Honors Thesis

Electric field control of magnetic moment induced in Pt

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Part1 Preface

1.1 Introduction

Nowadays, we see many devices using magnetic field or magnets in our daily lives. For example, motors are devices that turns magnetic repulsion into mechanical motion, IH heater uses magnetic field to generate thermal energy, and contactless IC cards (such as PASMO or SUICA) use magnetic field for activating the IC card. However, among the devices using magnetism, recording media are also one of the most important.

Some high density recording media, such as HDD, use magnetization direction to record information. Thin ferromagnetic materials are usually used for this type of devices. The magnets are divided into small segments, and each segment can record either 0 or 1, depending on the magnetic vector of the segment.

In the field of spintronics, many researchers are working to find more spatially, energetically, and financially efficient way of creating the recording media. One of the big problems listed is the energy issue. Conventionally, in order to record or rewrite information, magnetic field has to be applied externally. This action consumes a lot of energy, since countless numbers of the magnetic direction of the information segments has to be controlled, one by one, using electric currents. In addition, as the information segments become smaller to achieve spatially efficient solution, application of larger magnetic field is required for the magnetization direction reversal, which also results in larger energy consumption.

In order to solve this problem, the discovery of novel method for controlling the magnetic property has been long awaited. One way, which was recently discovered is magnetization reversal by spin torques. It uses the spin of the electrons to flip the direction of the magnetization [1]. However, it still uses electric current as a medium, and thus, becomes less efficient as the density of the information increases.

Compared to electric current controlling devices mentioned above, systems which use electric field are expected to consume less energy. This is because there is almost no electric current running. By creating a capacitor structure, the carriers stay at one place, spontaneously creating electric field without the need of exterior power. Therefore, controlling of the magnetic moment by electric field has been attracting attention lately.

In order to create a capacitor structure, an insulator is inserted between a gate electrode and a ferromagnetic material. Then, a gate voltage is applied to the circuit, which results in the change of carrier densities in the ferromagnetic material. This is considered to lead to transition in its magnetic properties.

At first, electric field control of magnetic properties of ferromagnetic semiconductors has
been investigated, since electric field effect has been a technique well used in semiconductor industry. As a result, change in the Curie temperature $T_C$ [2], coercivity $H_C$ [3], magnetic moment $m$ [4], and magnetization direction [5] has been reported.

Recently, not only the semiconductors, but also the ferromagnetic metals were shown to be controlled by electric field. To date, the changes in Curie temperature $T_C$ [6], coercivity $H_C$ [7], magnetic moment $M$ [8], magnetization direction [9], and domain wall velocity [10] has been reported.

As stated above, a number of changes in magnetic properties of ferromagnetic materials have been presented. However, control of magnetic properties of paramagnetic metals is yet to be widely investigated. This is due to the requirement of large modulation of carrier density could not be achieved by the conventional (electrode)-(oxide insulator)-(target metal) structure.

1.2 Purpose

The main purpose of this study is to make non-magnetic Pt ferromagnet with electric field effect. Pt has been chosen in this study since the characteristics of Pt are known to be close to that of ferromagnetic materials. In detail, Pt is often considered as an exchange-enhanced paramagnetic material which almost satisfies the Stoner’s criterion, which is the condition dividing ferromagnetic and paramagnetic.

In this bachelor’s assignment, electric field control of induced magnetic moment in Pt has been studied as an initial step to attain the final goal, control of magnetism of Pt alone on its own. Here, I focused on Pt/Co/Pt tri-layer structure in which magnetic moment is expected to be induced in both of the Pt layer through the ferromagnetic proximity effect. The enhancement or the reduction of the induced moment of the carrier modulated top Pt layer is expected to be observed as a difference in the magnetic moment.

Another purpose of this paper is to clarify the characteristics of ionic liquids, which are used for applying voltages. Since the application of ionic liquids as an insulator is relatively new, more research is necessary. The goal is to find out the accurate amount of carrier density modulation inside the target metal. In order to acquire that, the properties of ionic liquid, such as its electrostatic and electrochemical property was investigated.
Part 2 Theory and Previous Works

2.1 Electric field control of magnetism in ferromagnetic semiconductors

Although the ability to externally control the properties of the magnetic materials may bring huge technological progress considering the recent developments in spintronics, it was often assumed that it is not possible to alter the characteristics of magnetic properties once they are prepared. However, in 2000, electric field control of Curie temperature $T_C$ of ferromagnetic semiconductor was achieved [2].

The first electric field control of magnetism was observed with (In,Mn)As, which is a dilute ferromagnetic III-V semiconductor. The replacement of a part of indium by manganese results not only in the doping of the holes, but also in the appearance of localized magnetic moment. As Dietl suggests, the ferromagnetic correlations of the localized spins are mediated by the holes [11]. This correlation in the ferromagnetic semiconductor are equivalent to the Ruderman, Kittel, Kasuya, and Yoshida (RKKY) interaction, in which case, the modulation of the carrier densities would result in the change in the interaction between the localized spins. To be specific, the increase (decrease) of the holes was expected to result in the increase (decrease) of the hole mediated exchange interaction of the localized manganese spins.

Fig. 2-1-1 shows the Hall resistivity of (In,Mn)As versus magnetic field under different gate biases. At +125 V, the magnetic process seems linear which is a property seen with paramagnetic materials, while at -125 V, a clear hysteresis loop can be observed, which is a property of a ferromagnetic material. It should also be noted that the positive gate bias (direction of the depletion of holes in the (In,Mn)As layer) leads to the reduction of magnetic moment, while the negative gate bias (direction of the accumulation of holes in the (In,Mn)As layer) leads to the increase in magnetic moment, as has been expected by the theory.

Fig. 2-1-2 represents the spontaneous magnetic moment of (In,Mn)As at different temperatures under gate biases. The Curie temperature has noticeably changed by the gate biases. This shows that between 25.5 K and 27.5 K, the ferromagnetic-paramagnetic transition can be induced by the modulation of carrier densities.
Fig. 2-1-1 Hall resistivity as a function of magnetic field under different gate biases [2]. The ferromagnetic-paramagnetic transition has been observed without a change in temperature.

Starting with the control of Curie temperature $T_C$, up to date, many magnetic properties of ferromagnetic semiconductors were successfully controlled through application of electric field.

Coercivity is another characteristic which has been controlled [3]. The experiment was conducted using (In,Mn)As as a ferromagnetic semiconductor. Fig. 2-1-3 shows that the modulation
of carrier densities through the application of gate voltage results in the clear change in coercivity. Chiba has also showed that using the observed property, magnetization reversal can be triggered through the change in gate voltage biases. Although it is not yet practical, it has been proved to meet the most basic requirement as a rewritable memory device.

Fig. 2-1-3 Hysteresis curve of the electric field dependent (In,Mn)As gained by the Hall measurement [3].

Other examples of controlled magnetic properties include the magnetic moment [4] and the magnetic anisotropy [5]. In addition to these studies done from various aspects of the magnetic properties, the recent achievement of ferromagnetic-paramagnetic transition at room temperature makes the electric field control method a promising tool for the future devices [12].

2.2 Electric field control of ferromagnetic metals

The characteristics of electric field control of ferromagnetic metals are completely different from that of ferromagnetic semiconductors. Not only are the properties and theories behind magnetism different, one has to think about the screening effect of metals when applying gate voltage. When external electric field is applied to metals, itinerant electrons feels the potential, and moves around to cancel out the electric field inside. Therefore, it is believed that only the Thomas Fermi screening length from the metal surface feels the electric field and its potential gradation [13]. Thus, the experiment on electric field actuation on ferromagnetic metals are conducted using ultrathin films, in which the surface/volume ratio is large.

In 2007, modification of magnetic properties of ferromagnetic metals using electric field was first observed [7]. The experiment has been conducted using FePt(FePd) on top of Pt(Pd), and the accumulation of carrier in the alloy layer triggered the difference in coercivity as shown in Fig. 2-2-1.
Magnetic anisotropy can also be modified by the electric field [9]. In 2008, Maruyama succeeded in controlling the magnetic anisotropy of Fe ultrathin film. As shown in Fig. 2-2-2, anisotropy field and thus magnetic anisotropy energy have been modified. Assuming that the film has uniaxial crystalline anisotropy $K_u$ and surface anisotropy $K_{interface}$, the perpendicular magnetic anisotropy energy per unit volume $E_{perp}$ can be expressed as

$$E_{perp}d = \left(-\frac{1}{2}\mu_0M_S^2 + K_u\right)d + K_{interface} + \Delta K_{interface}(V) \cdots (2-2-1)$$

where $d$ is the thickness of the film, $M_S$ the saturation magnetization, $\Delta K_{interface}$ the change in interface anisotropy induced by the voltage application. According to the paper, $\Delta K_{interface}$ of 8.4 $\mu$Jm$^{-2}$ has been obtained. This difference in anisotropy energy may have originated from the change in the filling of electrons in Fe layer when voltage was applied. By applying 200 V, modulation of $2 \times 10^{-3}$ electrons per Fe atom has been achieved.
Fig. 2-2-2 Magneto-optical Kerr ellipticity for different applied voltages as a function of applied field [9]. The curve shows the perpendicular magnetic moment of 0.48 nm thick Fe ultrathin film. The left inset is an image of magnetization direction of Fe at point A and B. The right inset shows the difference of Kerr ellipticity between the voltages as a function of applied field. This shows that at point C, the difference of magnetic direction has been optimized by applying different voltages.

In 2011, the electric field control of Curie temperature has also been achieved [6]. The gate voltages of ±10 V were applied to MgO/Co/Pt/Ta (from the surface) structure with HfO$_2$ insulator, and gate electrode on top. Accordingly, the carrier density of the cobalt layer has been modulated. Hall measurement was conducted under different temperatures and spontaneous Hall resistance was measured as in Fig. 2-2-3. A modification of Curie temperature $T_C$ by over 10 degrees has been achieved. Not only does this show that Curie temperature has been controlled, it also suggests that within the range of the modulated Curie temperatures, phase transition from ferromagnetic behavior to paramagnetic behavior can be observed. Fig. 2-2-4 is the hysteresis loop of the film at different voltages. At 321 K, the voltage application of +10 V induces ferromagnetic behavior in the film, while the application of -10 V induces paramagnetic behavior.
Fig. 2-2-3 Spontaneous Hall resistivity with different gate biases near Curie temperature.

Fig. 2-2-4 Hall resistivity as a function of applied magnetic field at 321 K.

In addition, there are reports on electric field control of other magnetic properties such as the magnetic moment $m$ [8] and domain wall velocity [10]. Not only are these important result as basic science, but the control of ferromagnetic metals are also looked to for potential applications, especially in spintronics. The studies enhance the possibilities of better understandings of characteristics of ultrathin ferromagnets and possibilities of functional devices.

2.3 Electric field control of paramagnetic metals

It is natural to think that after the electric control of ferromagnetic materials has been proved possible, the electric field control of nonmagnetic materials are attracting attention. Until
now, when a magnet was necessary for devices, we had to plan out the uses and fabricate to acquire a magnet that can satisfy the obligations. However, if the electric field control of magnetism in nonmagnetic materials become possible, not only can we change the properties of the material, we may become capable to altering anything into a magnet. Without mentioning, this opens up a whole new possibility for material physics and its application fields.

In the past, the electric field control of magnetism and magnetic properties of nonmagnetic materials have not been investigated as intense as that of ferromagnetic metals. Therefore, the magnetization of nonmagnetic material by itself is yet to be accomplished. However, there has been signs of nonmagnetic materials becoming ferromagnetic-like materials.

In 2013, an electric field control of Pt has been observed [14]. Pt is often considered an exchange enhanced paramagnetic material, which nearly meets the conditions of ferromagnetism (see section 2.4). In this study, a 3.2 nm thick Pt layer has been deposited on Al₂O₃ substrate and gate voltage has been applied through ionic liquid on top of the Pt layer.

![Fig. 2-3-1 Hall resistivity ρ_H for different gate voltages and temperatures. Ionic liquid DEME-TFSI has been used for applying gate voltage.](image)

As a result, changes in magnetic behavior in Pt has been observed as in Fig. 2-3-1. When a Hall measurement is conducted on magnetic materials, the observed Hall signals will be expressed as

\[
V_{\text{Hall}} = V_{\text{NHE}} + V_{\text{AHE}} + V_{\text{PHE}} + V_{\text{offset}}
\]

where \(V_{\text{NHE}}, V_{\text{AHE}}, V_{\text{PHE}}, \text{ and } V_{\text{offset}}\) are normal Hall effect signal, anomalous Hall effect signal, planar Hall effect signal, and offset signal, respectively. Each element in the Hall signal can be
rewritten as

\[ V_{\text{NHE}} = \rho_{\text{NHE}} I_0 H_\perp \]  \hspace{1cm} \cdots(2-3-2)

\[ V_{\text{AHE}} = \rho_{\text{AHE}} I M_\perp \]  \hspace{1cm} \cdots(2-3-3)

\[ V_{\text{PHE}} = \rho_{\text{PHE}} I M_\parallel^2 \cos 2\varphi \]  \hspace{1cm} \cdots(2-3-4)

where \( \rho_{\text{NHE}} \), \( \rho_{\text{AHE}} \), and \( \rho_{\text{PHE}} \) are normal Hall resistivity, anomalous Hall resistivity, and planar Hall resistivity, respectively. Also, \( H_\perp \), \( M_\perp \), \( M_\parallel \), \( t \), \( I \), and \( \varphi \) each expresses the perpendicular element of the magnetic field, the perpendicular element of the magnetization, the in-plane element of the magnetization, the thickness of the film, the source-drain electric current, and the angle between \( M_\parallel \) and \( I \). In Fig. 2-3-1, the effect of planar Hall effect can be neglected, in which case, only the normal Hall effect and the anomalous Hall effect has to be considered.

When the applied gate voltage is 0 V, all the Hall resistivity at different temperatures seem to have the same linear relationship with the applied magnetic field \( H \). This is the effect of the normal Hall effect. Surprisingly, when gate voltage is applied, such as in Fig. 2-3-1(a) and (b), a clearly distinct data has been retrieved. This can be considered as the influence of the anomalous Hall effect, which, from equation (2-3-2), can be implied that the Pt thin film is magnetized when large magnetic field is applied. Although Shimizu concludes that the result shows somewhat superparamagnetic behavior, the mechanism of the induced local magnetic moments in Pt is has not been explained.

A similar study has been done on palladium as well [15]. Although ferromagnetic behavior of Pd is yet to be observed, Kudasov calculated and suggested that surface Pd can be magnetized by electron extraction, using the theory of itinerant magnetism.

Obinata and Hibino observed the changes in magnetic properties of Pd by electric field control of MgO/Pd/Co/Pt ultrathin film structure [16, 17]. The Co/Pt layer below Pd is known to have perpendicular magnetic moment. Through the magnetic proximity effect, Pd layer has induced magnetic moment. Considering the Thomas-Fermi screening length in metals, modulation of carrier density through application of voltage occurs only at the top Pd layer. The result shows that magnetic moment and magnetic anisotropy of induced moment in Pd has been successfully manipulated through electric field.

Fig. 2-3-3 shows the control of magnetic moment in Pd/Co/Pt layer [16]. When temperature \( T \) was sufficiently below the Curie temperature, change in magnetic moment has been observed. Applying positive gate voltage (adding of the electrons in Pd) increases the magnetic moment, regardless of the Co thickness, and vice versa. This implies that the magnetization of the topmost layer of Pd has been controlled electrically. The change in the effective ferromagnetic
thickness and the magnitude of the localized moment can be considered the cause of the change in magnetic moment. Although the result of doping electrons leading to an increase in the total magnetic moment does not agree with the calculated expectation of Kudasov, it may be considered that the difference arose from the complicated interaction between the Pd and Co/Pt layer.

![Graph showing temperature dependence of remanent magnetic moment of Pd/Co/Pt at different gate biases](image)

Fig. 2-3-3 Temperature dependence of remanent magnetic moment of Pd/Co/Pt at different gate biases [16]. Ionic liquid TMPA-TFSI was used for applying gate voltage.

In addition to magnetic moment, change in magnetic anisotropy by electric field in the same MgO/Pd/Co/Pt system has also been observed [17]. Hall measurement has been conducted and in-plane saturation magnetic field $H_S$ has been retrieved at different gate voltages. In plane saturation magnetic field corresponds to the perpendicular magnetic anisotropy. Fig. 2-3-4 shows that positive gate voltage (electron doping) strengthens the perpendicular magnetic anisotropy of the film.
In-plane saturation field as a function of gate voltage at different temperatures [17].

2.4 Stoner’s Criterion

The magnetizing mechanism in itinerant ferromagnetic materials has been revealed, and is known as the Stoner’s criterion. In ferromagnetic metals, the electrons contributing to the magnetization are itinerant electrons, therefore, the Stoner’s criterion can be applied. In the Stoner’s theory, the kinetic energy and the Coulomb repulsion are compared. When Coulomb repulsion is larger than the kinetic energy necessary to excite an electron to an unstable orbit, magnetic moment appears. The derivation of Stoner’s criterion are as follows.

When we simulate the magnetism inside a metal, we often use the Hubbard model. The Hubbard model considers the effect of tunneling from one site to the other inside the Hamiltonian. For example, ferromagnetic metals such as Fe, Co, and Ni has magnetic moment deriving from the 3d orbit. The 3d orbit is neither completely isolated from neighbor sites nor entirely stretched out. Therefore, possibility of electron hopping needs to be considered as the tunneling effect. The Hamiltonian in such a system can simply be expressed as

\[ \mathcal{H} = \sum_{i,j} \sum_{\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \]  \hspace{1cm} (2-4-1)

where \( t_{ij}, c_{i\sigma}^\dagger, c_{i\sigma}, \) and \( n_{i\sigma} \) represents an amplitude of the transition from site \( i \) to site \( j \), an operator which creates an electron at \( (i, \sigma) \), an operator which annihilates an electron at \( (i, \sigma) \), and the number of electrons at \( (i, \sigma) \), respectively. The first term of equation (2-4-1) expresses the kinetic energy of the electrons hopping from site \( i \) to site \( j \), while the second term represents the Coulomb interaction when two electrons are at the same orbit. By the way, electrons being fermions, the creation-annihilation operator satisfies the following equation.

\[ \{ c_{i\sigma}, c_{i\sigma'}^\dagger \} = \delta_{ij} \delta_{\sigma \sigma'} \]  \hspace{1cm} (2-4-2)
\{c_{i\sigma}, c_{i\sigma}^\dagger\} = \{c_{i\sigma}^\dagger, c_{i\sigma}\} = 0 \cdots (2-4-3)

Under magnetic field, equation (2-4-1) can be rewritten with the addition of a term for the Zeeman splitting.

\[ \mathcal{H} = \sum_{i,j} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} g \mu_B H \sum_{i} (n_{i\uparrow} - n_{i\downarrow}) \cdots (2-4-4) \]

Here, the Coulomb potential between the electrons in the same orbit can be simplified using the Hartree-Fock approximation, which is a popular method for solving many-body problems. The correlation term can be rewritten as

\[ U n_{i\uparrow} n_{i\downarrow} = U (\langle n_{i\uparrow} \rangle + n_{i\uparrow} - \langle n_{i\uparrow} \rangle)(\langle n_{i\downarrow} \rangle + n_{i\downarrow} - \langle n_{i\downarrow} \rangle) \]

\[ \cong U (\langle n_{i\uparrow} \rangle n_{i\downarrow} + \langle n_{i\downarrow} \rangle n_{i\uparrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle) \cdots (2-4-5) \]

Here, we think about replacing \( n_{i\uparrow} \) and \( n_{i\downarrow} \) with other quantities. Using \( n_{i\uparrow} \) and \( n_{i\downarrow} \), average number of electrons per site can be expressed as

\[ n = \langle n_{i\uparrow} \rangle + \langle n_{i\downarrow} \rangle \cdots (2-4-6) \]

Also, magnetization can be expressed using \( n_{i\downarrow} \) and \( n_{i\uparrow} \).

\[ M = g \mu_B \frac{1}{2} \sum_{i} (\langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle) \cdots (2-4-7) \]

Considering that \( g \mu_B \) is a unit of atomic magnet, magnetic moment can be represented as

\[ m = \frac{1}{2N} \sum_{i} (\langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle) \cdots (2-4-8) \]

where \( N \) is the number of sites per volume. Using equation (2-4-6) and (2-4-8),

\[ \begin{cases} \langle n_{i\uparrow} \rangle = \frac{1}{2} n - m \\ \langle n_{i\downarrow} \rangle = \frac{1}{2} n + m \end{cases} \cdots (2-4-9) \]

is deduced. By substituting equation (2-4-5) and (2-4-9) into the Hamiltonian (2-4-4), the Hartree-Fock approximation of the Hamiltonian is derived as

\[ \mathcal{H}_{HF} = \sum_{i,j} \sum_{\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + (Um + \frac{1}{2} g \mu_B H) \sum_{i} (n_{i\uparrow} - n_{i\downarrow}) + \text{const.} \]

\[ = \sum_{i,j} \sum_{\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + (Um + \frac{1}{2} g \mu_B H) \sum_{k} \sum_{\sigma} \sigma c_{k\sigma}^\dagger c_{k\sigma} + \text{const.} \]

\[ = \sum_{k} \sum_{\sigma} \left\{ \epsilon_k + \sigma(Um + \frac{1}{2} g \mu_B H) \right\} c_{k\sigma}^\dagger c_{k\sigma} + \text{const.} \cdots (2-4-10) \]

where
\[ \varepsilon_k = \sum_j t_{ij} e^{-i(k \cdot (r_i - r_j))} \]  \hspace{1cm} \cdots (2-4-11)

Therefore, the effective magnetic field can be expressed as
\[ g \mu_B H = 2U m + g \mu_B H \]  \hspace{1cm} \cdots (2-4-12)

Using the Fermi distribution function \( f(\varepsilon) \) and the density of states \( \rho(\varepsilon) \)
\[ f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \]  \hspace{1cm} \cdots (2-4-13)
\[ \rho(\varepsilon) = \frac{1}{N} \sum_k \delta(\varepsilon - \varepsilon_k) \]  \hspace{1cm} \cdots (2-4-14)

we can express \( m \) and \( n \) as the following self-consistent equation
\[ m = \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon) \left[ f(\varepsilon - \frac{1}{2} g \mu_B H) - f(\varepsilon + \frac{1}{2} g \mu_B H) \right] \]  \hspace{1cm} \cdots (2-4-15)
\[ n = \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon) \left[ f(\varepsilon - \frac{1}{2} g \mu_B H) + f(\varepsilon + \frac{1}{2} g \mu_B H) \right] \]  \hspace{1cm} \cdots (2-4-16)

By applying Sommerfeld expansion
\[ \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon g(\varepsilon) + \frac{\pi^2}{6\beta^2} g'(\varepsilon) + O\left(\frac{1}{\beta \mu}\right)^4 \]  \hspace{1cm} \cdots (2-4-17)

magnetic moment \( m \) can be expressed as
\[ m = \rho(\varepsilon_F) \left( \frac{1}{2} g \mu_B H \right) \left[ 1 - \frac{\pi^2}{3\beta^2} \left( \frac{\rho(\varepsilon_F)}{\rho(\varepsilon_F)} - \frac{\rho(\varepsilon_F)}{\rho(\varepsilon_F)} \right) + \cdots \right] + O\left(\frac{1}{2} g \mu_B H\right)^3 \]
\[ \cong \frac{1}{2} \rho(\varepsilon_F) g \mu_B H \]  \hspace{1cm} \cdots (2-4-18)

Using equation (2-4-12) and (2-4-18), permeability can be written as
\[ \chi = \frac{m}{H} = \frac{g \mu_B \rho(\varepsilon_F)}{1 - U \rho(\varepsilon_F)} \]  \hspace{1cm} \cdots (2-4-19)

The difference between paramagnetic and ferromagnetic materials are
\[ \{ \text{paramagnetic; } \chi \text{ positive and finite} \}
\[ \{ \text{ferromagnetic; } \chi \text{ negative or infinite} \} \]  \hspace{1cm} \cdots (2-4-20)

Therefore, the conditions of metals being ferromagnetic is given as below:
\[ U \rho(\varepsilon_F) \geq 1 \]  \hspace{1cm} \cdots (2-4-21)

Generally, the exchange-correlation integral \( U \) is fixed, leaving the density of states at Fermi level \( \rho(\varepsilon_F) \) the decisive factor for ferromagnetic-paramagnetic transition.

Platinum, which is the element investigated in this study, is recognized as the exchange-enhanced material whose density of states at Fermi level almost satisfies the Stoner’s criterion of ferromagnetism. Fig. 2-4-1 shows the calculation result of the density of states and the
number of occupied states of the bulk Pt [18]. The figure shows that a slight decrease in electrons (decrease in Fermi energy) can cause increase in the density of states, which may trigger a ferromagnetic-paramagnetic transition. Therefore, magnetism in paramagnetic materials may be effectively expressed through application of electric field.

Fig. 2-4-1 Density of states $D(\varepsilon)$ and number of occupied states $N(\varepsilon)$ for bulk Pt with spin-orbit interaction [18]. The orange line shows the Fermi energy.

Sigalas has calculated both the exchange-correlation integral and density of states for bulk Pt [19]. In fcc crystalized bulk Pt, the exchange-correlation integral $U = 0.0217$ and the density of states at Fermi energy $\rho(\varepsilon_F) = 13.587$. In this case, the Stoner’s criterion for ferromagnetism is not fulfilled, since $U\rho(\varepsilon_F) \approx 0.6$. Considering that the shape of the density of states looks like that of Fig. 2-4-1, it seems difficult to satisfy the Stoner’s criterion with small carrier modulation because even if the Fermi surface was modulated to the nearest peak, it is still smaller than $15$ (Ry · atom)$^{-1}$.

However, one has to remember that, in reality, conditions are much different. First, in order to modulate carrier densities, ultrathin film has to be prepared because the modulation only occurs on surface layers in metals. The dimension of the material seems an important issue, since the density of states may undergo large modification in such case. In palladium, which is also an exchange-enhanced paramagnetic material, it has been shown that the fine particles of few nanometers in size show ferromagnetic behavior [20, 21]. Second, the Pt ultrathin film will be affected by the neighboring materials. The orbital coupling with other elements cause not only a
difference in crystallizing structure, but also a direct influence to the direction of the spin of an
electron through spin-orbit interaction. Therefore, the change in dimensions and interfacial
interaction could cause an indispensable change in density of states and exchange-correlation
integral.

2.5 Magnetic Properties of Pt/Co/Pt

In this study, Pt/Co/Pt/Ta and MgO/Pt/Co/Pt/Ta ultrathin films are mainly used. The major
structure contributing to the magnetization of the film is the Pt/Co/Pt. The following section will
describe the basic magnetic properties of this structure.

2.5.1 Perpendicular magnetic anisotropy of Co/Pt

Magnetic anisotropy is an important magnetic property. It is necessary to understand the
magnetic anisotropy and direction to construct systems using magnets.

Magnetic anisotropy is known to originate from many factors. They include
magnetocrystalline anisotropy, shape anisotropy, interface anisotropy, elastic anisotropy, and induced
anisotropy. In an ultrathin film, the contribution of shape anisotropy cannot be ignored.

Shape anisotropy is created by diamagnetic field. Diamagnetic field exists in any magnet,
in the direction opposite of the magnetization direction. The diamagnetic field $H_d$ is created by
magnetization $M$, therefore, they can be expressed as

$$\mu_0 H_d = -N_i M_i \quad (i = x, y, z) \quad \cdots (2-5-1)$$

where $N_i$ is a diamagnetic constant in the direction $i$. $N_i$ is a factor only dependent on the shape
of the magnet. The diamagnetic field of thin film can be expressed using the physical quantities
defined in Fig. 2-5-1, supposing that the magnetization direction is perpendicular to the film. In such
a case, magnetic flux density $B$ inside and outside of the film must be continuous.

$$B_{in} = B_{ex} \quad \cdots (2-5-2)$$

Therefore,

$$\mu_0 H_{in} + M = \mu_0 H_{ex} \quad \cdots (2-5-3)$$

Also, the inner magnetic field can be expressed as

$$H_{in} = H_{ex} + H_d$$

$$= H_{ex} - \frac{N_z M}{\mu_0} \quad \cdots (2-5-4)$$

From equation (2-5-3) and (2-5-4),
\[ M(1 - N_z) = 0 \] \hspace{1cm} \cdots (2.5.5)

Therefore, \( N_z = 1 \) is obtained. However, in the case of in-plane magnetization, magnetic poles can be considered so far apart compared to perpendicular magnetization that the diamagnetic field originating from the magnetization can be ignored. In such a situation, \( N_x = N_y = 0 \). Hence it follows that in ultrathin films, magnetization direction is likely to face toward the x-y plane.

\[ \text{Fig. 2-5-1 Definition of physical quantities for calculating the diamagnetic field of a thin film.} \]

However, in the case of Co/Pt, interface anisotropy act to turn the magnetization of Co toward the perpendicular direction. Because the influence of this interface anisotropy is larger than that of shape anisotropy, Co/Pt ultrathin film is known to have perpendicular magnetic anisotropy [22-26].

It is difficult to fully understand the cause of this anisotropy, because the contributing factors cannot be separately evaluated. However, it is widely believed that the fcc(111) crystallized bottom Pt layer interacts with Co through electron orbits and aligns Co atoms in the fcc(111) direction. Reformed Co orbits then interacts with the electron spins through spin-orbit interaction, and faces the perpendicular direction.

It should be noted that there are conditions for Co/Pt having perpendicular magnetization. Kisielewski studied the Co thickness dependence of the Pt/Co/Pt structure [25]. It is stated that in Pt/Co/Pt structure, the thickness of Co is important. If Co is too thin, reduction of the Co coordinance results in vanishing of magnetization, while thick Co layer would result in decrease in perpendicular anisotropy. Fig. 2-5-2 shows the effective anisotropy of the film. The linear part with thickness over 1nm is considered to be hcp crystallized and faces in plane direction at about 1.6nm. The zone left of 1nm is believe to be fcc crystallized as an influence from the bottom Pt layer. The cause of decrease in anisotropy as the decrease in thickness of Co layer is not fully understood,
however such influence as magnetoelastic effects [27] and Co-Pt alloys [28,29] can be considered. Zeper also observed a similar curve with a 50nm thick Co/Pt superlattice structure [23].

Fig. 2-5-2 Effective anisotropy $K_{eff}$ times the Co layer thickness $d$ as a function of $d$ [25].

In 1992, Kyuno calculated the anisotropy of Co/Pt as a function of electron filling of the band [24]. It was proved theoretically that with the usual electron filling, the system is perpendicularly magnetized, as in Fig 2-5-3. It also implies that electrical field control of magnetic anisotropy is possible, although large amount of carrier modulation is necessary.

Fig. 2-5-3 Magnetic anisotropy energy of Co/Pt for wide range of bandfilling [24]. The arrow shows the number of valence electrons in Co/Pt, which is 29.

2.5.2 Magnetic proximity effect and induction of magnetic moment

As stated in section 2.4, Pt has large Stoner factor though not large enough to satisfy the criterion. However, due to the large exchange enhancement, Pt can be significantly magnetically
polarized in the vicinity of ferromagnetically ordered atoms. This is called the magnetic proximity effect.

Magnetic proximity effect is an important matter in spintronics and has been investigated [30-33]. Obinata compared the difference of magnetic moment between Co/Pt, Pd/Co/Pt, and Pt/Co/Pt as in Fig. 2-5-4 [33]. An increase in magnetic moment is believed to originate from the induced magnetic moment in Pt or Pd.

Fig. 2-5-4 Co thickness dependence of the magnetic moment per surface area at 10 K [33]. The structures of the samples are Co(t_{Co}^{eff})/Pt(4.1 nm), Pd(1.7 nm)/Co(t_{Co}^{eff})/Pt(4.1 nm), and Pt(4.1 nm)/Co(t_{Co}^{eff})/Pt(2.1 nm). The dotted line represents calculated value of the bulk Co directly applied to thin film thickness.

Geissler and Suzuki observed the induced magnetic moment of Pt in Co/Pt structure and discovered the relationship between the induced magnetic moment in Pt and the distance from Co layer using X-ray Magnetic Circular Dichroism (XMCD) [31, 32]. Geissler concluded that strong magnetic moment is induced in Pt up to 1nm from Co. Specifically, magnetic moment of about 0.21 \( \mu_B \) is induced per Pt atom within 0.3 nm from Co layer and decreases exponentially as the distance increases, as shown in Fig. 2-5-5. Suzuki has also done a similar experiment on Co/Pt and deduced the induced orbital moment and spin moment as in Fig. 2-5-6. Similar to Geissler’s results, induced magnetic moment almost vanishes over 1nm from the interface, which corresponds to 4 atomic layers. The Pt atom adjacent to the Co layer was calculated to have magnetic moment of 0.66 \( \mu_B \). Of this magnetic moment, 14 % was observed from the orbital moment and the other 86 % from spin
moment. The ratio was almost fixed for all the layers.

Fig. 2-5-5 Profile of the induced Pt 5d magnetic polarization per Pt atom (straight line) and per layer (dotted) [31]. The image of chemical density profile which corresponds to the roughness of the surface.

Fig. 2-5-6 Distribution of the Pt spin and orbital magnetic moments as a function of the distance from the Co-Pt interface [32].

The strong induced magnetic moment is believed to be as a result of the hybridization of Co 3d orbit and Pt 5d orbit. The strong spin-orbit coupling characteristic of Pt may be enhancing this
effect, which is implied in Fig. 2-5-6.

2.6 Characteristics of ionic liquid and electric double layer capacitor

2.6.1 Basic properties of ionic liquid and electric double layer capacitor

Ionic liquid, also known as room temperature molten salt, is a combination of cation (positive ion) and anion (negative ion) that exists as a form of liquid at room temperature. Usually, an ionically bonded material, such as sodium chloride, would have a high melting/freezing temperature because the strong ionic bond makes it stable. However, when the size of each ion becomes large enough, the bond between the cation and anion becomes unstable, lowering the melting/freezing point below or around room temperature.

Nowadays, ionic liquid is look upon as a promising solution for many fields of science [34-36]. This is because of its peculiar features, for example, it is liquid that only consists of ions, it has 0 vapor pressure, it is inflammable, and its density can be easily manipulated [36, 37]. It is very important in the field of electric field control as well, because ionic liquid creates electric double layer (EDL).

EDL is formed when ions in a substance can move around freely. When voltage is applied, the scattered ions in a substance gathers up to cancel the electric field created inside the substance, which is similar to the electrons inside metal. Then the ions gather around the surface and create capacitor structure as in Fig. 2-6-1(a).

Fig 2-6-1 (a) Ions in ionic liquid can move around freely and creates EDL at the interfaces. The distance between the carriers at the interface is very short, which implies that a capacitor with large
capacitance is created. (b) Conventional capacitor structure using solid insulator. Even if an insulator with large dielectric constant was used, the long distance between gate electrode and the thin film decreases the capacitance of the structure.

Thinking of applying gate voltage, the conventional way of inserting an insulator in between the target metal and the electrode may be the simplest solution (Fig. 2-6-1(b)). However, the use of ionic liquid enables us to dope more electrons/holes inside the target metal, compared to this conventional way. This comes from the difference in thickness of the capacitor structure. The capacitance is calculated by the following equation:

\[ C = \frac{\varepsilon_0 \varepsilon_r S}{d} \]  

\[ \cdots (2-6-1) \]

where \( \varepsilon_0 \), \( \varepsilon_r \), \( S \), and \( d \) stands for dielectric constant, relative permittivity, surface area of the capacitor, and the thickness of the capacitor, respectively. Since EDL capacitor is thin, meaning small \( d \), the total capacitance \( C \) of the system is large. Therefore, large modulation of carrier density is made possible.

2.6.2 Large carrier modulation through the use of electric double layer capacitor

The application of ionic liquids can drastically change carrier density, which induces large physical property modification. Shimamura used ionic liquid to modify the magnetic properties of the Co/Pt structure and succeeded in observing a change of nearly 100 K in Curie temperature (Fig. 2-6-2) [38]. This suggests a possibility of clear ferromagnetic-paramagnetic transition at room temperature.
Fig. 2-6-2 Temperature dependence of the magnetization at external magnetic field of 2 Oe [38]. The red, black, and blue dots each represents the magnetization at applied voltage of +2 V, 0 V, and -2 V.

Here, Shimamura calculated the difference in capacitance using an ionic liquid and a solid insulator. First, the capacitance $\text{HfO}_2$ is calculated as frequently used solid insulator. Assuming that voltage window of $\Delta V_G = +20 \text{ V}$ was applied to 50 nm $\text{HfO}_2$ whose dielectric constant is about 25, the carrier modulation per surface area can be calculated as

$$\frac{\Delta q}{S} = \frac{C}{S} \Delta V = \frac{\varepsilon_0 \varepsilon_r}{d} \Delta V \sim 5.6 \times 10^{13} \text{ cm}^{-2}$$

(2-6-2)

On the other hand, capacitor by ionic liquid can be calculated using a model as in Fig. 2-6-3. Here we suppose a series capacitor circuit. In such a circuit, assuming that $C_{GE} = C_{TF}$

(2-6-3)

two capacitors can be unified by

$$\frac{S}{C_{\text{total}}} = \frac{S}{C_{GE}} + \frac{S}{C_{TF}} = \frac{2S}{C_{TF}}$$

(2-6-4)

Shimamura measured the unified capacitance to be $6.3 \frac{\mu F}{\text{cm}^2}$. Therefore, with the application of voltage window of $\Delta V_G = 4 \text{ V}$, the carrier modulation per surface area can be calculated as

$$\frac{\Delta q}{S} = \frac{C_{TF}}{S} \Delta V = \frac{2C_{\text{total}}}{S} \Delta V \sim 3.1 \times 10^{14} \text{ cm}^{-2}$$

(2-6-5)

which is about 5 times larger than that of $\text{HfO}_2$. 

23
Fig. 2-6-3 Model of the capacitor structure of EDL. A capacitor created at the gate electrode side is put $C_{GE}$, while a capacitor created at the thin film is put $C_{TF}$.

Although the model for the EDL capacitor introduced above may be roughly correct, the physical picture in reality may need some modification to this model. McCafferty suggests that many systems including metal/solution interface system can be simplified to a capacitance-resistance parallel circuit (Fig. 2-6-4) [39]. The impedance of the circuit can be expressed as

$$Z = R_S + \frac{R_P}{1 + (i\omega CR_P)^{1-\alpha}} \quad \cdots (2-6-6)$$

where $0 \leq \alpha < 1$ is a measure of the departure from ideality. Each physical quantities can be separately deduced by measuring impedance at different frequencies and fitting it with the equation. Also, an innovative way of analyzing the data called Cole-Cole plot, has been introduced where plotting the imaginary part of the impedance by the real part of the impedance illustrates a semicircle that directly shows the separated physical quantities [40].

Fig. 2-6-4 Equivalent circuit for metal/solution interface [39]. $C$ is the double layer capacitance, $R_S$ the solution resistance, and $R_P$ the resistance of charge transfer process.
However, in an ionic liquid, two EDL capacitors are created, therefore model circuit needs to be expressed as in Fig. 2-6-5. Here, assuming that

\[ C_{GE} = C_{TF} = C_{EDL}, \quad R_{GE} = R_{TF} = R_{EDL}, \quad \alpha = 0 \]

the impedance of the circuit can be expressed as

\[
Z = R_{IL} + \frac{2R_{EDL}}{1 + i\omega C_{EDL}R_{EDL}}
\]

\[
= R_{IL} + \frac{2R_{EDL}}{1 + (\omega C_{EDL}R_{EDL})^2} - i\omega \frac{2C_{EDL}R_{EDL}^2}{1 + (\omega C_{EDL}R_{EDL})^2}
\]

\[
\cdots \ldots \ (2-6-8)
\]

In such a model, large \( R_{EDL} \) is necessary for decent capacitor characteristics as a whole circuit to increase the ratio between the imaginary and real part of the impedance. This agrees well with the qualitative solution, because less charge transfer process would ensure large accumulation of carriers, thus better quality as a capacitor.

![Fig. 2-6-5 Revised model circuit of ionic liquid. \( R_{IL} \), \( R_{GE} \), and \( R_{TF} \) stands for the resistance of ionic liquid, resistance of charge transfer process through gate electrode side of EDL, and resistance of charge transfer process through thin film side of EDL, respectively.](image)

### 2.6.3 Electrochemical properties of ionic liquid

In section 2.6.2, the electrostatic nature of EDL and ionic liquid has been observed. However, in reality, they are more sophisticated since electrochemical nature must also be taken into consideration. In the following text, some characteristics and measurement on chemical and electrochemical nature of ionic liquid will be shown.

#### 2.6.3.1 Glass transition
Glass transition is a reversible transition of amorphous materials from glass-like state to rubber-like state. Glass transition occurs when liquid is cooled at a certain speed and becomes a supercooling state. Above glass transition point, the molecules of the amorphous materials can move around, but are viscous, while below glass transition point, they become crystalized and the movement of molecules are regulated.

The glass transition point can be identified through calorimetry. Calorimetry is a scientific measurement for determining the changes in energy of a system by measuring the heat exchanged with the surroundings. Sato measured the temperature dependence of endothermic and exothermic properties of N,N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) and identified the glass transition point of DEME-TFSI to be -91 °C (Fig. 2-6-6) [41].

![Graph showing glass transition point](image)

Fig. 2-6-6 Glass transition point of DEME-TFSI measured by differential scanning calorimetry [41]. Heating and cooling rate were set 1 °C/min. $T_g$ stands for the glass transition point.

Glass transition point can also be figured out by its electric properties. Yuan has figured the glass transition point of ionic liquid through the change in leakage current [42]. At the transition point from rubber state to glass state, ideally, no current is supposed to flow. Therefore the change in electric properties can be considered one of the signals for determining the glass transition point.
2.6.3.2 Viscosity

When the ionic liquid is rubber-like state, the molecules can move around slowly, and viscosity arises. The viscosity of ionic liquids is an important factor for their electric characteristic as well. Ue observed the temperature dependence of the capacitance and conductivity for some ionic liquids [43]. The difference in temperature causes change in viscosity (i.e. higher temperature means low viscosity and vice versa), which effects the movement of ions. Fig. 2-6-8(a) shows that the conductivity increases as temperature increases. This is because at high temperature, ions can move around easily and can transmit carriers through the movement of ions. Fig. 2-6-8(b) shows that the capacitance also rises with temperature increase. The reason can be discusses similarly, that when the ions can move around easily, the accumulation of ions at the capacitor is quickly and easily done.
2.6.3.3 Cyclic voltammetry and electrochemical window

Cyclic voltammetry is an electroanalytical technique for the study of electroactive materials [44]. The measurement in electrochemical field of study is done using three electrodes as in Fig. 2-6-9. The desired potential is applied between a working electrode and a reference electrode. The current required to sustain the electrolysis is provided by the auxiliary electrode.
Voltage is applied between the working and reference electrode as a function seen in Fig. 2-6-10. The amplitude of the voltage, time width, and the number of cycles can be changed accordingly. By observing the current, reduction-oxidation reaction can be observed, since such reaction consumes or emits electrons. The graph is usually plotted against the voltage as in Fig. 2-6-11. It can be observed that TMPA-TFSI reacts at the voltage of around +2.6 V and -3 V and it is known as the decomposition voltage [45]. When decomposition occurs, electrolytes are broken down and its chemical and physical properties will be changed. Therefore, it is important to recognize the decomposition voltage and not to go beyond its limits during the experiment.

Fig. 2-6-10 Example of function of voltage application [44].

Fig. 2-6-11 Result of cyclic voltammetry measurement of ionic liquids [45]. Scan rate was set 50 mV/sec and temperature at 25 ºC. 1: trimethylpropylammonium bis(trifluoromethylsulfonyl)imide (TMPA-TFSI), EMI: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) (EMI-TFSI).

2.6.3.4 Frequency dependent measurement
Unlike an ideal capacitor where the system contains one capacitor and no resistive structure, ionic liquid contains multiple RC parallel circuits. In addition, chemical reaction at the interface may also have to be considered. Yuan measured the frequency dependence impedance of ionic liquid between Pt electrode and ZnO [46]. Fig. 2-6-12 shows the frequency dependence of the phase angle. The closer the values are to -90º, the better the efficiency of the circuit as a capacitor. From the figure, we can see that the circuit contains three frequency domains. The fastest switching regime accounts for the RC parallel circuit of the ionic liquid itself, as expressed as $R_{IL}$ and $C_{IL}$ in the inset of Fig. 2-6-12. The second frequency domain which has a peak at around 10 Hz is the EDL RC parallel circuit domain. Finally, the blue regime indicates the region where redox reaction at the interface of ZnO cannot be ignored. Irregular behavior observed at different DC biases may be due to the charging of electrochemical pseudocapacitance. A circuit with such a frequency dependent property can be expressed as shown in inset of Fig. 2-6-12. $W$ indicates the Warburg impedance for electrochemical pseudocapacitance.

Fig. 2-6-12 Room temperature impedance spectroscopy of Pt/ionic liquid/ZnO structure [46]. AC voltage of 5 mV has been applied with the DC bias which is indicated inside the figure. The upper inset shows the structure of the system. The bottom inset shows the equivalent electric circuit of the system.

As mentioned in section 2.6.3.1 and 2.6.3.2, the ionic liquid has temperature dependence. Therefore it is logical to think that the frequency dependence contains temperature as a variable. Fig. 2-6-13 shows the temperature-frequency mapping of the phase angle. As the temperature decreases, all the charging regions seem to shift to the lower frequency domain. The reasons can be attributed
to the low heat energy to induce chemical reaction, and more solid-like state in ionic liquid which make is difficult for the carriers to move around.

Fig. 2-6-13 Temperature-frequency mapping for the phase angle of the Bode plot [46]. The yellow curve, drawn by using valley points of phase angles, is the critical boundary to distinguish three charging mechanism.

2.6.3.5 The origin of the pseudocapacitance and Warburg impedance

The Warburg impedance is believed to originate from the chemical reaction of impurities at the surface of the ionic liquid. Yuan has produced proton induced ionic liquid by controlling the moisture of the atmosphere [47]. Some of the water molecules will be ionized inside the ionic film and work as a pseudocapacitance. Fig. 2-6-14 shows the frequency dependent capacitance of the proton induced ionic film. Compared to the normal ionic film, proton ionic film work as a better capacitor in the low frequency region. Considering the result shown in Fig. 2-6-12, the pseudocapacitance can be attributed to the chemical reaction of particles like water that becomes ionized at low frequency regime and work as a carrier of the EDL capacitor.
Fig. 2-6-14 Frequency dependence of EDL capacitance [47]. PIL stands for proton induced ionic liquid and IL stands for the normal ionic liquid. The experimented structure is Pt/ionic liquid/Pt. DEME-TFSI was used as an ionic liquid.
Part 3 Experimental Method

3.1 Sample Deposition

In this study, all the experiments were conducted using thin films. The films were deposited by using rf sputter.

3.1.1 rf sputter

Sputtering is a way to create thin films by scattering the target substances using the accelerated plasma particles. Rare gases, in this case, xenon, were used as the plasma particles.

All the depositing processes were conducted under 0.2 Pa xenon atmosphere. By applying voltage between the target and the substrate, xenon particles get ionized and are accelerated until they hit the target. Then, the target substances are emitted and deposited on the substrate.

rf sputter produces the film using AC voltage. Unlike the ones which apply dc voltages, called the dc sputter, rf sputtering is appreciated when depositing insulators.

This comes from the differences of the behavior of electrons in metal and non-metal substances when voltage is applied. In metal, the electrons moves toward the surface, trying to cancel out any electric field inside. However, in the case of insulators, the electrons do not gather around the surface. Instead, they scatter around the insulator, canceling out some of the electric field inside.

Therefore, when positive xenon ions hit the target, they stick to the surface of the insulator because they are attracted to the electrons inside the insulator. In order to tear off the xenon ions on the surface, we have to apply voltage other way around and attract the ions to the sample side. Once the surface of the target is clear, we can turn around the voltage to hit the target with xenon plasma particles. This process is continuously realized by applying AC voltage between the target and the substrate, which is the mechanism of the rf sputter device.

In this study, rf sputter was used because it was necessary to stack layers of MgO, which is an insulator.

3.1.2 Conditions and details of sample deposition

The electric power for depositing each substance is shown in Fig. 3-1-1. During deposition, the substrate is rotated at 15 rpm, in order to get rid of any bias on the thickness of the depositing substance.
The thickness of the layers were determined from the deposition rate of each material. However, this needs calibration. We measured the thickness of the thin film for each substance directly by using atomic force microscope (AFM). By comparing the thickness between the values from AFM and the values calculated from the deposition rate of the rf sputter, we were able to determine the actual thickness of the film through the deposition rate.

### 3.1.3 Preparing the samples for the experiment

After the sputtering process, the samples were taken out of the sputtering chamber, and were immediately covered with a resist (S1813). It is proved that the resist composition does not show any magnetic behavior, even if strong magnetic field is applied. The resist composition protects the thin films from oxidation, hydrogen adsorption, or other changes in physical or chemical properties. Then, the samples were put on a hot plate and baked for 5 minutes at 90 °C. Finally, the samples were cut into 2 mm × 5 mm segments. The samples were kept in a desiccator at around 100 Pa at an idle state to prevent annealing and contamination.

### 3.1.4 Composition of the film

Four different types of samples were mainly used in this study, as shown in Fig. 3-1-2. Two different types of experiments were conducted using the listed samples. First, using (a) and (b), experiments on the electrostatic and electrochemical properties of ionic liquid and its interface were conducted. Then, using (c) and (d), magnetic properties and electric field control of Pt/Co/Pt has been investigated. (e) is a sample with Pd on top of Co and they were also used for magnetic property measurement. In the following text, the sample structures will be referred to as sample (a)-(e) with sample thickness mentioned.

![Target Power Table]

<table>
<thead>
<tr>
<th>Target</th>
<th>Power [W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>40</td>
</tr>
<tr>
<td>Pt</td>
<td>40</td>
</tr>
<tr>
<td>Pd</td>
<td>35</td>
</tr>
<tr>
<td>Co</td>
<td>70</td>
</tr>
<tr>
<td>MgO</td>
<td>65</td>
</tr>
</tbody>
</table>

Fig. 3-1-1 Electric power for depositing each target substance
Fig. 3-1-2 Composition of the mainly used samples. \( t_{\text{Co}}, \ t_{\text{Pt}}, \) and \( t_{\text{MgO}} \) represent the thickness of Co layer, Pt layer, and MgO layer, respectively. Note that in the case where \( t_{\text{Co}} \) is set less than an atomic size, the Co atoms are expected to be in the island state. When experimenting the electric properties of the ionic film and electric field control of magnetism, ionic films were placed on top of the samples.

3.2 Measuring the properties of electric double layer capacitor

3.2.1 Basic characteristics of ionic film

The ionic liquid used in the experiment is TMPA-TFSI (N,N,N-Trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide). The cation and anion used in this ionic liquid are \([\text{Me}_3\text{PrN}]^+\) (TMPA) and \([\text{N(CF}_3\text{SO}_2)_2]^−\) (TFSI), respectively. The large
ions of TMPA-TFSI allows it to be stable in the form of liquid at low temperature. Specifically, the melting/freezing point of TMPA-TFSI is known to be about 295 K, which is around room temperature [48]. Other basic properties of TMPA-TFSI are shown in Fig. 3-2-2.

![Structure of ionic liquid TMPA-TFSI](image)

Fig. 3-2-1 Structure of ionic liquid TMPA-TFSI. (a) TMPA (cation) (b) TFSI (anion)

<table>
<thead>
<tr>
<th>Properties of TMPA TFSI</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical window</td>
<td>5.7 V</td>
</tr>
<tr>
<td>Melting point</td>
<td>22 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.44 g/cm²</td>
</tr>
<tr>
<td>Conductivity</td>
<td>3.27 mS/cm</td>
</tr>
</tbody>
</table>

Fig. 3-2-2 Basic properties of TMPA-TFSI [48, 49].

However, in the experiment, the ionic liquids were used in the form of ionic films. Ionic films, also known as ionic gels, are elastic polymer films which are soaked in ionic liquids (Fig.3-2-3). They are more stable and experimentally easier to handle compared to pure ionic liquid. In this study, ionic films are used to apply gate voltage to the magnetic thin films.
Fig. 3.2.3 Gelation process of ionic liquids [50]. Ionic liquid has various peculiar features (see section 2.6) and one of them are its characteristic as a catalysis. Ionic liquid helps synthesis of polymers which as a result, turns ionic liquids into ionic films.

In order to apply gate voltage, 50nm thick Au layer has been evaporated on top of the ionic film as an electrode.

3.2.2 Set-ups of the samples

After the baking of samples at section 3.1.3, the samples for electric field control measurement must have resist washed and ionic films placed on top. The procedures are as below;

1. The samples were put in acetone solution, then in ethyl alcohol solution, each for 1 minute to dissolve the resist composition.
2. The samples were put in the ashing apparatus, in order to detach the remaining resist composition on the surface. The process is done by turning oxygen molecule into plasma using electric power, and forcing chemical reaction between the resist (organic matter) and the active oxygen. Electrical power of 150 W has been applied for 90 seconds under 50 Pa oxygen atmosphere. The effect of active oxygen does not have an influence on the magnetic properties of the thin film.
3. The ionic films were placed on top of the samples. Once it was placed, it was kept untouched because unnecessary movement of the elastic film can cause undesirable changes to the thin film underneath. Finally, the samples were quickly put in the desiccator at 330 K, 200 Pa or wired
and put in the measuring equipment.

Process No.1 through No.3 was conducted quickly in order to get rid of unwanted contamination from the air. The ionic films are kept in a desiccator at 330 K, 200 Pa. The condition is known to be ideal for keeping ionic liquids, since the pressure keeps away unwanted contamination and the temperature keeps ionic liquids from solidifying [49].

3.2.3 Set-ups of the measurements of properties of ionic film

Measurements on the properties of ionic films were conducted under ultra-high vacuum pressure. This condition was realized by using a turbo-molecular pump. Under such an atmosphere, the effect of impurities, such as organic particles and H$_2$O, can be diminished.

The electric properties were measured using a source-measure unit (SMU). The equipment we used were B2901A from Agilent. SMU is an equipment, which can apply electricity as a source and measure at the same time. Also, it can be used for measuring high resistance electric circuit. Therefore, it is suited for measuring the properties of ionic film. B2901A was also used for applying voltage when measuring the effect of electric field to the magnetic moment.

The mainly used samples are sample (b). Most electric current is expected to run through Pt layer. Therefore, the electrical properties of the circuit is expected to be the same as the ones used for measuring magnetic moments, which are sample (d).

In this section, there are two different types of experimental methods. One is simply measuring under ultra-high vacuum atmosphere at room temperature, the other is at different temperatures.

The first experiment, ultra-high vacuum at room temperature, was conducted by using a sample holder shown in Fig. 3-2-4. The samples were fixed to the copper wire by silver paste. Silver paste is an adhesive liquid which has high conductance. The holder was simply connected to the turbo pump to achieve the atmosphere.
The temperature changing experiment was conducted using cryostat shown in Fig. 3-2-5(a). A turbo pump and a cryostat was connected and hence the experiments were conducted under the same pressure but with the ability to control pressure. However, the cryostat creates large electrical disturbances while cooling. Therefore, measurements which require extreme precision was done at room temperature using sample holder in Fig. 3-2-4.

3.3 Measuring the magnetic properties
3.3.1 MPMS

Magnetic properties of the samples were measured using the Magnetic Property Measurement System (MPMS) from Quantum Design Japan Inc. MPMS uses the superconducting quantum interface device (SQUID) to measure the magnetic moment of the samples.

A SQUID magnetometer is able to detect very weak magnetic signals. Therefore, the substances for holding and wiring the samples were picked carefully, so as not to show any unnecessary magnetic moment during the measurement. For example, silver paste and soldering iron, which were used for measurements on properties of ionic liquids, could not be used. Instead, nonmagnetic materials such as plastic straws (from Quantum Design Japan Inc.), Si blades, Au wires, and Au films were used for holding and wiring (Fig. 3-3-1). Fig. 3-3-1(a) shows a plastic straw holder used for normal magnetic property measurement using MPMS. Fig. 3-3-1(b) shows a Si blade holder used for magnetic property measurement with voltage application. In this study, accumulation of electrons on the bottom layer is considered positive gate bias and vice versa. The samples for the voltage application in MPMS were fabricated the same way as mentioned in section 3.2.2.

3.3.2 PPMS

At times, Hall measurement were also conducted to measure the magnetic properties of the samples. For the experiment, Physical Property Measurement System (PPMS) from Quantum
Design Japan Inc. were used. The Hall signal can be analyzed using equation (2.3-1) and anomalous Hall coefficient can be earned, which is proportional to the magnetic moment of the samples. Application of voltage is also possible with the use of PPMS, however it must be noted that the application of gate voltage may change the electric property, as well as the magnetic property, which might result in unwanted change in the Hall resistance. Since PPMS does not measure the magnetic moment itself, wiring with the use of conductive magnetic adhesives are allowed, which makes it more stable and easier to measure compared to MPMS magnetic measurement.

![Sample holder and wiring for measurements using PPMS.](image)

The following shows the procedures for the preparation of samples of Hall bar fabrication and photolithography. The processes are subsequent to the ones mentioned in section 3.1.3;

1. The Cr mask for making Hall bar structure was placed on top of the samples. Then, the ultraviolet rays were exposed for 40 seconds by an Hg lamp at 250 W.
2. The samples were put in a developing fluid and were shaken. The Hall bar still has resist covered and the resist at remaining places are washed away.

Up till here, the procedures were conducted in a room where ultraviolet rays cannot enter.

3. The resist uncovered places are washed away by ion milling. The samples were exposed to Ar ions for 80 seconds.
4. The samples were washed in an acetone solution and ethanol solution for 2 minutes and resist on top of the Hall bar were washed away.
5. The samples were put in the ashing apparatus, in order to detach the remaining resist composition on the surface. The process is done by turning oxygen molecule into plasma using electric power, and forcing chemical reaction between the resist (organic matter) and the active oxygen. Electrical power of 150 W has been applied for 90 seconds under 50 Pa oxygen atmosphere.
For the samples with the application of gate voltage, ionic films were placed on top. The wirings were done using indium fragments and conductive epoxy as adhesives as in Fig. 3-3-3.

Fig. 3-3-3 Hall bar fabricated sample seen from above. Ionic film has been placed on top of the Hall bar for application of gate voltage. Copper wire has been attached to the sample terminals using indium fragments and to the ionic film using conductive epoxy. The thickness of the Hall bar is 1 mm. The dotted line shows the image of the shape of the Hall bar.
Part 4 Characteristics of Ionic Liquids as Electric Double Layer Capacitor

Understanding the electrical properties of ionic liquids is crucial for two reasons. Firstly, determining the amount of modulated carrier density through the application of gate voltage is essential for calculating the modulated Fermi energy in the magnetic property measurement section 6. Secondly, establishing a clear method to apply gate voltage with minimal decomposition is necessary. The experimental results from various angles are presented below to elucidate the electrostatic and electrochemical nature of ionic liquids.

4.1 Impedance spectroscopy

Impedance spectroscopy involves measuring frequency-dependent capacitance for different MgO thickness samples. The experiment was performed at room temperature and under high vacuum. A 0.1 V sine wave was applied to the samples, and the resulting current was measured. From the current amplitude and phase, circuit elements like impedance, resistance, and capacitance can be deduced. A series RC circuit model was assumed, with the impedance equation given by:

\[ Z = \frac{V}{I} = R + \frac{1}{j\omega C} \]  

Capacitance \( C \) was calculated and divided by the surface area of the ionic film. Figure 4-1-1 displays the frequency dependence of capacitance with various MgO thickness samples. On a log-log plot, capacitance shows a linear increase against decreasing frequency, implying exponential growth. As MgO thickness increases, capacitance decreases. This trend is supported by Equation (2-6-1), which explains this phenomenon: the thicker the MgO, the lower the capacitance for the MgO part, bringing down the overall capacitance.
Fig. 4-1-1 Frequency dependent capacitance of MgO($t_{\text{MgO}}$)/ Pt(2.04 nm)/ Co(0.17 nm)/ Pt(4.08 nm)/ Ta(4.95 nm)/ Si substrate structure with different MgO thickness. Both x- and y-axis has been plotted against logarithm.

Fig. 4-1-2 shows the frequency dependence of the phase angle of the same samples. Equation (4-1-1) shows that the bigger the imaginary part of the impedance to the real part of impedance is, the better quality as a capacitance the circuit exhibits. Equation (4-1-1) can be rewritten as

$$Z = R - j\frac{1}{\omega C} \quad \cdots (4-1-2)$$

Therefore, as the phase angle of impedance becomes close to -90 degrees, the circuit as a whole becomes capacitance dominant. The phase angle in Fig. 4-1-2 is multiplied by -1, hence closer the phase angle is to 90 degrees, the more capacitance dominant structure the circuit exhibits. Fig. 4-1-2 shows that for almost all the samples, the most efficient frequency for the EDL capacitor is around 10 Hz.
Fig. 4-1-2 Frequency dependent phase angle of the impedance of MgO($t_{MgO}$)/ Pt(2.04 nm)/ Co(0.17 nm)/ Pt(4.08 nm)/ Ta(4.95 nm)/ Si substrate structure with different MgO thickness. -1 has been multiplied to the actual value, hence a value close to 90 degrees implies a better property as a capacitor. The arrow shows the point where the capacitor nature of EDL seems to be maximized.

Fig. 4-1-3 shows the voltage dependent phase angle of sample (b). In all the voltage range experimented, the most efficient frequency as a capacitor seems to be around 10 Hz, where the phase angle is closest to -90 degrees. However, there seems to be a trend that as the voltage amplitude increases, the efficient frequency increases. Also, the maximum phase angle decreases as the voltage amplitude increases.

However, it should be mentioned here that the effect of decomposition is likely to be stronger in the lower frequency region. In the experiment, the impedance was measured in the order of 0.1 V, 0.5 V, and 1 V. Therefore, impedance measurement at 1 V must be effected by the decomposition of ionic film which occurred during the impedance measurement of 0.1 V and 0.5 V. The effect of chemical reaction is strongest in the lower frequency region hence it is difficult to conclude whether the efficient frequency domain has shifted by the decomposition or the voltage amplitude. However, in any case, it can be stated that the most efficient frequency for any voltage amplitude is from 1 Hz to 10 Hz.
Fig. 4-1-3 Frequency dependent phase angle of the impedance of Pt/ Ta structure at different voltage amplitude.

In order to confirm the efficient frequency of the EDL to be 10 Hz, voltage was applied to the ionic film on sample (b) as a ramp function (Fig. 4-1-4). The experiment has been conducted under 0.1 V, 0.5 V, and 1 V. For each amplitude, responding electric current for the voltage raising time of 10 ms, 20 ms, 50 ms, 100 ms, 200 ms, 500 ms, and 1000 ms has been retrieved. Fig. 4-1-5 shows the amplitude of electric current for different voltage raising time and voltage amplitude. The result shows that as the raising time increases, the amplitude of the electric current decreases.
Fig. 4-1-4 Applied voltage as a function of time. The graph shows the case of 0.1 V. For the case of 0.5 V and 1 V, the voltage has been applied the same way, only the amplitude different.

When the voltage is applied to the ionic film at around the efficient frequency, the electric current should be linearly increasing. This is because the observed electric current is the sum of electric charging of the capacitor, which is constant, and the leakage current, which is proportional to the applied voltage. In Fig. 4-1-6, the observed electric current during the voltage increase was normalized and plotted against the normalized time. It is difficult to analyze the data for 0.1 V, since the time it takes for the electric current to be stable in the beginning takes up large part of the observed current. For 0.5 V, the most efficient raising time seems to be 10 ms, which is linear in almost all the region. For 1 V, the most efficient raising time seems to be 20 ms. In this case, even with the most efficient raising time, the normalized current goes out of linear relationship with the normalized time, from the normalized time of about 0.6. However, it should also be noted that in both the 0.5 V and 1 V cases, the slope and the shape of normalized current for 10 ms and 20 ms is almost the same.
Fig. 4-1-5 Electric current as a function of time for different raising time and voltage amplitude. (a) 0.1 V (b) 0.5 V (c) 1 V. y-axis has been plotted against log scale. Pt/ Ta with ionic film on top was used for the experiment.
Fig. 4-1-6 Normalized electric current plotted against normalized time for different raising time and voltage amplitude. The electric current observed during the applied voltage increase was taken and normalized against the largest electric current for normalized current. Normalized time was taken by dividing the actual time by the raising time. (a) 0.1 V (b) 0.5 V (c) 1 V. The black line for (b) and (c) shows the linear line that best fits the linear part of the most efficient curve.

4.2 Temperature dependent capacitance

Temperature dependent capacitance has been measured using sample (b). The capacitance had been continuously measured at 1 V, 100 Hz, while the temperature was dropped from 297 K at around 1 K/min. The result is shown in Fig. 4-2-1. The capacitance dropped monotonously until around 50 min where it was stabilized at around 1 nF.
Fig. 4-2-1 Temperature and capacitance change as a function of time. The figure above shows the temperature and the figure below shows the capacitance.

4.3 Leakage current

Leakage current has been measured using sample (b). Gate voltage of +1 V and -1 V was applied to the system at $t = 0$. The responding current was observed as in Fig. 4-3-1. Although it is difficult to estimate the true value of the leakage current for relaxation time for the charge is in the order of hours, it can be roughly approximated from the figure that the offset is 0 A and the leakage current for 1 V is $2 \times 10^{-9}$ A. The surface area of the ionic film of the sample was measured to be 7.88 mm$^2$. 
Fig. 4-3-1 Leakage current of ionic film on Pt/ Ta structure as a function of time. Above figure shows the leakage current for applied voltage of +1 V while the bottom one shows the leakage current for applied voltage of -1 V.

4.4 Cyclic voltammetry

Cyclic voltammetry measurement was conducted on sample (a) and sample (b). Auxiliary electrode was not used in this experiment. The working electrode was set as Au on top of the ionic film. The reference electrode was set as the Pt layer of the sample. The samples were first cooled down to the lowest measuring temperature. For each measuring temperature, 3 different cyclic voltammetry measurements were conducted before moving on to higher temperature. First, voltage has been applied between +3 V and -3 V at 200 mV/sec for 3 loops. Then, the same voltage has been applied at 2 V/sec for 3 loops. Finally, voltage between +4 V and -4 V has been applied at 20 mV/sec for 2 loops. The results are shown in Fig. 4-4-1 for sample (a) and Fig. 4-4-2 for sample (b).
Fig. 4-4-1 Cyclic voltammetry measured for MgO(0.72 nm)/ Pt(2.04 nm)/ Co(0.17 nm)/ Pt(4.08 nm)/ Ta(4.95 nm)/ Si substrate structure at different temperature. y-axis and x-axis represent the
current and the voltage, respectively. (a) Voltage between +3 V and -3 V swept at 200 mV/sec for 3 loops. For each temperature increase, an offset of $3 \times 10^{-7}$ A has been added. (b) Voltage between +3 V and -3 V swept at 2 V/sec for 3 loops. For each temperature increase, an offset of $1 \times 10^{-6}$ A has been added. (a) Voltage between +4 V and -4 V swept at 20 mV/sec for 2 loops. For each temperature increase, an offset of $1 \times 10^{-7}$ A has been added.
Fig. 4-4-1 Cyclic voltammetry measured for Pt(2.04 nm)/ Co(0.17 nm)/ Pt(4.08 nm)/ Ta(4.95 nm)/ Si substrate structure at different temperature. y-axis and x-axis represent the current and the voltage, respectively. (a) Voltage between +3 V and -3 V swept at 200 mV/sec for 3 loops. For each temperature increase, an offset of $2.5 \times 10^{-7}$ A has been added. (b) Voltage between +3 V and -3 V swept at 2 V/sec for 3 loops. For each temperature increase, an offset of $1 \times 10^{-6}$ A has been added. (a) Voltage between +4 V and -4 V swept at 20 mV/sec for 2 loops. For each temperature increase, an offset of $1 \times 10^{-7}$ A has been added.

In all the cases, the total current seems to be the smallest at 247 K or 254 K. Also, the electric current running is almost the same for every loop for all the cases.

With sample (a), a clear peak in current is observed at +4 V. However, the same cannot be observed as clear for the -4 V. With sample (b), the current does not seem to encounter a peak even at +4 V or -4 V.

**4.5 Discussion**

**4.5.1 Time constant of electric double layer and circuit analysis**

**4.5.1.1 Expected circuit structure of the system**

As explained in section 2.6.2, each capacitor-like structure can be replaced with RC parallel circuit in the ideal situation. Therefore, even if the structure in total was complicated, the circuit can be written with the series RC parallel circuit. In the case of the samples (a) and sample (b), the ideal circuits of the structures are estimated to be that of Fig. 4-5-1. The resistance structure in the parallel RC circuit expresses the charge transfer process of the electrons.
In the ideal situation, the time constant of each RC circuit should be different. For example, the time it takes for the bulk ionic film to be charged and for the EDL to be charged should be different according to the values of the capacitance and resistance of the RC circuit. The time constant $\tau$ is usually decided by

$$\tau = \frac{1}{\omega_E} = RC$$  \hspace{1cm} (4.5-1)

Here, $\omega_E$ is the most efficient angular frequency, which is the angular frequency where the phase angle of the impedance is closest to -90 degrees.

Assuming a simple situation, where the time constant of bulk ionic film and the time
constant of EDL is completely different and the time constant of EDL at the interface of Au and Pt are both the same, the frequency dependent phase angle of the impedance should encounter two peaks, one for the bulk ionic film and the other for EDL capacitor structure [46]. With the data retrieved from section 4.1, the time constant of EDL is assumed to be around 0.1 second.

However, it should be mentioned that, in reality, electrochemical element plays a large role in the circuit, especially in the low frequency region. To express the chemical properties, Warburg impedance is often used. As in Fig. 4-5-2, what used to be the resistance of the RC parallel circuit of the EDL is divided into the charge transfer resistance and the Warburg impedance. Warburg impedance contains resistance and capacitance inside, and responsible for the chemical actions in the circuit. For example, electric current consumed for redox reactions can be represented. In addition, the delaying element for the movement of ions at the interface of EDL is also included in the Warburg impedance.

Fig. 4-5-2 Circuit model of the samples with electrochemical properties taken into consideration. (a) Au/ ionic film/ Pt structure. (b) Au/ ionic film/ MgO/ Pt structure. $W$ represents the Warburg impedance at each interface and $R_{ct}$ represents the charge transfer resistance at each interface.

However, the structures of Warburg impedance being very complicated, it is difficult to discuss the circuit as Fig. 4-5-2. In the discussion below, the circuit in Fig. 4-5-1 will be
approximated and simplified in many ways to understand the characteristic of the structure.

4.5.1.2 Analysis on resistance

First, the value of resistance $R$ will be deduced. This is done by analyzing the Cole-Cole plot. When the applied frequency is high enough, electric current in all the RC circuit will pass through the capacitance. Therefore, in the high approximation, the only resistance in the circuit will be $R$. The approximation and calculation is easily done on Cole-Cole plot shown in Fig. 4-5-3. Cole-Cole plot takes the absolute value of the imaginary part of the impedance as y-axis and the real part of the impedance as x-axis [39]. In the high frequency region, the plots line up almost linearly. Therefore, the plots can be fitted with linear equation and the x-intercept of the fitting results shows the value of $R$.

![Cole-Cole plot](image)

Fig. 4-5-3 High frequency region of Cole-Cole plot of MgO($t_{MgO}$)/ Pt(2.04 nm)/ Co(0.17 nm)/ Pt(4.08 nm)/ Ta(4.95 nm)/ Si substrate structure with different MgO thickness. The lines represent the linear fitting results for each MgO thickness.

The value of $R$ has been attained for the different MgO thicknesses. It ranged from 180 $\Omega$ to 710 $\Omega$. Details are shown in Fig. 4-5-4. Here, $R$ is usually expresses as

$$R = \frac{\rho d}{S} \quad \cdots (4.5-2)$$

where, $S, \rho$, and $d$ stands for surface area, resistivity, and thickness of the ionic film, respectively.
Therefore, by multiplying $S$ to both sides,

$$RS = \rho d$$  \hspace{1cm} \cdots (4-5-3)

is achieved. The values of $\rho d$ has been deduced through the process. Fig. 4-5-4 shows the detailed values of $RS$ as well. Although considering an ideal circuit, the values of $RS$ should be fixed for all the MgO thickness, the difference is expected to originate from the accuracy of measurement, the fabricated condition of the samples, and so on.

![Graph showing MgO thickness dependence of resistance and product of resistance and surface area of the ionic film.](image)

The sum of the resistance of the circuit can also be attained. By applying constant current to the circuit, all the capacitance in the RC circuit will be saturated hence the current will flow through all the resistance of the structure. From the result of section 4.3, the total resistance of the circuit $R_{\text{EDLAu}} + R_{\text{IP}} + R_{\text{EDLPt}}$ is approximately $5 \times 10^8 \, \Omega$. Again, by multiplying the surface area,

$$RS = \rho d \approx 3.9 \times 10^7 \, \Omega \text{cm}^2$$  \hspace{1cm} \cdots (4-5-4)

Although, generally, the resistance depends on the surface area, resistivity, and the thickness of the resistance as in equation (4-5-3), it should be noted that the details may be different in this case. This is due to the electron hopping dominant characteristic of the EDL. Therefore, other factors such as the applied voltage may play an important role as well.

4.5.1.3 Analysis on capacitance

Now, the physical quantities of the capacitance will be discussed. Here, we will consider
the circuit of sample (a) at 10 Hz, when the capacitance property of the EDL is enhanced. Neglecting
the Warburg impedance, the bulk ionic film RC circuit and the rest of the resistance, only the
remaining series capacitance circuit needs to be considered. The total capacitance of this structure \( C \)
can be calculated as

\[
\frac{1}{C} = \frac{1}{C_{\text{EDL, Au}}} + \frac{1}{C_{\text{EDL, MgO}}} + \frac{1}{C_{\text{MgO}}} \quad \cdots (4.5-5)
\]

Here we simplify the equation by assuming that the interface does not affect the capacitance of the
EDL.

\[
C_{\text{EDL, Au}} = C_{\text{EDL, MgO}} = C_{\text{EDL}} \quad \cdots (4.5-6)
\]

The capacitance can be expressed as

\[
C_{\text{EDL}} = \frac{\varepsilon_0 \kappa_{\text{EDL}} S}{t_{\text{EDL}}} \quad \cdots (4.5-7)
\]

\[
C_{\text{MgO}} = \frac{\varepsilon_0 \kappa_{\text{MgO}} S}{t_{\text{MgO}}} \quad \cdots (4.5-7)
\]

where \( \varepsilon_0 \), \( \kappa_{\text{EDL}} \), \( \kappa_{\text{MgO}} \), \( S \), \( t_{\text{EDL}} \), and \( t_{\text{MgO}} \) represents the permittivity of vacuum, relative
permittivity of EDL, relative permittivity of MgO, surface area, thickness of EDL, and the thickness
of MgO, respectively. Using equation (4.5-7), equation (4.5-5) can be simplified.

\[
\frac{\varepsilon_0 S}{C} = \frac{2\varepsilon_0 S}{C_{\text{EDL}}} + \frac{\varepsilon_0 S}{C_{\text{MgO}}}
= \frac{2d_{\text{EDL}}}{\kappa_{\text{EDL}}} + \frac{t_{\text{MgO}}}{\kappa_{\text{MgO}}} \quad \cdots (4.5-8)
\]

By taking the MgO thickness dependent capacitance, the relative permittivity of MgO \( \kappa_{\text{MgO}} \) and the
ratio of the thickness of EDL and relative permittivity of EDL \( \frac{t_{\text{EDL}}}{\kappa_{\text{EDL}}} \) can be obtained. Fig. 4-5-5
shows \( \frac{\varepsilon_0 S}{C} \) plotted against the thickness of MgO \( t_{\text{MgO}} \).
Fig. 4-5-5 The product of permittivity of vacuum and surface area over capacitance $\frac{\varepsilon_0 S}{C}$ plotted against thickness of MgO $d_{\text{MgO}}$ for MgO($t_{\text{MgO}}$)/Pt(2.04 nm)/Co(0.17 nm)/Pt(4.08 nm)/Ta(4.95 nm)/Si substrate structure. The black line shows the slope of the ideal value of MgO dielectric constant, which is $\kappa_{\text{MgO}}=9.8$. The red line shows the linear fitting of the first two points of the data, whose reciprocal of the slope is calculated to be 11.7.

Although according to equation (4-5-8), the data should be plotted linearly, Fig. 4-5-5 shows that they are rather quadratic. To explain the result, the following causes can be considered:

- As the thickness of MgO layer increases, the electric field per molecules of ionic liquid decreases, resulting in the density of ions near the surface. The effect will enhance the thickness of EDL. The thickness is expected to diminish to a constant value as the applied voltage increases.

- As the thickness of MgO layer increases, the electric field per MgO molecules decreases, resulting in less polarization of the molecules. The polarization has positive correlation with relative permittivity hence the equation would be quadratic.

- In the experimented case, sputtered MgO is known to be a polycrystal when it is thin. However, as the thickness of MgO layer increases, the MgO may become ideally crystallized. The change in such characteristic may change the value of relative permittivity of MgO. However, more research on the crystal properties of MgO must first be attempted.
When MgO layer gets thicker, the leaking electric field becomes larger. Generally, when we consider a capacitor, we think of a thin structure whose electric field cancels out outside the capacitor structure. However, when the structure is thick, the electric field outside of the capacitor generated from the upper electrode cannot be canceled completely by the bottom electrode. This results in the leaking electric field, which means less effective electric field is applied to the MgO layer. Therefore, polarization behavior of MgO molecules will be weakened.

The function seems to be quadratic due to the thickness dependent property of MgO. Therefore, in Fig. 4-5-5, the two thinnest samples were taken and were fitted with a linear function. The red line shows the result and \( \kappa_{\text{MgO}} \) was calculate to be 11.7. Considering the ideal crystallized value of the MgO is 9.8, it seems a meaningful value. On the other hand, \( \frac{\kappa_{\text{EDL}}}{\kappa_{\text{EDL}}} \) was calculated to be 0.0857 nm.

Therefore, the capacitance of EDL can be determined

\[
\frac{C_{\text{EDL}}}{S} = \frac{\varepsilon_0 \kappa_{\text{EDL}}}{t_{\text{EDL}}} = 10.5 \mu F/cm^2
\]

\[\cdots(4.5-9)\]

4.5.2 Electrochemical window

From previous study, the electrochemical window of TMPA-TFSI is known to be 5.7 V (Fig. 2-6-11). Electrochemical window is the width of the amplitude of the voltage before the current due to the decomposition of the solution is observed. However, the results in section 4.4 shows that electrochemical window is larger than 5.7 V. The decomposition voltage has only been observed in sample (a) and it seems to be +3 V for the positive gate bias and -3.5 V for the negative gate bias. The electrochemical window for sample (b) seems to be larger than 8 V.

From the result, two facts can be deduced. First, by polymerizing TMPA-TFSI, the electrochemical window has been enlarged. This may be due to the fact that polymers get in the way of ions and disrupts them from chemical reaction. In other words, the polymers may be acting as a buffer. The other deduction is that the surface material can be a function of electrochemical window as well. It seems that Au/ ionic film/ Pt structure is more stable compared to Au/ ionic film/ MgO/ Pt structure. Chemical reaction in between the ionic liquid and oxide layers are known to be less stable compared to ionic liquid on chemically stable metal, as Yuan suggests [46].

As a conclusion, the electrochemical window of TMPA-TFSI can be enlarged by polymerizing the ionic liquid and selecting chemically stable metals for the interfaces. However, clarification of the electrochemical window of the Au/ ionic film/ Pt structure remains to be an assignment for the future studies.
4.5.3 Melting/freezing and glass transition point

From previous study, the melting point of TMPA-TFSI as an ionic liquid was 295 K [48]. However, the calorimetric behavior in the case of TMPA-TFSI in the experiment proved to be different as observed in Fig. 4-2-1. The capacitance decreased as the temperature dropped, until at around 240 K, when the capacitance became stable at around 1 nF. This shows that the glass transition point of the TMPA-TFSI ionic film is around 240 K. Below 240 K, the ionic film behaves like a glass structure, where ions are frozen and fixed as an amorphous crystal. Above 240 K, the ionic film should have a rubber-like property. In this state, although some ions are crystallized, other ions can still move around as a viscous liquid. This enables the creation of capacitor structure at the EDL interface. As the temperature increases, the viscosity of ionic liquid would decrease, enabling faster tracking. The freezing/melting point, that is the transition from rubber-like state to liquid state, was not clearly observed in the experiment. Therefore, as for the future studies, endothermic and exothermic property of ionic film should be measured using calorimetric techniques.

4.5.4 For the application to electric field control

Considering the results in section 4 and the discussions in section 4.5.1, 4.5.2, and 4.5.3, some ideal ways for realizing large capacitance structure with less decomposition and chemical reaction can be deduced.

From the electrochemical window, Au/ ionic film/ Pt structure is the most durable structure against decomposition. When changing the gate voltage, setting the temperature around 250 K may be ideal, because current leaking for the chemical reaction seems least in the region. Also, 250 K is above glass transition point deduced in section 4.5.3. The ionic film should be charged at around 10 Hz according to section 4.1. However, it should be reminded that the charging of EDL is most efficient around 10Hz only at room temperature. Therefore, there may be a different efficient frequency for different temperature.

Although in this study, the application of gate voltage was not conducted under such conditions (confer section 6), with more experiment and understanding, especially on the temperature dependent behaviors, we should be able to modulate larger amount of carrier density in Pt layers with more accuracy in knowing the amount of modulated carrier density.
Part 5 Magnetic Properties of Pt/Co/Pt Thin Film

Understanding the basic magnetic properties of Pt/Co/Pt and MgO/Pt/Co/Pt structure is necessary for discussing the electric field control of these samples. Here, the thickness dependence of magnetic moment has been studied and discussed.

5.1 MgO thickness dependence of magnetic properties

Magnetic moment was measured using MPMS as mentioned in section 3.3. External perpendicular magnetic field of 1.5 mT was applied and temperature was swept at the rate of 3K/min from 10 K to 300 K. The surface area of each samples was measured using stereo microscope and magnetic moment per surface area was calculated. The samples used in this experiment are sample (c) with different MgO thickness. The result is shown in Fig. 5-1-1.

![Fig. 5-1-1 Temperature dependence of perpendicular magnetic moment per unit area ($m_\perp/S$) of MgO($t_{\text{MgO}}$)/ Pt(2.04 nm)/ Co(0.17 nm)/Pt(4.08 nm) /Ta(4.95 nm)/ Si substrate structure. Thickness of MgO layer $t_{\text{MgO}}$ is as indicated.](image)

Here, we can see a trend that as the MgO thickness increases, the total magnetic moment per surface area decreases. Also the Curie temperature seems to share a same trend. For the sample with MgO thickness of 3.58 nm, coercivity of 25 mT for the in-plane direction has been observed at 10 K, implying that the magnetization direction of this sample is somewhat tilted to the in-plane surface direction.
5.2 Upper Pt thickness dependence of magnetic properties of Pt/Co/Pt structure

Perpendicular magnetization of sample (d) has been measured in this section. To understand about the induced moment in upper Pt and property of the film, magnetic properties of samples with different Co thickness and upper Pt thickness has been measured.

5.2.1 Co thickness of 0.17nm

Sample (d) with Co thickness of 0.17 nm has been created. Samples were created with different upper Pt thickness. The perpendicular magnetic moment of each samples were measured in MPMS. First, the samples were brought down to 10 K. Then magnetic field of 1T were applied to the samples for 2 minutes. Finally the magnetic field was brought down to 1.5 mT and the magnetic moment of each samples were measured as the temperature was swept from 10 K to 300 K at 3 K/min.

Although the Curie temperature steadily increase as the upper Pt layer gets thinner, magnetic moment at 10 K does not show a similar trend. Magnetic moment increases as the Pt thickness increases, however, at some point around 1.0 nm–1.3 nm, it seems to saturate. Also, the curve on the graph seems to become steeper near the Curie temperature as the Pt layer becomes thinner.

![Graph showing temperature dependence of perpendicular magnetic moment per unit area of Pt(t_Pt)/]

Fig. 5-2-1 Temperature dependence of perpendicular magnetic moment per unit area of Pt(t_Pt)/
Co(0.17 nm)/ Pt(4.08 nm)/ Ta(4.95 nm) structure. Thickness of upper Pt layer $t_{Pt}$ is as indicated. Hall measurement has been conducted on the samples at 10 K and has been concluded that the saturation magnetization equals remanent magnetization. Therefore, the magnetic moment indicated at 10 K can be regarded as the saturation magnetic moment at 10 K.

The magnetic moment at 10 K and Curie temperature $T_C$ has been plotted as a function of thickness of upper Pt layer in Fig. 5-2-2. The figure shows that there seems to be little relationship between the magnetic moment and Curie temperature when Pt is thin. Curie temperature seems to be decreasing in proportion to the film thickness while the magnetic moment has a clear peak at around 1.3 nm. However, after the peak, they seem to have positive correlation when Pt is thick.

**Fig. 5-2-2 Magnetic moment per unit area at 10 K and Curie temperature plotted as a function of thickness of upper Pt layer $t_{Pt}$. The sample composition is Pt($t_{Pt}$)/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm). The error bar indicates the possible thickness error of Pt layer.**

### 5.2.2 Co thickness of 0.10nm

The same experiment has been conducted on sample (d) with thinner Co layer. The result is shown in Fig. 5-2-3. The same trend in increasing Curie temperature for decreasing Pt thickness has been observed. However, the magnetic moment at 10K did not illustrate the same trend as in Fig. 5-2-1. The magnetic moment seems to be stable at $3.2 \times 10^{-10} \text{T} \cdot \text{m}$ for Pt layer thinner than 0.86 nm and did not decrease as was with the case of samples with Co thickness of 0.17 nm.
Fig. 5-2-3 Temperature dependence of perpendicular magnetic moment per unit area of Pt($t_{Pt}$)/Co(0.10 nm)/Pt(4.08 nm)/Ta(4.95 nm) structure. Thickness of upper Pt layer $t_{Pt}$ is as indicated.

The magnetic moment at 10 K and Curie temperature $T_C$ has been plotted as a function of thickness of upper Pt layer in Fig. 5-2-4. The magnetic moment and the Curie temperature seems somewhat related. The Curie temperature decreases linearly with the Pt thickness, which was a trend seen with Co 0.17 nm. However, this time, the peak in magnetic moment is not visible. The increase in magnetic moment was not visible within the experimented Pt thickness. Samples with less Pt thickness could not be created since the oxidization of Co atoms cannot be ignored because the Pt layer thinner than 1 atomic layer cannot cover the whole surface of the Co layer.
Fig. 5-2-4 Magnetic moment per unit area at 10 K and Curie temperature plotted as a function of thickness of upper Pt layer $t_{Pt}$. The sample composition is Pt($t_{Pt}$)/Co(0.10 nm)/Pt(4.08 nm)/Ta(4.95 nm). The error bar indicates the possible thickness error of Pt layer.

5.2.3 Co thickness of 0.25nm

Samples with thicker Co layer has also been created. This time, a thickness of about 1 atomic layer of Co has been deposited. The data has been retrieved for only two Pt thicknesses, but it showed a similar trend with the rest of the Co thickness samples. The decrease in upper Pt thickness lead to increase in both the magnetic moment and the Curie temperature.
Fig. 5-2-5 Temperature dependence of perpendicular magnetic moment per unit area of Pt($t_{Pt}$)/Co(0.25 nm)/Pt(4.08 nm)/Ta(4.95 nm) structure. Thickness of upper Pt layer $t_{Pt}$ is as indicated.

5.3 Upper Pt thickness dependence of magnetic properties of MgO/Pt/Co/Pt structure

Temperature dependence of magnetic moment of sample (c) has been measured using MPMS. The thickness of MgO and Co was fixed at 0.72 nm and 0.17 nm, respectively, and the thickness of upper Pt layer has been modified. The result is shown in Fig. 5-3-1. Fig. 5-3-2 shows the Pt thickness dependence of magnetic moment and the Curie temperature. Here we can see a similar trend between the magnetic moment and the Curie temperature. Both of them experience a severe drop at around 0.8 nm and encounters a low peak at around 1 nm. However, after that, magnetic moment and Curie temperature experience monotonic increase. It should be noted that the in-plane coercivity of 25 mT has been observed for sample with Pt thickness 0.86 nm. This indicates that the easy axis of magnetization is not completely in the perpendicular direction.
Fig. 5-3-1 Temperature dependence of perpendicular magnetic moment per unit area of MgO(0.72 nm)/Pt(\(t_{\text{Pt}}\))/Co(0.17 nm)/Pt(4.08 nm)/Ta(4.95 nm) structure. Thickness of upper Pt layer \(t_{\text{Pt}}\) is as indicated. Black line indicates the magnetic moment without the upper Pt layer.

Fig. 5-3-2 Magnetic moment per unit area at 10K and Curie temperature plotted as a function of thickness of upper Pt layer \(t_{\text{Pt}}\). The sample composition is MgO(0.72 nm)/Pt(\(t_{\text{Pt}}\))/Co(0.10 nm)/Pt(4.08 nm)/Ta(4.95 nm). The error bar indicates the possible thickness error of Pt layer.
5.4 Discussion

5.4.1 Magnetic properties of Pt/Co/Pt structure

Here, we discuss the magnetic properties of Pt/Co/Pt multilayer.

At first, an increase in magnetic moment as an increase in Pt upper layer was expected because of the ferromagnetic proximity effect in the top Pt as reported by Geissler and Suzuki [31, 32]. However, for all the Co thickness samples, monotonous increase in magnetic moment was not observed. In order to explain this phenomenon, other factors and reasons must be taken into consideration.

One of the possibilities for explanation is intermixing between the upper Pt layer and the Co layer. Although it depends largely on the condition of deposition, it was known that the variation of lattice constant between Co and Pt causes roughness of the surface, leading to intermixing [22]. The formation of Co-Pt alloys at the interface may be the cause of the behavior of magnetization.

Bandiera suggests that the interdiffusion are more likely to occur in top Pt/Co interface than in bottom Co/Pt interface [51, 52]. This may be due to the difference in the energy of Co and Pt atoms when they are sputtered. Co-Pt alloys have reduced Curie temperature but same magnetization at low temperature as pure Co.

The intermixing and induction of magnetic moment to the top Pt layer may be able to describe the phenomenon observed at section 5.2.1 and 5.2.2. First, we will discuss the sample with Co 0.17 nm. The constant decrease in Curie temperature can be attributed to the increase in intermixing and formation of Co-Pt alloys. On the other hand, magnetic moment first increases up to 1.3 nm due to the induction of magnetic moment to the top Pt layer. However, as the Pt layer gets thicker, the intermixing term becomes more and more dominant. The decrease in magnetic moment can be attributed to less coordination of Co atoms due to mixing.

Now, we will discuss the sample with Co 0.10 nm. The decreasing in Curie temperature can be explained similarly, that the formation of Co-Pt alloys may be the cause. As a matter of fact, the percentage decrease in the Curie temperature is the same as that of Co 0.17 nm samples, which is around 40 % in 1.7 nm Pt thickness variation. This may indicate that the percentage of Co atoms turning into Co-Pt alloys are the same in both cases. As for magnetic moment, the increasing trend could not be observed even when the Pt was thin. This may be due to the weakened induced moment, since the density of Co layer has decreased. Therefore, for all the thickness regime, the effect of intermixing became dominant.

However, it is difficult to attribute this phenomenon only to interdiffusion and induction of magnetic moment. Other possibilities such as the oxidization of Co with thin upper Pt samples and hydrogen absorption of Pt may also need to be taken into consideration to fully understand the
mechanism.

5.4.2 Magnetic properties of MgO/Pt/Co/Pt structure

5.4.2.1 MgO thickness dependence

Looking at Fig. 5-1-1, two effects of MgO/Pt interface effect can be considered.

First, the effect of deposition of MgO reduces the magnetic moment induced in Pt, or completely vanishes it. A few reasons can be considered for this phenomenon. Although most likely negligible considering the amorphous characteristic of sputtered MgO, the MgO layers, having a lattice constant different from Pt, can enhance the lattice constant of the neighbor Pt atoms, inducing magnetoelastic effect to the top layers of Pt. Also, oxidation of Co by MgO through baking processes can also be considered.

The other effect is MgO turning the magnetization direction of Pt to the in-plane direction. The sample with MgO thickness of 3.58 nm showed in-plane element of magnetization. For this phenomenon, reasons such as magnetoelastic effect, orbital interaction between MgO and Pt, and damaging of the Pt layers through long hour sputtering of MgO can be considered.

5.4.2.2 Pt thickness dependence

Similar to the discussion in section 5.4.1 on magnetic properties of Pt/Co/Pt thin film, there seems to be sophisticated properties and structures in this structure. Many factors seem to be influencing the results, hence it is difficult to ascribe the result to a simple cause. Therefore, the possible contributors to the manifestation of properties shown in Fig. 5-3-1 and Fig. 5-3-2 will be discussed.

- Effect of intermixing between upper Pt and Co layers is an issue which must be discussed. The decrease in magnetic moment and Curie temperature in the thin Pt region may be due to the decrease in Co coordination and Co turning into Co-Pt alloys. However, the effect seems suppressed in the thicker Pt region, which suggests that other factors are related to the thicker Pt region.

- As stated in 5.2.2.1, interface interaction between Pt and MgO may also be a contributor. When the Pt layer is thin, the effect of MgO to suppress the magnetization or to turn the magnetization direction toward in-plane direction spreads out to the entire Pt layer. From the Pt layer, the whole magnetic layer and its properties are changed, which results in the low peak around Pt thickness of 1nm. When Pt layer becomes thicker, the Pt atoms located near Co layer becomes independent from the MgO interaction. Therefore the increase in magnetization is observed. The possible reason for magnetic property change at the interface can be attributed to the magnetoelastic effect, orbit interaction, and oxidation of Co.
Induction of magnetic moment to upper Pt layer is another factor. The depth which the magnetic moment is induced is known to be around 1nm [31, 32]. However, considering the factors stated above, which is intermixing and interaction with MgO, the depth profile of induced moment may change. For example, if the magnetization of upper Pt layer was suppressed by MgO overlayer, the magnetic moment will not be induced. Therefore, the actual effect of magnetic moment induction will only appear when Pt layer is thick enough to alleviate the MgO interaction.

Fig. 5-4-1 shows the summarized data of MgO/Pt/Co/Pt system. Curie temperature has been plotted against the magnetic moment. The data shows that although many factors for the difference in increasing/decreasing trend of the Curie temperature and magnetic moment were listed, they seem to be on the slope for the most part. For Pt(t\textsubscript{Pt})/ Co(0.10 nm) /Pt(4.08 nm) /Ta(4.95 nm) samples (blue) and MgO(0.72 nm)/ Pt(t\textsubscript{Pt})/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) (black), the slope at which both the Curie temperature and magnetic moment are brought down is cloth to the one going up. For the part of Pt(t\textsubscript{Pt})/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) samples (red), the complex exchange balance between the contributors may be the cause of perplexing behavior.

![Graph showing Curie temperature plotted against magnetic moment per unit area for each Pt thickness. Red line, blue line, and black line represent the data from Pt(t\textsubscript{Pt})/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) samples, Pt(t\textsubscript{Pt})/ Co(0.10 nm) /Pt(4.08 nm) /Ta(4.95 nm) samples, and MgO(0.72 nm)/ Pt(t\textsubscript{Pt})/...](image-url)
Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm), respectively. The arrow shows the direction of increasing thickness of Pt.

Much has been mentioned as the possible contributors to the phenomenon observed in this section. However, more research must be conducted on Pt/Co, Co/Pt, MgO/Pt, and MgO/Co interfaces to learn more about this structure. Observations magnetic properties of samples with different depositing conditions should also be investigated to eliminate possible impurities and contamination from the processes.
Part 6 Electric Field Control of Magnetic Properties of Pt/Co/Pt Thin Film

The electric field control of Pt/Co/Pt thin films will be mainly discussed in this section. Gate voltage has been applied to the thin film through ionic film directly put on the sample and carrier modulation has been induced. It should be note that positive gate bias represents electron accumulation in magnetic layer and vice versa. First, experiment on electric field control of MgO/Pd/Co/Pt thin film was conducted. Although it is the replication of experiment already conducted by Obinata [16, 33], it has strengthened the statement that induced moment in Pd can be electrically manipulated. Then, from section 6.2, the electric field control of Pt/Co/Pt thin film will be discussed. In all the cases, the thickness of the upper Pd or Pt layers were chosen so that the magnetic moment seems to be induced in the uppermost layers, where carrier modulation is expected to occur.

6.1 Electric field control of magnetic properties of MgO/Pd/Co/Pt thin film

Magnetic moment of sample (e) has been measured by different gate biases. Samples were fabricated as stated in section 3.3.1. Gate voltages were applied in the order of 0 V, +2 V, 0 V, -2 V, and 0 V. First, the samples were stabilized at 300 K. The gate voltage was applied to the samples with the rate of 2 V/sec and after the voltage reached target value, the samples were left for 5 minutes for the gate current to stabilize. Then, they were brought down to 10 K with the applied magnetic field of 20 mT. At 10 K, the external magnetic field was changed to 1.5 mT and were brought up to 300 K at 3 K/min. The measurement on magnetic moment were only conducted when bringing the temperature up from 10 K to 300 K. The loop continued until measurement under all gate biases were completed.

Fig. 6-1-1 shows the temperature dependence of magnetic moment with the gate bias of +2 V and -2 V. Although the Curie temperature seems to be unchanged, magnetic moment at lower temperature region has been modified. The result indicate that the accumulation of electrons in the Pd layer lead to increase in magnetic moment, and depletion of electrons lead to decrease in the magnetic moment.
Fig. 6-1-1 Temperature dependence of magnetic moment per unit area of MgO(0.72 nm)/ Pd(1.70 nm)/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) thin film at $V_G = \pm 2 \, \text{V}$. At 10 K, magnetic moment has been modified by around $5.5\times 10^{-11} \, \text{T} \cdot \text{m}$.

Fig. 6-1-2 shows the difference in magnetic moment at 10 K at different gate biases. Here, we can see that total modification of $1 \times 10^{-10} \, \text{T} \cdot \text{m}$ per unit ionic film area has been earned at maximum. The magnetic moment at 0V after the +2 V is larger than that of +2 V and seems to illustrate a hysteresis loop.

Fig. 6-1-2 Difference in magnetic moment per unit area of the ionic film observed at 10 K as a
function of gate voltage. The magnetic moment at the first 0 V bias is set as the origin.

6.2 Electric field control of magnetic properties of MgO/Pt/Co/Pt thin film

First, samples with MgO on top of Pt/Co/Pt systems have been produced, as similar to the case of Pd/Co/Pt. Pt thickness has been chosen where the magnetic moment seems to be induced in the upper layer of Pt, which is 1.26 nm in this case (confer Fig. 5-3-2). The samples have been fabricated and their magnetic moment were measured at different gate biases. The measurement was conducted the same way as described in section 6.1. However, the gate voltages were applied in the order of 0 V, -2 V, 0 V, +1 V, +3 V, and 0 V. Fig. 6-2-1 shows the temperature dependent magnetic moment at different gate biases.

![Graph showing temperature dependence of magnetic moment per unit area.](image)

Fig. 6-2-1 Temperature dependence of magnetic moment per unit area of MgO(0.72 nm)/ Pt(1.26 nm)/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) thin film at indicated gate biases. The gate biases have been applied in the order of 0 V, -2 V, 0 V, +1 V, +3 V, and 0 V. The inset at the left bottom corner shows the magnetic moment magnified around 10 K. The inset at the right upper corner shows the magnetic moment magnified around the Curie temperature.

Neither clear difference in magnetic moment at 10 K nor the Curie temperature has been
observed. Fig. 6-2-2 is the magnetic moment and the Curie temperature plotted against gate voltage. The Curie temperature has been deduced by fitting around a point where differential is the largest by linear equation. Here, we can also see that the difference caused by gate bias is not significant.

![Graph showing magnetic moment and Curie temperature vs. gate voltage]

Fig. 6-2-2 Magnetic moment per unit area at 10 K and Curie temperature as a function of gate bias. The error bar in magnetic moment was derived from the fitting error of the MPMS. The arrow indicates the order of gate voltage change.

### 6.3 Electric field control of magnetic properties of Pt/Co/Pt thin film

Experiment of electric field control without the MgO layer on top has also been conducted. The measurement of temperature dependence of magnetic moment using MPMS and magnetic field dependence of magnetization using PPMS has been conducted.

#### 6.3.1 MPMS measurements

The Pt thickness has been carefully chosen, so that the magnetic moment is induced in the upper Pt layer. Looking at Fig. 5-2-2, the Pt thickness around peak magnetic moment at 10 K has been chosen, which is 1.25 nm in this case. The measurement has been conducted the same way as mentioned in section 6.1. However, the gate voltage has been applied in the order of 0 V, +1 V, +2 V, 0 V, -1 V, -2 V, and 0 V. Fig. 6-3-1 shows the result. Although it can be seen that a small amount of
change has been stimulated due to the carrier accumulation, a significant modification, as in MgO/Pd/Co/Pt systems, has not been observed.

Fig. 6-3-1 Temperature dependence of magnetic moment per unit area of Pt(1.25 nm)/Co(0.17 nm)/Pt(4.08 nm)/Ta(4.95 nm) thin film at indicated gate biases. The gate biases has been applied in the order of 0 V, +1 V, +2 V, 0 V, -1 V, -2 V, and 0 V. The inset at the left bottom corner shows the magnetic moment magnified around 10 K. The inset at the right upper corner shows the magnetic moment magnified around the Curie temperature.

Fig. 6-3-2 is the magnetic moment and the Curie temperature plotted against gate voltage. There seems to be a slight decrease in magnetization in the positive bias region as well as the Curie temperature. However, it is difficult to conclude that the magnetic moment surely changed by the electric field. The modification of magnetic moment has been observed only inside the error bar region. As for the Curie temperature, the roughness of the plots, which is 2 K per plot, overrules the small change in Curie temperature, which is 1 K.
6.3.2 PPMS measurements

Hall measurement has been conducted at 10 K using PPMS. Constant current of 0.3 mA was applied between the source and drain and Hall voltage were measured. Hall resistance were derived as the ratio of the Hall voltage and the source-drain current. Gate voltage was applied at 300 K a in the order of +1 V, +2 V, 0 V, -1 V, and -2 V. For each gate voltage, the temperature was dropped to 10K and external magnetic field was swept from 0.3 T to -0.3 T, then back from -0.3 T to 0.3 T.

First an experiment has been conducted on Pt/Co/Pt structure with upper Pt thickness of 1.34nm, which is almost same as the thickness of Pt used for the MPMS measurement. The result shows that coercivity seems to have increased from the gate voltage of +1 V to +2 V (Fig.6-3-3). Considering that the sweep rate is 0.5 mT/sec, change in coercivity of 1.5 mT seems a significant change. Fig. 6-3-4 shows the coercivity at different gate bias. A drop in coercivity has only been observed at 1V, and there seems to be a negative correlation at negative gate bias.
Fig. 6-3-3 Hysteresis loop of Pt(1.34 nm)/Co(0.17 nm)/Pt(4.08 nm)/Ta(4.95 nm) structure measured at 10 K. Area near the coercivity has been magnified. Note that y-axis is the Hall resistivity. The gate biases has been applied in the order of +1 V, +2 V, 0 V, -1 V, and -2 V. The sweep rate is 0.5 mT/sec.

Fig. 6-3-4 Coercivity plotted against gate bias. The arrow indicated the direction of the change of gate biases. Coercivity has been determined by the linear interpolation of Fig. 6-3-3 near coercivity.
Another experiment has been conducted on Pt/Co/Pt with thicker Pt, which is 2.38 nm. According to Fig. 5-2-2, this is in the area where both the magnetic moment and the Curie temperature is decreasing. Fig. 6-3-5 shows the hysteresis loop of the sample at different gate biases. It seems that coercivity does not change significantly in this case. The coercivity of the loop has been deduced from the linear interpolation, and was figured to be the values plotted in Fig. 6-3-6. The change in coercivity is smaller than 1 mT at maximum and smaller than the sweep rate of the external field.

Fig. 6-3-5 Hysteresis loop of Pt(2.38 nm)/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) structure measured at 10 K. Area near the coercivity has been magnified. Note that y-axis is the Hall resistivity. The gate biases has been applied in the order of +1 V, +2 V, 0 V, -1 V, and -2 V. The sweep rate is 2 mT/sec.
Fig. 6-3-6 Coercivity plotted against gate bias. The arrow indicated the direction of the change of gate biases. Coercivity has been determined by the linear interpolation of Fig. 6-3-5 near coercivity.

6.4 Discussion

6.4.1 Calculation of Thomas-Fermi screening length

Here, Thomas-Fermi screening length will be calculated to figure out the total length in which the carrier densities are modulated. The Thomas-Fermi screening length is calculated as $\frac{1}{k_s}$ [13], where $k_s$ can be expressed as

$$k_s^2 = 4\pi e^2 D(\varepsilon_F)$$

Here, $e$ and $D(\varepsilon_F)$ are elementary charge and density of states at Fermi energy, respectively. Assuming that the electrons follow the Fermi-Dirac distribution,

$$k_s^2 = \frac{6\pi n_0 e^2}{\varepsilon_F}$$

where $n_0$ is the charge density. From [18], Fermi energy is assumed to be 0.67 Ry in the bulk. The calculated values were 0.144 nm for electron density of $10^{23}$ m$^{-3}$ and 0.098 nm for $10^{24}$ m$^{-3}$. Therefore, the Thomas-Fermi screening length in Pt is less than that of the size of an atom, which is 0.28 nm. As a conclusion, only the uppermost layer of Pt atoms will feel the change in carrier density. However, this is not to say only the magnetic property of uppermost layer can be modified. The possibility that the modulated layer will influence the layers below through modified orbital interaction cannot be neglected.
6.4.2 Calculation of carrier density modulation

6.4.2.1 Without MgO

Without the MgO layer, the circuit can be simplified as two series EDL capacitor. Using equation (4-5-6), the total capacitance per unit area \( \frac{C}{S} \) can be expressed as

\[
\frac{C}{S} = \left( \frac{S}{C_{\text{EDL}}} + \frac{S}{C_{\text{EDL}}} \right)^{-1}
\]

\[
= 5.2 \ \mu F/cm^2 \quad \cdots (6-4-3)
\]

Suppose the Pt layer is facing fcc(111), the density of Pt atoms at the surface layer is calculated to be \( n = 1.5 \times 10^{15} \text{ cm}^{-2} \). Therefore the modulation of carrier density per Pt atom is calculated to be

\[
\Delta Q = \frac{C}{nS} V_G
\]

\[
= 2.2 \times 10^{-2} \times V_G \text{ electrons} \quad \cdots (6-4-4)
\]

When gate voltage of +2 V and -2 V was applied, the modulation of carrier density in total is calculated to be \( 8.8 \times 10^{-2} \text{ electrons} \).

6.4.2.2 With MgO (0.72 nm)

With the MgO layer, the circuit can be simplified as the series circuit of MgO capacitor and two EDL capacitor. Using equation (4-5-4) and (4-5-6), the total capacitance per unit area can be expressed as

\[
\frac{C}{S} = \left( \frac{S}{C_{\text{EDL}}} + \frac{S}{C_{\text{EDL}}} + \frac{S}{C_{\text{MgO}}} \right)^{-1}
\]

\[
= 3.8 \ \mu F/cm^2 \quad \cdots (6-4-5)
\]

\( \kappa_{\text{MgO}} = 11.7 \) was used. Similarly, the modulation of carrier density per Pt atom is calculated to be

\[
\Delta Q = \frac{C}{nS} V_G
\]

\[
= 1.6 \times 10^{-2} \times V_G \text{ electrons} \quad \cdots (6-4-6)
\]

When gate voltage of +2 V and -2 V was applied, the modulation of carrier density in total is calculated to be \( 6.4 \times 10^{-2} \text{ electrons} \).

6.4.3 Discussion of the result

The retrieved data for the electric field control of MgO/Pt/Co/Pt and Pt/Co/Pt systems have been summarized in Fig. 6-4-1 and 6-4-2. The values of magnetic moment has been calculated and modified into the change of magnetic moment per atom taking Bohr magneton as a unit. The
number of atoms per surface area has been calculated using the ideal Pt diameter and assuming they were fcc crystalized. Specifically, the number of Pt atoms at the surface was calculated to be $1.5 \times 10^{15} \text{ cm}^2$. The values of Curie temperature and coercivity has been normalized, with the first values taken as the normalizing factor for each figure. According to the figure, only the maximum of less than 3 % change of magnetic properties has been observed.

Fig. 6-4-1 Change in magnetic moment (above) and Curie temperature as a function of modulated electrons. For magnetic moment (above), the change in magnetic moment per atom, taking Bohr magneton as a unit, has been plotted. The values at first 0 V has been taken as the origin. The Curie temperature has been normalized with values at first 0 V set as 1. The red and blue plots show the data for MgO(0.72 nm)/ Pt(1.25 nm)/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) and Pt(1.25 nm)/ Co(0.17 nm) /Pt(4.08 nm) /Ta(4.95 nm) thin films, respectively. The arrows should the direction of the change.
Fig. 6-4-2 Change in coercivity as a function of gate bias. The first value at 1V has been taken as the origin and others were normalized. The red and blue plots show the data for Pt(2.38 nm)/Co(0.17 nm)/Pt(4.08 nm)/Ta(4.95 nm) and Pt(1.34 nm)/Co(0.17 nm)/Pt(4.08 nm)/Ta(4.95 nm) thin films, respectively. The arrows show the direction in which the gate bias was changed.

The modified magnetic moment seems large compared to the modulated electron density. The Bohr magneton represents the magnetic moment of an electron, however, the modified magnetic moment seems larger than the modulated magnetic moment. This suggests some possibilities. First, the electron modulated surface atoms may be interacting with the atoms below, changing their magnetic moment as well. Also, the electron modulation may not simply equal the amount of modified magnetic moment, in such a case where the exchange correlation is enhanced. For example, the change in magnetic anisotropy originating from the band filling can be considered. Finally, the accuracy of the number of modulated electrons and magnetic moment per atom should also be mentioned. Although both of them has been calculated from assumption based on data and previous studies, more accurate understanding is necessary to discuss precisely and quantitatively.

There seems to be a trend in all the cases that the magnetic properties weakens with positive gate bias and increases with negative gate bias. The trend agrees with the expected change from the calculated shape of the density of states of bulk Pt in Fig. 2-4-1. However the change is very small compared to the MgO/Pd/Co/Pt system. Although many elements are considered to be changed as a result of voltage application, in total, they seem to suppress the change in magnetic properties in this situation. The possible contributors to the change in magnetic properties will be
listed as follows;

- The change in density of states at Fermi energy can trigger the ferromagnetic-paramagnetic transition as mentioned in section 2.4. However, it is difficult to theoretically find out the density of states in this case because of the change in dimension, interface interaction from Co and MgO, and possibility of Pt turning Co/Pt alloys.

- Piezoelectric effect may be also influencing the system. Piezoelectric effect is the transition of voltage change to mechanical change and vice versa. Strong electric field will be applied to MgO and Pt topmost layer during the measurement. Thus the effect of mechanical property change such as change in lattice constant of Pt and MgO may be considered [53]. As Kyuno mentions, such strain would influence density of states, leading to the modification in magnetic properties of the film [27].

- Chemical property change of the film may also be considered as a factor. With the strong electric field applied, oxidization of Co from the oxygen atoms of upper MgO layer should be mentioned as an example. Oxidization of Pt can be ignored because Pt is known to be stable against chemical reaction.

Of all the possibilities considered above, the density of states may be able to explain the results the best. Considering the theoretical density of states of bulk Pt shown in Fig. 2-4-1, it may be appropriate to conclude that the density of states in the experimented case is flat near the Fermi energy compare to the case of Pd. In other words, even with the change in density of states from the bulk Pt value as a result of change in dimension and interface interaction, the energy derivative of the density of states was not enhanced. Although in the case of Pd, significant change in magnetic moment was observed, it may be appropriate considering that the energy derivative of the density of states near the Fermi level in bulk Pd is larger than that of bulk Pt (Fig. 2-4-1, 6-4-3). Considering that the magnetic moment in MgO/Pd/Co/Pt was enhanced by applying positive gate voltage and diminished by applying negative gate voltage, the trend is opposite from that of the theoretical bulk density of states. The change in dimension and interface interaction in the experiment may have moved the position of the peak.
Fig. 6-4-3 Density of states $D(\varepsilon)$ and number of occupied states $N(\varepsilon)$ for bulk Pd with spin-orbit interaction [18]. The orange line shows the Fermi energy.
Part 7 Conclusion

The purpose of the study was to control the magnetic moment induced in Pt through the application of electric field.

First, the properties of ionic film was investigated. From the result of the impedance spectroscopy, the characteristic of the capacitance of EDL was calculated to be $C_{\text{EDL}} = 10.5 \, \mu\text{F/cm}^2$.

In addition, other parameters of the circuit, such as the total resistance of the circuit ($3.9 \times 10^7 \, \Omega \text{cm}^2$) and time constant of the EDL (around 10 Hz) was figured out through leakage current and cyclic voltammetry experiment. The results were used for the calculation of the modulation of carrier density for the electrical field control of magnetic properties.

Then, the magnetic properties of MgO/Pt/Co/Pt and Pt/Co/Pt thin films have been investigated. The magnetic moment of the system with different MgO, upper Pt, and Co thickness have been measured. Among the many factors that seems to be contributing the magnetic moment of the film, the magnetic moment induced in Pt is one possibility for the increase in the magnetic moment. For the experiment on the electric field control of induced magnetic moment, the Pt thickness in which the magnetic moment was most likely induced was chosen.

Finally, the experiment on electric field control of MgO/Pt/Co/Pt and Pt/Co/Pt systems have been conducted. The observed change in magnetic properties was at maximum less than 3 %, which is insignificantly small compared to the result of MgO/Pd/Co/Pt systems. As one possible reason, the density of states near Fermi energy in this system may be flat, compared to the Pd systems.

In this study, electric field control of magnetic moment induced in Pt has been experimented. For the further understanding of physics associated with the system, the following studies should be conducted;

- Understanding of the electrochemical properties of ionic film
  Although a great part of electrostatic properties of the ionic film was revealed in this study, further research on the pseudocapacitance, Warburg impedance and the detail chemical behavior of the film must be understood for more accurate study of the electric field control.

- Specifying the reasons for the magnetic behavior of MgO/Pt/Co/Pt and Pt/Co/Pt systems
  More research on Pt/Co, Co/Pt, MgO/Pt, and MgO/Co interfaces should be conducted to learn about the magnetic properties of the system. They should also be compared to the result of the magnetic properties of systems using Pd. In addition, magnetic properties of samples with different depositing conditions should be investigated to eliminate possible impurities and contamination from the process.
Comparing the results of the electric field effect on Pt/Co/Pt and Pd/Co/Pt systems
Although electric field control of magnetic moment induced in Pd was successful, Pt did not come out to have the same result. The reasons should be specified to understand the physics associated in this system.

Electric field control of other exchange enhanced paramagnetic materials
Electric field control of exchange enhanced paramagnetic materials such as Ru and Rh should be conducted for further understanding of magnetic properties of paramagnetic materials [19].
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