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The Initial Growth Mechanism of LPCVD-Si_3N_4 on Si and SiO_2

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Ultra thin (less than 5nm) Si_3N_4 film is one of the key material for 256Mb DRAM capacitor. In order to use ultra thin film, it is significant to control the initial growth of the film. In this study, we make clear the initial growth mechanism of LPCVD-Si_3N_4 on SiO_2 and Si. On SiO_2, Si_3N_4 nuclei are generated and then Si_3N_4 film grows. On Si, on the other hand, Si_3N_4 film grows without nuclei generation. The nuclei generation rate is limited by gas pressure, and the film growth rate is limited by surface reaction rate.

1.Introduction

The composite SiO_2/Si_3N_4 film, formed by oxidation of low pressure chemical vapor deposition(LPCVD) Si_3N_4 film, has been widely used as the storage capacitor dielectric for dynamic random access memory (DRAM). With increase in the integration of DRAM, it becomes impossible to obtain sufficient storage capacitance using conventional capacitor cell and Si_3N_4 film. To overcome this problem, advanced cell structure which increase effective surface area of storage electrode has been studied[1].

And as for Si_3N_4 deposition process, rapid thermal nitridation and loadlock LPCVD deposition process have been proposed[2][3][4][5].

To use ultra thin film, it is essential to control the initial growth of the film. The great dependence of the initial Si_3N_4 film growth on substrate surface was demonstrated [6]; LPCVD-Si_3N_4 film grows initially on Si surface selectively, it does not on SiO_2 surface.

In this paper, the initial growth mechanism of LPCVD-Si_3N_4 is proposed, which can explain the effect of gas pressure and substrate material on initial Si_3N_4 growth. And atomic force microscopy(AFM) image of initial Si_3N_4 growth on SiO_2 are shown, which also certifies the growth mechanism.

2.Experimental result

Table.1 shows the condition of LPCVD-Si_3N_4 growth which was studied in this paper. Usually the growth of Si_3N_4 film has incubation time before linear film growth[1]. We deposited Si_3N_4 film on SiO_2 in various pressure, and measured Si_3N_4 film thickness by ellipsometer. As shown in Fig.1, we found that 1)incubation time depends on the total gas pressure, 2)linear growth rate is independent of the gas pressure.

In order to consider the above phenomena, we prepared two type substrate; Si substrate which has SiO_2 line pattern(SiO_2/Si substrate), and SiO_2 substrate which has poly-Si line pattern(Si/SiO_2 substrate). The sharp edge of substrate pattern is more exposed than the flat surface of substrate pattern to the reactive gas. So when the gas pressure limits the Si_3N_4 growth rate, the Si_3N_4 film is expected to grow thicker on the sharp edge of substrate pattern.

We deposited Si_3N_4 film on them in the pressure of 0.10Torr, for 8 minutes and for 24 minutes. The Si_3N_4 initial growth on Si and SiO_2, and on flat surface and sharp edge, was observed by transmission electron microscopy(TEM).

Fig.2(a) shows the TEM cross sectional view of Si_3N_4 film grown on SiO_2/Si substrate for 8 minutes. The selective LPCVD-Si_3N_4 growth is observed. Although 7nm thick Si_3N_4 film grows on Si, Si_3N_4 film does not grow on SiO_2.

Fig.2(b) shows Si_3N_4 film grown for 24 minutes. The selectivity is collapsed. Si_3N_4 grows as thick as 19nm on Si and 12nm on SiO_2.

These results are already reported[6]. The results, which we want to discuss in this work, are the followings.

The roughness of Si_3N_4 film surface is quite different between on Si and SiO_2 flat surface. Si_3N_4 film on Si flat surface has smooth surface. On the other hand, Si_3N_4 film on SiO_2 flat surface has rough surface.

And Fig.3 shows Si_3N_4 film grown on Si/SiO_2 substrate for 8 minutes. (The selective growth on Si is also observed.) Comparing with Fig.2(b), it is recognized that Si_3N_4 growth is quite different between on Si sharp edge and SiO_2 sharp edge. Si_3N_4 film grows thicker on SiO_2 sharp edge than on SiO_2 flat surface. On the contrary, Si_3N_4 film grows thinner on Si sharp edge than on Si flat surface.

3.Discussion

From the TEM observation of Si_3N_4 growth on substrate pattern, we propose the following model as shown in Fig.4. In the stage of Si_3N_4 initial growth on SiO_2, Si_3N_4 nuclei are generated, and then Si_3N_4 nuclei grow film. The nuclei generation step corresponds to the incubation time. Besides the generation rate of Si_3N_4 nuclei is supposed to be limited by gas pressure.

So Si_3N_4 film on SiO_2 has rough surface, and Si_3N_4 grows thicker on SiO_2 sharp edge. And the incubation time becomes longer when the gas pressure becomes lower.

On Si, on the other hand, Si_3N_4 film grows directly on Si surface from the first layer without nuclei generation. Besides the linear growth rate of Si_3N_4 film thickness is supposed to be not limited by gas pressure, but by the surface reaction rate on Si or Si_3N_4 surface.

So Si_3N_4 film on Si has smooth surface, and grows thinner on sharp edge. And the incubation time becomes zero, which leads the selective growth of Si_3N_4 on Si [6].

This model can also explain the study about oxigen resistance ability of ultra thin Si_3N_4 film[1][6]; H_2O or O_2 cannot penetrate bulk Si_3N_4. But Si_3N_4 film on SiO_2 has no oxigen resistance before a critical Si_3N_4 deposition time. Si_3N_4 film on Si has oxigen resistance from the film thickness is less than 1nm. Ultra thin Si_3N_4 film grown on SiO_2 is cosidered to have pin holes, through which oxigen can pass.

This model is confirmed by atomic force microscopy(AFM) observation, in addition. Fig.5 shows AFM image of Si_3N_4 grown on SiO_2 for 8 minute. Although Si_3N_4 film was not observed by TEM, something like nuclei was observed on SiO_2 surface. The left image is the magnification of the right image. By X-ray probe spectroscopy(XPS), nitrogen is detected on this SiO_2 surface, which suggests that the nuclei observed by AFM are Si_3N_4 growth nuclei.

4.Conclusion

From the above studies, the following are concluded;

1)On SiO_2, Si_3N_4 growth nuclei are initially generated, and then Si_3N_4 film are formed.

2)On Si, Si_3N_4 film grows from the first layer without nuclei generation.

3)The nuclei generation rate on SiO_2 is limited by gas pressure. And the film growth rate is limited by surface reaction rate.

In conclusion, this study has clarified the initial growth mechanism of Si_3N_4 film. These results are consistent with theoretical prediction[7]. To obtain ultra thin Si_3N_4 film which has less surface roughness and high oxigen resistance, LPCVD-Si_3N_4 should be deposited on Si surface after the complete removal of SiO_2.

5.References

[1]M.Yoshimaru, J.Miyano, N.Inoue, A.Sakamoto, S.Yoh, H.Tamura and M.Ino, IEDM Tech. Dig.(1990) 187.

[2]K.Ando, A.Ishitani and K.Hamano, Appl. Phys. Lett. 59 (1991) 1081

[3]N.Ajika, M.Ohi, H.Arima, T.Matsukawa and N.Tsubouchi, Symp. VLSI Tech. Dig.,(1991) 63.

[4]H.Kurogi, N.Inoue, M.Takahashi, H.Tamura, T.Ajioka, M.Yoshimaru and M.Ino, IEICE Tech. Report, SDM91-30 (1991) 43.

[5]M.Yoshimaru, N.Inoue, H.Kurogi, M.Itoh and M.Ino, IEDM Tech.Dig. (1992) 659.

[6]N.Inoue, M.Itoh, H.Tamura, N.Hirashita and M.Yoshimaru SSDM(1992) 205

[7]A.Ishitani and S.Koseki, SSDM.22(1990) 187.

750C

0.10Torr (/ 0.05Torr / 0.20Torr)

$NH_3 + SiH_2Cl_2$:
200sccm + 40sccm

on Si / on SiO_2

on flat surface / on edge

Table.1 The condition of LPCVD-Si_3N_4 film growth.

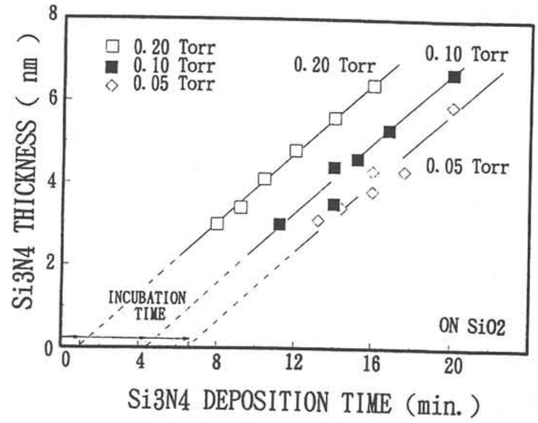

Fig.1 The dependence of the thickness on deposition time as a parameter of gas pressure.

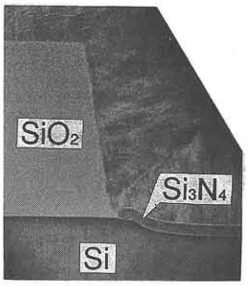

Fig.2(a) A TEM cross-sectional photograph of Si_3N_4 growth on SiO_2 /Si substrate (8 minutes).

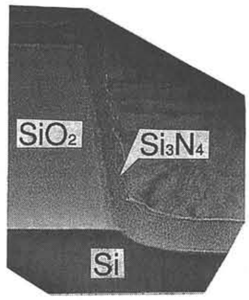

Fig.2(b) (24 minutes)

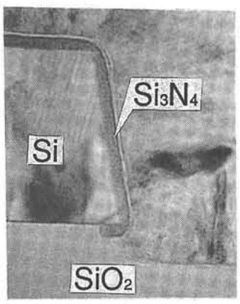

Fig.3 A TEM cross-sectional photograph of Si_3N_4 growth on Si/SiO_2 substrate (8 minutes).

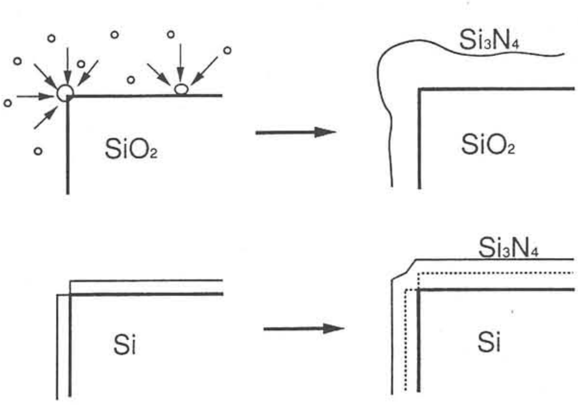

Fig.4 The initial growth mechanism of LPCVD-Si_3N_4 on Si or SiO_2.

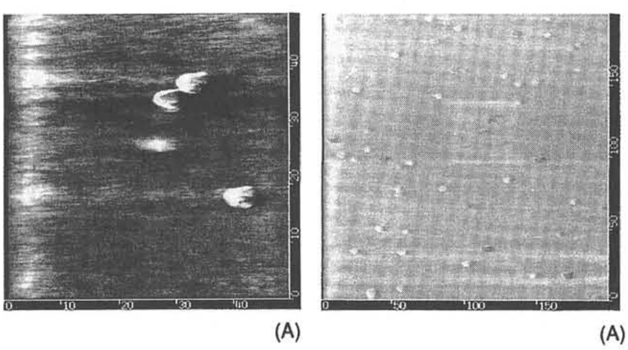

Fig.5 AFM images of LPCVD-Si_3N_4 growth on SiO_2 (8 minutes).