Graphene: Is It the Future for Semiconductors? An Overview of the Material, Devices, and Applications

by Yaw Obeng and Purushothaman Srinivasan

In this article, we attempt to summarize the graphene component of the ECS symposia series on "Graphene, Ge/III-V, Nanowires, and Emerging Materials for Post-CMOS Applications."[1] While not exhaustive and complete, a review of the papers presented at these symposia provides a brief glimpse of the state of graphene research over the last few years.

History of Graphene

As far back as in 1947, graphene was predicted to have extraordinary electronic properties, if it could be isolated.[2,3] For years, graphene (Fig. 1) 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 obtain the elusive free-standing graphene films,[4] 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 International Union of Pure and Applied Chemistry (IUPAC) defines graphene as a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size.[5] Thus, the term graphene should be used only when the reactions, structural relations, or other properties of a single layer are discussed. Previously, descriptions such as graphite layers, carbon layers, or carbon sheets have been used for the term graphene.

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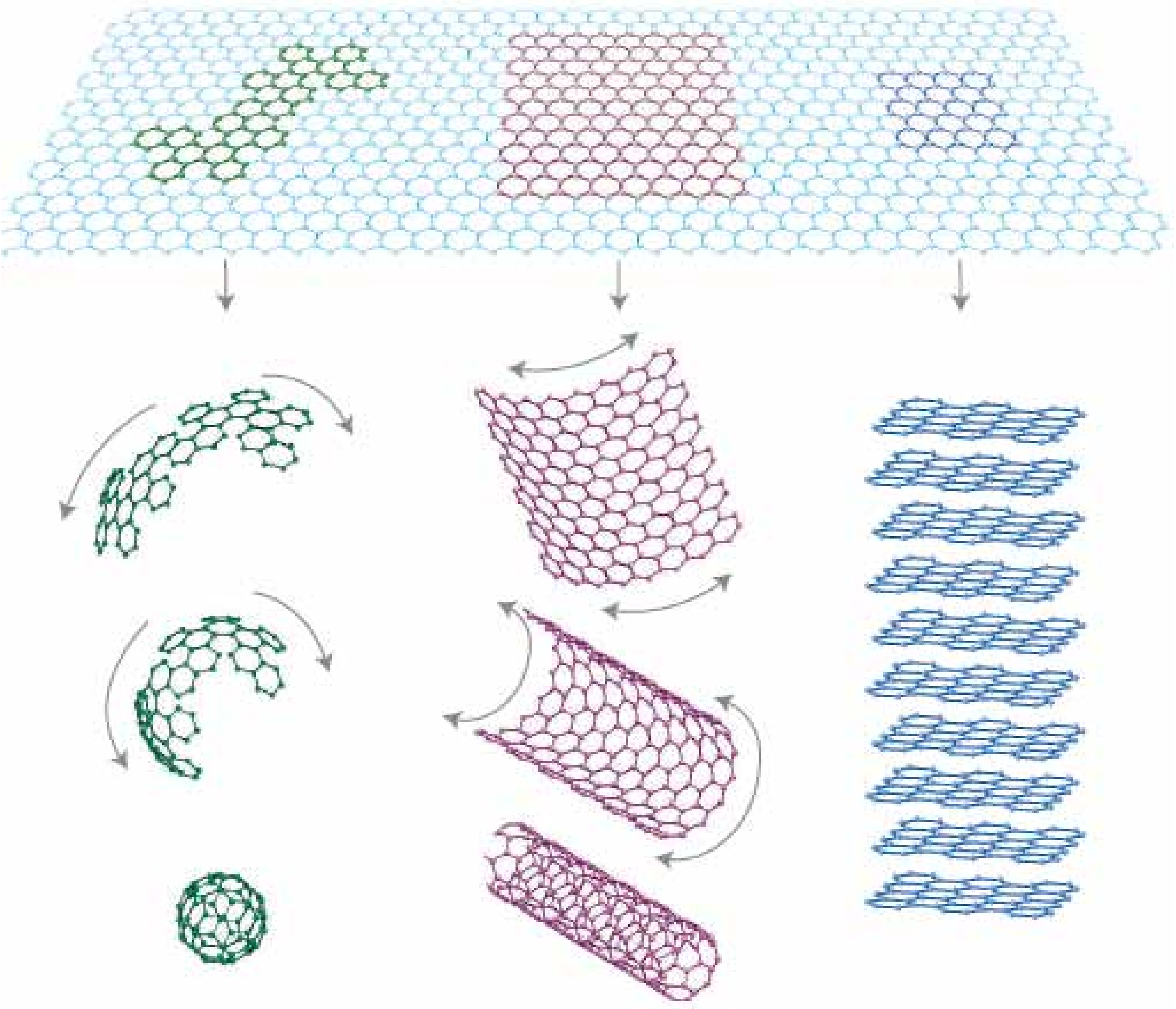

Fig. 1. *Graphene is a 2D building block for carbon-based materials. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes, or stacked into 3D graphite. Figure reproduced with permission from* Nature Mater., ***6****, 184 (2007).*

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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. One of the earliest documented attempts to isolate graphene was 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.[6] Graphite oxide was first prepared by Brodie in 1859, by treating graphite with a mixture of potassium chlorate and fuming nitric acid.[7,8] Boehm *et al.* described the formation of extremely thin lamellae of carbon, comprising of a few carbon layers as measured by TEM, by either "deflagration of graphitic oxide on heating or by reduction of graphitic oxide in alkaline suspension."[9] It has been argued that sample preparation techniques for making the TEM samples resulted in the agglomeration of the otherwise single layer of 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.

Geim's group (Fig. 2a) successfully isolated atomically thin graphite by using adhesive tape to peel off layers from 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 AFM. Their "Scotch tape" technique is very reminiscent of the use of adhesive tape to routinely peel layered crystals (*e.g.*, graphite, mica, etc.), held together by van der Waals forces, to expose fresh surfaces.[10,11]

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.[12] Furthermore, they showed that the epitaxial graphene exhibited 2D electronic properties as well as quantum confinement and quantum coherence effects. At the same time, Philip Kim's group at Columbia University used AFM to mechanically separate graphene layers from graphite. They succeeded in isolating a multi-layer structure comprised of about 10 layers.[13]

Recently, Ruoff's team successfully fabricated 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. In general, epitaxial growth of graphene offers the most promising route towards production, and rapid progress in this direction is currently in progress. Similarly, Kong's group at MIT has also grown graphene by epitaxy on metal surfaces, such as Ni or Pt (Fig. 2c).[15] In this epitaxy-on-metal technique, the graphene film is transferred onto suitable working substrates by chemical removal of the primary metallic substrate.

Properties of Graphene

Graphene is a flat monolayer of sp^2 carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, which 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.[3] 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 subsequent analyses conveniently applicable to the material that we now know as graphene.

The 2D system of graphene is not only interesting by itself; but it 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 in 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, $c^* \approx 10^6$ 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

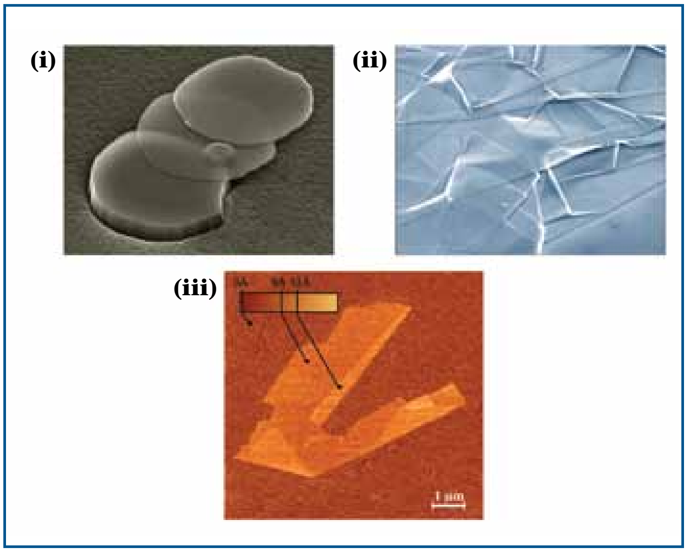

Fig. 2a. *(i) One of the first photographs of isolated graphene. They used the simple technique of ripping layers from a graphite surface (called as exfoliation) using adhesive tape. Courtesy of http://physicsweb.org. (ii) High resolution scanning electron micrograph image of graphene. Reproduced with permission from* Physics World, *Nov 2006, p 1. (iii) Atomic resolution of graphitic layers extracted using exfoliation method. Reproduced with permission from* Nature Mater., ***6****, 185 (2007).*

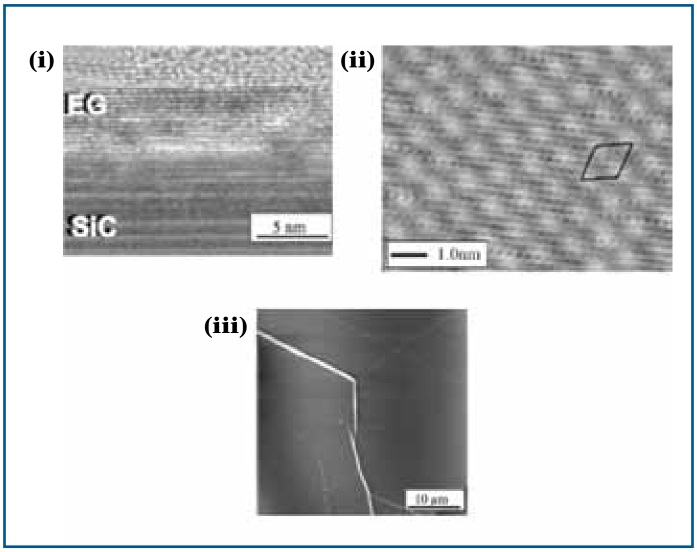

Fig. 2b. *Epitaxial graphene on the C-face of 4H-SiC. (i) TEM image of the cross section of multilayer epitaxial graphene. (ii) Atomic resolution STM image showing a hexagonal lattice. (iii) AFM image. The white lines are 'puckers' in the graphene sheets. Courtesy of* ECS Transactions, ***19****(5), 95 (2009).*

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 astrophysics, but direct tests of the Klein paradox using elementary particles had hitherto proved impossible. Katsnelson *et al.* showed that the effect can be tested in a conceptually simple condensed-matter experiment using electrostatic barriers in single- and bi-layer graphene.[17] 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 examples of new physics, graphene has demonstrated some amazing electronic properties, as illustrated below.

Charge carriers in graphene.—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 known analogies. They are massive Dirac fermions described by a combination of both Dirac and Schrödinger equations.

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

Thermal conductivity and mobility.—Graphene is a 2D material where there is little or no phonon scattering. In general, the low-energy phonons in the system are involved in heat transfer; hence, it offers higher thermal conductivity. Graphene 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 in excess of 15,000 cm^2 V^{-1} s^{-1} even under ambient conditions. The observed mobilities depend weakly 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 $\approx$100,000 cm^2 V^{-1} s^{-1}. In graphene, μ remains high even at high n ($>10^{12}$ cm^{-2}) in both electrically and chemically doped devices, which translates into ballistic transport on the sub-micrometer scale (currently up to $\approx$0.3 µm at 300 K).

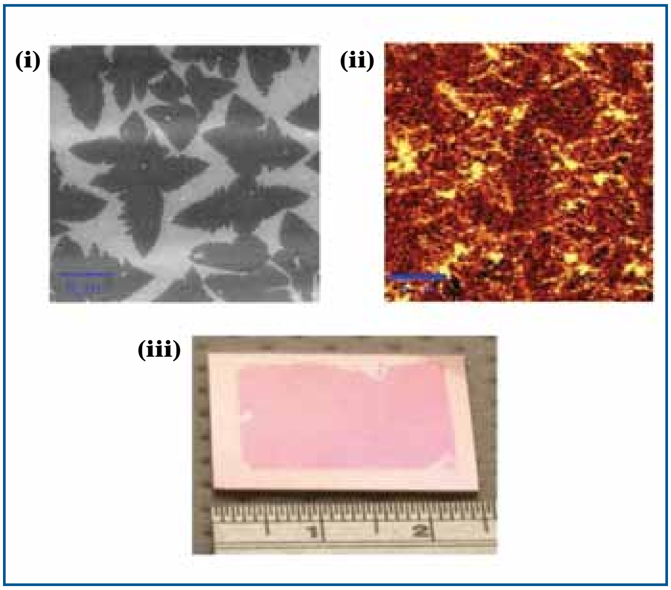

Fig. 2c. *Initial stages of graphene growth on Cu. (i) SEM of graphene on Cu. (ii) Raman maps of graphene on SiO_2/Si. Parts (i) and (ii) reproduced courtesy of* ECS Transactions, ***19****(5), 41 (2009). (iii) Graphene films grown on Ni and transferred onto a Si wafer. Reproduced with permission of* Nano Lett.*,* ***9****, 30 (2009).*

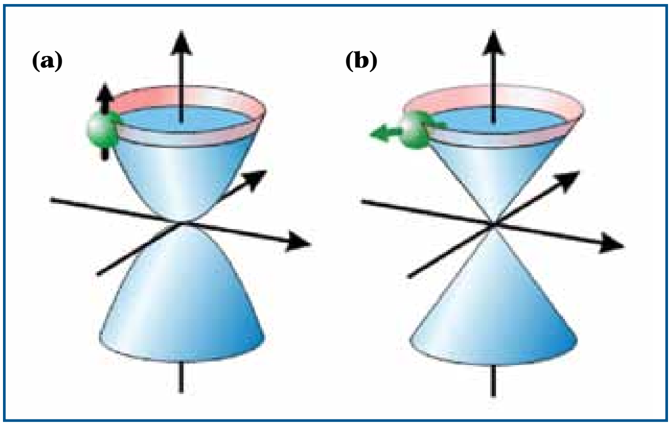

Fig. 3. *(a) Schrödinger's fermions; the green dot is the electron. (b) Dirac fermions in graphene. Reproduced with permission of* Science Review*,* ***324****, 1531 (2009).*

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.

Applications of Graphene

The unusual properties of graphene outlined in the preceding section coupled with its: (i) high optical transparency, (ii) chemical inertness, and (iii) low cost make it viable for a cornucopia of industrial applications. A cross-section of applications, that leverage specific graphene properties, is detailed below.

- The high mobility even at highest E-field-induced concentrations makes the carriers go ballistic giving rise to a ballistic FET device at 300 K
- Due to its e-h symmetry and linear dispersion it is suitable for RF and high frequency applications such THz detectors and lasers
- It also has its applications in chemical sensors and MEMS-based applications
- 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)
- Superconducting FETs and room-temperature spintronics
- Transparent electrodes

One of the commercially-viable devices based on graphene is the RF-FET, as its 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 and

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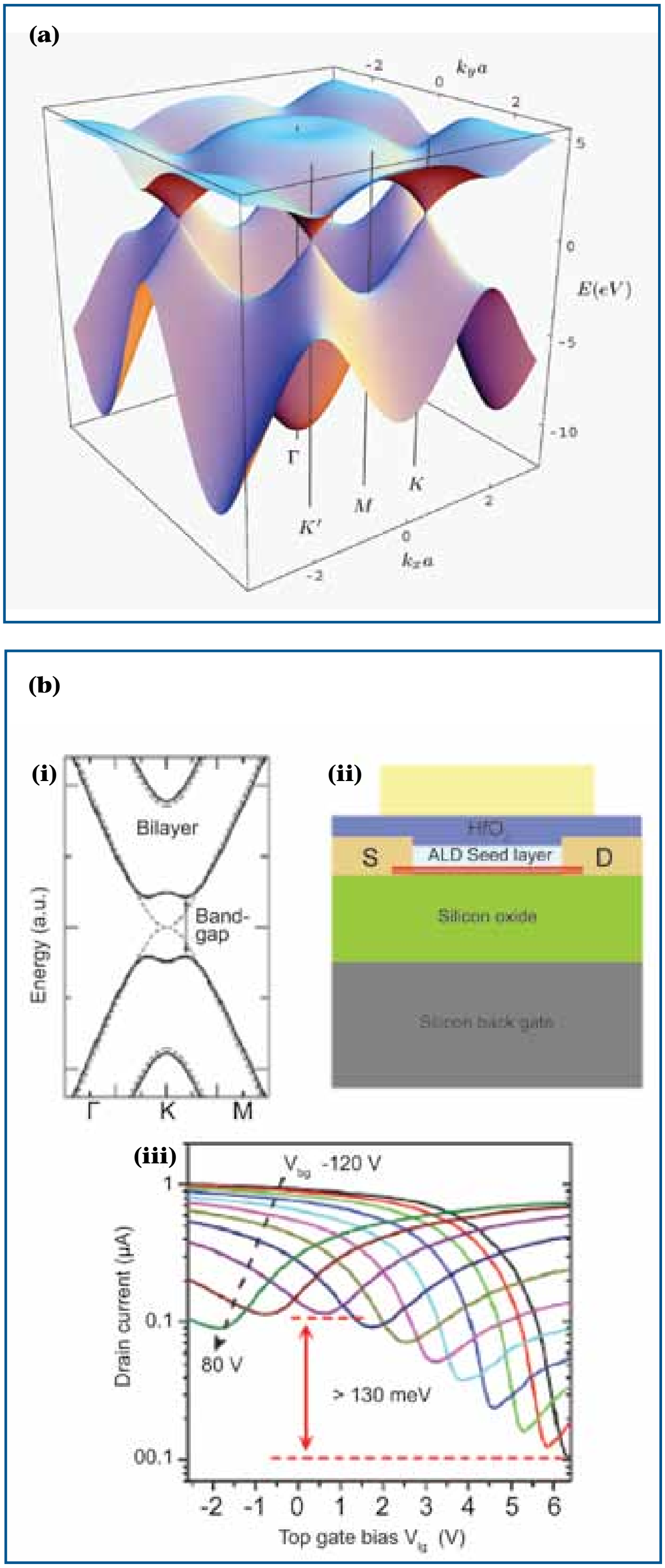

Fig. 4. *(a) Band structure of the graphene. The valence and conduction bands touch at discrete points in the Brillouin zone. Reproduced with permission of* Physics Today, ***59****(1), 21 (2006). (b) Schematic illustration (i) of bandgap opening in bilayer graphene by an electric field. (ii) Schematic of the device used to open the gap. (iii) Transfer characteristics of the graphene FET. Reproduced with permission of* IEDM Tech. Digest, ***23.1.1,*** *552 (2010).*

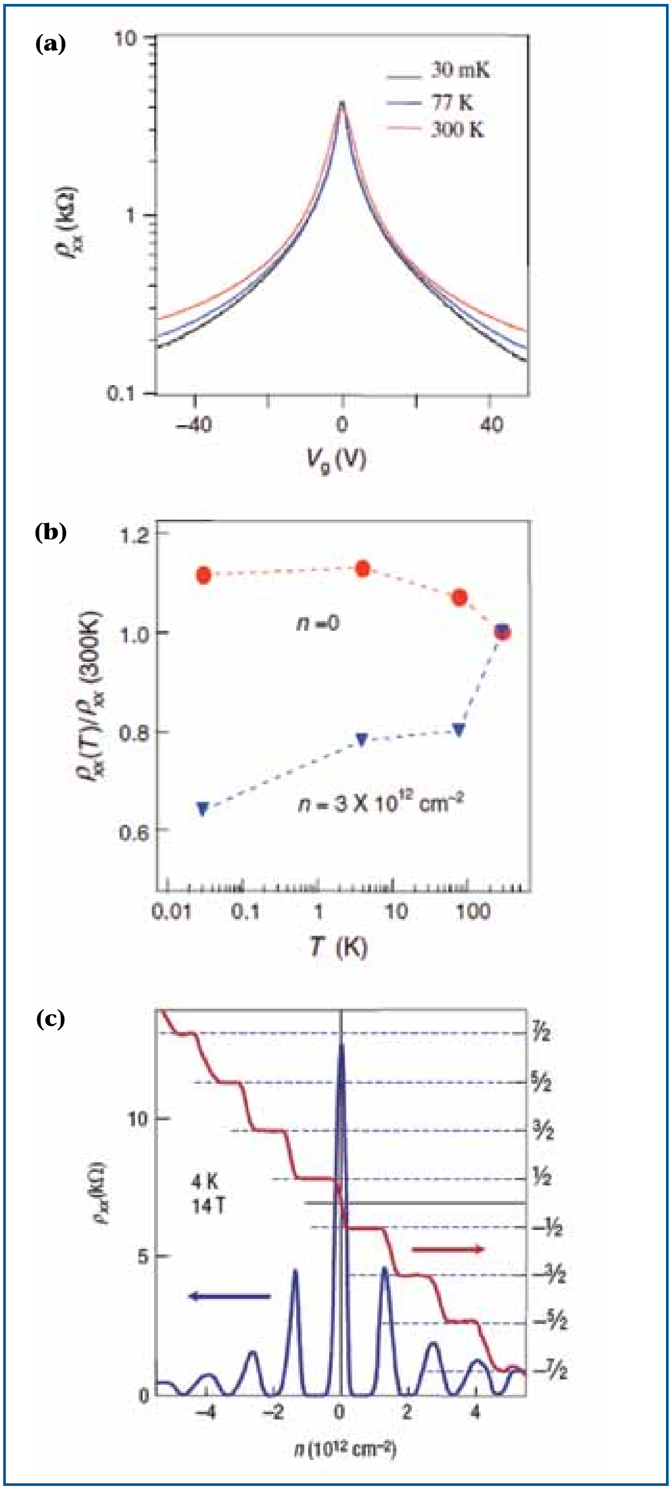

Fig. 5. *(a) Ambipolar E-field effect in single-layer graphene. The gate voltage and temperature dependence of resistivity of the high mobility sample (μ ≈ 20,000 cm² V-1s–1). (b) ρ versus Vg at three representative temperatures, T = 0.03K, 77K, and 300 K showing similar performances due to zero phonon scattering. Parts (a) and (b) reproduced with permission of* Eur. Phys. J. Special Topics, *EDP Sciences, Springer-Verlag,* ***148****, 15 (2007). (c) Graphene chiral quantum Hall effects. Reproduced with permission of* Physics Today, ***60****(8), 35 (2007).*

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 a high-k material was used as a gate dielectric in both the cases, h-BN seems to be a better choice since its 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, a major issue which limits 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 the transparent touch screen demonstrated by Samsung.[21] Using a roller, CVD-grown graphene has been transferred by pressing against an adhesive polymer support and the copper is then 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 can potentially replace the traditional transparent electrodes used in such applications, which are currently made from transparent conducting oxides such as ITO. However, the graphene electrode has better transparency and is tougher. Oxide materials such as ITO are usually fragile and weak leading to a finite life span; on the other hand, graphene-based screens should have a long life span. ■

About the Authors

Yaw Obeng has over 20 years of proven technical leadership in corporate, entrepreneurial and academic environments. Currently, he serves as a Senior Scientist with the Office of Microelectronics Programs at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland. He had previously worked with AT&T/Lucent Technologies/Agere Systems Bell Laboratories and Texas Instruments. He has also co-founded two start-up companies (psiloQuest, Inc. and Nkanea Technologies, Inc.) dedicated to the development of novel materials for semiconductor and optoelectronics fabrication. He is an inventor on over 50 U.S. and international patents, and has published over 100 papers in various technical publications. Dr. Obeng holds adjunct Professorships at Clemson University and the University of Central Florida, Orlando where he has advised several graduate students. He is a Fellow of the American institute of Chemists. He may be reached at yaw.obeng@nist.gov.

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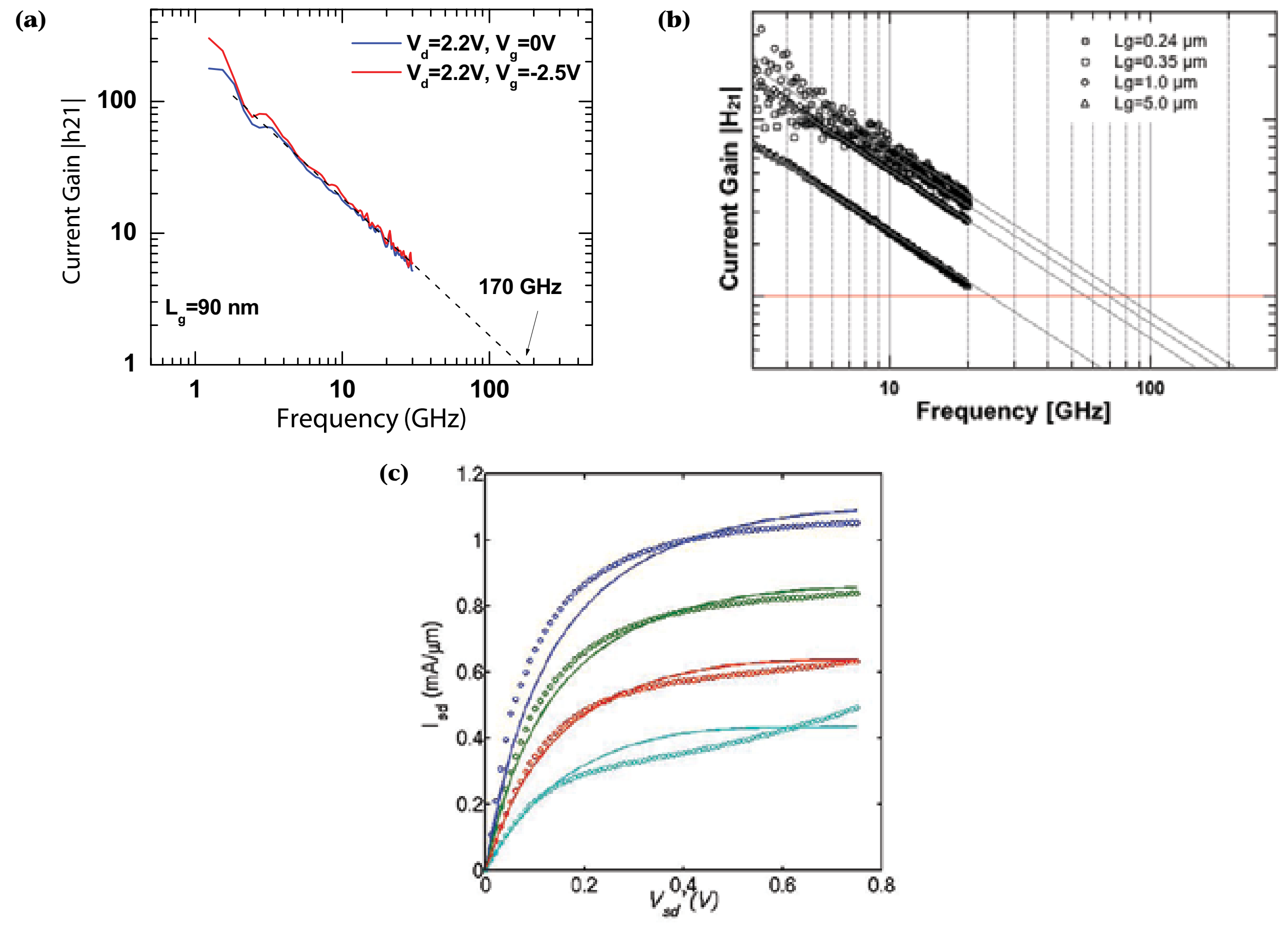

Fig. 6. *Current gain ft, max characteristics from: (a) IBM showing cut-off frequency of 170 GHz for gate length of 90 nm.[17] Reproduced by permission of* IEDM Tech. Digest, ***9.6.1-9.6.3****, 226 (2010); (b) Samsung showing cut-off frequency of 200 GHz for gate length of 0.24 μm.[18] Reproduced by permission of* IEDM Tech. Digest, ***23.5.1-23.5.4****, 568 (2010); and (c) Intrinsic I-V characteristics of 0.44 um device fabricated using B-N as gate dielectric. Solid lines indicate model fitting curves.[19] Reproduced by permission of* IEDM Tech. Digest, ***23.2.1-23.2.4,*** *556 (2010).*

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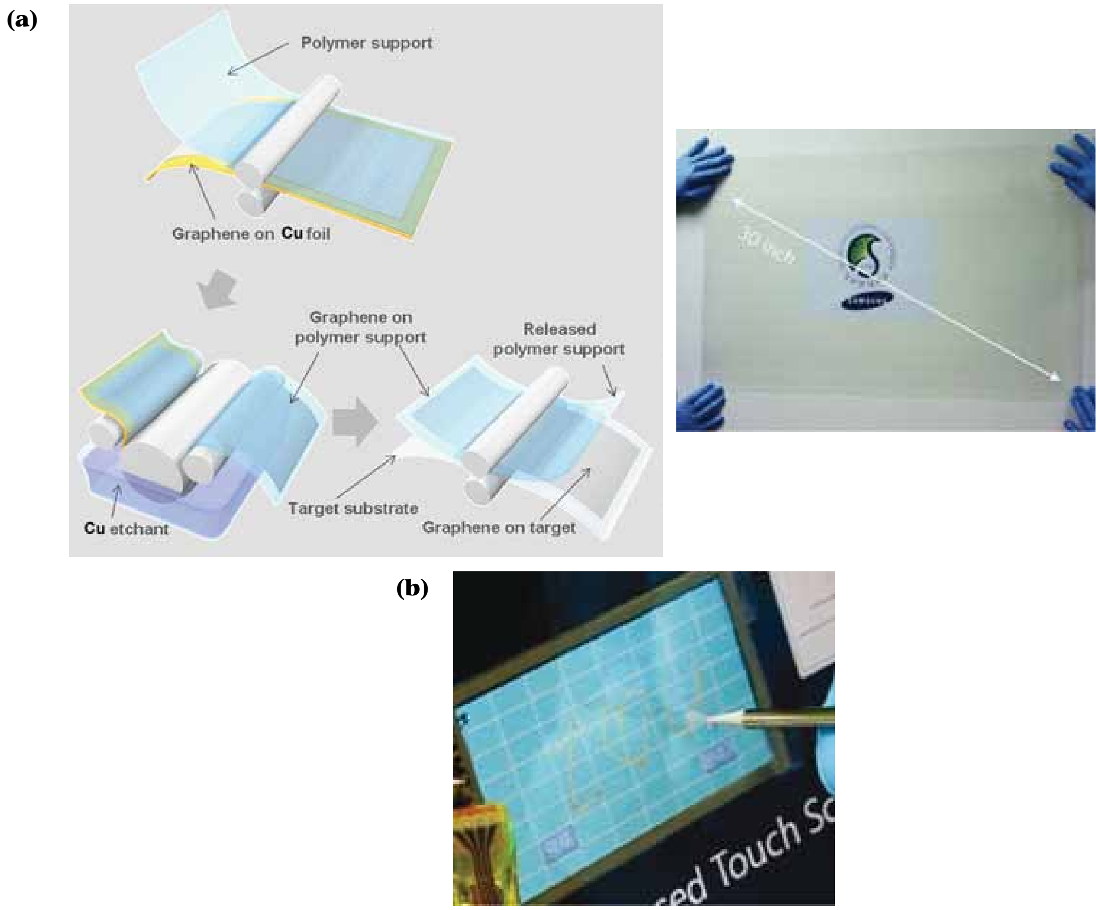

Fig. 7. *(a) Industrial production of graphene sheets. (b) Samsung's transparent touch screen technology using graphene. Reproduced with permission of* Nature Nanotechnology*, **5**, 574 (2010).*

summer of 2006 as a researcher at IBM T. J. Watson Research Center, Yorktown Heights, NY. He won the Hashimoto Prize for his best doctoral dissertation in 2007. He is a senior member of IEEE, has edited 2 books, authored and co-authored more than 50 international publications, has 3 patents and also serves as a reviewer for at least 6 journals, including the *Journal of The Electrochemical Society*. He may be reached at psrinivasan@ti.com.

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