Abstract

Dysprosium oxide ($\text{Dy_2O_3}$) were deposited by MBE on n-Si(100), and annealed at 200°C–600°C in vacuum in-situ for 90min. By in-situ vacuum anneal, negative $V_{FB}$ shift is observed. However, good C-V characteristics without hysteresis and accumulation capacitance decrease were observed. Dit was also improved by in-situ vacuum anneal.

1. Introduction

Rare earth oxides are thought to be promising candidates for next generation of gate dielectrics [1-3], and came to appear on the time table of ITRS 2001 [4]. Recently, good characteristics of Dy$_2$O$_3$ films were reported [5].

In general, interfacial layer are formed between the high-k film and Si substrate during the anneal process after the deposition, resulting in the EOT (Equivalent Oxide Thickness) increase. To suppress the interfacial layer growth, we have investigated in-situ vacuum annealing of the Dy$_2$O$_3$ films. In this paper, we report the effects of in-situ vacuum anneal for the improvement of the electrical characteristics of the films.

2. Experimental

Fabrication process of MIS capacitors is shown in Fig. 1. Dy$_2$O$_3$ thin films were deposited on HF dipped n-Si(100) substrate (HF-last) by MBE at room temperature (R.T.). The pressure in the chamber during depositions was $10^{-8}$-$10^{-10}$ Torr. Then, we have investigated different two annealing methods. In the conventional annealing method, the films were annealed ex-situ by RTA for 5min in O$_2$ atmosphere. On the other hand, in the new annealing method, the films were annealed in-situ in the vacuum at 200°C–600°C for 90min by the heater equipped in MBE system. (Fig. 1 (b)). The pressure in the chamber during annealing was $10^{-9}$-$10^{-10}$ Torr. Then, Al electrodes were formed by evaporation using a metal hard mask. Fabricated MIS capacitors were evaluated by C-V, J-V characteristics and surface morphology with AFM. Additionally, in order to investigate the effect of the different interfacial condition, Dy$_2$O$_3$ films were deposited on the chemical oxide. It was formed on the Si substrate by H$_2$O$_2$ (the film thickness is ~0.5nm).
3. Results and Discussions

3.1. Conventional Annealing (5min RTA)

Figure 2 shows the annealing temperature dependence of C-V and J-V characteristics for Al/Dy2O3/n-Si(100)/Al MIS structures fabricated by the conventional annealing method (5min RTA in O2).

Although a huge hysteresis was observed for as-deposited film, it disappeared in the C-V characteristics for the films after RTA. Both accumulation capacitance and leakage current decrease as annealing temperature increases. This result indicates that the interfacial layer was formed by the RTA.

3.2. In-situ Annealing Method

Figure 3 shows C-V and J-V characteristics for Dy2O3 thin films annealed in-situ vacuum at 400°C for 90min after deposition. It is observed that hysteresis in the C-V characteristics for the as-deposited film disappeared by the in-situ vacuum anneal without decreasing the accumulation capacitance. It is considered that the interfacial layer growth is suppressed during the in-situ vacuum anneal. On the other hand, leakage current increases by the vacuum anneal. However, notice that the C-V curve for the film after in-situ vacuum anneal is shifted to negative side. So, comparing the leakage current at the same electric field that effectively applied on the thin film, the leakage current for the film after in-situ vacuum anneal is lower than the as-deposited film as shown in Fig. 4. Figure 5 shows AFM images of surface morphology for Dy2O3 thin films. Surface roughness does not change by in-situ vacuum anneal.
Dy$_2$O$_3$ films were deposited on the chemical oxide and bare Si substrate (HF-last). Both were annealed in-situ in the vacuum at 400°C after deposition. Their C-V characteristics were compared in Fig. 6. The results for the conventional annealing method were also compared as a reference. It is found that in the case of in-situ vacuum anneal, the accumulation capacitance value for the film on the chemical oxide is lower than the film on HF-last because of its additional thickness due to the chemical oxide. However, negative $V_{FB}$ shift is smaller than that of the HF-last film. By inserting chemical oxide at the interface, the positive interfacial charges are suppressed. Figure 7 shows the dependence of interfacial state density $D_{it}$ on the annealing and wafer pretreatment method. The $D_{it}$ values were estimated by Terman method. It is found that in-situ vacuum anneal improves $D_{it}$. Chemical oxide also reduces the $D_{it}$. In terms of the $D_{it}$ improvement, combination of the vacuum anneal and chemical oxide is the best choice.

Figure 8 shows the C-V characteristics of the samples with in-situ vacuum anneal at 200°C and 600°C. Accumulation capacitance and $V_{FB}$ shift for the 200°C anneal does not show significant difference from those of the 400°C anneal (Fig. 6). On the other hand, C-V characteristics of the 600°C annealed sample changed dramatically. Figure 9 shows RBS measurement result for the film as-deposited and after 600°C in-situ vacuum anneal. The film thickness after 600°C in-situ vacuum anneal is about 50% to the as-deposited film. It is considered that Dy$_2$O$_3$ evaporates at high temperature such as 600°C.

### 3.3 O$_2$ RTA after in-situ anneal

Dy$_2$O$_3$ thin films were annealed by RTA(400°C and 600°C) in O$_2$, after 400°C in-situ vacuum anneal. In the case of 400°C RTA, (the same temperature with in-situ vacuum anneal) EOT slightly increased (about 0.1nm) by the RTA, but $V_{FB}$ were not improved. (Fig. 10) On the other hand, $V_{FB}$ shifts to positive direction from the initial position by the 600°C RTA. Additionally, it was found that the difference of capacitances for the film with and without chemical oxide is observed even after
This difference is not observed in the case of without in-situ anneal. This suggests that the chemical oxide quality is improved by the in-situ vacuum anneal.

EOT-J plot is shown in Fig. 11 as the summary of this work. Comparing with the case of the conventional annealing method (5min RTA in O2), the leakage current decreased by in-situ vacuum anneal at the same EOT.

Figure 8. C-V characteristics for the Dy2O3 films after in-situ vacuum anneal (a) at 200°C (b) at 600°C

Figure 9. RBS measurement for the Dy2O3 films as-deposited and in-situ vacuum annealed at 600°C

Figure 10. C-V characteristics for the Dy2O3 films annealed in O2 by RTA at 400°C and 600°C after in-situ vacuum anneal

Figure 11. EOT-J plot of the conventional RTA in O2 and in-situ vacuum anneal

4. Conclusion

Dy2O3 thin films were deposited by MBE and annealed in-situ in the vacuum at 200°C–600°C for 90min. Good C-V characteristics without hysteresis are obtained with suppressing the growth of the interfacial layer by in-situ vacuum anneal.

Acknowledgement

This work was partially supported by Semiconductor Technology Academic Research Center (STARC) and Grant-in-Aid for Scientific Research Priority Areas (A): Highly Functionalized Global Interface Integration. The authors are also grateful to Drs. N. Nakayama (STARC), T. Nishikawa (STARC), T. Arikado (Selete), J. Yugami (HITACHI), T. Kitano (NEC), K. Fujita (SANYO), Y. Tsunashima (TOSHIBA), H. Iishiwa (Tokyo Inst. of Tech.), K. Masu (Tokyo Inst. of Tech.), K. Tsutsui (Tokyo Inst. of Tech.), and Y. Horiike (The Univ. of Tokyo) for their useful discussion and support for this research.

References