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Effects of Oxygen Pressure on the Crystallization Behavior and Electrical Properties of $YMnO_3$ Thin Films

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ABSTRACT

The $YMnO_3$ thin films were prepared on platinized-silicon substrates by chemical solution deposition and annealed at 750 to 850°C for 1 h under various oxygen pressures, from 2 mTorr to 760 Torr. Effects of annealing oxygen pressures on the crystallization behavior and electrical properties of $YMnO_3$ thin films were investigated. Crystallinity and c-axis preferred orientation of $YMnO_3$ thin film were improved by decreasing the oxygen pressure but were deteriorated at extremely low oxygen pressure, 2 mTorr. Leakage current density of the $YMnO_3$ thin film decreased as the oxygen pressure decreased. The film annealed at 800°C under 2 Torr, which had the best crystallinity and the highest c-axis preferred orientation, showed the best-developed ferroelectric C-V hysteresis.

Key words : Ferroelectric properties, Annealing, $YMnO_3$, Chemical solution deposition

1. Introduction

Recently $YMnO_3$ thin film has been proposed as a new candidate for MFSFET(Metal Ferroelectric Semiconductor Field Effect Transistor)-type or MFISFET(Metal Ferroelectric Insulator Semiconductor Field Effect Transistor)-type non-volatile memory devices because it has a low dielectric constant and highly deoxidizing ability which could suppress the formation of SiO_2 interfacial layer when $YMnO_3$ thin films are formed directly on Si substrates.[1-4]

Even though C-V hysteresis in MF(I)S structure has been reported by several researchers,[5,6] it could be influenced by interfacial polarization and rearrangement of the space charge. Kitahata et al. reported the direct evidence of ferroelectricity, C-V hysteresis of a $YMnO_3$ thin film in a MFM (Metal/Ferroelectric/Metal) structure.[7] When they annealed the $YMnO_3$ thin film in vacuum, the film showed ferroelectric C-V hysteresis and low leakage current. Cheon et al. also reported C-V hysteresis of a $YMnO_3$ thin film annealed at Ar atmosphere in a MFM(Metal/Ferroelectric/Metal) structure.[8] These results imply that oxygen partial pressure in the annealing process could be an important factor on the ferroelectricity of the $YMnO_3$ thin film.

Therefore, the effects of oxygen partial pressure during the annealing process on the properties of $YMnO_3$ thin films, prepared by chemical solution deposition method on the platinized silicon substrates, were investigated in this work. They were crystallized in various oxygen pressure, from 2 mTorr to 760 Torr. The crystallinities, leakage currents, and C-V hysteresis of the thin films were examined.

2. Experimental

Yttrium acetate hydrate (99.9%, Aldrich) and manganese acetate tetrahydrate (99.99%, Aldrich) were used as raw materials and the mixed solution of DEA (diethanolamine, 98.5%, Aldrich) and 2EE (2-ethoyethanol, 99+%, Aldrich) as a solvent. Manganese acetate tetrahydrate was dissolved in the solvent and was distillated at 80°C for 1 h. It was mixed with an yttrium acetate hydrate solution prepared beforehand and refluxed at 120°C for 5 h. This stock solution was spin-coated on $Pt/Ti/SiO_2/Si$ substrates at 3000 rpm for 30 seconds and dried on hot plate in air. This process was repeated seven times. $YMnO_3$ thin films were annealed at 750~850°C for 1 h for oxygen atmosphere. Oxygen pressure of the annealing atmosphere was changed from 2 mTorr to 760 Torr. The thickness of the annealed thin film was about 120 nm. Crystallinity of the $YMnO_3$ thin films was examined using X-Ray Diffraction(XRD) analysis. Platinum top electrodes were sputtered on the annealed $YMnO_3$ thin films with a shadow mask. The top electrode area was about 2.54×10^{-8} m^2. The electrical properties were measured with MFM structure. Leakage currents were measured using an electrometer (Keithley 617), and capacitance-voltage characteristics were measured using an impedance analyzer (HP 4192A).

3. Results and Discussion

Fig. 1 shows XRD patterns of $YMnO_3$ thin films annealed at 800°C under various oxygen pressures. When the anneal-

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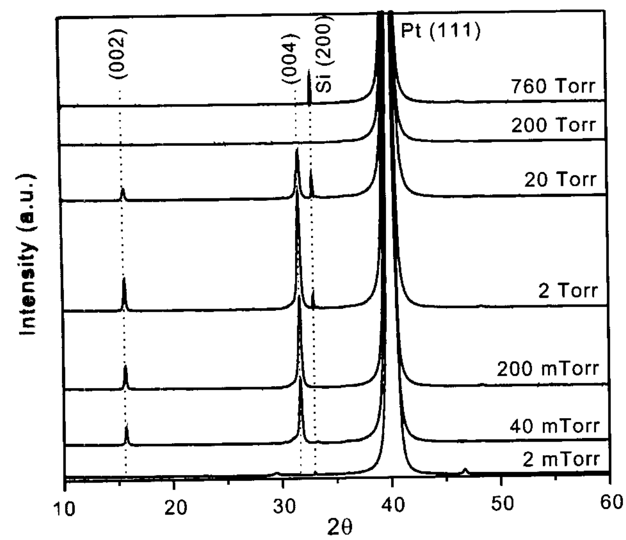

Fig. 1. X-ray diffraction patterns of $YMnO_3$ thin films annealed at 800°C under various oxygen pressure.

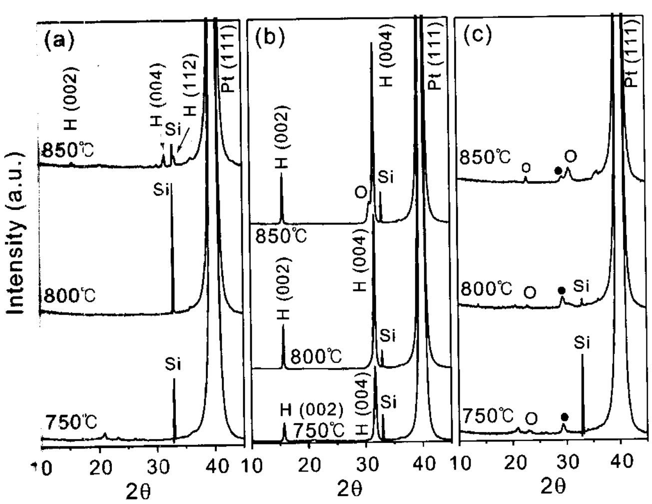

Fig. 2. Crystallization behavior of $YMnO_3$ thin films annealed at (a) 760 Torr, (b) 2 Torr, and (c) 2 mTorr of oxygen pressure (H : Hexagonal $YMnO_3$, O : Orthorhombic $YMnO_3$. ● : Y_2O_3).

ing oxygen pressure was higher than 200 Torr, the films were amorphous as shown in the figure. The films crystallized into highly c-axis oriented $YMnO_3$ hexagonal phase at the oxygen pressure between 40 mTorr and 20 Torr. The film annealed at 2 Torr showed the best crystallinity and the highest c-axis preferred orientation. Fig. 2 shows XRD patterns of $YMnO_3$ thin films annealed at 760 Torr, 2 Torr and 2 mTorr with varying annealing temperature from 750°C to 850°C. When the film was annealed at 760 Torr of oxygen pressure, the film was amorphous until annealing temperature was 800°C and was crystallized into polycrystalline film at above 850°C. At 2 Torr, the film was crystallized into highly c-axis oriented $YMnO_3$ beginning from 750°C. $YMnO_3$ orthorhombic phase were also observed in the film annealed at 850°C. Non-ferroelectric phases, Y_2O_3 and orthorhombic $YMnO_3$, were formed when the film was

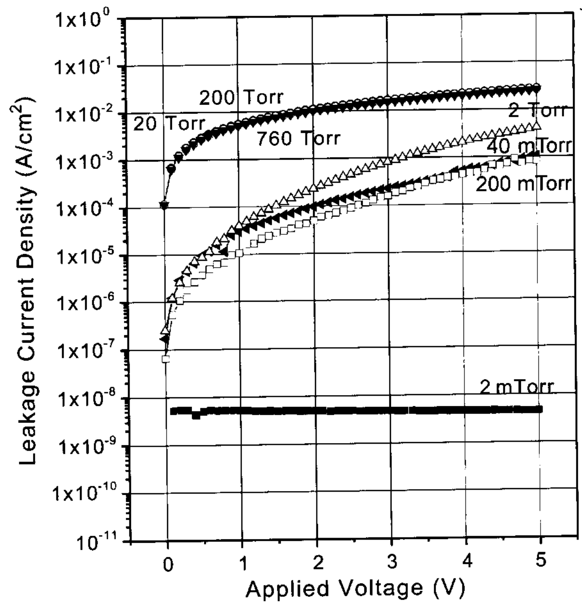

Fig. 3. The change of leakage current density of the $YMnO_3$ thin film annealed at 800°C by varying oxygen pressure.

annealed at 2 mTorr. From Figs. 1 and 2, it seems that crystallinity and c-axis preferred orientation of $YMnO_3$ thin film are improved by decreasing the oxygen pressure of the annealing atmosphere, but the crystallization of $YMnO_3$ hexagonal phase is suppressed at extremely low oxygen pressure because more stable other phases are formed.

Fig. 3 shows leakage current densities of $YMnO_3$ thin films annealed under various oxygen pressures. Leakage current density of the $YMnO_3$ thin film decreased as the oxygen pressure decreased. The change of leakage current density by varying the oxygen pressure in Fig. 3 suggests that the conduction mechanism might be the same as that of the $YMnO_3$ ceramic, a thermally activated hopping of small polarons between localized sites, Mn^{3+}–Mn^{4+}.[9] As oxygen pressure decreases, the density of Mn^{4+} which is a associate of Mn^{3+} and hole decreases and the leakage current density decreases. The film annealed at 2 mTorr shows extremely low leakage current density because nonferroelectric phases such as Y_2O_3 with very high resistivity were formed.

Capacitance-voltage characteristics of $YMnO_3$ thin films are shown in Fig. 4. The C-V characteristics of the films annealed at higher oxygen pressure than 2 Torr were not in the figure because of their high leakage currents. The $YMnO_3$ thin films annealed at 40 mTorr to 2 Torr show typical ferroelectric hysteresis in the C-V curve while the film annealed at 2 mTorr shows a flat C-V curve. In the ferroelectrics, the switching of the spontaneous polarization contributes to the total capacitance and is clamped by increasing the applied voltage. The difference between the maximum capacitance and the minimum capacitance in the Fig. 4 indicates the contribution by the switching of the spontaneous polarization. The best-developed ferroelectric

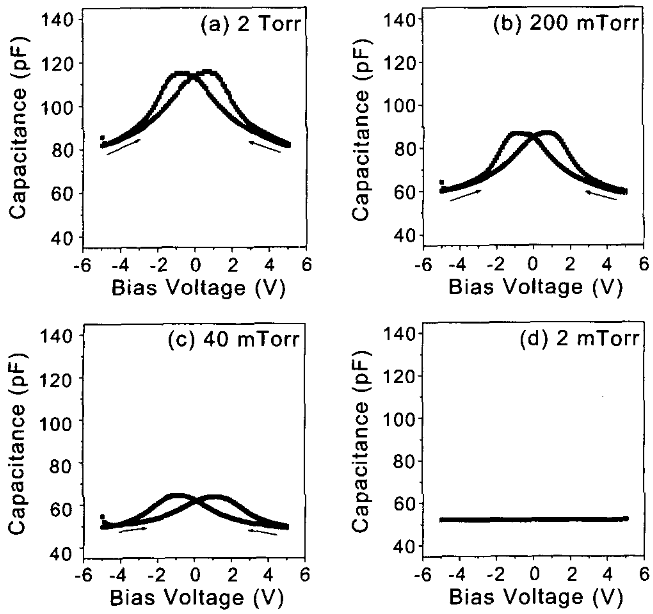

Fig. 4. Capacitance-voltage characteristics of $YMnO_3$ thin films annealed at 800°C under (a) 2 Torr, (b) 200 mTorr, (c) 40 mTorr, and (d) 2 mTorr of oxygen pressure.

C-V hysteresis curve in the film annealed at 2 Torr was due to the superior crystallinity and the strong preferred orientation along c-axis which is an unique polar axis in the $YMnO_3$ hexagonal ferroelectric phase. And the difference between maximum capacitance and minimum capacitance in the film annealed at 2 Torr of oxygen pressure is much higher than that of the film reported by others,[7,8] which was annealed in vacuum or Ar atmosphere. Nonferroelectric phases formed at 2 Torr of oxygen pressure results in the flat C-V curve, as shown in Fig. 4.

4. Conclusions

Crystallinity and c-axis preferred orientation of $YMnO_3$ thin film were improved by decreasing the oxygen pressure but were deteriorated at extremely low oxygen pressure. The film annealed at 800°C under 2 Torr of oxygen pressure showed the best crystallinity and the highest c-axis preferred orientation. Leakage current density of the $YMnO_3$ thin film decreased as oxygen pressure of the annealing atmosphere decreased. The conduction mechanism of the $YMnO_3$ thin film might be the same as that of the $YMnO_3$ ceramic, a thermally activated hopping of small polarons between localized sites, Mn^{3+}–Mn^{4+}. The film annealed at 800°C under 2 Torr of oxygen pressure showed the best-developed ferroelectric C-V hysteresis curve due to the superior crystallinity and the strong preferred orientation along c-axis.

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