Formation and Characterization of Ferroelectric $Sr_2Nb_2O_7$ Thin Film for MFMIS-FET Type Non-Volatile Memory

Y. Nakao [1] Y. Sekimoto and H. Matsuura [2]
Department of Engineering and Computer Science, Osaka Electro-Communication University,
18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan
E-mail: [1] m02124@isc.osakac.ac.jp, [2] matsuura@isc.osakac.ac.jp

Abstract: $Sr_2Nb_2O_7$ (SNO) ferroelectric thin films are deposited on Pt/SiO_2/Si by an MOD (metal-organic decomposition) method. From X-ray diffraction, some peaks corresponding to crystalline SNO are founded, and its polarization is confirmed from a Sawyer-Tower circuit. The densities and emission rates of traps in SNO layers are investigated by DCTS (discharge-current-transient spectroscopy). Three types of traps are detected, and also the density and emission rate of each trap are determined.

INTRODUCTION

Many types of structures for ferroelectric memories have been recently developed. Typical structures are a 1Tr/1Ca (one transistor plus one capacitor) structure and an MFS-FET(metal-ferroelectric-semiconductor field-effect transistor) structure. Although memory cells with the MFS-FET structure can be integrated more than those with the 1Tr/1Ca structure, it has not been realized yet because it is difficult to directly deposit good quality ferroelectric thin films on Si and to reduce the interface states between the ferroelectric film and Si. To solve these problems, an MFMIS (metal-ferroelectric-metal-insulator-semiconductor)-FET structure has been researched recently. Since the insulator is SiO_2 produced by thermal oxidation of Si, the interface states between the insulator and Si can be reduced. However, when the dielectric constant of the ferroelectric film is much higher than that of SiO_2 (dielectric constant of 3.9), almost of gate voltage is applied to the SiO_2 layer, indicating that high gate voltage is required to invert the polarization in the ferroelectric layer. Therefore, $Sr_2Nb_2O_7$ (SNO), which is ferroelectrics with a low dielectric constant, is investigated as one of gate ferroelectric layers for the MFMIS-FET structure.

SNO thin films are repureed to be deposited using sol-gel method using metal-alkoxide solutions [1], [2]. Since metal-carboxylic solutions are chemically stable more than metal-alkoxide solutions, SNO thin films are aimed to be deposited on Pt/SiO_2/Si substrates by the MOD (metal-organic decomposition) method using metal-carboxylic acid. From X-ray diffraction (XRD), the crystallinity of deposited thin films are checked. Moreover, the remanent polarization of the films are investigated from the Sawyer-Tower circuit.

The fatigues and imprints in those memory structures are considered to be related to traps in ferroelectric films. Therefore, in this study, the densities and emission rates of traps in SNO thin films are investigated by DCTS (discharge-current-transient spectroscopy).

THEORY OF DCTS

DCTS can determine the densities and emission rates of traps in a dielectric thin film from a transient discharge current $I_{\text{dis}}(t)$ in a capacitor consisting of a dielectric thin film between two electrodes at a constant temperature [3], [4]. When a charge voltage (V_{cha}) is applied to the capacitor, a charge current (I_{cha}), which fills traps with charged carriers (electron or hole), flows through the capacitor. After the applied voltage is changed from V_{cha} to a discharge voltage (V_{dis}), the transient discharge current flows, which is theoretically derived as

$$I_{\text{dis}}(t) = -qS\sum_{i=1} N_{ti} e_{ti} \exp(-e_{ti}t) + I_1(V_{\text{dis}}), \quad (1)$$

where $I_1(V_{\text{dis}})$ is the steady-state leakage current at V_{dis}, q is the electron charge, S is the electrode area, and N_{ti} and e_{ti} are the density per unit area and emission rate of the i th trap, respectively.

The signal of DCTS is defined as [4]

$$D(t, e_{\text{ref}}) \equiv \frac{t}{qS}\left[I_{\text{dis}}(t) - I_1(V_{\text{dis}})\right]\exp(-e_{\text{ref}}t + 1), \quad (2)$$

where we can shift the peak discharge time of the DCTS signal by changing the parameter (e_{ref}). Substituting $I_{\text{dis}}(t)$ in Eq. (1) for $I_{\text{dis}}(t)$ in Eq. (2) yields

$$D(t, e_{\text{ref}}) = \sum_{i=1} N_{ti} e_{ti} t \exp\left[-\left(e_{ti} + e_{\text{ref}}\right)t + 1\right]. \quad (3)$$

The peak value of the DCTS signal is

$$D(t_{\text{peak}}, e_{\text{ref}}) = N_{ti}\left(1 - e_{\text{ref}} t_{\text{peak}}\right), \quad (4)$$

at

$$t_{\text{peak}i} = 1/\left(e_{ti} + e_{\text{ref}}\right). \quad (5)$$

Using $t_{\text{peak}i}$ and $D(t_{\text{peak}i}, e_{\text{ref}})$, the values of N_{ti} and e_{ti} can be determined as

$$N_{ti} = \frac{D(t_{\text{peak}i}, e_{\text{ref}})}{(1 - e_{\text{ref}} t_{\text{peak}i})}, \quad (6)$$

and

$$e_{ti} = \frac{1}{t_{\text{peak}i}} - e_{\text{ref}}, \quad (7)$$

respectively. When two more than traps with close emission rates exist in a thin film, the DCTS signal become broader and each peak cannot be distinguished. In this case, from the maximum of the DCTS signal when e_{ref} is changed continuously, the density and emission rate of each trap can be determined.

EXPERIMENTAL PROCEDURE

After the surface of Si was thermally oxidized, 200-nm-thick Pt was deposited on 50-nm-thick SiO_2/Si by sputtering. SNO thin films were deposited on Pt/SiO_2/Si substrates.

The scheme outlining the formation of SNO thin films is depicted in Fig. 1. The MOD coating solution was prepared by 2-ethylehexanoate strontium and 2-ethylehexaanoate niobium, where the mol ratio was 1:1.

After a small amount of the solution was dropped onto the Pt/SiO_2/Si substrate, the substrate was rotated at 2000 rpm for 10 s, and continuously it was rotated at 6000 rpm for 60 s. This coated substrate was heated at 200 °C for 30 min., and then was pre-baked at 400 °C for 10 min. After this process is repeated between once and ten times, it was baked at 800 °C for 60 min.

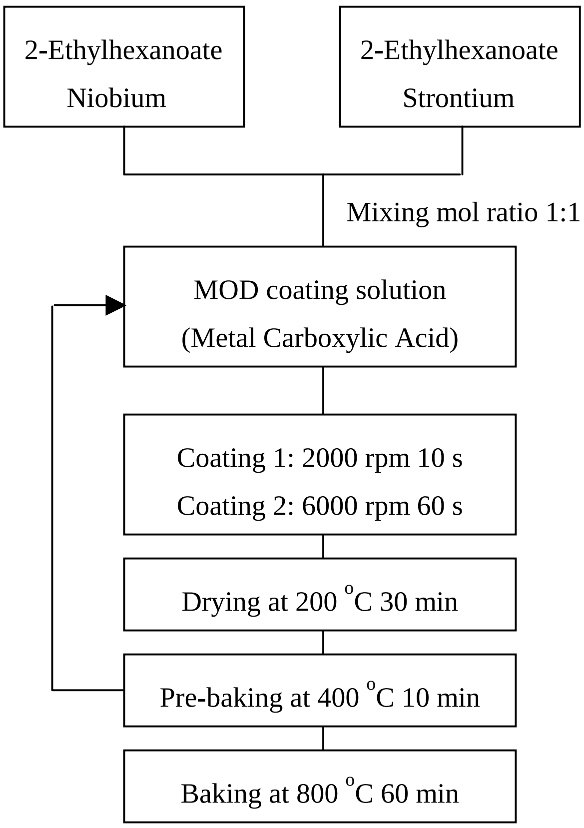

Fig. 1 Scheme outlining the formation of SNO thin film

The crystallinity of the obtained thin films was measured by XRD. In order to measure the electric characterization of the SNO films, Pt was deposited on SNO/Pt/SiO_2/Si by sputtering. Hysteresis loops of Pt/SNO/Pt capacitors were measured by the Sawyer-Tower circuit at 1kHz. The transient discharge current was measured at $V_{\text{dis}} = 0$ V at 290 K, after V_{cha} of 1.75 V was applied to the capacitor for 300 s. The densities and emission rates of traps in SNO thin films were determined by the DCTS method at 290 K.

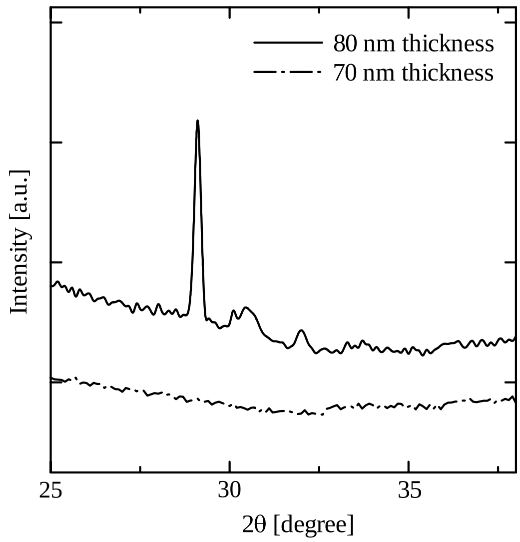

Fig. 2 XRD patterns of SNO thin film thickness at 70 nm and 80 nm

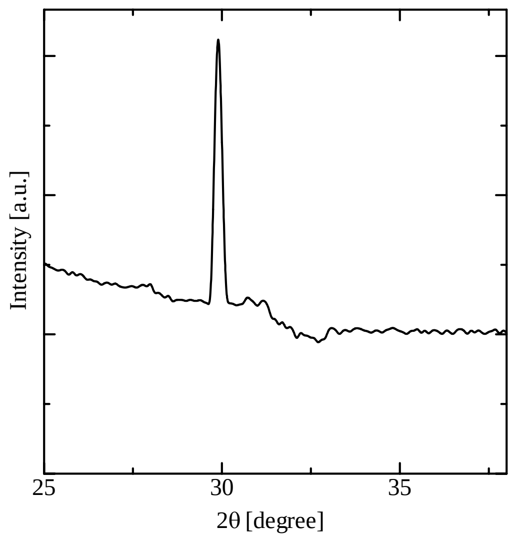

Fig. 3 XRD patterns of SNO thin film thickness at 100 nm

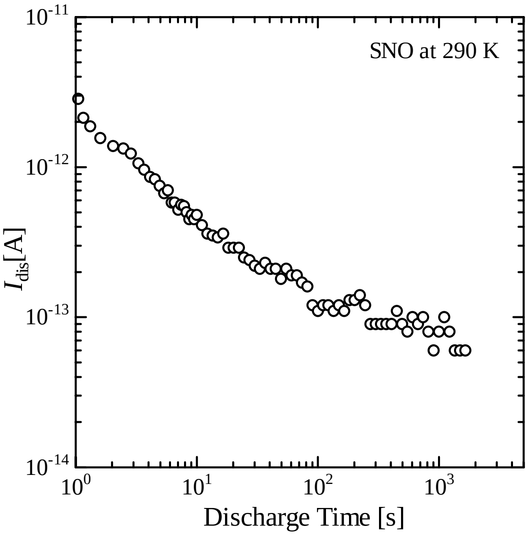

Fig. 4 The transient discharge current of SNO

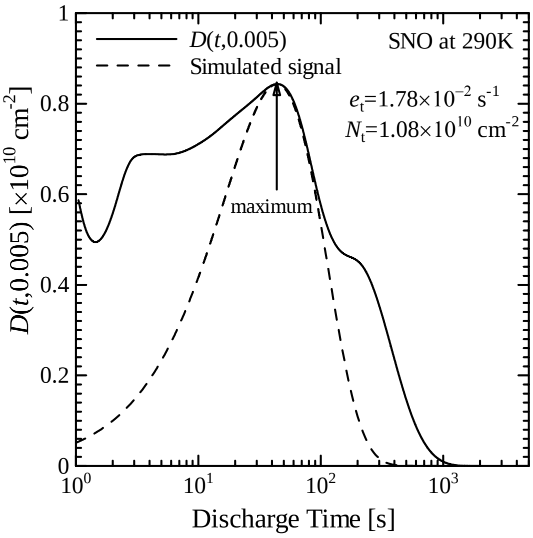

Fig. 6 DCTS signals with $e_{ref} = 0.005$ s^{-1}

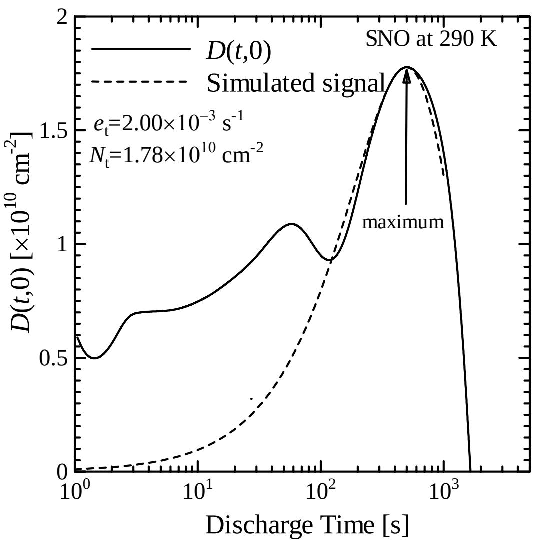

Fig. 5 DCTS signals with $e_{ref} = 0$ s^{-1}

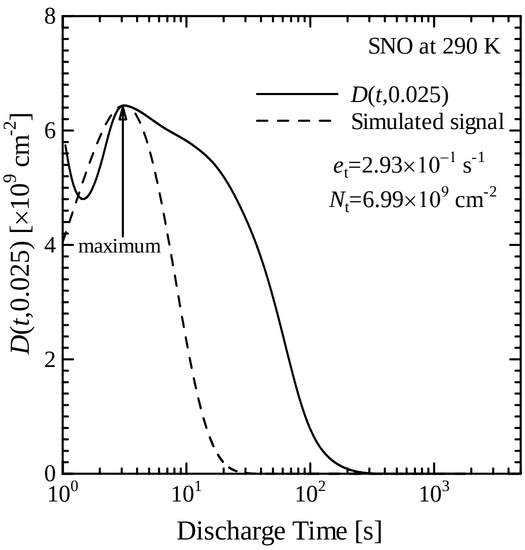

Fig. 7 DCTS signals with $e_{ref} = 0.025$ s^{-1}

RESULTS AND DISCUSSION

From ellipsometry, SNO film was obtained 10 nm at 1 time process. Figure 2 shows the XRD patterns of SNO films with 70 nm thickness (broken curve) and 80 nm thickness (solid curve). Since there are no peaks in the 70-nm-thick film, this film is considered to be amorphous. The films thinner 70 nm are also found to be amorphous. In the pattern of the 80-nm-thick film, on the other hand, a sharp peak is observed at 29.1^o, which corresponds to the (131) plane direction of crystalline SNO. Figure 3 shows the XRD pattern of the 100-nm-thick film. A sharp peak at 29.9^o corresponding to the (141) plane direction of crystalline SNO appears. These indicate that the film thicker than 80 nm is required to obtain polycrystalline SNO films.

Judging from hysteresis loops of a Pt/SNO/Pt capacitor using a Pt/SNO/Pt/SiO_2/Si structure with the 100-nm-thick SNO film, the remanent polarization (P_r) of this SNO film is determined to be 15 nC/cm^2. Since SNO is reported to be polarized along the c-axis direction [5], the value of P_r in the (141)-oriented SNO thin film is considered to be low.

Figure 4 shows the transient discharge current in the Pt/SNO/Pt capacitor. Figure 5 shows the DCTS signal calculated by interpolating $I_{dis}(t)$ with a cubic smoothing natural spline function. The solid

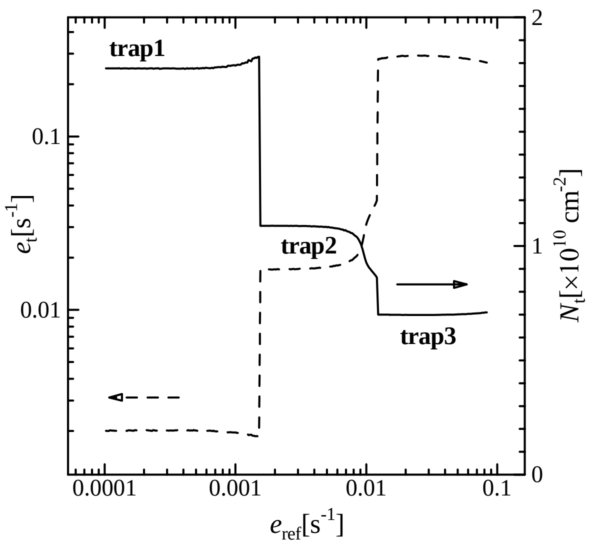

Fig. 8 The e_{ref} dependence of N_{ti} or e_{ti} determined from the DCTS signal.

curve represents the DCTS signal with $e_{ref} = 0$ s^{-1}. The maximum discharge time and maximum value are 501 s and 1.78×10^9 cm^{-2}, respectively. From Eqs. (6) and (7), N_{t1} and e_{t1} are determined to be 2.00×10^{-3} s^{-1} and 1.78×10^{10} cm^{-2}, respectively. In the figure, the broken curve represents the signal simulated using

$$N_{ti}e_{ti}t\exp[-(e_{ti}+e_{ref})t+1], \qquad (8)$$

with the obtained values. Since the solid curve is larger than the broken curve at < 100 s, the DCTS signal is considered to be affected by other traps.

In order to evaluate other traps, e_{ref} was changed. The solid curve in Fig. 6 represents the DCTS signal with $e_{ref} = 0.005$ s^{-1}. The maximum discharge time and maximum value are 44 s and 8.43×10^9 cm^{-2}, respectively. From Eqs. (6) and (7), N_{t2} and e_{t2} are determined to be 1.78×10^{-2} s^{-1} and 1.08×10^{10} cm^{-2}, respectively. In the figure, the broken curve represents the signal simulated using Eq. (8) with the obtained values. Since the solid curve is much broader than the broken curve, the DCTS signal is considered to be affected by another traps with close emission rates.

Figure 7 shows the DCTS signal (solid curve) with $e_{ref} = 0.025$ s^{-1}. The maximum discharge time and maximum value are 301 s at 6.43×10^9 cm^{-2}, respectively. From Eqs. (6) and (7), N_{t3} and e_{t3} are determined to be 2.93×10^{-1} s^{-1} and 6.99×10^9 cm^{-2}, respectively. In the figure, the broken curve , which are simulated using Eq. (8) with the obtained values.

Judging from these results, at least three kinds of traps are included in the SNO film. Figure 8 shows the e_{ref} dependence of N_{ti} or e_{ti} determined from the DCTS signal. Three discrete values of e_t or N_t clearly appear in the figure. Moreover, the e_{ref} range of the constant N_t clearly corresponds one to one to the e_{ref} range of the constant e_t. Therefore, it is found that DCTS can distinguish among three kinds of traps (trap1, trap2 and trap3) with close emission rates by e_{ref}. From the average of the e_{ref} range of the constant N_t and e_t, N_t and e_t of each trap can be determined; e_{t1} and N_{t1} of trap1 are 2.0×10^{-3} s^{-1} and 1.8×10^{10} cm^{-2}, respectively, and e_{t2} and N_{t2} of trap2 are 1.8×10^{-2} s^{-1} and 1.1×10^{10} cm^{-2}, respectively, and e_{t3} and N_{t3} of trap3 are 2.9×10^{-1} s^{-1} and 7.0×10^9 cm^{-2}, respectively.

In order to determine the energy levels of traps, DCTS is being measured at various temperatures. Moreover, the influence of these traps on the leakage current is investigated.

CONCLUSION

SNO thin films were deposited on Pt/SiO_2/Si by the MOD method. From XRD, it is found that polycrystalline SNO was created when its thickness was thicker than 80 nm. Although SNO films oriented along the c-axis could not be produced, the SNO film with the (141) plane direction showed the small remanent polarization.

Using the transient discharge current in the Pt/SNO/Pt capacitor, the densities and emission rates of three types of traps in the 100-nm-thick SNO film could be determined by DCTS.

REFERENCES

[1] A. V. Prasadarao, U. Selvaraj and S. Komarneni, “Fabrication of $Sr_2Nb_2O_7$ thin film by sol-gel method,” *J. Mater. Res.*, vol. 10, pp704-707, Mar. 1995.

[2] Y. Fujimori, N. Izumi, T. Nakamura and A. Kamisawa, “Study of ferroelectric materials for ferroelectric memory FET,” *IEICE TRANS. ELECTRON.*, vol. E81-C, pp. 572-576, Apr. 1998.

[3] H. Matsuura, M. Yoshimoto and H. Matsunami, “Discharging current transient spectroscopy for evaluating traps in insulators,” *Jpn. J. Appl. Phys.*, vol. 34, pp. L185-L187, Feb. 1995.

[4] H. Matsuura, T. Hase, Y. Sekimoto, M. Uchikura and M. Simizu, “Graphical peak analysis method for determining densities and emission rates of traps in dielectric film from transient discharge current,” J. Appl. Phys., vol. 91, pp. 2085-2092, Feb. 2002.

[5] S. Nanamatsu, M. Kimura and T. Kawamura, “Crystallographic and dielectric properties of ferroelectric $A_2B_2O_7$ (A=Sr, B=Ta, Nb) crystals and their solid solutions,” *J. Phys. Soc. Jpn.*, vol. 38, pp. 817-824, Mar. 1975.