Uniform and Reproducible MOCVD of Pb(Zr,Ti)O₃ Thin Films on 8"\u0396 Substrate for FeRAM Production

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1. Introduction

Extensive studies have been carried out on ferroelectric thin films for application in nonvolatile ferroelectric random access memories (FeRAMs). Among the various ferroelectric materials, PZT has attracted much attention as the best candidate for FeRAM for its promising ferroelectric properties [1]. Many deposition techniques, such as sol-gel, metalorganic decomposition (MOD), sputtering, laser ablation and metalorganic chemical vapor deposition (MOCVD), have been so far utilized in the preparation of PZT thin films. From the point of view of mass production for the near future, MOCVD is the best way for its feature such as accurate compositional control, uniform deposition over large area, conformal step coverage and so on [2,3].

In this study, we prepared PZT thin films on $8^{\circ}\phi$ substrate using ULVAC mass productive MOCVD module and evaluated capability such as uniformity, reproducibility and so on.

2. Configuration of MOCVD module

ULVAC MOCVD module has a single-slice type reactor with a liquid delivery system of multi component liquid precursors and fully temperature controlled gas lines, mixing box, shower plate, chamber wall, gas exhaust lines and dry-pump units. This setup enables continuous running over 1000 wafers without maintenance. This module has the capability of flow rate control of 3-6 different liquid precursors independently and enable composition control of the PZT thin films in lateral direction. Exact temperature control of every gas lines and valves are established using Aluminum block type heaters, within temperature distribution of 2°C–4°C at 220°C.

3. Experimental condition

PZT thin films were deposited at on $8"\phi$ Ir/SiO₂/Si substrates, whose Ir layer was formed by DC magnetron sputtering. After the PZT deposition, top electrodes (Pt) were also formed by DC sputtering and then annealed at the same temperature of PZT deposition for 60 min in O_2 ambient as the recovery annealing.

X-ray fluorescence (XRF) analysis was used for compositional analysis and scanning electron microscopy (SEM) was for microstructure observation. Electrical properties were evaluated using FCE-1 ferroelectric test system (Toyo corp.).

4. Results and Discussion

Improvement in uniformity

Uniformity is one of the most important factors for reliable mass production system. Among the several optimizing techniques, modifying the shower plate was thought to be effective and utilized for improvement in uniformity. Figure 1 shows the relationship between film thickness uniformity and the diameter of shower plate. As can be seen in this figure, there is optimum condition in the diameter. In case of 150 mm ϕ , flow rate of near center was relatively faster than periphery. While in case of 250 mm ϕ , that of near center was slightly slower than periphery. As a result, 200 mm ϕ was the optimum value in this module.



Fig. 1 Relationship between film thickness uniformity and shower plate diameter.

PZT composition uniformity is closely related to electrical performance and supposed to be required at least within $\pm 2\%$ for future generation (0.18 µm~). From the evaluation of composition uniformity in case of shower plate with 200 mm ϕ , Good uniformity of Pb/(Zr+Ti) of $\pm 0.9\%$ and Zr/(Zr+Ti) of $\pm 1.8\%$ were obtained and confirmed to be suited for future generation.

Effects of liquid source concentration

In so-called liquid delivery type MOCVD, organometallic sources were dissolved in appropriate solvent. While, effects of additives (solvents) on gas-transport type MOCVD were investigated by other group and it was reported that deposition process and growth mechanism were affected by additives [4]. Widely adopted THF is chemically active and also thought to affect the morphologies or electrical properties of PZT thin films. So, effects of liquid source concentration were investigated.

Figure 2 shows the P-V hysteresis loops of 120-nmthick PZT films. (a) and (b) are for standard and high concentration condition respectively. As can be seen in this figure, ferroelectricity was improved in case of high concentration condition (b).



Applied voltage (V)

Fig. 2 P-V hysteresis loop of 120-nm-thick PZT films. (a) and (b) are for standard and high concentration condition respectively.

Two samples were also compared by surface morphology. Figure 3 shows the SEM photographs of these samples. As can be seen in these figures, high concentration condition (b) is relatively smooth compared to standard condition (a). As mentioned earlier, it is thought that THF has some kind of relationship with growth mechanism and PZT growth was enhanced by removing the extra THF.



Fig. 3 SEM photographs of PZT thin films. (a) and (b) are for standard and high concentration condition respectively.

5. Conclusions

PZT thin films were deposited on $8^{\circ}\phi$ substrate using ULVAC mass productive MOCVD module and evaluate its capability. The results obtained in this study are as follows; (1) Relative good uniformity was achieved by adjusting the shower plate and (2) ferroelectricity and morphology of PZT thin films were improved by increasing the liquid source concentration. It is thought that PZT growth was enhanced by removing the extra THF. Further improvement will be continued to realize mass productive MOCVD with higher reliability.

References

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