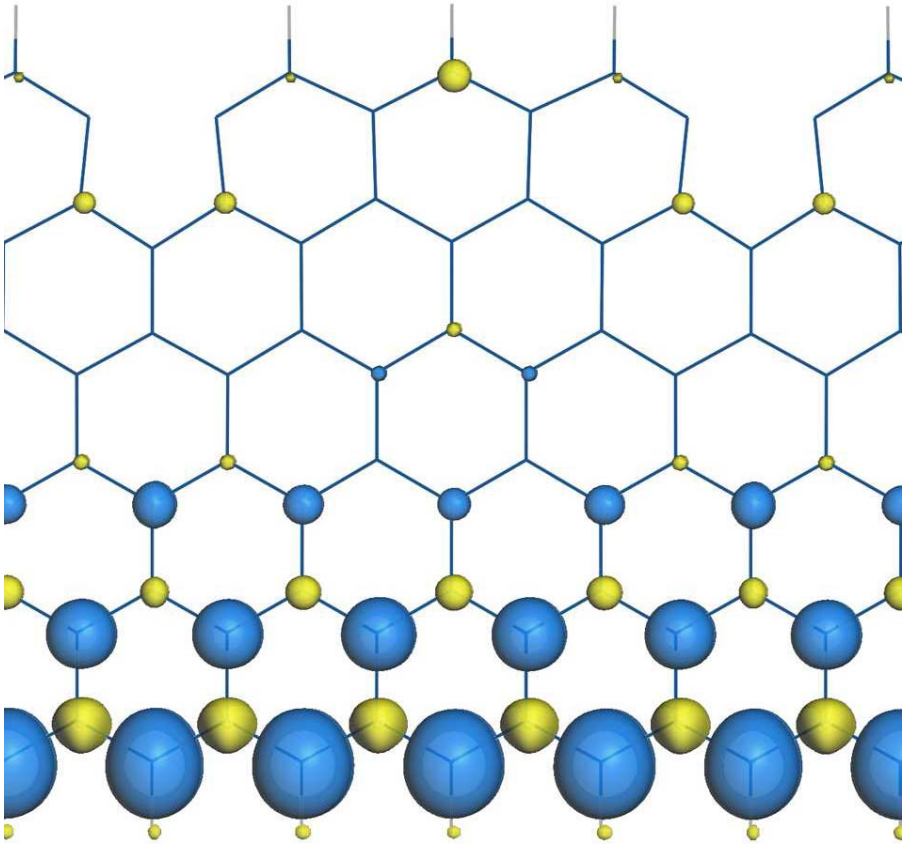
Correlation between defects

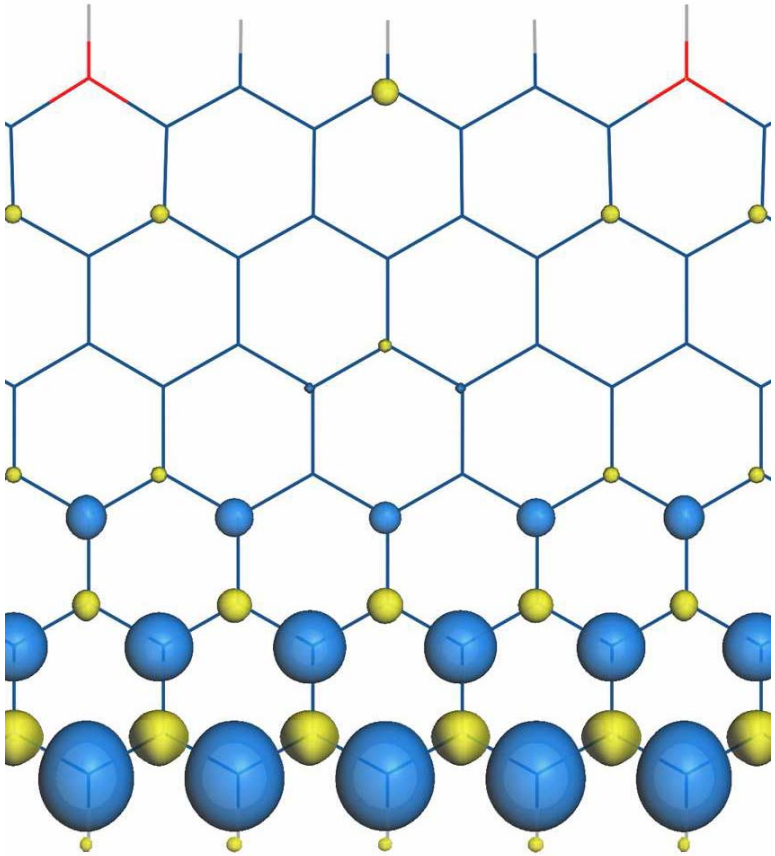


Local moment between two vacancies decreases as the two vacancies moving closer and completely vanishes.

Spin suppression is a rather localized effect!

Defects in only one edge





Conclusion and Summary

- Due to the similar quantum confinement effect, the electronic properties of GNRs exhibit a dependence on the ribbon direction and width that is the same as those of SWNTs do on the tube diameter and chirality.

  This provides the possibility of GNR-based electronics.

- The work function of GNRs is with different widths or directionality.

- GNR-based devices can be made with the atomic perfect-interface junctions and with controlled doping through edge termination, and may exhibit excellent performance comparable to the best case of nanotubes.

  The FETs made from intrinsic semiconductor zigzag ribbons can exhibit very high levels of performance, with On/OFF ratio up to 10^3, subthreshold swing as low as 60 meV per decade, and transconductance of 9.5×10^3 Sm^{-1}.

- Spin polarization can be greatly suppressed in the presence of edge defects and impurities.

Critical edge defect (impurity) concentration ~0.1 $Å^{-1}$.

A requirement on the GNR samples for spintronics applications.

- The spin suppression correlates closely with the reduction of DOS at the Fermi energy induced by defects (impurities).

A variety of device architectures as well as complete integrated circuits might be fabricated by nanopatterning of a single graphene sheet into the networks of GNRs.

Open up a new direction of nanoelectronics!

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Thanks !