Initial Stages of Growth of Organic Semiconductors on Graphene

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Outline

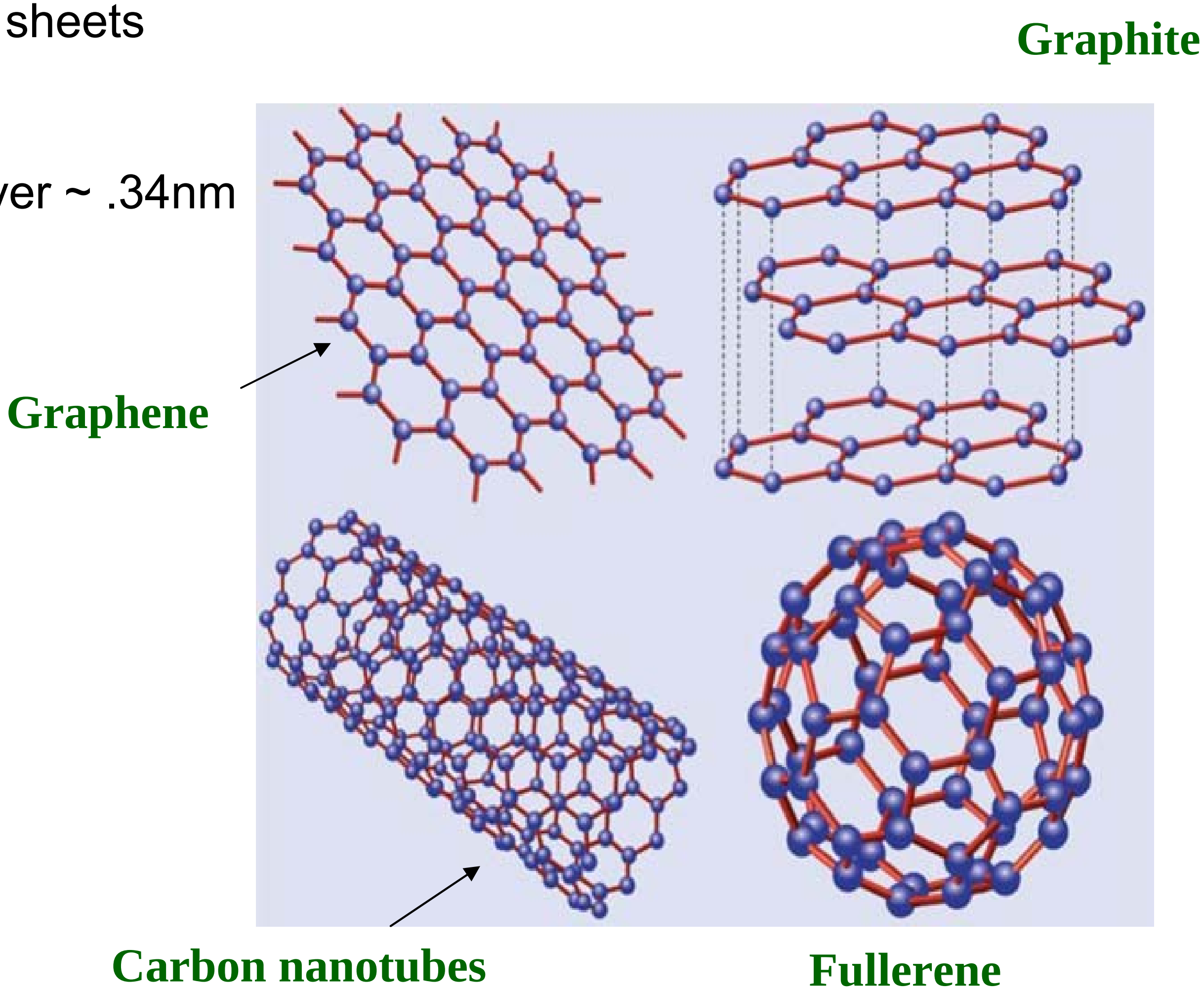
- **Introduction to Graphene**
  - Fabrication
  - Characterization: AFM (Atomic Force Microscope)
  - Properties: Electronic, Optical
  - Applications
- **Growth of organic semiconductors (OS) on Graphene**
  - OMBD (Organic Molecular Beam Deposition)
  - Growth Modes: Types
- **Conclusions**

Introduction to Graphene

- Hexagonal arrangement of carbon atoms forming an atom thick planar sheets

- C-C bond ~ 1.42 Å
- Thickness of one 1 atomic layer ~ .34nm (~ layer spacing of graphite)

- Strong
- Flexible
- High intrinsic carrier mobility ~ 200000 cm^2 /Vs
- High thermal conductivity

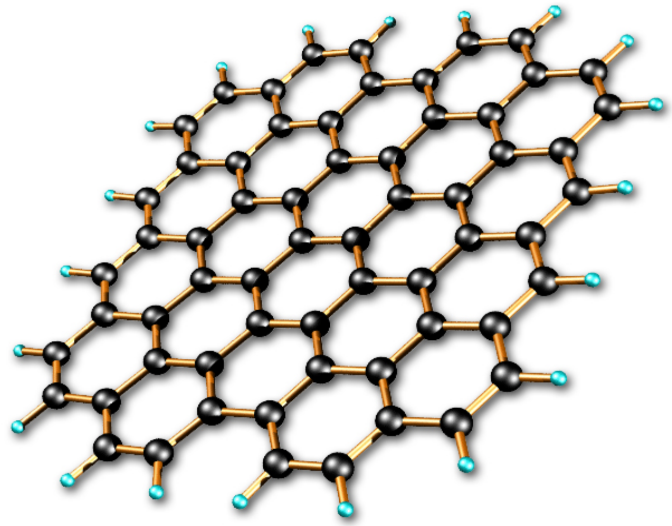


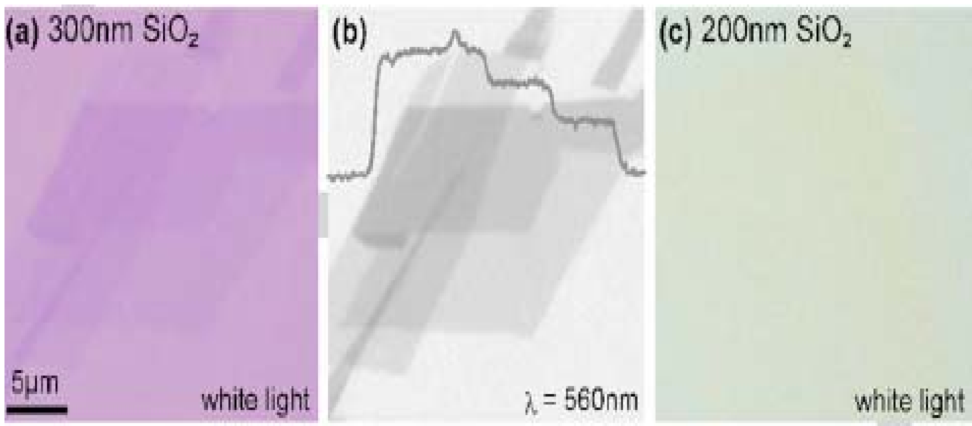
Late discovery of Graphene

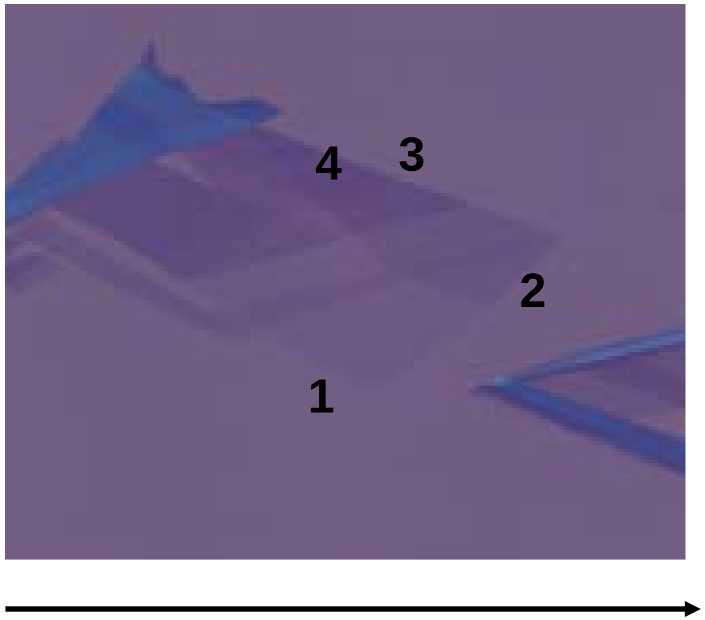
- **Discovered in 2004**

- Graphene monolayer in great minority among thicker flakes
- Unlike nanotubes, no clear signature by TEM
- Completely transparent on most of substrates
- The only method: AFM

very low throughput at high resolution



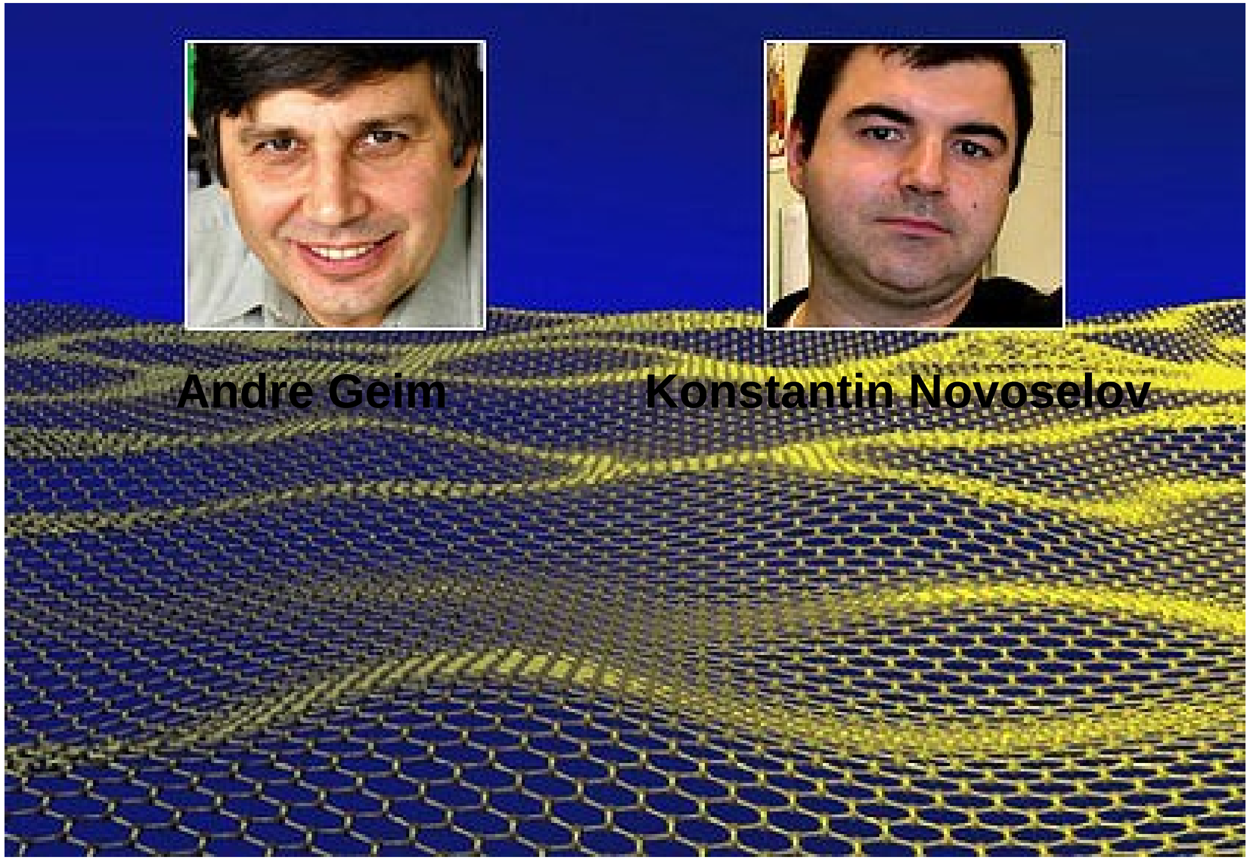




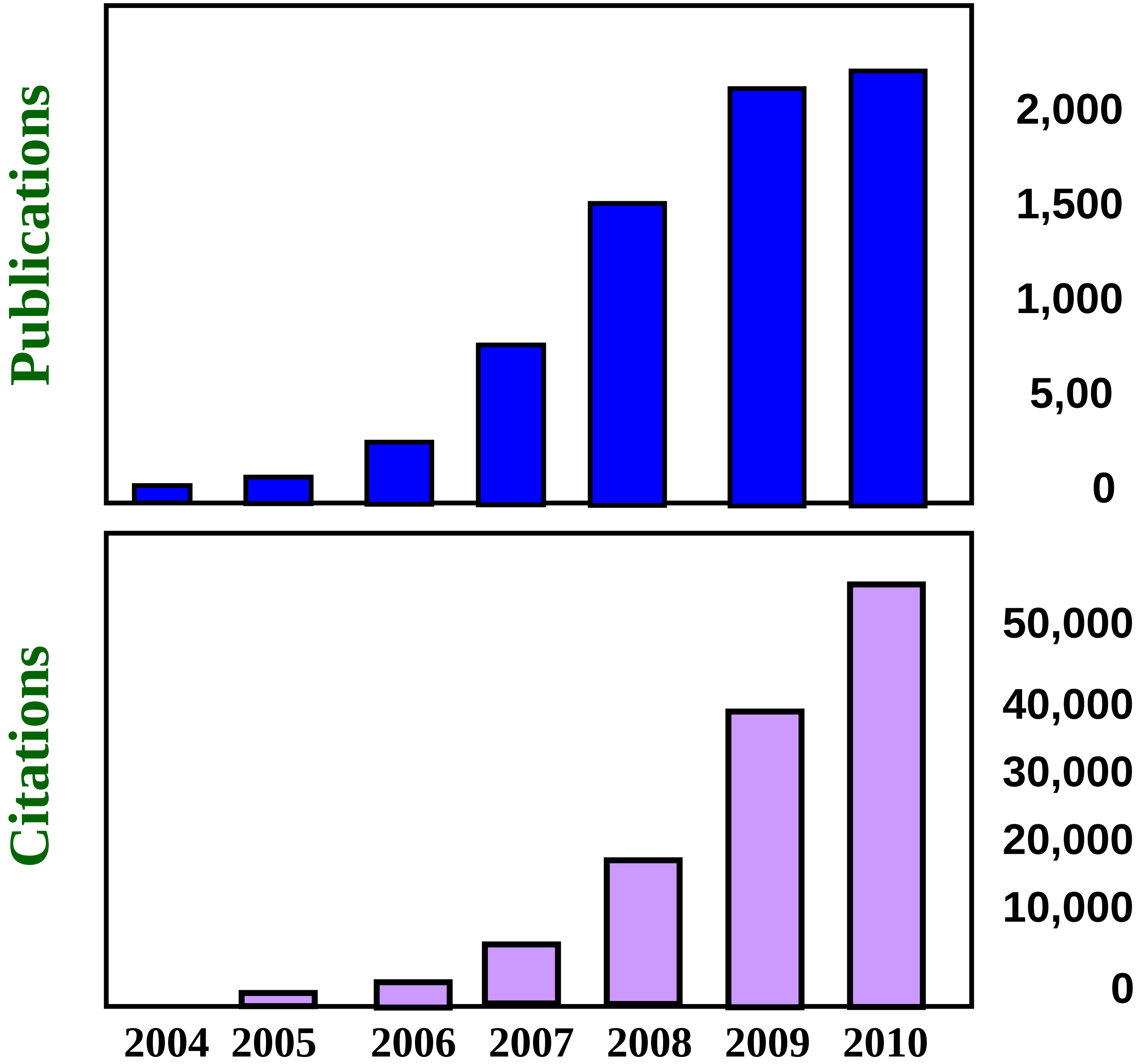
200μm

The Nobel Prize in Physics 2010

“ Graphene”



Impact of graphene in Scientific community



Fabrication Methods: Mechanical exfoliation

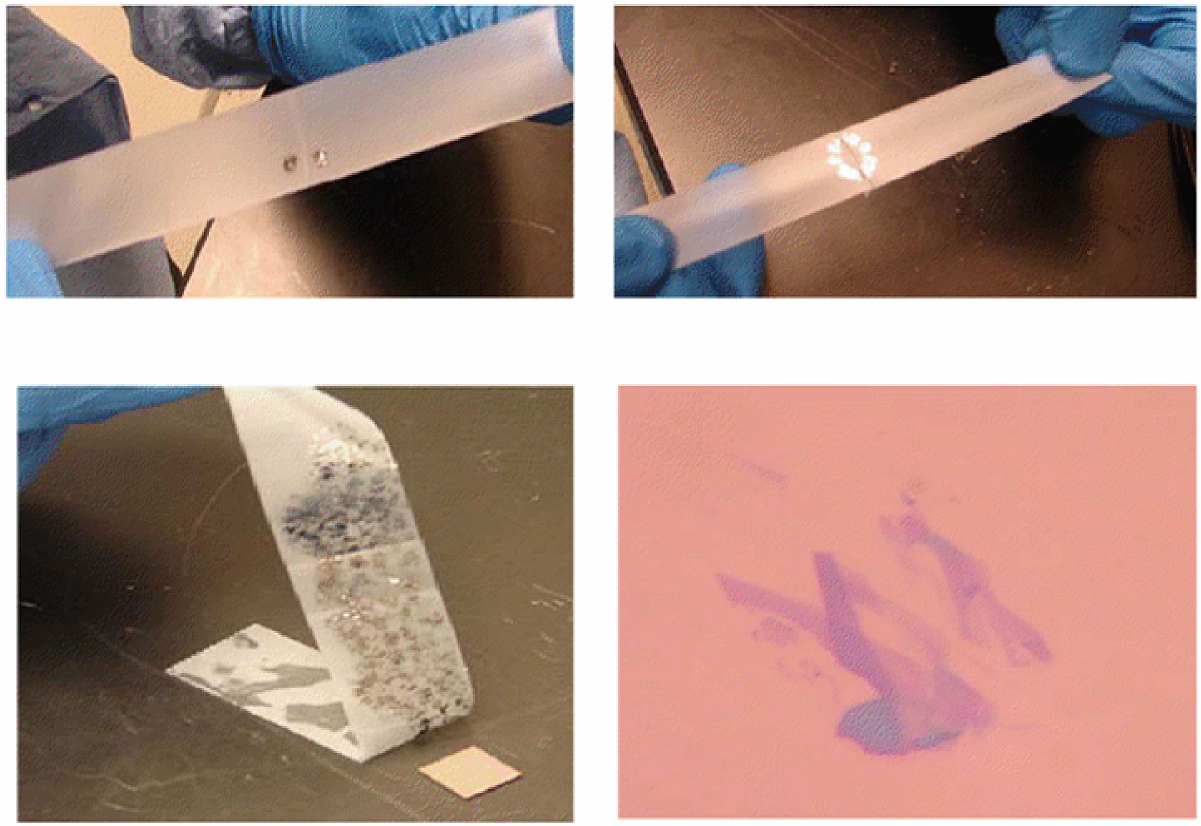
Advantages:

Cheap

Limitations:

Limited to small area
Many uneven films
Time consuming

Peel off technique



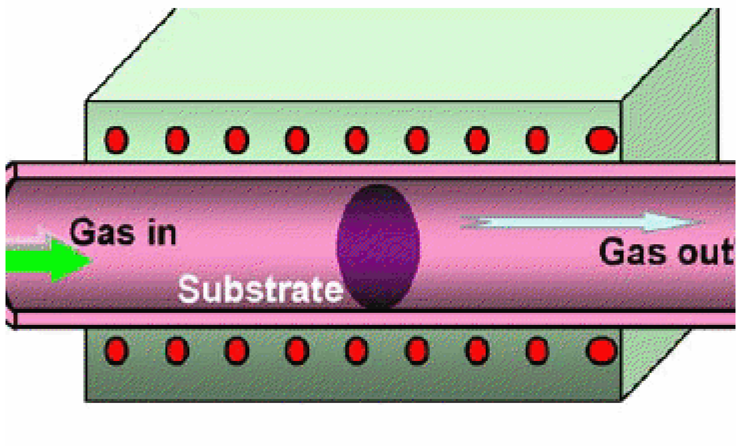
Chemical vapor deposition (CVD) method

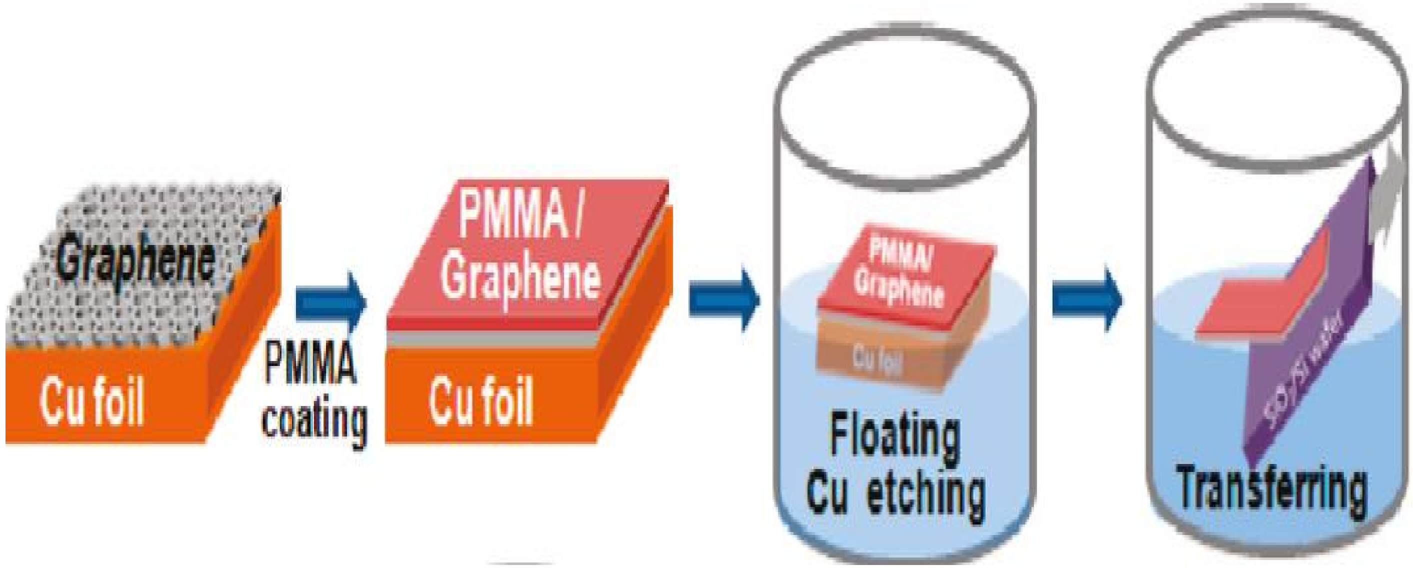
Advantages:

- Great technique for large area graphene
- Requires less labor
- Continuous films

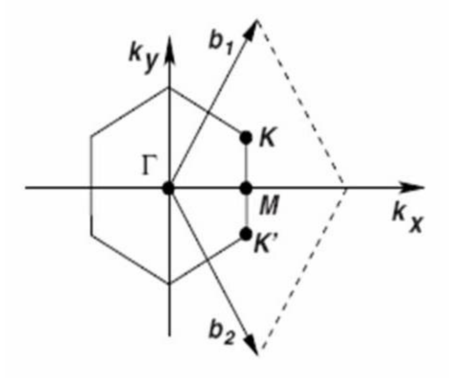
Limitation:

- Require high temperature





Band Structure of graphene

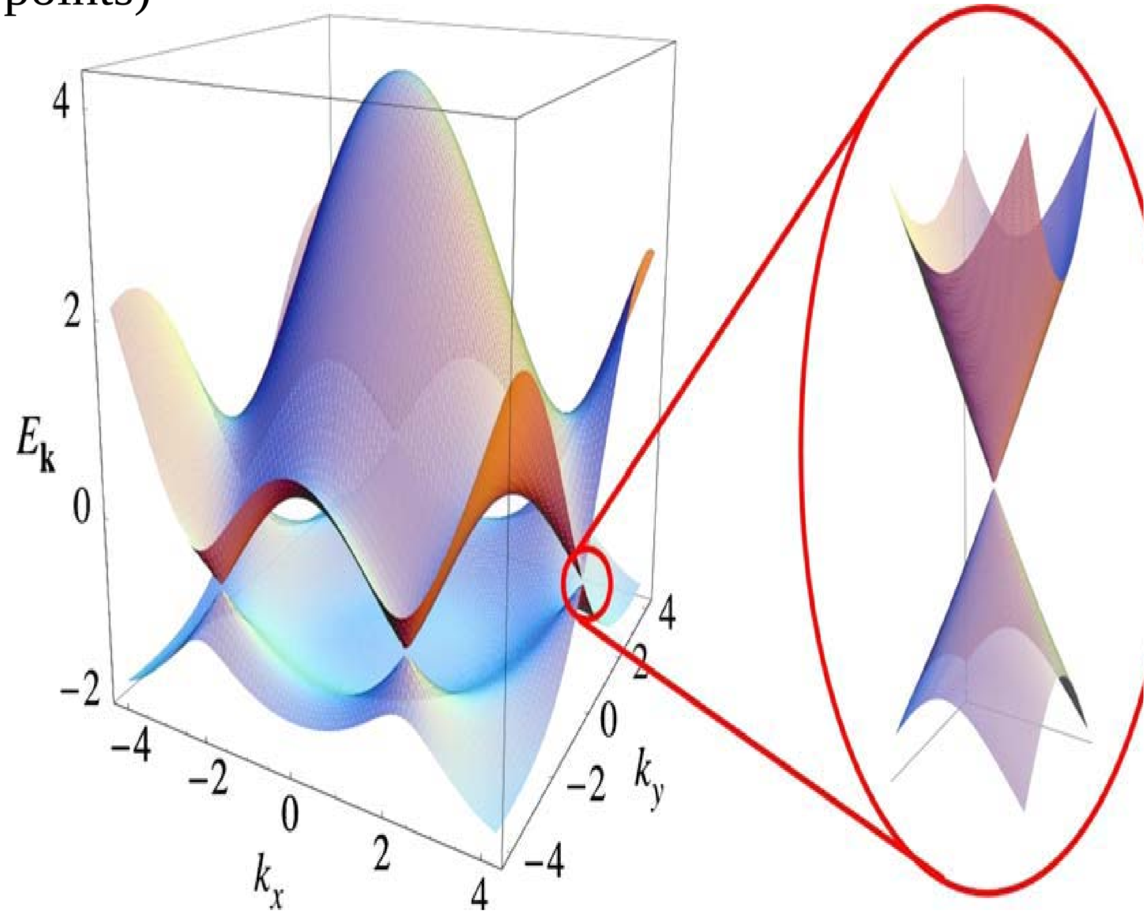


The spectrum is described by the tight-binding Hamiltonian on a hexagonal lattice

- Band crossing at K and K' (Dirac points)
- Dispersion is similar to that of relativistic particles, $E = h v_F k$

- Fermi velocity $v_F = 10^6$ m /s

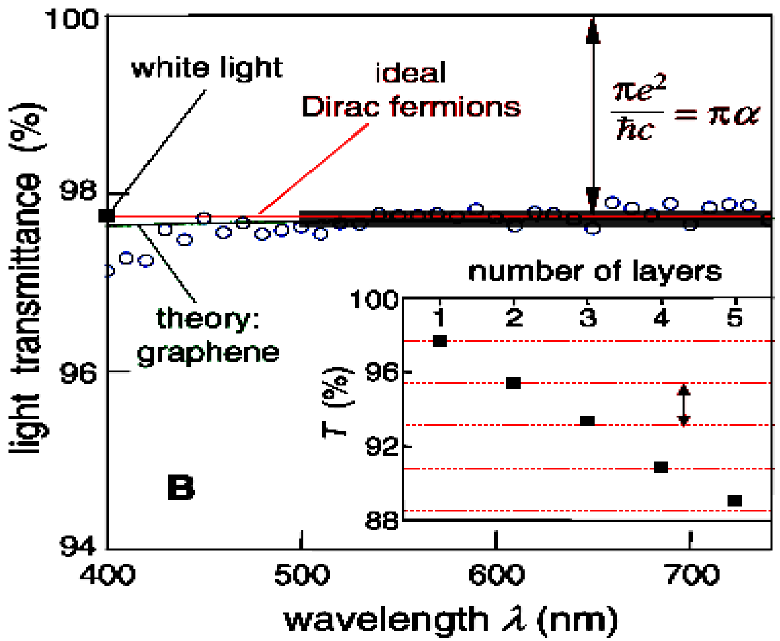
- Zero band gap semiconductor
- Charge carriers ~ massless Dirac Fermions

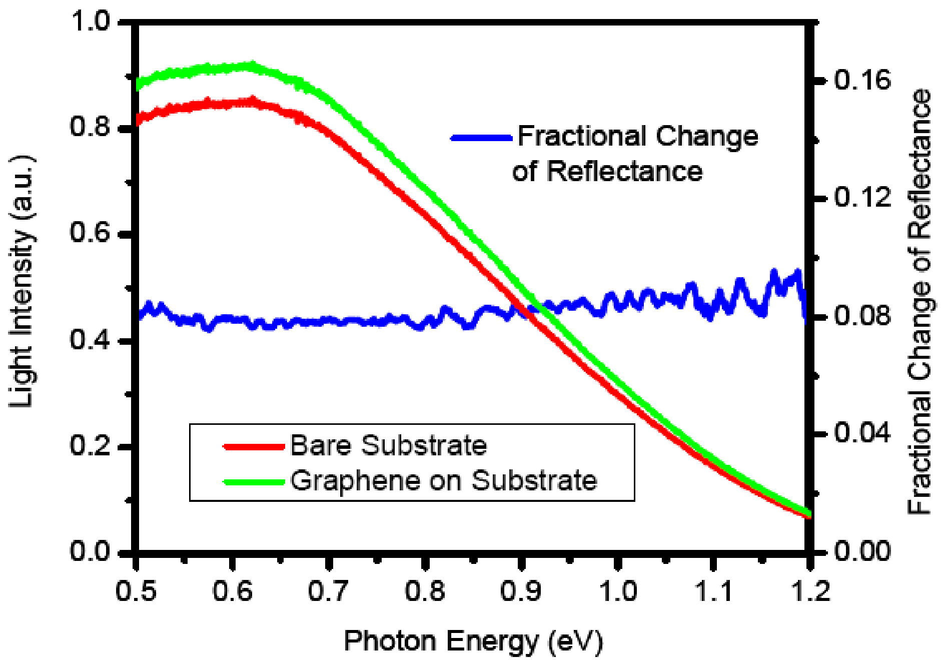


Optical properties of graphene

Absorption of light by 2D Dirac fermions

- Graphene absorbs πα ≈ 2.3% of white light, where α = fine structure constant
- Transmission, T = 1- πα , Reflection, R<<1





Possible applications of graphene

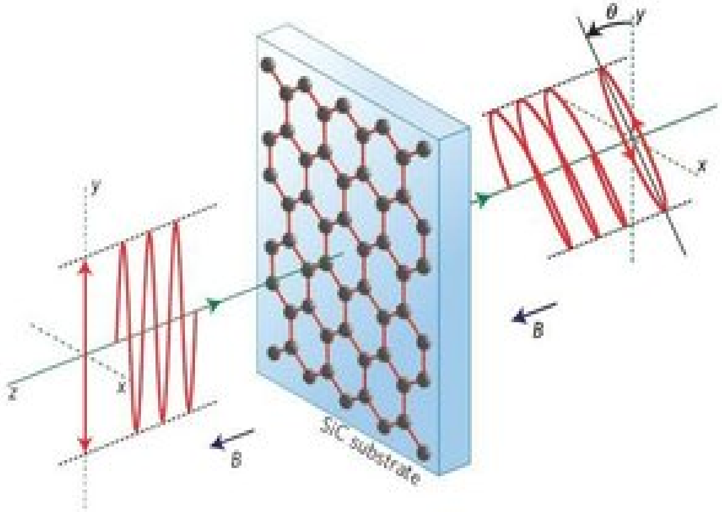
- TCO (Transparent conducting electrode)
  Alternative to ITO (expensive, difficult to recycle)

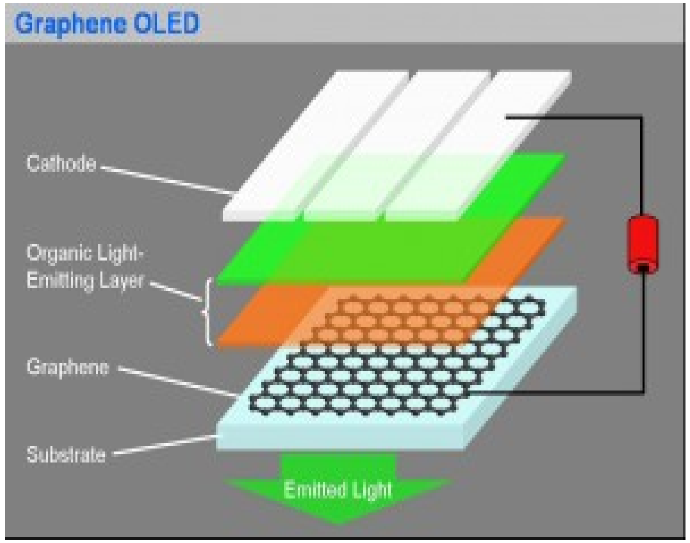
  Electrode very thin (couple of nm thick)

  Compatible with large scale manufacturing methods

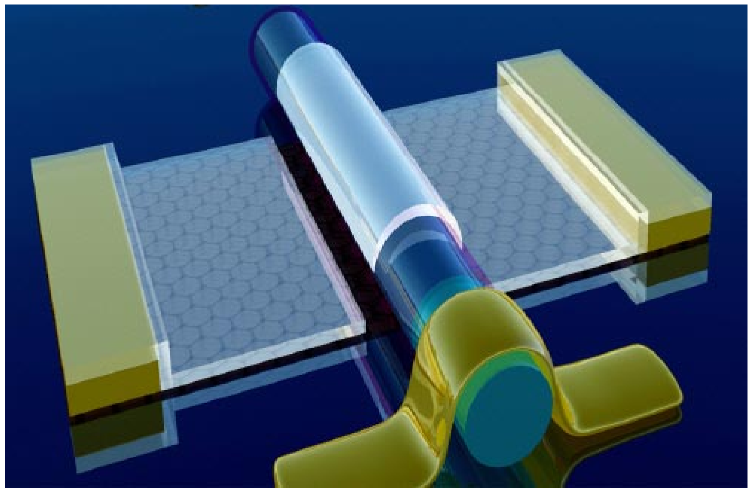
- Can be used to polarize light

- Saturable absorber





Graphene Transister



Characterization of graphene

AFM (Atomic Force Microscope)

- **Used to characterize the surfaces on nanometer scale**

The force acting on the cantilever,

$$F = -kz$$

k = spring constant of cantilever

z = deflection of cantilever

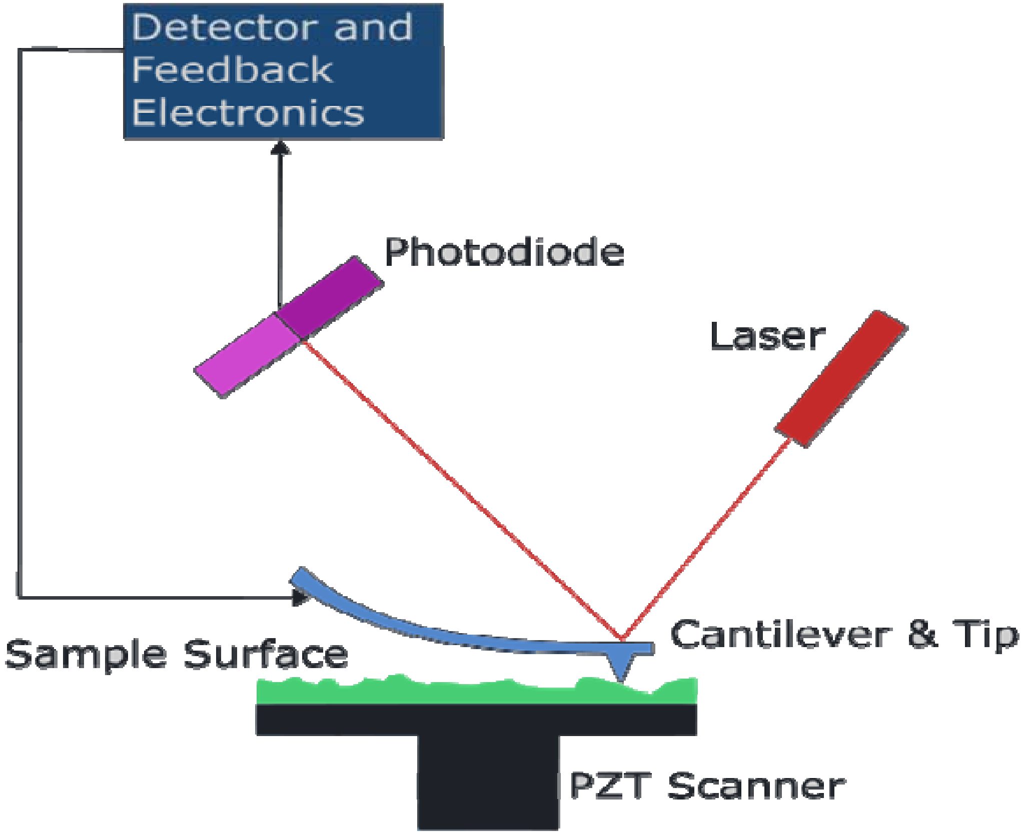


Fig. Scheme illustrating the working of AFM

Operating modes

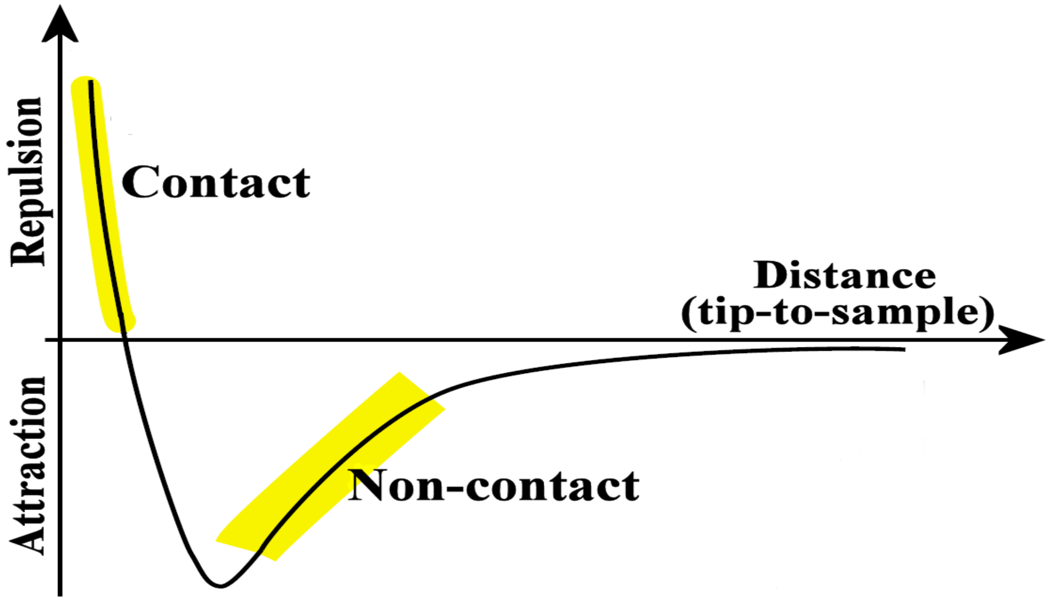
Contact mode

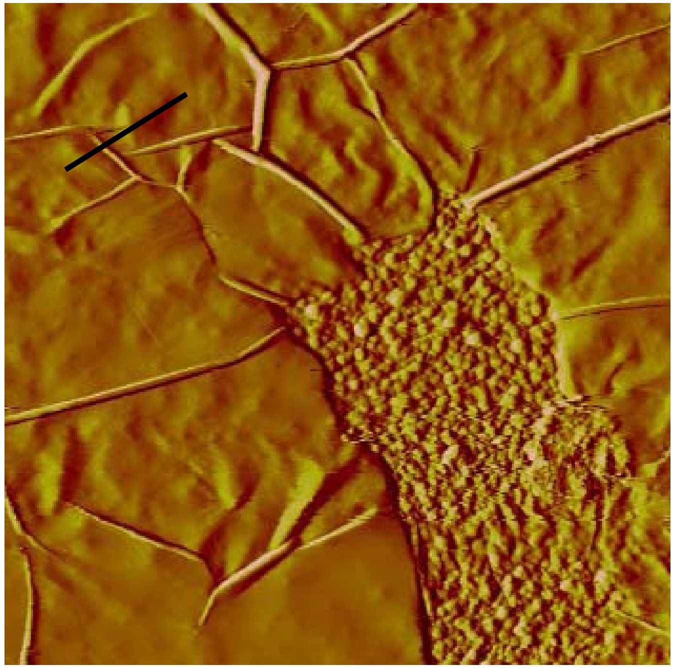
- S ~ few nm
- F ~ 10^{-8} to 10^{-6} N
- High resolution

Non-contact mode

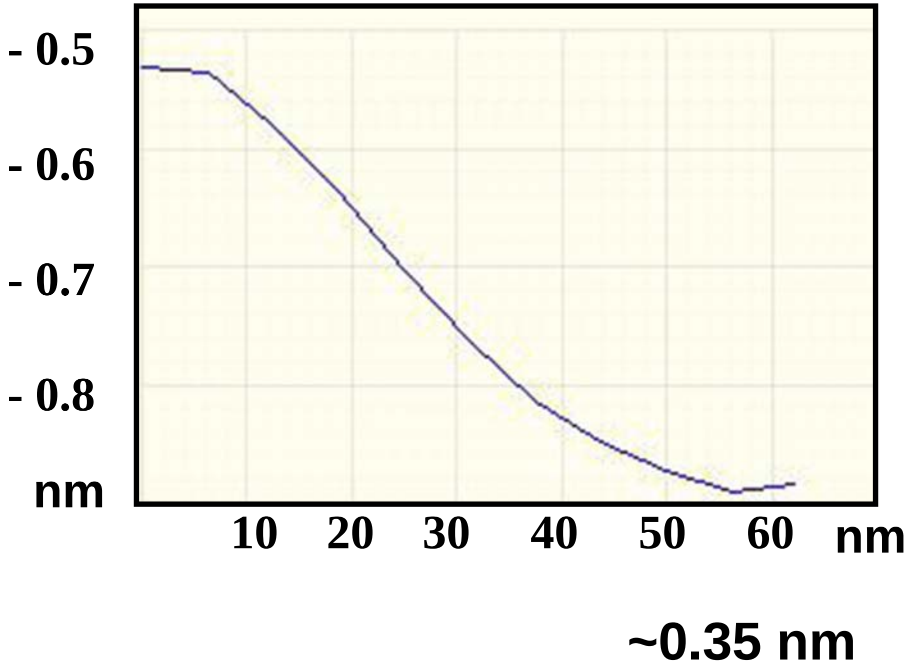
- S ~ 10 nm
- F ~ 10^{-12} N
- Suitable for soft samples

S = distance between tip and surface
F = force between tip and surface





AFM image of graphene



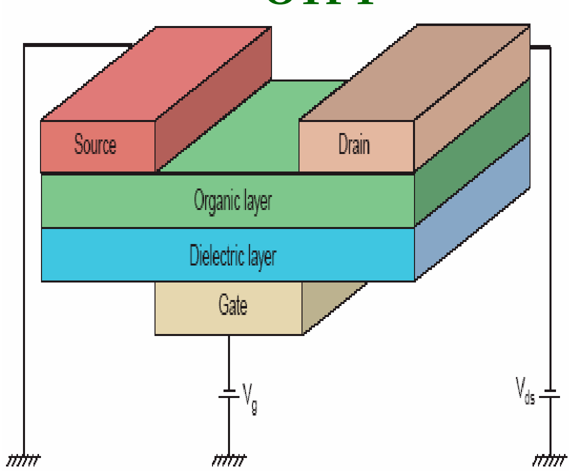
AFM measurement across a wrinkle confirming interlayer spacing of ~0.35 nm.

Growth of OS on graphene

- Low cost, mechanically flexible, easy to fabricate
- Aspects of interface

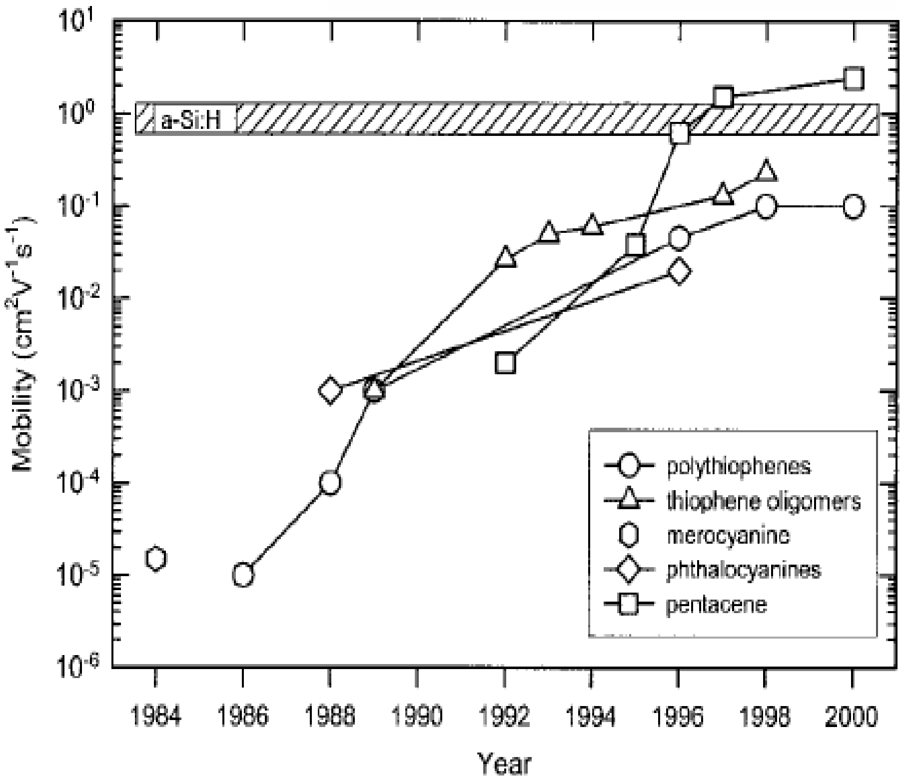
  Organic Solar cell, OLEDs, OTFTs

OTFT



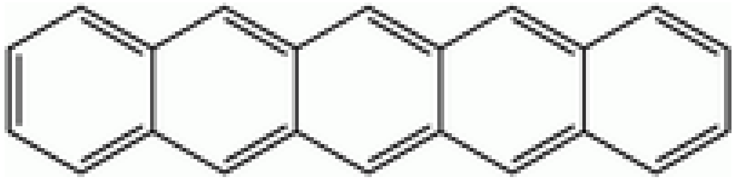
- Pentacene-based organic thin film transistors (OTFTs) reached charge carrier mobility of the order of 1 cm^2/Vs

- Graphene can be used as a substrate



Pentacene

- Crystal structure - **Triclinic**
- Band gap - **2.2eV**
- High carrier mobility
- Excellent interface properties with organic materials
- Form highly ordered organic films



Structural formula of Pentacene

Organic Molecular Beam Deposition

- The growth is controlled with the precision of a single molecular layer

- **Generation of the molecular beam**
- **Mixing zone**
- **Growth on substrate**

Sticking coefficient,

$s = N_{adh} / N_{tot}$

N_{adh} = no. of atoms adhering to substrate

N_{tot} = no. of atoms arriving

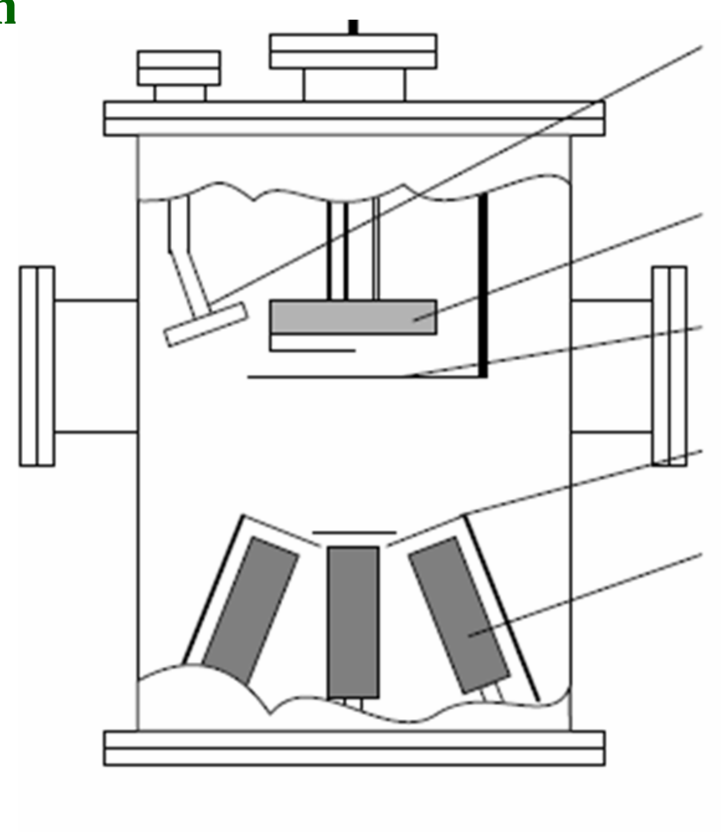


Fig. Organic Molecular Beam Setup

Practically, s <1

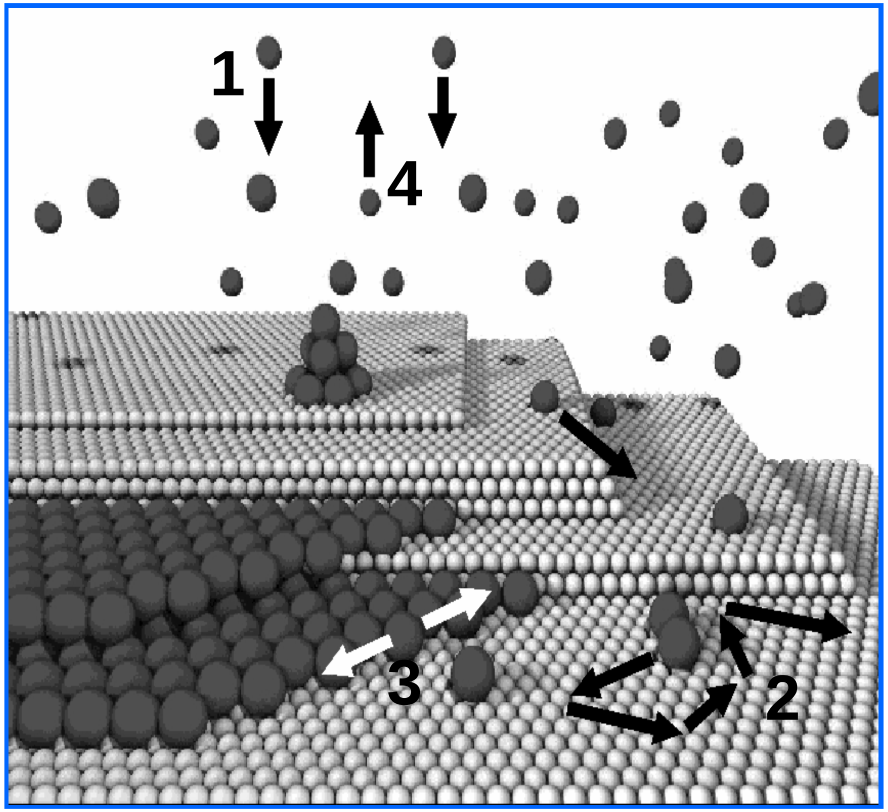
A series of process occur

1) Adsorption of atoms or molecules impinging on substrate surface
   - a) Physical adsorption- no electron transfer
   - b) Chemical adsorption-electron transfer

2) Surface migration and dissociation of adsorbed molecules

3) Incorporation of constituent atoms into crystal lattice

4) Desorption



Structure of organic films grown depends upon

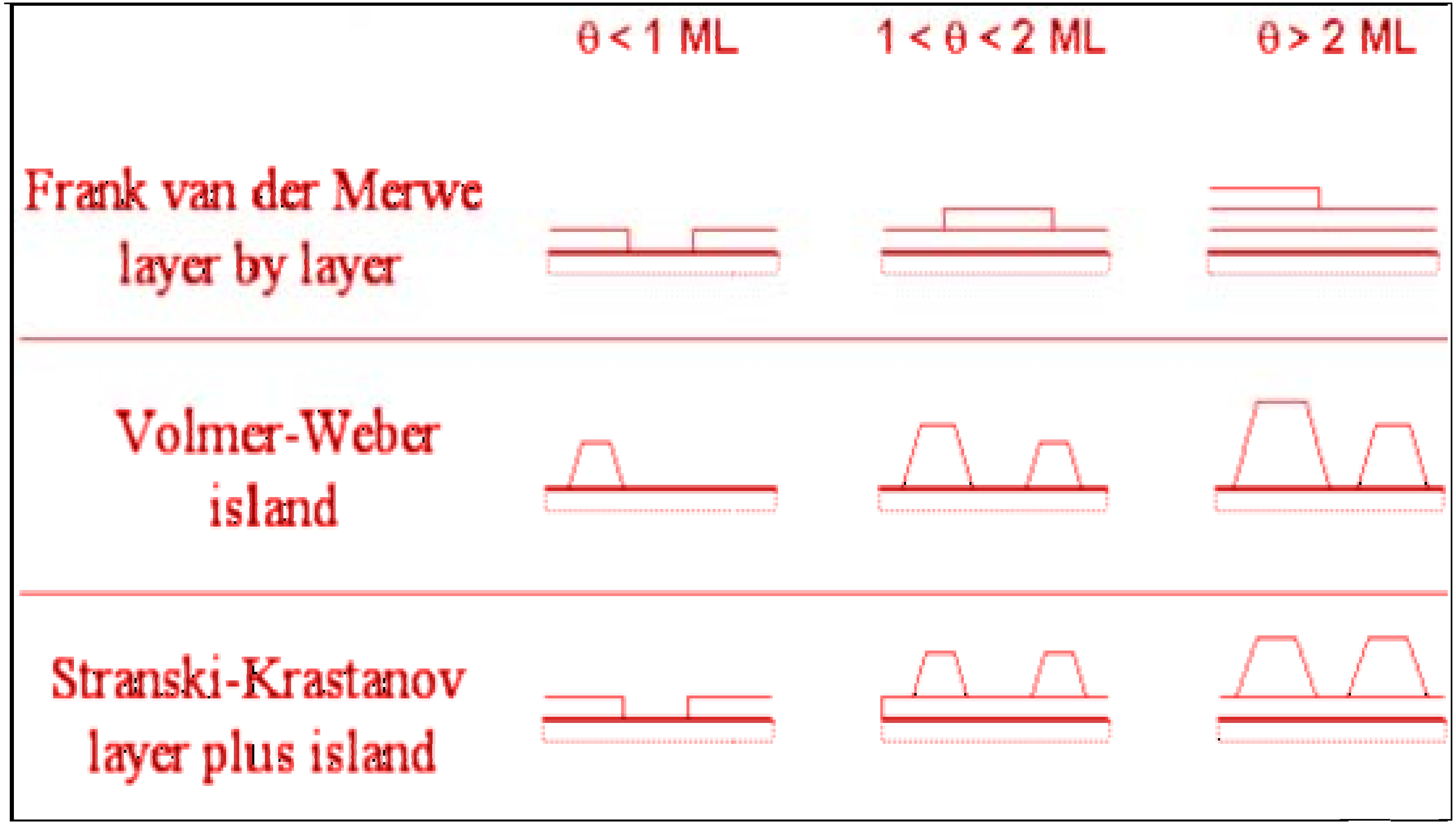
- Type of molecule/substrate interaction

  Layer-by-layer (Frank van der Merwe) growth mode
  if molecule/substrate interaction > intermolecular interaction

  Layer-plus-island (Stranski- Krastanov)- intermediate mode
  layer growth unfavorable after first few layers

  Islands (Volmer- Weber growth mode)
  if intermolecular interaction > molecule/substrate

- Substrate temperature
- Density of surface defects
- Surface energy



J. A. Venables et. al, Rep. Prog. Phys 47, 399 (1984)

Density of islands depends upon

- Deposition rate
- Substrate temperature and described as power law

$$N = R^p e^{\left(E_{nucl}/K_B T_s\right)}$$

p = critical exponent, K_B = Boltzmann constant

E_{nucl} = activation energy for homogenous nucleation

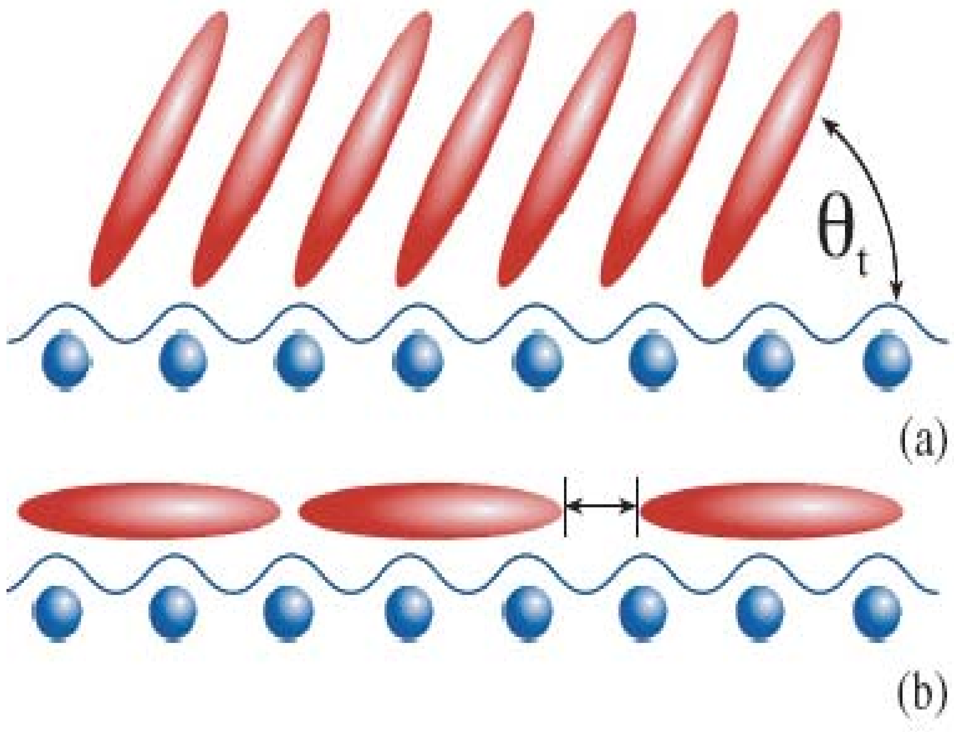
a) Surface diffusion (E_d)
b) Desorption from substrate surface (E_a)
c) Formation of island of critical size i with binding energy E_i

Specific issues to organic thin film growth

- **Internal degrees of freedom**
  Orientational degrees of freedom-orientation domain
  Vibrational degrees of freedom-impact on interaction with surface

- **Interaction potential**
  (Molecule-molecule and molecule-substrate)
  Strongly interacting surface-limited diffusion

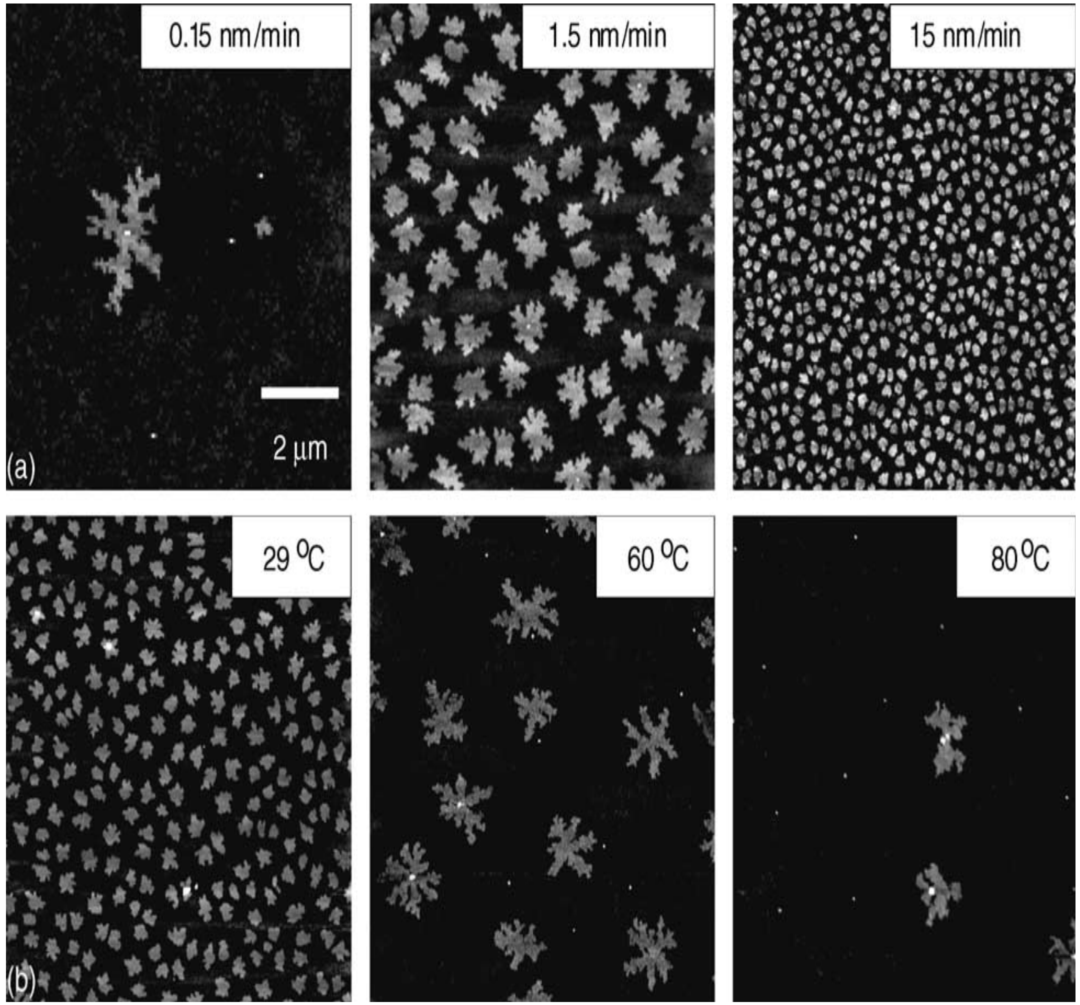
- **Size of the molecules**
  Multiple domains-disorder



Example 1: Pentacene on SiO_2

Experimental details:

- Si wafer with 200nm thick SiO_2 layer(roughness < 0.1nm)
- Pentacene evaporated from fused quartz crucible
- Film thickness, 0.5nm
- Base pressure ~ 10^{-7} mbar
- Substrate temperature, T_s ~ 338K
- Deposition rate ~ 0.45nm/min



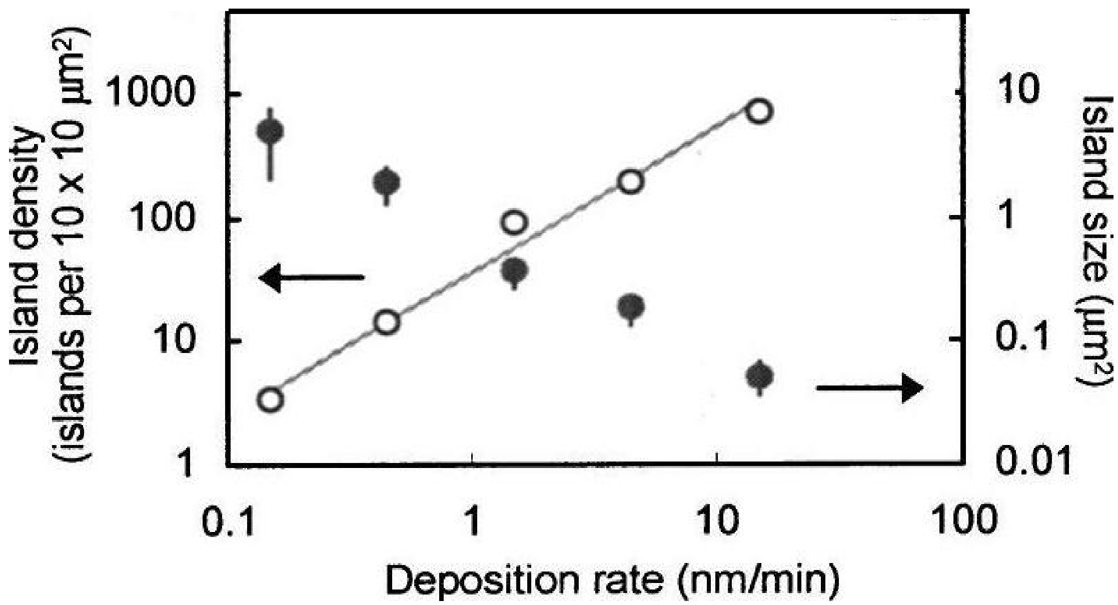
S. Pratontep et.al, PRB 689,165201(2004)

Effect of deposition rate

- Morphology of island becomes compact
- No. density of island increases

Effect of T_s

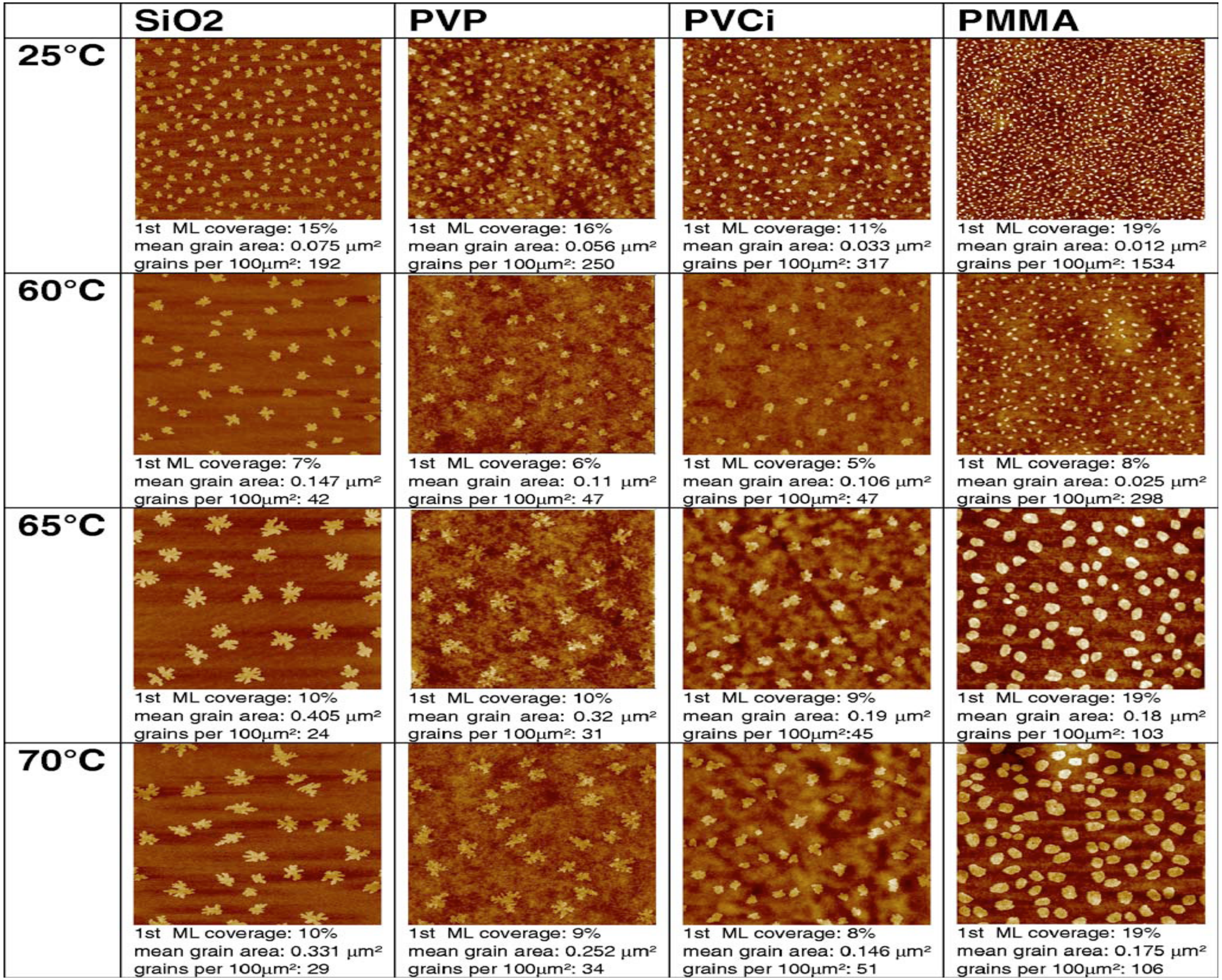
- Density N decreases by a few orders of magnitude as T_s increased from 29°C to 80°C



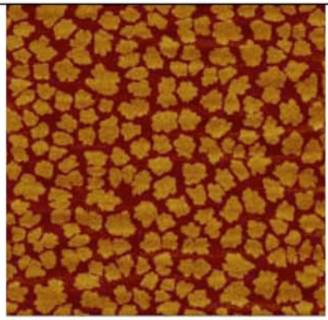
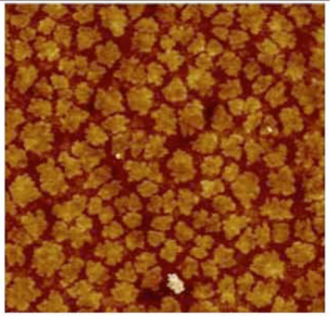
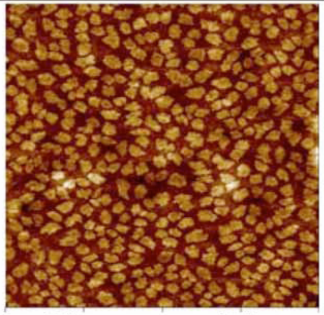
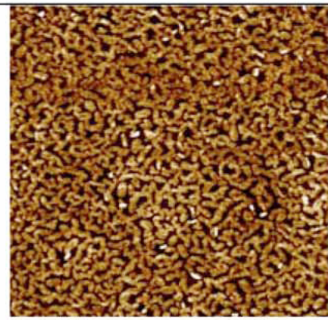
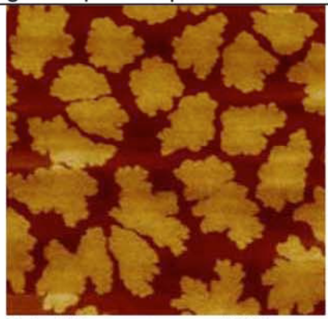
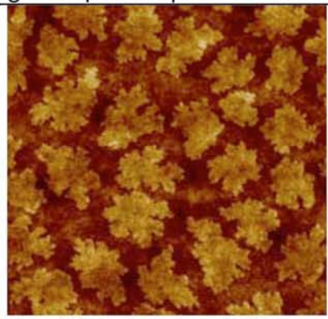
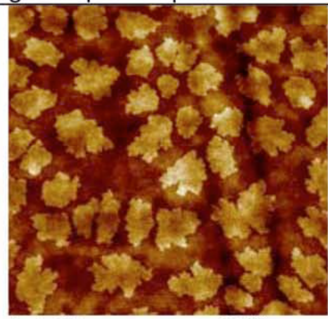
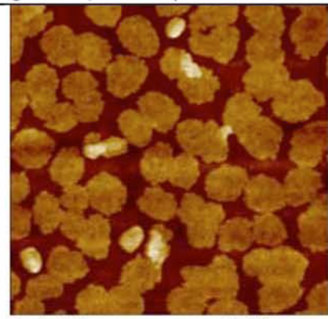
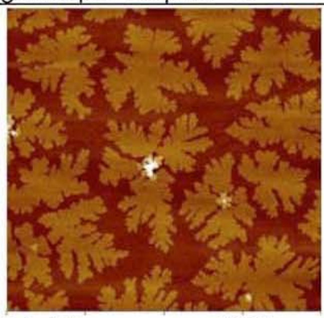
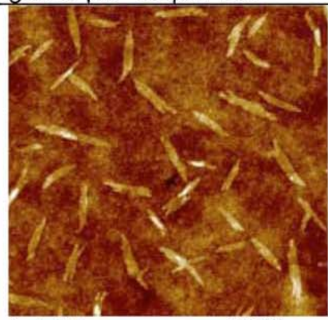
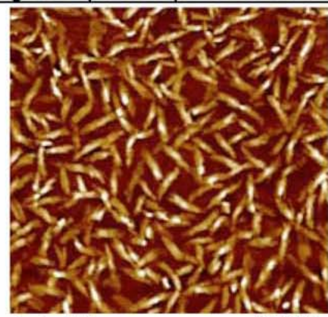
Conclusion: Nucleation density of islands can be tuned by both deposition rate and substrate temperature

S. Pratontep et.al, PRB 689,165201(2004)

Example 2: AFM images of Pentacene (0.2 ML) thick on different substrates

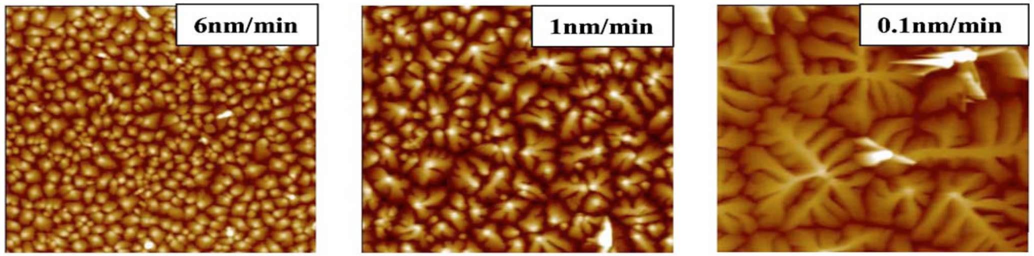


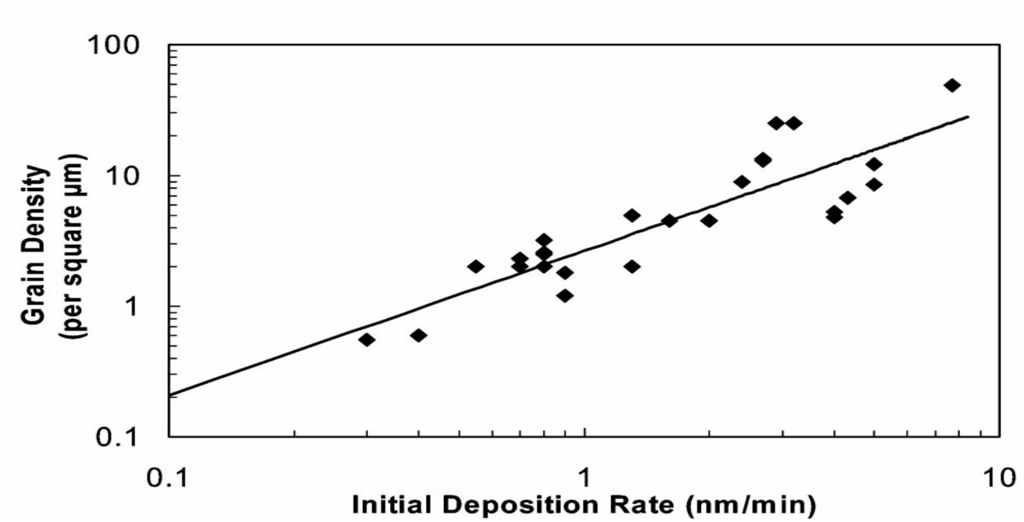
Pentacene on different substrates

	SiO_2	PVP	PVCi	PMMA
25°C 0.8ML	 1st ML coverage: 52% mean grain area: 0.331 µm² grains per 100µm²: 142	 1st ML coverage: 47% mean grain area: 0.441 µm² grains per 100µm²: 97	 1st ML coverage: 43% mean grain area: 0.087 µm² grains per 100µm²: 303	 1st ML coverage: 81% m. grain area: coalescing grains per 100µm²: coal.
65°C 0.8ML	 1st ML coverage: 53% mean grain area: 2.94 µm² grains per 100µm²: 13	 1st ML coverage: 41% mean grain area: 1.62 µm² grains per 100µm²: 25	 1st ML coverage: 37% mean grain area: 0.518 µm² grains per 100µm²: 31	 1st ML coverage: 57% mean grain area: 1.026 µm² grains per 100µm²: coal.
25°C 3.6ML	 1st ML coverage: 100%	 1st ML coverage: 100%	 1st ML coverage: 100%	 1st ML coverage: 100%

Transition from 2D to 3D- island growth

Film thickness ~ 33 ML
T_s = 25 ° C



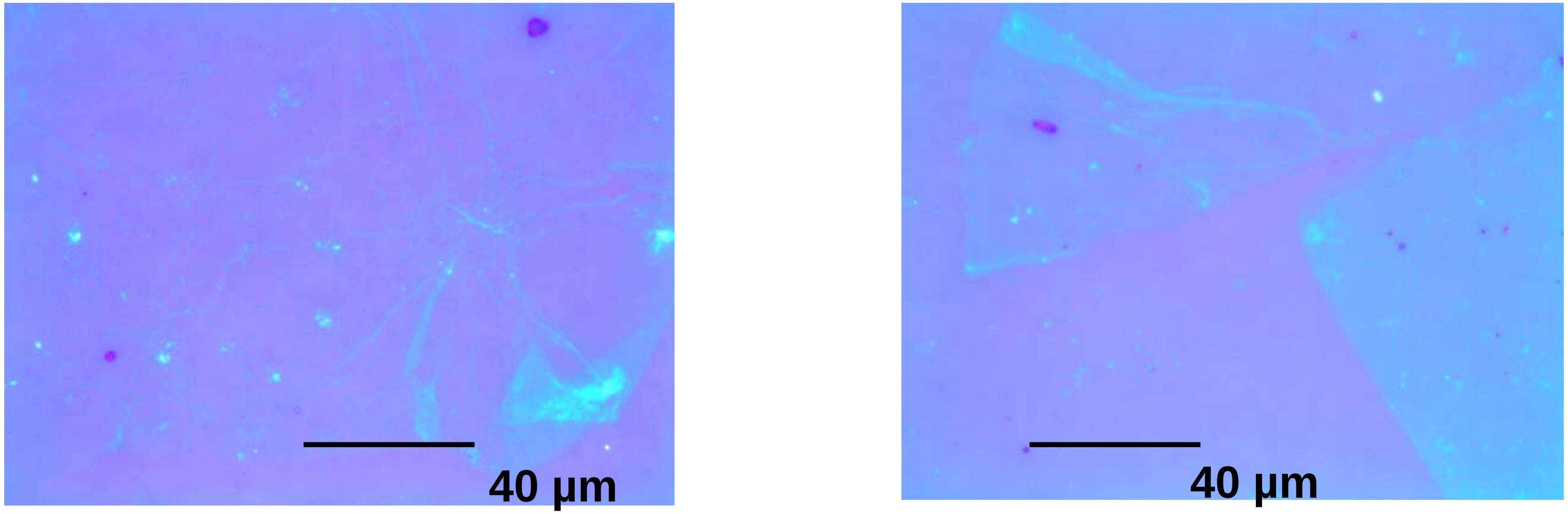


Conclusion: Pentacene growth on polymers is correlated
critical island size for substrates b/w 25-70 ° C is 3<i<4
Condensation is complete although reevaporation plays some role

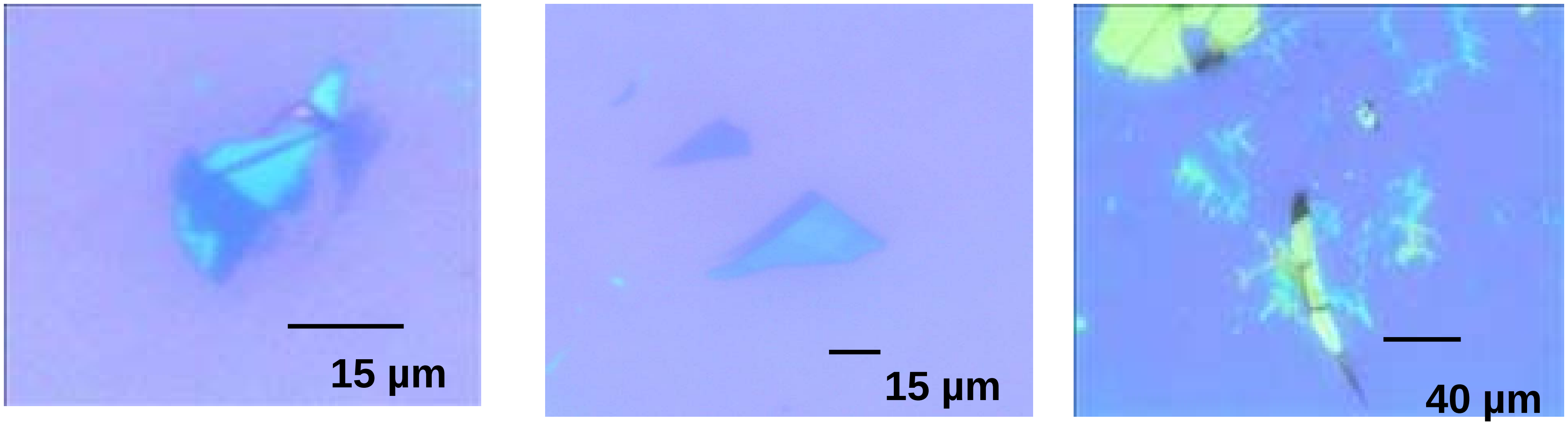
B. Stadlober et. al PRB B 74, 165302 (2006)

Optical microscope images of Graphene

Graphene prepared by CVD method



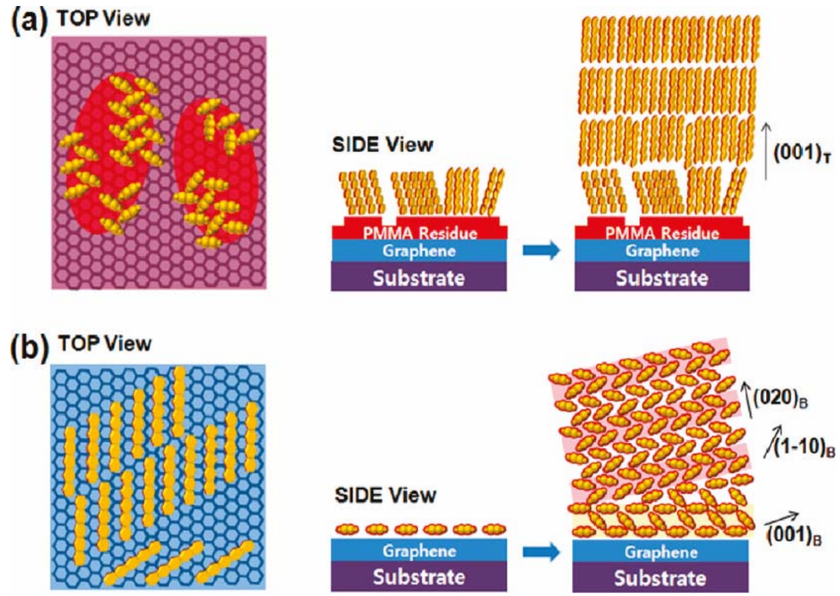
Graphene prepared by exfoliation



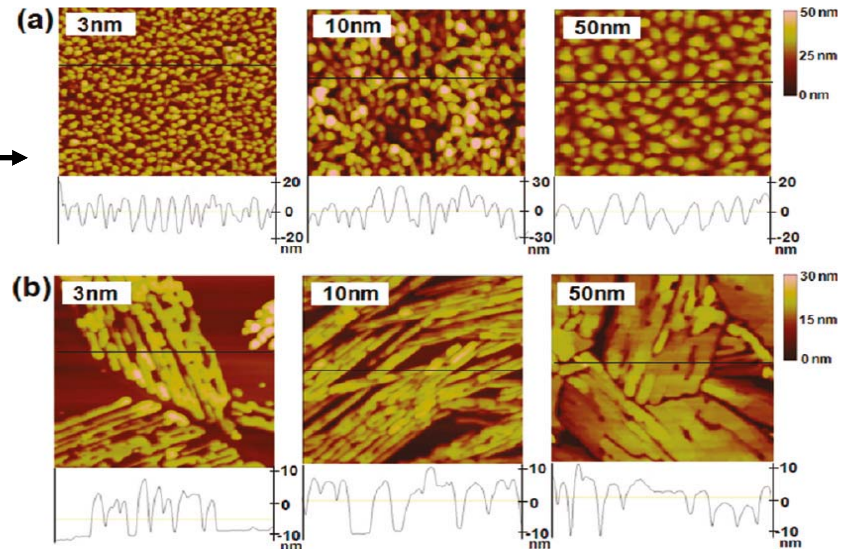
Pentacene on Graphene

- SiO_2 layer on Si wafer ~ 300 nm
- Pentacene deposition rate ~ 0.2 Å/ s

a) Untreated graphene films
b) Thermally treated graphene films



AFM images of pentacene films on graphene



W. H. Lee et. al., J. Am. Chem. Soc., 133, 4447 (07 March 2011)

Conclusions

- Graphene is an excellent 2D structure with unusual electronic and optical properties
- Organic semiconductors (OS) on substrates can be successfully grown in sub monolayer or more monolayer by OMBD
- AFM is an important tool to study initial stages of growth of organic semiconductor on substrates
- Graphene prepared by CVD and mechanical exfoliation methods can be used as a substrate