Hopping magnetoresistance in monolayer graphene disordered by ion irradiation

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Motivation

Study of magnetoresistance in the variable-range-hopping (VRH) regime including the case of 2D conductivity has a long history. However, investigation of known phenomenon in a new material leads sometimes to observation of new features.

**Choice of the new material: monolayer graphene (MG)**

1) Why monolayer graphene?

Carbon-based materials

- Pristine MG is a material with combination of unique properties, the best contender for the post-silicon electronics.

MG is a single atomic layer of carbon with hexagonal honeycomb lattice which consists of two interleaving triangular lattices. There are 2 atoms in a unit cell

**MG is true 2d material**

After extracting of a MG in 2004 by A. Geim and K. Novoselov, the number of publication increases exponentially.
### Mobility (cm²/V·s)
- Graphene: 200,000
- Silicon: 1400
- GaAs: 8500

### Transparency (%)
- Graphene: 97.7

### Bulk Resistivity (μΩcm)
- Graphene: 10
- Doped Gr: 4.2
  - Cu: 1.68
  - Tungsten: 5.6

### Current Density (A/cm²)
- Graphene: 10⁶
- Al: 800
- Cu: 4020

### Chemical Inertness (Bond enthalpies KJ/mol)
- Aromatic C-C: 518
- Si-Si: 348
- Si-Si: 176

### Surface Area (m²/g)
- Graphene: 2630
- Activated C: 500
- Silica: 800

### Thermal Conductivity (W/m · K)
- Graphene: 5300
- Silicon: 149
- Diamond: 2320

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MG is the best contender for the post-silicon electronics.

- Fast operating FET
- Transparent Electrode
- Interconnect
- Barrier Hard Mask
- Super capacitor
- Heat Sink
MG is a gapless semiconductor, conducting and valence bands meet in the Dirac point. $E(k)$ in MG is linear, as for massless photons, but the significant difference is that electrons and holes in MG are charged fermions. These electrons and holes are known as Dirac fermions, or Graphinos.

As a result, pristine MG is well conducting material. Even if the Fermi level crosses the Dirac point, and average concentration of carriers $\approx 0$, conductivity is not small. Minimal conductivity (maximal resistivity) of MG interferes with some applications in electronics.

The problem: small on-off ratio

high-resistance state can be achieved by introducing of disorder

- $\sigma_{\text{min}} \approx 4(e^2/h)$
- $R_{\text{max}} \approx \pi h/4e^2 \approx 20 \text{ kΩ/sq}$
3) Why ion irradiation?

- **Ion irradiation as a method of disorder** has an advantage due to high accuracy (ability to control the energy of ions, dose of irradiation) and possible reversibility using annealing the radiation damage.

### Sample preparation

**large-scale (5 x 5 mm) specimen of MG**
(supplied by “Graphenea” company)

#### Graphene Film
- Growth Method: CVD synthesis
- Transfer Method: Clean transfer method
- Quality Control: Optical Microscopy & Raman
- Transparency: >97%
- Coverage: >95%
- Number of graphene layers: 1
- Thickness (theoretical): 0.345 nm
- Field Effect Mobility on SiO2/Si: 2,000 cm²/V·s
- Hall Effect Mobility on SiO2/Si: 4,000 cm²/V·s
- Sheet Resistance: 350 Ohms/sq.
- Grain size: Up to 10 μm

#### Substrate SiO₂/Si
- Dry Oxide Thickness: 300 nm (+/-5%)  
- Type/Dopant: P/Bor
- Orientation: <100>
- Resistivity: <0.005 Ohm·cm
- Thickness: 525 +/- 20 μm
- Front surface: Single Side Polished
- Back Surface: Etched

**Ion irradiation:**
- C⁺ ions, 35 keV
- Xe⁺ ions, 35 keV

**CVD synthesis**
**Clean transfer method**
**Optical Microscopy & Raman**

**Transparency**: >97%

**Coverage**: >95%

**Number of graphene layers**: 1

**Thickness (theoretical)**: 0.345 nm

**Field Effect Mobility on SiO₂/Si**: 2,000 cm²/V·s

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**Resistivity**: <0.005 Ohm·cm

**Thickness**: 525 +/- 20 μm

**Front surface**: Single Side Polished

**Back Surface**: Etched

**C⁺ ions, 35 keV**

**Xe⁺ ions, 35 keV**
Raman scattering spectra in disordered MG

MG is a zero-gap material with linear dispersion at the unequivalent $K$ and $K'$ points of the Brilluion zone.

*Three main lines: D, G and 2D*

**2D**

**D**

*Intervalley two phonon scattering mode is allowed, because of momentum conservation, therefore 2D-band is associated with the perfect lattice*

*One-phonon scattering is forbidden, therefore D-band is associated with areas in the vicinity of defects like edge, vacancy and other*

*The G-band is graphite-like band, it is of the first order allowed and the most prominent peak in graphene and in all graphene-based structures.*

*The ratio of intensities of D- and G- lines, $(I_D/I_G)$, is used as a measure of disorder.*
Irradiation with heavy and light ions (Xe\(^+\) and C\(^+\))

Concentration of introduced defects: \(N_D = k\Phi\), the value of \(k\) depends on energy and mass of an incident ion.

\[ I_D/I_G = C_d e^{-\pi \lambda L_D} \left[ 1 - e^{-\pi (r_A^2 + r_I^2)/L_D} \right] + C_s \left[ 1 - e^{-\pi \lambda L_D} \right] \]

Luccece et al, Carbon 48, 1592 (2010)

RS for series of monolayer graphene samples irradiated by Xe\(^+\) ions with energy 35 keV.

\(\Phi\) (in units of \(10^{13}\) cm\(^{-2}\)): 0 – 0 (pristine), 1 – 0.15, 2 – 0.3, 3 – 0.5, 4 – 1.0, 5 – 2.0, 6 – 4.0

\(L_d \approx r_A\)

Maximal D/G

\(L_d \approx (N_D)^{1/2}\)
Correlation between concentration of irradiation induced defects $N_D$ and resistivity $R$ in C$^+$-irradiated series of monolayer graphene samples

Resistivity at room temperature for all samples

$$R_{\text{max}} \approx 1/\sigma_{\text{min}} = \pi h/4 e^2$$

$$= 20 \text{ kOhm/sq}$$

Temperature dependence of resistivity for samples 0 - 4

Sample 0 – metallic conductivity, $dR/dT > 0$
Sample 1 – conductivity of a “bad metal”, $dR/dT < 0$
Samples 2-4 – exponential dependence $R(T)$.

Sample # | $N_D(10^{12}\text{cm}^{-2})$
---|---
1 | 1
2 | 3
3 | 6
4 | 12
Regime of strong localization (samples 2,3,4)
Variable-Range-Hopping (VRH) conductivity

Mott VRH ("$T^{-1/3}$" law)

$$g(ε) = const = g(μ)$$

$$R(T) = R_0 \exp(T_M/T)^{1/3}, \quad T_M = C_M[g(μ)a^2]^{-1}$$

$$C_M = 13.8$$

Temperature dependence of resistivity plotted on the Arrhenius scale $\log R$ vs. $1/T$
Energy of activation continuously decreases with decreasing $T$ which is characteristic for the Variable-Range-Hopping conductivity (VRH).

In samples 2,3,4, magnetoresistance was measured in perpendicular and parallel magnetic fields up to 8 T at temperatures down to 1.8 K

Deviations from the straight line at low $T$ are due to existence of a soft Coulomb gap at the Fermi level in the density-of-states.
Hopping Magnetoresistance in irradiated graphene

Negative magnetoresistance (NMR) is observed in perpendicular magnetic fields and positive MR (PMR) in parallel fields at low temperatures.

This anisotropy shows that MR in perpendicular and parallel fields has different origin: NMR is determined by the orbital mechanism, while PMR is determined by spin polarization.
NMR in perpendicular magnetic fields: “orbital” model for NMR in VRH

Nguen, Spivak and Shklovskii, JETP Lett. 41, 42 (1985);

NMR of samples 2 (a), 3 (b) and 4 (c) at different temperatures \((T, K)\) shown near the curves. The density of structural defects \(N_D (cm^{-2})\): in sample 2 – 3x10^{12}, 3 – 6x10^{12}, 4 – 1.2x10^{13}.

The probability of the long-distance hop is determined by the interference of many paths of the tunneling through the intermediate states which include a scattering process. All scattered waves together with non-scattered direct wave contribute additively to the amplitude of the wave function \(\Psi_{12}\).

As a result of averaging over random distribution, the total contribution vanishes due to destructive interference. Perpendicular magnetic field suppresses the destructive interference which leads to increase of the hopping probability and NMR.

Theory predicts quadratic dependence \(-\Delta R/R \sim B^2\) at low fields and linear dependence at stronger fields.

NMR as a function of \(B\) plotted on the log-log scale for samples 2 (a), 3 (b) and 4 (c).

The arrows show the values of \(B^*\), where quadratic dependence of MR is replaced by the linear one.
NMR in perpendicular magnetic fields:
“orbital” model for NMR in VRH

One can assume that $B^*$ corresponds to the case when magnetic flux through the cigar-shape area $\Phi_B = B \cdot A$ achieves the flux quantum $\Phi_0 = \hbar/2e \approx 2.07 \times 10^{-15}$ T/m$^2$. This gives $B^* = \Phi_0/A = \Phi_0/r^{3/2}\xi^{1/2}$

In the Mott VRH, the width of the optimal band $\varepsilon(T)$ and the hopping length $r_h$ are

$$
\varepsilon(T) = T^{2/3}[g(\mu)\xi^2]^{-1/3}
$$

$$
r_h \approx [g(\mu)\varepsilon(T)]^{-1/2} \approx \xi(T_M/T)^{1/3}
$$

So, $r_h \sim T^{1/3}$, this gives $B^* = \Phi_0\xi^{-2}(T_M/T)^{-1/2} = \lambda T^{1/2}$, where $\lambda = \Phi_0\xi^{-2}T_M^{-1/2}$

The slope $\lambda$ of the straight lines allows to estimate the value of localization radius $\xi$.

For samples 2, 3, 4, $T_M = 70, 300$ and $6000$ K which gives $\xi = 50$ nm, $22$ nm and $7$ nm correspondingly.

$\xi$ decreases with increase of disorder (from sample 2 to 4).
Universal NMR curve for all samples and temperatures

It turns out that that value of \( B^* \) is a normalizing parameter.

NMR of samples 2 (a), 3 (b) and 4(c) at different temperatures (\( T, K \)) shown near the curves. The density of structural defects \( N_D \) (cm\(^{-2} \)):
- Sample 2 – \( 3 \times 10^{12} \)
- Sample 3 – \( 6 \times 10^{12} \)
- Sample 4 – \( 1.2 \times 10^{13} \).

The NMR data for different samples and different temperatures plotted as a function of dimensionless magnetic field \( B/B^* \).
PMR in parallel magnetic fields


Schematic representation of the possible hopping transition via the double occupied states where the double occupied is an initial $\varepsilon_i$ (a), final $\varepsilon_j$ (b) or both initial and final states (c). $\mu$ represents the position of the Fermi level, dashed lines show the width $\varepsilon(T)$ of the optimal band at given temperature

This effect can be observed only at low T, when the width of the optimal band $\varepsilon(T) < T$. If $T >> \varepsilon(T)$, participation of the double occupied states does not influence the value of hopping conductivity
Conclusions

- MR of disordered monolayer graphene with VRH mechanism of conductivity was measured in perpendicular $B_\perp$ and parallel $B_\parallel$ magnetic fields; it is shown that in $B_\perp$, MR is negative (NMR) while in $B_\parallel$, MR is positive (PMR) at low $T$.

- The NMR is explained on the basis of the “orbital” mechanism based on suppression in a magnetic field of the destructive interference of many paths through the intermediate state in the probability of the long-distance tunneling in VRH.

- At low fields, $B_\perp < B^*$, $MR \sim B^2$. The values of $B^*$ are determined for all samples and temperatures. It is found that MR curves plotted as a function of normalized magnetic field $B_\perp/B^*$, are merged in a universal dependence

- It is shown that $B^* \sim T^{1/2}$ in accordance with the “orbital” model, the slopes allowed to estimate the radius of localization for different disordered samples.

- The PMR effect in $B_\parallel$, is explained by suppression in strong fields the hopping transition via double occupied states due to spin polarization