# Study of the Metal-Ferroelectric-Insulator-Si Structure Device Formation by Controlling Properties of High Frequency and Microwave Excited Plasma

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#### 1. Introduction

Recently nonvolatile memory devices having ferroelectric gate structure (Metal-Ferroelectric-Insulator-Si Field Effect Transistor (MFIS-FET) structure) have attracted much attention from the viewpoints of high speed, nondestructive readout and high-packing-density memory LSIs. However, there are many problems to be solved, as follows. (a) It is difficult to crystallize ferroelectric on the insulator such as amorphous SiO<sub>2</sub>. (b) Because of small coercive field (weak ferroelectricity), the memory window of the MFIS device's CV hysteresys curve tends to be very small. (c) In order to obtain large memory window of it, thick ferroelectric film is needed. (d) As a result, low voltage operation is difficult. We have already reported the ferroelectric formation technology on amorphous insulator and MFIS structure device 3V with low dielectric constant ferroelectric  $Sr_2(Ta_{1-x},Nb_x)_2O_7$  (STN, x=0.3). These were realized by (1) the thin seed layer formed by rf-sputtering and microwave excited plasma treatment, and (2) the formation of the ferroelectric whose oxygen vacancy is reduced by the Ferroelectric Multi-Layer Stack (FMLS) deposition process [1]. This plasma treatment can oxidize the surface of the film and supply ion bombardment energy to the surface of the film.

In this work, we report the relation between rf-sputtering plasma condition and  $Sr_2(Ta_{1-x},Nb_x)_2O_7$  crystal phase on  $SiO_2$  and also reported MFIS structure device's electrical properties. Furthermore, we propose the application of high-density plasma to the ferroelectric improvement.

#### 2. Experimental

Figure 1 shows microwave excited (2.45GHz) high-density (>10<sup>12</sup>cm<sup>3</sup>) low electron temperature (<1eV) Kr/O<sub>2</sub> plasma system for improvement of ferroelectric. The detail of rf-sputtering condition of STN is shown in Table I. Figure 4 shows the device structure images and the process flows of MFIS structure device for rf-sputtering plasma dependency experiment. STN is formed on the 10nm STN seed layer/SiO<sub>2</sub>(10nm)/Si. The condition of the rf frequency electrode power was changed within the range from 8W to 22W. Based on the results of the experiment, the FMLS-MFIS structure device with STN (100nm, repeating 5nm STN deposition and the plasma treatment 20 times) was fabricated on the adequate plasma condition & shown in Fig. 10.

#### 3. Results and Discussions

Figure 2 shows Leakage current density of Al/as-deposited STN(20nm)/Pt capacitor. Basic rf-sputtering condition is fixed from the viewpoints of the reduction of the leakage current density as shown in Table I. Fig.3 shows our previous results of XRD measurement of the STN on  $SiO_2$  with (sample B) and without (sample A) 10nm STN seed layer [1]. In the case of the sample A, the pattern indicates that  $Sr_3(Ta,Nb)_6Si_4O_{26}$  phase grows. On the other hand, in

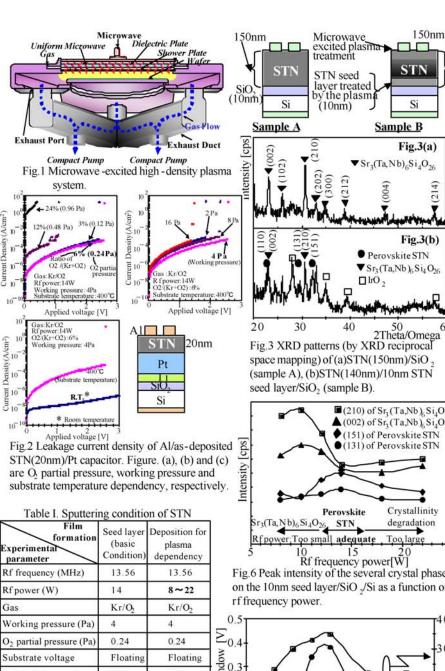
the case of the sample B, (151) peak of the perovskite STN appears and the peaks of Sr<sub>3</sub>(Ta,Nb)<sub>6</sub>Si<sub>4</sub>O<sub>26</sub> such as (210) are decreasing. This indicates that in order to obtain perovskite STN on SiO<sub>2</sub> it is indispensable to introduce the thin seed layer formed by microwave excited plasma treatment. However, the adequate rf-sputtering plasma condition to form the perovskite STN has not been researched. Figure 5 shows XRD patterns by XRD reciprocal space mapping of 140nm STN on the 10nm STN seed layer/SiO<sub>2</sub>/Si and those rf frequency power is 10W(fig. 5(a)), 14W(fig. 5(b)) and 18W(fig. 5(c)). In the case of the fig. 5(a), the XRD patterns are almost similar to those of sample A and this indicates that Sr<sub>3</sub>(Ta,Nb)<sub>6</sub>Si<sub>4</sub>O<sub>26</sub> phase grows. In the case of the fig. 5(b), (151) peak of perovskite STN appears and the peaks of Sr<sub>3</sub>(Ta,Nb)<sub>6</sub>Si<sub>4</sub>O<sub>26</sub> such as (210) are decreasing. On the other hand, in the case of the fig. 4(c), the peaks of perovskite STN such as (151) are decreasing. Fig. 6 shows the peak intensity of several crystal phases as a function of rf frequency power. This indicates that perovskite STN has well grown on the condition of 14W rf frequency power. Figure 7 shows the CV IrO<sub>2</sub>/STN(140nm)/seed the hysteresis curves of layer(10nm)/SiO<sub>2</sub>/Si devices. When rf frequency power is 14W, its memory window is the largest as shown in fig. 7(b). Figure 8 shows the memory window and dielectric constant of the total 150nm STN film as a function of the rf frequency power. The dielectric constant value of the STN that is formed on the condition of 14W rf frequency power is almost equal to those of STN reported previously [2]. These results indicatet that in order to fabricate perovskite STN on amorphous SiO2 it is important not only to introduce seed layer but also to give the surface of the film adequate Kr<sup>+</sup> ion bombardment energy that corresponds to those of 14W rf power in this case (fig. 9(a)). Another concept to obtain better perovskite STN is (1) to give low ion bombardment energy (below E<sub>a</sub>) and (2) irradiate Kr ion to the surface of the film a lot of times to supplement lack of the energy as shown in fig. 9(b). The FMLS-MFIS device formed by high-density low energy ion bombardment plasma shows effectiveness of the concept. Figure 11 (a) and (b) show XRD patterns and CV hysteresis curves of the FMLS-MFIS device, respectively. These results indicate that excellent perovskite STN phase is obtained.

### 4. Conclusion

We have clarified the relation between ferroelectric crystal phase on amorphous  $\mathrm{SiO}_2$  and rf high frequency plasma condition. We have successfully developed a new technology that crystallizes ferroelectric on amorphous insulator by control of the rf high frequency and microwave excited plasma properties.

## References

- [1] I. Takahashi et al, International Symposium of Integrated Ferroelectric 2005, 1-10-C, P.48 (2005)
- [2] Y. Fujimori et al., Jpn. J. Appl. Phys., vol. 38, p. 2285 (1999)



Bios Voltage[V] Bios Voltage[V] (sample A), (b)STN(140nm)/10nm STN Fig.7 CV curves of the IrO<sub>3</sub>/ Fig. 7(c) STN(140nm)/STN seed layer 8.0 0.6 (210) of Sr<sub>3</sub>(Ta,Nb)<sub>6</sub>Si<sub>4</sub>O<sub>20</sub> (10nm)/SiO<sub>2</sub>(10nm)/Si.  $\triangle$  (002) of Sr<sub>3</sub> (Ta,Nb)<sub>6</sub> Si<sub>4</sub>O<sub>2</sub> Rf sputtering power during ♦(151) of Perovskite STN 140nm STN deposition is 10W (131) of Perovskite STN -4 -2 0 2 4 Bios Voltage[V] (Fig. 7(a)), 14W (fig. 7(b)) and 18W (fig. 7(c)). High frequency (13.56MHz) excited plasma Crystallinity degradation Fig. 6 Peak intensity of the several crystal phase Rf frequency power Ion bombardment energy (e V) on the 10nm seed layer/SiO 3/Si as a function of Too small Too large Microwave (2.45GHz) excited plasma system 40 (1) Damage free of the film's surface  $E_m < 7eV < E_a$ constant (2) A lot of times irradiation Dielectric o [Em × Ni] ~ Large Possible to supplement shortage of the energy by a lot of times Kr<sup>+</sup> ions irradiations Possible to promoteferroelectric crystallization Perovskite STN Ni [ions/atom] : Kr ion irradiation times / one ferroelectric element Fig.9 Concept of the ferroelectric formation by controlling 5 10 15 20 25 Rf frequency power[W] Fig.8 Memory windows of the CV hysteresis the properties of the plasma excited by 13.56MHz high frequency (fig. 9(a)) and microwave (fig. 9(b)) curves of the IrO2/STN(140nm)/STN seed Fig.11(a) layer(10nm)/SiO<sub>2</sub>/Si devices and dielectric constant of the total 150nm STN film as Sr<sub>2</sub>(Ta<sub>0.7</sub>,Nb<sub>0.3</sub>)<sub>2</sub>O.

20

400

300

200

100

30

1MHz

STN: 100nm

SiO<sub>2</sub>: 10nm

4V operation

5V operation

and its CV hysteresis curves (b).

Microwave excited plasma-

STN seed layer (10nm)

treated by microwave excited plasma

· Dry Oxidation (900°C)

[Rf power: 14W]

· First crystallization

annealing at 950°C

for 60min

1.0 Fig. 7(a)

0.8 0.8 0.6 0.4 0.2

· STN(10nm) by sputtering

Microwave excited plasma

treatment at 400°C for 60min

for growth of perovskite STN phase.

2

treatment

☐ ☐IrO, electrodes

SiO<sub>2</sub> 10nm)

STN(140nm) by sputtering

(total STN thickness 150nm)

Microwave excited plasma

treatment at 400°C for 60min

[Rf power: 8~22W]

Second crystallization

annealing at 950°C for 90

· Sputtered IrO, electrodes

0

Fig. 7(b)

☐ IrO,

Bios Voltage [V]

Fig.11 XRD patterns of FMLS-MFIS device (a)

2Theta/Omega

0.4V(3V operation)

Fig.11(b)

Fig.4 Device structure images and the process flows of MFIS

00.6 00.4

structure devices. This experiment is performed in order to

find the most adequate sputtering condition (rf power)

150nm

 $\begin{array}{c|c} & & & & \\ \hline (000) & & & \\ \hline (010) & & & \\ \hline (000) & &$ 

R.T

RT

Fig.5(a) Rf power: 10W

 $\nabla \operatorname{Sr}_3(\operatorname{Ta},\operatorname{Nb})_6\operatorname{Si}_4\operatorname{O}_{26}$ 

Wemory 0.1

a function of rf frequency power.

Total STN

thickness

100nm

(Ferroelectricmulti -layer stack

MFIS (FMLS - MFIS) structure device)

ferroelectric multi-layer stack MFIS

Fig.10 Device structure images of the

TN (5nm) deposition Microwave excited plasma treatment

Low energy ion irradiation

A lot of times irradiation

The plasma

treated STN

 $(10nm, 5nm \times 2)$ 

structure device.

eed laver

IrO2 electrodes

Si

Sample C

Substrate temperature

20 30 40 50 2Theta/Omega 60 2Theta/Omega Fig.5 XRD patterns (by XRD reciprocal space mapping) of STN(140nm)/STN seed layer(10nm)/SiO<sub>2</sub> /Si. Rf power of the 13.56 MHz high -frequency electrode during 140nm STN deposition is (a)10W, (b)14W and (c)18W.