# Chemical vapor deposition of graphene

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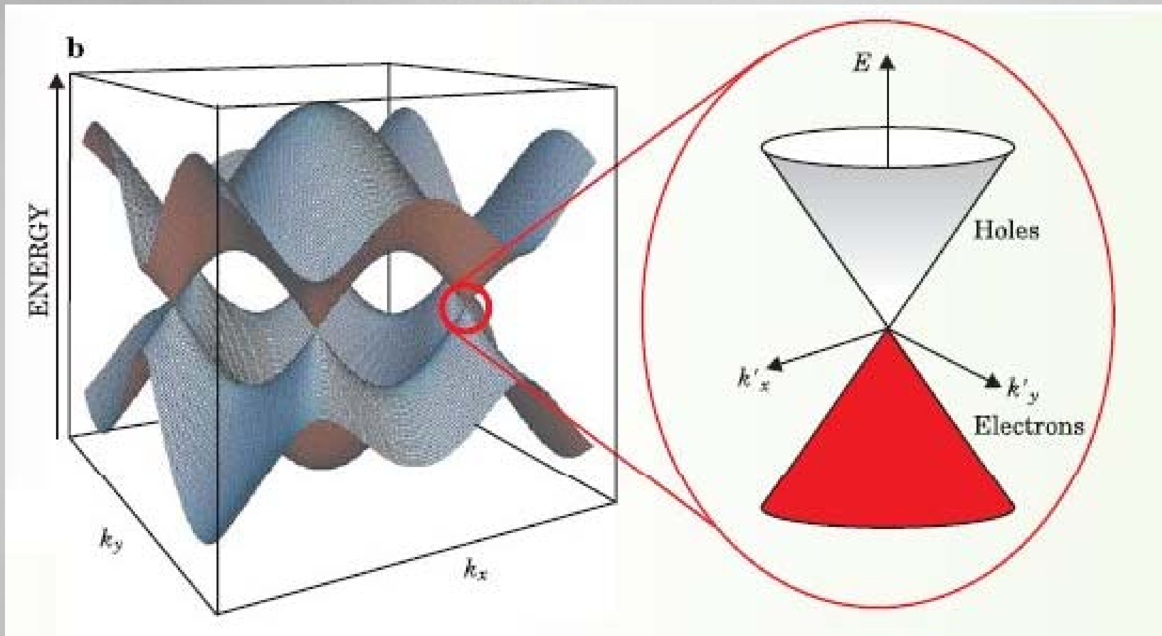
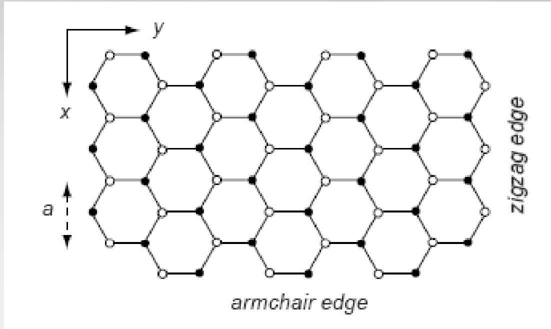
# Outline

- Introduction
- Catalytic CVD: graphene on Cu
- Noncatalytic CVD: graphene on $Si_3N_4$ and $HfO_2$
- Conclusions

# Introduction

# Graphene – a monolayer of $sp^2$ hybridized carbon atoms



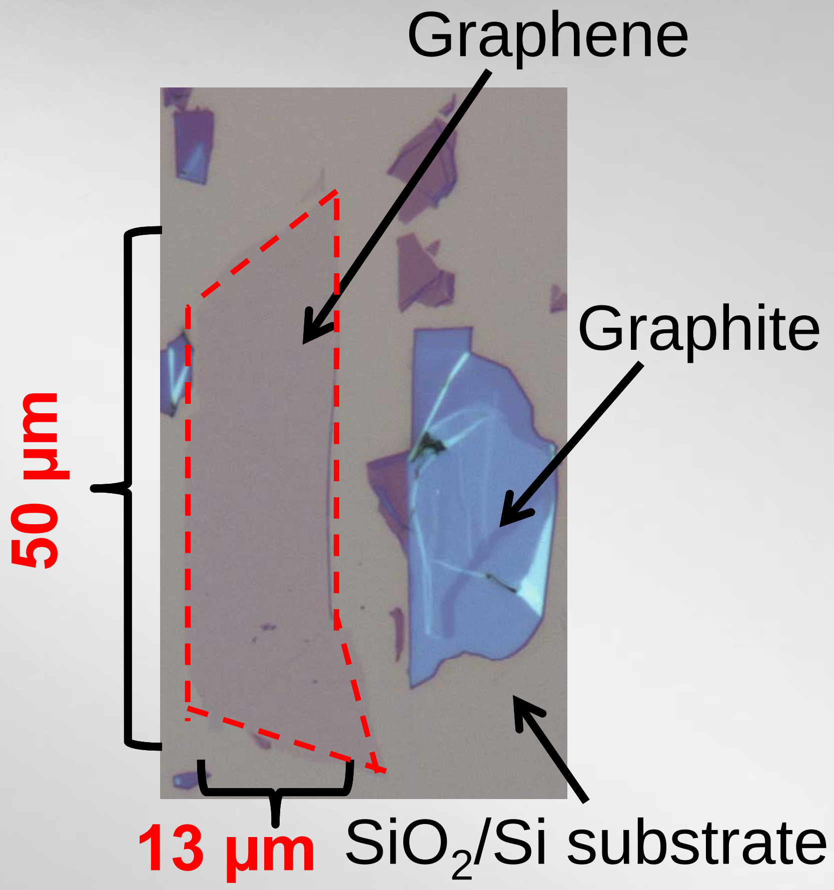




- Isolated in 2004
- THz transistors
- Transparent electrodes

*M. Wilson, Phys. Today (jan. 2006, vol. 59, p. 21-23).*

# Fabricating graphene

- **Mechanical exfoliation**
- **Reduction of graphene oxide and other wet chemical methods**
- **Desorption of Si on SiC**
- **Chemical vapor deposition on metals (Ni, Cu)**



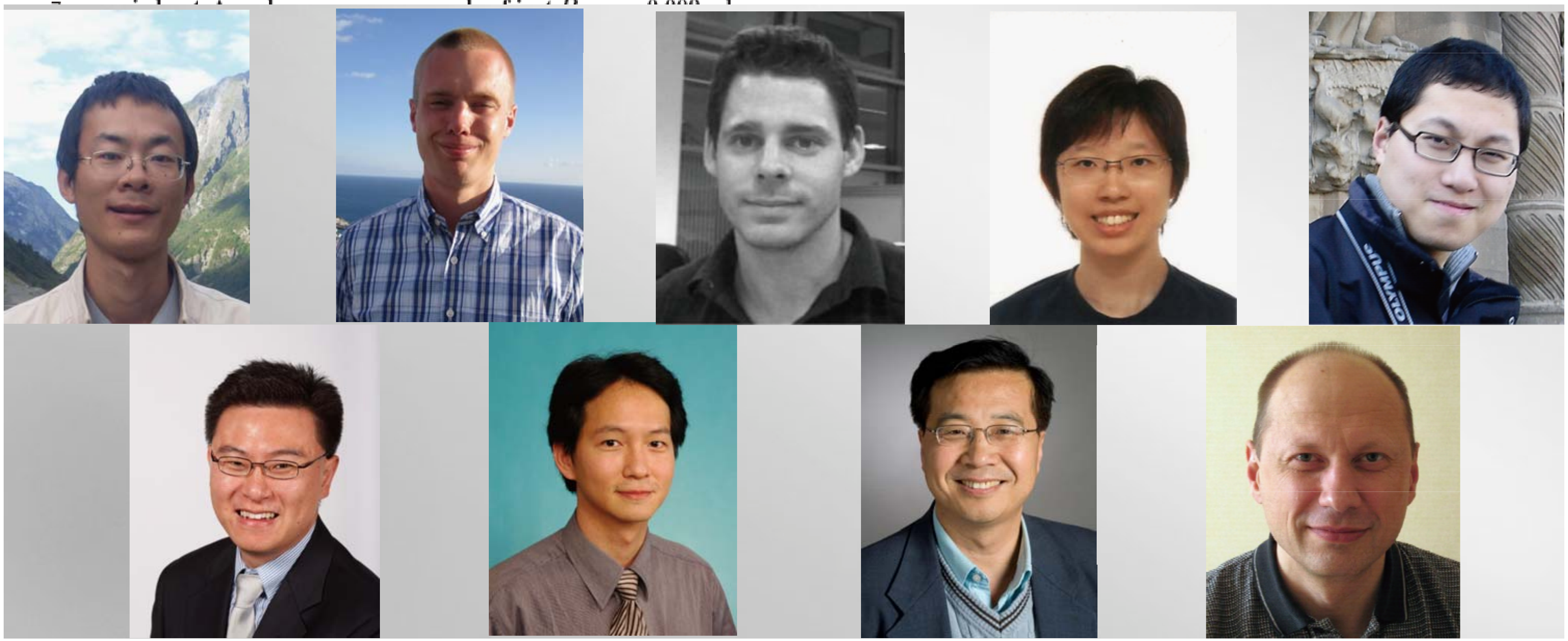
# Catalytic CVD on Cu

# Low Partial Pressure Chemical Vapor Deposition of Graphene on Copper

Jie Sun, Niclas Lindvall, Matthew T. Cole, Koh T. T. Angel, Teng Wang, *Student Member, IEEE*, Kenneth B. K. Teo, *Member, IEEE*, Daniel H. C. Chua, Johan Liu, *Fellow, IEEE*, and August Yurgens

***Abstract*—A systematic study of the Cu-catalyzed chemical vapor deposition of graphene under extremely low partial pressure is**

makes it a potential candidate material for channels of ultrafast transistors. Graphene is believed to play an important role in



# Mechanism of catalytic graphene CVD

- Graphite is made at >3000 $^{o}C$
- Inconvenient and costly
- Transition metal lower T to ~1000 $^{o}C$
- Solid carbon source [*Small* 5(2009)2291 & *Nature* 468(2010)549]
- Carbon segregation (Ni)
- Surface chemistry (Cu)

# Why Copper?

- **Science 324 (2009) 1312**
- **Mobility 4050 $cm^2/Vs$**
- **Small C solubility**
- **Dominantly monolayer**

13. H. Reiss, *J. Chem. Phys.* **19**, 482 (1951).
14. T. Sugimoto, *Adv. Colloid Interface Sci.* **28**, 65 (1987).
15. D. V. Leff, P. C. Ohara, J. R. Heath, W. M. Gelbart, *J. Phys. Chem. B* **99**, 7036 (1995).
25. K. L. Liu *et al.*, *Lab Chip* **8**, 1915 (2008).
26. N. de Jonge, D. B. Peckys, G. J. Kremers, D. W. Piston, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 2159 (2009).
27. Materials and methods are available as supporting material on *Science* Online.

Movies S1 and S2
References

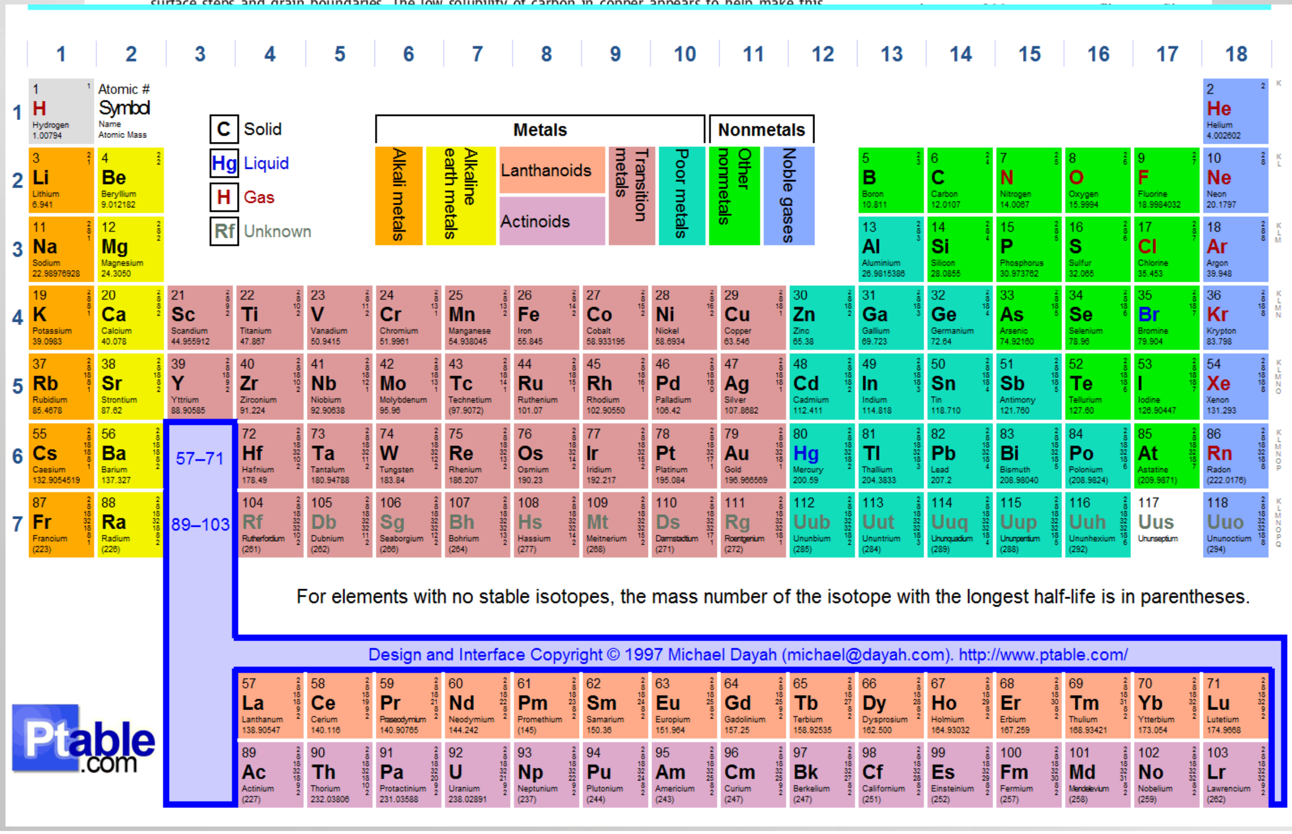
10 February 2009; accepted 8 April 2009
10.1126/science.1172104

## Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils

Xuesong Li,[1] Weiwei Cai,[1] Jinho An,[1] Seyoung Kim,[2] Junghyo Nah,[2] Dongxing Yang,[1] Richard Piner,[1] Aruna Velamakanni,[1] Inhwa Jung,[1] Emanuel Tutuc,[2] Sanjay K. Banerjee,[2] Luigi Colombo,[3]* Rodney S. Ruoff[1]*

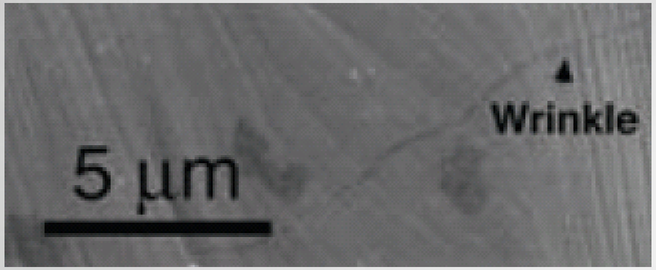
Graphene has been attracting great interest because of its distinctive band structure and physical properties. Today, graphene is limited to small sizes because it is produced mostly by exfoliating graphite. We grew large-area graphene films of the order of centimeters on copper substrates by chemical vapor deposition using methane. The films are predominantly single-layer graphene, with a small percentage (less than 5%) of the area having few layers, and are continuous across copper surface steps and grain boundaries. The low solubility of carbon in copper appears to help make this

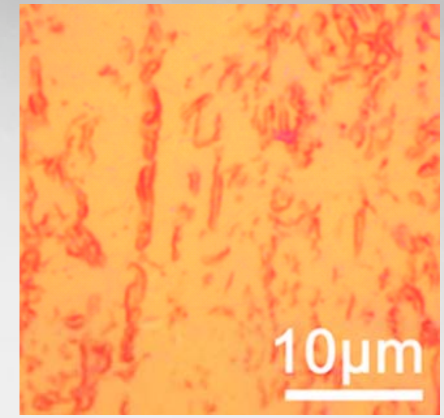
and transfer graphene grown on metal substrates (*5–7*). Although graphene has been grown on a number of metals, we still have the challenge of growing large-area graphene. For example, graphene grown on Ni seems to be limited by its small grain size, presence of multilayers at the grain boundaries, and the high solubility of carbon (*6*, *7*). We have developed a graphene chemical vapor deposition (CVD) growth process on copper foils (25 μm thick in our experiment). The films grow directly on the surface by a surface-catalyzed process, and the film is predominantly graphene with <5% of the area having two- and three-layer graphene flakes. Under our processing conditions, the two- and three-layer flakes do not grow larger with time. One of the major benefits of our process is that it can be used to



# Surface kinetics factor

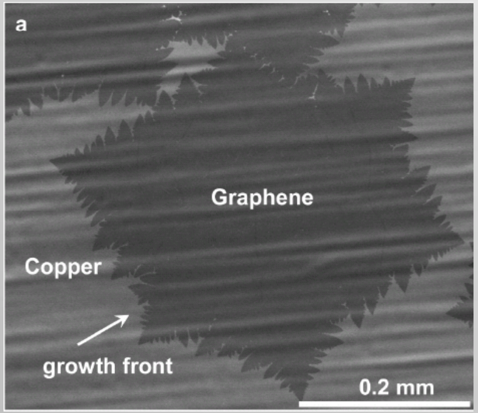
Science
324(2009)1312

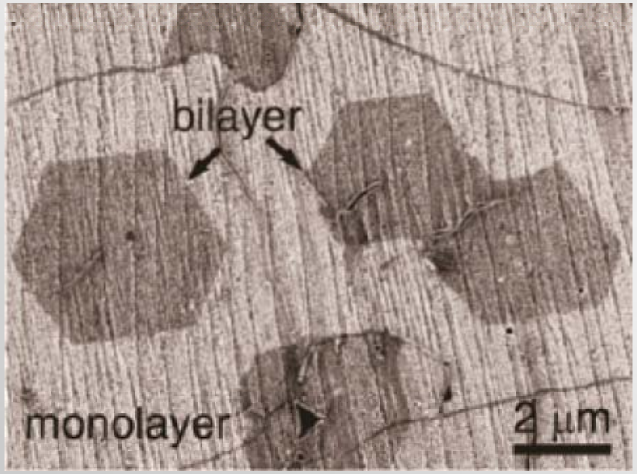



APL
97(2010)183109

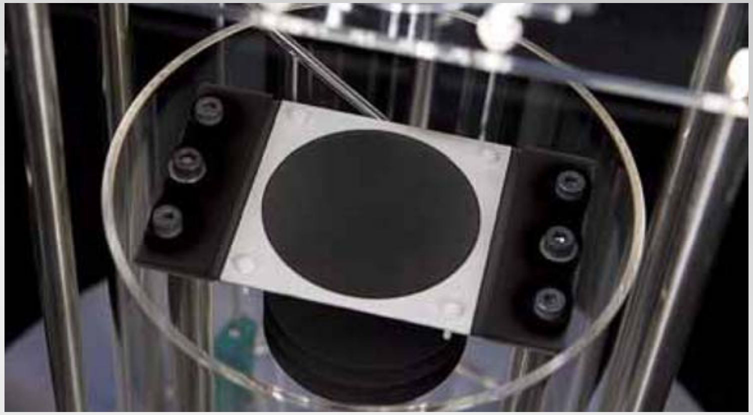
JACS
Xuesong Li et al
in press




Nano Lett.
Kai Yan et al
in press

# CVD graphene on Cu



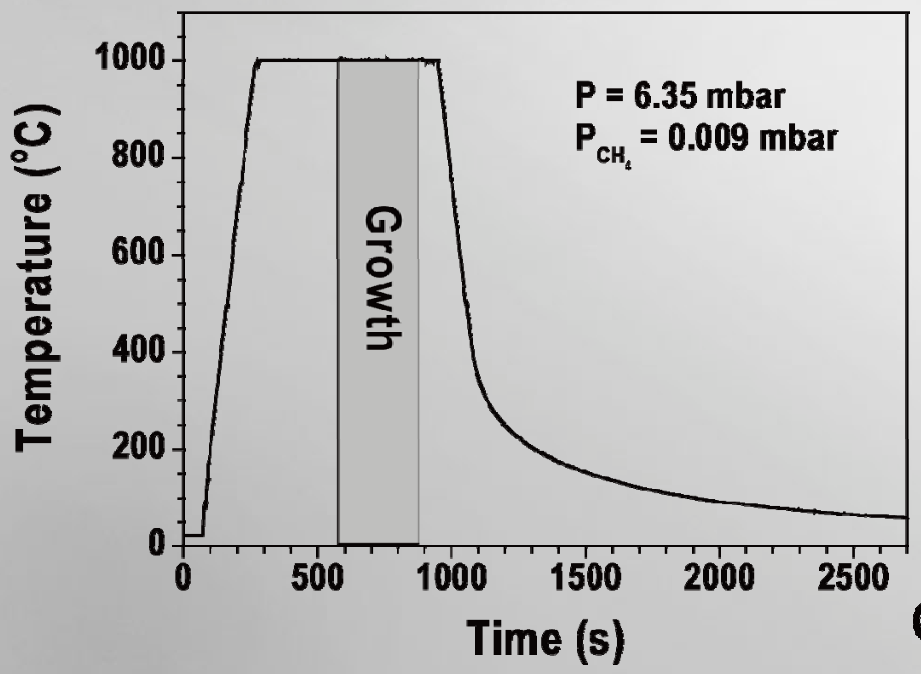
- Black Magic, AIXTRON
- Cold wall, low pressure CVD with graphite heater

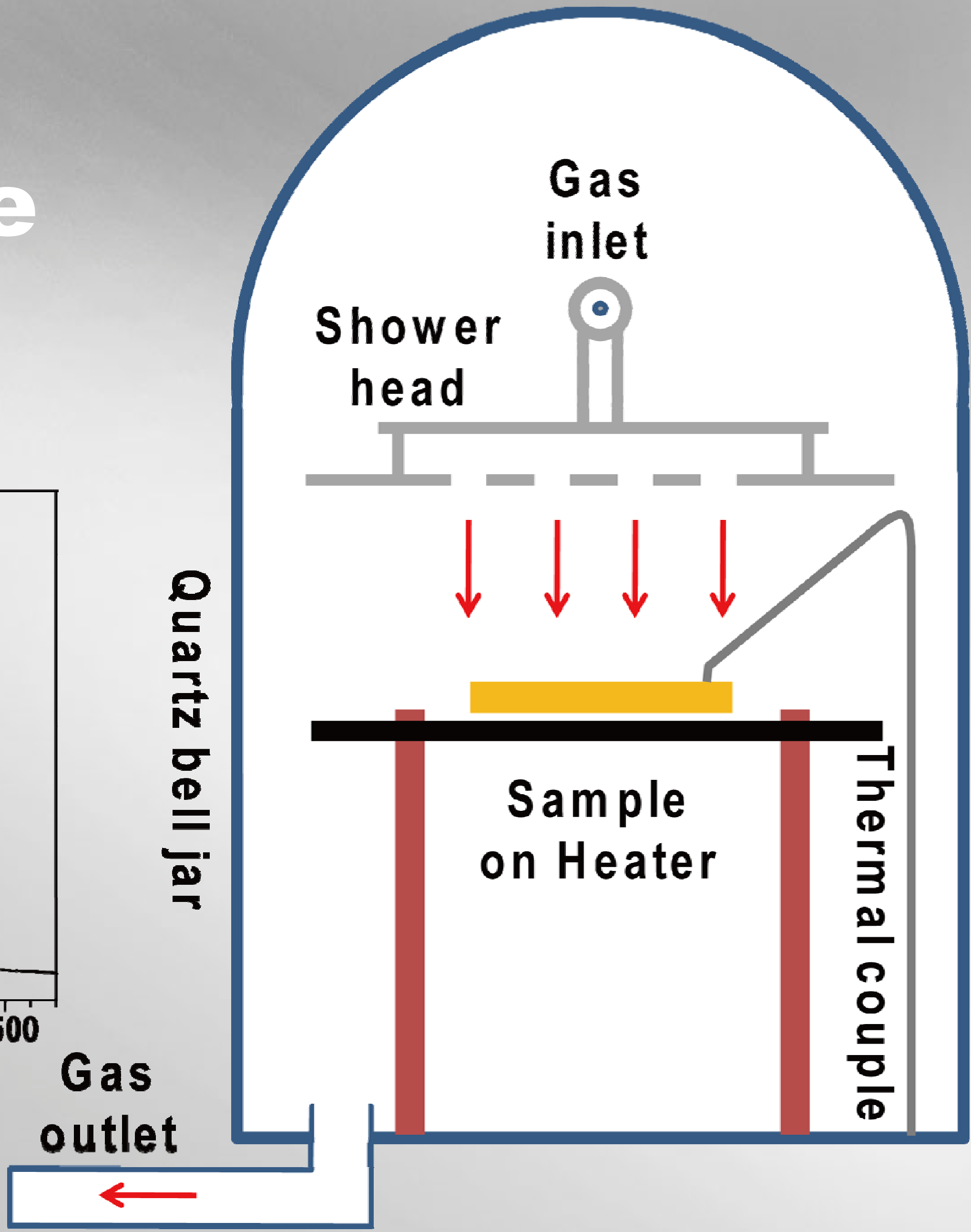
# Quality control: CVD graphene by $CH_4$

- Acetic acid, acetone, IPA
- High Temperature
- Low partial P
- Cold-wall

- Hi decompose T
- One C per molecule
- Long diffusion length
- High purity $CH_4$ 99.9995%
- Ar instead of $N_2$

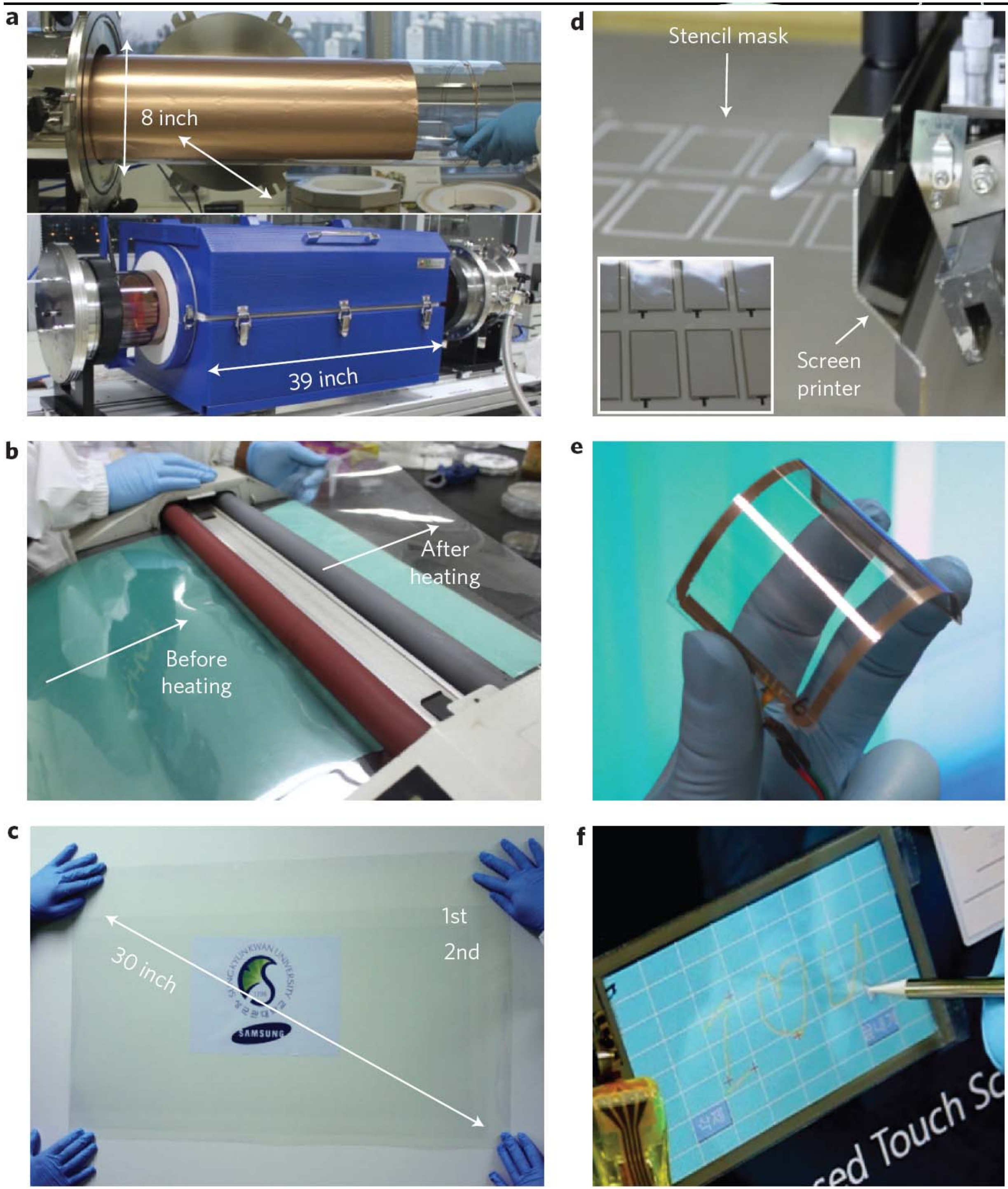
# Extremely low partial pressure of methane



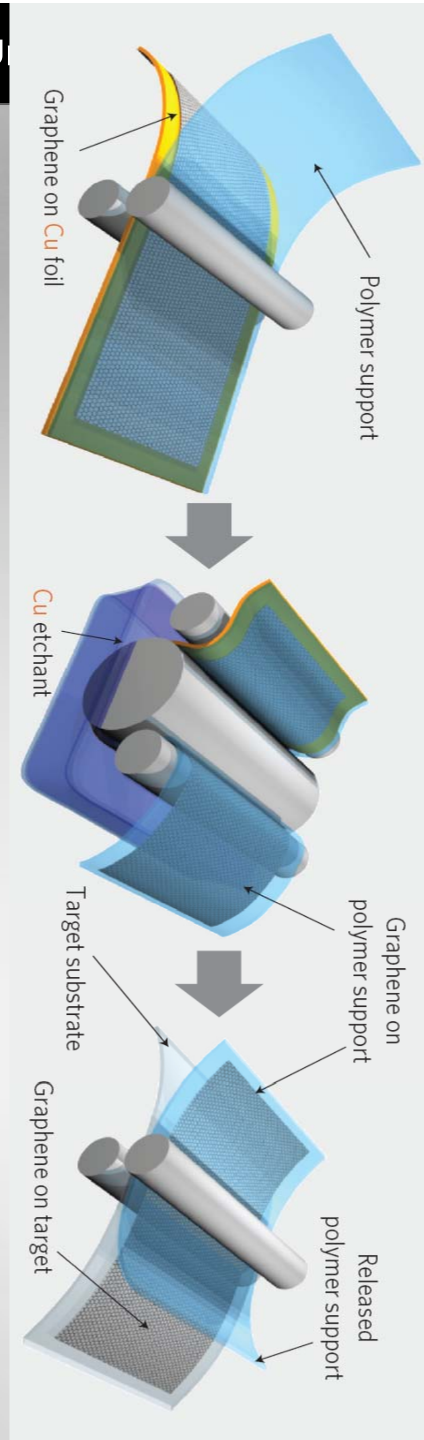



Chalmers U

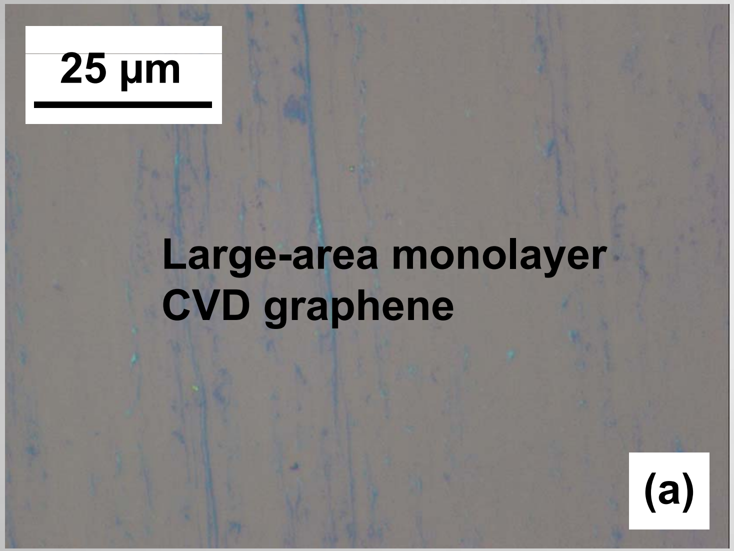
# 30-in. graphene by Samsung
# Nature Nanotechnol. 5 2010 574

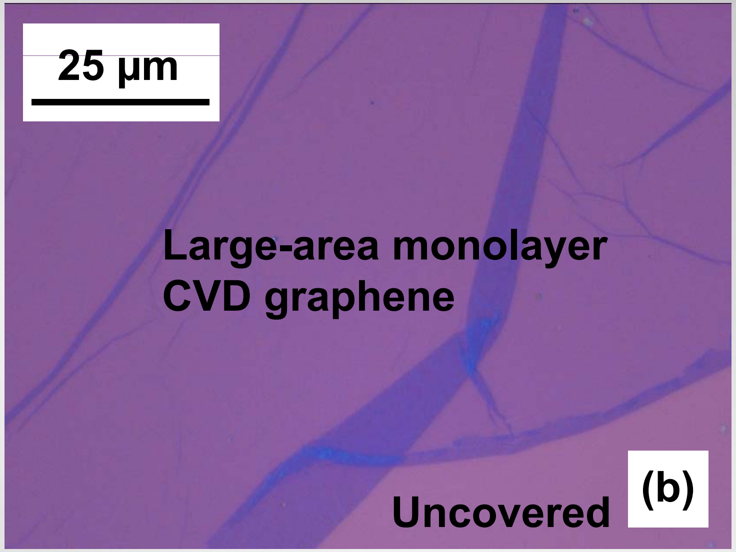



**Industrial graphene transfer**



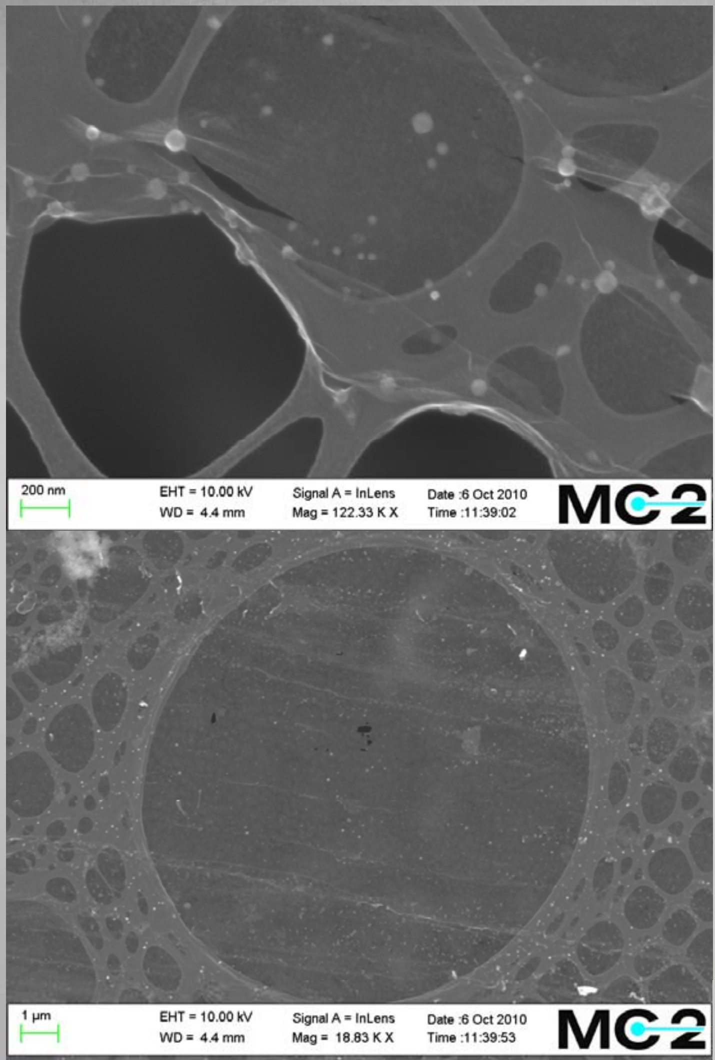
# Optical images of transferred graphene

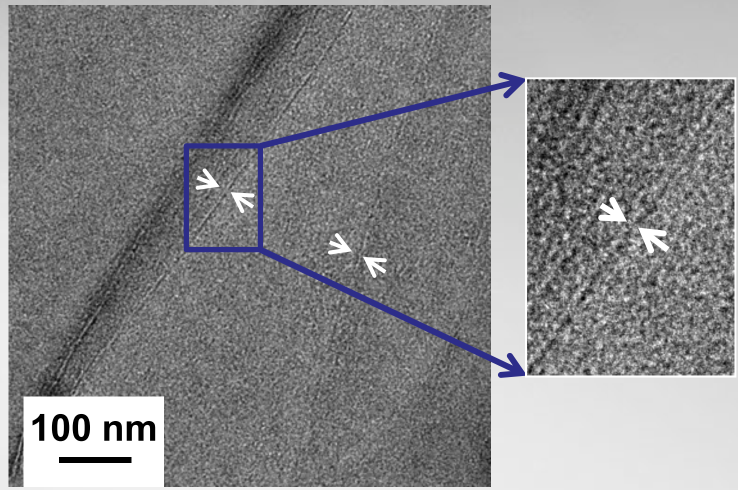



- Cu foil grown
- Cu film grown

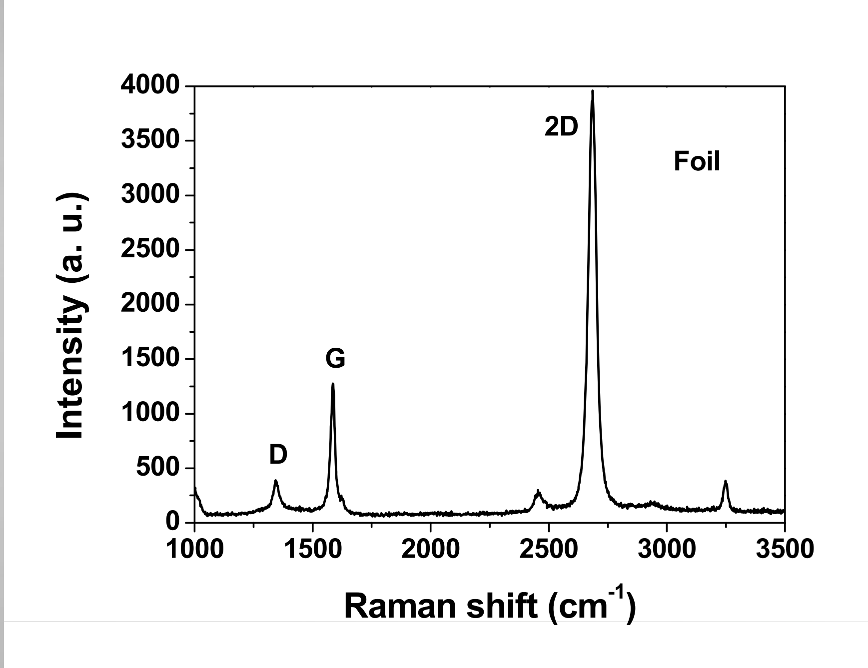
# Transfer to TEM grids

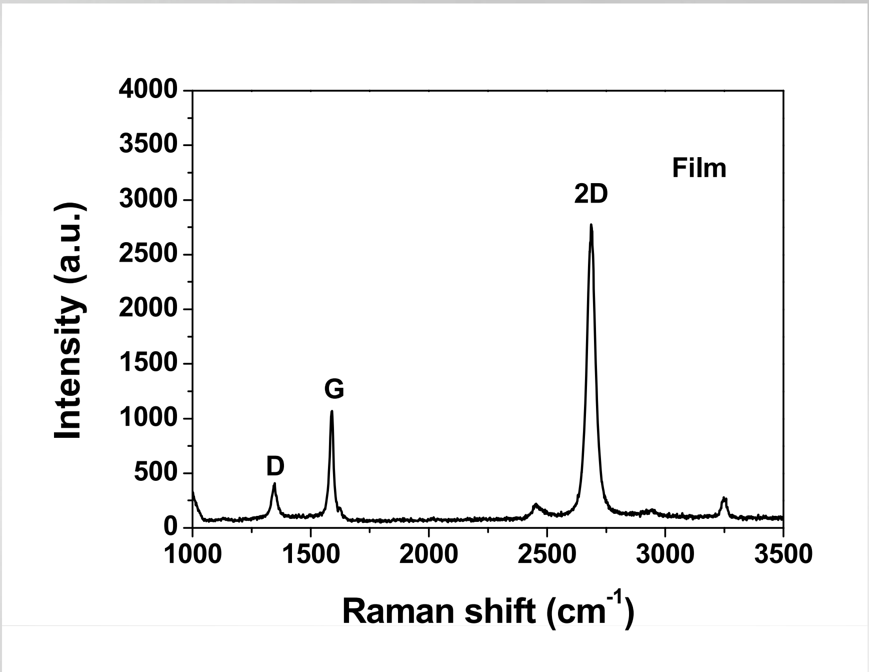



- **Graphene can cover holes with a diameter larger than 10 µm**

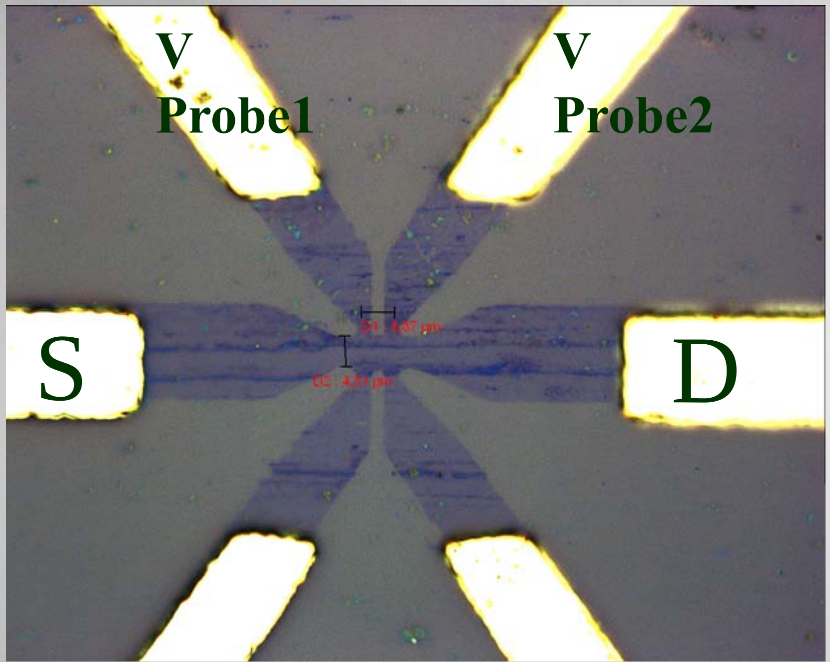
# Raman spectrascopy

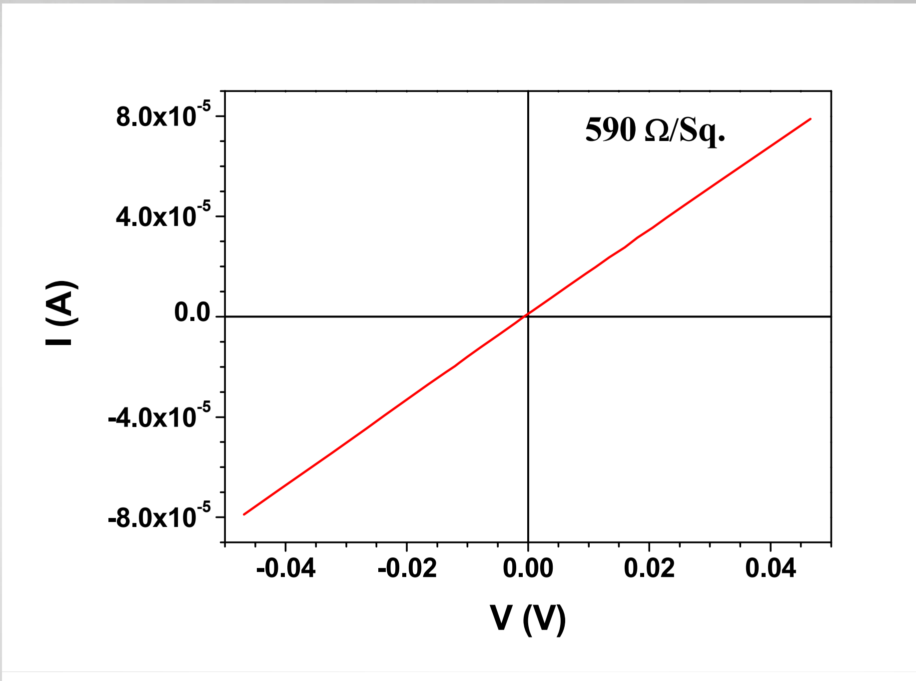



- Cu foil
- Cu film

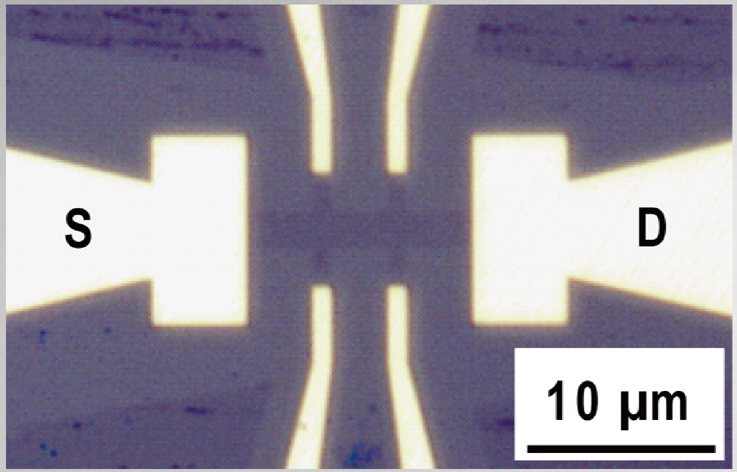
# Electrical measurements



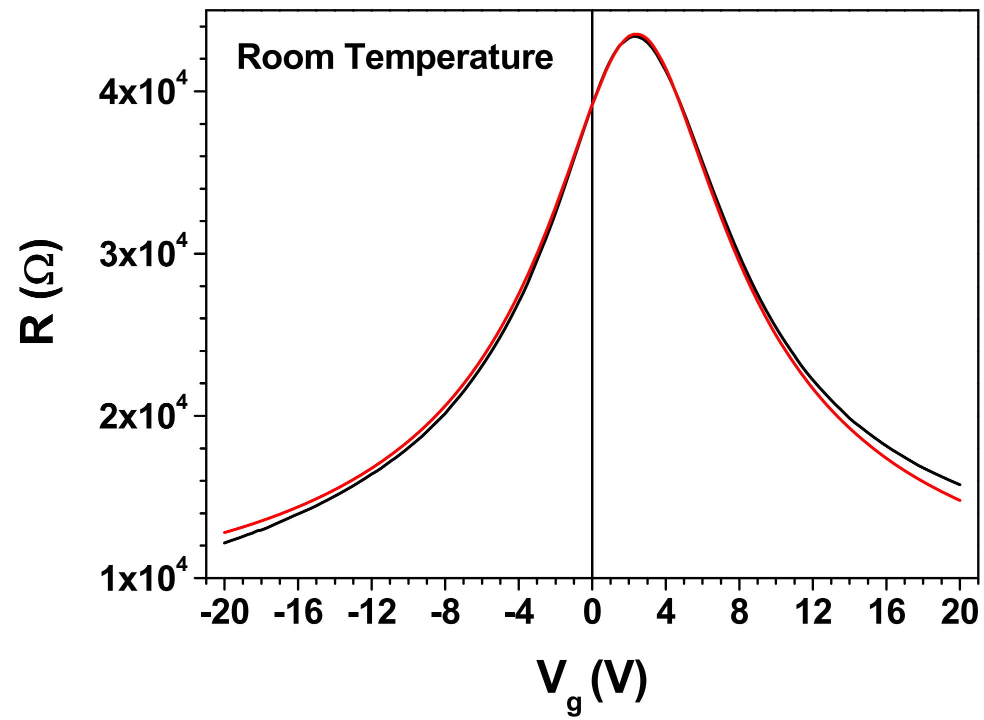




- **Sheet resistance below 1 kΩ per square (Room temperature)**

# Electrical measurements




- Kim et al.
  Appl. Phys. Lett. 94 (2009) 062107
- Electron & hole mobility ~2700 cm²/Vs



# Catalytic CVD summary

- CVD on Cu is a promising technique to make large area polycrystalline graphene,
- The graphene can be transferred to many substrates and the quality is good
- Optimizing the growth and transfer for more reproducible decent graphene

# Noncatalytic CVD on $Si_3N_4$ and $HfO_2$

APPLIED PHYSICS LETTERS **98**, 252107 (2011)

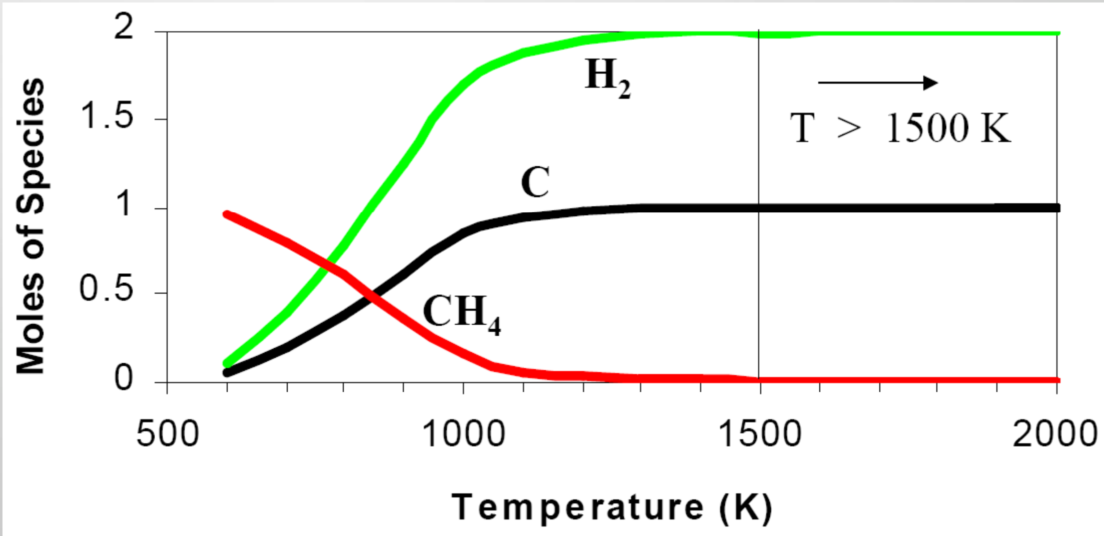
# Large-area uniform graphene-like thin films grown by chemical vapor deposition directly on silicon nitride

Jie Sun (孙捷),[1,a)] Niclas Lindvall,[1] Matthew T. Cole,[2] Kenneth B. K. Teo (张谋瑾),[3] and August Yurgens[1]
[1]*Department of Microtechnology and Nanoscience, Quantum Device Physics Laboratory, Chalmers University of Technology, S-41296 Gothenburg, Sweden*
[2]*Department of Engineering, Electrical Engineering Division, University of Cambridge, 9 JJ Thomson Avenue, CB3 0FA Cambridge, United Kingdom*
[3]*AIXTRON Nanoinstruments Ltd., Swavesey, CB24 4FQ Cambridge, United Kingdom*

(Received 1 April 2011; accepted 2 June 2011; published online 23 June 2011)

Large-area uniform carbon films with graphene-like properties are synthesized by chemical vapor

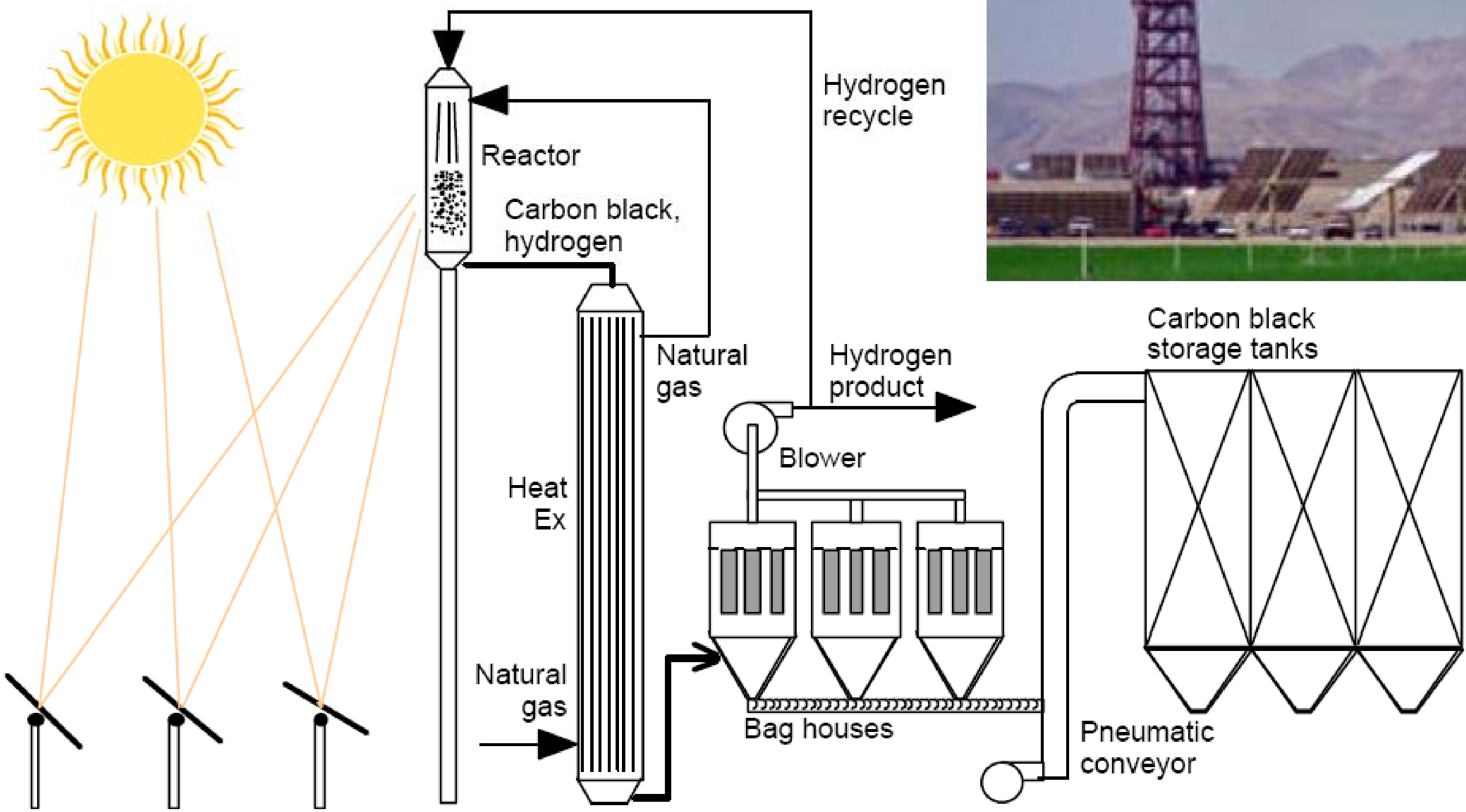
- **Transfer-free technique**
- **Catalyst free**
- **Display, solar cell**
- **Molecular electronics**




Proceedings of the 2001 US DOE hydrogen program review
NREL/CP-570-305350

# $CH_4=C+2H_2$ ($\Delta H^0=75.6$ kJ/mol)

a.




b.

**Proceedings of the 2001 US DOE hydrogen program review**
**NREL/CP-570-305350**

# What is carbon black?

## An X-Ray Study of Carbon Black

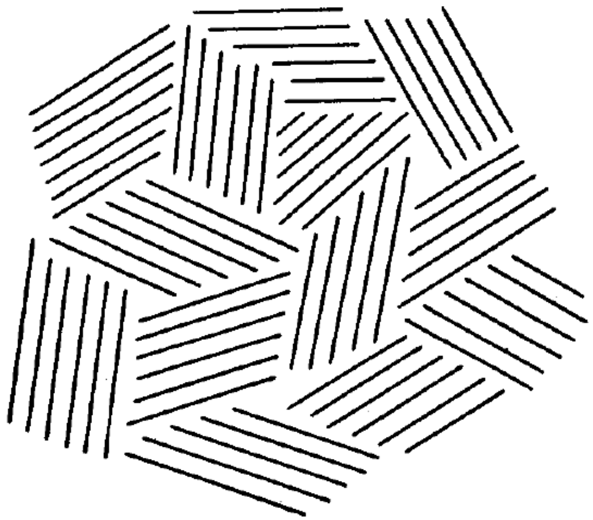
J. Biscoe and B. E. Warren
*George Eastman Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received February 16, 1942)

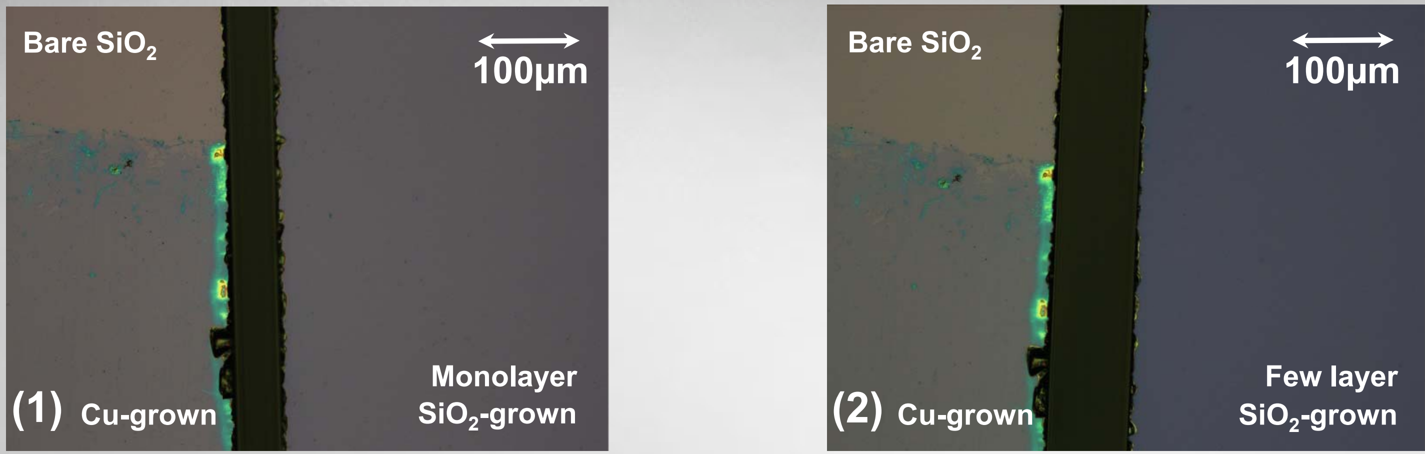
X-ray studies have been made of a number of carbon blacks, prepared under different conditions, and subject to various heat treatments. The patterns were made in evacuated cameras, using Cu *Kα* radiation monochromated by reflection from rocksalt. The patterns consist of crystalline reflections (00*l*), and two-dimensional lattice reflections (*hk*). The structure is one of true graphite layers arranged roughly parallel and equidistant, but otherwise completely random. The dimensions within a layer are the same as in graphite; the layer separation is somewhat larger than in graphite. The effect of heat treatment is to increase the size of the parallel layer groups. At graphitization the material changes discontinuously to the crystalline

- **Macroscopically amorphous**
- **Nano scale graphitic crystallites**
- **Random and porous**
- **Carbon black is black!**

**J. Appl. Phys. 13 (1942) 364**

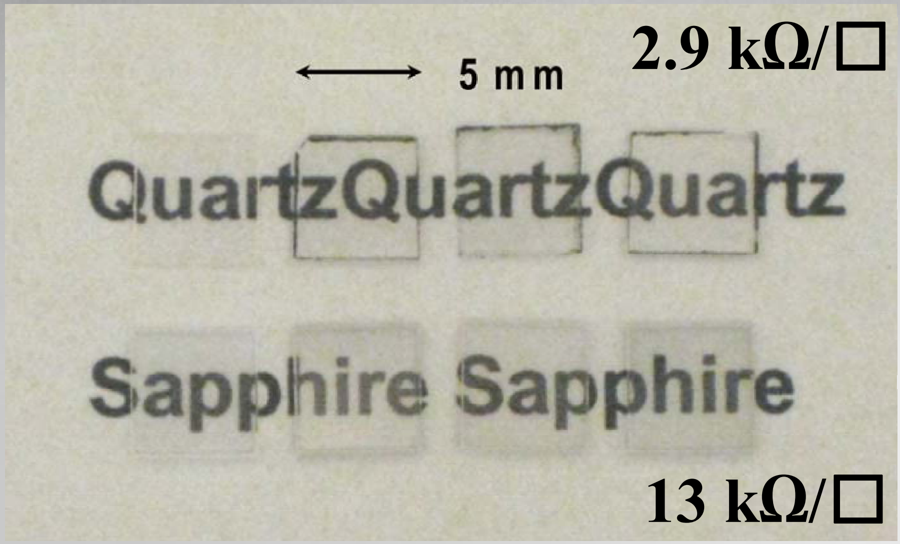


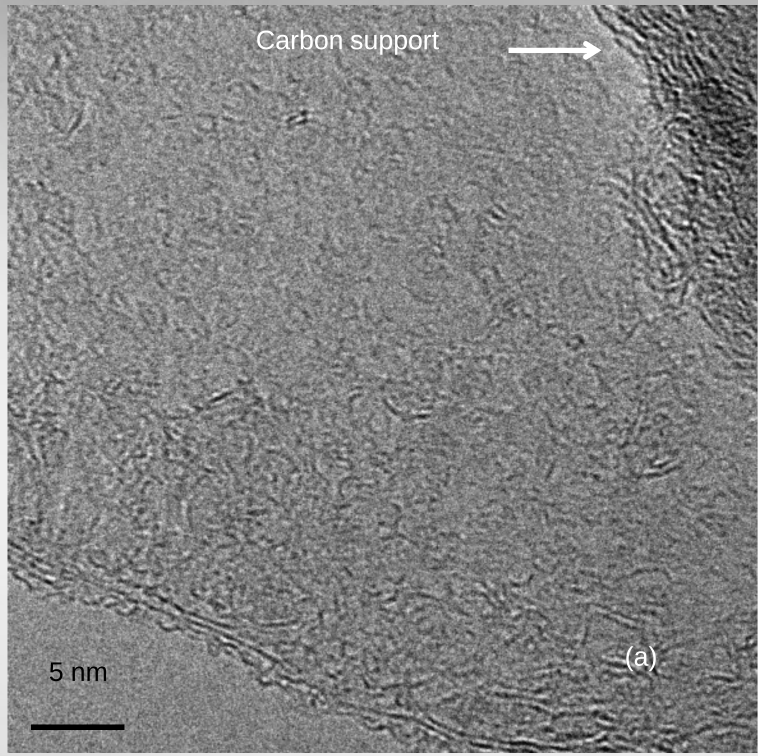
# Hot flat surfaces as templates

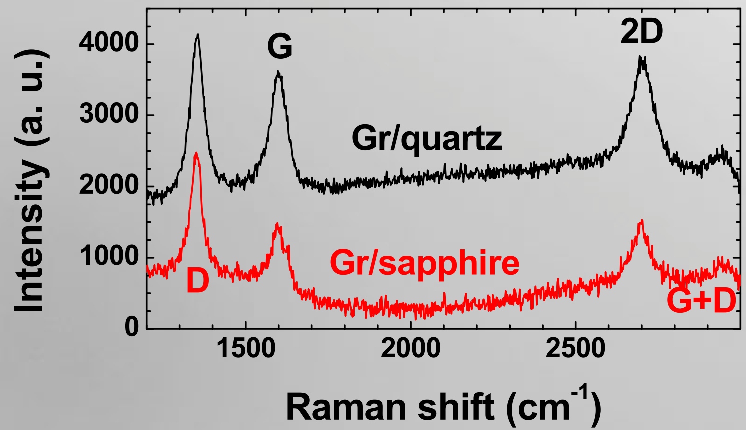


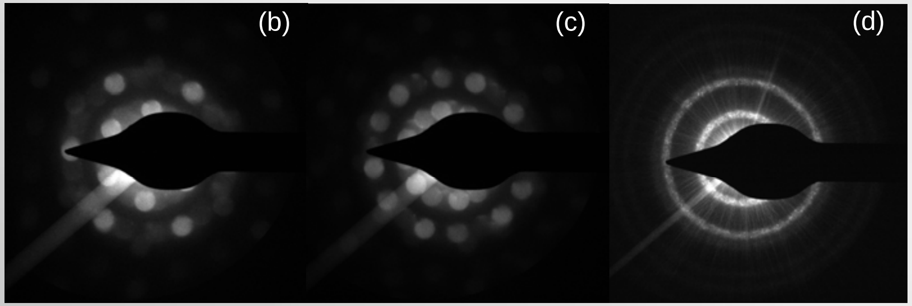

- Controllable thickness
- Large area
- Macroscopically uniform
- Similar transparency and conductivity as standard graphene

# Graphene on quartz and sapphire



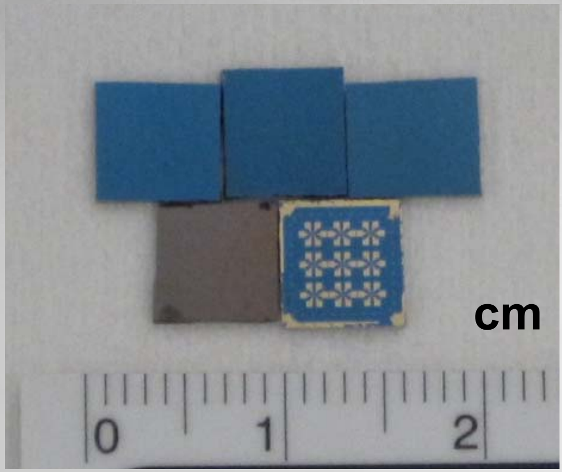



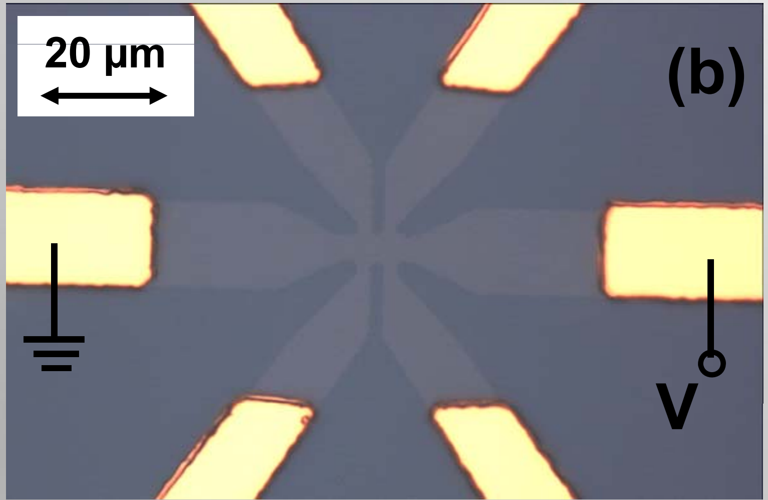



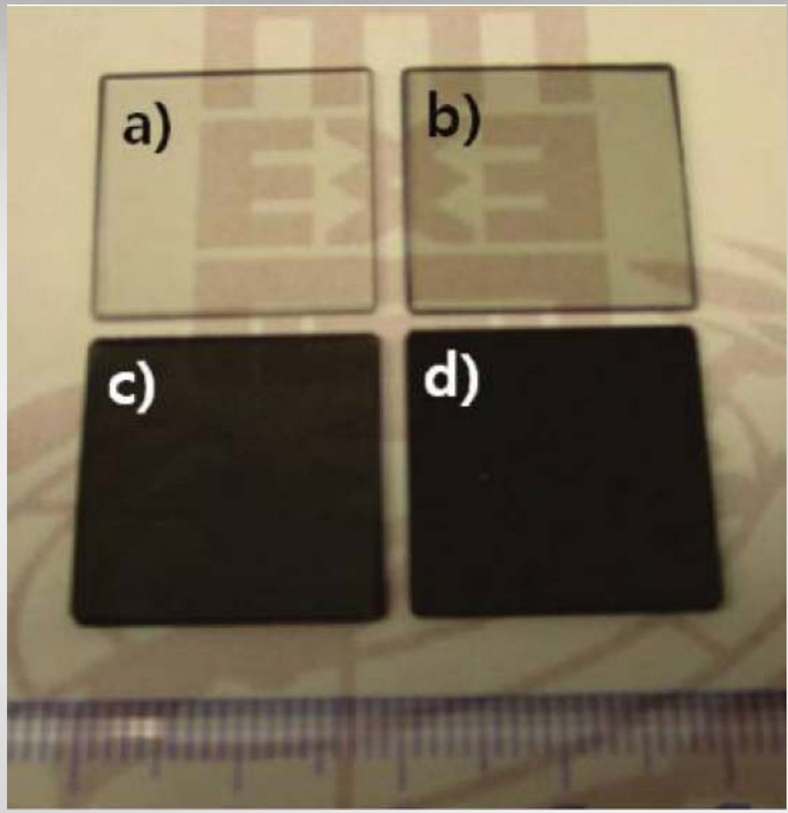



# Oriented graphite is not black

(a)

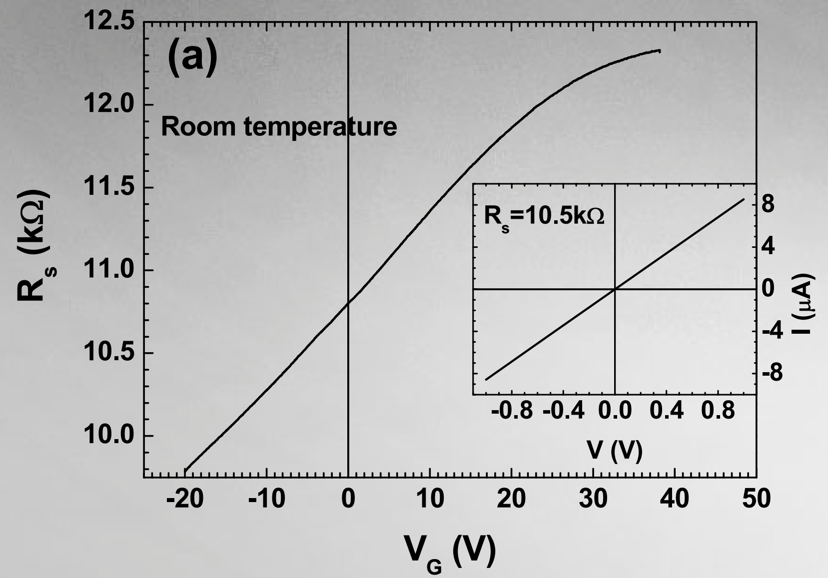


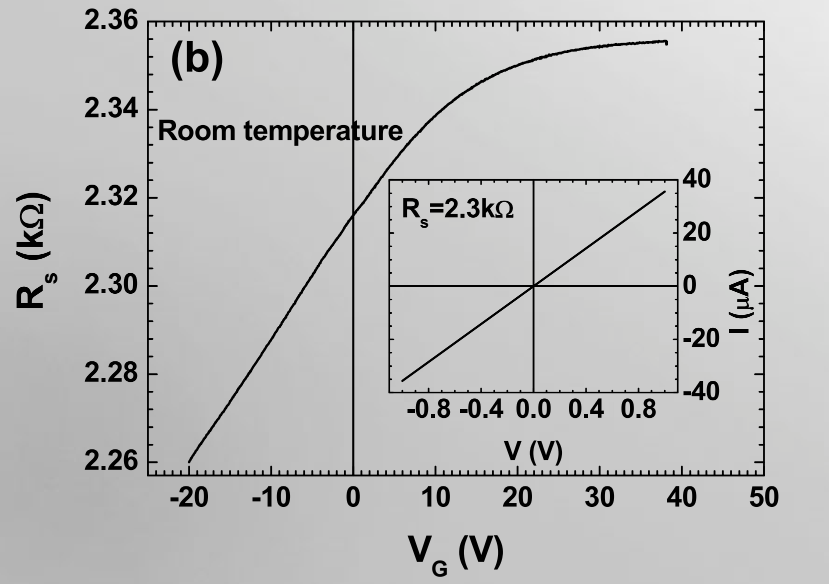



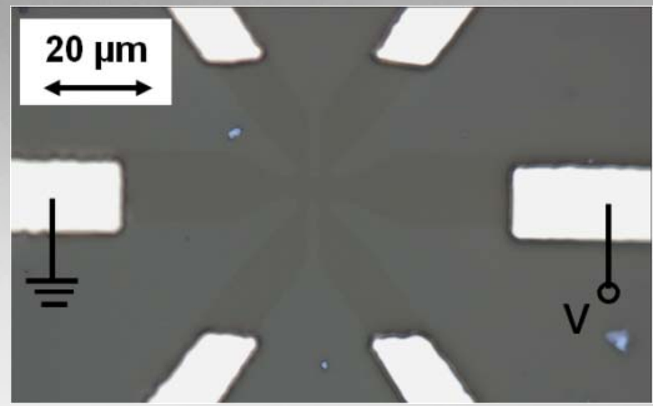

J. Phys. Chem. C 115 (2011) 14488

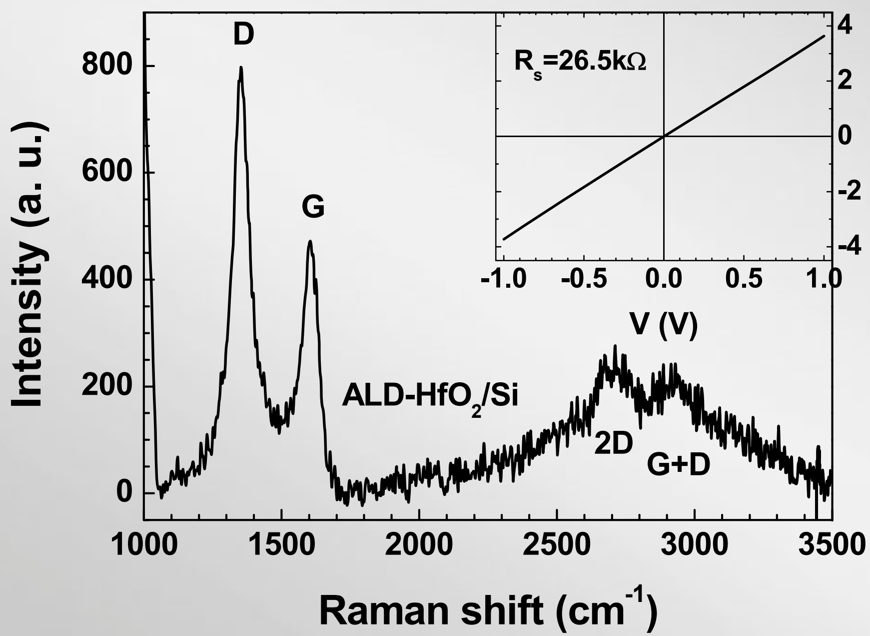
# $Si_3N_4$


(a)
Room temperature
$R_s$=10.5kΩ
$R_s$ (kΩ)
$V_G$ (V)
V (V)
I (μA)


(b)
Room temperature
$R_s$=2.3kΩ
$R_s$ (kΩ)
$V_G$ (V)
V (V)
I (μA)

# $HfO_2$


20 μm
V


D
G
ALD-$HfO_2$/Si
2D
G+D
$R_s$=26.5kΩ
V (V)
I (μA)
Intensity (a. u.)
Raman shift ($cm^{-1}$)

# Noncatalytic CVD summary

- Transfer free, semiconductor industry compatible
- Scalable
- Controllable thickness
- Macroscopically uniform
- Nanocrystalline textured thin films
- Similar transparency and conductivity as standard graphene
- Substrates withstanding ~1000 $^{o}C$

# Conclusion

| | Catalytic | Noncatalytic |
|---|---|---|
| Substrate | Metallic | Nonmetallic |
| High temperature | Yes | Yes |
| Transfer | Yes | No |
| Uniformity | Somewhat | Yes |
| Mobility | High | Low |
| Transparency/conductivity | High | High |
| Domain | µm | nm |
| Scalable | Yes | Yes |
| Novelty | No | Yes |
| Self-limiting | Conditionally yes | No |


Thanks