Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 929-931

Specialty Gas Interactions with Various Silicon Surfaces

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We have studied surface reaction between various silicon surfaces(non-dope Si, n+Si, p+Si) and specialty gases such as silane. The results indicated that even for the same gases, the starting decomposition temperature and decomposition rate were quite different. In this report, we present the low temperature surface reaction mechanism based on ionization potential of gas molecule, the energy level of solid surface and experimental results

1.Introduction

Scientific semiconductor manufacturing is available under ultraclean processing concept characterized by ultraclean wafer surface, ultraclean processing environment and perfect parameter controlled process[1][2]. In the CVD process, specialty gases such as silane and disilane have been extensively used. However their physical and chemical properties are very complex and not well understood. Process parameters such as flow rates, concentrations and temperature are mostly empirically determined. To achieve scientific semiconductor manufacturing, we have studied reactive specialty gas decomposition characteristics on various silicon surfaces[3][4].

2.Experimental

A schematic diagram of the experimental setup for evaluating the decomposition characteristics of specialty gases are shown in Fig. 1. All components used in the system are made of Cr2O3 treated stainless steel[5][6]. Dead space in the integrated parts was minimized to avoid trapping the gas, which tends generate impurities over a long period of time. Tube reactor was made of ϕ12.7mm x 40cm (reactor volume 32.8cc) Hastelloy and was heated with electric sheath heaters wrapped with aluminum foil and insulation. The temperature was controlled to within 2C by using several PID(Proportional-Integral-Differential) controllers along the tube reactor. The flow rate and dilution ratio were controlled by using precision mass flow controllers. A 100ppm SiH4 diluted Ar gas was supplied to the tube reactor and concentration of SiH4 gas came out from the tube reactor were measured using by FT-IR(Fourier Transform Infrared Spectroscopy) or GC-TCD(Gas Chromatography - Thermal Conductivity Detector).

In this study, we have prepared three kinds of Si surfaces, non-dope Si, n+Si and p+Si surface. The non-dope Si surface was formed by decomposition of SiH4, n+Si surface was formed by decomposition with PH3 and p+Si surface was formed by decomposition with B2H6. The flow rate was held constant until exit concentration reached a steady state as indicated by FT-IR measurements. Then gas flow rate was changed for the desirable residence time. The residence time was calculated based on the reaction volume and the gas flow rate at the reactor temperature.

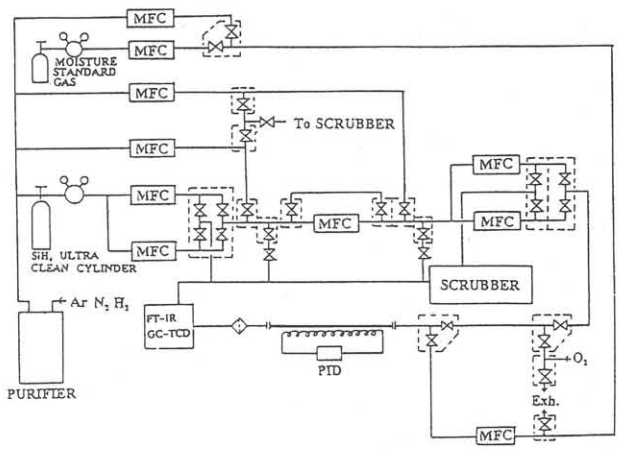

Fig.1 Schematic diagram of the experimental setup.

3.Results and Discussion

Fig.2 shows the semi-log plots of SiH4 decomposition behavior on p+ Si surfaces at various temperature. The vertical axis indicates the decomposition rate and the horizontal axis shows residence time. Due to the linearity plots, the decomposition rate follows the first-order kinetics. Its behavior can be reasonably well described by the equation

$$\ln[SiH4]t / [SiH4]t0 = -kt \quad (1)$$

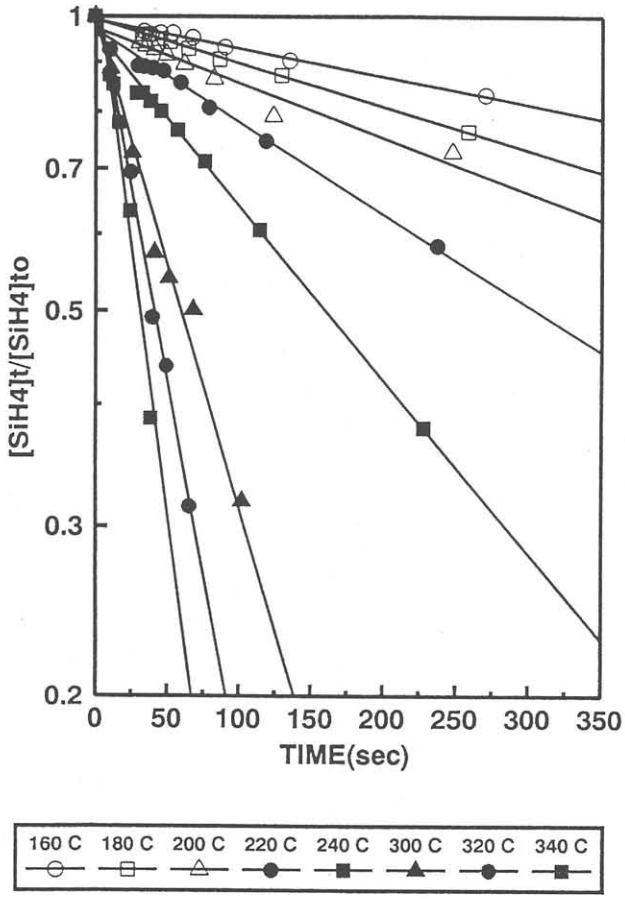

Fig.2 100ppm SiH4 decomposition characteristics on p+Si surface.

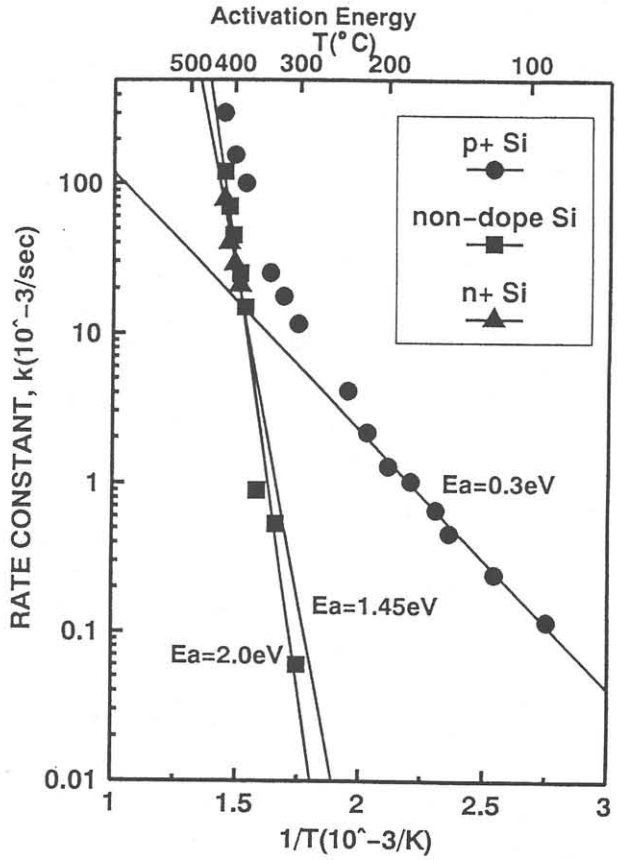

Fig.3 The activation energy of 100ppm SiH4 decomposition characteristics on non-dope Si, n+Si and p+Si surface.

where k is the rate constant and t is the residence time, [SiH4]t0 is the initial concentration of SiH4 before introduced to the tube reactor and [SiH4]t is the concentration of SiH4 from the tube reactor. From these results, all data were interpreted with first-order kinetic equation in this study.

We measured 100ppm SiH4 decomposition rate constant on non-dope Si, n+Si and p+Si surfaces as shown in Fig.3. SiH4 is not decomposed on non-dope Si and n+Si surfaces at temperatures lower than 300°C. On the other hand, SiH4 decomposed on p+Si surface at temperatures lower than 100°C and their activation energy is 0.3eV from 90°C to 200°C. And decomposition rate constant on p+Si surface almost same to non-dope Si and n+Si surfaces about 400°C. We have considered the low temperature SiH4 decomposition mechanism on p+ Si surface as follows (Fig.4). The ionization potential of isolated SiH4 molecules in gas phase is -11.6eV. But the SiH4 energy level has changed from -11.6eV to -5.45eV due to wave function interference between gas molecules and p+Si surface when gas molecules were getting close to the p+Si surface. Then the electron of adsorbed SiH4 molecule receives the thermal energy, 0.3eV, it recombines with the hole of p+Si surface and cause to SiH4 decomposition.

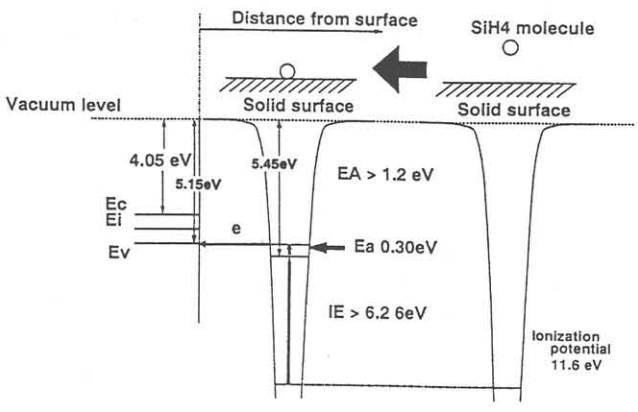

Fig.4 SiH4 decomposition mechanism on p+Si surface.

Furthermore, we measured 100ppm Si2H6 and Si3H8 decomposition characteristics on non-dope

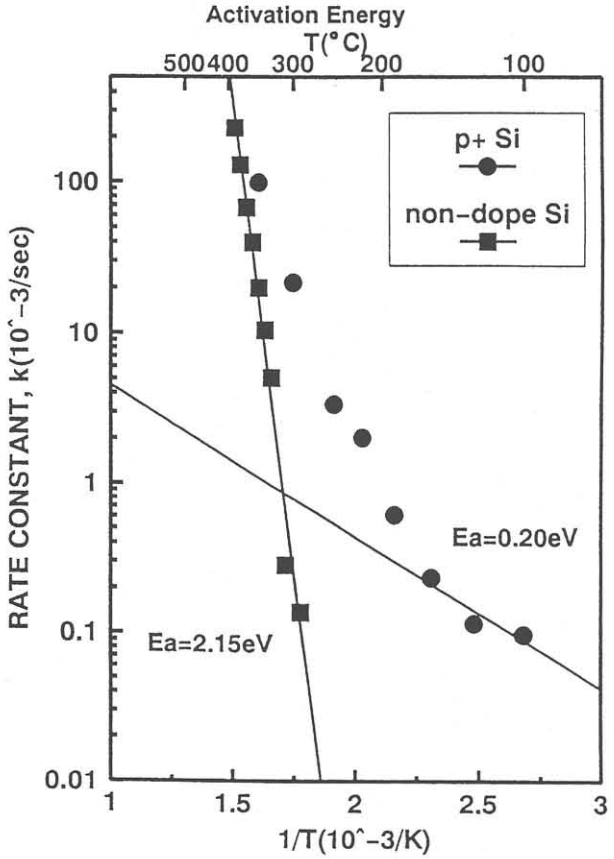

Fig.5 The activation energy of 100ppm Si2H6 decomposition characteristics on non-dope Si and p+Si surface.

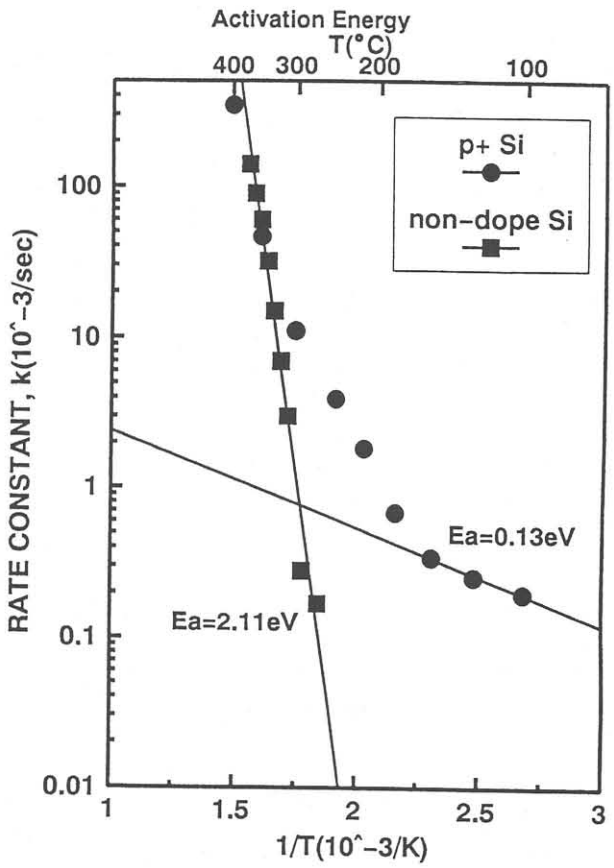

Fig.6 The activation energy of 100ppm Si3H8 decomposition characteristics on non-dope Si and p+Si surface.

Si and p+Si surfaces as shown in Fig.5 and Fig.6 respectively. In these figures, we can observe that the decomposition rate constant of SiH4, Si2H6 and Si3H8 on non-dope Si surface which increase in that order about 400°C. On the other hand, SiH4, Si2H6 and Si3H8 have almost same decomposition rate constant due to the interactions with p+Si surface at low temperature. From these results, we consider that -SiH3 group of Si2H6 and Si3H8 adsorbed on p+Si surface and cause to decomposition.

4.Summary

In this study, we reported SiH4 decomposition behavior on various Si surfaces. In particular, SiH4 decomposed on p+Si surface at low temperature. We interpreted this surface reaction by means of change of energy level due to wave function interference when gas molecules adsorbed solid surface. To achieve scientific semiconductor manufacturing, it will be important to understand specialty gas property in gas phase and adsorbed on solid surface.

5.Acknowledgments

This study was carried out at the Mini-Super Clean Room of Faculty of Engineering, Tohoku University

References

[1]T. Ohmi , 1989 International Electron Devices Meeting, Washington, D.C., pp.49-52, December 1989

[2]T.Ohmi, Microelectronic Engineering, Vol.10, pp.163-176, 1991.

[3]T. Watanabe, M. Nakamura, A. Ohki, K. Kawada, S. Miyoshi, S. Takahashi, M.S.K Chen and T. Ohmi , international Conference on Solid State Devise and Materials, pp.132-134, august 1992 Tsukuba, Japan

[4]R. C. Weast, "CRC Handbook of chemistry and physics 62nd edition" CRC Press, Inc.

[5] T.Ohmi, A.Ohki, M.Nakamura, K.Kawada, T.Watanabe, Y.Nakagawa, S.Miyoshi, S.Takahashi and M.S.K.Chen, Journal of the Electrochemical Society, Vol.140, No.6, pp.1691-1699, June 1993.

[6]A. Ohki, Y. Nakagawa, M. Nakamura, K. Kawada, S. Miyoshi, T. Watanabe, S. Takahashi, M. S. K. Chen and T. Ohmi, Contamination Control and Defect Reduction in Semiconductor Manufacturing 1, PV92-21, pp.416-437, The Electrochem. Soc., Pennington, NJ, 1992