Evaluation of resistive switching properties for BiFeO₃ film capacitors using Positive-Up-Negative-Down measurement

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Nd-doped BiFeO₃ (BNF) thin film of 170 nm thickness was deposited on SrRuO₃-coated (100) Nb-doped SrTiO₃ substrate by pulsed laser deposition. Resistive switching and ferroelectric properties of BNF film capacitor were investigated by using Positive-Up-Negative-Down measurement. Switched charge without influence of the leakage current was 121 $\mu\text{C}/\text{cm}^2$ with a maximum applied voltage of 9 V. The leakage current was estimated from the gradient of the pulse response when reading pulse was applied. After writing by voltages of -9 V and +9 V the current density at reading voltage of -1.8 V were 1.2 mA/cm^2 and 14 $\mu\text{A}/\text{cm}^2$, respectively. Maximum ON/OFF ratio of the leakage current was 86.

Key words: ReRAM, resistive switching, BiFeO₃, ferroelectrics

1. INTRODUCTION

Resistive switching behavior has attracted great attention due to excellent memory properties, such as non-volatile operation, high speed switching and large ON/OFF current ratio. Therefore, resistance random access memory (ReRAM) owing to the resistive switching behavior is a promising candidate for the future nonvolatile memory applications.

Recently, resistive switching behaviors have been reported also in ferroelectric materials, e.g., Pb(Zr_{0.52}Ti_{0.48})O₃, BiFeO₃ (BFO) and BaTiO₃.¹⁻⁶ The mechanism for the resistive switching in ferroelectric capacitor is still not completely elucidated, although several groups proposed the ferroelectric capacitors owing to ferroelectric polarization reversal model.³⁻⁹ It is well known that BFO is a lead-free ferroelectric material with excellent ferroelectric properties comparable to those of Pb(Zr,Ti)O₃.¹⁰⁻¹² In particular, large remanent polarizations P_r (over 80 $\mu\text{C}/\text{cm}^2$) have been demonstrated in the BFO thin films fabricated by various deposition methods.¹³⁻¹⁷ It is expected that the large P_r is an advantage in operation of the resistive switching with high ON/OFF current ratio in the ferroelectric ReRAM cell, because resistive switching in ferroelectric capacitor is induced by asymmetrical deformation of the barrier potential profile due to screening of polarization charge.⁵ Moreover, the ReRAM with ferroelectric switching is favorable for non-destructive readout operation compared with 1T-1C type non-volatile ferroelectric random access memory. Hence, BFO has potential as a promising material for ferroelectric ReRAM applications.

However, as a serious problem for detailed investigation of resistive switching and ferroelectric properties, there is huge leakage current in BFO thin film.¹⁸⁻²⁰ Usually, ferroelectric properties have been evaluated by hysteresis loop behavior in the polarization vs. electric field (P - E) curve. But the hysteresis loop of

Table I. PLD conditions of SRO and BNF films.

	SRO	BNF
Laser energy (mJ)	120	100
Repetition rate (Hz)	2	5
Substrate temperature (°C)	700	575
O ₂ pressure during deposition (Pa)	13.3	13.3
O ₂ pressure during cooling (Pa)	1330	1330

BFO film shows distorted and rounded loop because of the large leakage current in the film. Therefore, it is difficult to estimate the exact remanent polarization from P - E curve of BFO thin film. So far, the resistive switching properties have been mainly investigated by current vs. voltage (J - V) curve by using DC voltage sweep. However, the conventional J - V measurement method occasionally causes dielectric breakdown, because the specimen suffers from significant damage owing to the large current flow for a long time by applying the DC voltage. Moreover, it is not easy to evaluate essential properties of resistive switching because the current in the ferroelectric film capacitors is composed of ferroelectric, dielectric and leakage components, as shown in the Figure 1.

To solve these problems, we propose an evaluation of the resistive switching and ferroelectric properties using positive-up-negative-down (PUND) measurement technique. The PUND measurement can separate those current components and reduce the possibility of dielectric breakdown.²¹ Moreover, PUND measurement that can suppress the influence of joule heating is suitable to evaluate essential resistive switching property owing to ferroelectricity. In this paper, we have fabricated Nd-doped BFO (BNF) thin film capacitors on SrRuO₃ (SRO) bottom electrode and investigated the

Fig. 1. Equivalent circuit of ferroelectric capacitor.

Fig. 2. XRD pattern of BNF film grown on SRO-coated (100) Nb:STO substrate. Symbols in θ - 2θ scanning pattern indicate the SRO and Nb:STO substrate.

resistive switching and ferroelectric properties of specimen by using PUND measurement technique.

2. EXPERIMENTAL PROCEDURE

SRO and BNF thin films were deposited on 0.05 wt% Nb-doped (100) SrTiO₃ (Nb:STO) substrate using a pulsed KrF excimer laser deposition system, respectively. Ceramic targets with compositions of SrRuO₃ and BiNd_{0.03}FeO₃ were used as targets for SRO and BNF films, respectively. Here, Nd-doping for BFO was used to reduce the leakage current and formation of impurity phases.^{22,23} The detailed deposition conditions for SRO and BNF films are summarized in Table I. Before the deposition of SRO films, the Nb:STO substrate was soaked in the NH₄F-buffered HF solution and annealed in air at 1000 °C for 60 min.²⁴⁻²⁶ The thickness of deposited SRO film was 100 nm, and the BNF film thickness was 170 nm. Au top electrodes with an area of 2.0×10^{-5} cm² in square were deposited on the BNF thin film surface by thermal evaporation using a shadow mask to obtain ferroelectric film capacitor structure. The crystal structures of films were determined by X-ray diffraction (XRD; Rigaku Smart lab.) with Cu K α radiation. The electrical properties of BNF film capacitor were examined through PUND

Fig. 3. P - E curves of fabricated BNF film capacitor. The curves were measured with a measurement frequency of 20 kHz.

measurement of ferroelectric test system (Toyo FCE-3) and J - V measurement of pA meter (Agilent 4140B). All measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD θ - 2θ scanning pattern of BNF film grown on the SRO-coated Nb:STO substrate. The indices of the SRO and BNF diffraction peaks are based on the pseudocubic system. As shown in the figure, the BNF and SRO films were ($h00$)-oriented on the substrate without any impurity phases and other orientation components.

Figure 3 shows the P - E curves of BNF film capacitor. The P - E curves were measured with a measurement frequency of 20 kHz. As shown in the figure, distorted and rounded curves due to the influence of huge leakage current are observed, although the curves suggest ferroelectric hysteresis-like loop structure due to ferroelectricity. Therefore, it is difficult to evaluate essential ferroelectric property.

As shown in Fig.1, it is well known that the current in ferroelectric capacitor is composed of ferroelectric, dielectric and leakage components. Pulse response of each current component shows the specific behavior depending on the own origin. The PUND measurement not only has been used for evaluating remanent polarization but also can evaluate relative permittivity and leakage current by analyzing pulse response.²¹ Figure 4(a) shows the schematic illustration of employed voltage pulse train and the pulse responses in the PUND measurement. The integrated value of the three current components, namely the total charge value denoted by "Response" in the bottom of Fig.4(a) is measured in the PUND measurement. When a positive pulse was applied, the ferroelectric component (FC) and the dielectric component (DC) abruptly increase. On the other hand, leakage current component (LC) linearly increases. In order to explain the relation between the PUND response and conventional P - E hysteresis curve, the schematic illustration of P - E loop in ferroelectric capacitor is shown in Figure 4(b). Firstly, it is supposed that the initial state prior to the positive pulse is located at A state in Fig. 4(b). The Positive pulse causes a

Fig. 4. (a) Schematic illustration of employed voltage pulse train and the pulse responses in the PUND measurement. (b) Schematic illustration of P - E loop of ferroelectric capacitor.

change in polarization from A to B in Fig. 4(b). Then, the Up pulse causes a change in the polarization from C to B. Subsequent Negative and Down pulses similarly cause changes in the polarization with the opposite direction. As a result, the switched polarization P^* component caused by the Positive pulse includes ferroelectric, dielectric, and leakage components. The nonswitched polarization $P^\wedge$ component caused by the Up pulse includes only dielectric and leakage components. Therefore, the ferroelectric component (FC), namely the switched charge Q_{sw} , can be derived by difference between P^* and $P^\wedge$ ($Q_{sw} = P^* - P^\wedge$).

Figure 5 shows the applied pulse voltage dependences of Q_{sw} in the BNF film capacitor. Q_{sw} was measured with a pulse width of 50 μ s. As shown in the figure, with increasing the applied voltage, Q_{sw} was significantly increased from 4 V due to the polarization reversal in the BNF film capacitor. Q_{sw} was 121 μ C/cm² with a maximum applied voltage of 9 V. Observed Q_{sw} value is almost comparable with that of polycrystalline pure BFO thin film of 180 nm thickness measured by PUND measurement.²¹ This result indicates that essential ferroelectric property without influence of leakage current is observed by using PUND measurement technique.

Figure 6 shows the J - V curves of BNF film capacitor. The leakage currents were measured with a delay time

Fig. 5. Applied voltage dependences of Q_{sw} of BNF film capacitor with a measurement pulse width of 50 μ s.

Fig. 6. J - V curves for BNF film capacitor plotted on semi-logarithmic scales. The curves by open circle symbols were swept from positive to negative voltages, and the curves by solid circle symbols were swept from negative to positive voltages.

of 0.34 s. The J - V measurements were performed with 8 cycles by sweeping the bias voltage of the bottom electrode from 7 to -7 V and back to 7 V, repeatedly. The open circles indicate results of DC sweep from 7 V to -7 V. The solid circles indicate results of DC sweep from -7 V to 7 V. Here, in order to avoid the breakdown caused by the Joule heating at the large DC biasing, we measured J - V curves at less than 7 V. As shown in the figure, even by repeated measurement cycles, the J - V curves show a good reproducibility, and J - V curves show definite hysteresis behavior, indicating a large resistive switching. We defined ON and OFF states for upper and lower branches of the J - V hysteresis curves, respectively. The maximum ON/OFF ratio of the leakage current was 835 with bias voltage of -1.8 V. However, there is fear that observed result does not indicate the essential resistive switching property of specimen, because resistive switching behavior due to the redox reaction caused by joule heating has been reported.²⁷⁻²⁹ Hence, to characterize the essential resistive switching properties, we performed pulse measurement that can suppress the influence of Joule

Fig. 7. (a) Pulse train employed for pulse measurement of leakage current. (b) Reading pulse response of specimen measured by using pulse train.

heating due to current flow.

The pulse train for leakage current measurement is shown in Figure 7(a). Here, the voltage of reading pulse was less than the coercive voltage of BNF film for non-destructive readout. Figure 7(b) shows pulse response of specimen by applying the reading pulse. As mentioned above, when the reading pulse was applied, the charge was rapidly increased due to the dielectric component. After that, the charge was linearly increased due to leakage component. Then, the leakage current without influence of the other components can be estimated from the gradient of the pulse response. We estimated the leakage current from dotted line shown in Fig. 7(b).

Figure 8 shows the writing voltage dependences of the current density. The ON and OFF currents were defined as reading pulse responses after applying the negative and positive writing voltages, respectively. As shown in the figure, the ON current was significantly increased from 4 V with increasing the writing voltage. On the other hand, the OFF current shows almost constant value. Therefore, resistive switching behavior can be observed by using pulse measurement. The leakage current density was 1.2 mA/cm² and 14 μA/cm² after writing by voltages of -9 V and +9 V, respectively. The maximum ON/OFF ratio of the leakage current was 86.

Figure 9 shows the applied voltage dependences of the normalized Q_{sw} and ON/OFF current ratio. As shown in the figure, the normalized Q_{sw} and ON/OFF current ratio are increasing in similar manner. This result suggests that the leakage current was changed by ferroelectric polarization. On the other hand, ON/OFF current ratio measured by pulse measurement is one order of magnitude smaller than that in DC sweep

Fig. 8. Writing voltage dependences of current density of BNF film capacitors.

Fig. 9. Applied voltage dependences of normalized Q_{sw} and current ON/OFF current ratio. Q_{sw} and ON/OFF current ratio value in BNF film capacitor were normalized by 121 μC/cm² and 86 with an applied voltage of 9 V, respectively.

measurement shown in Fig. 6. This suggests that the resistance in specimen is changed by not only ferroelectric polarization but also other factors such as Joule heating and movement of oxygen vacancies in the DC sweep measurement.^{2, 27-29}

4. CONCLUSIONS

We have prepared the BNF thin films on the SRO-coated Nb:STO substrate by PLD and investigated the resistive switching and ferroelectric properties by PUND measurement technique. Essential ferroelectric property without influence of the leakage current was obtained by using PUND measurement. Q_{sw} was 121 μC/cm² with an applied voltage of 9 V. Resistive switching behavior in BNF film capacitors is successfully observed by using pulse measurement. The leakage current without the influence of the ferroelectric and dielectric components was estimated from the gradient of the pulse response. The current density was 1.2 mA/cm² and 14 μA/cm² after writing by voltages of -9 V and +9 V, respectively. The maximum ON/OFF ratio of the leakage current was 86.

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5. References

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