## The Improvement of CVD-WSi<sub>x</sub> Process by Preheating Method

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Kinetic studies were made on tungsten silicide chemical vapor deposition (CVD-WSix) process, focusing on the contribution of gas phase reactions. The preheating method was introduced to improve the  $WF_6/SiH_4$  process and WSix films were deposited at low temperature as 40°C. The silicon contents of deposited films by preheating procedure were richer than that of normally deposited films, and the residual fluorine concentration at the interface between the deposited film and the substrate was also reduced.

# 1. Introduction

Tungsten silicide (WSix) films are widely used in very large scale integrated circuit (VLSI) as low resistive gate electrodes and interconnection materials<sup>1)</sup>. They can be obtained by low pressure chemical vapor deposition (LPCVD) processes which utilize WF /SiH, (MS) or WF<sub>6</sub>/SiH<sub>2</sub>Cl<sub>2</sub> (DCS) as the source gases. MS process can deposit WSix films at relatively low temperature compared to DCS process, but the poor step coverage quality, high residual fluorine concentration, and high residual stress of deposited films are the major drawbacks of MS process. MS process is also known for a reaction system that is likely to produce particles in the gas phase<sup>2</sup>). The particle generation was also reported during CVD-W from WF<sub>6</sub>/SiH<sub>4</sub><sup>3)</sup>. These results suggest that some intermediate species formed by gas phase reactions are controlling MS process. In the present work, we have investigated the kinetics of this process and found some experimental evidences that show the contribution of gas phase reactions to this process. By introducing the preheating procedure to accelerate these gas phase reactions, the deposition temperature was decreased and the properties of deposited films were improved.

#### 2. Experimental

Experiments were performed in a tubular hot-wall type reactor, equipped with two resistive furnaces, as shown in Fig.1. The short furnace, 2cm long, located at the upper stream side of the reactor, was used only to preheat the source gases. The inner diameter of reactor was varied from 4mm to 22mm to change the surface area to volume ratio of the reactor. Si wafers with micron order trenches were used as substrate to observe the step coverage profile of the deposited films. The direct Monte Carlo simulation was performed to analyze the step coverage profile and the sticking probability of film forming species were obtained. The composition ratio and the residual fluorine concentration of WSix films were analyzed by Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS), respectively.

## 3. Results and Discussions

Several deposition runs were performed to investigate the temperature dependency of step coverage profile. The partial pressures of  $WF_6$ ,  $SiH_4$ , and Ar were fixed at 4mTorr, 400mTorr, and 2.0Torr, respectively. Figure 2 shows the sticking probability of film precursors analyzed from the step coverage profile. The reactivity of film precursors was relatively high and they had a low activation energy as 4 kcal/mol. Though an activation

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energy is small, the deposition rate drastically changed between 120°C and 110°C. As a result, we could not get any WSix film deposition below 110°C within a 11mm tube, i.e., 120°C is a threshold temperature (T<sub>th</sub>) for 11mm tube. This phenomenon can be explained by two kinds of reaction mechanisms, the one is a radical chain reaction, the other is a self-catalytic reaction. If a radical chain reaction occurred in the reactor, the active radical species would be balanced by both producing in the gas phase and quenching at the wall of the reactor. Hence, the change of surface area to volume ratio (S/V ratio) of the reactor will result in the change of T<sub>th</sub>, while if the selfcatalytic reaction is the case, S/V ratio will not affect to the threshold temperature. Other experiments were made to investigate if T<sub>th</sub> is affected by S/V ratio or not, by changing the reactor diameter. Table 1 summarizes the results. T<sub>th</sub> is decreased by increasing the reactor diameter and this is the direct evidence that the gas phase reactions are dominating the process.

An attempt was made to accelerate the gas phase reactions by adding preheating zone in the reactor. Low temperature deposition, as low as 40°C, was achieved by 360°C preheating treatment, also shown in Table 1. The low temperature deposition at 40°C were also accomplished with 130°C and 240°C preheating furnace. The sticking probabilities with different S/V ratio or preheating procedure is also plotted in Fig.2. Sticking probabilities were almost in the same rate and showed similar temperature dependency. These results are characteristic feature of radical chain reactions. That is, once reactions start, gas phase conditions does not affect the following reactions and the radical species produced by the chain reactions often show high reactivity and low activation energy.

The compositions of the deposited films analyzed by RBS were shown in Fig.3 as a function of deposition temperature. The Si contents of as deposited WSix films were increased by increasing the temperature, which is previously reported by Shioya *et al.*<sup>4)</sup>. Moreover, we found, for the first time, that Si contents after 360°C preheating was richer than that of normal heating method. The composition ratio of x = 2.5 (x of WSix), which is required in ULSI fabrication process, can be obtained at 180°C by preheating method and uniform step coverage can also be achieved because of the low sticking probability at this temperature.

Figure 4 shows the typical depth concentration profile of the deposited films measured by SIMS. Residual fluorine was almost uniform in the film and showed segregation at the interface between the deposited film and substrate. The bulk fluorine concentrations are summarized in Table 2. They did not show any tendency to be changed by the preheating method and reactor size. The concentration range of 10<sup>21</sup> atoms/cm<sup>3</sup> is a typical value for MS process<sup>5)</sup>. However, the films deposited at 40°C after 360°C preheating contain ten times as much as that of the others. It suggests that the residual fluorine concentration was not controlled by gas phase reaction, but some surface reactions, which should be enhanced between 40°C and 150°C, dominated the fluorine concentration. Figure 5 shows the segregation ratio of the residual fluorine defined as the fluorine concentration at the interface to the bulk. The preheating method and the reactor size control contribute to reduce the segregation ratio. The residual fluorine in WSix films at the interface causes peeling and deteriorate the capacity of gate electrode<sup>6)</sup>. The control on gas phase reactions is one of the successful way to improve these problems.

# 4. Conclusion

The WSix films with suitable composition and low interface fluorine concentration can be deposited at relatively low temperature by controlling the gas phase reactions. The preheating method can contribute to improve the MS process in good deal.

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## References

- K. C. Saraswat *et al.*: IEEE Trans. Electron Devices <u>30</u> (1983) 1497.
- D. L. Brors *et al.*: Proc. Ninth Int. Conf. on CVD, edited by McD. Robinson, C. H. J. van den Brekel, G. W. Cullen, J. M. Blocher, Jr., and P. Rai-Choudhury (Electrochem. Soc., Cincinnati, OH, 1984), p.275.
- 3) Y. Nakamura et al.: Extended Abstracts of the 1991

Int. Conf. on SSDM, (Jpn. Soc. of Appl. Phys., Yokohama, 1991), p.216.

- 4) Y. Shioya et al.: J. Appl. Phys. 61 (1987) 561.
- 5) Y. Shioya et al.: J. Appl. Phys. 58 (1985) 4194.
- P. J. Wright *et al.*: IEEE Trans. Electron Devices <u>36</u> (1989) 879.







Fig. 2 Temperature dependence of sticking probability of film precursors.



Fig. 3 Temperature dependence of composition ratio.



Fig. 4 The typical depth profile of fluorine.



Fig. 5 The segregation ratio of residual fluorine.

Table 1 The variation of threshold temperature.

Inner Dimeter [mm]	Preheating Temperature [°C]	Threshold Temperature [°C]	
4.0	No	140	
11.0	No	120	
16.5	No	100	
22.0	No	80	
11.0	360	40	
11.0	240	40	
11.0	130	40	

Table	2	The	bulk	residual	fluorine	concentration.
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Inner Diameter [mm]	Preheating Temperature [°C]	Substrate Temperature [°C]	Fluorine Concentration [atoms/cm <sup>3</sup> ]	
11.0	No	360	3.2 × 10 <sup>21</sup>	
11.0	No	150	1.5 × 1021	
16.5	No	150	1.7 × 10 <sup>21</sup>	
22.0	No	150	2.3 × 1021	
11.0	270	150	3.0 × 10 <sup>21</sup>	
11.0	360	150	1.7 × 10 <sup>21</sup>	
11.0	450	150	3.6 × 1021	
11.0	360	40	14.0 × 10 <sup>21</sup>	