Injected Charge Modulation Using Magnetic Filtering Effect in Au/Cr₂O₃/FeCr/CeO₂/Si Capacitor

Takeshi Yokota,* Koji Ichikawa, Shotaro Murata, and Manabu Gomi
Department of Material Science and Engineering, Graduate School of Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya City, Aichi 466-8555, Japan
(Received 6 July 2013; Accepted 18 October 2013; Published 16 November 2013)

We investigated the influence of an external magnetic field for the carrier injection process of a metal (Au)/insulator (Cr₂O₃/FeCr/CeO₂)/semiconductor (Si) capacitor, in which the insulator consists of magnetic materials. By applying an electric field, electrons propagating through the CeO₂ layer from Si were injected into the FeCr or an oxygen deficiency layer formed around the FeCr layer. When a magnetic field was applied, the hysteresis window width of this capacitor was increased. I–V curve analyses under a magnetic field revealed that this increases was more likely due to the magnetic state of the FeCr layer. [DOI: 10.1380/ejssnt.2013.122]

Keywords: Magnetic films; Magnetic interfaces; Metal-oxide-semiconductor (MOS) structures

I. INTRODUCTION

Magneto-electronics employing magneto-electric (ME) materials have become attractive as a new generation of non-volatile data storage devices because their magnetic or ferroelectric properties can be controlled by an external electric or magnetic field [1–5]. Although many researchers are investigating ME materials, there are only a few reports of electric devices using the ME feature [6–9]. Previously, we proposed the possibility of ME capacitors (MECs) consisting of Pt/Cr₂O₃ (ME material:gate insulator)/Fe (magnetic filtering layer: MFL)/CeO₂/Si. We also reported the carrier injection process and the memory effects of this capacitor [10]. However, the relationship between magnetism and the charge injection mechanism were unclear. Hence, in this present study, we demonstrate the injection charge modulation of the Au/Cr₂O₃/FeCr/CeO₂/Si Metal-Insulator-Semiconductor (MIS) capacitor by the application of an external magnetic field. We also discussed the charge injection mechanism of this capacitor by analyzing the I–V characteristics.

II. EXPERIMENTAL

The sample was prepared using the three-gun radio-frequency magnetron sputtering method. Cr₂O₃ and CeO₂ sintered ceramics were used as the target. The base pressure before introducing the sputtering gas was 3.0×10⁻⁴ Pa and the gas pressure during deposition was 8.0×10⁻¹ Pa. The first layer was a 5-nm-thick CeO₂ tunnel layer and it was deposited on an n-type Si (111) substrate (resistivity: 20 Ωcm) cleaned using improved Radio Corporation America methods. A 0.25-nm-thick FeCr layer was then deposited using only Ar as the sputtering gas. Finally, a 45-nm-thick Cr₂O₃ layer was deposited.

The magnetic properties of the sample were measured using a superconducting quantum interface device. Structural analysis of the films was performed by X-ray diffraction (XRD) utilizing Cu Kα radiation. The surface morphology was measured by atomic force microscopy (AFM). The leakage current was measured using a picoammeter (Keithley, 6487), while the capacitance was measured using an LCR meter (Agilent, E6480A). The top and bottom electrodes consisted of Au and were 200 µm in diameter. To avoid deviations in the measurements of the electric properties, they were performed using about 40 electrodes, which were constructed on the sample. A magnetic field was also applied perpendicular to the film’s surface during the electric properties measurement.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a XRD pattern. It reveals that the film consists of polycrystalline Cr₂O₃ and highly oriented CeO₂. Figure 1(b) shows an AFM image of the surface morphology and the surface profile along the dotted line in the AFM image.

*Electronic address: yokota.takeshi@nitech.ac.jp
have been injected into the FeCr layer or some defects layer existed around the FeCr layer. According to the thickness of FeCr layer, defects layer more likely works as a floating layer. With the increases of a magnetic field, the hysteresis window width (HWW) of the C–V curve becomes wider and the flat band voltage was shifted toward positive voltage. These charge injection behavior under the magnetic field does not change for a direction of magnetic field. The ME effect of Cr$_2$O$_3$ is generated along to c- or a-axis. If the Cr$_2$O$_3$ film has highly oriented crystal structure, the both direction of electric field and magnetic field is important [11]. Since the Cr$_2$O$_3$ gate insulator has polycrystalline structure in our sample, the carrier injection process was not affected by the external magnetic field direction.

Figure 3 shows applied magnetic field dependence of HWW and flat band voltages. The flat band voltage of each C–V curve was estimated by the depletion layer approximation [12]. Changes in the HWW and the flat band voltage have the same tendency against the applied magnetic field. Basically, there should be no relationships between the flat band voltage and the amount of injected carriers, because occurrence of the hysteresis window could be explained by a threshold voltage shift due to the stored charge in the floating gate and the flat band voltages is defined by the band gap of each insulator and work function of top electrode, which is Au in this sample.

In order to investigate these behaviors, the current–voltage (I–V) characteristics with/without a magnetic field, the so-called magneto-resistance (MR), were measured. Figure 4 shows I–V curves of the sample with/without a magnetic field of 10 mT. In response to application of the magnetic field, the current values at the voltages from 0 to 2 V decreased. Since the electron was under a charge injection process into the FeCr layer within the measurement voltages, this I–V behavior can be analyzed using both tunneling and the Schottky emission conduction model. In general, the F.G.-type MIS capacitor can store charges in the F.G. according to the Fowler-Nordheim (FN) tunneling mechanism. Since a magnetic field should affect only a charge injection process propagating through the CeO$_2$ tunneling layer and injecting into the floating gate within measurement voltages, we regard the Cr$_2$O$_3$ top gate insulator as an ideal dominated by Schottky emission conduction. The currents due to the FN tunneling (FNT), $J_{DT}$, and the Schottky emission (SE) conduction, $J_{SE}$, are given as follows [13–15].

\[
J_{DT} = A^* \frac{E_{tox}^2}{\varphi_{CeO_2}} \exp \left[ -B \left( \frac{\varphi_{CeO_2}^{3/2} - (\varphi_{CeO_2} - |qV_{tox}|)^{3/2}}{|E_{tox}|} \right)^{1/3} \right],
\]

\[
J_{SE} = AT^2 \exp \left[ -\frac{q(\varphi_B - \sqrt{qE/4\pi\varepsilon_{Cr_2O_3}\varepsilon_0})}{kT} \right].
\]

Here, $A^* = \frac{q^3m_0}{8\pi\hbar m_{ox}}$, $B = 8\pi \sqrt{2m_{ox}/(3\hbar q)}$, and $q = 1.602 \times 10^{-19}$ [C]. $m_{ox}$ is the effective electron mass in the tunneling layer, $m_0$ is the free electron mass, and $\varphi_{CeO_2}$ is the tunneling barrier. $A$, $T$ and $k$ are Richard-
son constant, temperature and Boltzman constant, respectively. \( \phi_B \) is the Schottky barrier height for junction of \( \text{Cr}_2\text{O}_3 - \text{FeCr} \), and \( \varepsilon_{\text{Cr}_2\text{O}_3} \) is the dielectric constant of \( \text{Cr}_2\text{O}_3 \).

In the case of common F.G. type MIS capacitor, the experimental I–V curves can be analyzed using each conduction mechanism. Figure 5 shows I–V curves replotted using (a) FNT conduction and (b) SE conduction mechanism. FNT conduction plots of both samples have a negative slope above 1.0 V. On the other hand, SE conduction plots of both samples always have a positive slope. This means that the SE mechanism dominate the current–voltage characteristics within the measurement voltage. However, the conduction mechanism above 1.0 V was dominated by the both mechanisms. In the case, it is difficult to distinguish which conduction mechanism dominates the charge injection properties under the magnetic field. The experimental I–V curves could be fitted by the linear combination of each conduction model regarding \( m_{\text{ox}} \) as a fitting parameter. The \( m_{\text{ox}} \) does not appear to be affected by the external magnetic field. In the case of the magnetic layer/tunneling layer hetero system, however, the electron tunneling probability changed depending on the magnetic ordering state of the ferromagnetic layer. In addition, the \( m_{\text{ox}} \), which corresponds to tunneling the probability, should be changed. It is also taking into accounts the ratio of liner combination to understanding which mechanism dominates the system.

Figure 6(a) shows the I–V curve fitted by only SE model and (b) fitted by both SE and FNT model. According to the result of Fig. 6(a), it could not be fitted well above 1.0 V. This result supported the results of Fig. 5, which is indication of FNT conduction existence above 1.0 V. The ratio of liner combination of SE part is monotonically decreased until 1.0 V. The ratio of FNT part has opposite tendency. Since the ratio of FNT part above 1.0 V become larger than that of SE part, it is revealed that the conduction mechanism above 1.0 V is dominated by FNT conduction.

Using these results, we also estimated the \( m_{\text{ox}} \) of each magnetic field. Figure 7 shows the magnetic field dependence of the values of \( m_{\text{ox}} \). With the increase in the applied magnetic field, the \( m_{\text{ox}} \) decreases. The light tunneling electron mass means that the electron easily propagates the tunneling layer. These results support the results of the HWW increase under the magnetic field, as shown in Fig. 3. Although the increase in HWW is explained by the mechanism mentioned above, the shift of flat band voltage cannot be explained. Although we have not yet determined the physical origin of this behavior, one possible explanation can be proposed. The \( \text{Cr}_2\text{O}_3 \) can produce an induced polarization by applying an external magnetic field due to its ME feature and can induce an apparent change of the relative permittivity of \( \text{Cr}_2\text{O}_3 \). Or the magneto-electric domain of \( \text{Cr}_2\text{O}_3 \) might be aligned electromagnetically with the existence of both an external magnetic field and electric field, which are applied for the C–V measurement \[16–18\]. In this case, we can expect an increase or decrease in the relative permittivity of \( \text{Cr}_2\text{O}_3 \). Upon application of a voltage \( V_G \) to the gate, which is top electrode on this system, an electric field is established in each of the two insulators. In other words, we have that \( V_G = V_1 + V_2 \) where \( V_1 \) and \( V_2 \) are the voltages developed across \( \text{Cr}_2\text{O}_3 \) and \( \text{CeO}_2 \). Therefore, increases or decreases of the relative permittivity of \( \text{Cr}_2\text{O}_3 \) give rise to an increase or decreases the voltages applied on \( \text{CeO}_2 \) layer \[12\]. The voltage for band bending of \( \text{CeO}_2 \) then will be changed.

Anyway, these results indicate that the charge injection process of this capacitor can be controlled by the magnetization of the FeCr layer and by the amount of the
FIG. 6: I–V curves without magnetic field fitted using (a) SE conduction, (b) SE and FNT conduction mechanism. The open squares indicate experimental results. The solid line is represented calculations using each conduction mechanisms.

FIG. 7: Magnetic Field Dependence of tunnel electron effective mass estimated using both the FN tunneling and Schottky emission conduction equation.

FIG. 8: Retention Properties of the capacitor memorized at various magnetic field.

We investigated the relationship between the charge injection process and an applied magnetic field on the Cr$_2$O$_3$/FeCr/CeO$_2$/Si MIS capacitor. Upon applying a magnetic field, the HWW in the C–V curve increased. A negative magneto-resistance was observed in the same magnetic field range. According to the analyses using direct tunneling and the Schottky emission conduction model, the increase in the HWW is more likely related to the lighter effective electron mass due to the internal or the external magnetic field. The retention properties revealed that the injected carrier by the different magnetic field was retained within the measurement period. The amount of injected charges can be modulated by the application of a magnetic field.

IV. CONCLUSIONS

We investigated the relationship between the charge injection process and an applied magnetic field on the Cr$_2$O$_3$/FeCr/CeO$_2$/Si MIS capacitor. Upon applying a magnetic field, the HWW in the C–V curve increased. A negative magneto-resistance was observed in the same

Acknowledgments

This work was supported in part by a Grant-in-Aid for Young Scientists (A) (23686094) from the Japan Society for the Promotion of Science (JSPS) and the JSPS International Training Program (ITP), “Young Scientist-Training Program for World Ceramics Network,” and in part by a grant from Institute of Ceramics Research and Education, NITECH.