学位論文の要旨

Abstract of Thesis

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学位論文題目 Title of Thesis（学位論文題目が英語の場合は和訳を付記）

Study on electronic properties of two-dimensional materials by using electric double-layer transistors
（電気二重層トランジスタを用いた二次元物質の電子状態の研究）

学位論文の要旨 Abstract of Thesis

Electric double-layer transistors (EDLTs), in which the gate voltage is applied through the liquid electrolyte, have been widely utilized for controlling the electronic properties of various two-dimensional materials (2DMs). The gate voltage drops across the extremely thin EDL, which enlarges the geometrical capacitance $\bar{C}_{\mathrm{tg}}$ to enable the accumulation of high-density carriers over 10^{14} cm^{-2} in the target 2DMs. The control of carrier density in a wide range has induced various intriguing phenomena such as superconductivity, ferromagnetism, Mott transition, and ambipolar transport [1–3]. An ionic liquid (IL) or ionic gel (IG) has often been utilized for the electrolyte owing to chemical and thermal stabilities within the chemical window [4–6].

In this doctoral thesis, the dual-gate structure, which consists of the top gate with the EDL of IL or IG, and the bottom gate with the conventional solid dielectric, has been adopted for 2DMs to distinguish the electric-filed effect from the carrier-doping effect. The effect of the electric field has not yet been explored extensively, because the electric field cannot penetrate the bulk metals or semiconductors. From this point of view, few-layer graphene (FLG) and topological insulators (TIs) are ideal 2DMs to study the electric-field effect, because FLG is thinner than the penetration depth [7,8] and TIs have the surface gapless states in addition to the insulating bulk state [9,10].

The doctoral thesis is organized as follows. In chapter 1, the author introduces the background of this study. The operation principle of the field-effect transistors (FETs) and the advantages using EDLTs are explained [1–3]. The electronic properties of monolayer graphene (MLG), bilayer graphene (BLG), and TIs [7–10] which are the target 2DMs in this doctoral thesis, are also introduced in chapter 1. In chapter 2, the purpose of this study, *i.e.*, the significance of electric-field effects on 2DMs is fully described. In chapter 3, the experimental methods to fabricate and characterize EDLT devices are explained. The detailed results and discussion for the study on four topics are described in chapters 4 – 7.

In chapter 4, the electric field produced in the dual-gate FET is quantitatively evaluated by using BLG for the target material [11]. BLG is a zero gap semiconductor, whereas it exhibits the bandgap (E_g) under the electric field. BLG was placed on electron-donating self-assembled monolayers with NH_2-terminal group (NH_2-SAMs). For comparison, BLG was also prepared on the neutral SAMs of hexamethyldisilazane (HMDS) which do not donate any carriers. Both the SAMs were grown on SiO_2/Si so that the bottom gate voltage (V_{bg}) could be applied for BLG through SiO_2 dielectric. By adding the top gate voltage (V_{tg}) through IL or IG, the minimum conductivity ($\sigma_{\min}$) at the charge neutrality point (V_{n}) was detected for each V_{bg}. The E_g values at different V_{bg}'s were estimated from temperature (T) dependence of $\sigma_{\min}$ for each V_{bg}. The

value of E_g for BLG on HMDS was minimum at $V_{bg} = 0$ V and it was enhanced with increasing $|V_{bg}|$. On the other hand, the value of E_g for BLG on NH_2-SAMs was minimum at $V_{bg} = -55$ V, and it was monotonically enhanced with increasing V_{bg}. The results indicated that the value of E_g was dominated by the total electric field applied for BLG. Comparison between the two BLG devices showed that *n*-doping from NH_2-SAMs produced the additional upward electric field. It was confirmed that the combination of electron transfer from the bottom side and the EDL gating from the top side can create the large uniform electric field.

In chapter 5, the dual-gate technique is applied for MLG to study the effect of the electric field on the transport properties, although the electronic state of MLG is prospected not to be influenced by the electric field. In the same manner as chapter 4, MLG devices were prepared on the NH_2-SAMs and HMDS. In addition to σ_{min}, the mobility (μ_e and μ_h) was evaluated at electron and hole regimes by sweeping V_{tg} at fixed V_{bg}. The σ_{min} and μ_e (or μ_h) for MLG on HMDS were minimum when V_{bg} provided V_n around 10 V, and they were enhanced with increasing $|V_{bg} - V_n|$. In contrast, those for MLG on NH_2-SAMs were minimum at $V_{bg} = -100$ V, and they were monotonously enhanced with increasing V_{bg}. Considering that NH_2-SAMs produced an additional upward electric field, it was concluded that the values of σ_{min} and μ_e (or μ_h) increased in accordance with the absolute magnitude of electric field. The measurements also showed that μ_e is smaller than μ_h at the downward electric field, or *vice versa*. These results indicated that the electrons (or holes) in MLG were predominantly scattered by the cations (or anions) in the IG [12,13]. The electric field changed the arrangement of the ions to control the transport in MLG.

In chapter 6, the difference in $\bar{C}_{tg}$ for the IG on MLG and BLG is verified. Assuming that the penetration depth of the electric field is appended to the EDL thickness, $\bar{C}_{tg}$ is predicted to be smaller in BLG than in MLG [14] because of the penetration of the electric field into the interlayer of BLG to effectively increase the EDL thickness. To confirm the prediction, the author proposed the method to evaluate $\bar{C}_{tg}$ experimentally, which was inspired from the measurement of V_n as functions of V_{bg} and V_{tg}, as described in chapters 4 and 5. The value of V_n was determined from the condition that the total charge induced by the top and bottom gate voltages, $\bar{C}_{tg}V_{tg} + \bar{C}_{bg}V_{bg}$, was constant, where $\bar{C}_{bg}$ is capacitance of SiO_2 for the bottom gate dielectric. In other words, the value of $\bar{C}_{tg}$ was given by $-\bar{C}_{bg}dV_{bg}/dV_{tg}$ as a condition expressing V_n. This method allows the evaluation of $\bar{C}_{tg}$ without the contribution from the quantum capacitance. The MLG/BLG devices were prepared to minimize the effect of stray capacitance, and the measurement method was devised to reduce the experimental errors of V_n, *i.e.*, by sweeping V_{tg} slowly at the vicinity of V_n. As a result, $\bar{C}_{tg}$ in BLG was found to be smaller than that in MLG, indicating that $\bar{C}_{tg}$ depends on not only the electrolyte itself but also the penetration depth in 2DMs.

In chapter 7, the EDL gating technique is extended for a TI, $Bi_{1.5}Sb_{0.5}Te_2Se$, to identify the surface transport characteristic of TIs by controlling the Fermi level (E_F). The EDLTs were prepared from thin flakes of $Bi_{1.5}Sb_{0.5}Te_2Se$, and temperature dependence of the sheet resistivity $\rho_s(T)$ was measured to discuss the change in the E_F. The pristine $Bi_{1.5}Sb_{0.5}Te_2Se$ showed a semimetallic behavior in $\rho_s(T)$. By applying the positive V_{tg} through the IG gate, $\rho_s(T)$ curve changed to be metallic, suggesting the upward shift of the E_F. In contrast, the application of negative V_{tg} changed $\rho_s(T)$ curve to be insulating by lowering the E_F. Thus, a tuning of the E_F was successfully achieved, which is the first step toward the fundamental research and practical application of the surface transport in TIs.

In chapter 8, the author summarizes the results obtained in chapters 4 – 7. Throughout the studies, the effects of the electric field on the electronic properties of MLG, BLG, and TI were systematically investigated. So far, the EDL gating had mainly been used for the accumulation of high-density carriers. The author demonstrated that the dual-gate EDLT technique allows not only carrier accumulation in the rigid band picture but also band engineering under the electric field. The control of the electronic properties in 2DMs with the dual-gate EDLT technique provides a versatile platform for exploring unprecedented electronic phenomena as well as developing new functional devices.

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