Spin-charge multi injection mechanism of a magneto-electric capacitor

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We investigated a multiple charge-injection mechanism of a magneto-electric (ME) capacitor. Although the capacitor showed a multi-step charge-injection process with regard to its capacitance–voltage (C–V) characteristics, the behaviors were found to be different depending on the tunneling layer thickness. Detailed analyses of current–voltage (I–V) characteristics revealed the presence of multi-step behavior in a sample exhibiting a Fowler–Nordheim (FN) tunneling mechanism. With decreases in the tunnel layer thickness, the FN tunneling behavior shifted to a high voltage region, at which point the multi-step behavior became unclear. These results indicate that the tunnel layer thickness plays an important role in this multi-step mechanism.

1. Introduction

Information-processing devices that use semiconductor random access memories generally operate using electric charge, without utilizing the electric spin. In these devices, however, spin becomes important for dimensions smaller than approximately 100 nm. Consequently, a new information technology that utilizes spin, known as spintronics, has begun to be developed.1)–3) In order to make efficient use of electric spin in semiconductor information-processing devices, we have proposed the possibility of ME capacitors (MECs) consisting of Pt/Cr2O3 (ME material: gate insulator)/Cr2O3/Fe/ Cr2O3 – x (floating gate: F.G.)/Fe (magnetic filtering layer: MFL)/CeO2/Si.6) We have confirmed that the MECs can store electrons in the F.G., magneto-electrically.7) We have also reported that the spin density of state matching between the F.G. and the MFL layer is important for the charge-injection process.8) Based on these results, if we could change the spin density of state of the F.G. using a stronger ME effect than that of single Cr2O3, we could expect variations in the charge-injection process. Here, we investigate the multiple charge-injection process using a Cr2O3/LiNbO3/Cr2O3/Cr2O3 – x/Fe/CeO2/Si capacitor with different CeO2 thicknesses. In this structure, [Cr2O3/LiNbO3/Cr2O3], [Cr2O3 – x], [Fe], and [CeO2] work as a ME gate insulator, F.G., MFL, and tunnel layer, respectively.

2. Experiment

MECs were prepared using a three-gun radio-frequency magnetron sputtering method. Cr2O3 and CeO2-sintered ceramics and commercial LiNbO3 (KOJUNDO CHEMICAL LAB CO., LTD, Tokyo) ceramic were used as the target. The base pressure before deposition was 8.0 × 10−10 Pa. The first layer was a 5-nm or 3.5-nm-thick CeO2 tunnel layer, and it was deposited on an n-type Si (111) substrate cleaned using improved Radio Corporation of America methods. These samples were named as sample (a) and sample (b), respectively. A 250-nm-thick Fe layer was then deposited using only Ar as the sputtering gas. In order to prevent this Fe layer from oxidizing, a 1-nm-thick Cr2O3 – x layer was deposited, also by using only Ar as the sputtering gas. Since Cr2O3 – x showed ferromagnetism, this Cr2O3 – x layer also functioned as a ferromagnetic F.G. layer.9) For a multilayered gate insulator, a 16-nm Cr2O3 layer was deposited, then a 100-nm LiNbO3 layer, and finally, a 16-nm Cr2O3 layer. Structural analysis of the films was performed by X-ray diffraction (XRD; Rad-B, Rigaku, Tokyo) utilizing Cu Kα radiation. The surface morphology was measured by atomic force microscopy (AFM). The leakage current was measured using a picoammeter (model# 6497, Keithley), while the capacitance was measured using an LCR meter (model# E4980, Agilent, Santa Clara, CA, USA). The top and bottom electrodes consisted of Au and were 0.2 mm in diameter. To avoid deviations in the electric properties, the measurements were performed using about 40 electrodes, which were patterned on the sample.

3. Results and discussion

Figure 1 shows C–V characteristics of the samples having different CeO2 thicknesses of (a) 5 nm and (b) 3.5 nm. Both of the samples showed hysteresis loops having clock-wise traces, which means that the charges were injected into ferromagnetic F.G. and they also showed multistep traces. Although these samples showed multistep traces, there were differences between the two samples. The trace of sample (a) still showed charge-injection process (process 2) after the first injection process (process 1). In contrast, the trace of sample (b) showed asymmetry hysteresis and the charge injection occurred only during the first process. The hysteresis window width (HWW) of sample (a) is also larger than that of sample (b). Figures 2(a) and 2(b) shows tanδ–V curves corresponding to Fig. 1. Stepwise behavior was also observed in the curve. The tanδ is the dissipation factor, which means a loss rate of energy for alternative voltage. If the tanδ shows flat against a voltage, as in Fig. 2(a), it means that an injectable state in F.G. was filled by injected charge. Therefore, there are at least two types of injectable states in sample (a). The step-like behavior can also be observed in Fig. 2(b), as indicated by an arrow. It seems that the injectable site is one. Since the number of injected charges

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DOI http://dx.doi.org/10.2109/jcersj2.121.1008
is the same as the number of electrons, which, in turn, the current during the injection process, we believe that an analysis of I–V characteristics is important for understanding the charge-injection mechanism. We chose two models for analyzing the I–V curves. One is the space-charge-limited-current (SCLC) model, because the electron follows the capacitor via the trap site, which is F.G. in this sample. If the injectable site in the F.G. is filled up by the charges, these regions limit the current flow, which is referred to as SCLC and can be expressed as Eq. (1).

\[
J_{SCLC} = \frac{9\mu\varepsilon_0 K_B}{8d^3} V_n \left( \frac{1}{n-1} \right)^{1/n} \quad \text{(1)}
\]

\(\mu\): mobility, \(d\): thickness, \(\varepsilon_0\): permittivity, \(K_B\): Boltzman constant.

We can therefore expect that the charge-injection behavior can be described by analyzing the SCLC plot. The other mode is the FN conduction plot. In general, the F.G.-type MIS capacitor can store charges in the F.G. according to the FN tunneling or hot electron mechanism. Since we only changed the thickness of the CeO2 tunnel layer between samples (a) and (b), we also analyzed the I–V curves using FN tunneling. The FN tunneling is expressed as Eq. (2).

\[
J_n = \frac{A E_{OX}^2}{\sinh^2 \phi_b} \left( \frac{\phi_b}{V_{OX}} \right) \left( \frac{2\phi_b}{V_{OX}} - 1 \right) e^{-B \left( \frac{V_{OX}}{\Phi_b} \right)^{1/2}} \quad \text{(2)}
\]

\(B = \frac{8\pi \sqrt{2m_{ox}}}{3\hbar} \Phi_b^{3/2} A = \frac{q^3 m_0}{8\pi \hbar m_{ox}} \quad \text{(2)}
\]

\(\Phi_b\): tunnel barrier height, \(V_{OX}\): Electric potential in oxide, \(m_{ox}\): effective electron mass in oxides, \(h\): plank constant, \(q\): Elementary charge, \(m_0\): electron mass. This equation is simply re-expressed as Eq. (3)

\[
\ln \left( \frac{J}{V^2} \right) = -B/V + \ln A \quad \text{(3)}
\]

\(A, B\): Constant.

Since the charge-injection process was observed from negative to positive voltage in the C–V curves, we analyze the I–V curves at both voltage regions. For the negative voltage region, we used absolute values. Figure 3 shows I–V curves replotted using the SCLC model. The broken and solid lines indicated in Fig. 3 show the calculated line using Child’s Law \((J \propto V^2)\) and the Ohmic Law \((J \propto V)\), respectively. In the sample (a), the current values monotonically increased with increases in the measurement voltages, which suggest that the injectable site in the F.G. was not filled up within the measurement voltages. In contrast, the transition from monotonic behavior to Child’s law from 0.2 to 0.7 V was observed in sample (b). This change in the current means that the trap levels were occupied with electron. In other words, charge injection occurred only in this region. In the negative voltage region of the sample (a), the current values also monotonically decreased in the low voltage region, meaning that the charge-injectable site was not filled up in this region. Figures 4(a) and 4(b) shows I–V curves of sample (a) and (b) replotted using the FN conduction model. The solid line indicates a negative slope region, which corresponds to FN conduction. In the sample (a), FN tunneling behavior is observed from 0.1 to 0.3 V with positive voltage and from −0.1 to −0.3 V in the negative voltage region. In contrast, FN tunneling behavior was observed from 0.4 to 0.6 V at the only positive voltage region in the sample (b). From the SCLC results, the FN tunneling behavior and the C–V characteristics, we can propose the charge-injection process differences between the sample (a) and (b). In the sample (a), the FN tunneling dominates in the most of charge-injection process. The FN tunneling behavior wasn’t observed above 0.4 V. We believe that the FN tunneling still occurs above 0.4 V, but it could be small, with the hot electron mechanism being dominant in the charge-injection process. In this case charges can be injected into a higher energy state than that achieved with FN tunneling. In contrast, in the case of the sample...
the FN tunneling dominates from 0.4 to 0.6 V. From the analysis of the SCLC mechanism, the transition from the monotonic behavior to Child’s law was observed at the same voltage region. After that, the conduction mechanism changes to SCLC. A remarkable point is that the increase in current in sample (b) during the FN tunneling is larger than that of sample (a). This difference can be explained by the thickness of the tunneling layer. If the CeO$_2$ layer becomes thinner, the effective voltage applied to CeO$_2$ become small. In this case, FN tunneling doesn’t dominant the injection process until the voltage become sufficiently high. Since the charge injection occurred from −1 V from the result of the C−V curve of sample (b), the dominant charge-injection mechanism of sample (b) should be the hot electron type. Above 0.4 V, the charge injections occur with both injection mechanisms at the same time. There still remains, however, a question as to why the multi-step behavior is clearly observed in sample (a), but not (b). Figure 5 shows the magneto-resistance (MR) of samples (a) and (b). The negative MR was clearly observed in sample (a). On the other hand, sample (b) shows no

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MR. The negative MR of the sample (a) is observed below 0.4 V, which corresponds to the FN tunneling behavior. In contrast, the MR ratio from 0.4 to 0.9 V is decreased. From these results, we
can conclude the mechanism of the multi-step injection behavior in the ME capacitor. The F.G., which is Cr$_2$O$_3$, should modulate the spin state by the ME effect of the Cr$_2$O$_3$/LiNbO$_3$/Cr$_2$O$_3$ gate insulator. In addition, the carrier from the semiconductor should gradually propagate through the tunnel layer using an FN tunneling mechanism. As long as the carrier is injected using the FN tunneling mechanism, carriers are affected by the spin-filtering effect of Fe, which is revealed in the results of the negative MR. The spin-polarized carrier can then be injected into the spin state of F.G. modulated by the ME effect. If the injection mechanism dominates by the hot electron mechanism, carriers are not affected by the spin-filtering effect. In this case, the carrier can injected evenly into the spin state modulated by F.G.; in other words, the spin state of F.G. modulated by ME effect works as a simple floating gate just like a normal semiconductor F.G.-type MIS capacitor. Therefore, the negative MR shows only below 0.4 V of sample (a). Although a negative MR was observed above 0.4 V, the ratio is small due to the dominance of the hot electron mechanism.

4. Conclusions

We have investigated the multiple charge-injection processes of an ME capacitor. The detailed I–V analyses revealed that the FN tunneling plays an important role for multiple charges in injection behavior. In addition, injected carriers appear to be influenced by the filtering effect of Fe. On the other hand, the carrier injected using the hot electron mechanism was not affected by the spin-filtering effect of Fe. To obtain the multiple charge-injection behavior of this ME capacitor, the ME gate insulator, the spin state of F.G. modulated by the ME effect, the spin-filtering layer, and the tunneling layer thickness are important, and spin band engineering is also necessary.

**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 the Institute of Ceramics Research and Education, NITECH.

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