Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 105-107



# The Suppression of Precipitation in Boro-Phospho-Silicate-Glass Films by Surface Control by Silylation (SCS) Process

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Simple surface control by silylation (SCS) process is developed for suppression of precipitation in high impurity concentrations BPSG films. Increase in impurity concentrations causes a precipitation problem by moisture penetration. This process employs exposure to the vaporized hexamethyldisilazane or that spin coating after BPSG films deposition. Silylation then occurs at the BPSG surface. Silyl radicals change BPSG surface from a hydrophilic to a hydrophobic one.

## 1. Introduction

Quarter micrometer VLSI devices have the high aspect ratio structures and transistors with shallow dopant profiles. In such devices, boro-phospho-silicate-glass (BPSG) films offer good planarity at low glass flow temperature for Inter Layer Dielectrics. Ozone and tetraethoxysilane based BPSG was developed for improving the step coverage of the glass prior to flowing [1]. Glass flow at very low temperatures of 850 °C or less in $N_2$ requires high impurity concentrations of $B_2O_3$ and $P_2O_5$ in the BPSG films [2)3)] . BPSG films have a precipitation problem which results in small particle generation. This was suppressed by low temperature deposition and high oxygen concentrations reactant gas flow [4]. However, high concentration of impurity causes more precipitation problem even at ambient conditions after BPSG film deposition [5]. This problem results from a water absorption of phosphosilicate glass films [6].

This paper reports the suppression of precipitates in BPSG films by Surface Control by Silylation (SCS) process. After SCS process, BPSG surface changes from being hygroscopic to being hydrophobic.

## 2. Experiments and results

BPSG films were deposited on patterned polysilicon substrate by Atmospheric Pressure Chemical Vapor Deposition using $SiH_4$, $B_2H_6$ and $PH_3$ gas. The impurity concentrations in BPSG films were controlled by the flow ratio of each gas and were measured by X-ray fluorescence analysis. The planarization of BPSG films after glass flow was evaluated by observing cross sectional views under scanning electron microscopy. Figure 1 shows the planarization of BPSG films after glass flow.

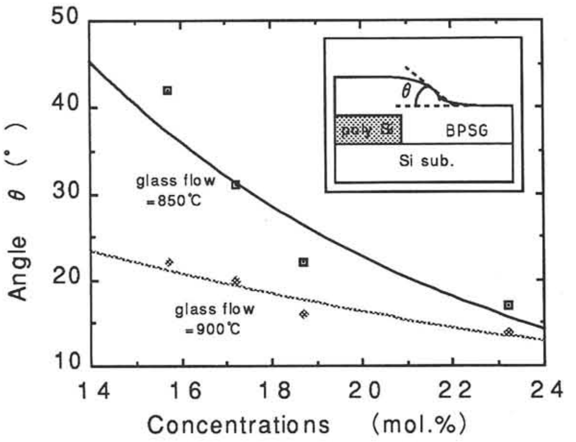


Fig. 1 The flow angle versus impurity concentrations dependence. The BPSG films flow at 850℃ and 900℃ in $N_2$.

The thickness of patterned polysilicon was 350nm and that of BPSG films was 400nm. Increase in impurity concentrations tends to decrease the slope angles. The slope angle of 18mol.% impurity concentrations when flows at 850 °C is similar to that of 15mol.% impurity concentrations at 900 °C glass flow. The latter is a comonly uses condition.

Increase in impurity concentrations causes precipitates in BPSG films during atmospheric exposure after BPSG films deposition. Figure 2 shows the impurity concentrations and the atmospheric exposure time dependence of the precipitates. Precipitates were measured as particle counts by particle inspection measurements and show an increase in number with time. Moisture penetrates the BPSG films during the atmospheric exposure [5], and it changes $B_2O_3$ and/or $P_2O_5$ to metaborate and/or metaphosphate, respectively. Figure 3 shows the typical SEM photograph of precipitates.

To suppress moisture penetration, SCS process was devised. It uses a silylation reaction by hexamethyl-disilazane (HMDS). The process employs exposure to the vaporized HMDS or HMDS spin coating within a hour after BPSG films deposition. The experimental SCS process sequence is shown in figure 4. BPSG films of 23.1 mol. % impurity concentrations were deposited on Si wafers after washing, and were coated with HMDS. A BPSG film without HMDS coating was also observed for the reference. Particle inspection measurement was carried out to evaluate the suppression of precipitation by the SCS process. The presence of silyl radicals was evaluated by thermal desorption spectroscopy (TDS) using non-doped silicate glass (NSG) films. NSG films was used for excluding the outdiffusion effect of the impurities. Figure 5 shows the suppression of the precipitates by SCS. After BPSG film deposition with 23.1 mol. % impurity concentrations, two samples, the reference and SCS, were exposed to atmosphere for 95.5 hours. The amount of the precipitates was counted over 0.45μm size. SCS suppresses the number of the

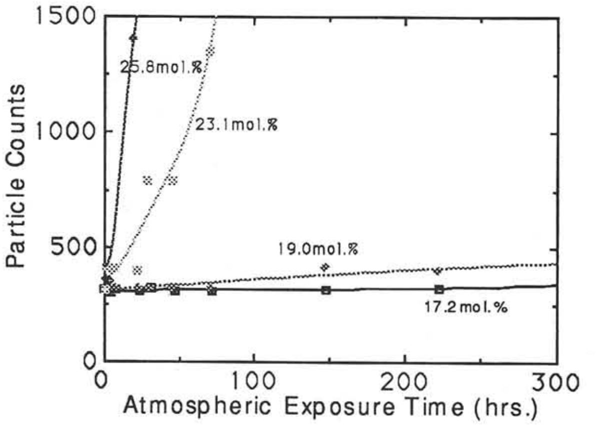


Fig. 2 Concentration dependence of the precipitates on atmospheric exposure time. Precipitates are measured as particle counts.

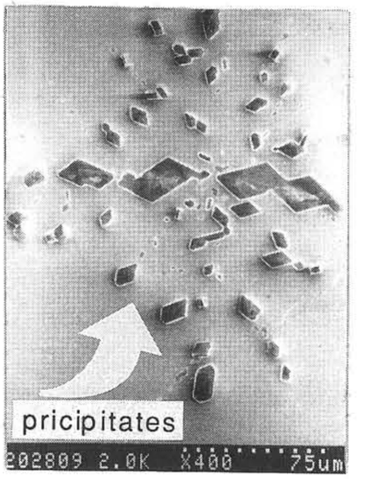


Fig.3 Characteristic scanning electron microscopy photograph of the precipitates.

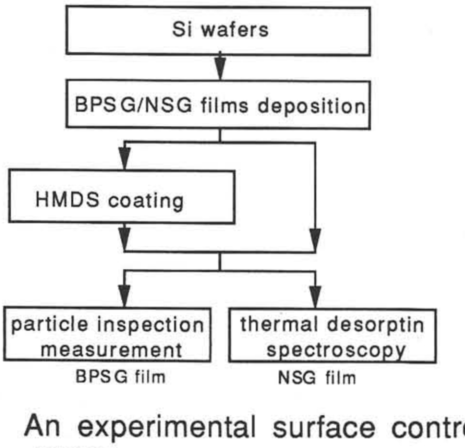


Fig. 4 An experimental surface control by silylation (SCS) process sequence.

precipitates to less than 2%. This number of particles is similar to 17 mol. % BPSG films. Figure 6 shows the TDS of NSG film with HMDS coating and that without HMDS coating as a reference. The desorped gas from reference is shown for the background. The desorption of mass number 15 was measured with TDS. The value of HMDS coated sample increases in comparison with that of reference over 300 °C. This indicates the presence of methyl radical desorped from HMDS termination.

Figure 7 shows a model for this silylation terminated surface. BPSG surface is covered with OH radicals, Si-OH, B-OH and P-OH. This surface is hydrophobic. Silyl reaction shows as below.

$$X\text{-}OH + (CH_3)_3SiNHSi(CH_3)_3 \rightarrow X\text{-}OSi(CH_3)_3 + NH_3$$
$$(X = Si, B \text{ or } P.)$$

Also silyl radical ($-Si(CH_3)_3$) changes BPSG surface from a hydrophilic to a hydrophobic one. This reaction plays a role in the protection of moisture penetration. This results in the suppression of precipitation by the SCS process.

## 3.Conclusion

Simple Surface Control by Silylation is applied to the VLSI process technology to suppress precipitates in BPSG films. It realizes low temperature glass flow at 850°C in $N_2$ using high impurity concentrations BPSG films. The low temperature glass flow enables low thermal budget. The glass flow in $N_2$ suppresses oxidation of under layer. The SCS process then provides a precipitate free process for 0.25 $\mu$m technology.


Reference

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6)R.M.Levin , J.Electrochem. Soc. Vol.129, No.8,p.1765('82).


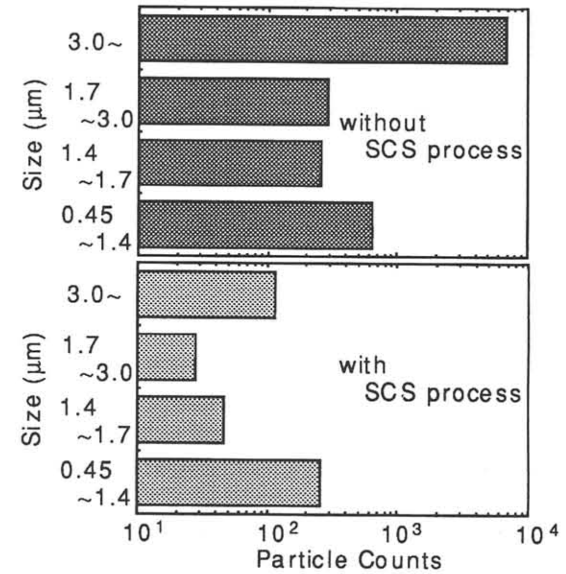


Fig. 5 Suppression of precipitation by the SCS process after atmospheric exposure for 95.5 hours. Precipitates are shown as particle counts of usual BPSG film (a) and STS BPSG film (b).

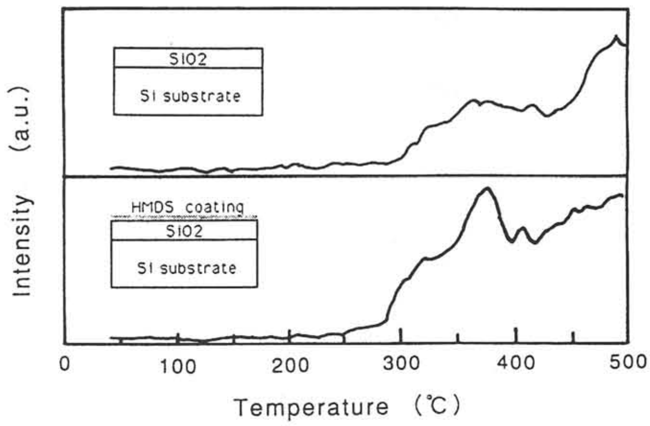


Fig. 6 The thermal desorption spectroscopy (TDS) of NSG films with HMDS coating and that without coating. The TDS measured the value of mass number 15.

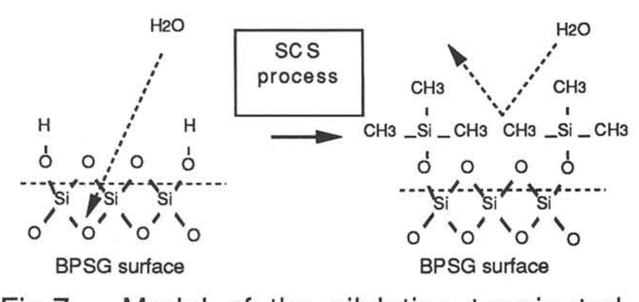


Fig.7 Model of the silylation terminated surface by the SCS process. Si-OH on the BPSG surface is substituted for $Si\text{-}O\text{-}Si(CH_3)_3$.