Indo-French Workshop on Multifunctional Molecular and Hybrid Devices

# Field Effect Transistors based on Poly(3-hexylthiophene) with 3-aminopropyltrimethoxy silane multilayer modified gate dielectric

by

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# Outline

- Introduction
- Role of self-assembly monolayers (SAM) in OFETs
- APTMS Multilayers /monolayer:

  ***Growth and characterization***

- Influence of surface modification on P3HT
- FET: Fabrication and characterization
- Conclusions

# OFET: Key Features

- Tailoring properties as per demand
- Easy processing
  spin coating, inkjet printing, screen printing etc.
- Low-temperature deposition
- Flexibility
- Applications in switching devices, flexible sensors, printed electronics such as RF-ID tags, integrated circuits

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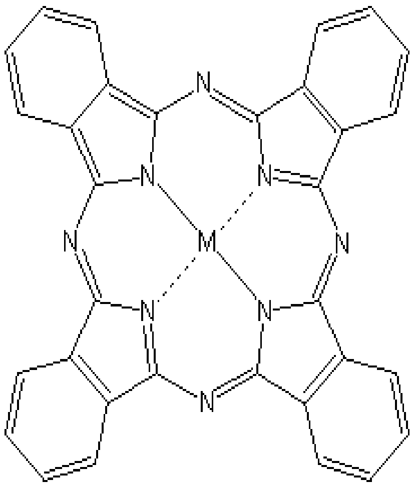
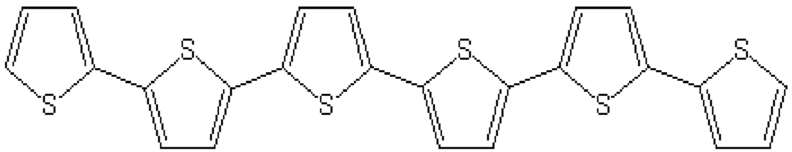
# Materials

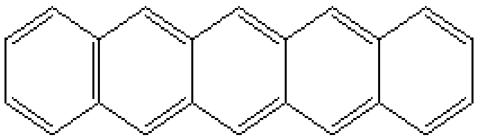
## Small molecules



Phthalocyanine

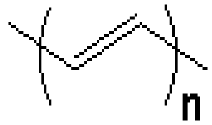


Sexithiophene

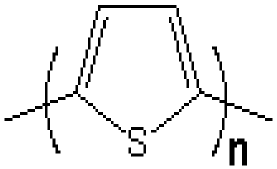


Pentacene

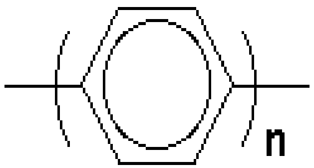
## Large Molecules



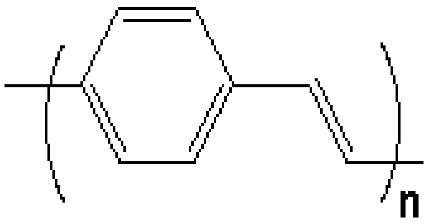
Polyacetylene



Polythiophene



Polyphenylene



Polyphenylenevinylene

# Parameters

- Mobility
- ON/OFF Ratio
- Threshold voltage
- Subthreshold slope
- Transconductance
- Current leakage

# Important Issues

**Material Science**

Charge transport

Novel Materials

Structure

**Device Physics**

Dielectric

Fabrication Details

Device Geometry

# Why is structure important?

## *Structure influences electronic properties*

### *Information Requirements*

| | |
|---|---|
| **Molecular orientation** | ***(few Å)*** |
| **Interfacial structure** | ***(few Å)*** |
| **Crystal/ Amorphous domains** | ***(few nm)*** |
| **Macroscopic Defects** | ***(few nm)*** |
| **Grain boundaries, traps** | |

# Interfacial Engineering: *SAM*

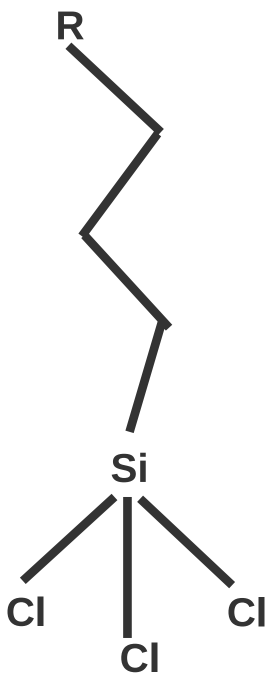
**Interface between dielectric and semiconductor**

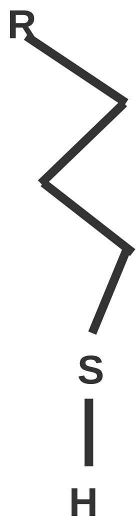
*Change in morphology, molecular ordering and packing, crystallinity of semiconductor*

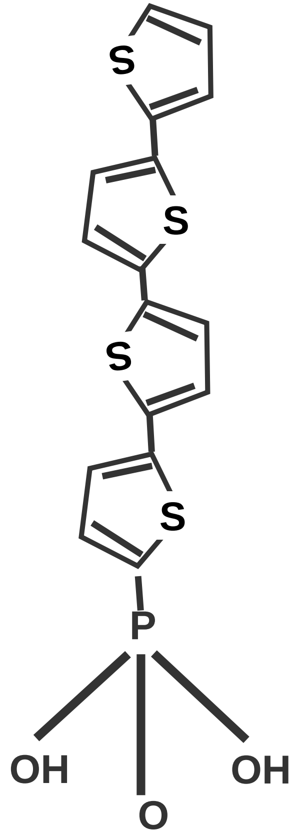
**Interface between metallic contacts and semiconductor**

*Better charge injection at the interface*

# Some SAM Structures



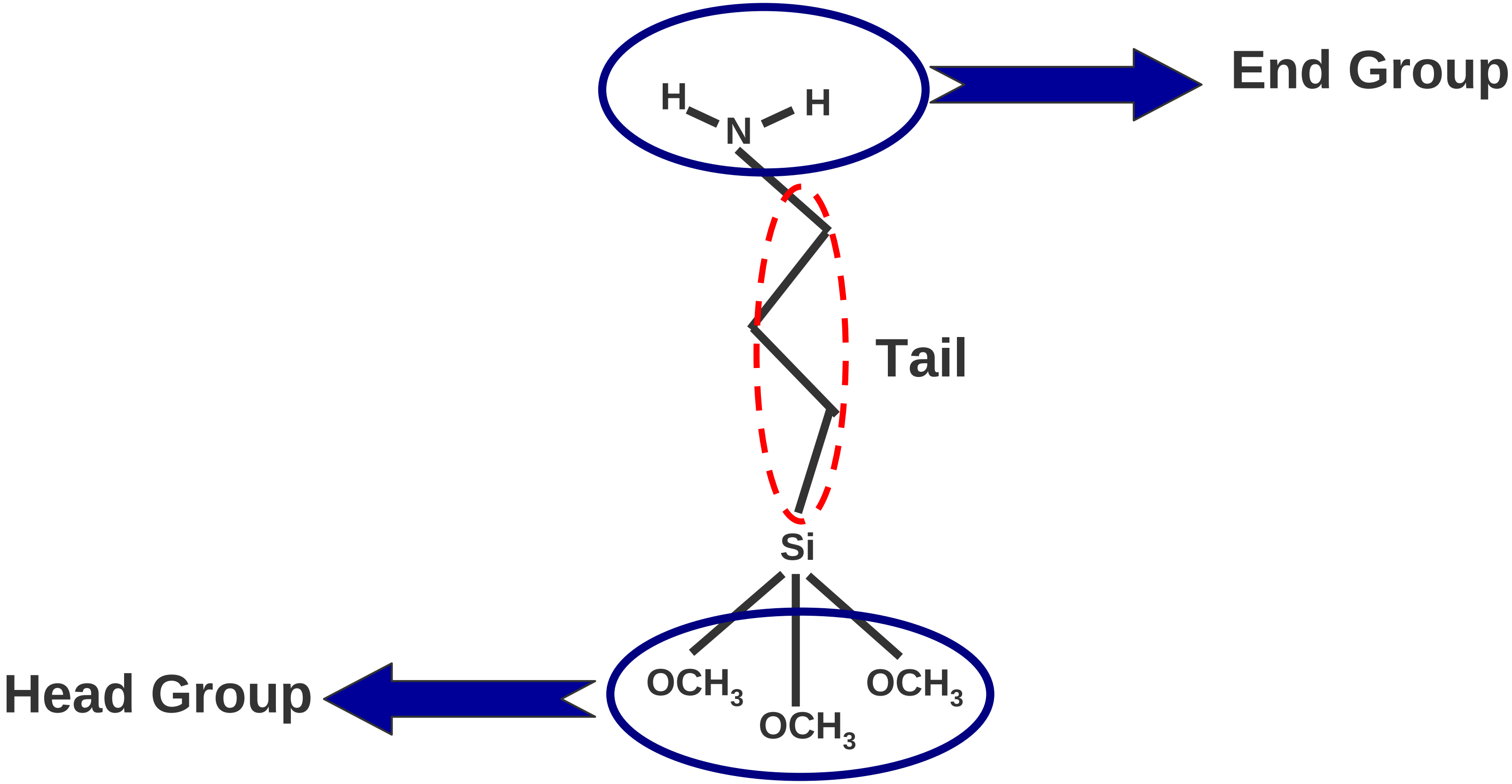




**Organic trichlorosilanes** **Organothiols** **(quarterthiophene) phosphonic acid**

R: $CH_3$, $C_2H_5$, etc

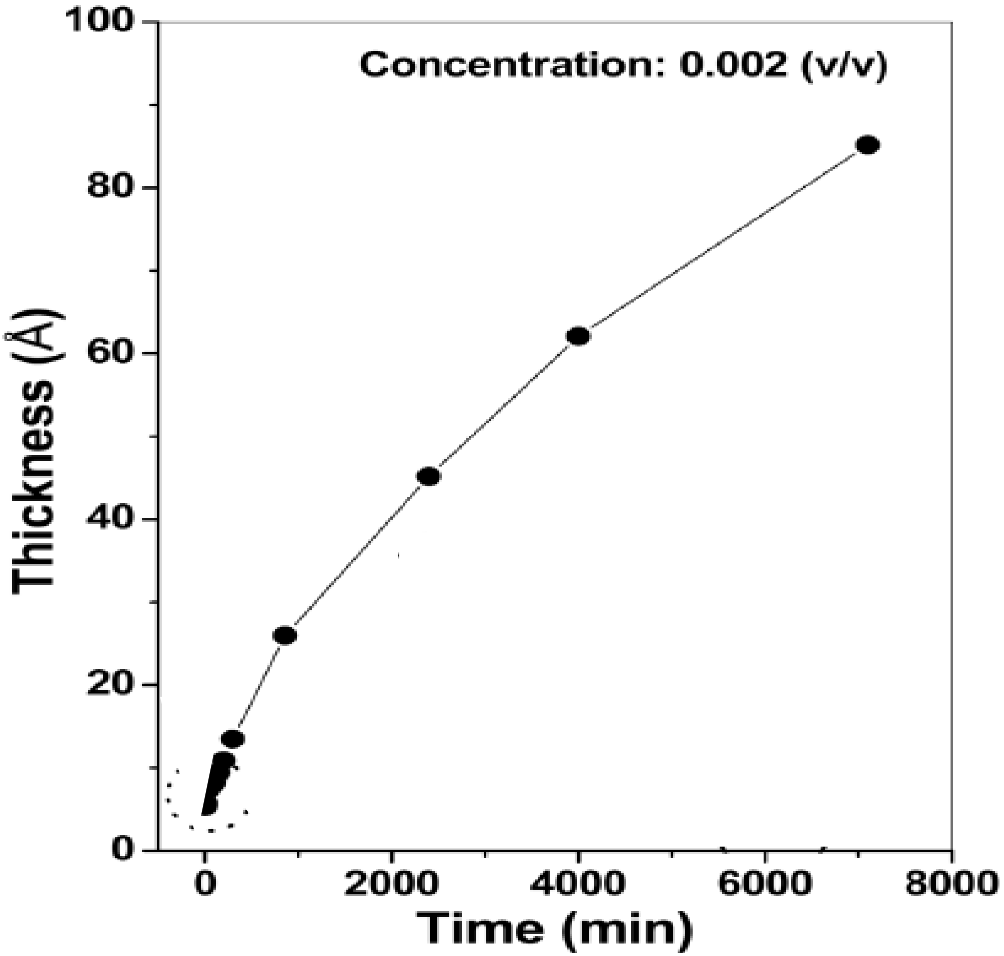
# APTMS : *Molecular Structure*



# APTMS Growth : ***Monolayer/ Multilayers***

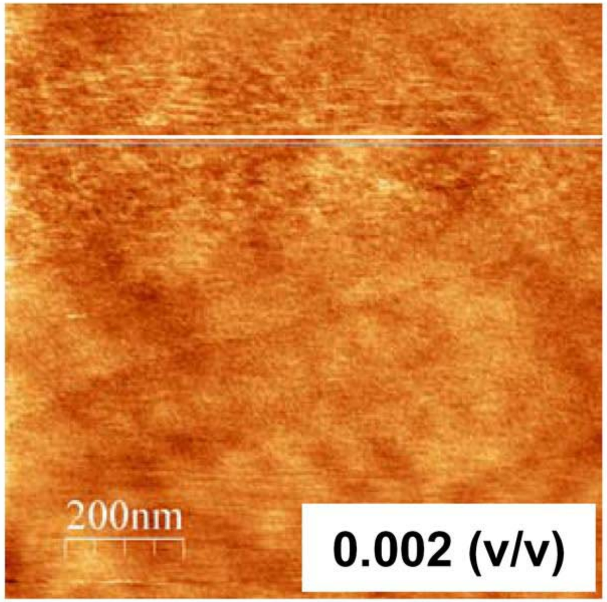
## Solution Growth:

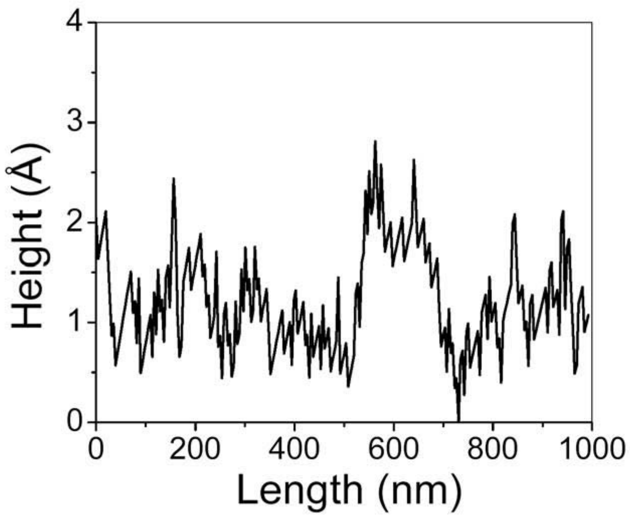
- *APTMS in dry toluene under inert atmosphere for 30 mins.*
- *Thickness depends on concentration and time*




Chauhan et al, Phys. Stat. Sol. (A), 1– 5 (2007)

# APTMS Monolayer: ***Characterization***



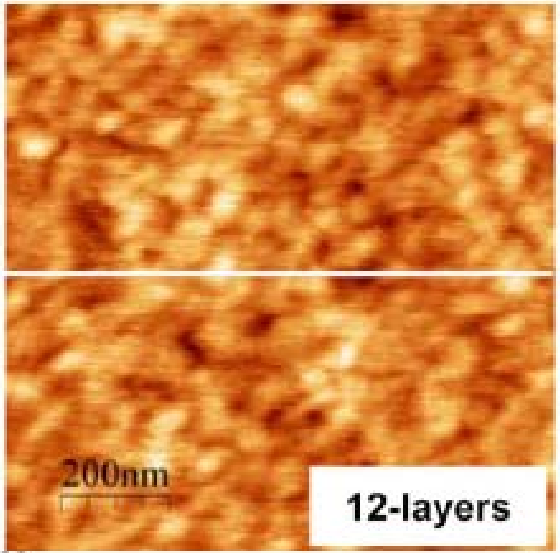

**Roughness < 1 Å**

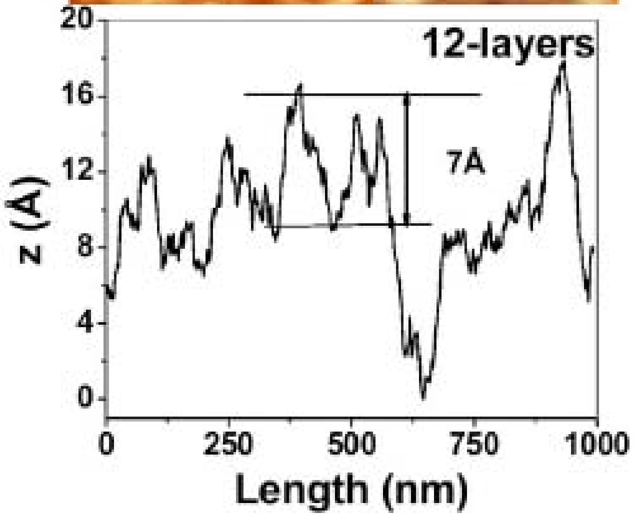
**DI water contact angle < 15º**

**Molecule Thickness ~ 6.5 Å,**

indicates formation of well organized monolayer

# APTMS Multilayers: *Characterization*



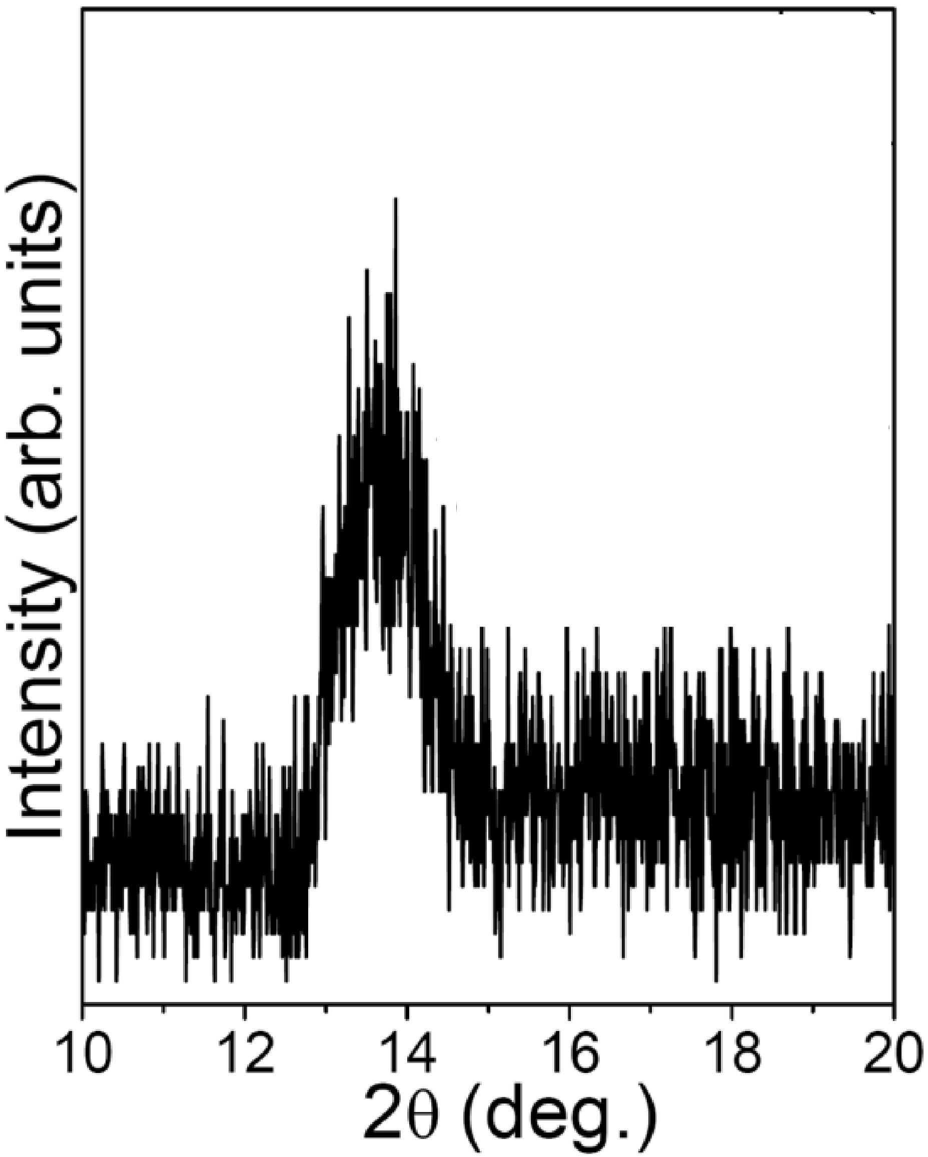

**Roughness** **7Å**

**DI water contact angle** **<42º**

**Thickness** **~ 78.5 Å**

***corresponds to 12 monolayers***

# APTMS Multilayers: ***XRD Characterization***



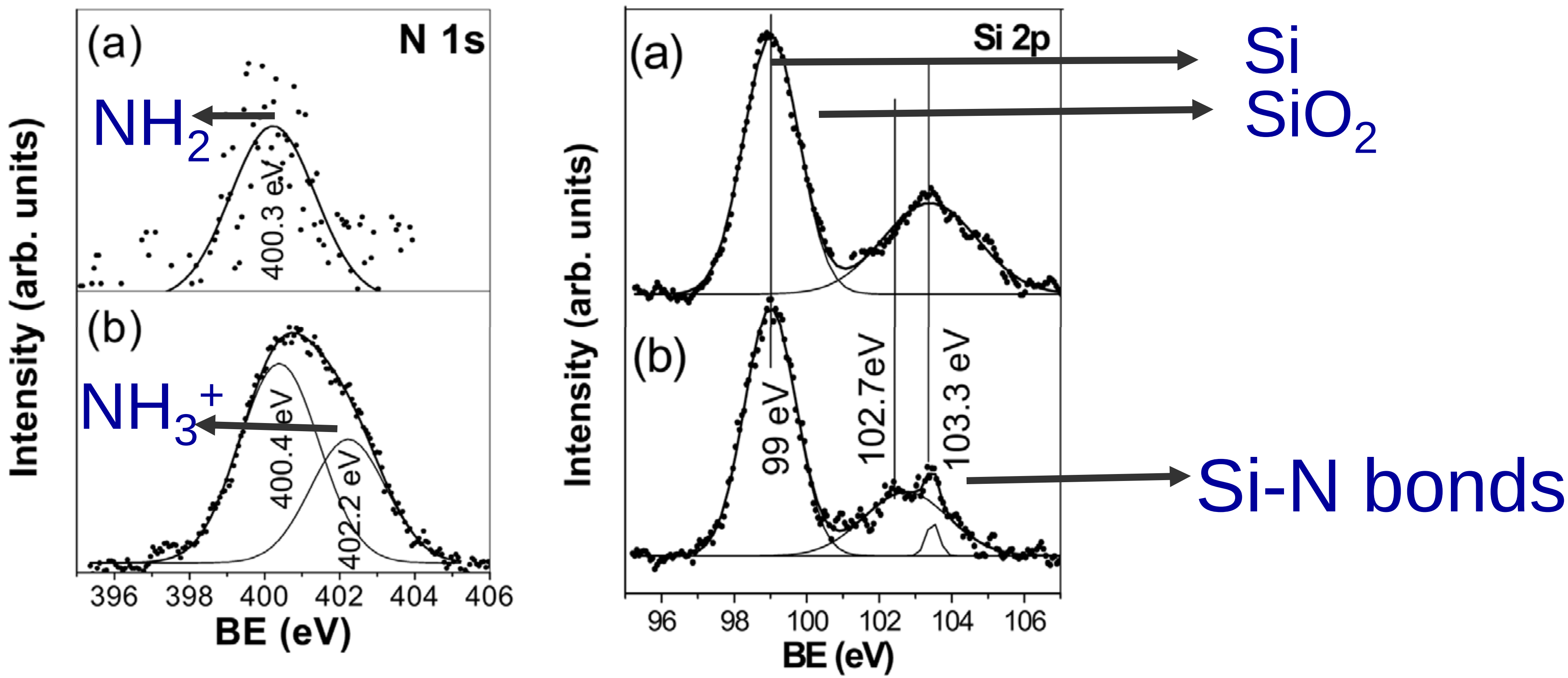

Length of APTMS molecule~6.4 Å

**Layer by layer self- assembly of APTMS multilayer**



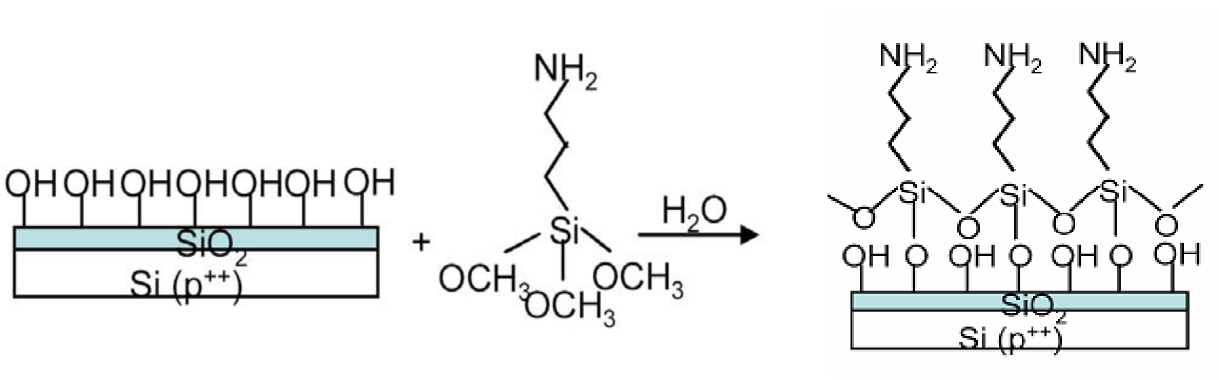
Chauhan et al, Appl. Phys. A, 90 (3) 581-589 (2008)

# APTMS : *XPS Characterization*



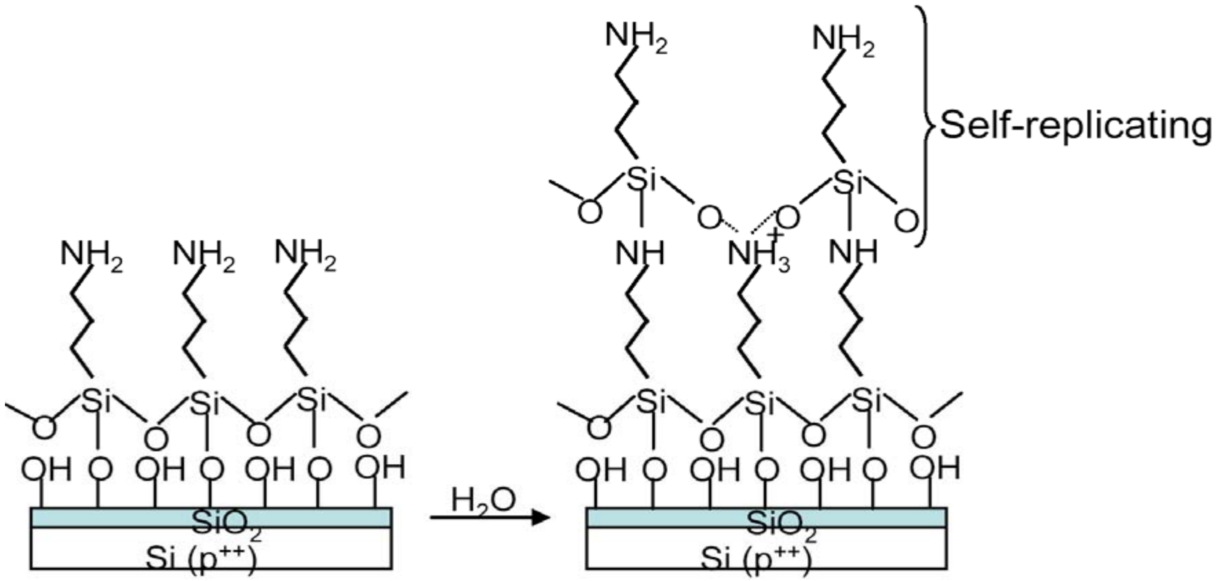

**(a) Monolayer** **(b) 12-layered APTMS**

# Growth Mechanism




*APTMS molecule gets chemisorbed on $SiO_2$…..*

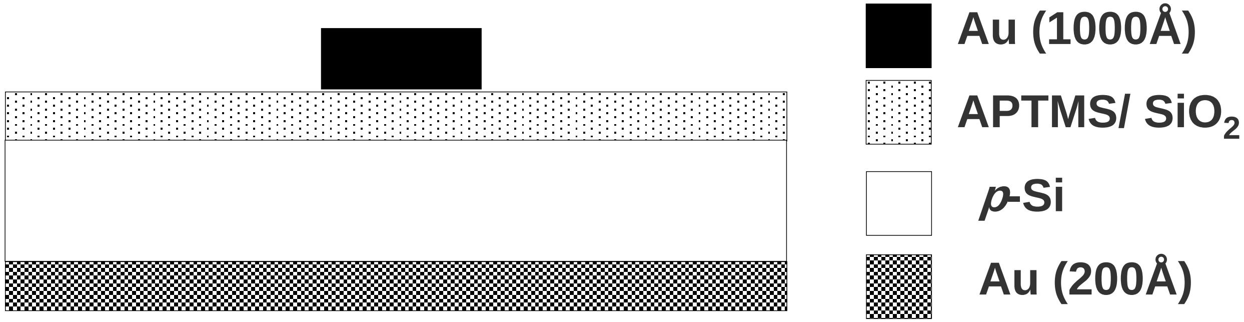
*…….. $NH_2$ group of APTMS gets protonated by $H_2O$ or by slight acidity of solvent to form $NH_3^+$ ions…..*




*…….Hydrolyzed APTMS molecule can also react with $NH_2$ group of monolayer via Si-N bonding…….*

*….Bilayer formation takes place through Si-N bonds & $NH_3^+$ ions*

# APTMS Multilayers: *C-V on MIS Structure*

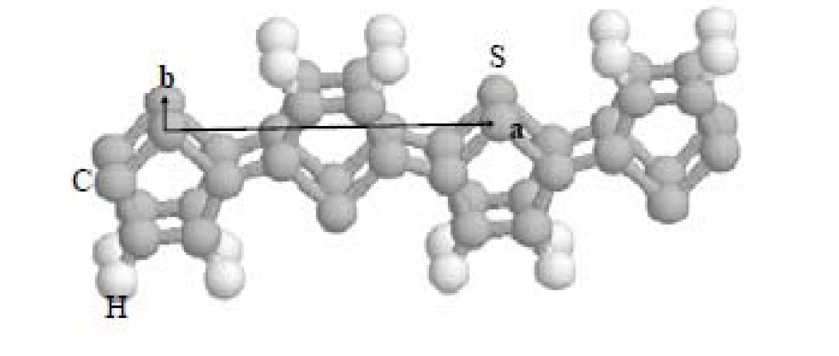



| Structure | $C_i$ (nF/cm$^2$) | ε |
| --- | --- | --- |
| $SiO_2$ | 15 | 3.8 |
| APTMS | 70 | 4.19 |

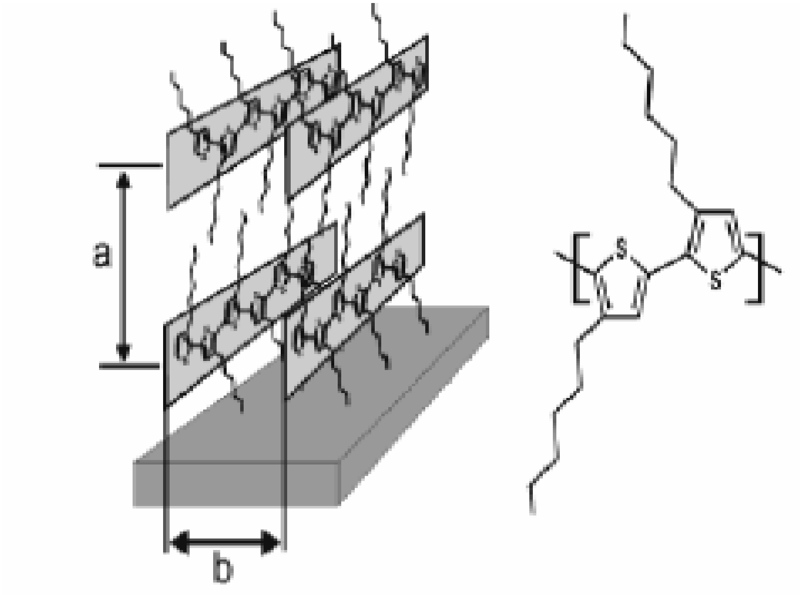
# P3HT Film

**P3HT**

a = 33.6 Å, b = 7.66 Å

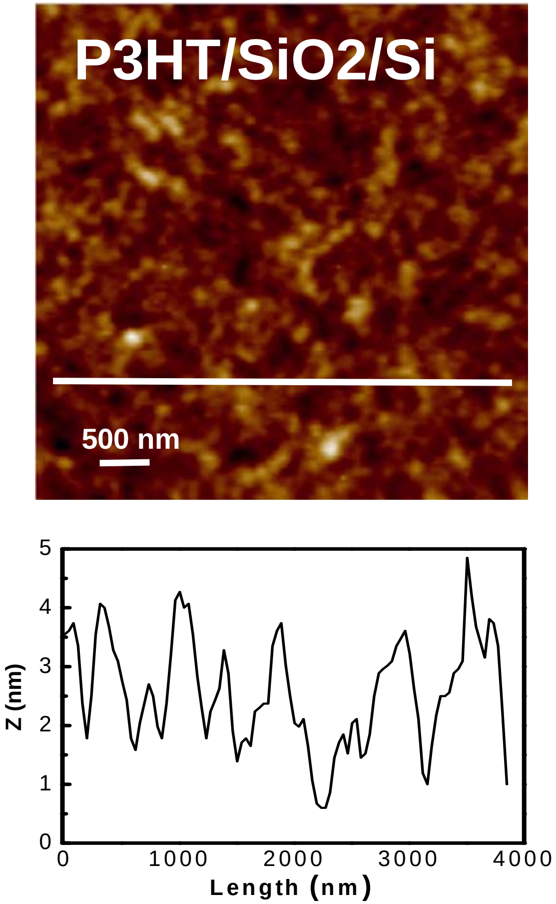


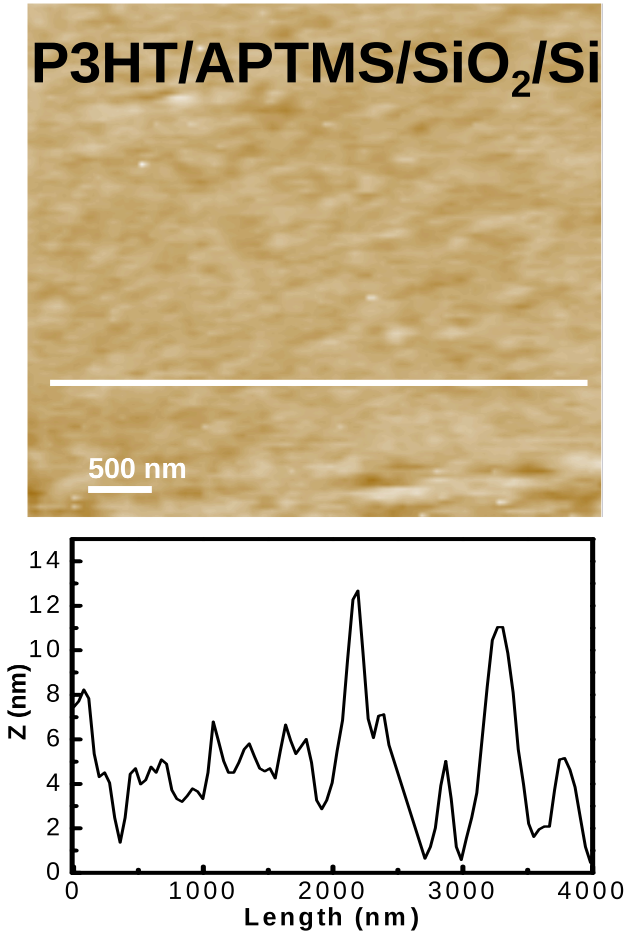

Electric properties of P3HT films degrade in ambient




But we need devices working in ambient conditions!!

# P3HT on APTMS Multilayers: *AFM Study*



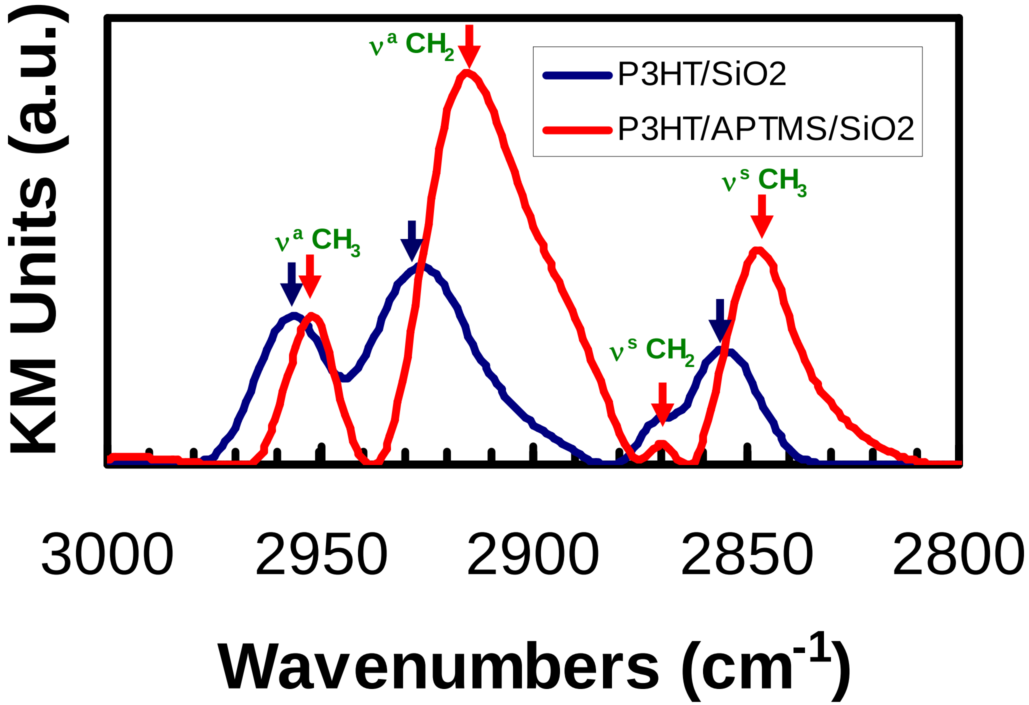




**Roughness:** Without APTMS ~ 40 Å

With APTMS ~ 7 Å

# P3HT on APTMS Multilayers: *FTIR Study*

***Aliphatic hexyl stretching region***



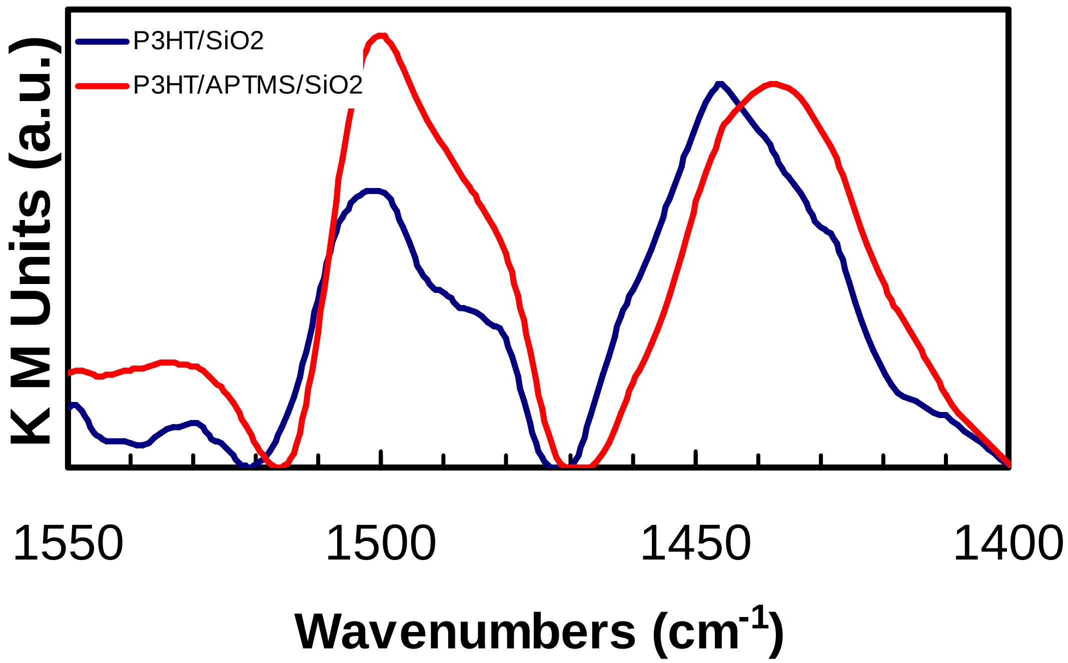

**Reduction in wave numbers of $\upsilon^a$ $CH_2$ 2916 $cm^{-1}$.**

**Reduction in peak width and an increase in intensity of 2916 $cm^{-1}$ peak.**

**<u>Transformation from disordered to crystalline films!</u>**

# P3HT on APTMS Multilayers: *FTIR Study*

***Fingerprint region***

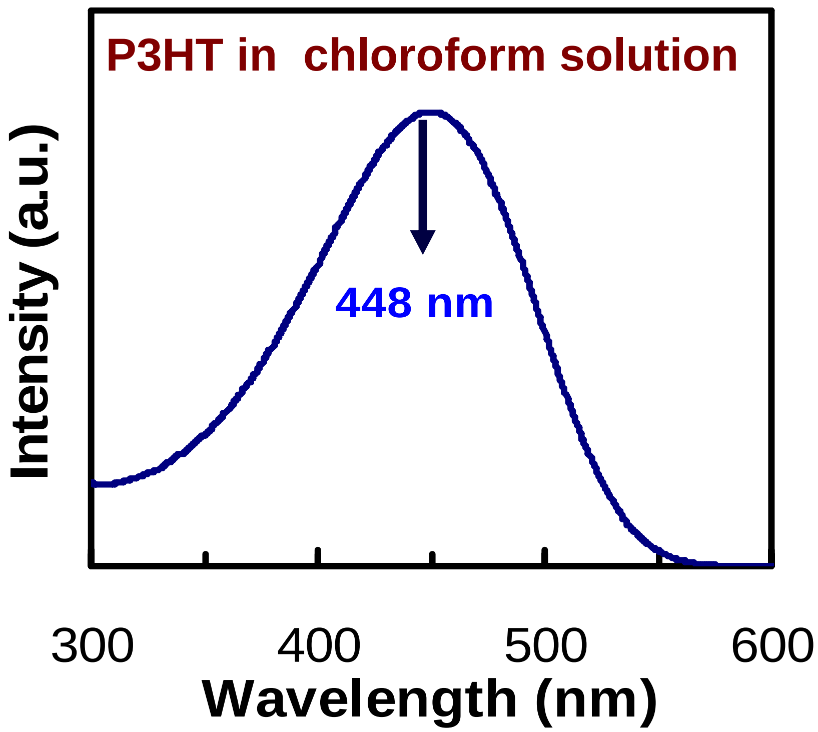



**Intensity peak ratio = $\nu^a/\nu^s$ ↑**

**corresponding to C=C vibrations of thiophene ring**

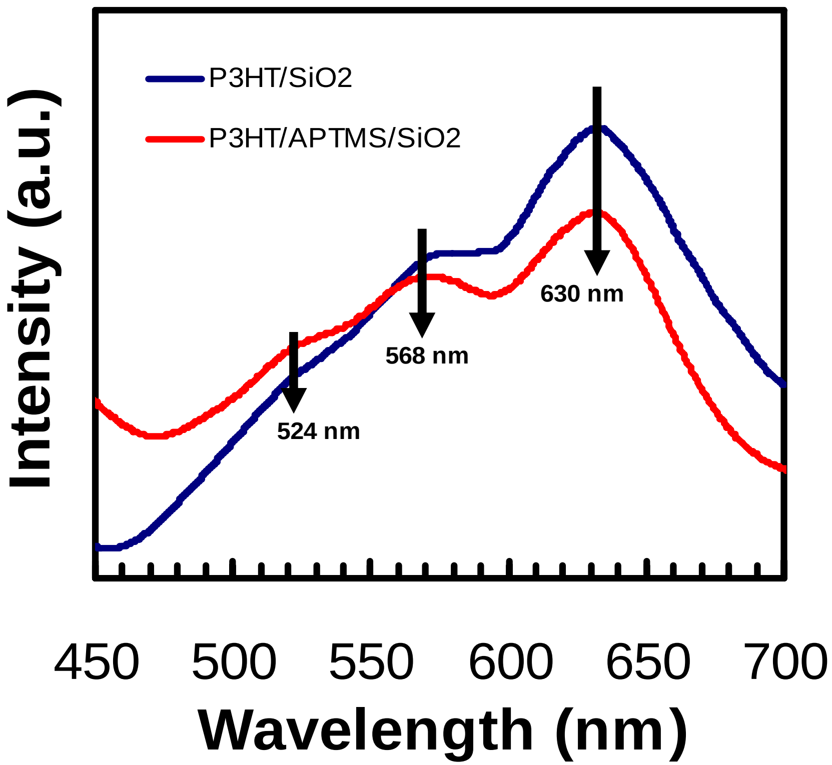
**Increase in conjugation length of polymer backbone after APTMS modification!**

# P3HT on APTMS Multilayers: *UV-Vis Study*




**Peak at 448 nm due to π–π* electronic transition**

# P3HT on APTMS Multilayers: *UV-Vis Study*

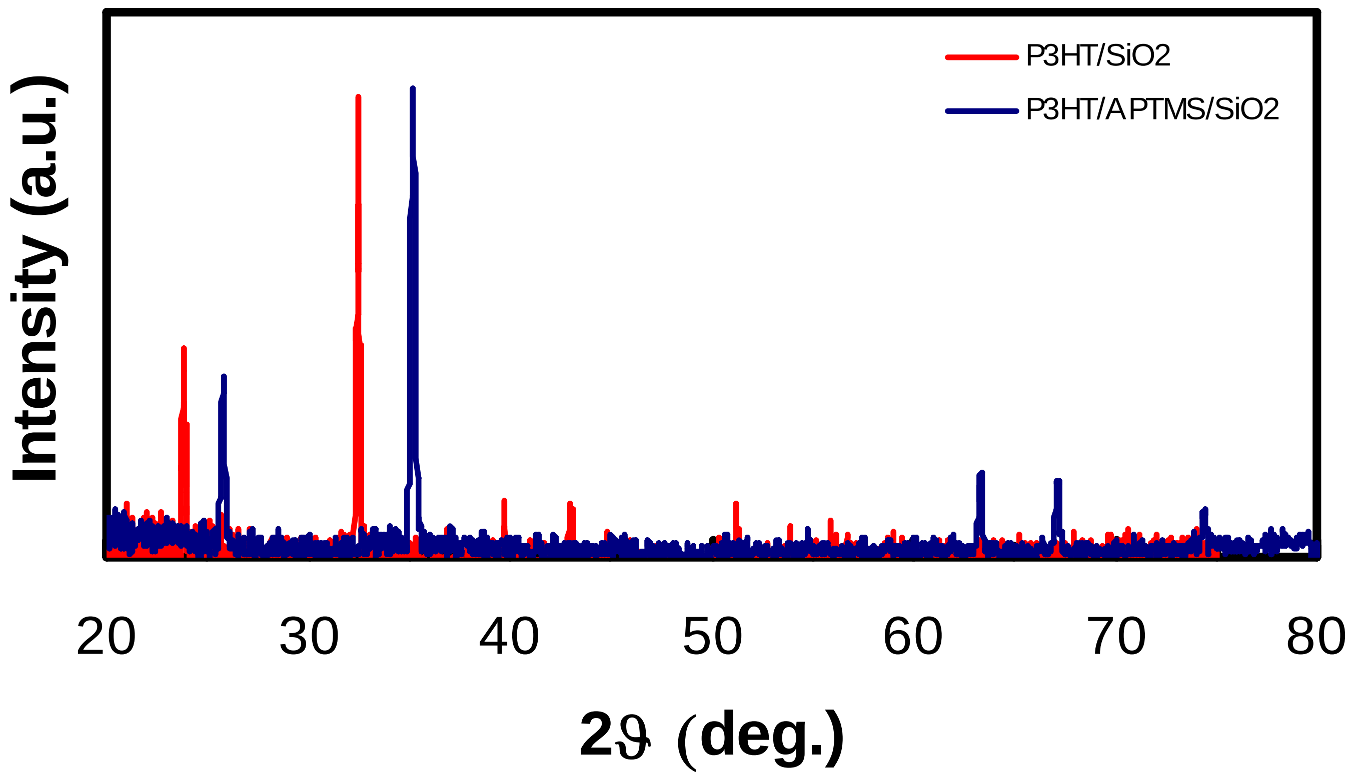



**Red shift in the optical spectra**

**Additional peaks observed in films**

**Increase in conjugation length & crystalline order after APTMS modification!**

# P3HT on APTMS Multilayers: *XRD Study*



# Why is the improvement?

**Crystallinity, molecular ordering and conjugation length**

- **$SiO_2$ surface energy~ 72 mN/m**
- **Chemical Modification of SAM with APTMS, (water contact angle ~ 42º), surface energy ~46-50 mN/m**
- **This is not sufficient as chemical modification with apolar ($-CH_3$) group terminated surface result in reduced surface energy (23-25 mN/m).**

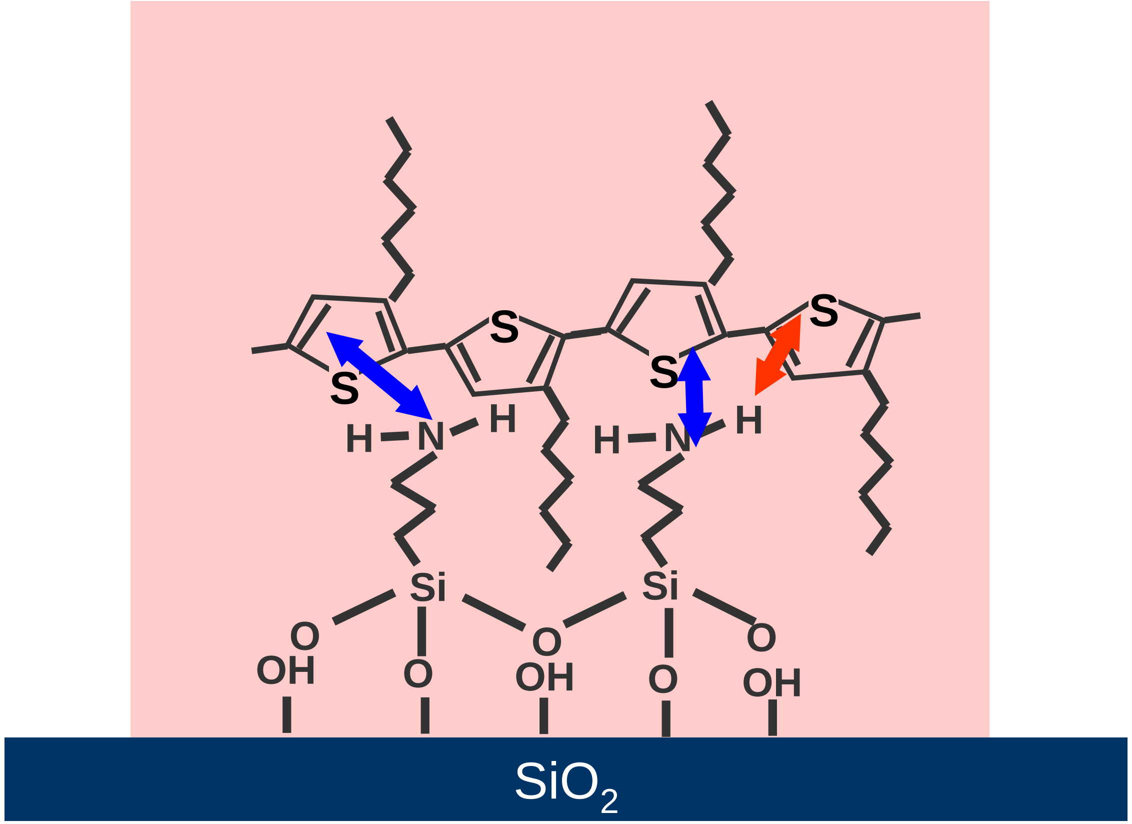
# What is the deciding factor?

Improvement may be the result from a combination of a number of effects, such as changes in surface energy, surface roughness, molecular orientation, and reduced defects

Role of dielectric surface treatment is still not entirely clear

More information is needed to get a clear picture

# Role of –$NH_2$ group




Presence of –$NH_2$ group at interface between P3HT and substrate results in

edge-on conformation

**Better charge transport**

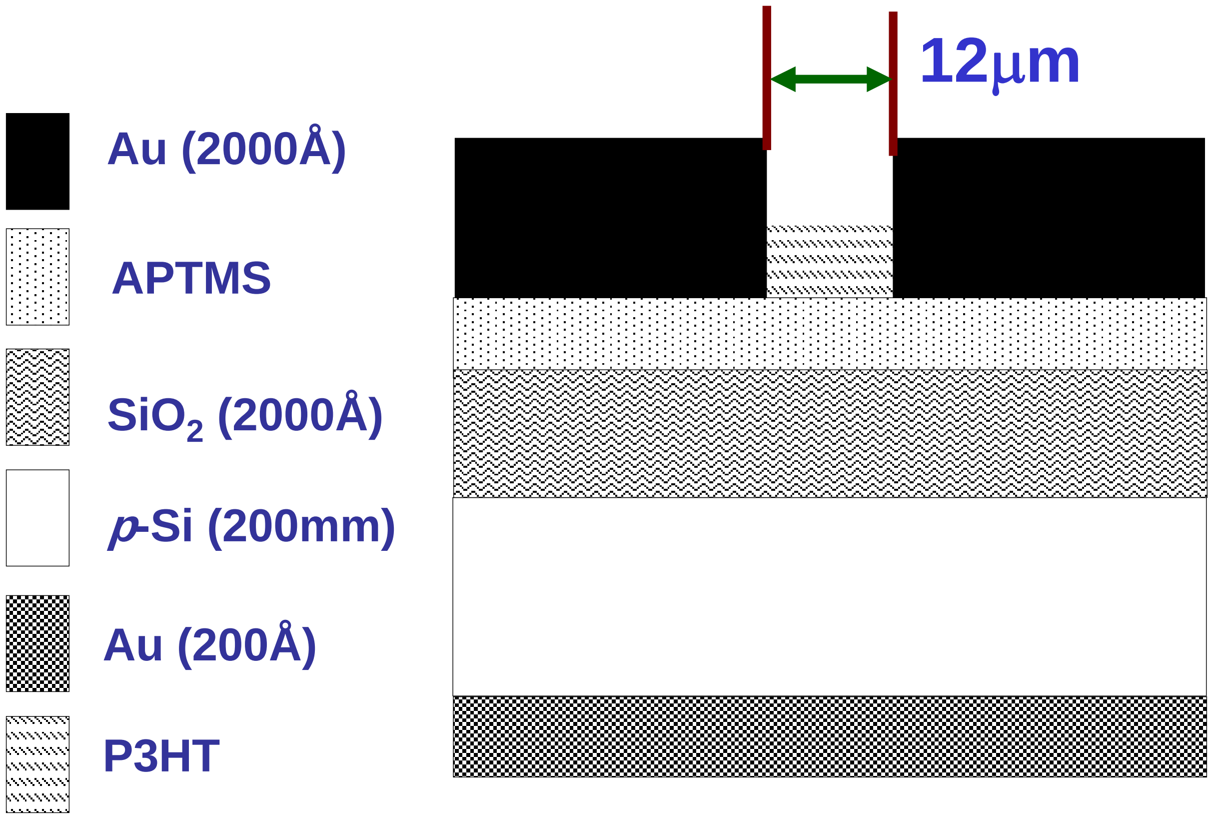
**Leads to higher mobility in P3HT films!**



Kim, D. H., *et al.*, *Langmuir* (2005) **21**, 3203

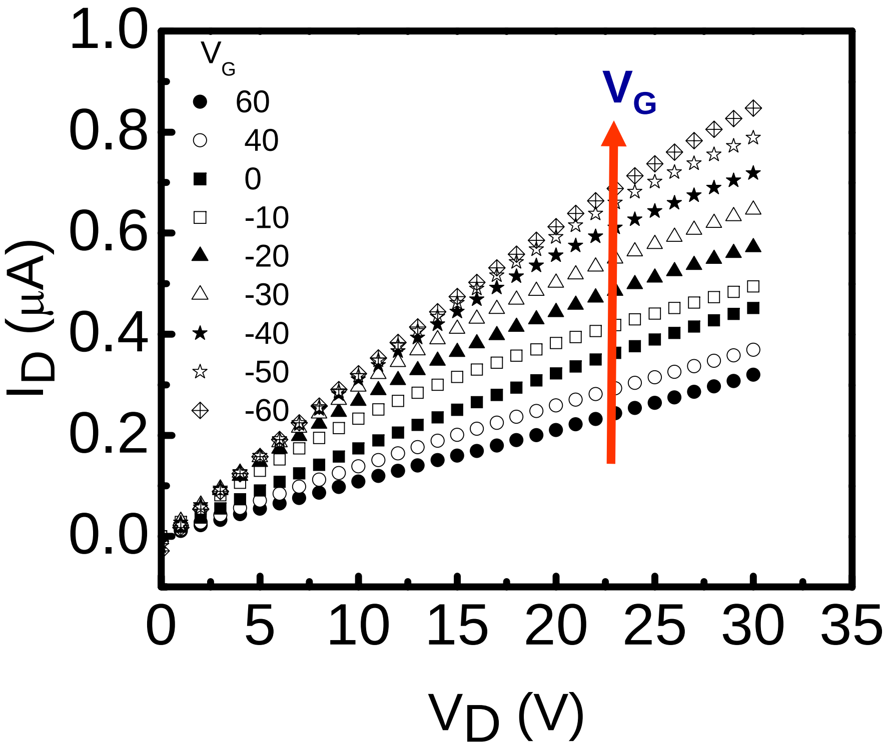
# Schematic Diagram of OFET

## Top contact Geometry

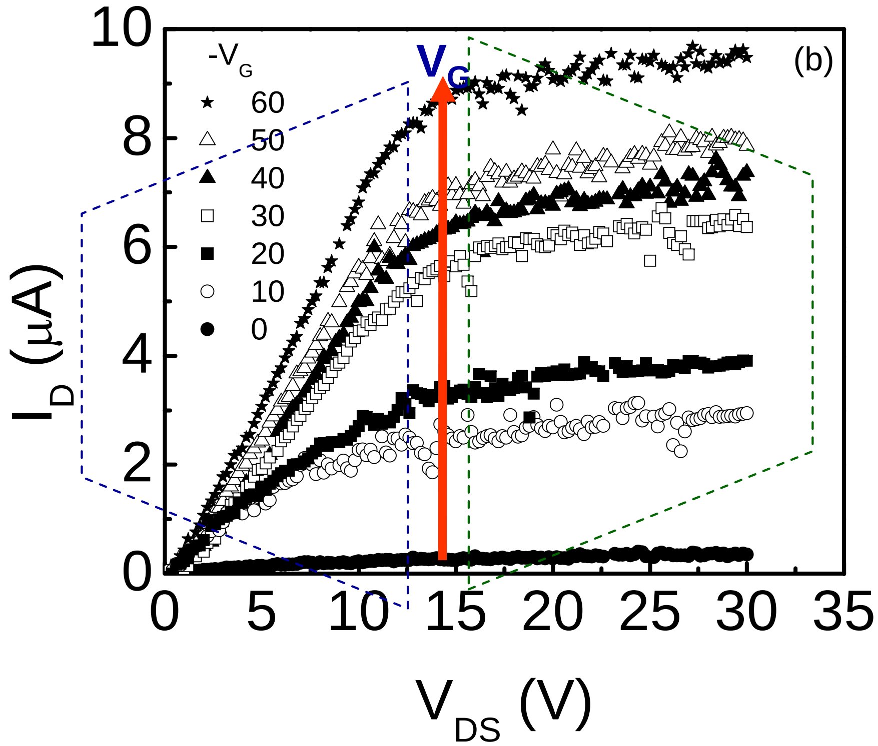


# OFET: *Output Characteristics*

**Unmodified dielectric**




**APTMS-Modified dielectric**

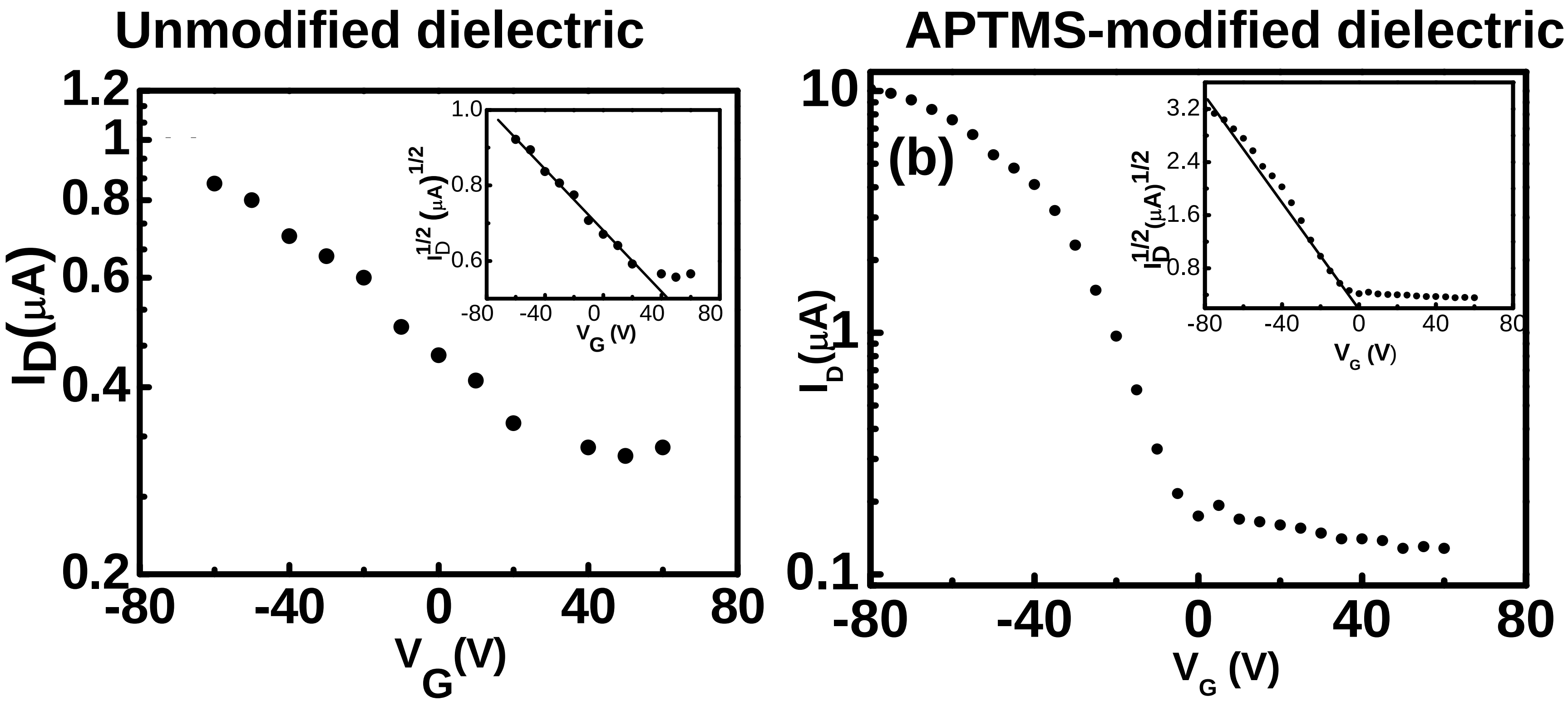



**Good ohmic contact between P3HT layer and gold.**

**$I_D$ for APTMS-modified OFET at $V_G$=0 is much lower.**

**Clear saturation region for OFET with an modified dielectric surface**

# OFET: *Transfer Characteristics*




**On/Off Ratio enhanced by two orders of magnitude**

**Low density of charge traps at the interface and low bulk carrier density.**



Vibha et al, Thin solid films (communicated)

# Calculated Parameters

| OFET using dielectric | Mobility | $V_t$ (V) | Trap density ($eV^{-1}$ $cm^{-2}$) x $10^{15}$ | S (V/ decade) |
|---|---|---|---|---|
| APTMS +$SiO_2$ | $3.2x10^{-2}$ | -1.2 V | 0.21 | 31 |
| $SiO_2$ | $0.56x10^{-4}$ | 38.5 | 1.5 | 112 |

Low threshold voltage and trap density suggests a good interface between P3HT & APTMS.

Increased mobility for APTMS-modified FET is due to better intergranular connectivity and uniformity as well as better crystallinity and enhanced conjugation length.

# Conclusions

I

***Very uniform and smooth P3HT films can be prepared on APTMS modified Si/$SiO_2$ substrates***

II

**Spectroscopic studies show high degree of molecular ordering and crystallinity in P3HT films deposited on APTMS-modified substrates**

III

***APTMS-modified gate dielectric, shows an enhanced mobility and increase in on/off ratio by two orders of magnitude***

**APTMS-modified substrates can significantly improve structural properties of P3HT yielding better mobility and device characteristics**

# Acknowledgements

Dr. Anil K. Chauhan

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Dr. J V Yakhmi

# Thank You