Graphene—Novel Material for Nanoelectronics

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Graphene is a flat monolayer of carbon atoms with a two-dimensional honeycomb lattice, and many layers of it constitute graphite. Single-layer graphene has been discovered recently and found to have excellent electrical and thermal properties, making it a promising material for future electronics. We performed first-principle calculations which do not use empirical parameters and elucidated the electronic states of graphene under an electric field. We also clarified the electronic states of graphene at the interface with an electrode. We further simulated electron transport in graphene and found that it can be a channel material for high-speed and high-frequency transistors with a performance better than InP-HEMT. Moreover, we succeeded in synthesizing graphene and a composite structure consisting of graphene and vertically aligned carbon nanotubes on a substrate. In this paper, we describe our theoretical and experimental approaches aimed at future applications of graphene.

1. Introduction

Carbon is a well-known element and is contained in a great many things in this world such as organic materials that constitute organisms. Carbon is an interesting element because, even if some material is made of carbon atoms only, it can have various morphologies and characteristics depending on how carbon atoms bind together. While both diamond and graphite (which is used in pencil lead) are made of carbon as indicated in **Figure 1**, their characteristics are completely different. Graphite is a layer material and its monolayer is called graphene. As shown in Figure 1, graphene has a honeycomb structure consisting of carbon atoms. It is an ideal two-dimensional material as it is as thin as the thickness of the monolayer atoms. When graphene is given a round geometry, it forms a carbon nanotube (CNT) which is a well-known material in the field of nanotechnology.

Several years ago, it was a widely accepted argument that, while graphene does exist, isolating it is impossible because its monolayer structure is very unstable. However, a research team at the University of Manchester successfully isolated the material and clarified its electronic characteristics in 2004.[1] Electrons in graphene behave as Dirac Fermions without mass and display the half-integer quantum Hall effect.[2,3] Because of these physically interesting characteristics, many studies have been conducted on graphene since its successful isolation. On the other hand, from the viewpoint of using it in electronic devices, graphene is an attractive material because of its high electron mobility, which is theoretically estimated to be 2 000 000 cm^2/Vs[4] at the maximum. Based on an experiment, a mobility as high as 200 000 cm^2/Vs[5] has been confirmed. The mobility of an electron in silicon is around 1000 cm^2/Vs at

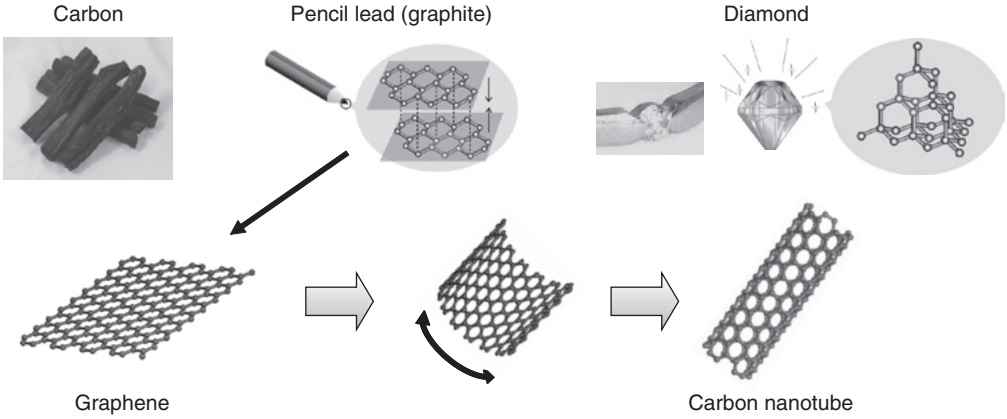

Figure 1
Various materials made from carbon.

the maximum, meaning the electron mobility in graphene is more than 100 times higher. This fact suggests that, if graphene is used as a channel material, a transistor allowing extremely high-speed operation and with low electric power consumption can be obtained. Graphene is regarded as a promising and novel channel material for large scale integration (LSI) circuits, since it is pointed out that LSIs will soon reach their limit in terms of performance enhancement through size reduction. In addition, because graphene has a high tolerance to current density and a high thermal conductivity, it is regarded as promising material for use in wiring and heat dissipation applications, too. It is also regarded as an excellent "green electronics" material because using it reduces the consumption of rare metals that are used in electronic devices, and also the amount of power consumed can be lowered when it is used.

Because the high carrier mobility in graphene is attributable to its electronic states, CNT based on a rolled graphene structure also shows a high mobility. Graphene's two-dimensional characteristics have been attracting attention in a different way to that of CNT. Because semiconductor processes currently focus on thin-layer processing, graphene, as a novel thin-layer material, would seem to have a high affinity with the semiconductor process. This is an advantage that graphene has over CNT.

Although graphene has many excellent advantages as mentioned above, there are several challenges to overcome in the actual commercialization of this material as a transistor channel. One of them is to clarify the effects of an electric field and interface on the electronic states of graphene, because such effects are important in nano-scale devices. In this situation, computer simulations are very useful because they allow us to visualize electrons and atoms and estimate their characteristics. The authors started a simulation-based study on graphene ahead of experimental ones. Fujitsu Laboratories clarified the electronic states of few-layer graphene in an electric field, as well as the electronic states at the interface with a metal electrode, using a methodology called "the first principles calculation" which does not use parameters obtained by experiments. Transistor characteristics were estimated based on this approach. In addition, we demonstrated that few-layer graphene can be an attractive material for high-speed and high-frequency transistor channels that exceed InP-HEMT, which has thus far been regarded as the best available material from the aspect of high-frequency response.[6)]

In our experiment, our recent focus has been to synthesize graphene and fabricate a transistor using graphene. Currently, there is no

established technology to synthesize graphene on a desired substrate in a uniform manner.

In this report, we will introduce some of the issues we have been focusing on recently including the following: simulation-based clarification of electronic states and electron transport characteristics in graphene; and technology to synthesize graphene.

2. Electronic states of graphene obtained through first principles calculation

As mentioned above, the first principles calculation presents the states of electrons and atoms based on a computer simulation through quantum theory without using parameters obtained in experiments. Therefore, it is possible to simulate the ideal situations where a strong electric field is applied to graphene or graphene is connected to a clean metal electrode.

In the current approach, we studied the dependence of electronic states of 1–4 layer graphene upon the vertical electric field. The characteristic band structure of single-layer graphene, which is linear around the Fermi level without mass, varied depending on the number of layers and the vertical electrical field. It is easily predicted that the transport characteristics of electrons will be degraded accordingly. In some cases, graphene forms a band gap. As shown in **Figure 2**, this band gap increases in proportion to the vertical electric field only in bilayer graphene, while there is little change in 1-, 3-, and 4-layer graphene.

In addition, we studied the electronic states of graphene in contact with a metal electrode under a vertical electric field. We calculated the electronic states based on the first principles calculation under a vertical electric field for a structure where a titanium electrode is connected to 1–4 layer graphene. **Figure 3** indicates the results for 3-layer graphene. The atomic configuration at the interface between the graphene and the metal electrode was optimized to ensure the lowest total energy. First of all,

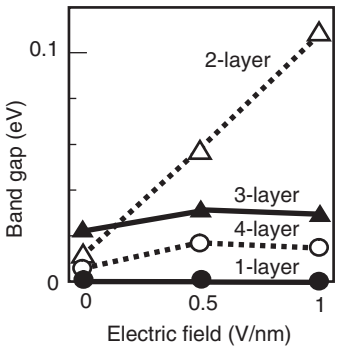

Figure 2
Bandgaps of various layers of graphene under a vertical electric field.

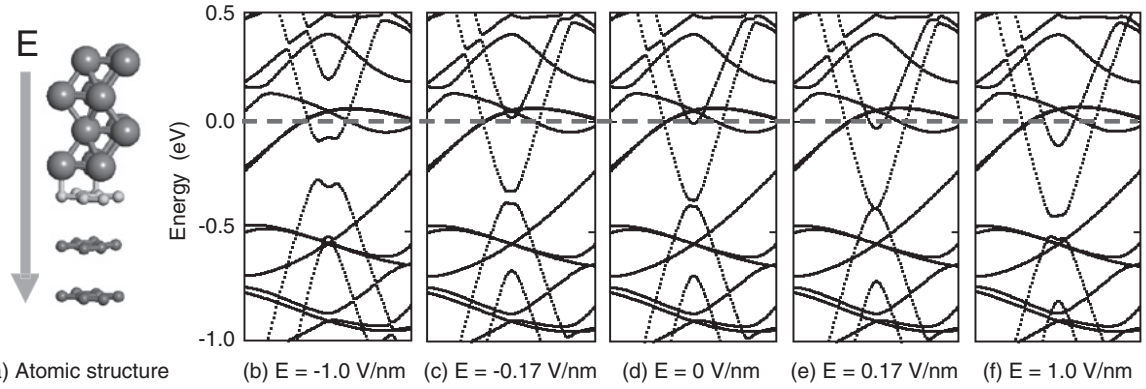

Figure 3
Atomic structure of 3-layer graphene with Ti contact and energy band structures near the Fermi level in various conditions of vertical electric fields.

when no electric field is applied, a drop in energy (of approx. 3 eV) is observed at the energy band formed by the electrons in the graphene that contacts the titanium electrode. This means that electrons are doped to the graphene. For instance, for 3-layer graphene, a band structure similar to that of bilayer graphene appears (one layer less than three layers) in the vicinity of the Fermi level that accounts for the electron conduction. In this case, unlike the case without the electrode, a small band gap is formed even when no electric field is applied. Upon applying an electric field, the band gap disappears. However, if a higher electric field is applied, the band gap appears again. In addition, when applying a reversed electric field, the larger scale of band gap opens in a monotonous manner.

In this way, with the first principles simulation it is possible to express and estimate unknown nano-level behaviors of electrons and atoms in a visible manner. Also, by conducting a further simulation using these results, it is possible to obtain transistor characteristics that can be compared with experimental results. The details of this approach are explained in the next section.

3. Simulation of electron transport in graphene

To explore electron transport phenomena in graphene in the presence of actual scattering bodies, we carried out a Monte Carlo simulation based on the assumption that there is impurity scattering, optical phonon scattering and acoustic phonon scattering. It is known that with monolayer graphene it is difficult to control the number of carriers because such graphene is a semi-metal. However, as mentioned above, bilayer graphene generates an energy gap when a vertical electric field is applied. Accordingly, by comparing the transport characteristics of monolayer graphene and bilayer graphene, we predicted the performance of an FET channel using such materials.

We used the Monte Carlo method to calculate the scattering processes and used the results for the band structures obtained through the first principles calculation as a table. **Figure 4** shows the time response of the electron speed in monolayer and bilayer graphene in a uniform horizontal electric field at room temperature. In monolayer graphene, a significant overshoot phenomenon appears and

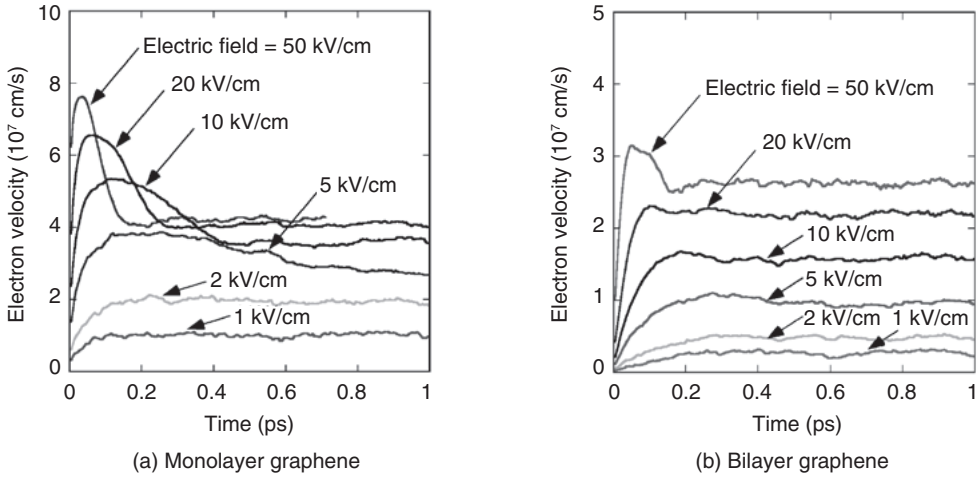

Figure 4
Electron velocity in a monolayer graphene channel and a bilayer graphene channel, as a function of the time elapsed after the application of a horizontal electric field. The bilayer graphene is under a vertical electric field of 1 V/nm.

the maximum speed reaches 7.6×10^7 cm/s when the strength of the electric field is 50 kV/cm. A high saturation speed can be maintained even in a high electric field, which is attributable to the band structure. Figure 4 (b) indicates some bilayer graphene to which a vertical electric field of 1 V/nm is applied. In this situation, the band gap is 0.16 eV. Band bending occurs when there is a gap. Because the electron has a limited effective mass in this situation, the saturation speed drops to approx. 60% of the saturation speed in monolayer graphene. Nevertheless, a still relatively high value (2.6×10^7 cm/s) is obtained which well exceeds the value obtained for silicon (1×10^7 cm/s). **Figure 5** indicates the estimated transit time of a graphene channel FET obtained by this simulation. In this situation, assuming that the channel electric field is uniform (50 kV/cm), the transit time was obtained based on the average speed and the channel length. For comparison purposes, the experimental values for InP-HEMT are also shown. InP-HEMT has been considered as the material that has the best high-frequency response. In monolayer graphene, a transit time less than 0.1 ps can be achieved with a channel length less than 65 nm, while bilayer graphene shows equivalent behaviors to those of HEMT, exhibiting a transit time shorter than 0.1 ps with a channel length less than 25 nm. These facts suggest that graphene is an attractive nano-channel material for high-speed and high-frequency transistors.

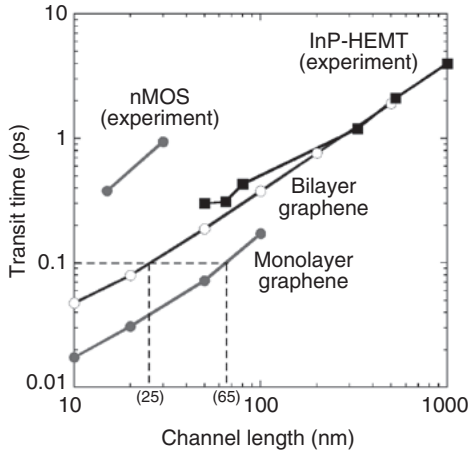

Figure 5
Electron transit time of graphene channel FETs.

4. Formation of graphene on substrate

In addition to its advantages as a transistor channel material mentioned above, graphene is also a promising material for use in interconnect and heat dissipation applications thanks to its high tolerance to current density and high thermal conductivity. However, as already mentioned, the technology to synthesize graphene on a substrate has not been established yet. In fact, various characteristics of graphene have been measured using graphene exfoliated from graphite crystals using adhesive tape. As one of the methods to synthesize graphene on a substrate, high-temperature annealing of an SiC substrate has been used, as this process causes Si atoms to sublime and produces graphene on the surface of the substrate.[7] However, this method may not be universally accepted because it requires an expensive SiC substrate. In this report, we will briefly introduce our approach to synthesize graphene on a substrate.

Recently, during an experiment to synthesize CNTs on a substrate by the chemical vapor deposition (CVD) method, we discovered a structure shown in **Figure 6**, where a thin film was observed on vertically aligned CNTs.[8] When analyzing the thin film's cross section by transmission electron microscopy (TEM), we confirmed that it is comprised of multi-layer graphene composed of several tens of layers. Further, in microscopic observation of the multi-layer graphene, we confirmed that it is not only located on the CNTs but also bonded to the CNTs. This was the first time this structure had been discovered. This structure was obtained by depositing titanium nitride and cobalt films on a substrate and carrying out thermal CVD

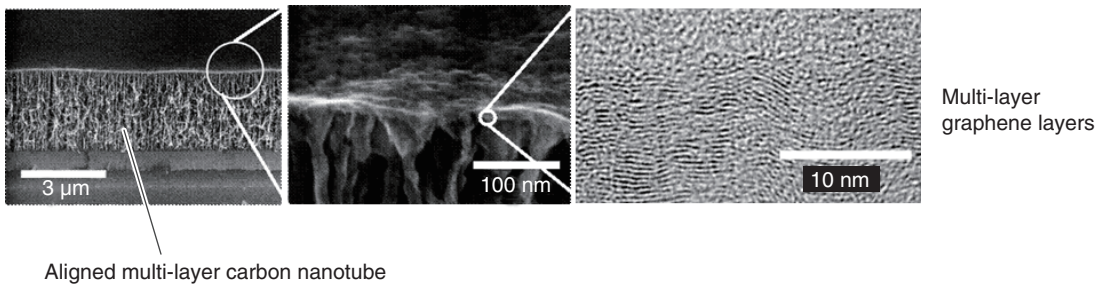

Figure 6
Electron micrographs of a nano-carbon composite structure.

(substrate temperature: 510°C) using acetylene as the source gas. The graphene formation mechanism can be considered as follows. When a substrate with a catalyst film is heated, the catalytic film first decomposes the source gas while keeping its thin-film structure, which leads to the formation of graphene on the catalyst film. Then, the cobalt film turns into particles at a certain timing and CNTs are grown downwards from those particles. If this mechanism actually takes place, the timing of turning into particles is accelerated when the cobalt layer is thinner. As a result, this experiment should lead to the thinning of graphene layers. The experimental results verified this model and we demonstrated that the thickness of the graphene layers can be controlled by altering the thickness of the cobalt layer.

Because a CNT has a linear, one-dimensional structure, it has almost no electric conductivity or heat conductivity in the directions vertical to the tube axis. However, graphene has electric conductivity and heat conductivity in the planar or two-dimensional direction. Accordingly, the novel nano-carbon composite structure we discovered here can conduct electricity and heat in every direction; i.e. from the vertical to the horizontal, or from the horizontal to the vertical. This means the material has wide-ranging applications.

While the above-mentioned composite structure is sure to be very useful, CNTs are not always necessary when graphene is used as a transistor channel. In fact, we have succeeded in synthesizing graphene as a single body. One example is shown in **Figure 7**, which is a cross-sectional TEM image of graphene formed on a substrate using an iron film as a catalyst. While the formation of graphene on a metal catalyst has been practiced for a long time in the field of surface physics,[9] those methods are not always practical because they require time-consuming processes such as cleaning the surface of a nickel crystal in an ultra-high vacuum. On the other hand, our method can be widely used because the iron catalyst is deposited on a substrate using the conventional spattering method.

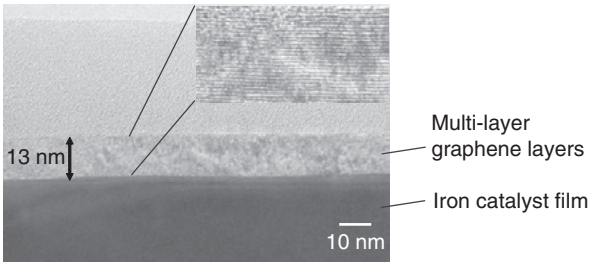

Figure 7
Cross-sectional transmission electron micrographs of multi-layer graphene formed on a substrate with an iron catalyst film.

The method using a catalyst is not an ideal method for transistor applications, because the catalyst film will remain between the graphene and the substrate. However, since the catalyst can be removed easily with acid treatment, it is possible to make a transistor by transferring the graphene onto other substrates. Some research

institutes have recently reported studies using this method.[10] We have also fabricated a graphene channel transistor using a similar method. Giving consideration to the future development of applications, the transferring method is not the best method due to factors such as the wrinkling of graphene. There are expectations for a new method of forming graphene directly on a substrate and we are currently making efforts to do that.

5. Conclusion

Graphene has been attracting public attention in recent years. We, Fujitsu Laboratories, introduced our approach to this novel material based on a simulation and through experiments. It is well known that graphene is an extremely promising material in the field of electronics. However, when using it as a material for a transistor channel without any further improvement, the insufficient ON-OFF ratio has been pointed out as an issue due to insufficient band gaps. Nevertheless, many potential solutions to band gap formation have been proposed, such as application of the vertical electric field, which is discussed above, and forming graphene in a ribbon structure. We believe that this band gap issue will be solved in the future. Fujitsu Laboratories is committed to promoting its R&D activities to realize "green" carbon electronics using graphene and CNTs in the near future.

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