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Low-Temperature Preparation of Ferroelectric $Sr_2(Ta_{1-x}, Nbx)_2O_7$ Thin Films by Pulsed Laser Deposition and Their Application to MFIS Structure

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1. Introduction

In recent years, nonvolatile memory devices having ferroelectric gate structure (Metal- Ferroelectric- (Insulator)- Semiconductor Field Effect Transistor (MF(I)S-FET) structure) have attracted much attention from the viewpoints of nondestructive readout and large scale integration. However, a high temperature fabrication process of the ferroelectric degrades 1) the performances of memory device by diffusion of the elements to Si side and 2) device characteristics of pre-fabricated CMOS in the same chip. On the other hand, 3) the voltage applied to ferroelectric film becomes small when the ferroelectric film has a high dielectric constant. For 1) and 2), we have tried to fabricate ferroelectric films by pulsed laser deposition method (PLD) [1], at low temperature compared to the sol-gel methods. For 3), $Sr_2(Ta_{1-x}, Nb_x)_2O_7$ (STN)[2] has attracted much attention as bismuth- and lead-free ferroelectric material having a low dielectric constant, where both Bi in SBT and Pb in PZT are very diffusive into the substrate side. However, STN film was prepared at very high temperate.

In this work, we report a low temperature preparation of ferroelectric $Sr_2(Ta_{1-x}, Nb_x)_2O_7$ thin films by pulsed laser deposition and their application to MFIS structure.

2. Experimental

The laser used for PLD was ArF excimer laser and the targets were $Sr_2(Ta_{1-x}, Nb_x)_2O_7$(x=0.2-0.4) ceramic disks. The substrates were Pt/Ti/SiO_2/Si(100) wafers for Metal- Ferroelectric- Metal (MFM) structure, and SiO_2/Si(100) or SiON/Si(100) wafers were fabricated for MFIS structure by dry oxidation or oxinitridation. The substrate temperature during the deposition (T_s) was varied from 500 to 650 °C. The ambient gas during deposition was O_2 or N_2O and the pressure was varied from 0.03 to 0.2 Torr. The detail of PLD condition is shown in Table I. Pt(250 μmφ, 100 nm) was deposited by rf sputtering on the STN films as a top electrode.

Table I. Deposition condition of STN films by pulsed laser deposition.

Substrate temperature	**500 - 650 °C**
Gas	**O_2, N_2O**
Gas pressure	**0.05 - 0.2Torr**
Laser	**ArF excimer**
Repetition frequency	**3 - 8Hz**
Beam size	**0.03cm^2**
Strength	**3.7 J/cm^2 shot**
Deposition time	**90 - 150 min**
Target-substrate distance	**15 mm**

3. Results and Discussion

Figure 1 shows XRD patterns of STN(x=0.3) films deposited on Pt/ Ti/ SiO_2/ Si(100) and SiO_2/ Si(100) substrates at 600 °C in N_2O ambient gas of 0.08 Torr under ArF laser irradiation with repetition frequency of 5 Hz. On Pt/Ti/SiO_2/ Si(100), (151) peak of STN appears in the film deposited at 600°C but is not observed using O_2 ambient gas. Therefore, it is found that radical oxygen is very effective for low temperature preparation of STN thin films because N_2O gas is more activated than O_2 gas by ArF excimer laser. Also it is noted that STN films show (151) peak on SiO_2/ Si(100) and SiON/ Si(100) substrate. SiON is preferable as insulator layer in MFIS-FET[3] compared to SiO_2 from the viewpoints of bar-

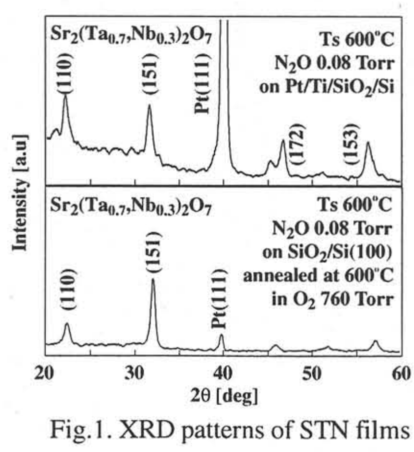

Fig.1. XRD patterns of STN films

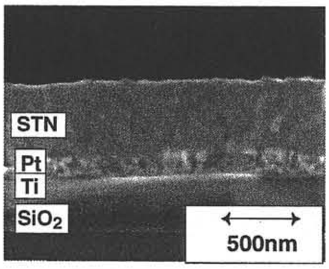

Fig.2. Cross sectional view of STN film.

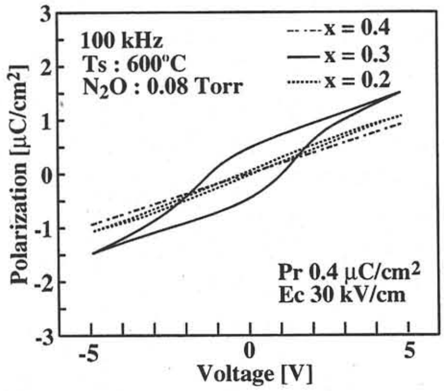

Fig.3. D-E hysteresis loops of STN films of X = 0.2 and 0.3.

rier against diffusion and dielectric constant. Figure 2 shows cross sectional view of a STN film deposited at 600°C in N_2O. STN film has dense column structure.

Figure 3 shows D-E hysteresis loops of STN capacitors measured by Sawyer-Tower circuit at 100 kHz. Symmetrical ferroelectric hysteresises were confirmed at composition (x) of 0.2 and 0.3 but no hysteresis was observed at x=0.4. For x=0.3, the remanent polarization (P_r) was 0.4 $\mu C/cm^2$ and the coercive force (E_c) was 30 kV/cm. The dielectric constant (ε) was about 55 at 1 MHz and is much lower than those of SBT and PZT. The fatigue properties of the remanent polarization of STN (x=0.3) thin films were shown in Fig. 4. P_r of as-deposited STN film disappears at switching cycles over 10^8 , however, P_r of the film post-annealed at 800°C in O_2 for 20 minutes after preparation of top electrodes did not change after 10^{10} cycles.

Figure 5 shows C-V characteristics of MFOS (Pt/ STN (x=0.3)(400nm)/ SiO_2(27nm)/ n-Si(100)) and MOS structures at 1 MHz. A counter clockwise C-V hysteresis was observed and its memory window was about 1.3V at sweep voltage width of 10 V. The C-V hysteresis is spread symmetrically without voltage shift and does not change in sweep rate ranging from 0.2 to 5.0 V/sec. It was therefore thought that this memory window is due to ferroelectricity of STN whose polarization controls the Si surface potential.

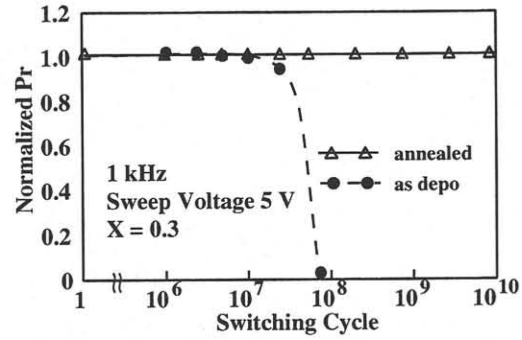

Fig.4. Fatigue properties of as-deposited and annealed STN films.

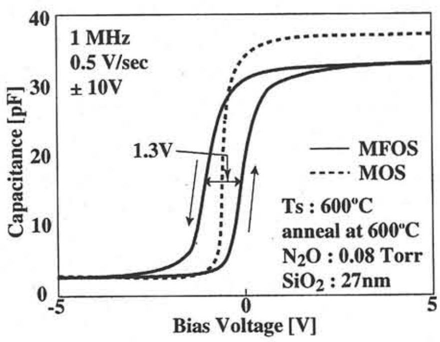

Fig.5. C-V characteristics of MFOS and MOS structures.

4. Conclusion

$Sr_2(Ta_{1-x}, Nb_x)_2O_7$ (STN) thin films have been prepared by pulsed laser deposition method on Pt/ Ti/ SiO_2/ Si(100), SiO_2/ Si(100) and SiON/ Si(100) substrates at lower temperature than the other reported process. These films have preferential (151)-orientation. D-E hysteresis loops are observed for STN thin films on Pt/ Ti/ SiO_2/ Si substrates when composition ratio is 0.2 and 0.3. For $Sr_2(Ta_{0.7},Nb_{0.3})_2O_7$ thin films, P_r is 0.4 $\mu C/cm^2$, E_c is 30 kV/cm and ε is as low as 55. P_r of $Sr_2(Ta_{0.7}, Nb_{0.3})_2O_7$ film annealed at 800°C did not change after 10^{10} cycles of polarization reversal. A counter clockwise C-V hysteresis was observed in an MFIS structure and its memory window was about 1.3V. It is indicated that the STN ferroelectric thin films can be well applied to MFIS-FET memory devices.

References

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