# The Role of Hydrogen during Rapid Vapor-Phase Doping Analyzed by FTIR-ATR

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The surface of boron- doped layers formed by Rapid Vapor-phase Doping were analyzed by XPS and FTIR-ATR, and the role of the hydrogen carrier gas was examined. Using hydrogen carrier, no evidence of boron segregation was observed in the XPS spectra and FTIR-ATR analysis confirmed that the hydrogen termination of the surface was maintained during doping. The hydrogen termination should promote the surface migration of adsorbed species. A hydrogen carrier gas plays an important role in terminating the dangling bonds, thus preventing excessive chemisorption of boron.

#### 1. Introduction

As the performance of high-speed silicon devices continues to be advanced, interest in developing processes for ultrashallow pn junctions of less than 50 nm has been increasing. For example, source and drain extensions of  $0.1\mu$ m-MOS transistors should have diffusion depth of 20 nm and surface carrier concentration of  $10^{20}$  cm<sup>-3</sup>. It is especially difficult to achieve such shallow and high-concentration doping through ion implantation for boron because of the channeling effect of the boron ions. Hence, a great deal of research has focused on finding a process to form shallow p-type layers <sup>1)-3)</sup>.

To meet the requirements of shallow junctions for future LSIs, we have developed Rapid Vapor-phase Doping (RVD) and have applied it to device fabrication <sup>4)5)</sup>. RVD is a kind of gas source diffusion in which a hydrogen carrier gas is used. Most other methods that use B<sub>2</sub>H<sub>6</sub> as a diffusion source for boron shallow-doping suffer from boron segregation and poor controllability of the concentration. In RVD, however, the boron concentration can be controlled over a wide range, and by choosing suitable doping conditions, no segregation of boron occurs. The difference between RVD and other methods is the use of a hydrogen carrier gas. In this paper, to clarify the role of hydrogen during RVD, the surface of the boron-doped layer is analyzed using Xray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared spectroscopy Attenuated Total Reflection (FTIR-ATR).

### 2. Experiment

The doping experiments were carried out using equipment that included a lamp annealing system <sup>4)</sup> as shown in Fig. 1. CZ(100), n-type (10  $\Omega$ cm) wafers were used in our experiments. The off angle from (100) plane

was 4°. Before doping, the wafer was treated by a conventional method that involved chemical cleaning, HF dipping and rinsing with de-ionized water. The doping sequence was reported previously <sup>5</sup>). The most notable feature of the process is that a wafer is rapidly heated after  $B_2H_6$  is introduced into the reaction chamber using a hydrogen carrier gas for the doping. The doping conditions are summarized in Table 1. The one-minute post annealing after the  $B_2H_6$  injection was stopped was done to reduce the boron adsorption during cooling. To clarify the role of hydrogen, a nitrogen carrier gas was also used. Boron doped layers were characterized by secondary ion mass spectroscopy (SIMS), XPS, and FTIR-ATR. In FTIR-ATR analysis, germanium prism attached to the samples was used for



multiple internal reflections element. The FTIR analysis was done twice, just after doping and after HF treatment of the doped samples.

# 3. Results and discussions

The boron profiles from the SIMS analysis are shown in Fig. 2. In both atmospheres, the lower temperature led to higher boron concentration at the surface because of lower probabilities of out-diffusion and re-evaporation. Since 800°C doping in nitrogen led to a very high surface concentration of over 10<sup>21</sup> cm<sup>-3</sup>, the obtained boron profile may not be correct because of the knock-on effect of boron during SIMS analysis.

The XPS spectra for the 800°C-doped samples are shown in Fig. 3. For the 900°C-doped samples, data are not shown because almost identical spectra were obtained. When a hydrogen carrier gas was used, no B(1s) peak was observed, showing that the boron concentration at the surface was below the detection limit of XPS which is a few percent of silicon. But in the case of nitrogen, a B(1s) peak at 188 eV and another broad peak at the higher energy shoulder of Si (2p) around 102 eV have appeared. From the SIMS and XPS data, the surface of the samples doped in nitrogen



appear to have been covered with thin layer that consists mainly of boron and silicon. However, doping in hydrogen does not cause such undesirable layers.

FTIR-ATR spectra measured just after the doping are shown in Fig. 4. Due to the absorption by free carriers, broad peak at lower wavenumbers can be seen in all spectra. In the spectra of the sample doped in hydrogen, there is a sharp peak due to the Si-H<sub>x</sub> bond at 2100 cm<sup>-1</sup>. This peak is due to either the Si-H bond on the Si(2x1) dimer 6) or the Si-H<sub>2</sub> bond 7). The existence of the peak related to the Si-H<sub>x</sub> bond indicates that the hydrogen termination of the dangling bonds of silicon was maintained during doping, as it is in epitaxial growth <sup>6)</sup>, even though the processing temperature is much higher than that at which terminated hydrogen desorbs. On the other hand, the spectra of the sample doped in nitrogen show no peak due to the Si-H, bond, which indicates that the terminated hydrogen had desorbed. Instead, a B-O peak was observed. A B-O peak is due to the oxidation of segregated boron at the



Fig. 4 FTIR-ATR spectra for as-doped samples







surface that occurs while the samples are being carried to the FTIR equipment. A small B-H peak was seen at 2540 cm<sup>-1</sup> when the doping temperature was  $800^{\circ}$ C regardless of the carrier gas. This fact suggests that B<sub>2</sub>H<sub>6</sub> gas does not completely dissociate at this temperature and the precursors adsorb on silicon surface as a form of boron hydrides.

The doped samples were treated by 0.5%-HF dipping and rinsed with de-ionized water, then they were analyzed by FTIR-ATR again. At that time, the samples doped in hydrogen were repelling water, while those doped in nitrogen were not. The changes in the FTIR spectra caused by the 0.5%-HF treatment of the samples doped in hydrogen are shown in Fig. 5. After HF treatment, a Si-H<sub>2</sub> peak at 2110 cm<sup>-1</sup> and a Si-H<sub>3</sub> peak at 2140 cm<sup>-1</sup> appeared instead of the sharp peak at 2100 cm<sup>-1</sup>. The wavenumbers of these peaks are identical to those for the sample before doping. This indicates the existence of Si atoms at the surface without boron segregation when the hydrogen carrier gas was used. On the other hand, when the nitrogen carrier gas was used, there were no Si-H<sub>x</sub> peaks even after HF treatment although the B-O peak decreased. This also suggests that boron segregation occurred with the nitrogen carrier gas.

As mentioned above, when a hydrogen carrier gas is used, hydrogen termination of Si dangling bonds is maintained during doping and boron segregation is suppressed. Considering these results, the surface reactions which may occur during doping in hydrogen can be described as follows. This model is based on the surface reactions during CVD of a-Si proposed by Matsuda<sup>8)</sup>. Here, Si-H stands for a silicon atom at the surface whose dangling bonds are terminated by hydrogen, and Si<sup>o</sup> stands for a silicon atom with dangling bonds. BH<sub>3</sub> molecules are assumed to be the precursors generated by thermal dissociation of B<sub>2</sub>H<sub>6</sub> gas<sup>9)</sup>. Reactions between the adsorbed species and hydrogen in the atmosphere are ignored. (2) Reflection

Si-HBH<sub>3</sub> --> Si-H + BH<sub>3</sub>

(3) Migration

Si-HBH<sub>3</sub> +Si-H --> Si-H + Si-HBH<sub>3</sub>

- (4) Recombination Si-HBH<sub>3</sub> + Si-HBH<sub>3</sub> --> 2Si-H + B<sub>2</sub>H<sub>6</sub>
- (5) Chemisorption  $Si^{\circ} + BH_3 SiBH + H_2$
- (6) Diffusion or  $Si^{\circ} + BH_{3} --> SiB + 3H$ SiBH --> Si-H + B(diffused) or SiB --> Si^{\circ} + B (diffused)

This reaction model is shown schematically in Fig. 6. Hydrogen which terminates the dangling bonds of silicon reduces the reactivity of the surface. Thus, BH<sub>3</sub> precursors can physisorb and migrate on the surface. When the BH<sub>3</sub> precursors meet the small number of silicon dangling bonds, they chemisorb and make Si-B bonds. Since the boron chemisorption on silicon is not self-limiting <sup>10</sup>, a surplus of dangling bonds causes continuous chemisorption and thus boron segregation when a nitrogen carrier gas is used. A hydrogen carrier gas probably plays an important role in terminating the dangling bonds, thus promoting the surface migration of adsorbed species and preventing excessive chemisorption of boron.

# 4. Conclusions

To clarify the role of the hydrogen carrier gas during Rapid Vapor-phase Doping (RVD), the surface of boron-doped layers were analyzed by XPS and FTIR-ATR. When a hydrogen carrier gas was used, the hydrogen termination of the surface was maintained during doping and the segregation of boron could be suppressed as compared with the case of nitrogen carrier gas. This hydrogen termination may promote the surface migration of the adsorbed species. The hydrogen carrier gas plays an important role in terminating the dangling bonds, thus preventing excessive chemisorption of boron.

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