Defect evolution in graphene induced by He^{+} and He^{++} ion irradiation

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Defect kinds

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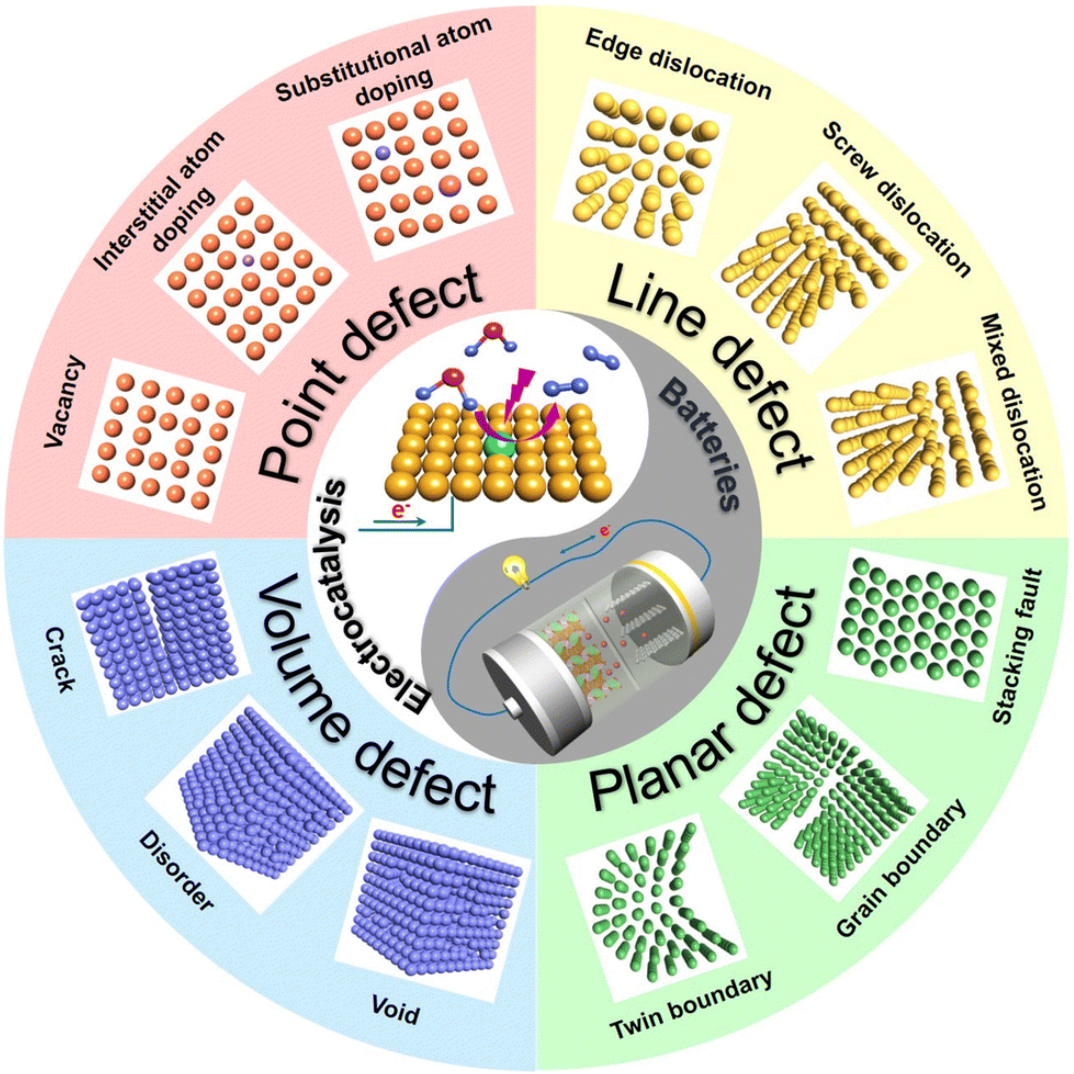
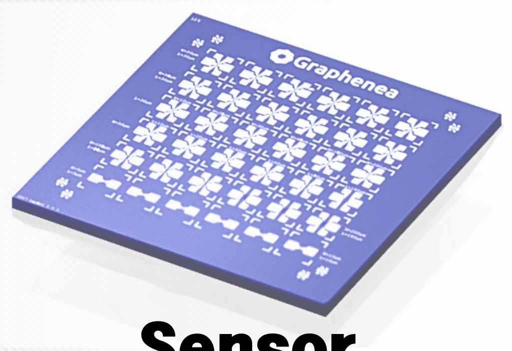


Materials 2018, 11, 1885

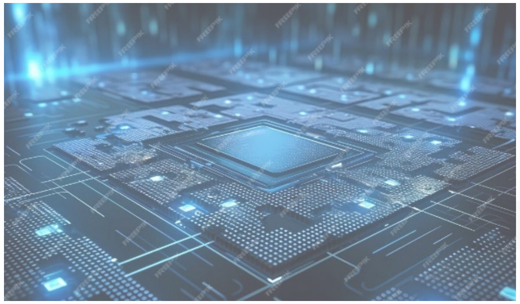
- Many people want materials with no imperfection.
- However, defects are ubiquitous in macroscopic samples
- Moreover, defects play an important role for the performance of any device.

Defect engineering

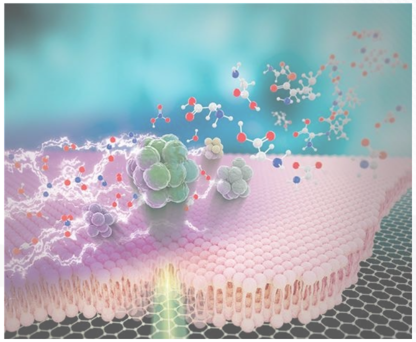
Defects can change many properties such as electrical, optical, mechanical properties



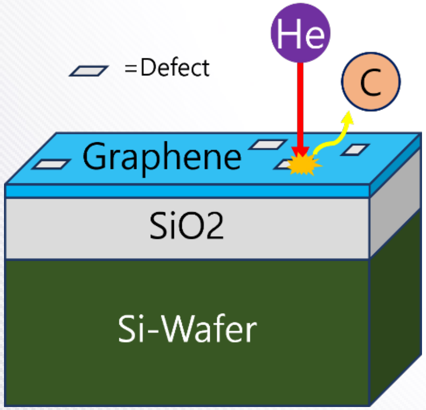
Sensor



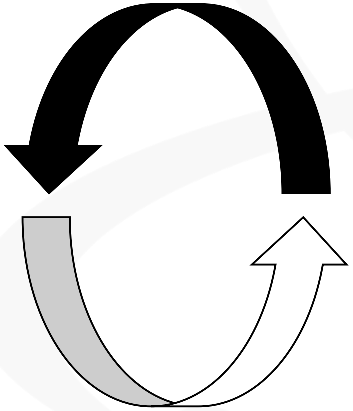
Nano electronics



Medical device



Formation



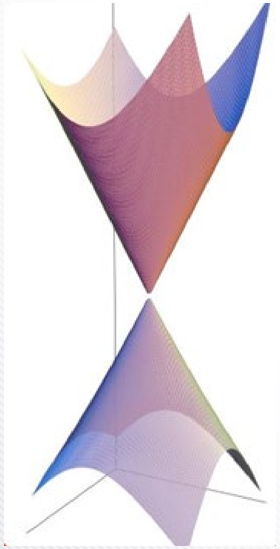
Control

Application

Defects on Graphene

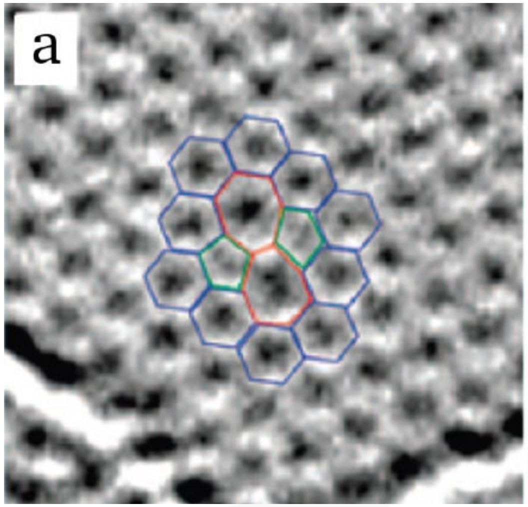
Graphene

- Carbone hexagonal networks with sp2 bonding
- High carrier mobility (2 x 10^5 cm^2/Vs)
- Perfect 2D Materials
- Zero rest mass near Dirac point

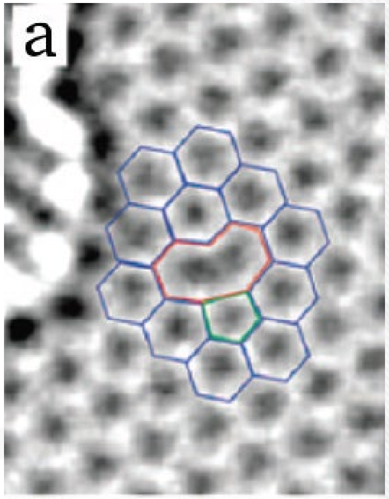


Defects

- Defects affect electrical, optical, and mechanical properties



Stone –Wales defect
: the defects without carbon atoms loss
: This is caused by the 90 degree rotation of C-C bond



Point defect

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Defects on graphene

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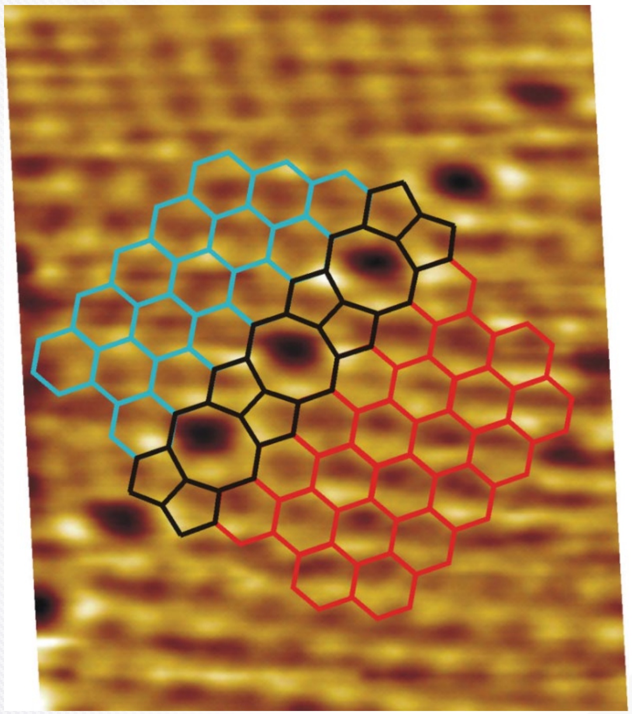
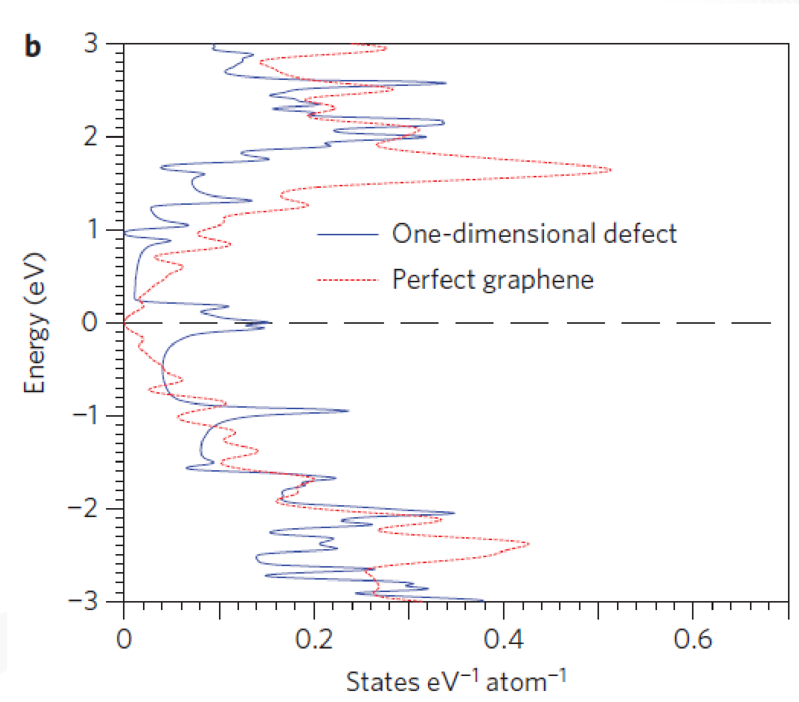
Linear defects



STM (scanning tunneling microscope image)



Calculated band structure

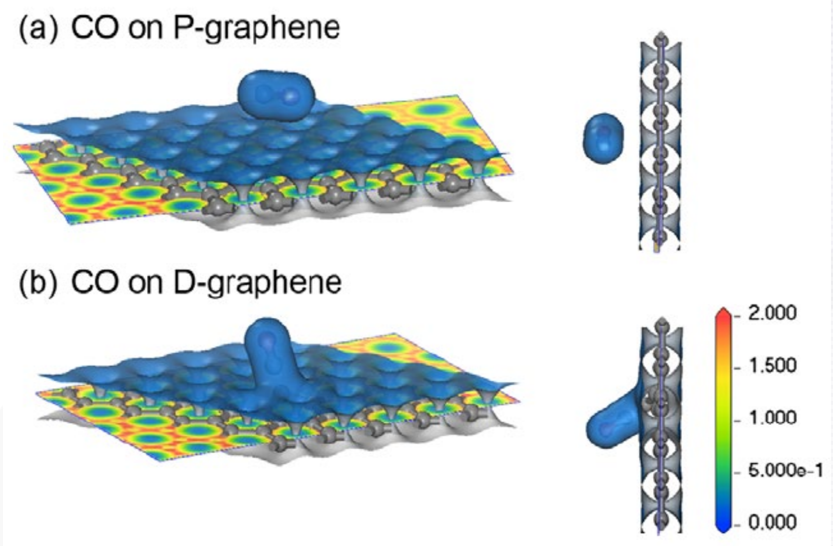
- The linear defects can be used as 1-D metallic wire

Nature Nanotech. 5 (2010) 326

Example of defective graphene

System	E_{ad}	d (Å)	Q (e)[a]
CO on P-graphene	−0.12	3.02	−0.01
NO on P-graphene	−0.30	2.43	0.04
NO_2 on P-graphene	−0.48	2.73	−0.19
NH_3 on P-graphene	−0.11	2.85	0.02
CO on B-graphene	−0.14	2.97	−0.02
NO on B-graphene	−1.07	1.99	0.15
NO_2 on B-graphene	−1.37	1.67	−0.34
NH_3 on B-graphene	−0.50	1.66	0.40
CO on N-graphene	−0.14	3.15	0
NO on N-graphene	−0.40	2.32	0.01
NO_2 on N-graphene	−0.98	2.87	−0.55
NH_3 on N-graphene	−0.12	2.86	0.04
CO on D-graphene	−2.33	1.33	0.26
NO on D-graphene	−3.04	1.34	−0.29
NO_2 on D-graphene	−3.04	1.42	−0.38
NH_3 on D-graphene	−0.24	2.61	0.02

Nanotechnology 20 (2009) 185504
Improving gas sensing properties of graphene by dopants and defects



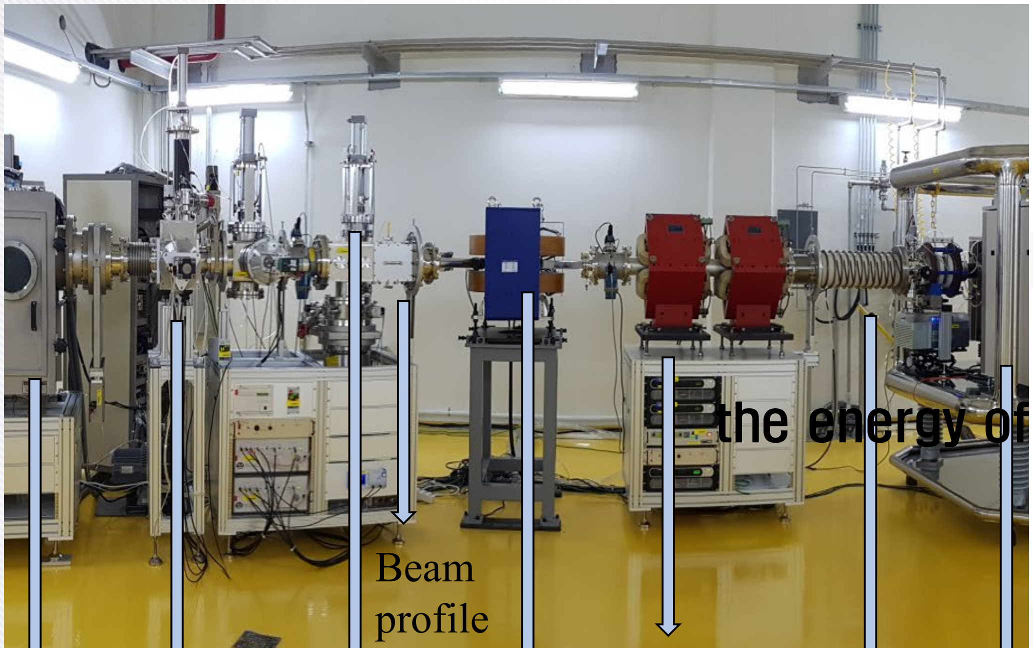
Calculation method: Density Functional Theory (DFT)

The adsorption energy difference between pristine graphene and defective graphene

	P-Graphene	D-graphene	
CO :	−0.12	−2.33	~20 times
NO2 :	−0.48	−3.04	~ 6 times
NH3 :	−0.11	−0.24	~ 2 times

Experimental apparatus

Gas ion implanter



Raman Spectrometer

We used the energy of 60 keV for He^{++} and the energy of 120 keV for H^{+}.

Typical Raman data for the ion irradiation

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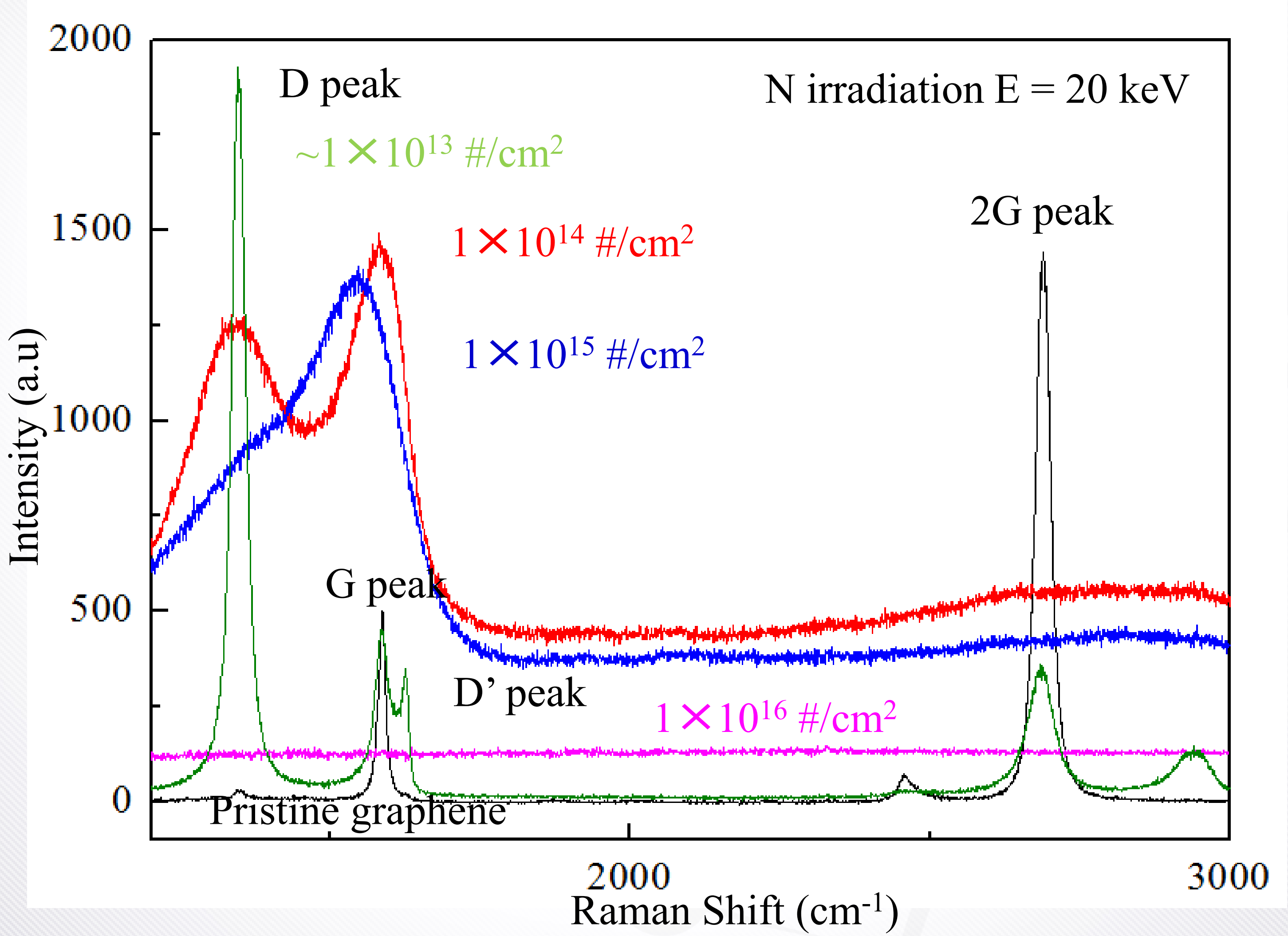
Raman spectroscopy of graphene by N implantation



Raman data for the He ion irradiation

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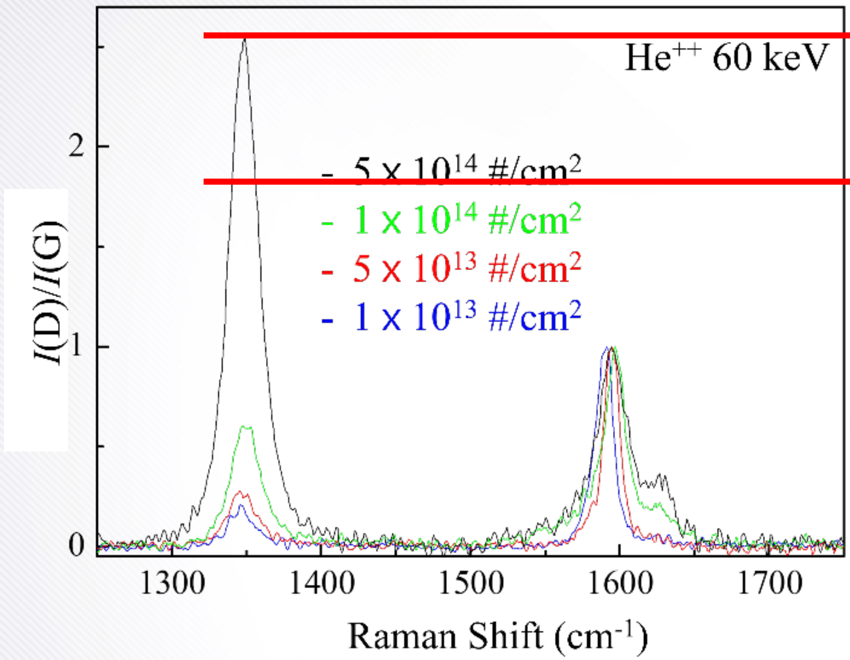
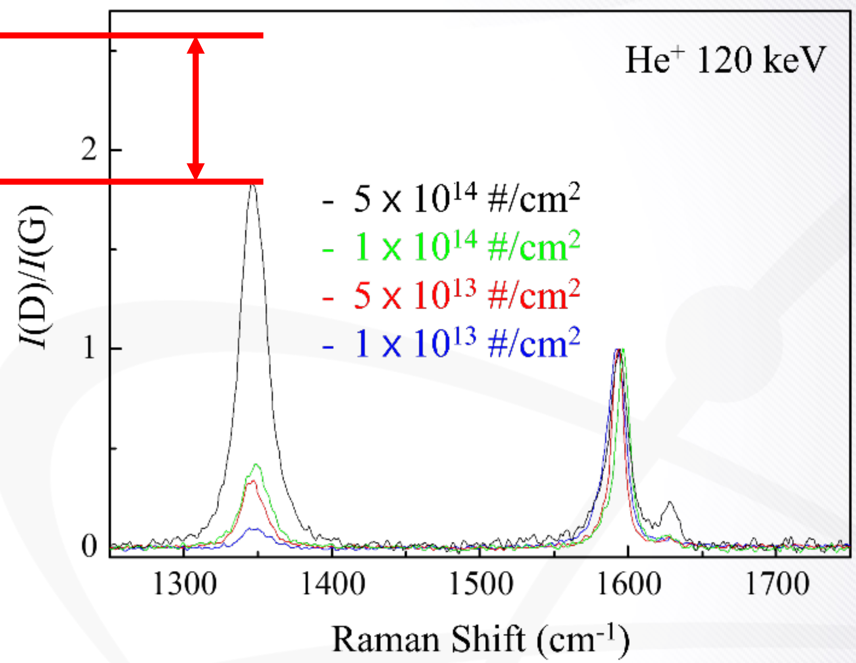
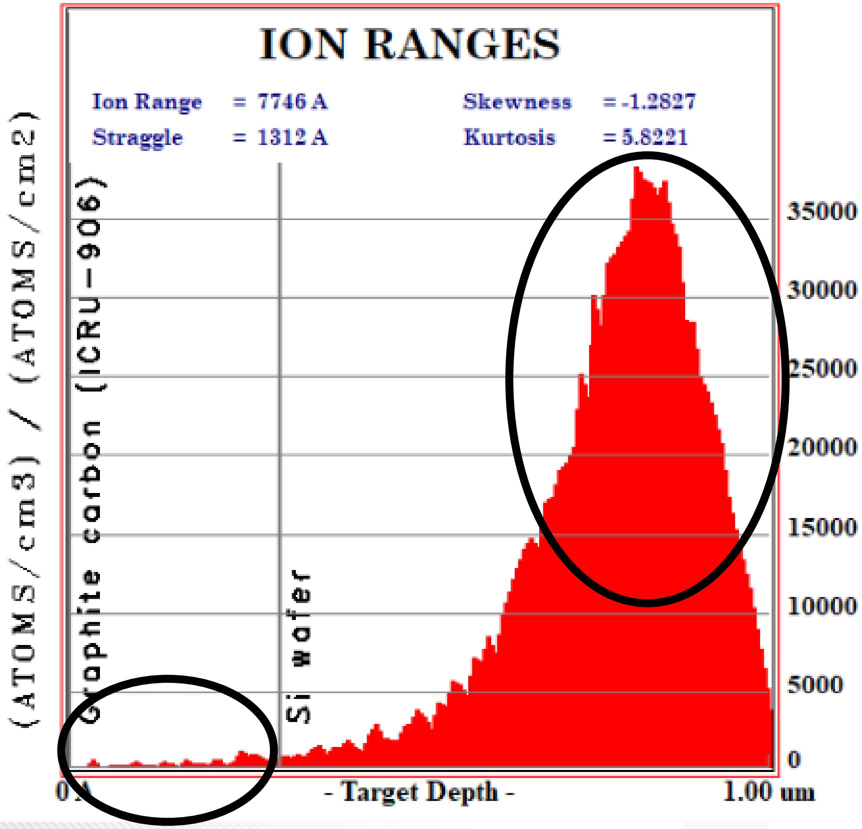


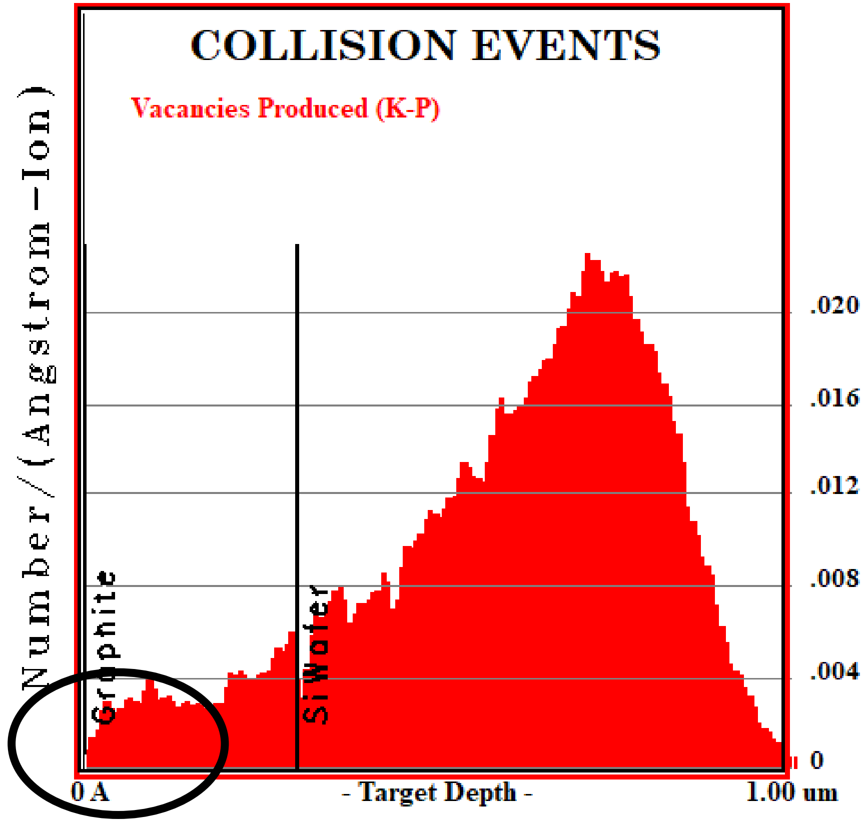


So, Why does this difference occur?

SRIM calculation

SRIM simulation result





Ion Ranges

Most ions pass through the graphene layer and come to a stop in the Si-wafer layer

Damage Events

The Damage occurring on the graphene surface is the cause of lattice defects

Linear Energy transfer

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Nuclear LET

Elastic scattering

$$S_n = \left(\frac{dE}{dx}\right)_{nuclear} = N \cdot \int_0^{E_{T,max}} E_T d\sigma$$

where $E_T = \frac{4m_1 \cdot m_2}{(m_1 + m_2)^2} \cdot E_0 \cdot \sin^2\frac{\vartheta}{2}$

N the number of target atoms per unit volume, and $d\sigma$ the differential cross section.

Electronic LET

Inelastic scattering

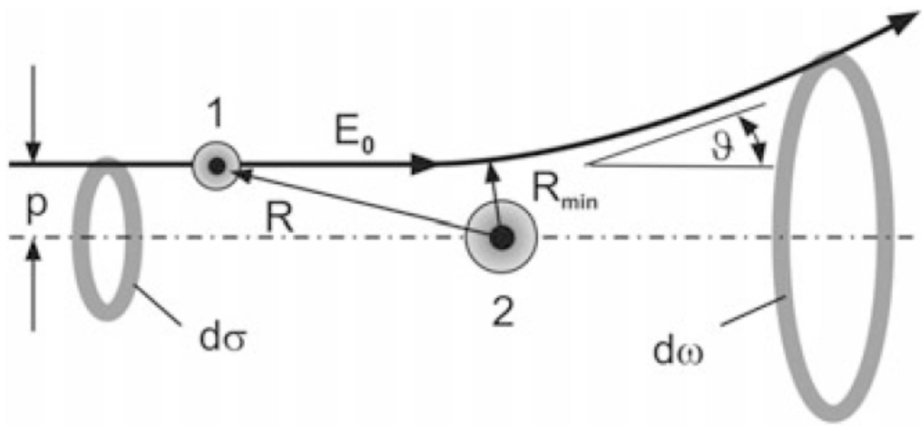
$$S_e = \left(\frac{dE}{dx}\right)_{electronic} = \frac{2\pi \cdot Z_1^2 \cdot e^4}{E_0} \cdot N \cdot Z_2 \cdot \left(\frac{m_1}{m_2}\right) \cdot \ln\frac{2m_e \cdot v_2}{I}$$

with m_1—ion mass, m_2—target atom mass, m_e—mass of a target-atom electron, Z_1—atomic number of the ion, Z_2—atomic number of the stopping target atom, and I—average excitation energy.

Nuclear LET is important for graphene.

Cross-section formula

Collision between accelerated ions and nuclears in target material



Rutherford Cross-section formula

$$\left(\frac{d\sigma}{d\omega}\right)_R = \frac{1}{16} \cdot \left(\frac{Q_1 \cdot Q_2 \cdot e^2}{4\pi \cdot \varepsilon_0}\right)^2 \cdot \frac{1}{E_c^2} \cdot \frac{1}{\sin^4 \frac{\vartheta}{2}} .$$

Simple calculations at 90 degree

$$\left(\frac{d\sigma}{d\Omega}\right)_{He^{++}} = \left(\frac{k \times 1.602 \times 10^{-19} \times 6 \times 10^{-19} \times e^2}{4 \times 120 \times 10^3}\right)^2 \frac{1}{sin^4\left(\frac{\pi}{2}\right)}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{He^{+}} = \left(\frac{k \times 2 \times 1.602 \times 10^{-19} \times 6 \times 10^{-19} \times e^2}{4 \times 120 \times 10^3}\right)^2 \frac{1}{sin^4\left(\frac{\pi}{2}\right)}$$

$\left(\frac{d\sigma}{d\Omega}\right)_{He^{++}} - \left(\frac{d\sigma}{d\Omega}\right)_{He^{+}}$ $=1.806 \times 10^{-33}\ [m^2]$ ~ **20 μbarn**

- This difference is not negligible !!

Summary

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1. Defects can change the properties of 2D materials.

2. 2D material with defects can be applied to various sensors such as gas sensors.

3. Although the kinetic energy of 60 keV He^{++} ion is the same as that of 120 keV He^{+} ion, the defect amount for He^{++} ion irradiation is larger than He^{+} ion irradiation.

4. The reason is that nuclear linear energy transfer of He^{++} ion is larger than that of He^{+} ion.