Electrical Characteristics of Gd_2O_3 thin film deposited on Si substrate.

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Abstract

Gadolinium oxide (Gd_2O_3) for high- k gate dielectric films were deposited on n-Si(100) substrates by e-beam evaporation to investigate their electrical characteristics. The electrical characteristics of Gd_2O_3 films were evaluated by fabricating Metal-Oxide-Semiconductor (MOS) capacitors. Gd_2O_3 thin films were confirmed amorphous after post deposition anneal in oxygen ambient at 400°C for 5min by XRD measurement. Formation of chemical oxide on Si substrate before the deposition of the Gd_2O_3 films improved the electrical characteristics and surface roughness.

1. Introduction

The International Technology Roadmap for Semiconductors (ITRS) describes about the necessity of the replacement of the SiO_2 gate dielectric films by high- k materials. HfO_2 [1] or ZrO_2 [2] have been widely studied for next generation gate dielectric materials, because they have high dielectric constant (10-20) and wide band gap. Rare earth oxide have also high dielectric constant and have been studied as promising candidates. Recently, excellent results of rare earth oxide, such as La_2O_3 [3], Gd_2O_3 [4,5] and Pr_2O_3 [6] have been reported. However, these materials – i.e. including HfO_2 , ZrO_2 , and rare earth oxides -- have some problems, such as interfacial layer growth during the thermal process of the CMOS fabrication [2].

In this paper, we report the properties of amorphous Gd_2O_3 films deposited on n-Si(100) substrate. In order to suppress the interfacial layer growth, we investigated the effect of Si surface treatment before the deposition -- formation chemical oxide and oxynitride film on Si surface.

2. Experiments

Figure 1 shows the fabrication process for MIS capacitors. Amorphous Gd_2O_3 films were deposited on HF last, chemically oxidized or oxynitrided n-Si(100) substrate by e-beam evaporation. After deposition,

Gd_2O_3 films were annealed by rapid thermal annealing (RTA) and aluminium electrodes were formed by evaporation.

The substrate resistivities were 13-15 and 0.8-1.2 Ωcm . Chemical oxide was formed by H_2O_2 dip for 30min at room temperature (R.T.), and oxynitride was formed by RTA in NH_3 ambient at 1050°C for 10 sec. The Gd_2O_3 film deposition temperatures were R.T. and 250°C and its annealing condition was O_2 ambient at 400°C for 5min. The pressure in MBE chamber during deposition were $\sim 10^{-8}$ Torr.

C-V, J-V characteristics, atomic force microscopy (AFM) and X-Ray Diffraction (XRD) measurements were carried out to characterize the films.

Figure 1. Fabrication process

3. Results and Discussions

Figure 2 shows XRD pattern for thick Gd_2O_3 films (Physical thicknesses were 52 nm and 25 nm) were deposited at R.T. XRD pattern of as-deposited films were amorphous for both 52 nm and 25 nm cases. After the annealing, 52nm film exhibits a peak near $2\theta=28.6^\circ$. The peak corresponds to the crystal of cubic(222) Gd_2O_3 . However, this peak was not observed for the 25 nm film. Thus, we estimated that the Gd_2O_3 films with thickness less than 25 nm stays in the amorphous state after the 400°C in O_2 anneal.

Figure 2. XRD pattern for Gd_2O_3 films

Effect of chemical oxide

To improve the electrical characteristics, we investigated the effect of using chemically oxidized Si substrate.

Figure 3. shows C-V characteristics for HF-last and chemically oxidized Si substrate. The films were deposited at 250°C and their physical thickness were 5.3 nm. After the annealing, the films thicknesses of the HF-last and chemical oxide samples were 2.02 nm and 2.05 nm, respectively. This indicates that the annealing in O_2 oxidized the $\text{Gd}_2\text{O}_3/\text{Si}$ interface and formed the interfacial layer. Considering that the EOT values of the HF-last and chemical oxide samples after the anneal were almost same, the thickness of the interfacial layer the HF-last sample would be almost the same as that of the chemically oxidized samples. Figure 4. shows J-V characteristics for these samples. Although the EOT values were almost the same, the leakage current of the chemical oxide sample shows three orders of magnitude smaller than that of the HF-last samples. It seems that the interfacial layer of the chemical oxide sample has better quality.

Figure 3. C-V characteristics for $\text{Al}/\text{Gd}_2\text{O}_3/\text{Si}$ and $\text{Al}/\text{Gd}_2\text{O}_3/\text{SiO}_2/\text{Si}$ (T_{phy} : 5.3 nm)

Figure 4. J-V characteristic for $\text{Al}/\text{Gd}_2\text{O}_3/\text{Si}$ and $\text{Al}/\text{Gd}_2\text{O}_3/\text{SiO}_2/\text{Si}$ (T_{phy} : 5.3 nm)

Figure 5. shows surface morphologies measured by AFM for these samples before and after annealing. In the case of as-deposition, both HF-last and chemical oxide showed flat surface. However, after the annealing, root mean square (RMS) values of surface roughness of the HF-last samples significantly increased from 0.187 nm to 0.942 nm. On the other hand, chemical oxide sample kept flat surface and small RMS value.

Figure 5. AFM images (500x500 nm, z:5 nm/dev)

- (a) HF last, As depo.
- (b) HF last, after annealing
- (c) Chemical oxide, As depo.
- (d) Chemical oxide, after annealing

Figure 6. shows the relation between the EOT and leakage current density for the samples with various experimental conditions. In the case when the physical thickness of the deposited Gd_2O_3 films are thicker than 3.5 nm the leakage current density of the chemical oxide samples were three orders of magnitude smaller than that of the HF-last samples. However, in the case when the physical thickness of the deposited film is 2.8 nm, the leakage current of the HF-last sample improved significantly and reached the level of the chemical oxide sample. We assume that high quality chemical oxide like interfacial layer is formed during the O_2 anneal, when the deposited Gd_2O_3 films are thin.

In addition, we studied the case of nitrogen annealing. However, we have not obtained good results as shown in the figure. It seems that annealing in N_2 , is not sufficient to form a high quality interfacial layer.

Figure 6. Plots of leakage current and EOT

Effect of oxynitride

We have also studied the effect of oxynitrided thin film on the Gd_2O_3 film properties. Figures 7, 8 and 9 show C-V characteristics for chemically oxidized and oxynitrided Si substrate, respectively. The C-V curves of the oxynitrided samples show significant distortion due to interface states as well as hysteresis. It is difficult to obtain high quality oxynitride interfacial layer.

Figure 10. shows the plots of negative flat band shift and interface state density for HF-last, chemical oxide and oxnitride samples. Negative flat band shift and interface state density of the oxnitride samples were significantly larger than those of HF-last and chemical oxide samples. This indicates the bad interfacial quality of the oxnitrided samples.

Figure 7. C-V characteristics for $\text{Al}/\text{Gd}_2\text{O}_3/\text{Si}$ (T_{phy} : 3.5 nm, EOT: 1.86 nm)

Figure 8. C-V characteristics for $\text{Al}/\text{Gd}_2\text{O}_3/\text{SiO}_2/\text{Si}$ (T_{phy} : 3.5 nm, EOT: 1.89 nm)

Figure 9. C-V characteristics for $\text{Al}/\text{Gd}_2\text{O}_3/\text{SiON}/\text{Si}$ (T_{phy} : 2.8 nm, EOT: 1.85 nm)

Figure 10. Negative flat band shift and interface state density

Figure 11. shows J-V characteristics of the HF-last, chemical oxide and oxynitrided samples. Leakage current of the HF-last, chemical oxide and oxynitride samples were 1.0×10^{-2} A/cm², 1.7×10^{-4} A/cm² and 6.0×10^{-6} A/cm², respectively. Although, the quality of the oxynitrided layer is not good, the layer helps to suppress the leakage current. The chemical oxide shows better suppression of the leakage current than that of the oxynitride. Fig. 12. shows P-F (Poole-Frenkel) plot of these samples. The effective barrier height obtained from the plot were 0.72 eV, 0.89 eV and 0.81 eV, respectively.

Figure 11. J-V characteristic for Al/Gd₂O₃/Si, Al/Gd₂O₃/SiO₂/Si and Al/Gd₂O₃/SiON/Si

Figure 12. Pool-Frenkel plots

4. Conclusions

We reported electrical characteristics of MIS capacitor using amorphous Gd₂O₃ film on n-Si(100). It was confirmed that the film stays in the amorphous state after the 400°C 5min O₂ anneal when its thickness is less than 25 nm. The effect of the chemical oxide and oxynitride thin films on Si substrate before the deposition was investigated. The chemical oxide suppress the Gd₂O₃ film roughness and reduced the leakage current three orders magnitude. As the result we obtained excellent characteristics of Gd₂O₃ MIS capacitor (EOT: 1.89 nm, Leakage current: 6.0×10^{-6} A/cm²). The oxynitride suppressed the leakage current by 1.5 orders of magnitude. However, interface state density and flat band voltage shift were significantly large because of bad interfacial quality of the oxynitride film.

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