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A Noble SiON/AlO Structure at High-κ/poly-Si Interface for Storage Capacitors of High Density DRAMs

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1. Introduction

The decreasing scales of DRAM memory cells are placing increasingly strict demands on the capacitor dielectric. Although high-κ materials are used to compensate for the decrease in physical thickness, an interfacial layer is also needed for the following reasons ; The interfacial layer functions as an oxygen barrier, prevents reactions between the Si and the high-κ material, and provides a high energy barrier relative to Si. The interfacial layer should be made as thin as possible, since this lets us suppress leakage current by increasing the high-κ layer's thickness. So far, SiN has been used as this interface. However, it is too permeable to oxygen and has too low an energy barrier for further decreases of interface thickness of this material. We thus propose introduction of AlO, which provides a better barrier against oxygen and higher energy barrier. We found that a SiN/AlO structure is an appropriate interfacial material in terms of suppressing interfacial oxide. We found key parameters that lead to reduced leakage current by finding those that lead to high SiON permittivity and good insulating qualities.

2. Results and Discussion

2.1 *SiN/AlO interface for MIS capacitors*

To reduce thickness of the insulator, controlling the production of interface oxide by annealing is important. Since AlO blocks the diffusion of oxidizing species, it should be suitable for use as an interface with the high-κ materials. On the other hand, depositing AlO by ALD (atomic layer deposition) on hydrogen-terminated silicon is difficult due to non-linear growth components. It is possible to control the initial stage by forming thin SiO_2 layer on Si, but this leads to an increase in the insulator's thickness. We thus suggest the SiN/AlO/high-κ structure shown in Figure 1. This interface structure shows higher energy barrier and higher permittivity than that of SiN.

2.2 *Restriction of interfacial oxide growth and enhanced barrier height*

The increase in the thickness of interfacial oxide with annealing of the high-κ material in a thermal SiN/ALD-AlO is shown in Figure 2. No thickness increase was found even with annealing at 860˚C, although the thickness increases with annealing at only 800ºC in the cases of the SiN-only or AlO-only layers annealed for reference. Si *2p* absorption spectra measured by XPS (X-ray photoelectron spectroscopy) are shown in Figure 3. As SiN is annealed at increasing temperatures, the Si^{4+} peak is shifted towards higher energy. This shows that much oxygen was being introduced into the SiN. However, the introduction of oxygen into SiN/AlO was controlled. Thus, since the SiN/AlO structure effectively restricts growth of the interfacial oxide, this structure makes a thinner insulator possible.

Next, we discuss control of the leakage current. Firstly, the insulating ability of AlO was evaluated. In Figure 4, the energy-barrier height of AlO deposited by ALD is evaluated by using the F-N (Fowler - Nordheim) plot. The energy-barrier height of AlO was 2.8 eV. This value is greater than those for SiN, HfO and TaO, and is almost the same as that of SiO_2 [1,2]. In Figure 5, the band-gap was evaluated as 6.6 eV by subtracting the O *1s* peak energy from the loss peak energy [3]. We found that AlO deposited by ALD provides a good enough insulator.

2.3 *Key parameters for optimization of interface layers*

Figure 6 shows the dependence of the voltage at 10^{-4}A/cm^2 on the conditions of CVD-TiN. The deposition rate and order of gas flow were varied. The leakage current was suppressed by introducing the $TiCl_4$ after the NH_3. The $TiCl_4$ contains reactive Cl so that introducing it after the NH_3 probably also reduces damage to the surface. The leakage current also decreases with the deposition rate. This is probably because decreasing the deposition rate lowered the intensity of the chemical reaction, which in turn suppressed damage to the surface and thus improved the interface. Since the leakage current was decreased as the conditions of TiN deposition were improved, even in the case of AlO, which is a stabler material, this technique will be applicable to the deposition of TiN on high-κ materials in general.

The improvement in the case of AlO is now discussed. Leakage-current variation in relation to the proportion of aluminum in AlO is shown in Figure 7. The compositional ratio of AlO deposited by $Al(CH_3)_3$ and H_2O as source gases was very far from stoichiometric.

Annealing was found to bring it close to stoichiometric, and this greatly improved the effective field for a given leakage current.

The relation between permittivity and effective field at 10^{-6}A/cm^2 as measured for SiN/AlO capacitors is shown in Figure 8. The weak field for as-nitrided SiN is attributed to defects in the SiN. We tried improving the effective field by annealing to place oxygen in the defects.

Weak oxidation improved the effective field by 25%; that is, the thickness of the interfacial layer can be decreased by 25%. On the other hand, strong oxidation leads to too much interfacial oxide. It is found that the optimal permittivity of SiON exists in the range from 5.5 to 6.0. A TEM image of the sample with permittivity of 6.0 is given in Figure 9, to confirm the effect of annealing on interface morphology and crystallization. The morphology of the interface was pretty good and crystallization had not occurred; the film was thus effective in terms of controlling leakage current.

3. Conclusion

In this report, the application of SiN/AlO as an interface with the high-κ layers of DRAM capacitors had been discussed.

SiN/AlO structure was proved to be stable during oxidation up to 860˚C. This enables deposition of various high-κ materials on the interface structure. We also investigated improvements of leakage current of the SiN/AlO. In addition to the annealing of AlO and moderate deposition of TiN, it was found to be particularly important to reduce the defects in SiN. We applied noble weak oxidation of SiN before the deposition of AlO. As a result, we increased the effective field by 25% while decreasing the thickness of the interface layers by the same amount, so that leakage current can be suppressed by increasing the high-κ layer's thickness.

References

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[2] J. Robertson, *J. Vac. Sci. Technol.*, **B 18** (3)(2000)1785.
[3] H. Itokawa, T. Maruyama, S. Miyazaki, et. al., *SSDM* (1999)158.

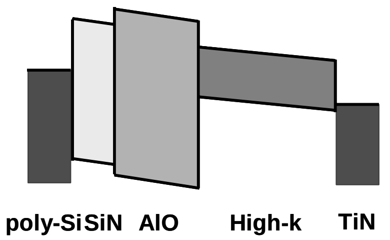

Fig. 1 Band structure of suggested capacitor dielectric.

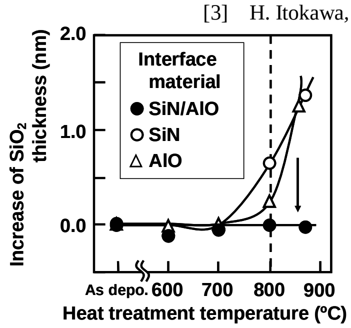

Fig. 2 Increase in interfacial oxide thickness with heat treatment.

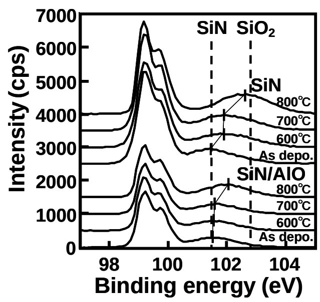

Fig. 3 Si *2p* spectra of annealed samples.

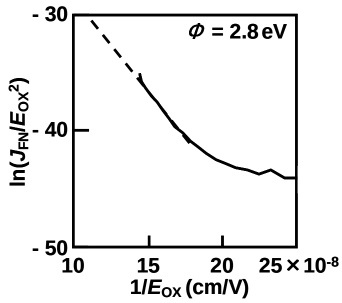

Fig. 4 Barrier-height evaluation by Fowler-Nordheim plot.

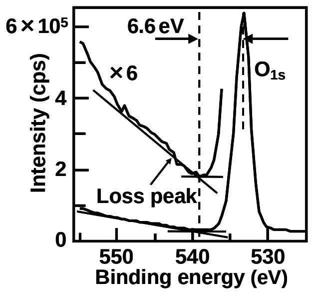

Fig. 5 Band-gap evaluation by O *1s* peak.

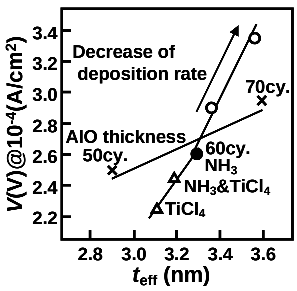

Fig. 6 Increase in voltage for a given leakage current with improved conditions of TiN deposition; the first application of chemicals is indicated.

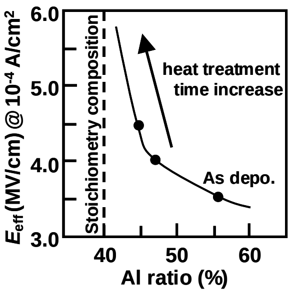

Fig. 7 Increase in field for a given leakage current with increasing period of AlO heat treatment.

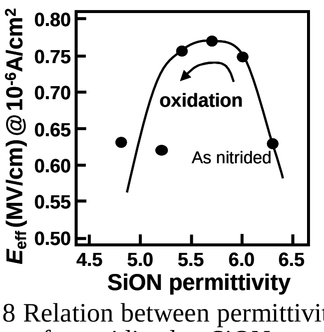

Fig. 8 Relation between permittivity of oxidized SiON and effective field strength of SiON/AlO capacitors.

Fig. 9 Cross-sectional TEM image of a weakly oxidized SiN and AlO capacitor.