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Phosphorus Direct Doping from Vapor Phase into Silicon for Shallow Junctions

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ABSTRACT

Characteristics of shallow n-type layers formed by direct doping of phosphorus from the vapor phase are presented. Shallow doped layers can be formed with depths less than 100 nm using PH_3 as a source gas and hydrogen as a carrier gas. It is found that the phosphorus concentration on the surface is constant with the doping time and is determined by the flow rate of PH_3 , not by the solid solubility. By varying the flow rate of PH_3 , the surface phosphorus concentration is controlled in the range of 10^{16} to 10^{19} cm^{-3} . These results show that impurities with low sticking coefficients to silicon and high vapor pressure, such as phosphorus, can be incorporated using this process, although the doping efficiency of phosphorus is low.

Increasingly smaller silicon large scale integrated circuits (LSIs) are produced by using advanced lithography. For achieving still faster and smaller devices, shallow junctions are indispensable. Ion implantation, which is widely used in LSI fabrication, has the disadvantage of the channeling effect of ions, especially in the case of boron. To overcome this problem, some new p-type doping processes have been reported.^{1,2} For n-type doping, low-energy arsenic ion implantation is effective for shallow junctions because the arsenic ion is so heavy that it reduces the channeling effect. Source and drain regions of high-performance n-channel metal oxide field effect transistors (MOSFETs) are usually fabricated by arsenic ion implantation.³ However, ion implantation has a basic drawback: annealing is necessary after implantation in order to activate the implanted ions and restore the crystal structure. This requirement is one reason that it is difficult to reduce the temperature during fabrication of LSIs. New doping processes are therefore required even for n-type shallow junctions. These processes should not suffer from channeling and damage, and they should provide controllability of impurity concentration.

One candidate for making shallow junctions is the diffusion method. Diffusion of phosphorus is usually performed by using POCl_3 or PH_3 at about 1000°C . This high temperature makes it difficult to form shallow junctions. In this conventional diffusion, the oxygen is needed to form $(\text{P}_2\text{O}_5)_2$ which acts as the diffusion source on the wafer. Hsueh reported other effects of oxygen to prevent segregation of phosphorus and variation of sheet resistance.⁵ Using this conventional method, solid-source diffusion of phosphorus occurs from the oxide layer to silicon, although the gaseous dopant is used. The surface phosphorus concentration is determined by the solid solubility which is a function of temperature, not by the flow rate of the source gas. This feature makes it easy to form doped layers with high concentration as in the gate electrode of MOS devices. However, it is difficult to form doped layers with relatively low concentration as in a base region of pnp bipolar devices.⁴

We have developed a new doping method called rapid vapor-phase doping (RVD) which is a kind of vapor source

diffusion.⁶⁻⁸ It is carried out in a hydrogen atmosphere using a doping gas such as PH_3 or B_2H_6 . This method has the following features: (i) the impurity atoms directly diffuse from the vapor phase into silicon, (ii) the impurity concentration is controlled by changing the flow rate of the source gas, (iii) hydrogen carrier gas has roles for cleaning the silicon surface before doping and for preventing unnecessary layers which include impurities during doping, and (iv) the doping time is shortened to a few minutes. We have shown that 30 nm p-type layers could be formed and that the surface boron concentration of the doped layers can be controlled by varying the flow rate of B_2H_6 .

In this paper, we give the results for phosphorus doping by RVD using PH_3 gas. By varying the doping time and the PH_3 flow rate, shallow n-type layers less than 100 nm deep were successfully formed. It was found the doping efficiency of phosphorus was lower than that of boron because of the low sticking coefficient.

Experimental

The experimental setup consists of a vertical-type atmospheric pressure chemical vapor deposition (APCVD) system.⁹ Eight 4 in. wafers can be loaded at once in this system. The CZ (100), p-type, 10- Ωcm wafers were used as substrates. The wafers were cleaned by rinsing in conventional chemical solutions. The final steps of this cleaning were in HF and deionized water. After the wafers were loaded into the chamber, the atmosphere was changed from nitrogen to hydrogen. The flow rate of hydrogen was 50 liter/min. The wafers were then heated on a graphite susceptor by RF induction to the doping temperature. The heating rate was $100^\circ\text{C}/\text{min}$. Next, PH_3 source gas was mixed with the hydrogen carrier gas and supplied to the chamber. Typical doping conditions are given in Table I. The hydrogen flow rate was maintained until the wafers were cooled to about 200°C after doping. The cooling rate was also about $100^\circ\text{C}/\text{min}$. The PH_3 gas was obtained as a 1% in hydrogen mixture, which was further diluted by mixing with the carrier gas. The doping temperature was 900°C , and the doping time and flow rate of PH_3 were varied. The doping temperature was determined to obtain a uniform doping across the

Table I. Doping conditions for rapid vapor phase doping.

H ₂ flow rate	50 liter/min
PH ₃ (1%) flow rate	30 to 200 ml/min
Doping temperature	900°C
Doping time	10 to 30 min

wafer and the repeatability of the data. At lower temperatures, the variation of sheet resistance across the wafer was so large that it was difficult to characterize the doped layer.

The phosphorus profiles were measured by secondary ion mass spectroscopy (SIMS) with the Hitachi IMA-3000 spectrometer in which the primary ion was 13 keV C_s⁺. The carrier profiles and the sheet resistance were measured by differential Hall effect measurements and the four-probe method.

Results

Dependence of the doping characteristics on the flow rate of PH₃.—Secondary ion mass spectroscopy (SIMS) profiles for various PH₃ flow rates are shown in Fig. 1. The flow

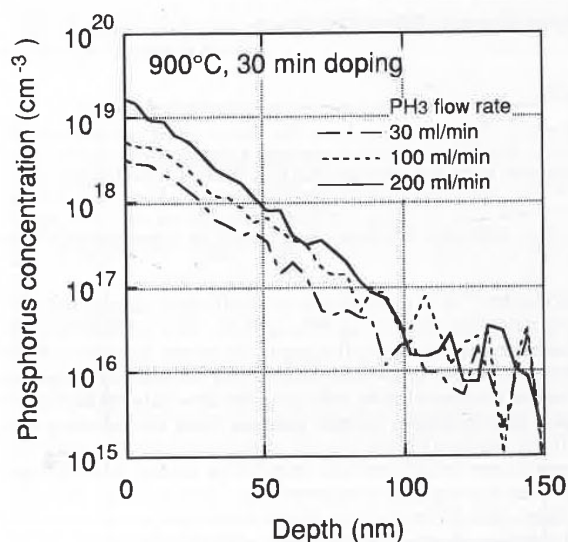


Fig. 1. SIMS profiles of phosphorus. Doping was carried out at 900°C for 30 min. PH₃ flow rate was varied from 30 to 200 ml/min.

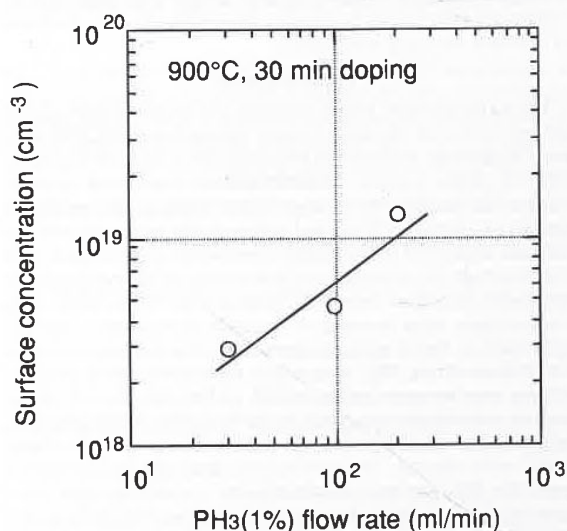


Fig. 2. Dependence of surface phosphorus concentration on PH₃ flow rate.

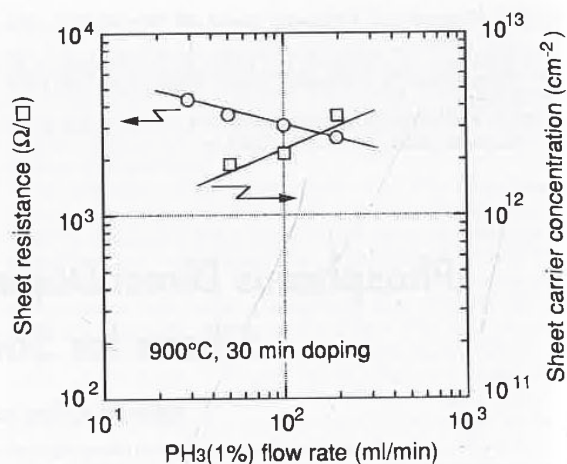


Fig. 3. Dependence of sheet resistance and carrier concentration on PH₃ flow rate.

rates of PH₃ were 30, 100, and 200 ml/min. The doping time was 30 min. Shallow phosphorus-doped layers were formed about 100 nm deep. The phosphorus concentration on the surface was controlled by the flow rate of PH₃. As shown in Fig. 2, it changes from 3.0×10^{18} to $1.3 \times 10^{19} \text{ cm}^{-3}$ as the flow rate of PH₃ is increased from 30 to 200 ml/min. These values are lower than the solid solubility of phosphorus at 900°C, $3 \times 10^{20} \text{ cm}^{-3}$.⁹ These results show that RVD provides various impurity concentrations below the solid solubility by changing the flow rate of the source gas. This feature is useful for making the base region of pnp bipolar and the extended source and drain region of n-channel MOS transistors. Under these experimental conditions, the partial pressure of PH₃ in the atmosphere is not sufficient to form highly doped layers, such as source and drain, and re-evaporation of phosphorus may be occurring. Hence, the surface phosphorus concentration is determined by the difference between the number of adsorbed phosphorus on silicon and that of re-evaporated ones. By increasing the flow rate of PH₃ and supplying sufficient phosphorus to reduce the effect of re-evaporation, the surface phosphorus concentration would be at solid solubility. The sheet resistance and carrier concentration of the doped layers are

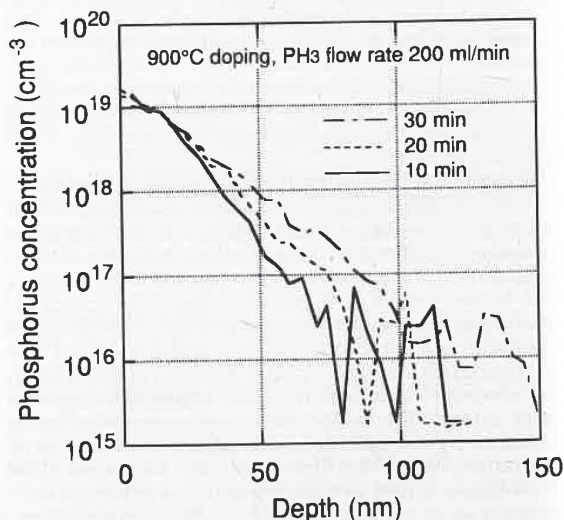


Fig. 4. SIMS profiles of phosphorus. Doping was carried out at 900°C, PH₃ flow rate of 200 ml/min. The doping time was varied from 10 to 30 min.

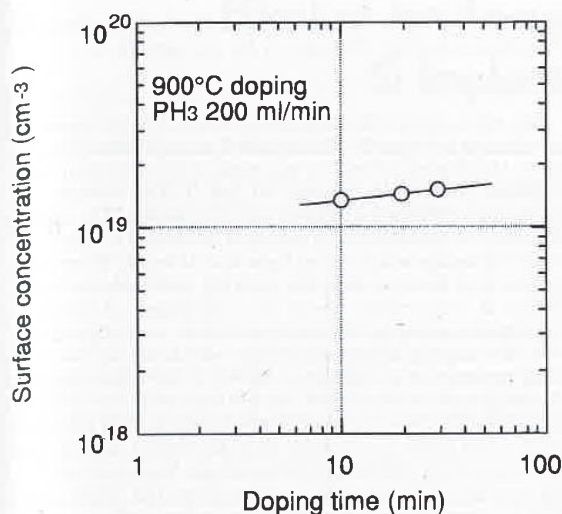


Fig. 5. Dependence of surface phosphorus concentration on doping time.

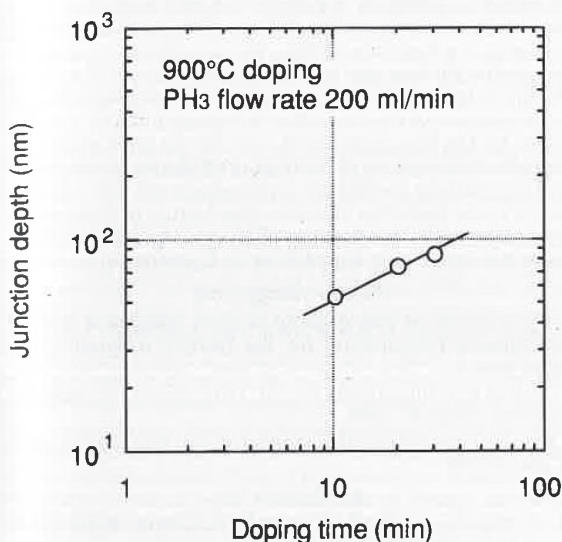


Fig. 6. Junction depth of phosphorus doped layer (defined as the point where the phosphorus concentration is $1 \times 10^{17} \text{ cm}^{-3}$) vs. doping time.

shown in Fig. 3. For a sample with PH_3 flow rate of 30 ml/min, it was difficult to measure the carrier concentration because of such small amounts of carriers. The sheet resistance, a few $\text{k}\Omega/\square$ are suitable for the intrinsic base region of a bipolar LSI. By increasing the flow rate of PH_3 , the carrier concentration increased as well as the phosphorus concentration.

Dependence of the doping characteristics on doping time.—SIMS profiles of samples with various doping times are shown in Fig. 4. The flow rate of PH_3 was 200 ml/min. The junction depth increases with doping time, but the surface phosphorus concentration is almost constant at $1.3 \times 10^{19} \text{ cm}^{-3}$ as shown in Fig. 5. In boron doping, the surface boron concentration increased with the doping time.⁷ These results show the difference in the characteristics of phosphorus and boron and are discussed later. The junction depth is defined as the point where the phosphorus concentration is $1 \times 10^{17} \text{ cm}^{-3}$, and this is plotted in Fig. 6. The junction depth increases linearly with the square root of the doping time. These characteristics are identical to those

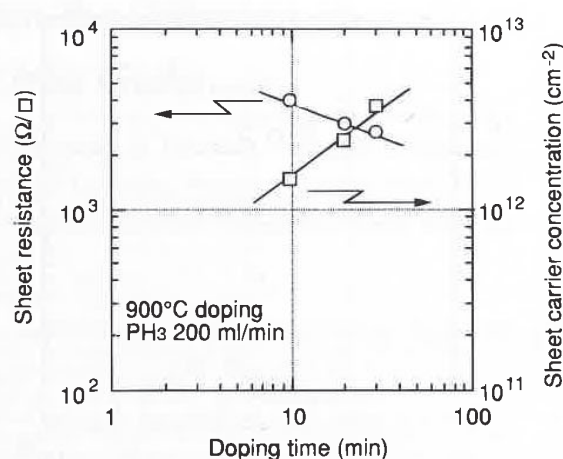


Fig. 7. Dependence of sheet resistance and carrier concentration on doping time.

of conventional diffusion except that the surface concentration is less than the solid solubility. For future LSIs, it will be necessary to form still shallower junctions below 50 nm which are obtained by reducing the doping time. In our experimental setup, however, the slow cooling rate after doping due to a large thermal mass of the susceptor causes an excessive impurity diffusion. A doping system with lamp annealing apparatus is preferred to reduce thermal budget and to form shallower junctions.⁸ The sheet resistance and the sheet carrier concentration of the doped layers are shown in Fig. 7. Since the concentration of phosphorus on the surface is almost constant, the increase in carrier concentration is caused by an increase in junction depth.

Discussion

Process simulation.—Since the phosphorus concentration on the surface is constant as shown in Fig. 5, the diffusion profile can be simulated by the solution of the following differential equation (Fick's law of diffusion)

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \quad [1]$$

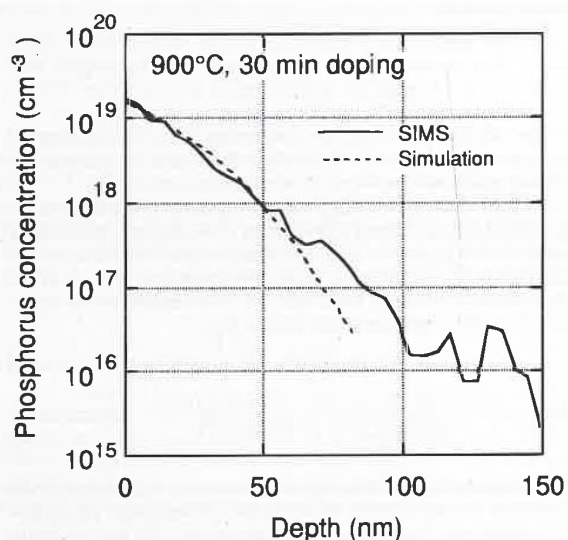


Fig. 8. Simulated phosphorus doping profile. The doping time was 30 min and temperature was 900°C. The surface phosphorus concentration is maintained at $1.3 \times 10^{19} \text{ cm}^{-3}$ according to the experimental SIMS data.

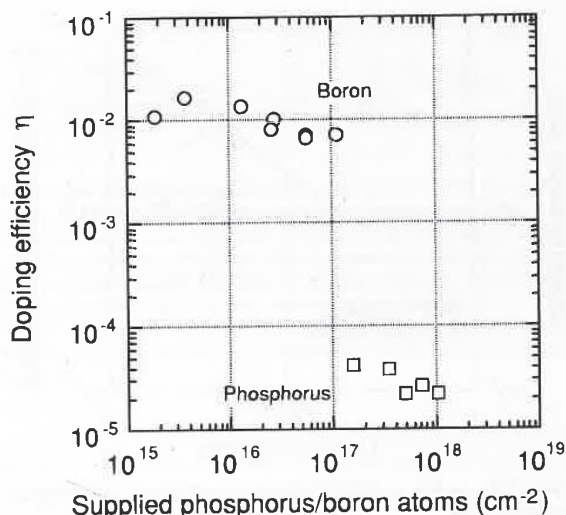


Fig. 9. Phosphorus and boron doping efficiency as a function of the number of supplied atoms.

When the initial condition is $C(x, 0) = 0$, and the boundary conditions are $C(0, t) = C_s$ and $C(\infty, t) = 0$, the solution of the above equation is a complementary error function

$$C(x, t) = C_s \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad [2]$$

where C_s is the surface concentration (in atom/cm³), D is the phosphorus diffusion constant (in cm²/s), x is the distance from the surface (in cm), and t is the doping time (in seconds). The value of the diffusion constant in the literature¹⁰ was used. The results for the calculation including an actual SIMS profile are shown in Fig. 8. The RVD conditions were 900°C, 30 min with a PH₃ flow rate of 200 ml/min. The phosphorus concentration on the surface, C_s , was maintained at 1.3×10^{19} cm⁻³ in the simulation according to the actual SIMS data which is shown in Fig. 1. The simulated curve provides a good fit to the SIMS profile. This shows that the profile follows a complementary error function distribution. These results show that the phosphorus doping by RVD is a diffusion with constant surface concentration.

Doping efficiency.—PH₃ gas easily dissociates below 400°C into hydrogen and compounds of hydrogen and phosphorus.¹¹ Under the experimental temperature, 900°C, it is believed that PH₃ gas completely dissociates into hydrogen and phosphorus. By assuming this, the number of phosphorus atoms introduced into the chamber can be calculated and used in the following calculation.

The phosphorus doping efficiency was investigated as described below. Using the density (1.40 kg/m³), molecular weight (34.0 g/mol) of PH₃ gas and Avogadro's number, we calculated the number of phosphorus atoms N in 1 ml of PH₃ gas (diluted with hydrogen to 1%) and the total number of supplied phosphorus atoms N_{total}

$$N = 2.48 \times 10^{17} \quad (\text{atom/ml}) \quad [3]$$

$$N_{\text{total}} = \frac{N \times (\text{PH}_3 \text{ flow rate}) \times (\text{doping time})}{(\text{surface area of susceptor})} \quad (\text{atom/cm}^2) \quad [4]$$

To compare with the integrated intensity I_{total} of the SIMS spectrum (in atom/cm²), the number of supplied phosphorus atoms was divided by the surface area of the graphite susceptor in the reaction chamber. The size of the susceptor

was 430 mm diameter and 10 mm thick. Therefore, the phosphorus doping efficiency η for our system is

$$\eta = I_{\text{total}}/N_{\text{total}} \quad [5]$$

This value shows the ratio of the amount of incorporated phosphorus atoms and the supplied phosphorus atoms. In Fig. 9, the doping efficiency η is plotted as a function of the supplied phosphorus atoms (in cm⁻²). For comparison, boron data obtained at 900°C are also shown. The doping efficiency of phosphorus is constant between 10^{-5} and 10^{-4} . These values are much lower than that of boron. From these results, it is derived that the sticking coefficient of phosphorus is lower than boron in a hydrogen atmosphere. Phosphorus atoms do not easily adhere to a silicon surface. This low doping efficiency is also explained by the high vapor pressure of phosphorus. At 900°C, the vapor pressure of phosphorus is above 100 Pa, but that of boron is below 10^{-6} Pa.¹² This high vapor pressure indicates that phosphorus is more stable as a vapor than as a solid. Using RVD, impurities with high vapor pressure can be doped into silicon because the impurity is doped from the vapor phase without forming an impurity layer on the surface.

Conclusions

Characteristics were obtained for shallow phosphorus-doped layers formed by rapid vapor-phase doping (RVD). Phosphorus atoms are successfully doped into silicon and shallow junctions less than 100 nm deep were formed. By changing the flow rate of PH₃, the phosphorus concentration on the surface was controlled from 3.0×10^{18} to 1.3×10^{19} cm⁻³. It was found that the phosphorus concentration on the surface was independent of doping time and is determined by the flow rate of PH₃, not by the solid solubility. From the calculations of the doping efficiency, it was found that the sticking coefficient of phosphorus on a silicon surface is lower than that of boron. One feature of RVD is that impurities with low sticking coefficients can be doped because the impurity is doped directly from the vapor phase.

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