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Sticking Configuration of Boron Atoms from B2H6 on Silicon during Rapid Vapor-Phase Doping

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1. Introduction

To achieve high-speed performance of silicon devices, shallow junctions with high impurity concentrations are inevitable. Low-energy ion implantation has recently been used for this purpose, however, for future requirements such as few-nanometer doping and atomic-layer doping, dopants with almost zero energy should be supplied to the Si surface. In this case, diffusion by using a gas source may be more effective than ion implantation.

We have developed Rapid Vapor-phase Doping (RVD) to meet these requirements [1]. Although its advantages have been shown by the resulting device performance [2], the reaction kinetics is not yet clarified because it involves complicated reactions; that is, dissociation of gas, adsorption and desorption of species on the surface, and diffusion of impurities into Si. There are some studies on the reactions between B_2H_6 gas and silicon surface [3, 4], however, little has been reported on their reactions in a hydrogen atmosphere. We have reported that the hydrogen termination of the surface is maintained during RVD [5]. In this paper, we evaluate the sticking coefficients of B_2H_6 gas in order to show the configurations of boron on a hydrogen-terminated silicon surface.

2. Experiment

RVD uses a hydrogen carrier gas and a B_2H_6 doping gas. The experimental setup consists of a lamp-heated atmospheric pressure system [1]. The most notable feature of the process is that the wafer is rapidly heated after B_2H_6 is introduced into the reaction chamber at the same time as the hydrogen carrier gas for the doping. The doping conditions are summarized in Table 1. Boron-doped layers were characterized by secondary ion mass spectroscopy (SIMS) and Auger electron spectroscopy (AES).

3. Results and discussions

SIMS profiles for B_2H_6 concentrations from 1 to 10 ppm are shown in Fig. 1. Above 6 ppm, the boron concentration on the surface exceeds the solid solubility at 900°C (about 5×10^{19} cm^{-3}). In this case, boron atoms are segregated on the surface. Figure 2 shows the AES spectra of boron-doped samples. Below 4 ppm, we could not see the boron peaks, however above 6 ppm, a boron (KLL) peak appeared at 185 eV. By comparing the intensity of Si(KLL) and B(KLL), we can speculate that more than one monolayer of boron exists on the surface. The sheet boron concentrations obtained from the SIMS profiles are shown in Fig. 3. Here, sheet concentration increases with increasing B_2H_6 concentration.

In general, the incident flux of gas molecules to the unit area of the chamber wall is calculated by the following equation.

$$Z_n = \frac{n}{2\sqrt{\pi}} \sqrt{\frac{2kT}{m}} = 2.66 \times 10^{20} \cdot \frac{P}{\sqrt{MT}} \text{ (molecules/s/cm}^2\text{)}.$$

Here, n is molecular concentration (cm^{-3}), m is molecular weight (g), M is molecular mass (g/mol), and P is pressure (Pa). The sticking coefficient is defined as the ratio of the sheet boron concentration in Fig. 3 and the incident B_2H_6 flux obtained from the equation. The calculated results are shown in Fig. 4. The sticking coefficient increases with increasing B_2H_6 concentration. Especially between 4 and 6 ppm, a drastic change is seen, which suggests a change in sticking configuration of boron. The relation between doping time and sticking coefficient is shown in Fig. 5. The sticking coefficient for 10 ppm B_2H_6 is about one and half orders of magnitude higher than those for 1 and 2 ppm. Note that when the B_2H_6 concentration is 1 or 2 ppm, a low sticking coefficient is maintained even when the doping time is extended.

From these data, we can conclude that there are two types of sticking configuration of boron on silicon: a low-B_2H_6-concentration case and a high-B_2H_6-concentration case. These configurations are schematically shown in Fig. 6. Here, BH_3 is assumed as the precursor as in the thermal CVD of boron [6]. Figure 6(a) shows the sticking configuration of BH_3 on hydrogen-terminated silicon, which represents the low-B_2H_6-concentration case. Here, the desorption of hydrogen opens more sites for BH_3 chemisorption [3]. Figure 6(b) shows the other configuration of BH_3 on adsorbed boron, which represents the high-B_2H_6-concentration case. To provide shallow doping layers with controlled boron concentrations, the configuration in Fig. 6(a) is preferable. And suppressing the sticking coefficient by keeping the hydrogen-terminated surface is necessary to avoid boron segregation.

4. Conclusion

Two types of boron sticking configurations during Rapid Vapor-phase Doping were clarified by evaluating the sticking coefficient. Doping conditions with low sticking coefficient $(\sim 10^{-6})$ are preferred in order to avoid boron segregation and to obtain concentration controllability.

References

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Table 1 Experimental conditions

Temperature (°C)	900°C
Doping time (s)	5 - 1800
B_2H_6 concentration (ppm)	1 - 20
H_2 flow rate (l/min)	25
Pressure	atmospheric

900°C, 40 s

B_2H_6
— 10 ppm
-- 6 ppm
— 4 ppm
···· 2 ppm
—·— 1 ppm
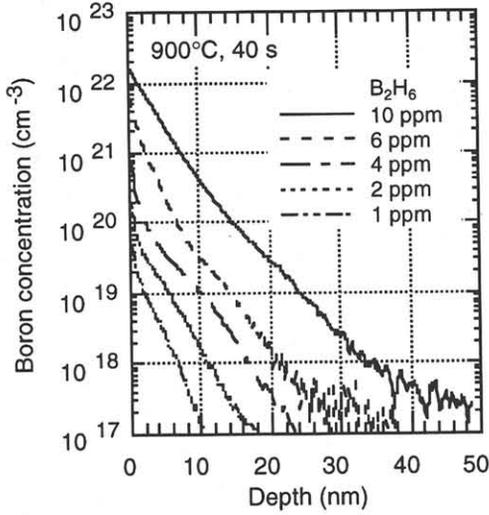
Fig. 1   SIMS profiles.

B(KLL) 185 eV

Si(LVV) 96 eV   Si(KLL) 1621 eV

B_2H_6 = 4 ppm

B_2H_6 = 10 ppm

Fig. 2 AES spectra.

900°C, 40 s

Fig. 4 Sticking coefficient vs. B_2H_6 concentration.

900°C, 40 s

Fig. 3 Sheet boron concentration.

B_2H_6
○ 1 ppm
△ 2 ppm
□ 5 ppm
● 10 ppm

Fig. 5 Sticking coefficient vs. doping time.

physisorption   chemisorption

○ Si
⊘ B
● H
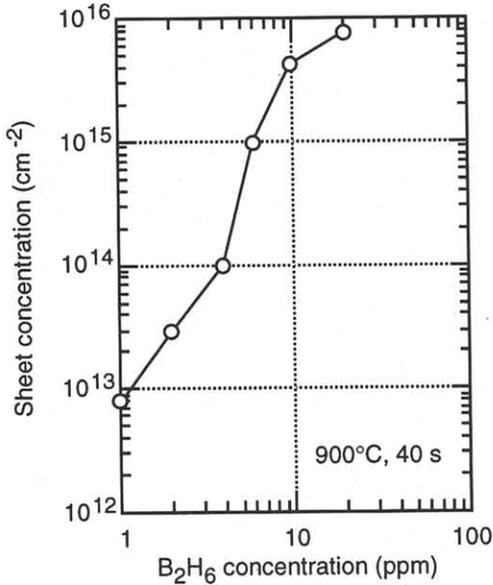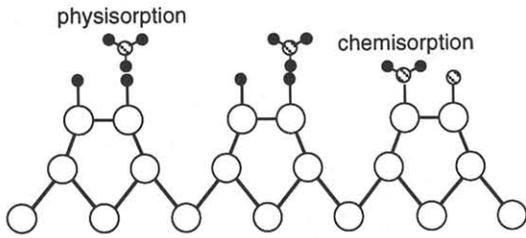
(a) on hydrogen-terminated surface
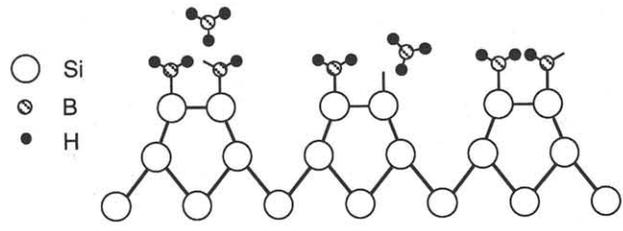
(b) on boron-adsorbed surface

Fig. 6 Sticking configurations of boron on silicon.

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