Graphene - Is it the future for semiconductors?

A High Level Overview of Materials, Devices and Applications

Y. Obeng[1] and P. Srinivasan[2]
[1] Semiconductor Electronics Division, Physical Measurements Laboratory,
NIST, Gaithersburg, MD 20899

[2]Technology Design Integration, External Development and Manufacturing
Texas Instruments, Dallas, TX 75243

1. Introduction

In this paper, we attempt to summarize the graphene component of the first two of the ***GRAPHENE, Ge/III-V AND EMERGING MATERIALS FOR POST-CMOS APPLICATIONS*** symposia [1, 2]. While not exhaustive and complete, a review of the papers presented at these symposia provides a high level overview of the state of graphene.

2. History of graphene

Predicted by theory as far back as 1947, graphene had been known to exhibit extraordinary electronic properties, if ***it could be isolated*** [3, 4]. For years grapheme was considered an academic material that existed only in theory and presumed not to exist as a free standing material, due to its "unstable nature". A. Geim, K. Novoselov and co-workers, were among the first to successfully isolate graphene [5], which was a remarkable achievement. Thus, the 2010 Nobel Prize for Physics awarded to Geim and Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene" must be celebrated as recognition of remarkable ingenuity in experimental physics.

The IUPAC defines grapheme as a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size [6]. Previously, descriptions such as graphite layers, carbon layers or carbon sheets have been used for the term graphene. Because graphite designates that modification of the chemical element carbon, in which planar sheets of carbon atoms, each atom bound to three neighbors in a honeycomb-like structure, are stacked in a three-dimensional regular order, it is not correct to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure. The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed.

3. The race to isolate graphene

There has been a long and sustained effort to realize free standing graphene films. Different ways for isolating graphene have been studied. There have number of attempts and different techniques to either isolate or grow graphene. One of the earlier attempts to isolate graphene is through exfoliation by physical or chemical methods. For example, graphite was first "exfoliated" in 1840, when C. Schafheutl tried to purify 'kish' from iron smelters by treating it with a mixture of sulfuric and nitric acids.[7] Graphite oxide was first prepared by B. C. Brodie in 1859, by treating graphite with a mixture of potassium chlorate and fuming nitric acid [8,9]. Boehm *et al.* described the formation of extremely tin lamellae of carbon, comprising of a few carbon layers as measured by TEM, either by "*deflagration of graphitic oxide on heating or by reduction of graphitic*

oxide in alkaline suspension" [10]. It has been argued that the sample preparation techniques for making the TEM samples resulted in the agglomeration of the otherwise single layer graphene into the lamellae described by Boehm *et al.* In none of these early works was free-standing graphene or graphene-oxide files isolated or identified as such.

In the past decade or so, the group at Georgia Tech led by Walter de Heer used the method of epitaxial growth to isolate graphene (Fig 2b). Silicon carbide was chosen as a substrate and the group demonstrated that epitaxial graphene could be produced by thermal decomposition of SiC which can be patterned and gated [11]. Furthermore, they showed that the epitaxial graphene exhibit 2D electronic properties as well as quantum confinement and quantum coherence effects. At the same time, Philip Kim's group at Columbia University has studied using AFM to mechanically separate graphene layers from graphite. They succeeded in isolating a multi-layer comprising of about 10 layers [12].

Geim's group (Fig 2a) successfully isolated atomically thin graphite by using adhesive tape to peel off layers from a graphitic crystal flakes and then gently rub those fresh layers against an oxidized silicon surface. They were also able to determine the thickness of this layer which was few angstroms' thick, using atomic force microscopy. This technique was first proposed by Ruoff's group in 1999 [13].

Recently, Ruoff's team successfully isolated graphene using epitaxial growth by chemical vapor deposition of hydrocarbons on metal substrates. In this case, the metal

substrate was Cu (Fig 2c) [14]. The advantage of this technique is that it can be easily extended to large areas by just increasing the Cu metal substrate size and growth system. Further, one can also use Cu films deposited on silicon wafers as is routinely done by the semiconductor industry using an electrochemical deposition process.

In general, epitaxial growth of graphene offers the most promising route towards production and rapid progress in this direction is currently in progress. The other approach is the use of epitaxy on catalytic surfaces, such as Ni or Pt, as demonstrated by the Kong's group at MIT (Fig 2c) [15], followed by the deposition of an insulating support on top of graphene and chemical removal of the primary metallic substrate.

4. Properties of Graphene

Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for carbon based materials (Fig. 1). In 1947 Wallace, used band theory of solids with tight binding approximation, to explain many of the physical properties of graphite [4]. In that paper, the author makes a rather clairvoyant assumption "*Since the spacing of the lattice planes of graphite is large (3.37A) compared with the hexagonal spacing in the layer 1.42A, a first approximation in the treatment of graphite may be obtained by neglecting the interactions between the planes, and supposing that conduction takes place only in layers*." This assumption makes the subsequent analyses conveniently applicable to what we are calling graphene.

The 2D system of graphene is not only interesting by itself but also allows access to the subtle and rich physics of quantum electrodynamics in a bench-top experiment. Novoselov *et al*. [16] showed that electron transport graphene is essentially governed by Dirac's (relativistic) equation. The charge carriers in graphene mimic relativistic particles with zero rest mass and have an effective 'speed of light' $c^* \approx 3 \times 10^{10}$ $cm^{-1}s^{-1}$. Their study revealed a variety of unusual phenomena that are characteristic of 2D Dirac fermions. In particular, they observed that graphene's conductivity never falls below a minimum value corresponding to the quantum unit of conductance, even when concentrations of charge carriers tend to zero. Furthermore, the integer quantum Hall effect in graphene is anomalous in that it occurs at half-integer filling factors; and the cyclotron mass m_c of massless carriers in graphene is described by $E = m_c c_*^2$.

One of the most fascinating aspects of the physics enabled by the isolation of graphene is the experimental demonstration of the so-called Klein paradox—unimpeded penetration of relativistic particles through high and wide potential barriers. The phenomenon is discussed in many contexts in particle, nuclear and astro-physics but direct tests of the Klein paradox using elementary particles had hitherto proved impossible. Katsnelson *et al* [17] showed that the effect can be tested in a conceptually simple condensed-matter experiment using electrostatic barriers in single- and bi-layer graphene. Owing to the chiral nature of their quasi-particles, quantum tunneling in these materials becomes highly anisotropic, qualitatively different from the case of normal, non-relativistic electrons. Massless Dirac fermions in graphene allow a close realization of Klein's gedanken experiment, whereas massive chiral fermions in bilayer graphene offer an interesting complementary system that elucidates the basic physics involved.

Besides these new physics, graphene has demonstrated some interesting electronic properties, as illustrated below:

(i) Charge carriers in graphene

Graphene is an exception — it has a unique nature in terms of charge carriers. Electrons propagating through the honeycomb lattice completely lose their effective mass, which results in quasi-particles called as "*Dirac-fermions*" that are described by a Dirac-like equation rather than Schrödinger equation as shown in Fig 3a and 3b. These can be seen as electrons that have zero mass m_0 or as neutrinos that acquired the electron charge e. Bilayer graphene shows another type of quasi-particles that have no analogies. They are massive Dirac fermions described by a combination of both Dirac and Schrödinger equations.

(ii) Band structure of graphene:

Graphene is a semi-metal and is a zero-gap semiconductor (Fig 4a). In addition, bilayer graphene is the only known material in which the electronic band structure changes significantly via the electric field effect and the semiconducting gap ΔE can be tuned continuously from zero to ≈ 0.3 eV if SiO_2 is used as a dielectric. A recent study by IBM provided evidence where the bandgap was tuned to the order of 0.13eV using the structure as shown in Fig 4b.

(iii) Thermal conductivity and mobility:

Graphene is a 2D system where there is no phonon scattering. In general, the low-energy phonons in the system are involved in heat transfer and hence graphene offers higher thermal conductivity. Graphene also exhibits ambipolar electric field effect (Fig 5a) such that charge carriers can be tuned continuously between electrons and holes with

concentrations as high as 10^{13} cm^{-2} (Fig 5b) and their mobilities μ can exceed 15,000 cm^2 V^{-1} s^{-1} even under ambient conditions. Moreover, the observed mobilities weakly depend on temperature T, which means that μ at 300 K is still limited by impurity scattering, and therefore can be improved significantly, perhaps, even up to ≈100,000 cm^2 V^{-1} s^{-1}. In graphene, μ remains high even at high n (>10^{12} cm^{-2}) in both electrically and chemically doped devices, which translates into ballistic transport on the sub-micrometer scale (currently up to ≈0.3 μm at 300 K).

A further indication of the system's extreme electronic quality is the quantum Hall effect (QHE) that can be observed (Fig 5c) in graphene even at room temperature, extending the previous temperature range for the QHE by a factor of 10.

5. Applications of Graphene

Graphene properties - (i) high transparency (ii) good conductivity (iii) chemically inert and (v) low cost makes it viable for various industrial applications. These unique properties of graphene give rise to cornucopia of applications, each leveraging a specific property, as illustrated below:

i. The high mobility even at highest E-field induced concentrations makes the carriers go ballistic giving rise to a ballistic FET at 300 K.

ii. Due to its e-h symmetry and linear dispersion it is suitable for RF and high frequency applications such THz detectors and lasers.

iii. It also has its applications in chemical sensors and MEMS based applications.

iv. Another route to graphene based electronics is to consider graphene as a conductive sheet rather than a channel material which can be used to make a single-electron-transistor (SET).

v. Superconducting FETs and room temperature spintronics.

One of the commercially viable devices based on graphene are RF-FETs as their properties are well suited for low power / high speed applications. IBM has demonstrated a successful fabrication of an RF-FET on 2 inch wafers using SiC as substrate [18] . They obtained a superior electrical performance when the device was self-yielding better Hall mobility, higher I_D and g_m. In addition, they obtained f_t max of 170 GHz at 90 nm gate lengths (Fig 6a). Samsung also obtained good characteristics for an RF device on 6 inch wafers [19] with current gain close to 200 GHz at 0.24 um (Fig 6b).

While high-k was used as a gate dielectric in both the cases, h-BN seems to be a better choice since their material properties [20] are close to graphene (Fig 6c). The structure is an insulating isomorph of graphite which enhances the mobility of graphene device. However, one of the major issues which limit the performance of these devices is poor contact resistance. The contact resistance values are currently in the order of kilo-ohms.

Another potential near term application of graphene is transparent touch screens demonstrated by Samsung [21]. Using a roller, the CVD grown graphene has been transferred by pressing against an adhesive polymer support and the copper etched away, leaving the graphene film attached to the polymer. The graphene can then be pressed

against a final substrate - such as polyethylene terephthalate (PET) - again using rollers, and the polymer adhesive released by heating. Subsequent layers of graphene can then be added in a similar way, creating a large graphene film. The graphene was doped by treating with nitric acid, to afford a large, transparent electrode which was demonstrated to work in a touch-screen device application (Fig 7). This graphene electrode will potentially replace the traditional transparent electrodes used in such applications are made from indium tin oxides (ITO). But graphene electrode has better transparency and is tougher. Since, oxide materials like ITO are usually fragile and weak, ITO-based touch screens have a finite life span, whereas, a graphene-based screen should last essentially forever.

References:

1) ECS transactions, 19, 5, **2009.**
2) ECS transactions, 28, 5, **2010.**
3) D.R Dreyer, R. S. Ruoff, C. W. Bielawski, Angew. *Chem. Int. Ed.,* 49, 996-9344, **2010.**
4) P. R. Wallace, *Phys. Rev.,* 71, 622, **1947.**
5) K.S. Nososelov, A. K. Geim, S. V. Marozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva; A. A. Firsov, *Science* 306, 666, **2004**.
6) IUPAC, 1995, 67, 473 (Recommended terminology for the description of carbon as a solid (IUPAC Recommendations 1995)) on page 491 http://goldbook.iupac.org/G02683.html
7) C Schafhaeutl ., Phil. Mag. 1840; 16, 570-90; Boehm, H. P.; Stumpp, E., *Carbon* 45, 1381-1383, **2007.**
8) B. Brodie Phil. Trans. Roy. Soc. London, 149, 249 (1859); B. Brodie, Ann. Chem. Liebigs, 114, 6 (1860)
9) William S. Hummers Jr., Richard E. Offeman, *J. Am. Chem. Soc*., 80, 6, 1339, **1958.**
10) H. P. Boehm, A. Clauses, G. Fisher, U. Hofman in Proceedings of the fifth conference on carbon vol 1: S. MROZOWSKI, P. L. WALKER and M. L. STUDEBAKER. Eds., Pergamon, 1962 New York, Oxford, London and Paris.
11) C. Berger et al., *J. Phys. Chem. B,* 108, 19912, **2004**.
12) Y. Zhang et al., *Phys. Rev. Lett,* 94, 176803, **2005.**
13) X. K. Lu, M. F. Yu, H. Huan and R. S. Ruoff, *Nanotechnology* 10, 269, **1999.**
14) X. Li et al, *Science*, 324, 1312, **2009**.

15) A. Reina et al., *Nano Lett.,* 9 (1), 30-35, **2008.**
16) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos , A. A. Firsov, *Nature* 438, 197-200, **2005.**
17) M. I. Katsnelson, K. S. Novoselov , A. K. Geim*, Nature Physics* **2**, 620, **2006.**
18) Y.Q. Wu, Y.-M. Lin, K.A. Jenkins, J.A. Ott, C. Dimitrakopoulos, D.B. Farmer, F. Xia, A. Grill, D.A. Antoniadis and Ph. Avouris, *Proceedings of IEDM Tech. Digest,* **2010.**
19) J. H. Lee, H. J. Chung, J. Lee, H. Shin, J. Heo, H.Yang,Sung-Hoon Lee, S.Seo, J. Shin, U-in Chung, I.Yoo and K. Kim, Proceedings of IEDM Tech. Digest, 2010.
20) I. Meric, C. Dean, A. Young, J. Hone, P. Kim, and K. L. Shepard, Proceedings *of IEDM Tech. Digest,* **2010.**
21) J-H Ahn et al, *Nature Nanotechnology*, **2010.** DOI: 10.1038/NNANO.2010.132

Figure Captions:

Fig 1: Graphene is a 2D building material for carbon materials. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.

Fig 2a: (i) First photographs of isolated graphene. They used the simple technique of ripping layers from a graphite surface (called as exfoliation) using adhesive tape. (ii) High resolution images of graphene under Scanning Electron Micrograph. (iii) Atomic resolution of graphitic layers extracted using exfoliation method.

Fig 2b: Epitaxial graphene on the C-face of 4H-SiC (a) TEM image of the cross section of multilayer epitaxial graphene. (b) Atomic resolution STM image showing a hexagonal lattice (c) AFM image. The white lines are 'puckers' in the graphene sheets.

Fig 2c: Initial stages of graphene growth on Cu (i) SEM of graphene on Cu and (ii) Raman maps of graphene on SiO_2/Si and (iii) Graphene films grown on Ni and transferred onto a Si wafer.

Fig 3a: Schrodinger's fermions. The green dot is the electron. **3b:** Dirac fermions in graphene.

Fig 4a: Band structure of the graphene. The valence and conduction bands touch at discrete points in the Brillouin zone. **4b:** Schematic illustration of bandgap opening in bilayer graphene by an electric field. Schematic of the device used to open the gap. Transfer characteristics of the graphene FET.

Fig 5a: Ambipolar E-field effect in single-layer graphene. The gate voltage and temperature dependence of resistivity of the high mobility sample ($\mu \approx 20{,}000$ cm^2 $V^{-1}s^{-1}$). **b:** ρ versus Vg at three representative temperatures, T = 0.03, 77, and 300 K showing similar performances due to zero phonon scattering **(c)** Graphene Chiral Quantum Hall effects.

Fig 6: Current gain ft, max characteristics from (a) IBM showing cut-off frequency of 170 GHz for gate length of 90 nm (b) Samsung showing cut-off frequency of 200 GHz for gate length of 0.24 um (c) Intrinsic I-V characteristics of 0.44 um device fabricated using B-N as gate dielectric. Solid lines indicate model fitting curves.

Fig 7: Industrial production of graphene sheets. Samsung's transparent touch screen technology using graphene.

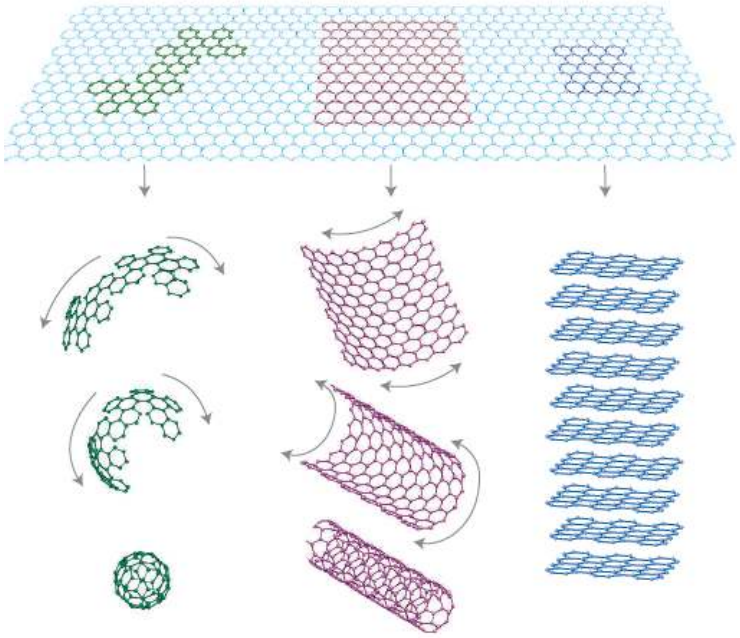
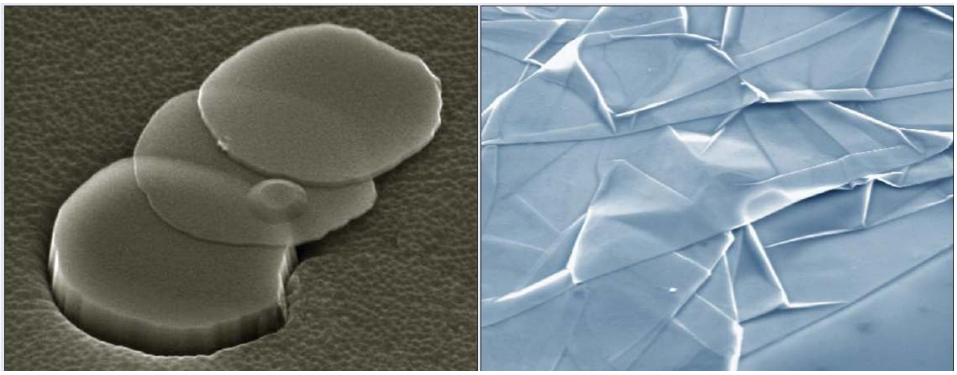
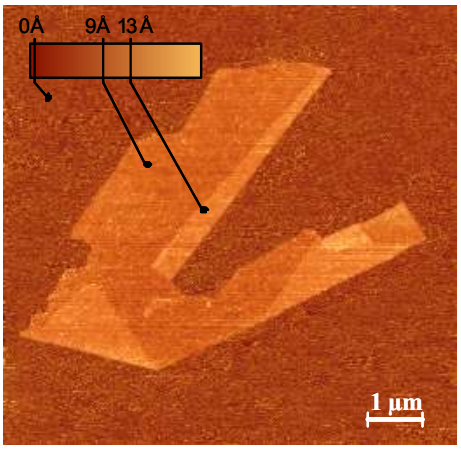


Fig 1

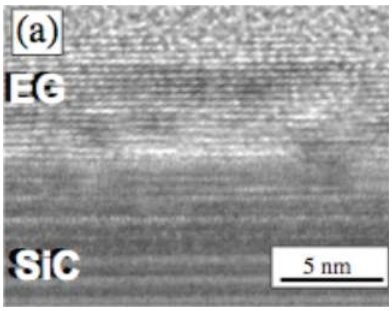


(i) (ii)

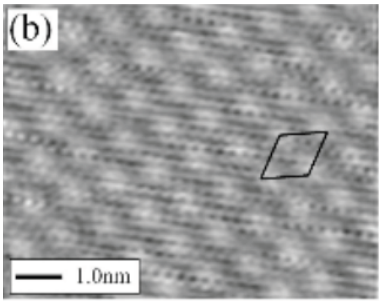


(iii)

Fig 2a



(i)



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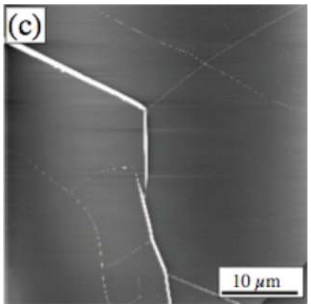
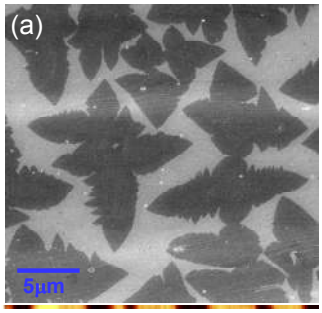
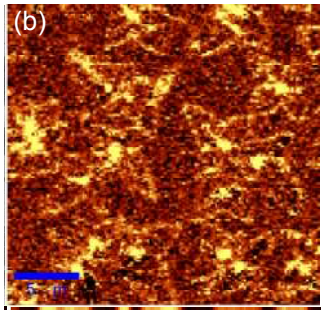


(iii)

Fig 2b



(a)



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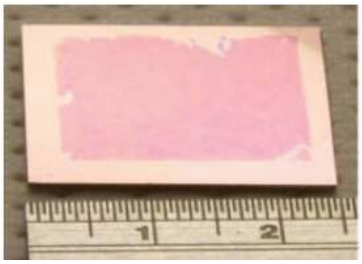
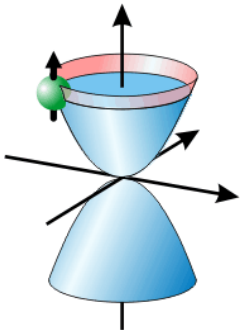
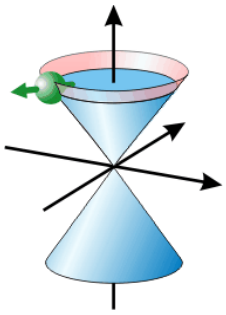


(c)

Fig 2c

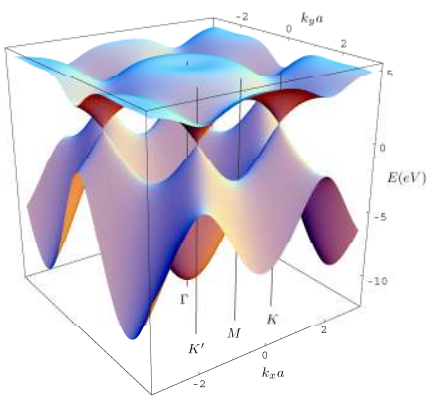


(a)

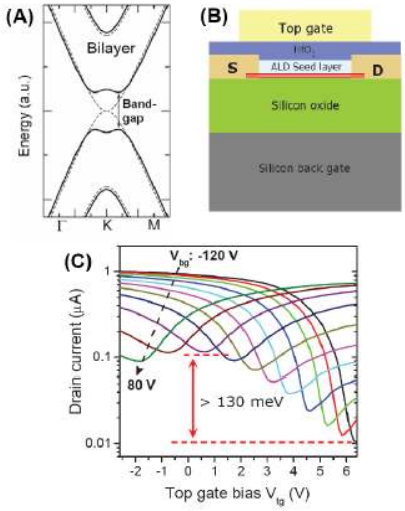


(b)

Fig 3

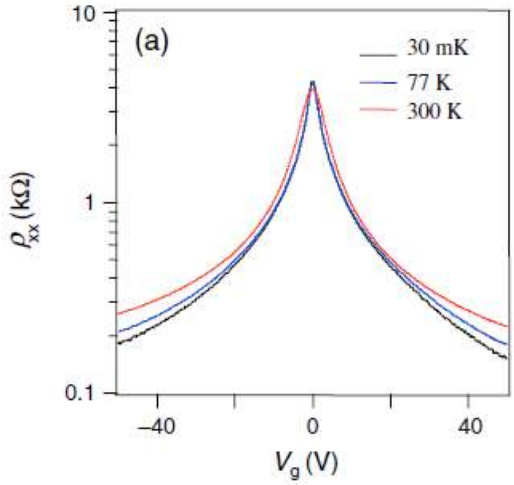

$k_y a$
$E(eV)$
Γ
K'
M
K
$k_x a$

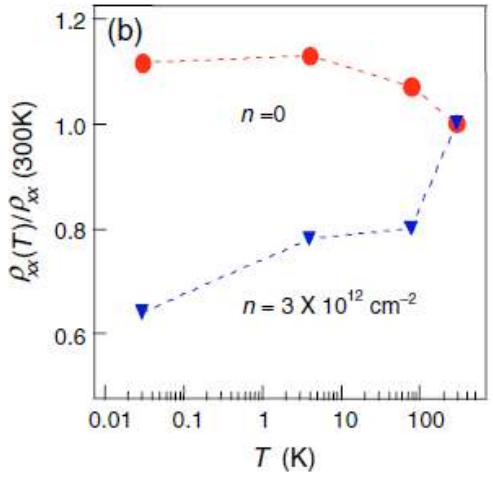
(a)

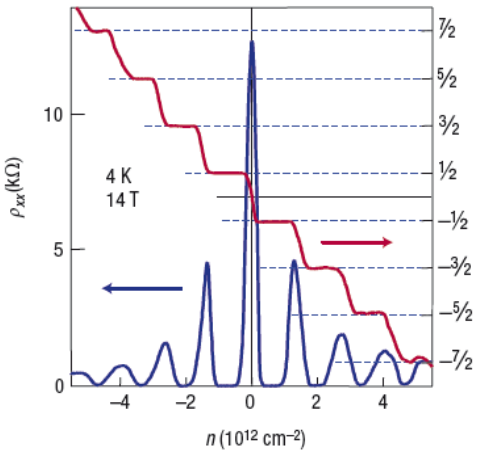

(A)
Bilayer
Band-gap
Energy (a.u.)
Γ
K
M
(B)
Top gate
S
D
ALD Seed layer
Silicon oxide
Silicon back gate
(C)
V_{bg}: -120 V
80 V
> 130 meV
Drain current (μA)
Top gate bias V_{tg} (V)

(b)

Fig 4

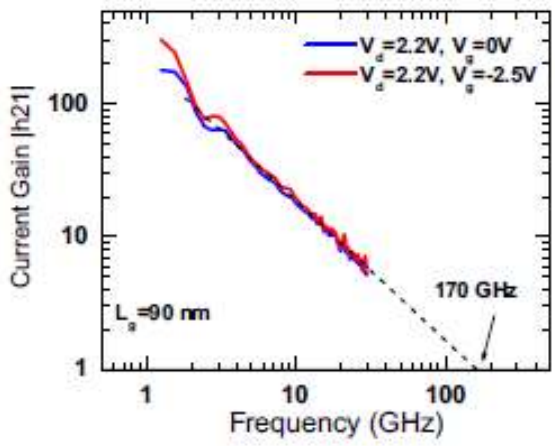

(a)
30 mK
77 K
300 K
10
1
0.1
ρ_{xx} (kΩ)
–40
0
40
V_g (V)

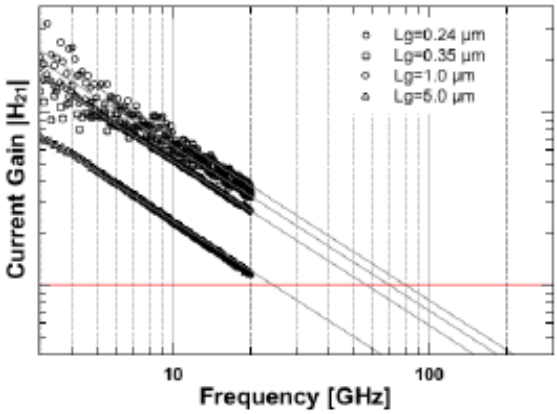

(b)
1.2
1.0
0.8
0.6
$\rho_{xx}(T)/\rho_{xx}$ (300K)
n =0
n = 3 X 10^{12} cm^{-2}
0.01
0.1
1
10
100
T (K)


10
5
0
ρ_{xx}(kΩ)
4 K
14 T
7/2
5/2
3/2
1/2
–1/2
–3/2
–5/2
–7/2
–4
–2
0
2
4
n (10^{12} cm^{-2})

(c)

Fig 5


V_d=2.2V, V_g=0V
V_d=2.2V, V_g=-2.5V
Current Gain |h21|
100
10
1
L_g=90 nm
170 GHz
1
10
100
Frequency (GHz)


Lg=0.24 µm
Lg=0.35 µm
Lg=1.0 µm
Lg=5.0 µm
Current Gain |H21|
10
100
Frequency [GHz]

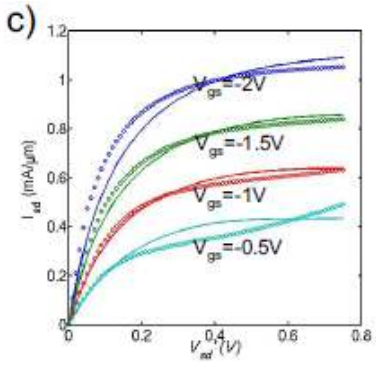
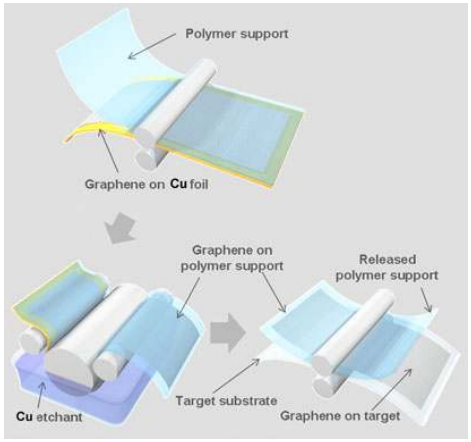
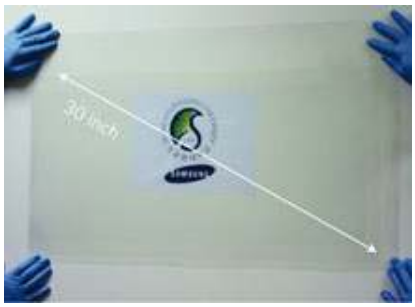

c)
1.2
1
0.8
0.6
0.4
0.2
0
I_{sd} (mA/µm)
V_{gs}=-2V
V_{gs}=-1.5V
V_{gs}=-1V
V_{gs}=-0.5V
0
0.2
0.4
0.6
0.8
V_{sd} (V)

Fig 6


Polymer support
Graphene on Cu foil
Graphene on polymer support
Released polymer support
Target substrate
Graphene on target
Cu etchant


30 inch

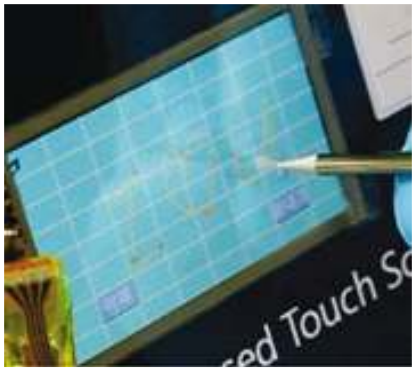


Fig 7