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Effect of annealing pressure on the growth and electrical properties of $YMnO_3$ thin films deposited by MOCVD

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Abstract – Ferroelectric $YMnO_3$ thin films were deposited on Y_2O_3/Si(100) substrates by metalorganic chemical vapor deposition. The $YMnO_3$ thin films annealed in vacuum ambient (100 mTorr) above 750°C show hexagonal structured $YMnO_3$. However, the film annealed in oxygen ambient shows poor crystallinity, and the second phase as Y_2O_3 and orthorhombic-$YMnO_3$ were shown. The annealing ambient and pressure on the crystallinity of $YMnO_3$ thin films is very important. The C-V characteristics have a hysteresis curve with a clockwise rotation, which indicates ferroelectric polarization switching behavior. When the gate voltage sweeps from +5 to 5 V, the memory window of the Pt/$YMnO_3$/Y_2O_3/Si gate capacitor annealed at 850°C is 1.8 V. The typical leakage current densities of the films annealed in oxygen and vacuum ambient are about 10^{-3} and 10^{-7} A/cm^2 at applied voltage of 5 V.

I. Introduction

Ferroelectric random access memory (Fe-RAM) with Metal/Ferroelectric/Semiconductor field effect transistors (MFSFET) structure have the advantage of saving electricity power and decreasing memory cell size, and this type of memory utilizes the remanent polarization of a ferroelectric thin film to control the surface potential of a silicon substrate. This type of memory could make possible non-destructive read out (NDRO) and a single transistor per cell. However, this structure has not demonstrated yet due to difficulty in forming reliable ferroelectric thin films on silicon directly. Elements in the film may diffuse into silicon [1], forming uncontrollable oxide layer and thus degrading the interface characteristics. In order to solve these problems, Metal/Ferroelectric/Insulator/Semiconductor field effect transistors (MFISFET) structure have been suggested and increasingly studied these days. Among insulators (inter-dielectric layers), there are silicon nitride, Y_2O_3, CeO_2, ZrO_2, and so on [2-6]. Particularly, Y_2O_3 films are epitaxially grown on Si (111) or Si (100) substrates [7], and the Y_2O_3/Si shows excellent interface properties [8]. The dielectric constant of bulk Y_2O_3 ranges from 14 to 17 [9]. It is also expected that the Y atoms in Y_2O_3 films reduce the thickness of the interfacial SiO_2 layer. Hence, Y_2O_3 films are expected to use as a buffer layer in the ferroelectric gate structure. Among ferroelectric materials, $YMnO_3$ does not have any reaction between the Silicon substrate. This material have a low dielectric constant, one axis polarization, heavy and easily oxidized elements [10-13]. In addition, a self-aligning process should be used to fabricate the source-drain regions of regions of high density MFS, MFIS FET memories. It is necessary to keep the ferroelectric materials from degrading during the source-drain activation annealing above 850°C. The $YMnO_3$ thin film is Pb and Bi free and is stable at high processing temperature. Hence, it is expected that $YMnO_3$ films can be used as a ferroelectric in the Metal/Ferroelectric/Insulator/Semiconductor field effect transistors (MFISFET) structure.

In this letter, we have described the dependence of the heat treatment conditions on the crystallinity and ferroelectric properties of $YMnO_3$ thin film deposited on Y_2O_3/Si (100) substrates by metalorganic chemical vapor deposition (MOCVD).

II. Experiments

The Y_2O_3 thin films were first deposited on *p*-Si(100) substrates using metalorganic chemical

Table 1. Deposition conditions of Y_2O_3 and $YMnO_3$ thin films by MOCVD.

Deposition parameter	Deposition condition
Deposition temperature	500°C
Deposition pressure	3 Torr
Bubbling temperature of Y source[a]	162°C
Ar gas flow rate for Y delivering	100 sccm
Bubbling temperature of Mn source[b]	20°C
Ar gas flow rate for Mn delivering	20 sccm (0 sccm for Y_2O_3)
Oxygen gas flow rate	500 sccm
Deposition time	30 min (10 min for Y_2O_3)
Substrate	*p*-type Si (100)

[a] $Y(C_{11}H_{19}O_2)_3$
[b] $(CH_3C_5H_4)Mn(CO)_3$

vapor deposition (MOCVD), and then the ferroelectric $YMnO_3$ thin films were *in situ* deposited on the Y_2O_3 thin films. During the Y_2O_3 deposition, the deposition temperature and system pressure were fixed at 500°C and 3 Torr, respectively. In order to eliminate native oxide, silicon wafers were etched with following procedure. The Si wafers were etched for 20 sec using a HF 2.5 mol % solution and then rinsed with deionized wafer for 5 min in ultrasonic cleaner. After the rinse, the wafers were again etched for 5 sec in 6:1 HF solution buffered using C_2H_5OH. Finally, they were blowed with nitrogen gas (99.9999% purity). For the $YMnO_3$ and Y_2O_3 growth, $Y(C_{11}H_{19}O_2)_3$ and $(CH_3C_5H_4)Mn(CO)_3$ were used as starting materials of Y and Mn respectively. The typical Y_2O_3 and $YMnO_3$ deposition conditions are summarized in Table. After the deposition, the samples were annealed at 700-900°C for 60 min in various atmospheres. The film thickness and composition of the $YMnO_3$ films was determined by Rutherford backscattering spectroscopy (RBS, NEC 3SDH), and transmission electron microscope (TEM, CM20T/STEM, Philips) was used to characterize the microstructure of the films. X-ray diffraction (XRD, Rigaku D/MAX-RC) using Cu Kα radiation and a Ni filter was used to determine the crystal phase of the films. The C-V characteristics were measured as a function of frequency with a Hewlett-Packard (4194A) impedance-gain phase analyzer. The current-voltage (*I*-V) measurements were performed with a Keithley 617 programmable electrometer. Top Pt electrode was prepared at room temperature by dc sputtering using the shadow mask with a diameter of 0.15 mm.

III. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of $YMnO_3$ thin films on Y_2O_3/Si(100) substrates with annealing temperature in oxygen ambient. As shown in Fig. 1(a), (b) and (c), there are no hexagonal $YMnO_3$ peaks except for (111) Y_2O_3 peak at the 29.2°. After annealing above 850°C in oxygen ambient, the hexagonal $YMnO_3$ phase were formed with Y_2O_3 and orthorhombic-$YMnO_3$ phase, as shown in Fig. 1(d) and (e). However, $YMnO_3$ thin films annealed in vacuum ambient (lower than 100 mTorr) show hexagonal structured $YMnO_3$, as shown in Fig. 2. $YMnO_3$ thin films show a polycrystalline structure in vacuum ambient above 750°C. This result suggests that the annealing conditions on the crystallinity of $YMnO_3$ thin films is very important. Yi *et al.* reported that the $YMnO_3$ thin films deposited by chemical solution deposition were crystallized by conventional furnace annealing in oxygen ambient with rapid thermal annealing at 850°C [14], and Kitahata *et al.* reported that the heat treatments in vacuum improved the crystallinity because the low pressure annealing enhanced the elimination of residual organics [15]. Our thin films were also improved the crystallinity in vacuum annealing.

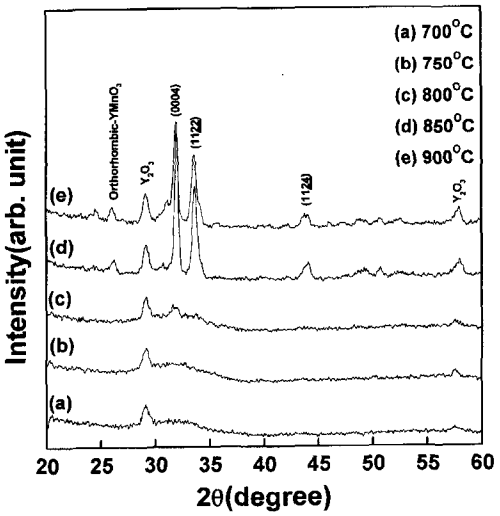

Fig. 1. XRD patterns of $YMnO_3/Y_2O_3$/Si structure with annealing temperature in oxygen ambient.

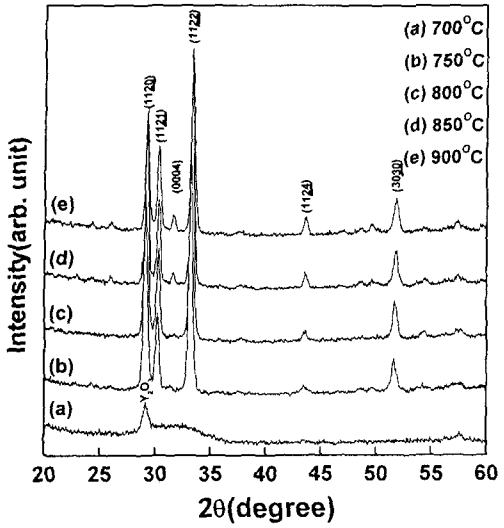

Fig. 2. XRD patterns of $YMnO_3/Y_2O_3/Si$ structure with annealing temperature in vacuum ambient.

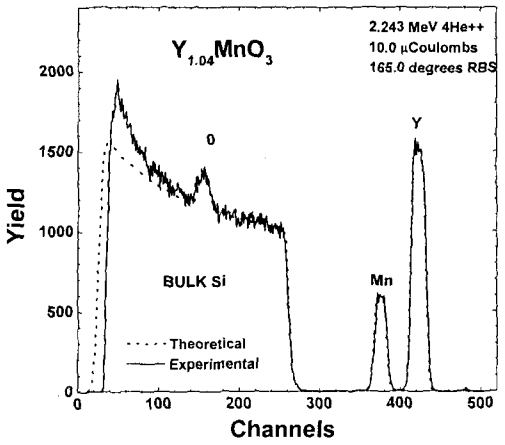

Fig. 3. RBS spectrum of $YMnO_3/Y_2O_3/Si$ structure annealed in vacuum ambient at 850°C.

However, the precursor used film deposition decomposed during the deposition at 500°C. Therefore, improvement of crystallinity in vacuum annealing needs another explanation. The annealing in oxygen ambient makes the thin films in the oxygen excess state. But many oxides composed of transition metals are in an oxygen deficient state, and this excess oxygen state prevents the crystallization of $YMnO_3$ thin films. Therefore, while the film heat treated in oxygen ambient shows an insufficient crystallinity, and the second phase as Y_2O_3 and orthrhombic-$YMnO_3$ were formed. However, $YMnO_3$ thin films annealed in vacuum ambient show hexagonal structured $YMnO_3$ phase. We can conclude that vacuum annealing has a positive influence on the crystallinity of $YMnO_3$ thin films. These results indicate that the annealing ambient and pressure on the crystallinity of $YMnO_3$ thin films is very important.

Fig. 3 shows RBS spectrum of $YMnO_3/Y_2O_3/Si$ structure annealed at 850°C in vacuum ambient. The detector angle was 165° with respect to the direction of the 2.25 MeV $4He^{++}$ incident particle. Analysis of RBS spectrum showed that a stoichiometric $YMnO_3$ thin film was grown with an interfacial layer suspected to be Y_2O_3. The ratio of Y/Mn is about 1.04.

The microstructure of the interface structure of $YMnO_3$ thin films on the Y_2O_3/Si substrate annealed

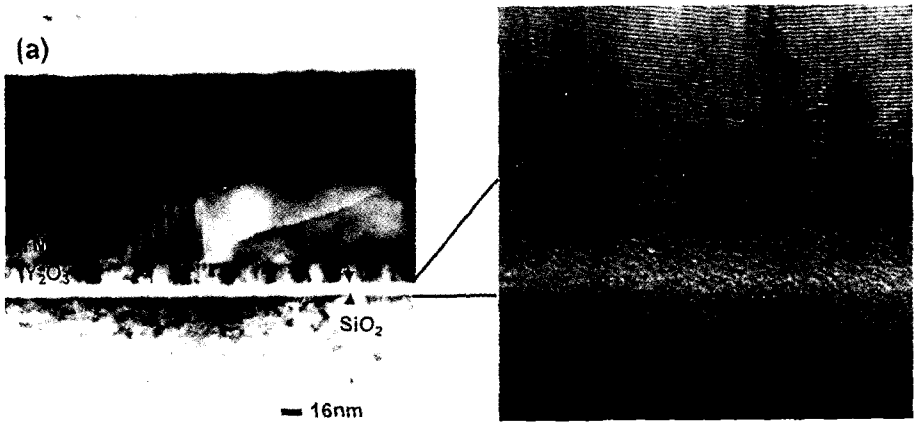

Fig. 4. TEM cross section images of (a) the $YMnO_3/Y_2O_3/Si$ structure annealed in vacuum ambient at 850°C, and (b) the high resolution image between Y_2O_3 and Si.

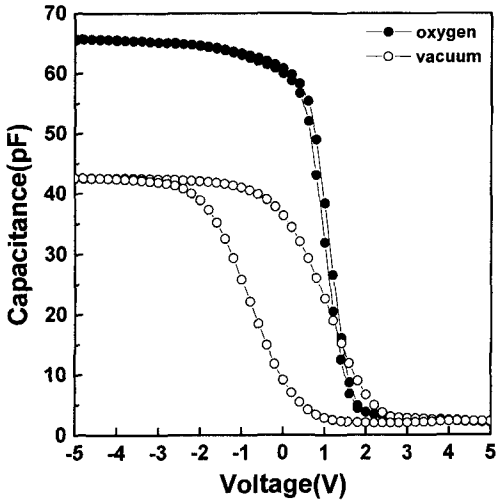

Fig. 5. C-V characteristics of $Pt/YMnO_3/Y_2O_3/Si$ structure with annealing ambient at 850°C.

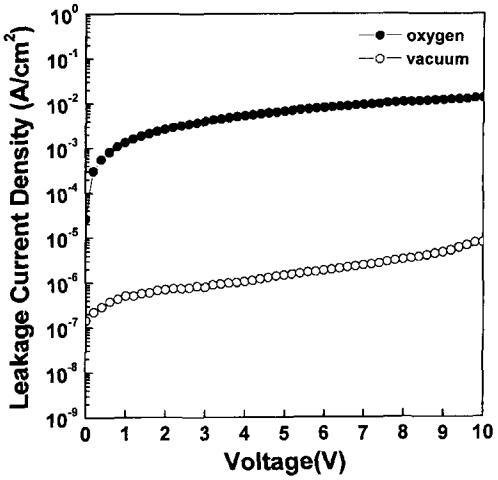

Fig. 6. Leakage current density of $Pt/YMnO_3/Y_2O_3/Si$ structure with annealing ambient at 850°C.

at 850°C in vacuum ambient was observed with HR-TEM as shown in Fig. 4. The figure shows the clean and smooth interface between Si and Y_2O_3 with the native oxide of 6 nm thickness, and the thickness of $YMnO_3$ and Y_2O_3 thin films are estimated as 140 and 15nm, respectively.

C-V measurements were performed for the $Pt/YMnO_3/Y_2O_3/Si$ structure by a frequency signal of 1MHz. C-V characteristics of the $Pt/YMnO_3$ (140 nm)/Y_2O_3 (15 nm)/Si structure with annealing ambient at 850°C are shown in Fig. 5. The C-V characteristics have a hysteresis curve with a clockwise rotation, which indicates ferroelectric polarization switching behavior. The stability in the inversion region depends on the trap charges at the interface between ferroelectrics and Si. The stable inversion at the annealing temperature of 850°C suggests that there are no interactions at the interfaces of $YMnO_3/Y_2O_3/Si$ as shown in Fig. 4. When the gate voltage sweeps from +5 to –5V, the memory window of the $Pt/YMnO_3/Y_2O_3/Si$ gate capacitor annealed at 850°C is 1.8 V. In the C-V characteristics, the accumulation region appears below the bias voltage –2V. The capacitance in the accumulation regions approximately corresponds to the series capacitance of $YMnO_3$, Y_2O_3, and SiO_2 capacitors. The dielectric constant of $YMnO_3$ films calculated from flatband capacitance in the accumulation regions. The evaluated dielectric constant of $YMnO_3$ thin films is about 45 at room temperature.

The leakage current characteristics of MFIS structures with different annealing ambient at 850°C were shown in Fig. 6. Pt electrodes of 0.15 mm in diameter were sputtered for electrical measurements. In this measurement, the time interval of each step voltage was 1s. The typical leakage current densities of the films annealed in oxygen at 850°C is about 10^{-3} A/cm^2. However, the leakage current density of the samples heat treated in vacuum at 850°C is drastically improved, which is about 10^{-7} A/cm^2 at applied voltage of 5 V. These results is very similar with Kitahata *et al.* [15] The annealing in oxygen ambient makes the $YMnO_3$ thin films in the oxygen excess state. This excess oxygen in films makes the change in the valence of Mn ion 4+ from 3+. This variation of Mn valence state from 3+ to 4+ resulted in the increase of leakage current. However, The $YMnO_3$ thin films annealed in vacuum ambient is maintained at Mn ion 3+. From these results, the leakage current density is drastically decreased the annealing in vacuum ambient.

IV. Conclusions

The ferroelectric $YMnO_3$ and Y_2O_3 thin films were deposited by using metalorganic chemical vapor deposition (MOCVD) for the Metal/Ferroelectric/Insulator/Semiconductor field effect transistors (MFISFET) structure. The ferroelectric capacitors

deposited at 500°C were annealed under various atmospheres and temperature for 60 min. The capacitors of Pt/$YMnO_3$ (140 nm)/Y_2O_3 (15 nm)/Si structure heat treated in vacuum (100 mTorr) above 750°C showed superior crystallinity and ferroelectric properties, lower leakage current than those heat treated under oxygen ambients. The ferroelectric films annealed in vacuum were single phases of hexagonal $YMnO_3$. The MFIS structure with the stoichiometric $YMnO_3$ capacitors annealed in vacuum showed a high memory window of 1.8 V at the gate voltage of 5 V. The leakage current densities of the films annealed in vacuum showed almost four orders of magnitude lower than those annealed in oxygen. The structural and electrical properties of $YMnO_3$ depend greatly on the annealing conditions.

Acknowledgments

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