Transient Photocurrent Measurements of Graphene Related Materials

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Contents:

Electrical conductivity

Electrical conductivity is a measure of how well a material accommodates the transport of electric charge. It is the ratio of the current density to the electric field strength.

$$\sigma = J/E \quad (V = IR)$$

The electrical conductivity σ satisfies:

$$\sigma = ne\mu_e \text{ for electrons,}$$

$$\sigma = pe\mu_h \text{ for holes.}$$

The electrical conductivity σ can be defined as a sum of two terms:

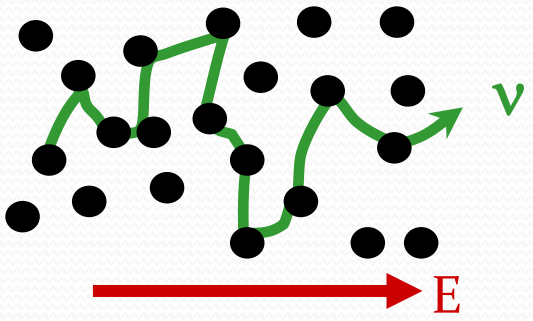
$$\boldsymbol{\sigma = (ne\,\mu_e + pe\,\mu_h)} \qquad \textbf{in } 1/\Omega cm$$

n and p = density of charge carriers (n for electrons and p for holes) in cm^{-3} e = unitary charge (C)

Electrical mobility- definition

❒ When an electric field E is applied across a piece of material, the electrons respond by moving with an average velocity called the drift velocity. Then the electron velocity

$$v=\mu_e E \quad cm/s$$

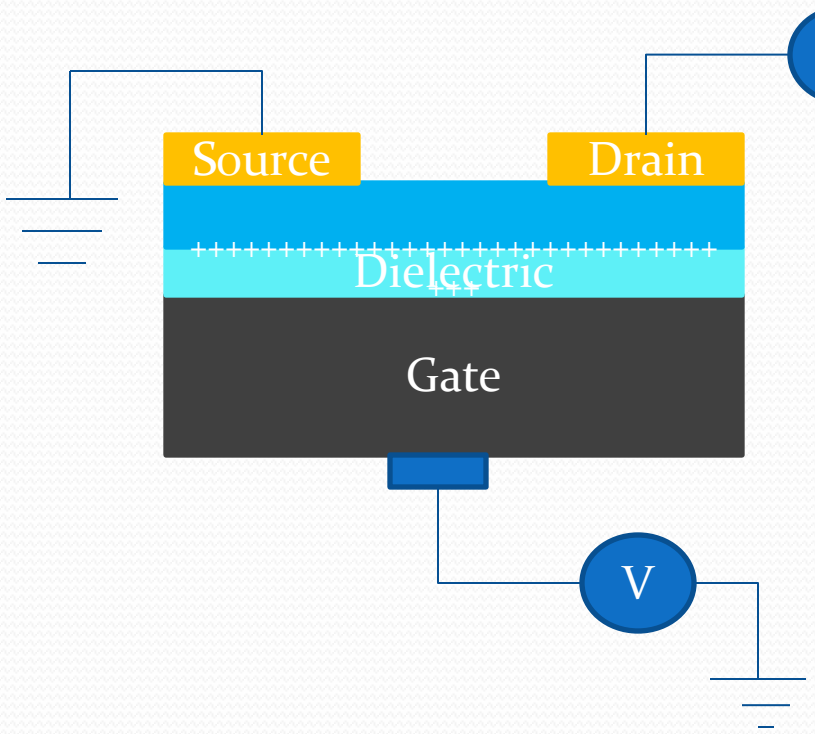


❑ The mobility **μ** of the charge carriers is the average speed of diffusion **|ν|** or net drift velocity of the charge carrier (cm/s) as a function of applied electric field **E**(V/cm).

$$\mu = |\nu|/E \qquad \textbf{in } cm^2/V\cdot s$$

FET mobility

The mobility can also be measured using a field-effect transistor (FET), the result of the measurement is called the “field-effect mobility”.



The measurement can work in two ways:

1. saturation-mode measurements

$V_{gs}-V_{th}<V_{ds}$

2. linear-region measurements

$V_{gs}-V_{th}>V_{ds}$

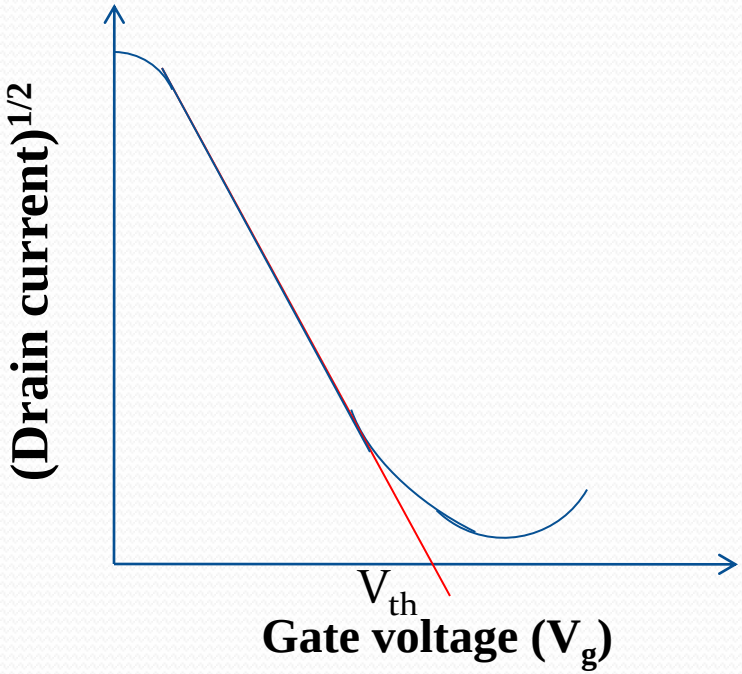
For the linear region,

$$I_{ds} = \mu C_i \frac{W}{L}((V_{gs} - V_{th})V_{ds} - \frac{V_{ds}^{\ 2}}{2})$$

For the saturation region,

$$I_{ds} = \mu C_i \frac{W}{2L}(V_{gs} - V_{th})^2$$

where W and L are the width and length of the channel, C_i is the capacitance per unit area, V_{gs} is the gate source voltage and V_{ds} is the drain source voltage.



FET configuration: bottom contact interdigitated electrodes .

Dielectric Thickness :230 nm
Dielectric Constant of SiO_2=3.9
W=10 mm
L=20 μm
I_{ds} =-1 *10^{-6} Amp
V_{gs} = -80V
V_{th} = -30V
V_{ds}= -0.01V

Estimated field effect mobility
μ= 145,000$cm^2/V{\cdot}s$

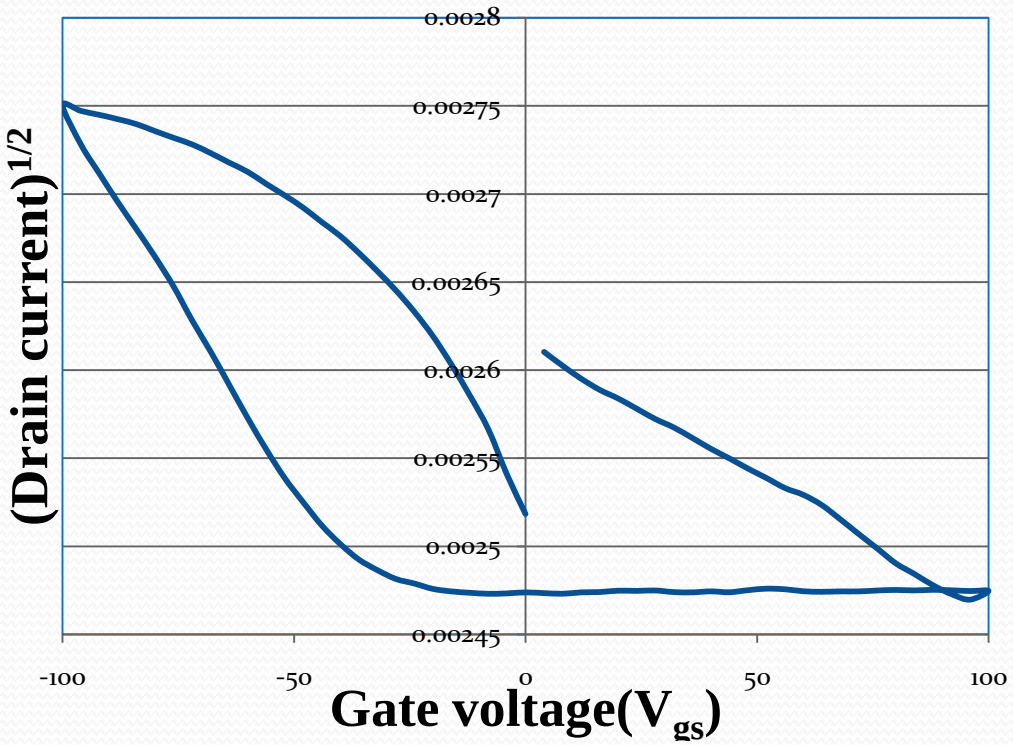
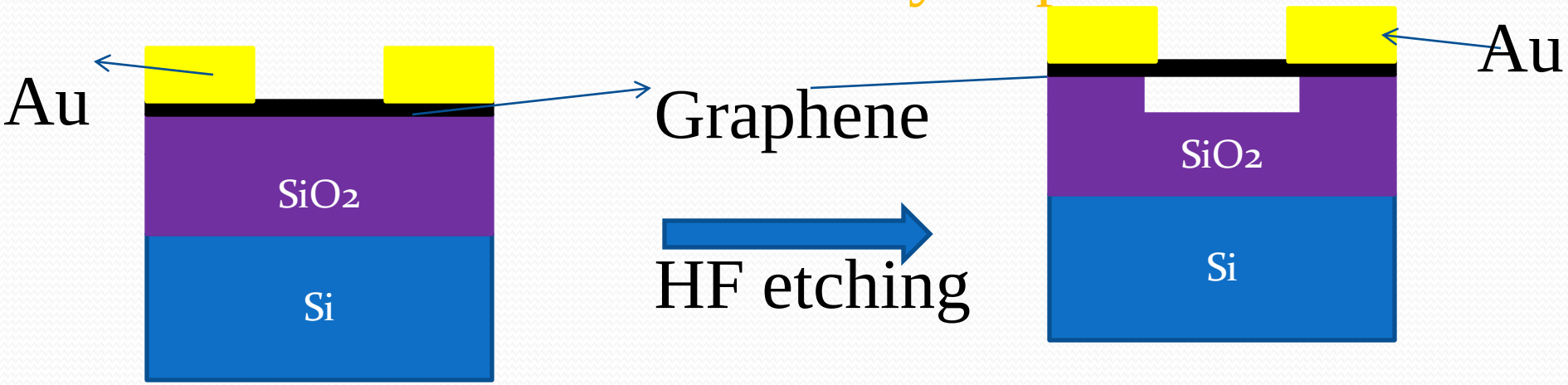


Fig: I_{ds} ½ vs V_{gs} characteristics of bottom contact graphene field effect transistor

Effect of dielectric: mobility improvement

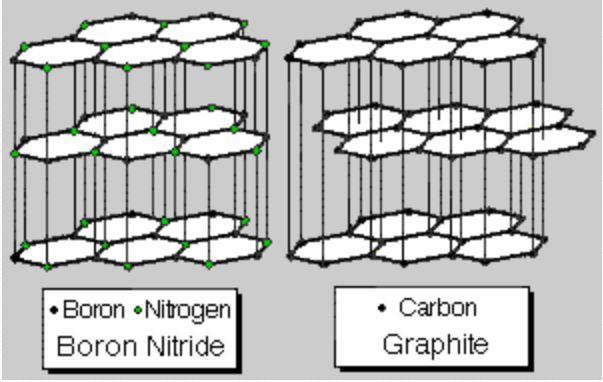


Suspending samples

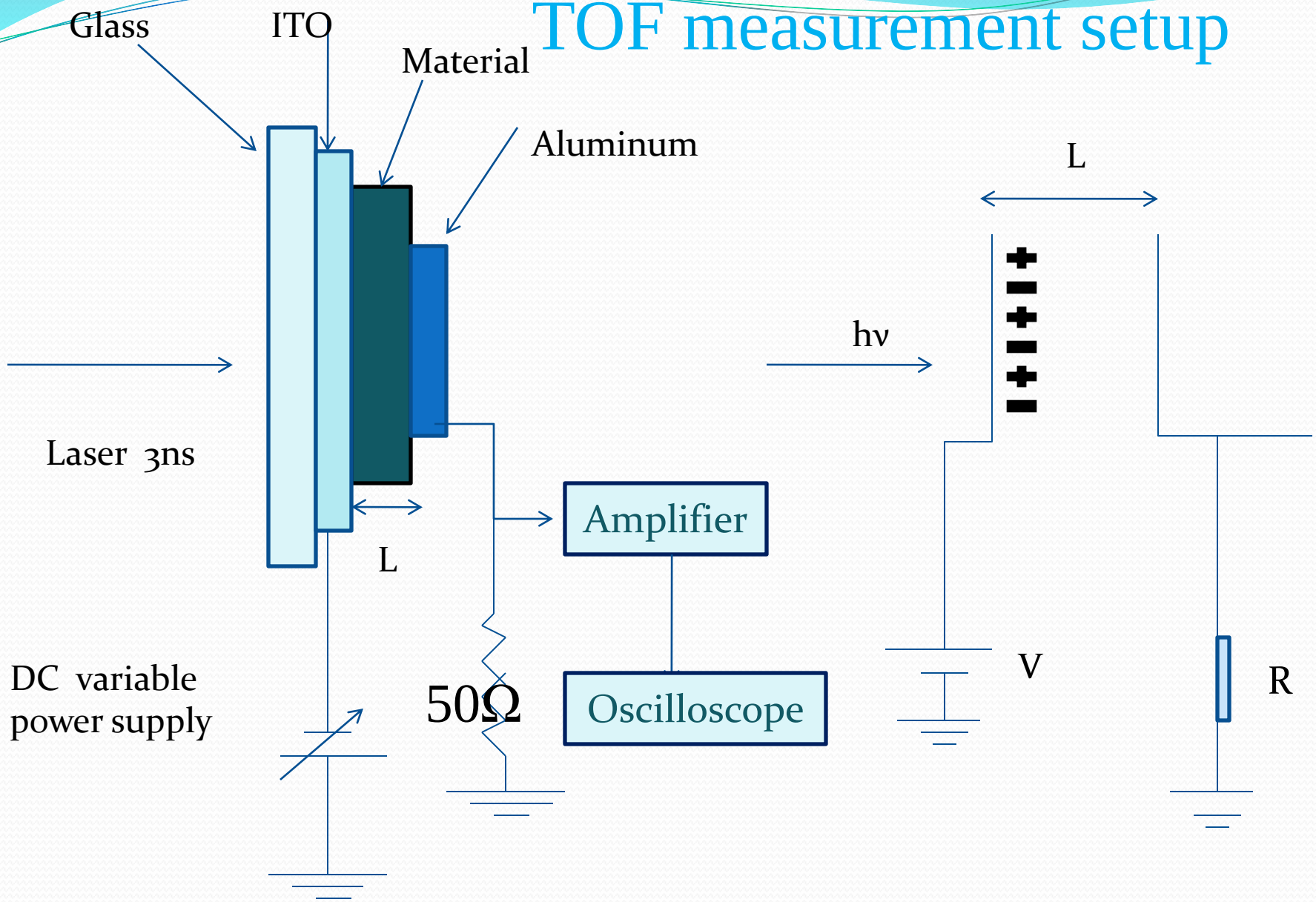
- Hexagonal boron nitride (h-BN) is an interesting substrate, because it has an atomically smooth surface that is relatively free of dangling bonds and charge traps.
- It also has a lattice constant similar to that of graphite and a large electrical band gap.

Lattice constant of graphene – 2.46A^{o}
and h-BN – 2.5 A^{o}

Lattice misfit is only 1.7 %



TOF measurement setup



Definition of mobility of free charges

Mobility is estimated from the time taken by the photoexcited carriers created at one electrode to reach the opposite electrode.

$$\mu = \frac{v}{E} = \frac{\frac{L}{t_{tr}}}{\frac{V}{L}} = \frac{L^2}{V * t_{tr}}$$

μ = Mobility of the carriers

v = Drift velocity of the carriers

L = Separation between the electrodes

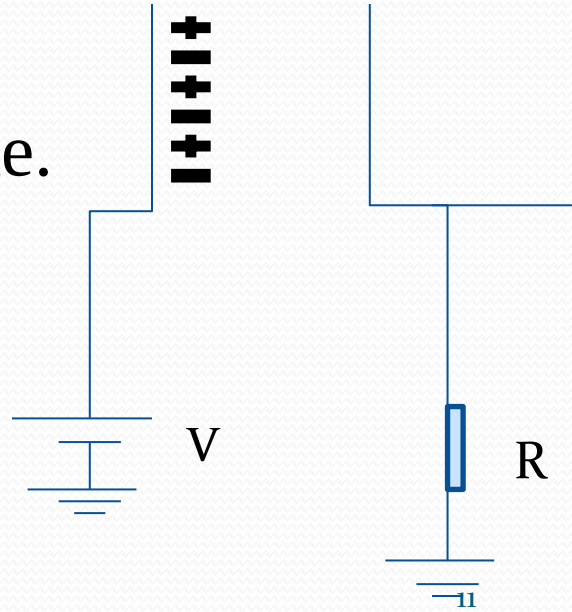
E = Electric field strength

V = Voltage applied

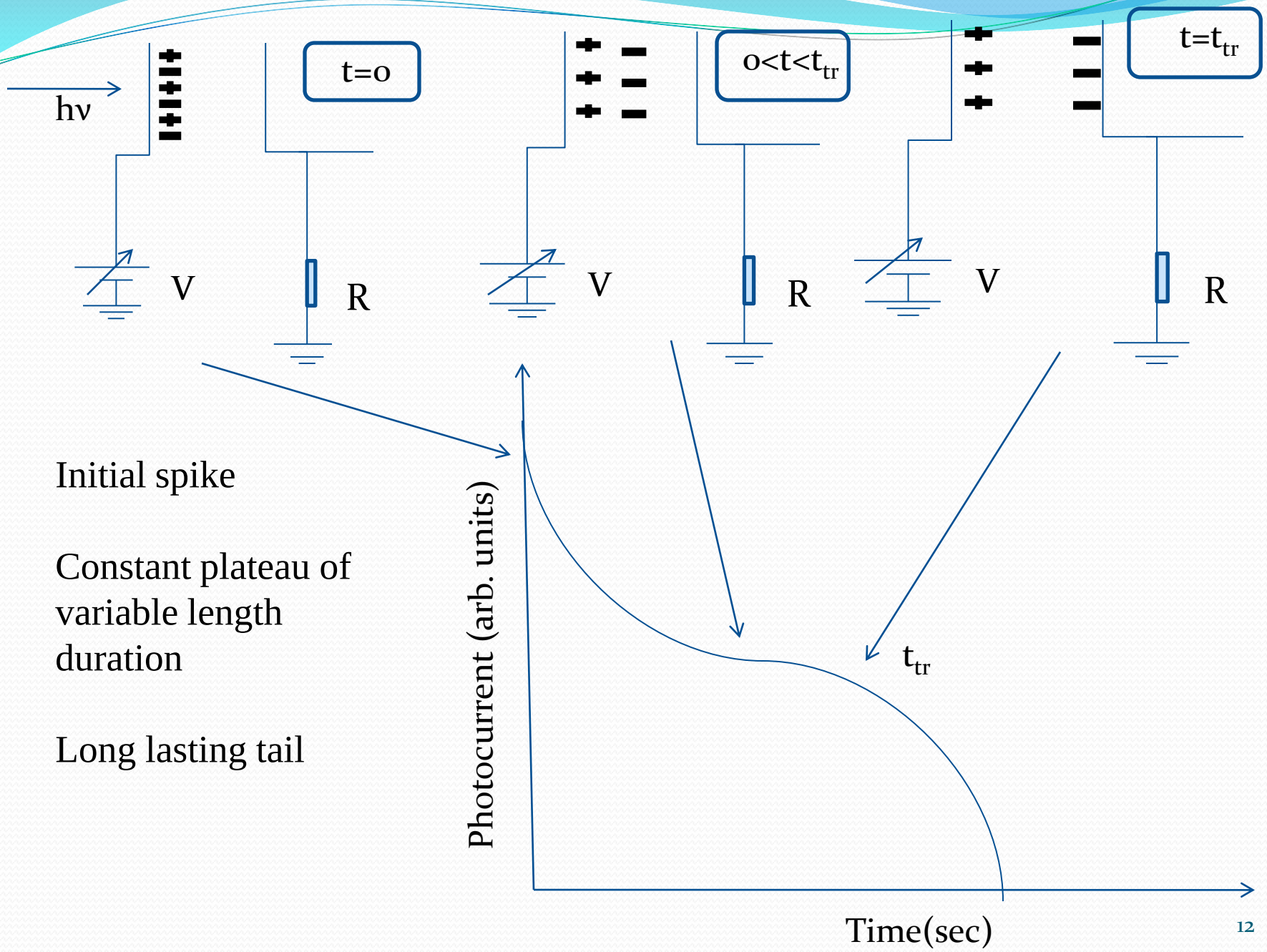
t_{tr} = Transit time

Requirements:

1. Total photoinjected charge << CV (capacitor charge).
2. Electrodes – blocking contacts- non injecting electrodes.
3. One electrode must be semitransparent.
4. Excitation laser pulse width << transit time.
5. Light absorption within 10% of the sample-thin sheet of carriers << d (film thickness).
6. Carrier recombination time >> transit time.
7. Dielectric relaxation time >> transit time.
8. Circuit reaction time RC << transit time.



Typical TOF curve



Initial spike

Constant plateau of variable length duration

Long lasting tail

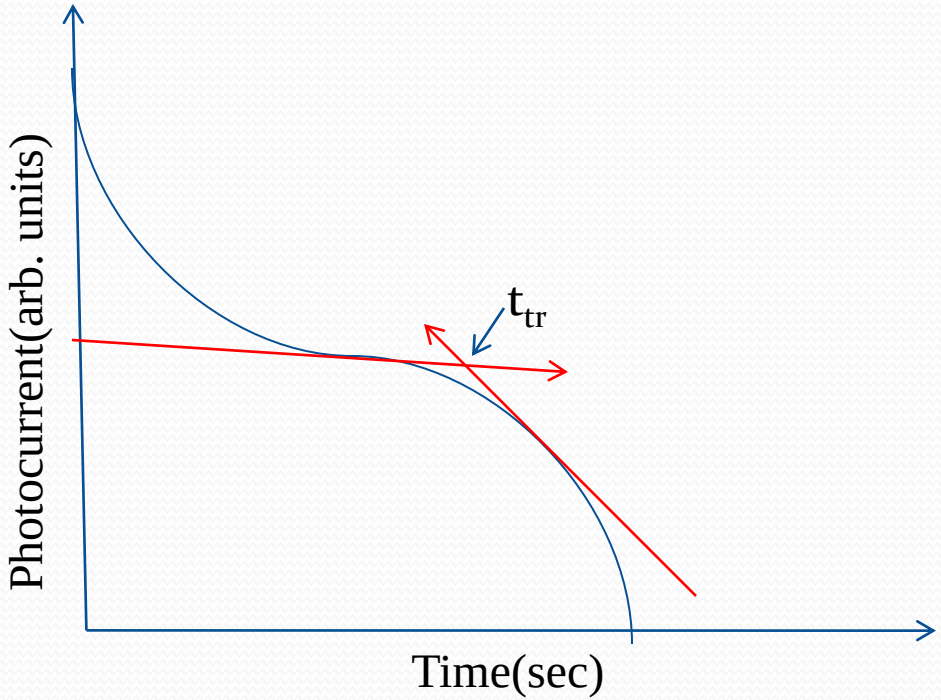
Transit time:

The time required for the photoinjected carriers to traverse from one electrode to the other in the presence of electric field.

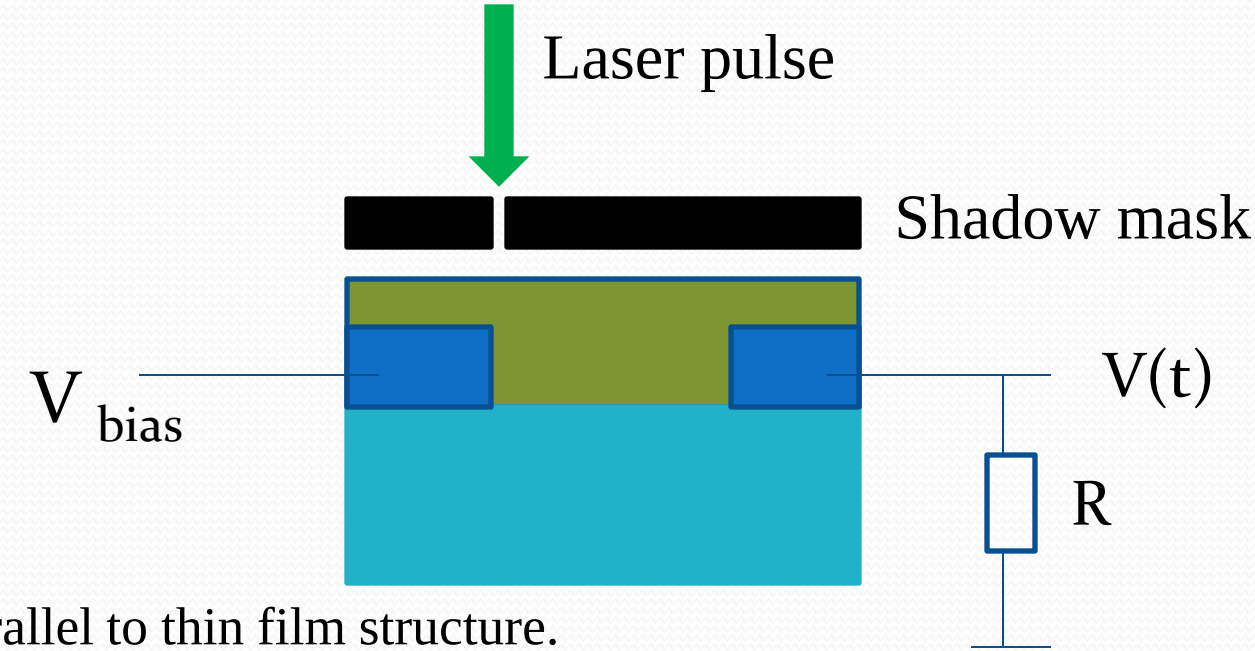
Determination of the transit time:

Transit time is determined from the intersection of asymptotes drawn to the constant plateau region and the long tail of the photocurrent transient.

Logarithmic plot of photocurrent vs time



Thin film time of flight (T- TOF) measurement setup



Benefits:

- Charge transport parallel to thin film structure.
- Large availability of substrates (glass, PET, sapphire, silicon, PMMA ...).
- Variable channel length (limited with light diffraction on the shadow mask).
- Semiconductor deposition with different methods (spin-coat, OMBE …).
- Top-contact or bottom-contact electrodes.

Limits:

- Charge carrier mobility $>10^{-4}$ $cm^2/V \cdot s$.
- Charge injection blocking electrodes.

What's so special about graphene

Graphene is a single atomic layer of graphite and it is the thinnest material.

Graphene is a semimetal or a zero band gap semiconductor.

Graphene shows a mobility of 200,000 $cm^2/V \cdot s$.

High electrical conductivity.

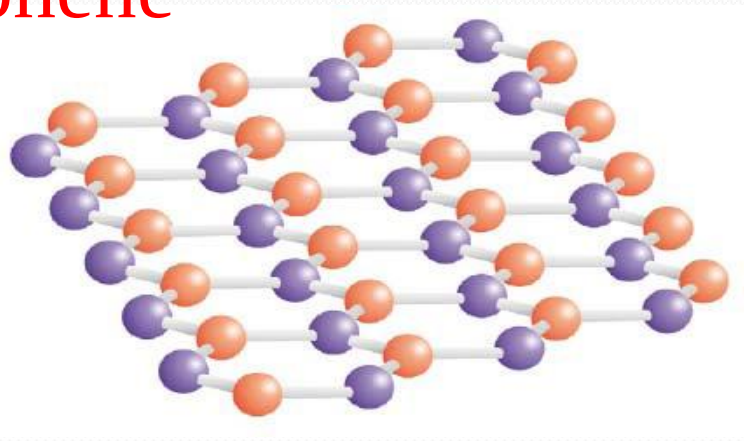
Extremely large mechanical strength.

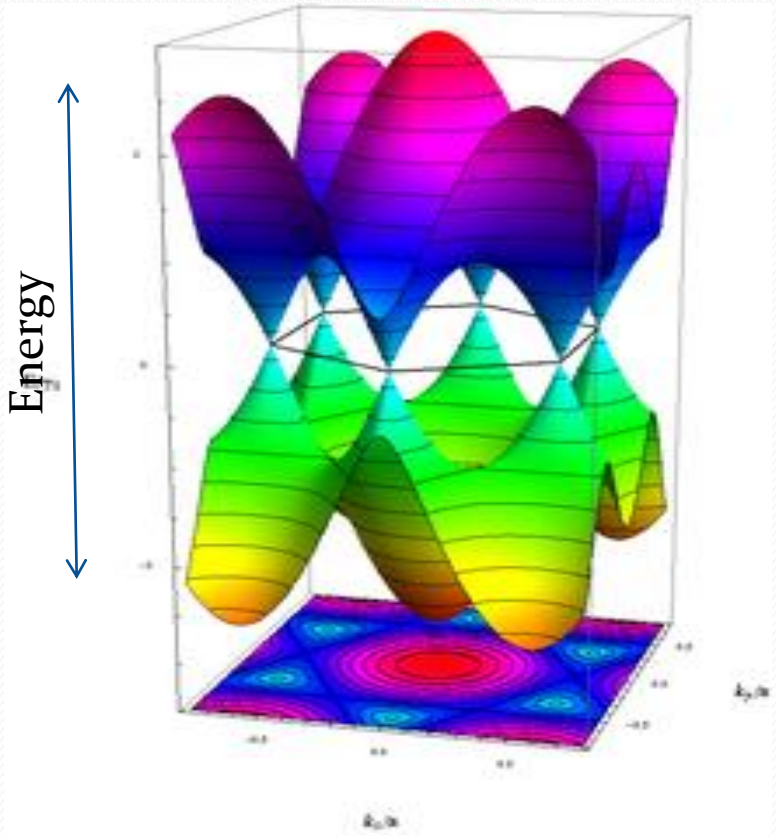
Graphene is an ambipolar material.

Graphene is a transparent material and hence it can be used as a transparent electrode.

Band structure of graphene

Crystal honeycomb symmetry with two sublattices A and B.

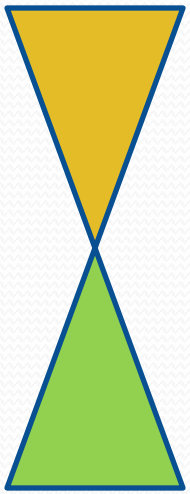




It has two atoms per unit cell.
It has two conical points per Brillouin zone.
At these particular points (Dirac points) the charge carriers behave like relativistic particles.
They are massless Dirac fermions (1/300 of the speed of light).

Relativistic charge carriers

Conduction band



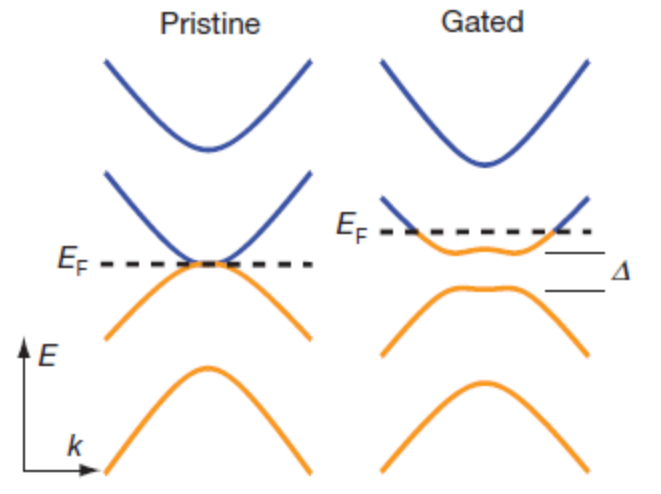
Valence band

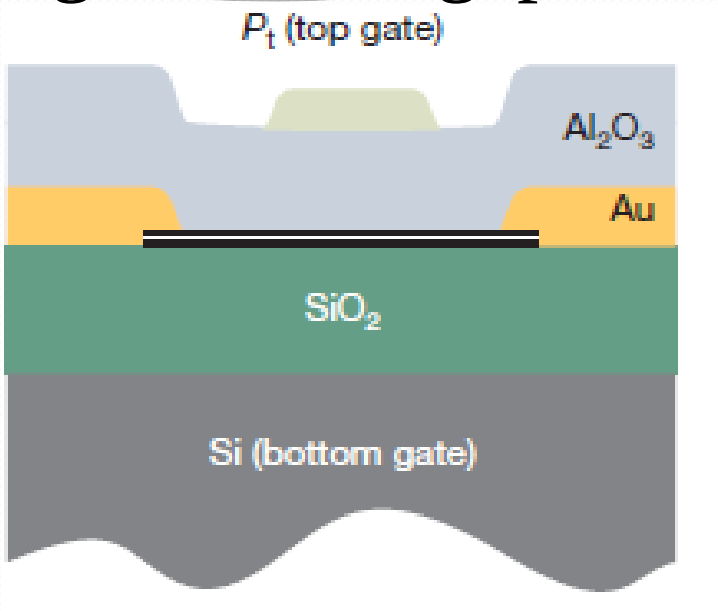
- Charge carriers behave like massless Dirac fermions with an effective speed of light $c^* \sim 10^6$.
- Relativistic behavior comes from interaction with lattice potential of graphene, not from carriers moving near speed of light.
- Behavior only present in monolayer graphene, disappears with 2 or more layers.

Dispersion relation $E = \hbar k c^*$

K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, & A. A. Firsov. Two-dimensional gas of massless Dirac fermions in graphene. ***Nature, 438*** 197-200 (2005)

Bilayer graphene gets a bandgap





Stacking bilayer of graphene gives the possibility of tuning the energy gap by a vertical electric field.

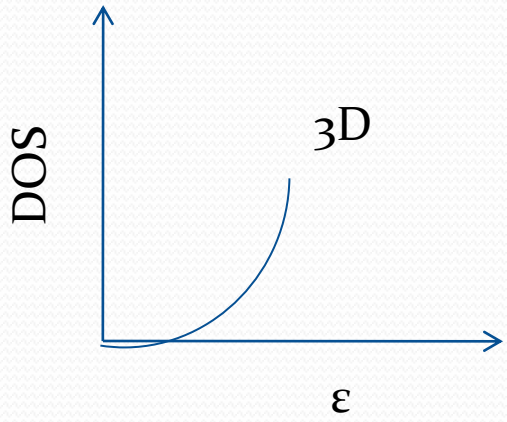
Band gap can be tuned upto 250 meV.

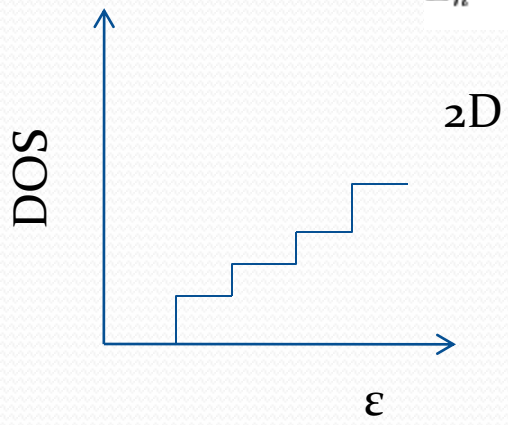
By using both bottom and top gates in the graphene FET, we can control the bandgap and doping concentration.

Anomalous quantum Hall effect

- Graphene shows integer quantum Hall effect.
- 2DEG has stair case like density of states distribution.
- When magnetic field is applied Landau levels will be formed.

$$E_n = \hbar\omega_c\left(n + \frac{1}{2}\right), \quad n \geq 0.$$





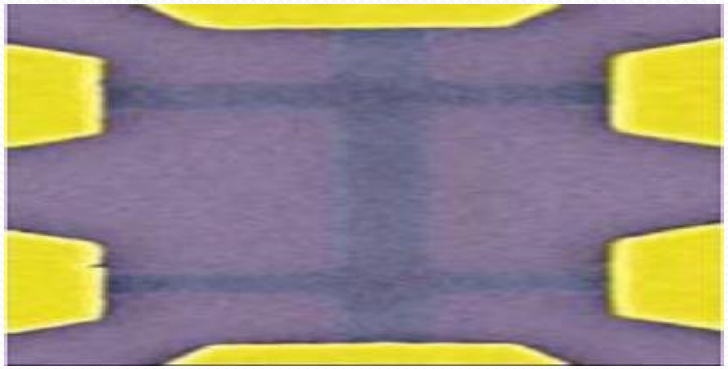
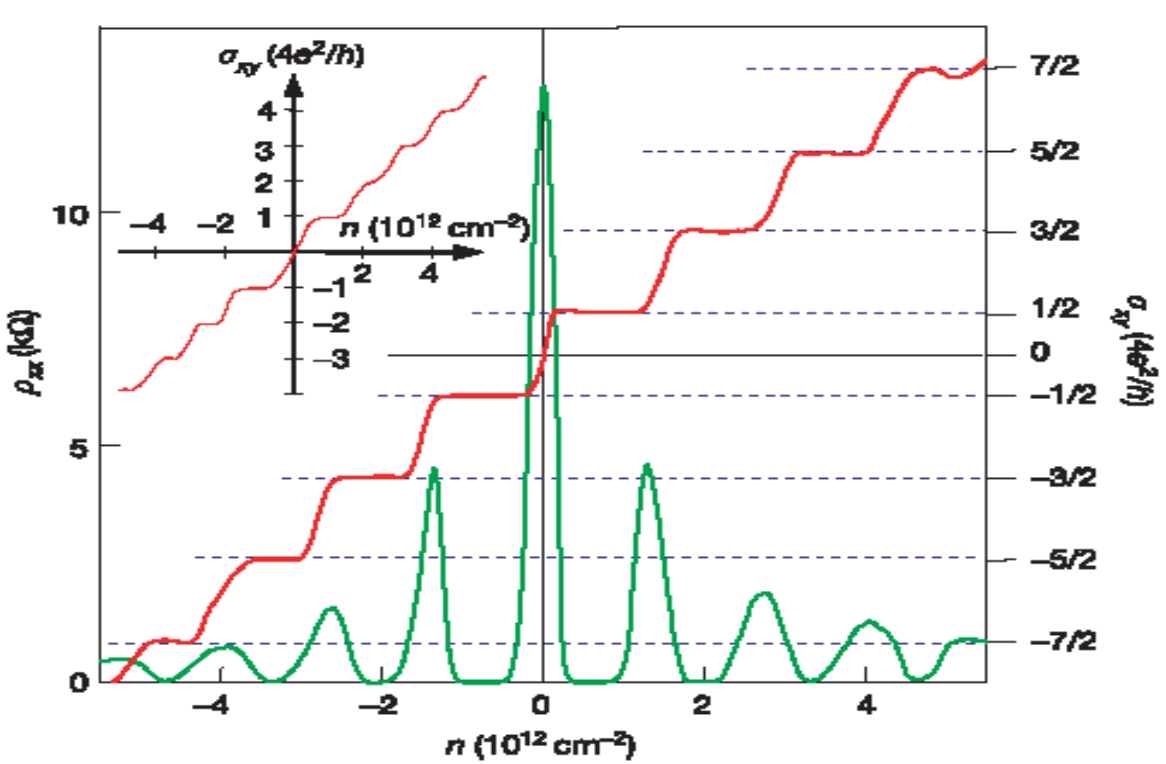
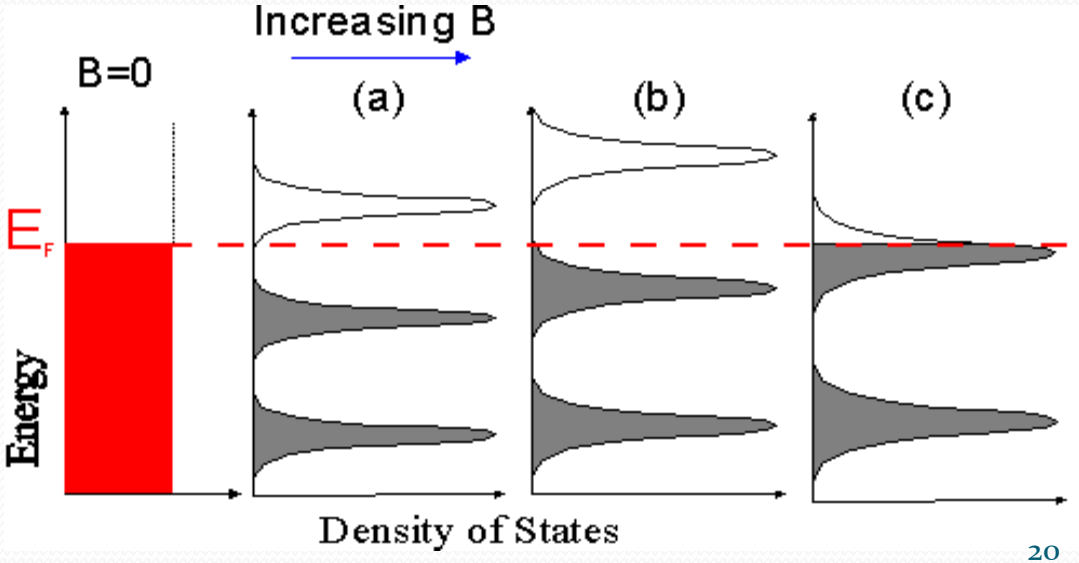


Fig. Graphene on Si/SiO_2 substrate etched into a Hall-bar structure.


σ_{xy} ($4e^2/h$)
4
3
2
1
−4
−2
n (10^{12} cm^{-2})
2
4
−1
−2
−3
10
5
0
ρ_{xx} (kΩ)
−4
−2
0
2
4
n (10^{12} cm^{-2})
7/2
5/2
3/2
1/2
0
−1/2
−3/2
−5/2
−7/2
σ_{xy} ($4e^2/h$)

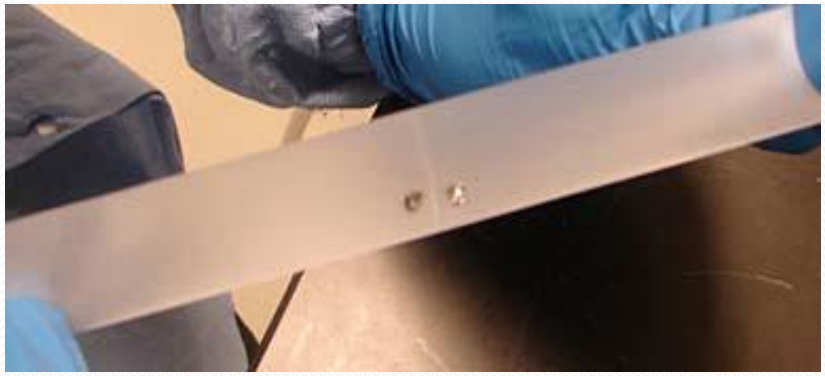

Increasing B
B=0
(a)
(b)
(c)
E_F
Energy
Density of States

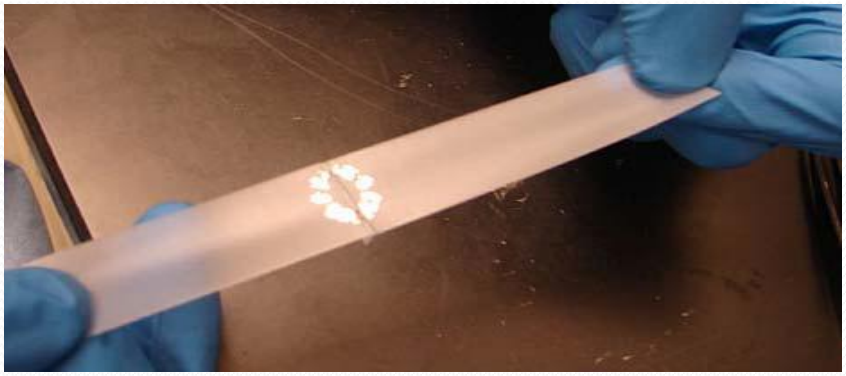
Production of graphene

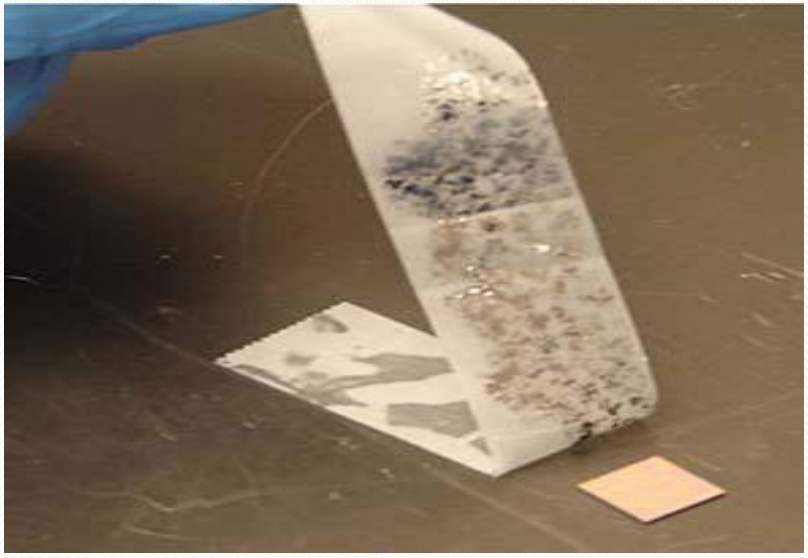
1. Peel off method

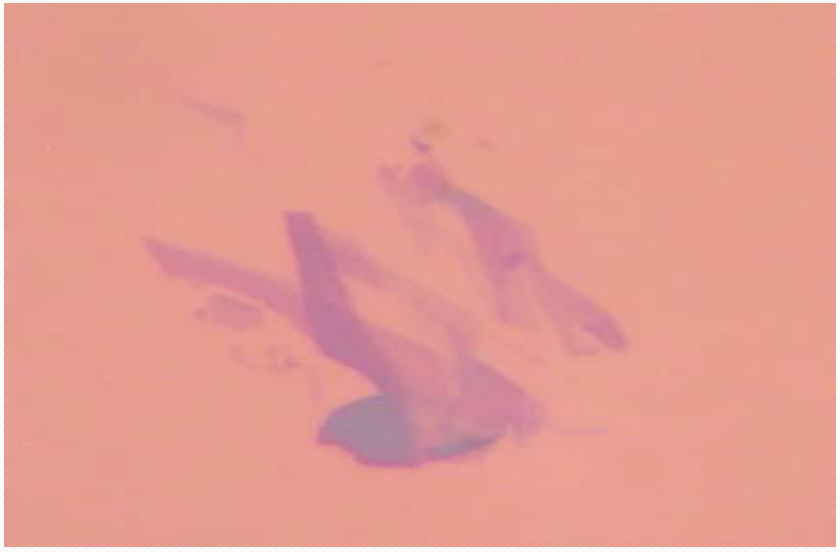
- By repeatedly peel with scotch tape or a sticky tape.
- Place samples on specific thickness of Si/SiO_2 wafer. The wrong thickness of silicon dioxide leaves graphene invisible.
- Graphene visible through feeble interference effect, different thicknesses are in different colors.

Peel off technique







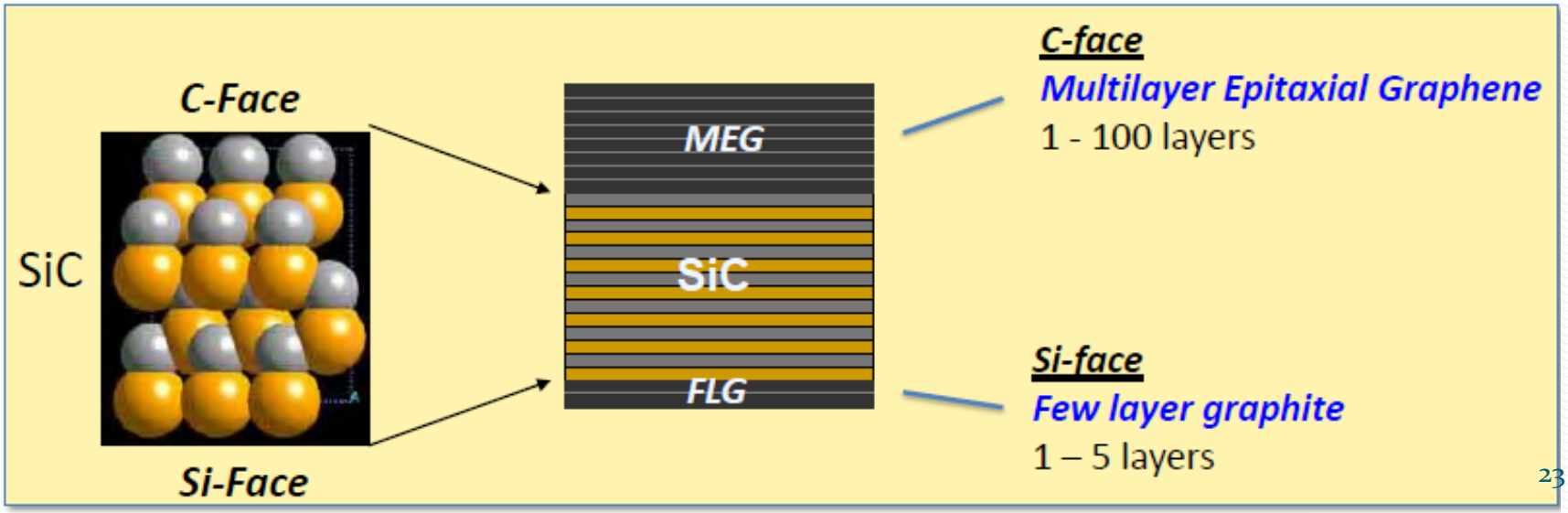


2. SiC decomposition

In this method SiC was decomposed at high temperature and at high vacuum.

1. Scaleable electronics platform.
2. Graphene is grown in situ (not transferred)
3. Very high mobilities (low dissipation).
4. THz electronics is possible.

But we can't transfer onto other substrates, because of the strong interaction between graphene and SiC and also it has lot of defects.



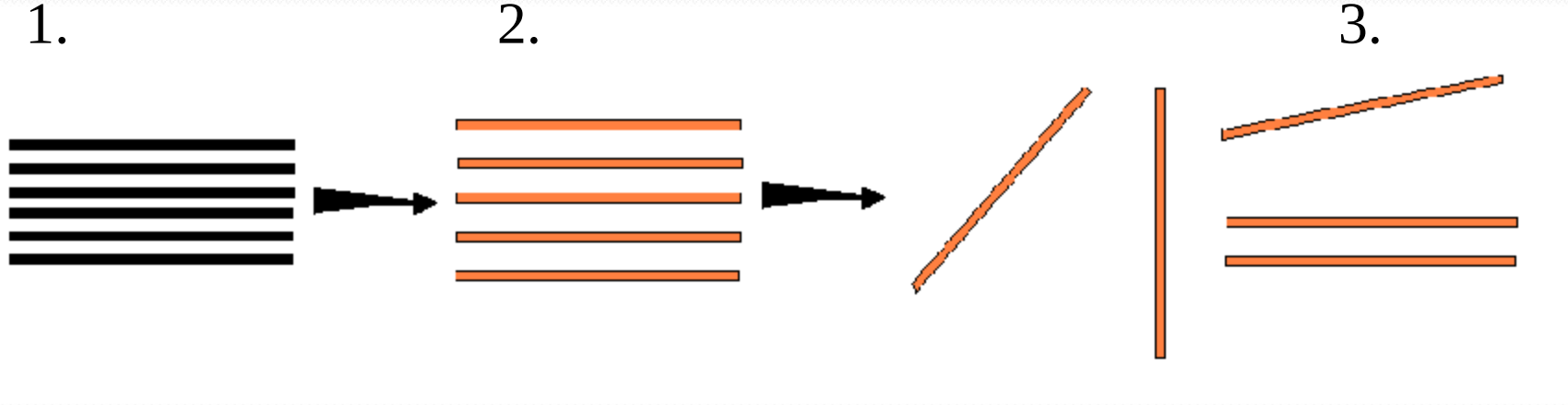
3. Chemical method for graphene

Top- down formation of single layer graphite oxide from bulk graphite powder.

1. Bulk graphite.

2. The oxidative procedure incorporates oxygen functionalities between the carbon layers forcing them apart.

3. Heavy sonication in solution separates these layers forming single layers of GO.

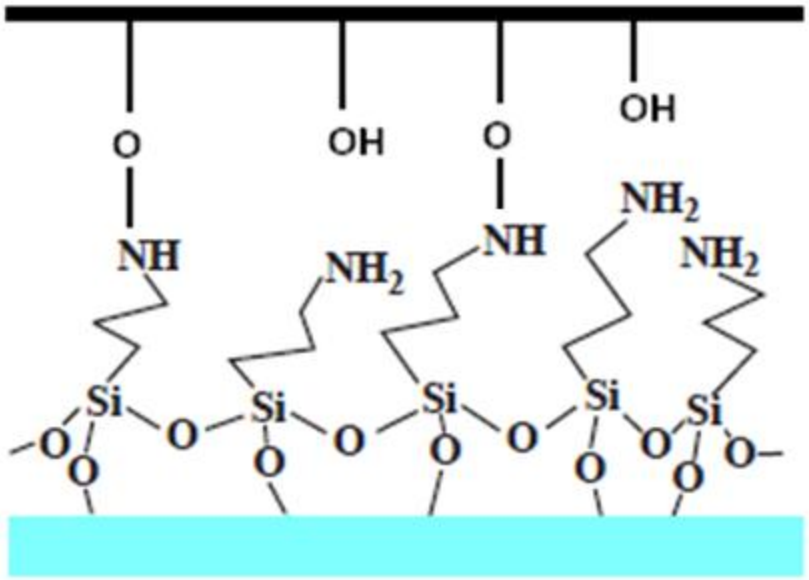


Reduced/conducting top side

Graphite oxide flake →

3-Aminopropyltriethoxysilane →

Quartz substrate →



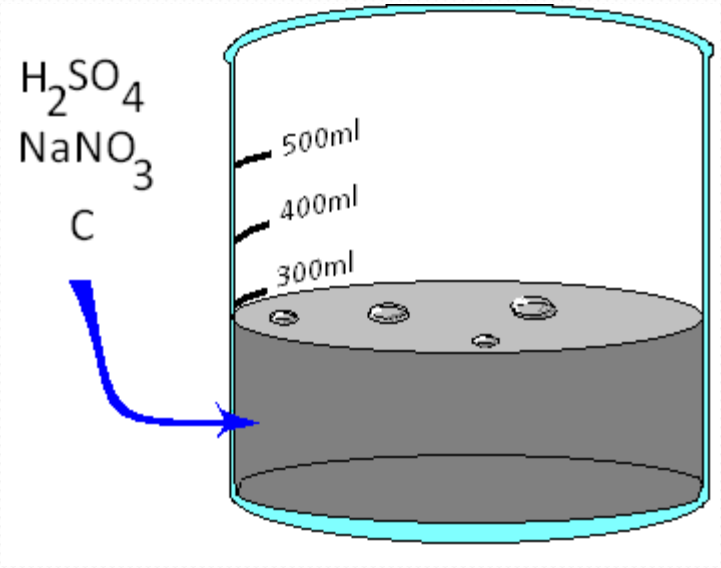
Chemical and thermal reduction:

1. Reduction by chemical treatment using hydrazine vapour and thermal annealing .

2. Removes a majority of the oxygen functionalities and produce a conducting layer.

Synthesis of graphite oxide (GO) via a modified Hummers method.

- Recovered product is subsequently washed with a total 0f 40L of dilute acid solutions



$KMnO_4$
add very slowly

Bulk graphite oxide

•These solutions can now be:

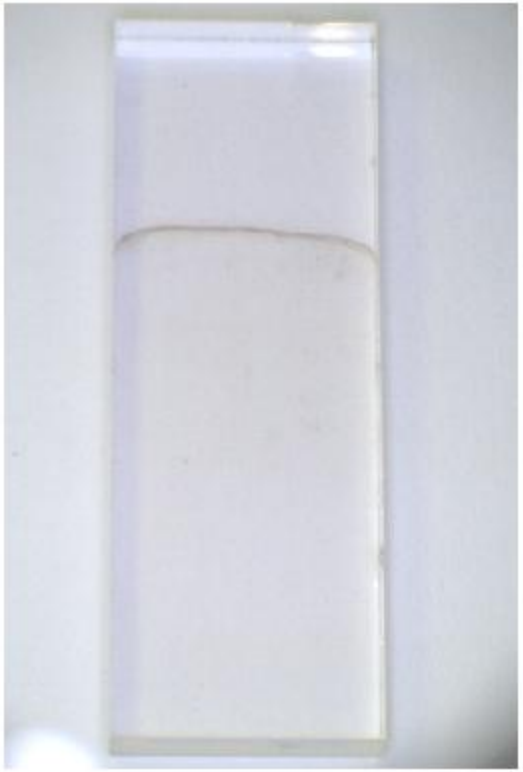
- Evaporation cast

- Spin coated

- Dip coated

• Multiple dip coats can be used to increase layer thickness .

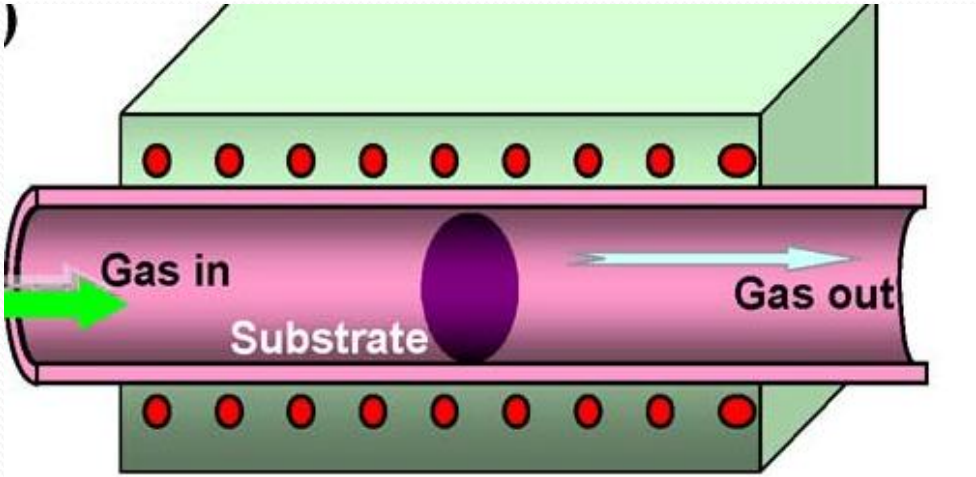
• Dip coating of pre-prepared quartz substrates using GO solutions.



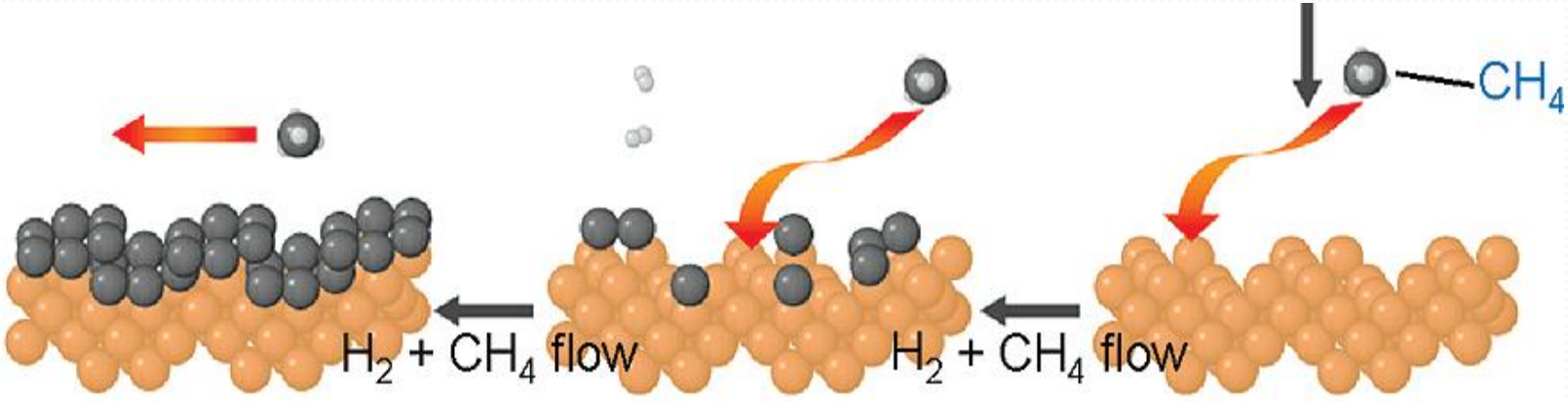
Dip coated quartz in GO

4. Chemical vapor deposition technique

$Ar+CH_4+H_2$



We can grow on metallic thin films (foils) like Iridium, Ruthenium, Nickel, Copper.



Catalytic decomposition of methane takes place at high temperature.

Advantages:

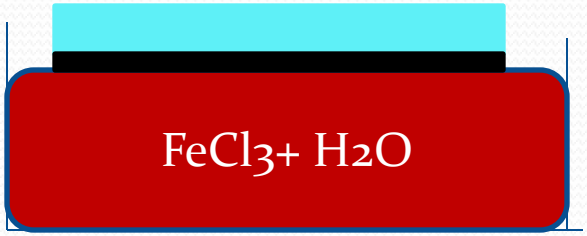
- Using CVD technique, we can deposit large area single layer graphene films.
- Because of the low solubility of graphene in copper, the process is self limited.
- Chemically inert and stable.
- These films can be transferred onto other substrates.
- These films showing excellent electrical conductivity and optical transmittance.

Graphene transfer

1. Graphene on copper foil

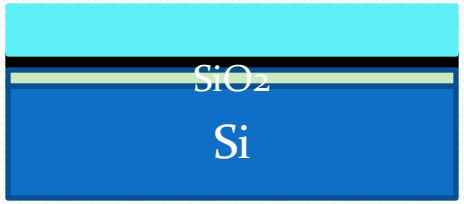
2. PMMA coating

3. Copper etching

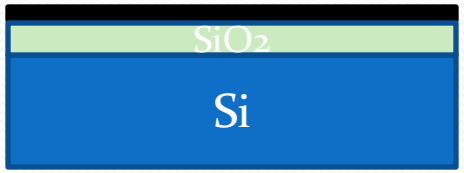


4. Transfer into arbitrary substrate

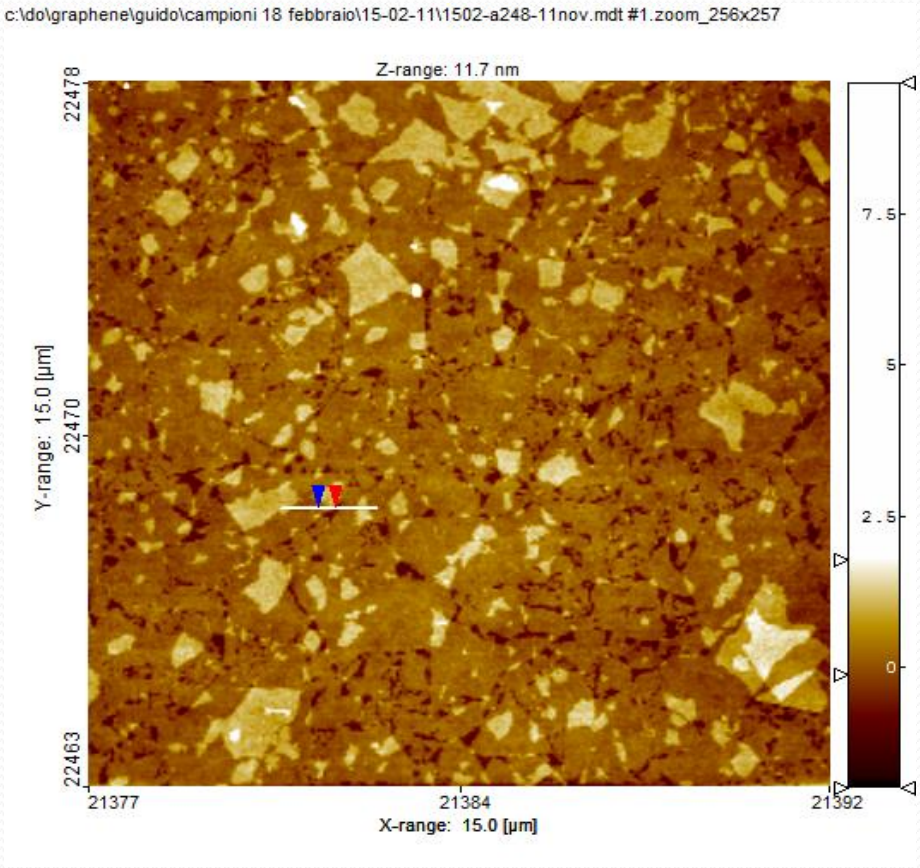
5. PMMA coating

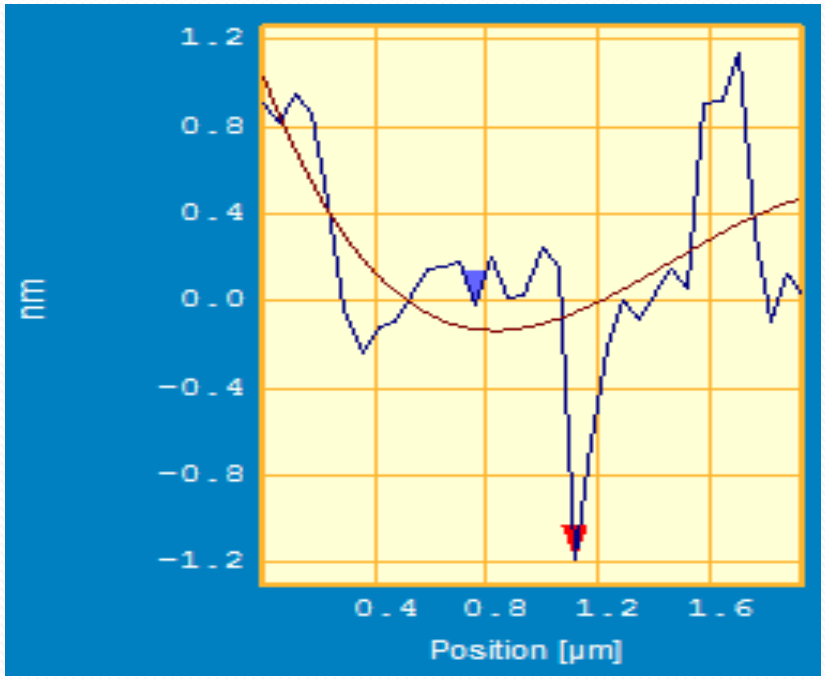


6. Dip in acetone



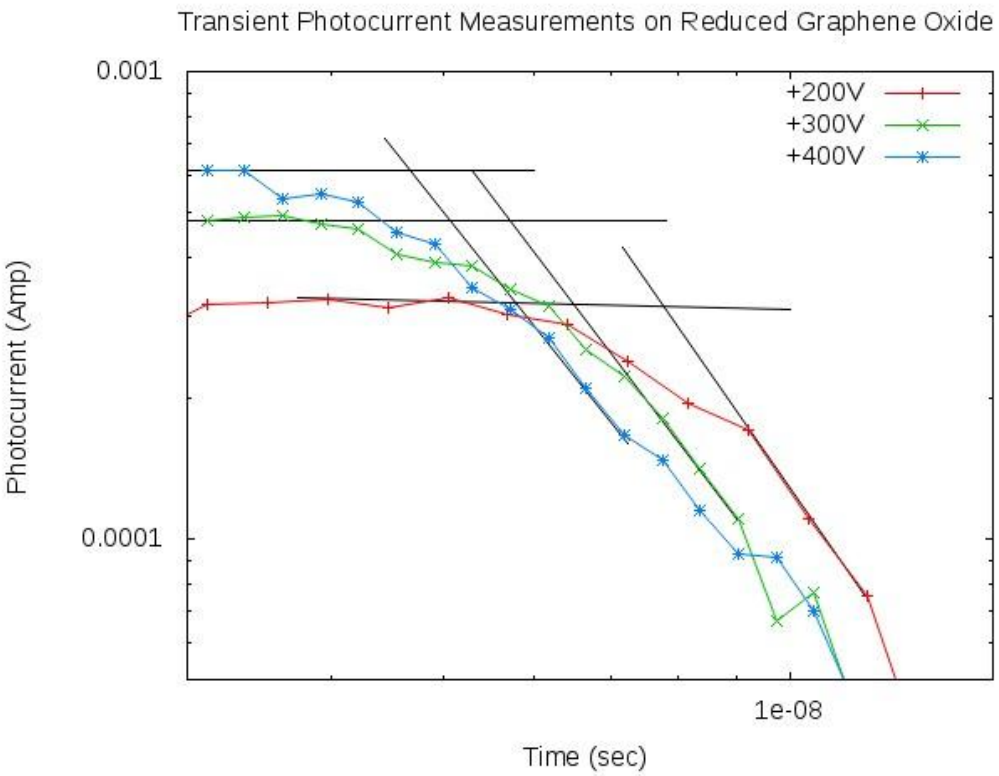
Graphene oxide





Before reduction the thickness of the film is around 1 nm.

Transient photocurrent measurements on reduced graphene oxide



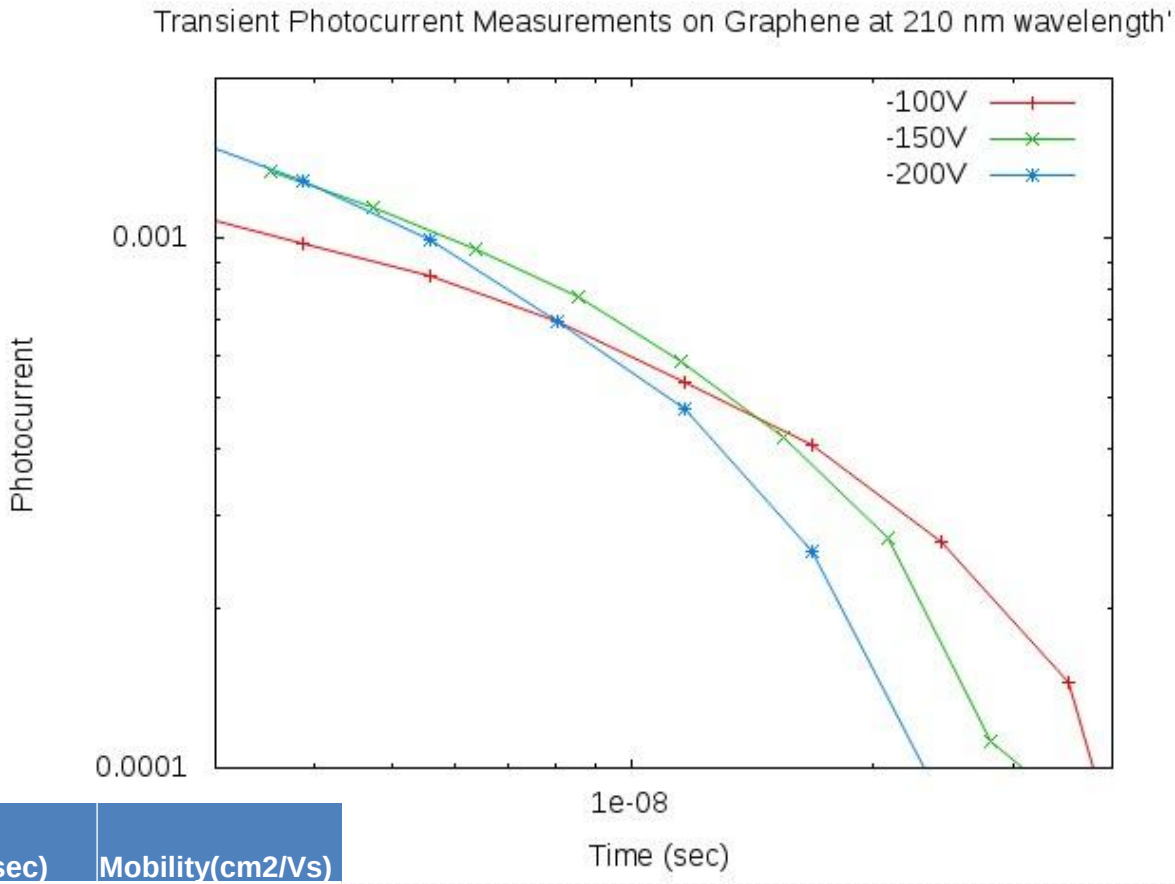
Logarithmic plot of photocurrent vs time

Nd:YAG Laser
Pulse width=3ns
Channel length=3mm
R=50Ω C=16pF
RC=0.8 ns
Amplifier is used because of the low signal
Wavelength =210nm
Xlecroy oscilloscope

Voltage(Volts)	Transit time(sec)	Mobility(cm^2/Vs)
200	7.7E-9	58000
300	5.7E-9	52500
400	4.7E-9	48000

Transferred graphene from copper foil to the sapphire crystal - Transient response

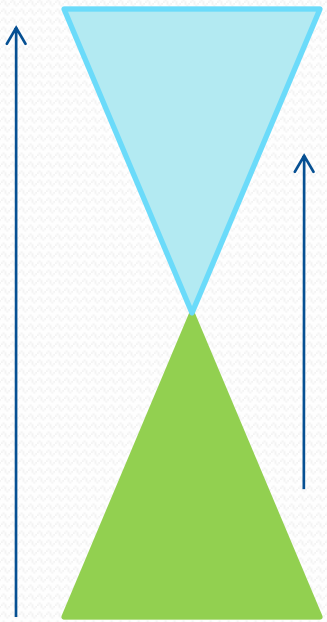
Nd:YAG Laser
Pulse width=3ns
Channel length=4mm
R=50Ω C=16pF
RC=0.8 ns
Amplifier is used because of the low signal

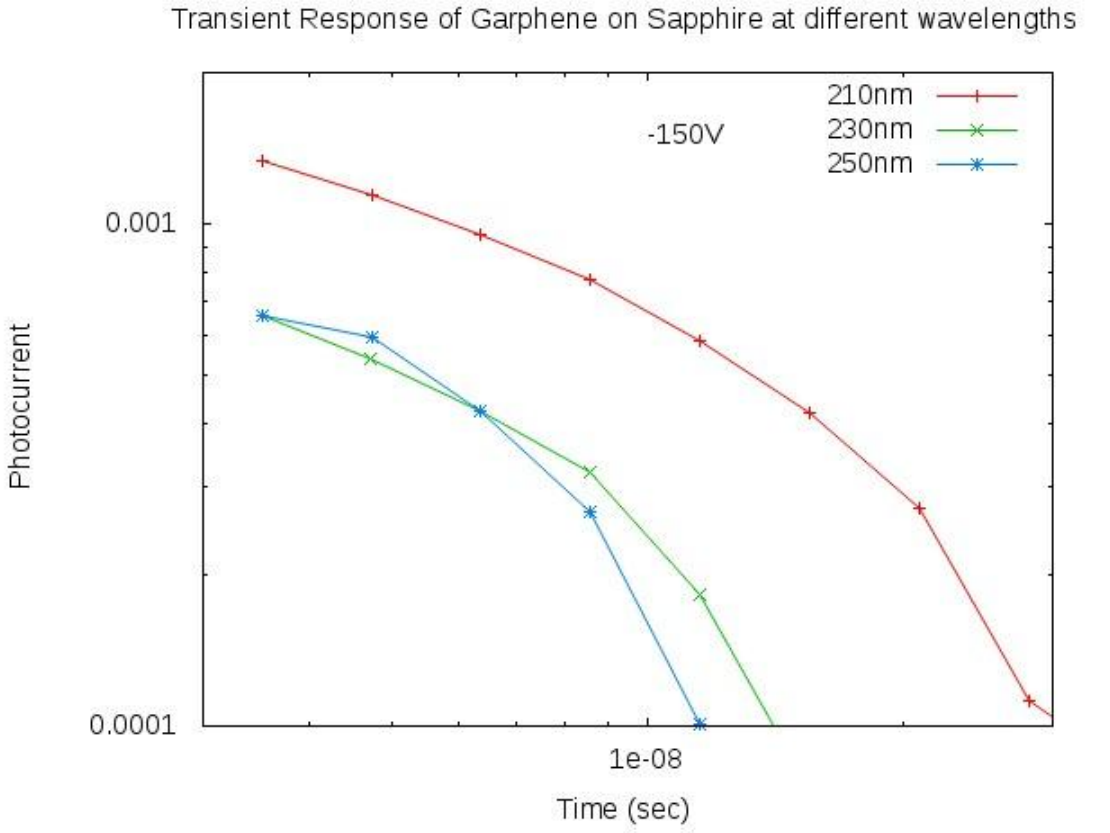


Voltage(Volts)	Transit Time(sec)	Mobility(cm2/Vs)
-100	2.09E-8	76500
-150	1.6E-8	66500
-200	1.4E-8	57000

Logarithmic plot of photocurrent vs time

Transient photocurrent measurements at different wavelengths





wavelength(nm)	Energy(eV)	Transit time(sec)	Mobility(cm^2/Vs)
210	5.91	1.6E-8	66000
230	5.63	9.8E-9	108000
250	5.39	7E-9	152000

Conclusions:

1. Electrical mobility of the materials can be estimated by using FET configuration and TOF method.
2. Graphene is showing excellent conductivity and mobility.
3. Mobility can be improved by suspending graphene and hexagonal boron nitride dielectric substrates.
4. Graphene can be produced by the peel off method, modified Hummers method, SiC decomposition and chemical vapor deposition techniques.
5. Graphene mobility can be estimated from the time of flight measurements and FET configuration.

Many thanks for your attention