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The Selective Growth of LPCVD-Si_3N_4 on Cleaned Si Surface

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Ultra thin(less than 5nm) Si_3N_4 film is one of the key materials for 64Mb DRAM capacitor. It is formed by thermal reaction of NH_3 and SiH_2Cl_2 on Si surface. Control of Si surface is essential for the formation of ultra thin LPCVD-Si_3N_4. In this study, we make it clear that initial Si_3N_4 growth depends on the treatment of substrate surface, and newly demonstrate the ability of selective deposition of LPCVD-Si_3N_4.

1. Introduction

Si_3N_4 film is widely used as the storage capacitor dielectric for dynamic random access memory (DRAM). It is considered that Si_3N_4 film thickness less than 5nm is required for 64 Mbit DRAM. As currently studied, the Si_3N_4 film thickness can not be reduced less than 5 nm because of the degradation of oxidation resistance and leak current increasing.[1],[2] This means that thin Si_3N_4 film is made up of initial reaction layer which is different film quality from bulk Si_3N_4. Therefore, it is important to clear the initial reaction of NH_3 and SiH_2Cl_2 on Si or SiO_2 surface, to use such a thin Si_3N_4 film.

Recently, in order to change the initial reaction , rapid thermal nitridation (RTN) process has been proposed as a pretreatment before Si_3N_4 deposition. It can avoid the native oxide growth on Si surface. [3],[4],[5]

In this paper, in-situ HF vapor cleaning system has been used to avoid the native oxide growth completly. The effects of surface treatment of Si or SiO_2 on the initial Si_3N_4 film growth was confirmed, and the selective growth of low pressure chemical vapor deposition (LPCVD) Si_3N_4 film was demonstrated.

2. Experimental

Si substrates with line and space patterned thermal SiO_2 were prepared. Si_3N_4 film was deposited on them by two types of LPCVD reactor, the conventional reactor and the load lock reactor. In the case of using the conventional reactor, the Si surface is exposed to air and is oxidized during loading. On the other hand, in case of using the load lock reactor which has in-situ HF vapor cleaning system in the same apparatus, the sample surface can be free from uncontrolled oxidation. NH_3 and SiH_2Cl_2 were used as the reaction gases. The deposition was performed at 650°C or 750°C.

The thickness and roughness of Si_3N_4 film grown on various surfaces were estimated by ellipsometer and transmission electron microscopy (TEM). The Si-N bond formation was measured by fourier transform infrared spectroscopy (FTIR).

3. Results & Discussion

Fig.1 shows the dependence of thickness on deposition time at 650°C as a parameter of LPCVD reactor type. It is found that incubation time of Si_3N_4 film growth has not been observed in the load lock reactor, but observed in the conventional reactor.

The oxidation resistance ability of Si_3N_4 film is shown in Fig.2. Oxidation was carried out in wet O_2 at 850°C for 30 min. The thickness, where the deposition time is zero, means the thickness of oxidized bare Si,and Si_3N_4 films thinner than critical thickness were oxidized as thick as bare Si. They have no oxidation resistance ability. The critical thickness depends on the reactor type as the same as the incubation time variation. These differences between reactor types are caused by the surface condition, whether native oxide exists or not.

Si_3N_4 films were deposited at 650°C for 20 min on substrate with Si and SiO_2 patterned. Fig.3(a) shows the TEM cross sectional views of Si3N4 deposited in load lock LPCVD reactor with in-situ HF vapor cleaning. Fig.3(b) shows the TEM cross sectional views of Si_3N_4 deposited in conventional LPCVD reactor.

The selective growth of Si_3N_4 film occurs, as shown in Fig.3(a). 5 nm thick and smooth Si_3N_4 film was grown on Si surface, because the surface with oxide free can be obtained, when wafers are in-situ cleaned with HF vapor. On the other hand, it was not seen in Fig.3(a), in the case of using a conventional reactor. We consider that the air exposure changes the surface conditions of both Si and SiO_2.

Fig.4(a) shows the same phenomena with deposition at 750°C for 8 min. This selective growth is not affected by deposition temperature. For 24 minutes Deposition, Si_3N_4 film grown thickness was about 18 nm on Si, the selectivity of Si_3N_4 growth is collapsed during deposition.(Fig.4(b)) On in-situ cleaned SiO_2, Si_3N_4 is deposited as thick as 10nm.

The film grown on cleaned SiO_2 is very rough though the film on cleaned Si is very smooth, which suggests that the mechanism of initial Si_3N_4 growth is quite different between on in-situ cleaned Si and SiO_2.

It is thought that on clean Si, the surface reaction is dominant and this leads the layer-like Si_3N_4 growth, on clean SiO_2, the vapor phase reaction is dominant and this leads the nuclei-like Si_3N_4 growth. We suppose that the nucleation step causes the surface roughness and the incubation time of Si_3N_4 growth on an oxidized surface.

Next, focused on the formation of Si-N bond, the Si_3N_4 film growth was estimated. Fig.5(a),(b) shows the infrared absorption peaks of Si-N bond formed on the above-mentioned samples, respectively.

The FTIR peak heights correspond to the thickness measured by TEM, also indicating the selectivity of Si_3N_4 growth, as shown in Fig.4(a). Although the Si-N bond main peak of LPCVD Si_3N_4 is normally appearing at wave numbers $840cm^{-1}$. The main peak of Si_3N_4, grown on SiO_2 , shifts to $810cm^{-1}$(Fig.5(a)). It is reported that when the composition of Plasma Si_3N_4 becomes Si-rich, the Si-N main peak shifts to lower site of wave numbers.[6] Fig.5(a),(b) suggest that the thin Si_3N_4 formed on SiO_2 is Si-rich, as compared with bulk Si_3N_4, and it is stoichiometric composition formed on native oxide free Si surface.

4. Conclusion

From above studies, the follows are concluded;

1) LPCVD Si_3N_4 film grows initially on clean Si surface selectively, it does not on clean SiO_2 surface.

2) On SiO_2, a Si rich transition layer is formed, and then a stoichiometric Si_3N_4 layer grows.

In conclusion, this study has clarified that the initial Si_3N_4 growth depends greatly on the surface treatment. These results are consistent with theoretical predictions.[7] For achieving the ultra thin Si_3N_4 film in 64 Mbit DRAM, the surface treatment to avoid the native oxide is a key factor in process technology.

5. References

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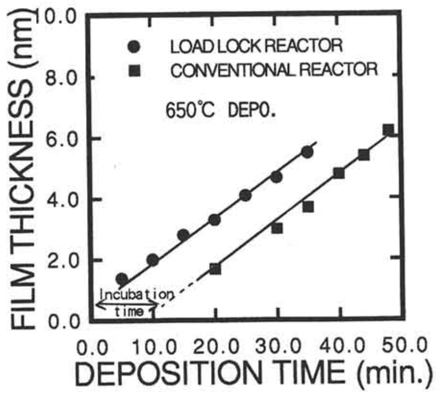

Fig.1 The dependence of the thickness on deposition time as a parameter of reactor type.

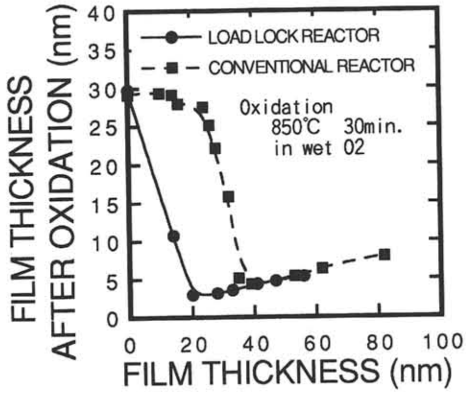

Fig.2 The oxidation resistance ability of Si_3N_4 film as a parameter of reactor type.

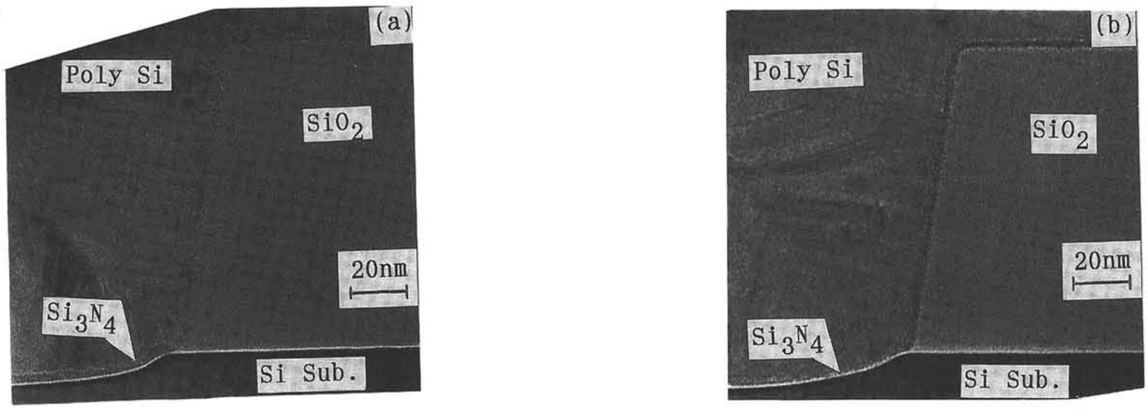

Fig.3 TEM cross-sectional photographs of Si_3N_4 growth on Si and SiO_2 surfaces by load lock reactor(a) and conventional reactor(b).

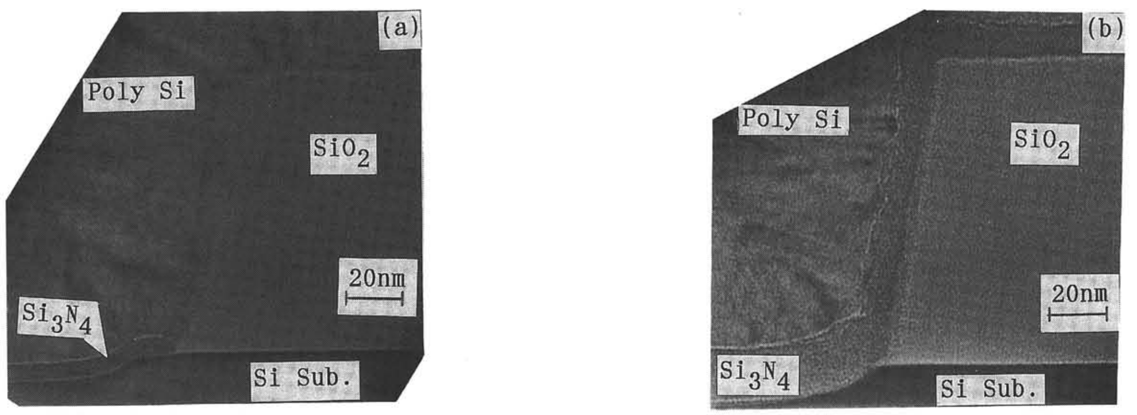

Fig.4 TEM cross-sectional photographs of Si_3N_4 growth on Si and SiO_2 surfaces by load lock reactor at 750°C for 8 min. deposition(a) and for 24 min. deposition(b).

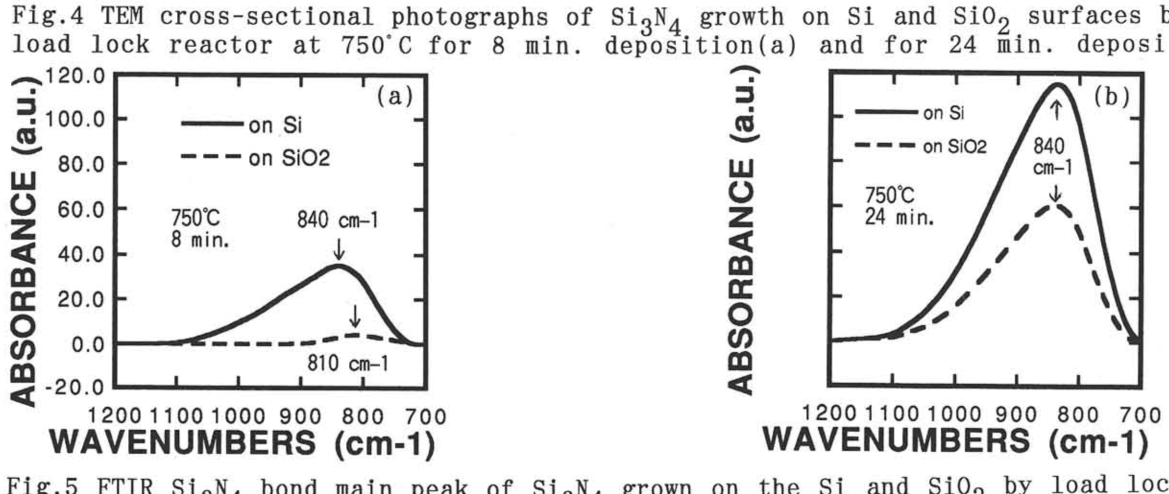

Fig.5 FTIR Si_3N_4 bond main peak of Si_3N_4 grown on the Si and SiO_2 by load lock LPCVD at 750°C for 8 min. deposition(a) and for 24 min. deposition(b).