# Graphene – Towards Nanoscale Devices –

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[Summary] Graphene, a single-atom-thick sheet of carbon atoms, is attracting a great deal of attention from both fundamental researches and applications because of its remarkable electronic, photonic and mechanical properties. When reducing the size of devices to nanometer scale, effects, such as edge and substrate friction, that are generally overlooked at larger scales should be considered. There are two types of edge structure in graphene: zigzag and armchair. Since each edge shows different electronic properties, control of the edge structure and understanding of their physical properties are indispensable for development of an ultra-small graphene devices. This article outlines the properties of graphene and introduces the processing as well as the characteristic electronic state of the zigzag edge.

### 1 Graphene

Graphene is the thinnest imaginable material with a thickness of just one atom, in which carbon atoms are bonded covalently in a honeycomb lattice (Figure 1(a)). One distinguishing feature of graphene is that it is a stable 2-dimensional material even at room temperature and appears on surfaces. There are clear differences from conventional 2-dimensional electron systems, which exist at a few hundred nm deep from the surface only at very low temperatures where thermal excitation is suppressed. This is because such systems are formed in a confinement potential between two different semi-conductors. On the other hand, graphite, a well-known material used as pencil "lead", is a stack of graphene layers. Due to the honeycomb lattice formed by covalent bonds between carbon atoms, graphene is not only mechanically strong but also resists doping with impurities in the crystal structure, while being flexible with very high crystallinity. Consequently, electrons in graphene can travel long distances without scattering, with graphene displaying 100 times more electron mobility than silicon, and 10 times more thermal conductivity than silver.

Another notable feature of graphene is its linear energy dispersion (Dirac cone) crossing at charge-neutrality points called the Dirac point (Figure 1(b)). Therefore, quasiparticles (Dirac fermions) responsible for graphene conduction is not only massless but also connote relativistic effects. Moreover, the conductivity can be largely manipulated by controlling the Fermi energy ( $E_{\rm F}$ ) using the gate-voltage field effect (Figure 1(b)). Because the electronic density of state is zero at the Dirac point, the resistance diverges greatly as  $E_{\rm F}$  approaches the Dirac point. Since the Dirac cone has no natural bandgap, a high on/off ratio cannot be obtained as electronic devices for graphene as it is. On the other hand, since graphene absorbs light over a wide spectrum range from UV to infrared, it is an extremely attractive material for photonics applications.

Here, the Dirac cone originates from so-called bipartite property of honeycomb lattice which consists of stacked triangle lattices turning rightwards (sub-lattice A) and leftwards (sub-lattice B) (Figure 1(a)). Consequently, there is some hope of being able to create a gap by breaking the sub-lattice symmetry. It is also discussed to create a gap by electronic confinement using quantum interference to apply graphene to nanoscale devices.

This article first introduces graphene and its types in sections 1 and 2, followed by a summary of graphene research trends and device applications in section 3. Section 4 comments on graphene edge states, which cannot be avoided at production of nanoscale graphene devices.



Figure 1 (a) Graphene Honeycomb Lattice with Overlapping Triangular Sub-lattices A and B Facing Different Directions
(b) Schema of Dirac Cones and Gate Voltage Dependence of Resistance; Dirac point at crossing point (charge neutrality point) between upper and lower cones. Graphene resistance changes as *E*<sub>F</sub> changes with gate voltage.
(c) Optical Microscope Image of Graphene Exfoliated on SiO<sub>2</sub> Substrate; Graphene is folded at the lower part of the image.

## 2 Graphene Types

Although we have discussed graphene as one material, it is important to realize that there are several types of graphene, depending on the production method. Graphene can roughly be classified into four: exfoliated graphene (Figure 1(c)), SiC graphene, chemical vapor deposition (CVD) graphene, and reduced graphene oxide. Unlike the first three, which are in a sheet form, reduced graphene oxide is a common powder form and is dispersed rather easily in water or several other polar solvents for use as a paste.

Exfoliated graphene (Figure 1(c)) is obtained by exfoliating a graphite source block. This was the first successful experimental method to obtain graphene in  $2005.^{1), 2}$  In this case, although one need to look for graphene since it is obtained at any place on a substrate and the size is limited to only several hundred  $\mu$ m, almost ideal graphene with excellent crystallinity can be obtained.

On the other hand, graphene is a carbide which can be produced by heating any carbon-containing material, such as an organic material. SiC and CVD graphenes are methods using this mechanism. In other words, SiC graphene is formed to precipitate carbon (C) atoms by evaporating silicon (Si) of SiC, a layered crystal of Si and C, at high temperatures. CVD graphene, on the other hand, is produced by heating methane (CH<sub>4</sub>) gas to deposit a carbon film on a metal substrate. Although SiC graphene has a large and relatively uniform single crystalline size depending on the original SiC, there is a C-rich layer between graphene and Si substrate, and graphene is strongle interacting with the substrate. In comparison, CVD graphene can be produced in larger sheets than SiC graphene and it is possible to torn and separate from the substrate rather easily due to the weak affinity with the metal substrate. However, the uniformity is not necessarily high because it is produced by depositing C atoms on a substrate.

Since there are several types of available graphene, it is important to choose proper type that matches the application. Exfoliated graphene is tend to be used at the fundamental R&D stage, while the production trend is to use CVD graphene due to its large surface area, as well as reduced graphene oxide which can be sprayed as an inkjet.

## 3 Graphene Device Applications

As well as its own unique properties, graphene can be processed directly to exploit the material properties since it is exposed to the air. As a result, graphene can be applied in many fields and it is not an exaggeration to say that the research fields are infinite. Thanks to its high electrical conductivity, the power consumption can be suppressed when it is applied to electronic devices. In addition, since it consists of carbon, a common element, it offers industry the benefit of being a relatively low-cost raw material. Actually, the graphene market is growing exponentially.<sup>3)</sup>

With a visible-light transmittance of about 98% and high electrical conductivity, graphene is an ideal transparent conductor for touch panels and transparent antennas, which have been focused on since the early stage of the graphene research. As an application to a touch panel, graphene mobilphone displays with high sensitivity, low power consumption and good color reproduction had already been developed.

Because of its high mobility and two dimensionality, graphene is introduced especially to the semiconductor industry. By applying graphene into the field effect transistors (FET), FET with THz operation speeds has been reported. Attention is also focused on FET-type graphene devices for gas and biosensing applications capable of measuring minute trace gases and viruses from changes in graphene properties. Compared to the electronic data transfer based on electrons, attention is also focused on next-generation "spintronics" devices using the spin properties of electrons. This application is based on a property that spins in graphene can travel over long distances keeping their information (phase), and it is theoretically possible to implement devices that do not consume electric power because there is no electron flow. The spin polarized zigzag edge state of graphene, which will be discussed later, makes it a useful candidate material for these applications.

At the same time, graphene is expected to demonstrate higher vibration responsivity than conventional materials when used in Micro Electro Mechanical Systems (MEMSs) applications, since graphene is another form of the lightweight element, carbon, and has an order-of-magnitude larger Young's modulus (index of rigidity) than other semiconductors, such as silicon. Although the use of graphene for MEMS<sup>1)</sup> is still limitted compared to FET devices, expansion of graphene MEMS applications is thought to be essential considering the importance of MEMS in modern technologies such as mobile-phones. Graphene MEMS R&D is still within  $\mu$ m-sizes, but once nano-scale processing of graphene becomes possible in future, it should lead to development of higher performance and lower power-consumption devices than ever, as Nano Electro Mechanical Systems (NEMSs).

It is important to note that, since graphene is exposed to the outside, it is also easily affected by the environment. Above all, the impact cannot be ignored for graphene substrates because graphene is extremely thin. For example, the mobility of graphene is easily changed by surface irregularities, consistency between substrate crystals and graphene crystals, and the ingress of water or other impurities between graphene and substrate. Although silicon dioxide (SiO<sub>2</sub>) is used as the substrate in most cases, there are a few instances when the expected mobility is not obtained. On the other hand, hexagonal boron nitride (h-BN) is commonly used as a substrate for graphene R&D, since it has a similar crystal structure to graphene and shows high consistency with graphene.

Leading graphene research started with work on the various atomically thin sheets and then widened to cover research into new materials based on these discoveries. Moreover, work on novel materials and industrial applications is progressing by physically stacking graphene and other monoatomic materials (van der Waals heterostructures).

Note 1: Due to the atom-level thinness of graphene, there is a trend towards calling  $\mu$ m-size graphene MEMS nanoscale components or NEMS, but this article uses the terms MEMS for  $\mu$ m-scale components, and NEMS for nano-scale components.

#### 4 Graphene Edge State

#### 4.1 Zigzag Edge State

MEMS and other electronic devices will probably become smaller in the future, and the effects that can be ignored for  $\mu$ m-scale devices become apparent for devices operating at the nanoscale. For instance, since the edge area relative to the surface area becomes larger, it is important to correctly evaluate the edge effect. Graphene in particular has two types of edge structure reflecting its honeycomb structure: a zigzag type (Figure 2(a)), and an armchair type (Figure 2(b)). The symmetry between sub-lattice A and B is broken close to the zigzag edge (there is an imbalance between the numbers of the two sub-lattices), while the armchair type maintains the symmetry. Consequently, it is known that the two different edge structures display completely different electronic properties. When thinking about a graphene nanoribbon (GNR) sandwiched between the zigzag edges (Figure 2(a)) and armchair edges (Figure 2(b)), the electronic state of the armchair GNR (A-GNR) is essentially the same as that of bulk graphene<sup>Note 2</sup>, whereas the zigzag GNR (z-GNR) forms a flat band at the Dirac point, indicating that an electronic state localized at the zigzag edge appears.<sup>4)</sup> Here, it is important to note that there is only sub-lattice A at one z-GNR edge (top edge in Figure 2(a)) while there is only sub-lattice B at the other edge (bottom edge in Figure 2(a)).







The existence of the zigzag edge state can be confirmed from atomic-scale measurements of the electronic state using a scanning tunneling microscope (STM). Figures 2(c) and (d) show the local electronic density of state obtained near the zigzag edge and armchair edge<sup>Note 3</sup>, respectively, found on the graphite surface.<sup>4)</sup> While no spatial change is observed near the armchair edge (Figure 2(d)), a peak appears at E = 0 (corresponds to  $E_F$ ) approaching close to the zigzag edge, clearly showing the zigzag edge state (Figure 2(c)).

Note 2: To be precise, electronic property of A-GNR changes either metal or semiconductor depending on the ribbon width.

Note 3: To be precise, edge where either the zigzag edge or armchair edge is dominant.

## 4.2 Producing Graphene Zigzag Edge

Since the armchair edge is more stable energetically, it is

not generally easy to manufacture the zigzag edge. However, a zigzag edge can be preferentially manufactured by exposing graphene and graphite to hydrogen plasma at high temperatures.<sup>6)</sup> Figures 3(a) and (b) show a hydrogen plasma etching system and light emitted by hydrogen plasma, respectively. Figure 3(c) is an STM image of the graphite surface etched by this hydrogen plasma clearly showing the formation of many hexagonal holes (nanopits) in the surface. Each of these nanopits is one atom deep (about 0.3 nm) and the zigzag edge structure can be confirmed by atomic scale observation with an STM.



Figure 3 (a) Hydrogen Plasma Etching Equipment; hydrogen gas is supplied from the right side to the left. The graphene and graphite are placed in the electric furnace and hydrogen gas is excited into plasma by applying radio-frequency (13.56 MHz) power to a coil located at upstream of the furnace.

(b) Light Emitted by Hydrogen Plasma

(c) STM Image of Surface of Hydrogen-Plasma Etched Graphite<sup>(i)</sup>; hexagonal nanopits with a depth of one atomic layer (0.36 nm) and a zigzag edge are formed. Z-GNR is obtained in the region between nanopits.

Although several graphene processing methods have been proposed, it is practically impossible to control the edge structure at the atomic scale using physical methods such as cutting. In addition, the edge must be terminated with one hydrogen atom to maintain graphene honeycomb structure to the edge. In this respect, hydrogen plasma etching, a chemical technique, can control the edge at the atomic scale and there are high expectations that edges are terminated by hydrogen. The edge is considered to be terminated by a single hydrogen atom by calculating chemical potentials, although there still be no experimental verifications.<sup>7)</sup> There are two functions in hydrogen plasma etching. One serves to create defects in graphene and graphite, while the other expands these defects into hexagonal nanopits. Therefore, if the position of the defects can be predetermined, the hexagonal nanopits might be freely arranged. It possibly offers an easy method to design and fabricate z-GNR and z-GNR network, that to create defects in a lattice arrangement by either electron-beam irradiation or oxygen-plasma etching then to expand the defects into a hexagonal nanopit with zigzag edges by hydrogen plasma etching. By configuring a free-standing GNR beam as a resonator, NEMS applications could be supported. Electronic devices using energy gaps evoked by electron confinement in nanoscale and spintronic devices using the spin polarized edge state described below are also the focus for use.

#### 4.3 Latest Research in Zigzag Edge State

It is theoretically expected that electron-spins are polarized to create a ferro-magnetic state (flat-band ferro-magnetism) even at infinitesimally small electron correlation, when there is localized electronic state at  $E = E_{\rm F}$  (Stoner criterion). The graphene zigzag edge is a good example. Although the spin polarization is unstable with a single zigzag edge, it can be stabilized with z-GNR due to the sandwiching by two zigzag edges with different sub-lattices (Figure 2(a)). Here, spins interact ferro-magnetically within an edge, while anti-ferromagnetically between edges, and overall magnetism of z-GNR becomes zero. In such spin-polarized zigzag edges, the spin unpolarized zigzag edge state is divided and the double-peak structure appeares in the electronic density of state. The peak gap depends on the spin polarization strength and should be larger as the ribbon width narrows. Spontaneously spin-polarized z-GNR is expected to be a useful spintronics material by using the zigzag edge for spin transport.

Since creation of a zigzag edge is difficult, experimental verification of the spin polarized state has long been a problem in graphene research, but scanning tunnelling microscopy/spectroscopy (STM/S) of z-GNR created by hydrogen plasma etching has provided results strongly suggestive of the spin polarized state.<sup>8)</sup> Figure 4(a) shows the local electronic density of state measured at the zigzag edge of z-GNR fabricated by hydrogen plasma etching of a graphite surface. Because graphite consists of graphene stacking slightly shifted each other, the sublattice symmetry had already been broken, and, corresponding to graphene sub-lattice A (B), there is a top (hollow) site which sits on top of another atom (on hollow site) in underneath layer. Different from the single-peak structure in the local electronic density of state measured at the isolated zigzag edge (i.e., zigzag edge without any counter zigzag edge as z-GNR in Figure 2(a)), a double-peak structure is observed at the zigzag edge in the z-GNR. The gap between the double peak at the top site ( $\Delta_{p\cdotp}^{(top)}$ ) is smaller than that at the hollow site ( $\Delta_{p\cdotp}^{(hollow)}$ ) due to the correlation with the carbon atom in the underneath layer. Moreover, as shown in Figure 4(b),  $\Delta_{p\cdotp}$ is clearly inversely proportional to the z-GNR width, indicating that the spin polarized state is stabilized as opposite zigzag edges locate closer.



Figure 4 (a) Local Density of State Measured at ZigZag Edge of z-GNR Manufactured on Graphite Surface; red (blue) dots indicate measured results for top (hollow) sites. Double-peak positions are indicated by ▼∇.
(b) Inverse Relationship between Local Electronic Den-

(b) Inverse Kelatonship between Local Electronic Defsity Of State Double-Peak Gap  $(\mathcal{A}_{p\cdot p})$  and Nanoribbon Width;  $\mathcal{A}_{p\cdot p}$  increases as width narrows.<sup>7</sup>

## 5 Conclusions

This article overviewed the properties of graphene followed by the introduction of the graphene edge structure and its electronic state which are important in applications to nanoscale graphene devices. The application range for graphene crosses many fields and almost all devices and mechanical elements could be replaced by graphene. However, there are still major hurdles to be overcomed before implementation. In particular, graphene nanoscale processing technologies and understanding and controlling obscure nanoscale effects, such as the zigzag edge state, are essential for the development of nanoscale devices. The graphite processing using hydrogen plasma etching and the evaluation of physical properties with the scanning probe techniques such as STM, introduced in this article, are expected to help overcome these problems.

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