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Properties of LaAlO Film after Waterless Process using Organic Solvent containing Anhydrous HF

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Introduction

To achieve high performance and low stand-by power applications, the integration of a high-k dielectric film is necessary for LSI devices 22nm technology node and beyond. Recently, Lanthanum based oxide films such as La_2O_3 and LaAlO have been studied as a high-k gate dielectric. Minimum equivalent oxide thickness (EOT) value of 0.5 nm has been achieved by means of direct oxidation of La deposited on Si . Especially, LaAlO, as a compound of La_2O_3 and Al_2O_3, has some advantages such as a high dielectric constant of 25-27, high band gap of 7 eV and amorphous structure up to a high temperature of 850 °C[1]. However, the moisture absorption is a serious problem for oxide films containing La. [2] A water based solution such as diluted HF (DHF) is used to remove residual high-k film and post-dry etching residues in FEOL process. Therefore, the removal and post water rinse process caused the damage in the side of the LaAlO gate dielectric, as shown in Fig 1.

In this study, we have attempted to use waterless solutions in the removal wet process for suppress the damage of the LaAlO film. We report the effect of the anhydrous HF (AHF) and Isopropyl Alcohol (IPA) mixture as etching solution, and hydrofluoro ethers (HFE) as rising solution.

Experimental procedure

The process flow of this experiment is shown in Fig.2. LaAlO film was deposited on p-Si (100) by physical vapor deposition and annealed at 500℃. The composition ratios of the LaAlO film was La 18%, Al 22% and O 60%. To investigate waterless wet process, AHF and IPA mixture (AHF+IPA) and HFE were prepared as etching and rinse solution, respectively. AHF30%+IPA was produced by dissolving the vapor AHF in IPA solvent as shown in fig.3. AHF concentration in the mixture was adjusted by adding IPA. We also prepared DHF5% and H_2O for comparison as water base solutions. The etching rates of LaAlO and SiO_2 were investigated for AHF5%+IPA and DHF5% at room temperature by ellipsometry. To examine the electric characteristics of LaAlO films after the wet process, current-voltage (I-V) characteristics were measured by using metal- insulator-semiconductor (MIS) structure. The atomic bonds and the surface morphology of the LaAlO film after H_2O and HFE rinsing were also investigated by XPS and AFM respectively. As the HFE solution has high removal effects for residual halogen and low surface tension, this solution is useful for not only an effective rinsing but also suppression sticking for fine gate pattern.

Results and discussion

LaAlO etching rates and selectivity for LaAlO relative to SiO_2 (LaAlO/SiO_2) with DHF5% and AHF5%+IPA is shown in Table.1. LaAlO etching rate with AHF5%+IPA is smaller than that of DHF5%, however the selectivity with AHF5%+IPA can be improved to 0.35 from 0.062 with DHF5%. Therefore, this solution is useful to suppress etching of the SiO_2 under layer for Sallow Trench Isolation (STI).

Figure 4 shows I-V characteristics of LaAlO films before wet process and after H_2O rinsing and HFE rinsing. The leakage current increases after H_2O rinsing. On the other hand, the leakage currents with HFE rinsing was unchanged. This indicates that the HFE can suppress the degradation of LaAlO films by the moisture absorption.

Figure 5 shows that XPS spectra (O 1s) of LaAlO films with (a) H_2O dipping and (b) HFE dipping, respectively. Hydroxy peak is observed for the samples dipped in H_2O, in contrast, it didn't appeared from samples with HFE dipping.

Figure 6 shows AFM image of surface of LaAlO film with H_2O dipping and HFE dipping. The surface roughness of LaAlO with H_2O dipping is larger than that with HFE dipping.

This result indicates that the smooth surface can be kept due to suppress La bonds with hydroxy by waterless rinsing using HEF.

Figure 7 shows I-V characteristics of LaAlO films with (A) DHF5% etching and H_2O rinsing processes and with (B) AHF5%+IPA etching and HFE rinsing processes. The leakage current drastically increases for rhe sample etched with DHF and rinsed with H_2O. In contrast, it increases slightly etched with AHF+IPA and rinsed with HFE.

Conclusion

We have succeeded in drastically suppressing degradation of LaAlO film by using AHF+IPA etching and HFE rinsing in the wet etching process to remove residual LaAlO film.

References

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2) Jin Hyung Jun, Doo Jin Choi, Thin Solid Films 504 (2006) 205-208

Acknowledgements

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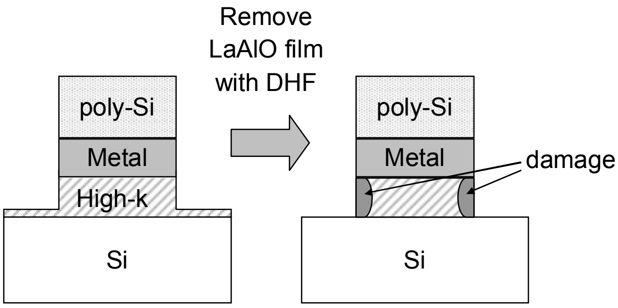

Fig.1 Process flow of removing High-k gate dielectric film.

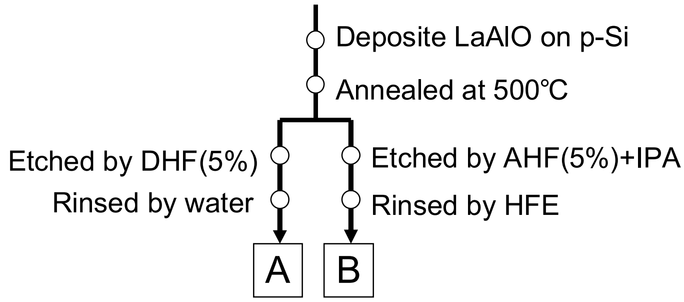

Fig.2 Process flow of this experiment.

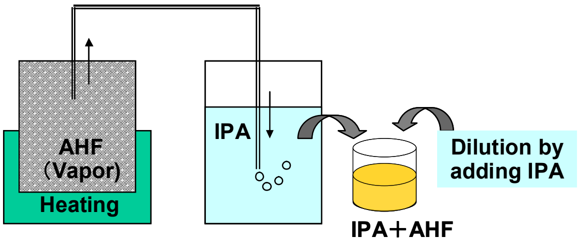

Fig.3 Manufacture method of IPA containing Anhydrous HF.

Table.1 Etching rate of LaAlO and Selectivity (LaAlO/SiO_2) with DHF(5wt%) and AHF(5wt%)+IPA.

Solution	Etching rate (LaAlO) [nm/min]	Selectivity (LaAlO/SiO_2)
DHF(5%)	1.45	0.062
AHF(5%)+IPA(95%)	0.80	0.35

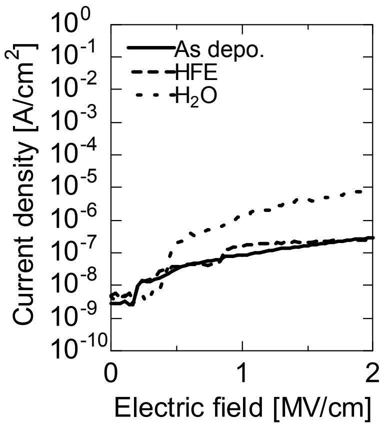

Fig.4 I-V characteristics of LaAlO films without wet prpcess, with H_2O dipping, with HFE dipping.

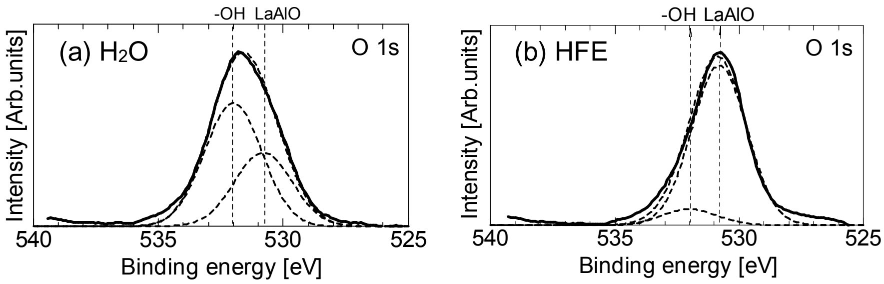

Fig.5 XPS spectra (O1s) of LaAlO films with (a) H_2O dipping and (b) HFE dipping for 3 hours, respectively.

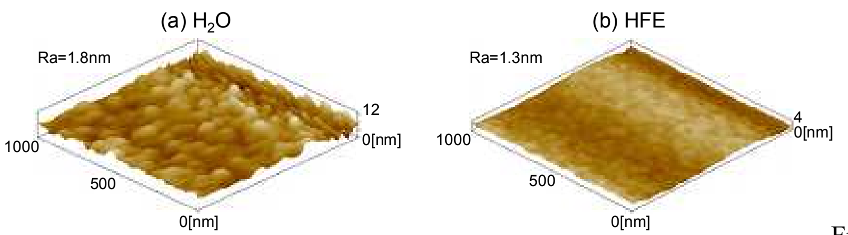

Fig.6 AFM of LaAlO film with (a)H_2O dipping and (b) HFE dipping, respectively.

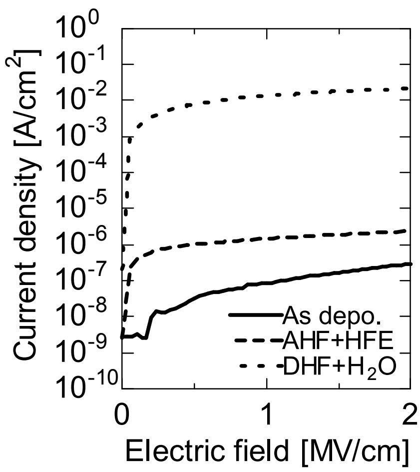

Fig.7 I-V characteristics of LaAlO films without wet process, with DHF dipping and H_2O rinse, with AHF+IPA dipping and HFE rinse.