Silane Thermal Decomposition Characteristics on Various Si Surface

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In this paper, we studied the SiH_4 thermal decomposition behaviors (100 ppm in Ar) on various modified polysilicon surfaces. We found the decomposition rates on Si-H and poly-Si surfaces are essentially the same while the rates on n+ and Si-O surfaces are slower. Rates on p+, Si-F and Si-Cl surfaces are very reactive even at low temperature. Thus it is possible to achieve a high selective film deposition by controlling the surface conditions and temperatures.

1. Introduction

It is essential to have perfect uniformity and reproducibility of process conditions for high performance ULSI manufacturing. In the CVD and RIE process, various kinds of very reactive and corrosive speciality gases such as silanes and halogens are used. Their properties, especially on various surfaces, are not well understood. The process parameters such as flow rates, concentrations, pressure and temperatures are mostly empirically determined. To improve the process performance, we need more fundamental understanding of these paramaters. Previously we reported the effects of dilution gas and dilution rate on silane decomposition¹). In this paper, we would like to report our further study on the characteristics of SiH₄ decomposition on various modified polysilicon surfaces. We will show the surfaces play an important role on the behaviors of silane decomposition.

2. Experimental

Figure 1 shows a schematic of the experiment. All parts were made of electropolished and mirrored– finished SUS316L. Plastic materials which tend to trap moisture were replaced by all-metal parts. Dead space in the integrated parts was minimized as much as possible²⁾. Reactor tubes were made of 1" electropolished SUS316L or 1/2" Hastealloy X tubings. The reactor was heated with electric sheath heaters and wrapped with the aluminium foil and insulator. The temperature was controlled to within 2°C. Ultra pure silane with a moisture less than 6ppb and argon with a moisture of about 50ppt were used³⁾. The flowrate and dilution rate were controlled by using precision mass flow controllers. Silane concentration was measured by using a high sensitivity GC equipped with TCD. Thermal decomposition of 100ppm of SiH₄ in Ar was evaluated on 7 different surfaces including poly–Si surface by decomposition of SiH₄, H– terminated Si surface by H₂ annealing the polysilicon surface, Si–O surface by oxidizing poly–Si in dry oxygen gas, n+ surface by depositing poly–Si with PH₃, p+ surface by depositing poly–Si with silane and B₂H₆ mixtures, Si–F by fluorinating the poly–Si surface and finally Si–Cl surface by cracking SiCl₄.



Fig.1 Schematic diagram of decomposition evaluation system.

3. Results and discussion

Figure 2(a) shows the semi-log plots of SiH_4 thermal decomposition at 420°C for 4 differnt surfaces: poly-Si, Si-H, Si-O and n+. The vertical axis is the decomposition rate and the horizontal axis is the reaction time. The rates appear to follow the first-order kinetics reasonably well: $\ln[SiH4,/SiH4,_0] = -kt$, where k is the rate constant and t the reactor

residence time. From this figure, we obserbed that the rates on poly–Si and Si–H are essentially the same while the rate on n+ is slower and the rate on Si–O is significantly slower. Figure 2(b) shows the Arrhenius plots, from which the activation energies were calculated: 2.0 and 1.9 eV for the poly–Si and the Si–H respectively, about 1.45 eV for the n+ surface and 0.9 eV for the Si–O surface.

These results indicate that the surface conditions for poly–Si and Si–H are essencially the same, while n+ surface is slightly more electron rich, which tends to repel the silane molecules. On the other hand, Si–O surface, a good electric insulator, attract and break less easily the silane molecules.

Next, we describe the othe three more reactive surfaces: p+ surface, Si–F, Si–Cl. Figure 3 shows the silane concentration at the reactor effluent as a function of time as the temperature was ramped at 1.7° C/min from 25°C to 100°C on p+ Si surface. Silane began to disapper around 40°C. Figure 4 and 5 show similar experimental results on the Si–F and Si– Cl surfaces at about 2°C/min. Each time, the temperature was raised from one level to another, silane concentration dipped and the valleys became deeper and deeper with temperatures.

These surfaces have a common feature in that they are very reactive toward silane at fairly low temperatures. The probable reason is that holes at the p+ surface tend to recombine electrons in the silane molecule while halogen silicon surfaces, due to their large electronegativity of halogen atoms, have a





tendency to form halogen-hydrogen bonds or halogensilicon bonds with silane molecules and attract and break the silane molecules more easily.

For comparison, Figure 6 shows the silane concentration on the poly–Si surface. We observed that there was no reaction of any sorts as temperature was

SiH4 THERMAL DECOMPOSITION (P+-Si SURFACE)





SiH4 THERMAL DECOMPOSITION (SI-F SURFACE) SiO2-4.5%HF/Ar at RT, ANNEALING AFTER ETCHING



reaction as the temperature varied from R.T. to 300°C.

SIH4 THERMAL DECOMPOSITION ON SI-CI SURFACE



Fig.5 The time transition of Si–Cl surface and SiH₄ reaction as the temperature varied from R.T. to 350° C.

raised in a step-wise manner from 25 to 300°C. Poly-Si surface is not reactive at low temperature.

To further investigate the effect of the temperature rise rate and to pin-point the starting "decomposition" temperature more precisely, we ran further experiments on the Si-F and Si-Cl surfaces at 0.1°C/min lower rates. Figure 7 shows that on the Si-Cl surface, silane concentration did not change at a 100 ppm feed level at temperature below 200°C and 300cc/min flow. This is consistent with the previous

experiment (Fig.5). At 200°C, we raised the temperature to 280°C for 80 minutes and observed a sudden drop in concentration to the zero level and then followed by a dramatic recovery to 96ppm as the flow was raised to 1060cc/min. Beyond the peek concentration, the silane began to fall gradually again as the temperature reached 514°C. Note that at 380°C, 74ppm point and 450°C, 400ppm points some behavior changes in silane concentrations were evident. From these results, we found that the starting decomposition temperature appered to lie between 200 to 280°C.

Figure 8 shows the behavior on Si–F surface. Silane concentration appered to decrease around 170° C and fall to a 50% level at 280°C(60ppm) and to zero at 305°C. After a complete disapperance, we raised the flow. Twice we observed a quick recovery of silane concentration. From these results, we confirmed silane began to decompose at 170°C.

Considering the quick recovery and the subsequent disappearance of silane concentration with flow changes on both Si–Cl and the Si–F surfaces, we think that even the surface was guradually deposited with polysilicon and the surfaces were modified to some extent, the surface is probably still very electronegative and remained very reactive.

UNCHANGED SIH4 CONCENTRATION ON SI SURFACE 100 ppm SIH4/Ar SI Surface



Fig.6 The time transition of poly–Si surface and SiH₄ reaction as the temperature varied from R.T. to 300°C.



Fig.7 The time transition of Si-Cl surface and SiH₄ reaction as the temperature varied from R.T. to 530°C.



Fig.8 The time transition of Si-F surface and SiH₄ reaction as the temperature varied from R.T. to 500° C.

4. Summary

We have studied the silane decomposition baheviors on 7 different surfaces and revealed that the starting decomposition temperature and the rates varid widely depending the surface properties. High electronegative surfaces such as p+, Si–F and Si–Cl are far more reactive than poly–Si, Si–H, n+ and Si–O surfaces. The implication of these results is that a selective film deposition is possible in the CVD by a careful control over the surface condition and the temperature.

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