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Electrical control of Curie temperature in cobalt using an ionic liquid film

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The electric field effect on magnetization properties and Curie temperature of Co ultra-thin films has been investigated. An electric field is applied to a Co film by using an electric double layer (EDL) formed in a polymer film containing an ionic liquid. The change in the Curie temperature is ~100 K by applying the gate voltage of ±2 V, suggesting that the observed large modifications of magnetization properties are attributed to the significant change in the Curie temperature, which is induced by a large amount of carrier density control due to the formation of the EDL. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3695160]

The electric field effect on magnetism opens up a new dimension for the research field of spintronics. Using field effect capacitors (FEC) consisting of a gate electrode, an insulator layer, and a ferromagnetic layer, controls of ferromagnetic properties have been achieved through the modulation of the carrier density in the ferromagnetic layer by applying gate voltage.[1–12] Ferromagnetic semiconductors have been most intensively investigated from this viewpoint[1–3,5,7,8,11] because their ferromagnetic properties are the function of carrier concentration.[13] More recently, even in FECs with an ultra-thin ferromagnetic metal layer, electric field controls of coercivity,[4,9,12] magnetic anisotropy,[6,9] and Curie temperature[12] have been demonstrated at room temperature. Since ferromagnetic metals have a larger electron density than ferromagnetic semiconductors, FECs with a large capacitance are required to dramatically change ferromagnetic properties. A conventional way to obtain a large capacitance is to adopt high-κ (κ: relative permittivity) materials (e.g., Al_2O_3, HfO_2, or ZrO_2),[5,7,9,12] although an electric double layer (EDL) formed between a liquid electrolyte and a material to be gated has attracted a lot attention[4,8,11,14–22] because it has a huge capacitance and has been recently used for controlling ferromagnetic properties.[4,8,11]

To understand the electric field effect on magnetism in ferromagnetic metals, it is significant to quantitatively investigate how the magnitude of the magnetization as well as the Curie temperature[12] is electrically modulated by changing the electron density[10] in terms of the physical chemistry of magnetism. In this letter, we show the electric field effect on the magnetization properties of Co ultra-thin film at room temperature by an EDL formation at the interface between a cobalt layer and a polymer film containing an ionic liquid,[17,23,24] a transparent and flexible electrolyte sheet known as an ion film. The magnetization value (M) of the ferromagnetic layer during the EDL formation was directly measured by using a conventional superconducting quantum interference device (SQUID) magnetometer.[7] Our method of using a polymer film containing an ionic liquid to modulate the electron density of ferromagnetic layers makes it easy to measure the direct magnetization under an electric field.

Figure 1 shows a schematic of the device structure. The device consists of a Pt gate electrode, the polymer film containing the ionic liquid (the ionic liquid film), and a cobalt ferromagnetic layer. The ionic liquid film we used here contained the following cation and anion: 1-ethyl-3-methylimidazolium (EMI^+) and bis(trifluoromethylsulfonyl)imide ($TFSI^-$), and the film was made in the conventional way.[17,23,24] To fabricate the device, the ionic liquid film was first placed onto sputter-deposited layers consisting of MgO (2.0 nm)/Co (0.4 nm)/Pt (1.2 nm)/Ta (3.0 nm) from the surface on an undoped Si substrate. Next, to form the gate electrode, a commercially available ~25-μm-thick Pt thin film was directly placed on top of the ionic liquid film. The surface of the ionic liquid film is sticky, which naturally prevents all the parts from peeling apart. The total area of the device (S) was ~4×4 mm^2. Cu wires were finally attached to the gate electrode and the bottom cobalt layer to apply the gate voltage (V_G). Based on this design, ~30% of S remained uncovered by the Pt film. The devices were introduced into the SQUID magnetometer and the magnetization was measured while applying various V_Gs ranging from −2 to +2 V.

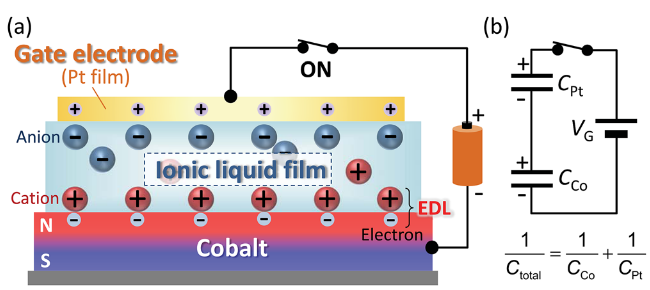

FIG. 1. (Color online) (a) Schematic illustration of the device structure consisting of the gate electrode, the polymer film containing the ionic liquid (ionic liquid film), and the Co (cobalt) thin film. The electric double layers (EDLs) are formed at the interface between the cobalt thin film and the ionic liquid film and also at that between the platinum film (gate electrode) and the ionic liquid film. (b) The equivalent circuit schematic of the present device.

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Magnetization curves measured at several V_Gs are displayed in Fig. 2. The measurements were carried out at 300 K and an external magnetic field (H) was applied perpendicular to the sample plane. The vertical axis of Fig. 2 indicates M normalized by S. Note that the curves contain the contribution of M of the uncovered (thus ungated) region. To rule out the drift of the sample properties, the V_G was gradually increased to approach the values listed in the figure and kept at each level for 30–60 min before each magnetization measurement. One can see that the application of V_G considerably modified the magnetization properties, i.e., larger coercivity (H_c) and larger M were obtained by applying a higher positive V_G. Figures 3(a) and 3(b) show V_G dependence of the remanent magnetization (M_r: M at $H = 0$ Oe) and H_c, respectively. The initial M_r value at $V_G = 0$ V is nearly zero. By increasing V_G, the M-H curve enlarges as shown in Fig. 2. Appreciable M_r value appears at $V_G = +1.5$ V and it further increases at 2.0 V. Then, as V_G is reduced, the value decreases and finally drops to zero at $V_G = -1.0$ V. The H_c shows similar dependence on V_G [Fig. 3(b)]. Thus, it is clear that applying electric fields enabled us to control the magnetization properties. The results shown here were reproduced in more than five similar but different devices fabricated on Si or GaAs substrates.

One possible explanation for the observed modulations of magnetization properties is the change in the Curie temperature (T_C). To check whether T_C can be changed by applying V_G, the temperature (T) dependence of M was measured using another device. Figure 4 shows the temperature dependence of M measured at $V_G = -2$, 0, and $+2$ V under the application of moderately small perpendicular H of 2 Oe. The T_C at 0 V can be roughly estimated to be ~325 K, where M drops to nearly zero. Such a T_C much lower than the bulk value (>1000 K) is due to two-dimensional magnetism.[12,25] T_C at -2 and $+2$ V were ~280 and 380 K, respectively, i.e., the amount of the change in T_C (ΔT_C) was ~100 K. We, therefore, conclude that the significant

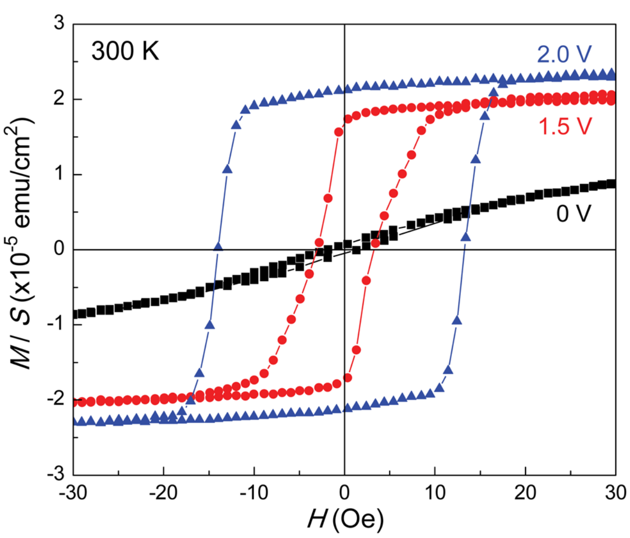

FIG. 2. (Color online) Magnetization (M) versus external magnetic field (H) curves at 300 K under different gate voltages (V_G). The vertical axis represents M divided by the total area of the sample (S). V_G was applied in an order of 0 V, 1.5 V, and 2.0 V. H was applied perpendicular to the sample plane.

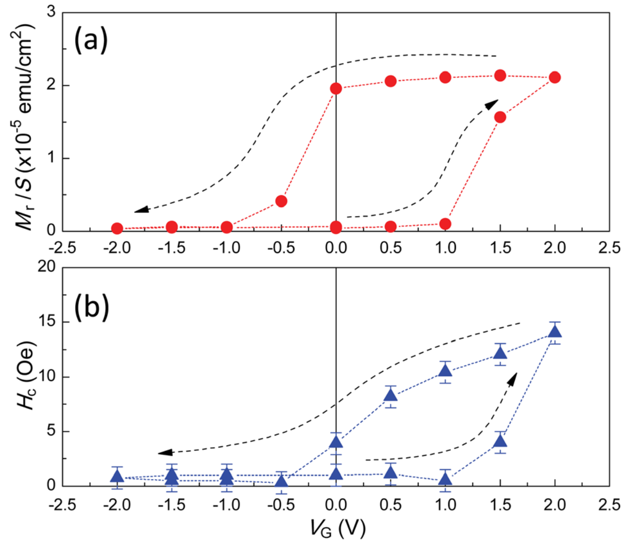

FIG. 3. (Color online) Gate voltage (V_G) dependence of (a) the remanent magnetization (M_r) and (b) coercivity at 300 K. The vertical axis of (a) represents M_r divided by the total area of the sample (S).

modulations of M_r and H_c observed at 300 K can be attributed to the observed large ΔT_C.

In the present experiment, T_C is enhanced by applying positive V_G in the direction of the electron accumulation at the Co layer surface. This is consistent with our previous results, in which a HfO_2 high-κ gate insulator was used.[12] This electric field control of T_C can be explained by the surface critical phenomena[26] or a change in magnetocrystalline anisotropy in a 2 dimensional ferromagnetic film.[27] The observed ΔT_C in the present device (~100 K) by applying V_G of only ±2 V (i.e., the total amount of V_G, $\Delta V_G = 4$ V) is larger than the result in the FEC with the 50 nm HfO_2 gate insulator we used in our previous work ($\Delta T_C = 12$ K), where $\Delta V_G = 20$ V was needed. The total capacitance C_{total} of the present device is 6.3 μF/cm^2. In the present EDL capacitor,

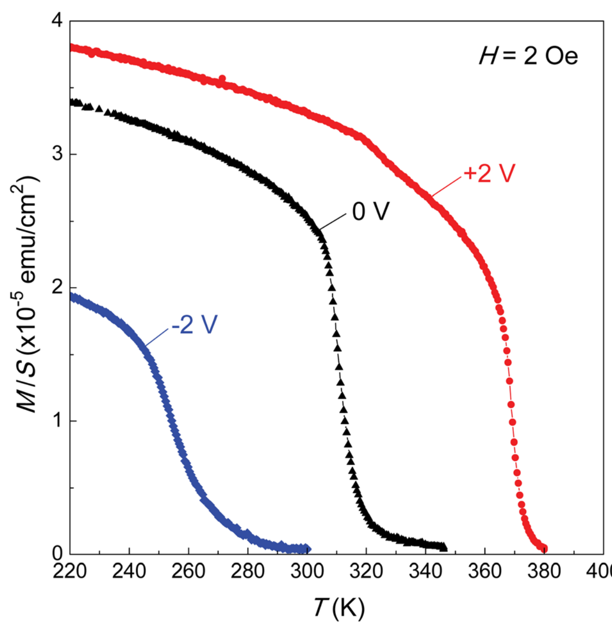

FIG. 4. (Color online) Temperature (T) dependence of the magnetization (M) at $H = 2$ Oe under $V_G = -2$ (diamonds), 0 (circles), and $+2$ V (triangles).

C_{total} can be determined by two double-layer capacitors formed on the Pt interface (C_{Pt}) and the Co interface (C_{Co}): $1/C_{total} = 1/C_{Pt} + 1/C_{Co}$ [see Fig. 1(b)]. If we assume $C_{Co} = C_{Pt}$, $C_{Co} = 2C_{total}$, then the modulated sheet electron density per 1 V ($= C_{Co}/e$, where e is the elementary charge) is estimated to be $7.9 \times 10^{13}\,\mathrm{cm}^{-2}$. This value is $\sim$7 times larger than that in the FEC for the 50-nm HfO_2 gate insulator at 1 MV/cm. The change in the number of electrons per Co atom in the surface can be derived as ± 0.084 by applying $V_G = \pm 2$ V under the assumption that the Co on the Pt layer orders as a fcc(111) structure. The amount of the change in the number of electrons achieved here is about 8 times larger than that expected in the HfO_2-FEC at $\Delta V_G = 20$ V, indicating that the giant modification of T_C in the present device is due to this large modification of the electron numbers. The amount of the carrier modulation is limited by the breakdown voltage in the solid-state-EFCs, while the EDL-FEC presented here has a further potential for controlling wider T_C.

In summary, the direct magnetization measurements have revealed that the magnetization properties and the Curie temperature of Co can be significantly controlled by applying a few volts of the gate voltage through forming an EDL. This low-voltage control of magnetism at room temperature is a significant step towards realizing future low-power magnetic applications.

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