

## 論文の内容の要旨

論文題目      Fabrication and Characterization of Carbon Nanotube  
and Graphene Field-Effect Transistors  
(カーボンナノチューブおよびグラフェン  
電界効果トランジスタの制作と評価)

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The semiconducting industry has been able to improve the performance of electronics systems by making smaller devices. However, this approach will soon encounter both scientific and technical limits, which is why the industry is exploring a number of alternative device technologies. For the next semiconducting industry, we have to study and find a new material which has excellent properties and high performance, for instance, graphene and carbon nanotube. First of all, there have been many advantages of using graphene for electronic and optoelectronic devices due to its outstanding electrical, mechanical, and optical transparent properties. Its many physical and electrical properties, such as extraordinarily high carrier mobility (up to  $200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ), ballistic transport distance up to  $1 \mu\text{m}$ , half-integer quantum Hall effect, superior mechanical elasticity, open up possibilities as a promising candidate to substitute silicon in the next generation electronics. However, the full potential of graphene in device industry is still restricted by several challenges. For example, it is crucial to open a bandgap in graphene to realize the “ON” and “OFF” states in electronic devices. Solutions to this challenge involve tailored

nanoribbon structure, bilayer graphene with a vertical electric field, graphene nanomeshes, etc. Moreover, due to the fact that ambient condition makes graphene behave as p-type semi-metal, to facilitate the electronic transport properties in graphene-based devices, the positive and negative carrier concentrations of graphene must be adjusted by shifting the Fermi level away from its Dirac point, so that the device can also behave as n-type and be assembled into circuits. Several approaches to locally change the carrier density have been explored using different dopants, such as gases, alkali metals, polymers, and so on. However, these approaches show disadvantages in device fabrication, such as difficult to process or pattern, or low device stability and so on. For instance, potassium doping has led to the fabrication of n-type graphene field-effect transistors (FETs) and enabled the integration of more complex devices such as intra-graphene p-n junctions with different device functions. However, such alkali dopants suffer from immediate degradation upon exposure to air, making them unapplicable for n-type doping of graphene in practical device applications. In the chapter 2, we present a protocol of tunable n-type doping of graphene by functionalizing its surface with polyvinyl alcohol (PVA) film. Using high-quality graphene grown from alcohol catalytic chemical vapor deposition (ACCVD), functionalization of its surface by this hydroxyl anion-rich polymer results in an evolution of the FETs from p-type to ambipolar or n-type. The doping level of graphene is strongly related with the treatment procedure of the PVA film, such as the solution concentration, spin-coating speed and hardening time. This PVA coating proves to be a simple and stable approach of tuning the Dirac point and doping level of graphene, and this environmentally free n-type doping enable us to fabricate more complex electronic devices such as p-n junction diodes, complementary inverters, and numerous complicated logic circuits.

Carbon nanotubes (CNTs) is one of the leading materials for next electronics and optoelectronics due to its extraordinary properties, such as electrical, mechanical, and optical properties. CNT field-effect transistors using horizontally aligned single-walled carbon nanotubes (HASWNTs) is relatively easy with high performance to fabricate devices on desired location and substrate compared with other method. CNTFETs are also expected to enable fabrication complementary circuits with high performance by control of carrier type or density using several techniques. Compared to conventional metal-oxide-semiconducting FETs, CNTFETs have several advantages. First, near ballistic

transport of carriers can be achieved which makes possible ultra-fast and high efficient devices due to its one dimensional structure. Second, high-k dielectric materials can be used as gate dielectric without degrading carrier transport in the active channel because of the absence of dangling bonds in carbon nanotubes. This leads to efficient gate field coupling that results in low subthreshold swing.

CNTFETs have been previously reported and have achieved high performance. Simple logic gates, such as, inverter, NOR, SRAM and ring oscillator, and analog circuit using CNTFETs have been demonstrated. Although these circuits show potential and a lot of challenges exist for nanotubes to fully replace CMOS technology. As different techniques point of view, individual nanotube mobility ( $\sim$  in  $10,000 \text{ cm}^2/\text{Vs}$  range) is higher than as-deposited random network one ( $\sim$  in  $100 \text{ cm}^2/\text{Vs}$  range). For CNT devices to be practically implemented in electronics, a full control of carrier type (hole or electron) and carrier concentration is fundamentally required. In this regard, the charge transfer from/to physically or chemically adsorbed species has been widely studied. Amine-containing molecules, potassium, or Benzyl viologen have been shown to n-type characteristics of CNTFETs. Some of non-chemical doping methods have also investigated, for instance, metal work function, electrostatic, and ion implementation. However, adsorption of water or oxygen have been believed to be the origin of p-type behaviors of nanotube FETs. Water or oxygen molecules induce a hole doping in the CNTs channel as well as reduce the Schottky barrier between the metal and nanotubes contact. Due to this reason, carbon nanotube FETs need to a more stabilized control carrier density of SWNTs.

Nitrogen atom has naturally been considered a good electron donor. Previous simulation results suggest the substitutional atom has been shown different phenomena compared to chemically adsorbed adatom or pyridinelike configurations. The former would lead to n-type nanotubes, whereas the later induces the p-type doped nanotubes. Recently we reported that heterostructure SWNTs were directly grown on the silicon substrate at  $800 \text{ }^\circ\text{C}$  using ethanol and acetonitrile by chemical vapor deposition system. It was characterized by x-ray photoelectron spectroscopy that nitrogen atoms are doped in our SWNTs. In the chapter 3, we report the synthesis and fabrication of nitrogen-doped horizontally aligned single-walled carbon nanotubes FETs. The growth of N-HASWNTs using CVD on an r-cut crystal quartz substrate, followed by peel off and transfer to a target substrate. Nitrogen

dopant, either in the form of a chemical adatom or the pyridinelike configuration, would lead to p-type, whereas the substitutional nitrogen dopant induces the n-type doping. Although our N-HASWNT FETs show p-type behaviors, the resulting N-HASWNTs have well-controlled density and a unique morphology, consisting of small diameter nanotubes with large bandgap ( $\sim 1$  eV). N-HASWNTs can be This FET simultaneously demonstrates a mobility of  $1,284 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and an on/off ratio  $\sim 10^6$ . We also demonstrate flexible FETs using N-HASWNT with high performance.