Low-Temperature Preparation of Ferroelectric Sr$_2$(Ta$_{1-x}$, Nb$_x$)$_2$O$_7$ 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(F)IS-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$_x$)$_2$O$_7$ (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 temperature.

In this work, we report a low temperature preparation of ferroelectric Sr$_2$(Ta$_{1-x}$, Nb$_x$)$_2$O$_7$ 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$_x$)$_2$O$_7$ 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$_2$O and the pressure was varied from 0.03 to 0.2 Torr. The detail of PLD condition is shown in Table I. Pt (250 µm, 100 nm) was deposited by rf sputtering on the STN films as a top electrode.

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$_2$O 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$_2$O 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 barrier...
rier against diffusion and dielectric constant. Figure 2 shows cross sectional view of a STN film deposited at 600°C in N₂O. 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 (Pᵣ) was 0.4 μC/cm² and the coercive force (Eᵥ) was 30 kV/cm. The dielectric constant (ε) was about 55 at 1 MHz and is much lower than those of STB and PZT. The fatigue properties of the remanent polarization of STN (x=0.3) thin films were shown in Fig. 4. Pᵣ of as-deposited STN film disappears at switching cycles over 10⁶, however, Pᵣ of the film post-annealed at 800°C in O₂ for 20 minutes after preparation of top electrodes did not change after 10⁶ cycles.

Figure 5 shows C-V characteristics of MFOS (Pt/ STN (x=0.3)(400nm)/ SiO₂(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.

4. Conclusion
Srₓ(Taₓ₋₁₋y, Nbₙ)yO₇ (STN) thin films have been prepared by pulsed laser deposition method on Pt/Ti/SiO₂/Si(100), SiO₂/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/SiO₂/Si substrates when composition ratio is 0.2 and 0.3. For Srₓ(Ta₀.₇₅, Nb₀.₂₅)O₇ thin films, Pᵣ is 0.4 μC/cm², Eᵥ is 30 kV/cm and ε is as low as 55. Pᵣ of Srₓ(Ta₀.₇₅, Nb₀.₂₅)O₇ film annealed at 800°C did not change after 10⁶ 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