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A Ferroelectric $Sr_2(Ta_{1-x}, Nb_x)_2O_7$ with a Low Dielectric Constant by Plasma PVD and Oxygen Radical Annealing

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1. Introduction

Recently nonvolatile memory devices having ferroelectric gate structure (Metal- Ferroelectric- Metal- Insulator Field Effect Transistor (MFMIS-FET) structure) have attracted much attention from the viewpoints of nondestructive readout and high-packing-density memory LSIs. However there are many problems that must have been solved still more so that it may be put MFMIS FETs to practical use. The voltage applied to ferroelectric film becomes small when the ferroelectric film has a high dielectric constant. $Sr_2(Ta_{1-x},Nb_x)_2O_7$ (STN) has attracted much attention as bismuth and lead-free ferroelectric material having a low dielectric constant [1], [2]. However a dielectric constant needs to be lower to make MFMIS FETs operate in a low voltage. Although previous preparation of STN is sol-gel method and pulsed laser deposition, when it is thought of that can be installed in a semiconductor manufacturing line, STN film formation by plasma PVD is indispensable.

In this work, we report a new STN film (having a very low dielectric constant) formation technology by using plasma PVD and a new improvement technology of the ferroelectric films by oxygen radical annealing using microwave-excited (2.45GHz) high-density ($>10^{12}cm^{-3}$) low electron temperature (<1eV) Kr/O_2 plasma.

2. Experimental

Sputtering target was a $Sr_{2.5}(Ta_{0.7},Nb_{0.3})_2O_7$ ceramic disk. The detail of rf-sputtering condition of STN is shown in Table. I . Device structure image of each samples and process flow are shown in Fig.1. The substrates were $Pt/IrO_2/SiO_2/Si(100)$wafers (Pt substrates) and $IrO_2/SiO_2/Si(100)$wafers (IrO_2 substrates) for Metal-Ferroelectric- Metal (MFM) structure. The STN films were post-annealed at 950℃ for 90min in the oxygen ambient. Pt was deposited by rf-sputtering on the STN films as a top electrode.

For another experiment (Fig.1), very thin STN(20nm) films were deposited on Pt substrates and subsequently annealed in the Kr/O_2 mixed plasma employing microwave exited (2.45GHz) high density plasma system at 400℃ (Fig.2) [3]. Then STN was deposited on the oxygen radical annealed STN (20nm) thin films by same condition. The condition of the post-annealing and the preparation of top Pt electrodes were also same.

3. Results and Discussions

Fig.3 shows XRD patterns of STN films deposited on Pt substrates and IrO_2 substrates. The peaks of STN appear in the both films.

Fig.4 shows cross sectional view of STN film deposited on Pt substrates. Clear interfaces were kept during crystallization of 950℃.

Fig.5 shows D-E hysteresis loops of STN capacitors measured by Sawyer-Tower circuit at 1000Hz. Symmetrical ferroelectric hysteresises were confirmed for both films. For IrO_2 substrates, the average remanent polarization (P_r) was $0.5\mu C/cm^2$ and the coercive force (E_c) was 52kV/cm. The dielectric constant (ε) was 35 at 1MHz and is much lower than those of STN of previous reports. These properties of hysteresis indicate that this can be applied to MFMIS FET memory devices. It has not been reported yet that STN was deposited on an electrode except Pt. Hydrogen content atmosphere such as passivation process degrades properties of ferroelectric films when Pt electrode is used [4]. For Pt substrates, P_r was $0.3\mu C/cm^2$, E_c was 17kV/cm and ε was 44. The small hysteresis width suggests that STN on Pt substrate includes crystal defects or lack of oxygen.

Fig.6 shows D-E hysteresis loops of STN capacitors with and without oxygen radical annealing in the Kr/O_2 plasma. For the film with oxygen radical annealing, P_r was $0.45\mu C/cm^2$, E_c was 35kV/cm and ε was 39. The STN thin film was oxidized by large amount of oxygen radical in the Kr/O_2 plasma and the STN film could be also deposited as a film of high quality on the 20nm thin STN film.

Fig.7 shows J-E characteristic of STN capacitor. The leakage current density of the film with oxygen radical annealing was reduced by one order of magnitude in a low electric field.

4. Conclusion

A ferroelectric $Sr_2(Ta_{1-x},Nb_x)_2O_7$ (STN) films have been formed by plasma PVD for the first time on $IrO_2/SiO_2/Si(100)$wafers (IrO_2 substrates) and on $Pt/IrO_2/SiO_2/Si(100)$wafers (Pt substrates). For IrO_2 substrates, the average P_r was $0.5\mu C/cm^2$ and E_c was 52kV/cm, and ε was 35. The E_c is larger and the ε is much smaller than those of STN of previous reports. The oxygen radical annealing by using microwave-excited (2.45GHz) high-density ($>10^{12}cm^{-3}$) low temperature (<1eV) Kr/O_2 plasma effectively improves the performance of the STN films. Because this new technology can make E_c large and ε small and can reduce leakage current density by one order of magnitude, it is expected very much as a process technology applied to MFMIS FETs formation. The STN films having a very low dielectric constant by plasma PVD can be well applied to MFMIS-FET memory devices.

References

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[2] T. Nakaiso, M. Okuyama et al., Jpn. J. Appl. Phys., vol. 39, p. 5517 (2000)
[3] K. Sekine, T. Ohmi et al., IEEE T-ED, vol. 48, p.1550 (2001)
[4] Y. Shimamoto, et al., Appl.Phys. Lett., vol.70, p.3069 (1997)

Frequency (Target Bias)	13.56(MHz)
Power (Target Bias)	18(W)
Gas	Ar/O_2
Working pressure(mTorr)	30(mTorr)
O_2 partial pressure(mTorr)	1.8(mTorr)
Substrate voltage	Floating
Substrate temperature(℃)	R.T.

Table I. Sputtering condition of STN.

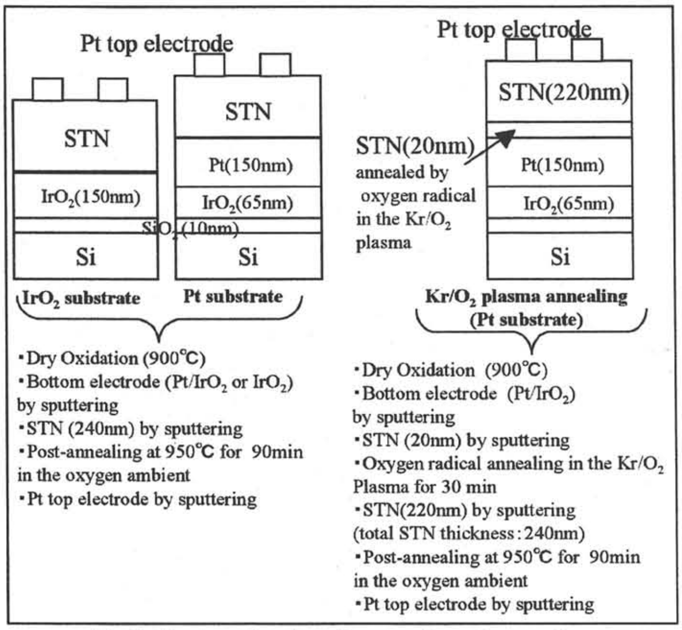

Fig.1 Device structure image of each samples.

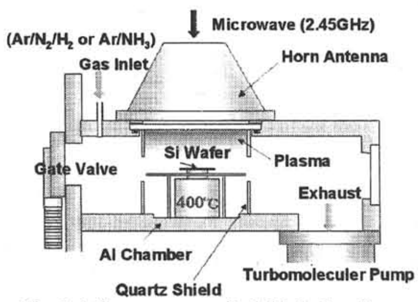

Fig.2 Microwave-excited high-density plasma system.

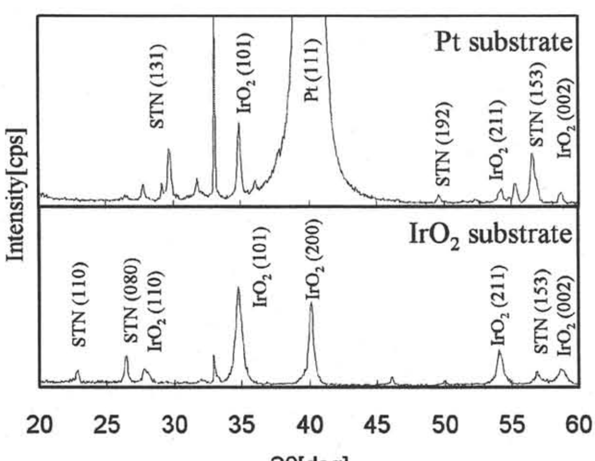

Fig.3 XRD patterns of STN deposited on Pt and IrO_2 substrate

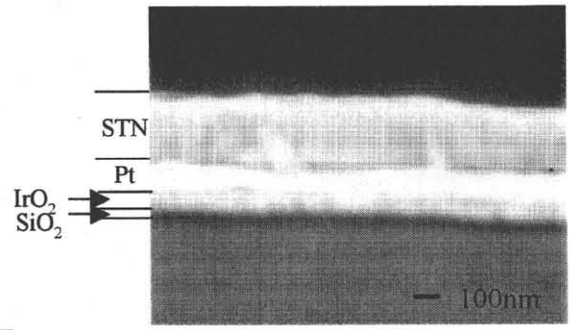

Fig.4 Cross sectional view of STN deposited on Pt substrate.

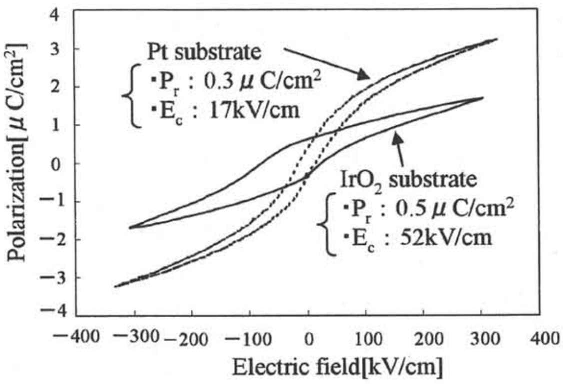

Fig.5 D-E hysteresis loops of STN capacitors of Pt and IrO_2 substrate.

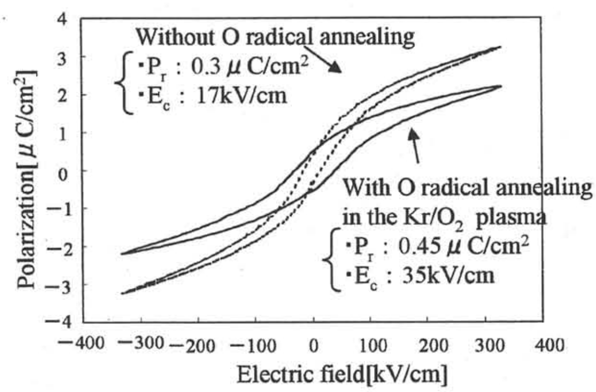

Fig.6 D-E hysteresis loops of STN capacitors of Pt substrate with and without Oxygen radical annealing in the Kr/O_2 plasma.

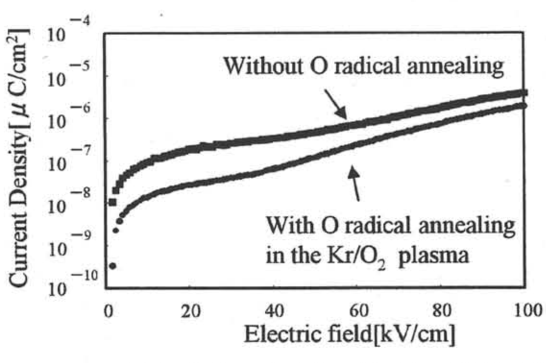

Fig.7 J-E characteristics of STN capacitors of Pt substrate with and without oxygen radical annealing in the Kr/O_2 plasma.