Low Temperature Chemical Vapor Deposition of Dielectric Films using Ozone and Organosilane

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The silicon dioxide film was chemically vapor deposited at low temperature below 450°C using ozone and silicon alkoxide as a source. The conventional pyrolytic decomposition of TEOS (Tetraethylorthosilicate) has required temperature above 650°C to form this film.

The doped oxide film such as PSG, BSG, or BPSG was also formed by adding alkoxide of phosphorus or boron as a dopant. This doped oxide film is very useful as the interlayer dielectric film for high density devices. The step coverage on the fine pattern can be enhanced because this CVD method enables isotropic deposition and self-planarization. This paper outlines the study of each parameter to control this CVD reaction, consideration of the reaction mechanisms and evaluation results of film properties.

1. Introduction

The silicon dioxide film and the doped oxide film have been widely used as the interlayer dielectric films for semiconductor devices. Today, these films are deposited in various methods as the insulators between Al layers and between Al and polysilicon or silicide layers. Among these methods, the low temperature CVD method using the SiH_4-O_2 system at deposition temperature below 450°C is the most popular.

On the other hand, the CVD oxide film deposition using pyrolysis of TEOS (Tetraethylorthosilicate) at temperature above 650° C has already been put into practical use. ¹)~⁴)

The authors have been studying deposition of the CVD SiO₂ film and CVD doped oxide film with pyrolysis or oxidation of organosilane and found that the CVD film could be deposited by using ozone as an oxidant within the temperature range almost same as that of the CVD reaction with the SiH₄-O₂ system. $5) \sim 6$) This paper describes experimental the result of the 100 temperature CVD of oxide films using ozone

and organosilane including the study of various conditions to control the reaction, doping characteristics, and the evaluation results of step coverage and other film properties.

2. Experimental Procedure

In this experiment, atmospheric pressure CVD system, which could process one 125 mm diameter silicon wafer, was used as a reactor. The substrate was placed on the hot plate heated by the resistance heating method and controlled at the temperature ranging from 300°C to 450°C. The chamber was kept at atmospheric pressure and the reactant gas was uniformly supplied onto the wafer surface from the porous gas dispersion plate facing the wafer. The space between the wafer and the gas dispersion plate was made variable from 4 to 6 mm.

The following three organic compounds, all of which are liquid at room temperature, were used as the materials:

Tetraethylorthosilicate (TEOS); Si(OC₂H₅)₄ Trimethylphosphate (TMOP); PO(OCH₃)₃

Trimethylborate (TMOB); B(OCH₃)₃

These materials were stored in the quartz vaporizer and kept at a certain temperature in the thermostatic oven. They were vaporized by bubbling dry nitrogen and introduced to the chamber. The vaporized source amount was calcuated by the saturated vapor pressure determined by the temperature of each liquid and the flow rate of the nitrogen carrier gas.

Ozone was generated by passing dry oxygen through the conventional discharge type ozonizer available in the market and the concentration of ozone in oxygen was monitored by the ozone meter.

Ozone was mixed with the reactant gas at the entrance of the gas dispersion plate. The concentrations of phosphorus and boron in the deposited films were obtained as mole% of P_2O_5 and B_2O_3 by the flourescent X-ray analysis and infra-red absorption spectra analysis.

In this experiment, the substrate temperature, the amount of supplied source, the concentration of ozone, and the mixing ratio of dopants were used as parameters to control the reaction.

3. Results and Discussion

Figure 1 shows the dependence of deposition rate for the CVD film using TEOS on the deposition temperature.⁵⁾

Figure 2 shows the dependence of the deposition rate on the temperature and dopant as the results of this experiment.

It shows that the peak deposition rate of the BSG film is shifted to the temperature higher than the peak values of the NSG and PSG films. It also shows that the PSG film has the gentle slope of deposition rate to indicate the activation energy of the reaction lower than that of the NSG or BSG film deposition. This means that doping of



Fig. 1. Dependence of Deposition Rate on Temperature

boron causes film deposition to be more surface catalytic while doping of phosphorus enhances the vapor phase reaction and causes deposition to be more diffusion limited. In addition, the increase of boron causes the peak deposition rate to be shifted to the higher temperature though the activation energy is unchanged.



Fig. 2. Dependence of Deposition Rate on Temperature and Dopant

Figure 3 shows the dependence of the deposition rates of PSG and BSG on the dopant concentration in the reactant gas. Doping of boron increases the deposition rate while doping of phosphorus activates the vapor phase reaction to limit the actual deposition rate of film. In addition, as shown in Figure 4, the concentration of phosphorus



Fig. 3. Dependence of Deposition Rate on Dopant Concentration in Reaction Gas

transferred from the gas phase to the solid phase is quite lower than that of boron. That is, boron is incorporated into the film with high efficiency.



Table 1 shows the comparison of step coverage between PSG, NSG and BSG films deposited on the trench of approx. 2µm in width and approx. 4µm in depth in the silicon wafer. It is shown in this table that the BSG film has the highest ratio of the thickness of the film outside of the trench to the thickness of the film on the bottom and sidewall of the trench among the three films. Following the BSG film, the NSG film has higher coverage ratio and the PSG film has the lowest coverage ratio. Even the coverage ratio of the PSG film, however, is much better than that of the low temperature oxide film with the SiH4-O2 system or the plasma enhanced CVD film. As the results, it can be understood that surface catalytic reaction is closely related to the step coverage condition.



D: Depth of Trench W:Width of Trench A,B_{max}, B_{min}, C: Thickness of CVD Film D/W: Aspect Ratio

Deposition Temperature: 400°C PSG: P_2O_5 6.0 mole % BSG: B_2O_3 7.0 mole %

FILM TYPE	A	B _{max}	B _{min}	С	D	w	D/W	B _{max} /A	B _{min} /A	C/A	B _{min} / B _{max}
PSG	7000Å	5400Å	3900Å	3900Å	44000Å	19000Á	2.32	77.1%	55.7%	55.7%	72.2%
NSG	6400Å	5500Å	4800Å	5000Å	42000Å	18000Å	2.33	85.7%	75.0%	78.1%	87.3%
BSG	6200Å	5600Å	4900Å	5100Å	42000Å	19000Å	2.21	90.3%	79.0%	82.3%	87.5%

Table 1. Comparison of Step Coverage for PSG, BSG and NSG

Photograph 1 shows the comparison of step coverage between the PSG films using the TEOS-TMOP-O₃ and SiH₄-PH₃-O₂ systems (both doped with P₂O₅ at 4 mole%) deposited on the fine A1 pattern at 400°C. The PSG film using the SiH₄-PH₃-O₂ system has a very rough surface and causes a large number of voids. On the other hand, the PSG film using the TEOS-TMOP-O₃ system has a very smooth surface and causes no void. This also indicates that the film is deposited by surface catalytic reaction.





a) SiH₄-O₂ System b) TEOS-O₃ System Photo 1. Step Coverage on Al Patterns (400°C, 4 mole% PSG)

Photograph 2 compares the step coverage on the trench structure. The relationship between doping of boron and phosphorus and the step coverage can be explained by the surface limited reaction characteristic.

In the reaction of TEOS and ozone, ozone seems to be combined with alkyl radicals of TEOS absorbed on the substrate surface to remove these radicals.

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 a) SiH₄-O₂ System
b) TEOS-O₃ System
Photo 2. Step Coverage on Silicon Trench Patterns (400°C, 4 mole% PSG)

Photograph 3 shows the step coverage of the film deposited on the Al and polysilicon device patterns. On the Al patterns, the inside is completely filled with oxide without causing any void even if the pattern has negative profile. On the polysilicon patterns, isotropic deposition is attained and if the film become thicker it can be expected to cause the condition called self planarization.





a) Polysilicon b) Aluminum

Photo 3. Step Coverege on Fine Device Patterns (400°C, 4 mole% PSG)

4. Conclusion

By using TEOS-TMOP-O₃, TEOS-TMOB-O₃, TEOS-O₃ systems and TEOS-TMOB-TMOP-O₃ system, the PSG, BSG, NSG and BPSG films were deposited at the low temperature below 450° C.

The results are summarized as follows:

- High quality oxide and doped oxide films can be deposited at the low temprature below 450°C.
- The surface catalytic factor plays an important role in reaction and varies by doping of phosphorus and boron.
- 3) The surface catalytic reaction is closely

related to the step coverage, particulate, and surface roughness.

- Very conformal step coverage is obtainable for high aspect ratio and small geometory patterns.
- 5) No carbon is detected in these films.
- No special issues has been found for device application.
- 7) This method will be put into practical use in the VLSI device fabrication process replacing the method using the SiH₄-O₂ system.

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