

Phosphorus Diffusion from Doped Polysilicon through Ultra-Thin SiO₂ Films into Si Substrates

Yumiko Tsubo, Yukio Komatsu, Kazumasa Saito, Satoru Matsumoto*,
 Yoshiyuki Sato¹, Ikunao Yamamoto² and Yoshifumi Yamashita²

Department of Electrical Engineering, Keio University, Hiyoshi, Yokohama 223-8522, Japan

¹NTT Laboratories, Midori-cho, Mushashino, Tokyo 180-8585, Japan

²Okayama University, Faculty of Engineering, Tsushima-cho, Okayama 700-8530, Japan

(Received June 26, 2000; accepted for publication July 28, 2000)

The diffusion of phosphorus into ultra-thin oxides from phosphorus-doped polysilicon sources was studied. The two-boundary diffusion model can be applied to the diffusion of phosphorus in ultra-thin oxides, and the diffusivity and segregation coefficient were obtained based on the model. The dependence of the diffusivity on oxide thickness and drive-in ambients was investigated. The enhanced diffusion, which has been observed for boron diffusion in ultra-thin oxides, was not observed for phosphorus diffusion. For the diffusion in dry O₂ and wet O₂ ambients, the enhanced diffusion due to high phosphorus concentration in the polysilicon was observed.

KEYWORDS: phosphorus diffusion, ultra-thin oxides, doped polysilicon, Si, segregation coefficient

1. Introduction

In deep sub-micron gate metal-oxide-semiconductor field effect transistors (MOSFETs), a high-quality gate oxide less than 3 nm thick is required.¹⁾ However, impurity penetration through such a thin gate oxide to the channel region becomes a serious problem. That is, high-temperature annealing for activation of dopants in the doped polysilicon gates causes dopant diffusion from the gates. Diffusion of boron into thermally grown SiO₂ from a doped polysilicon source has been found to be dependent on drive-in ambients (in H₂, wet O₂) and oxide thickness (<80 Å).²⁾ To explain this behavior, Fair proposed the diffusion model of boron in SiO₂.³⁾

On the other hand, few studies have been performed on phosphorus diffusion through a thin gate oxide because the diffusivity of phosphorus is smaller than that of boron in SiO₂. Recently, it has been reported that hole trap formation at the phosphorus-doped polysilicon/SiO₂ interface is due to phosphorus diffusion into SiO₂ from the doped polysilicon gates⁴⁾ and hole traps cause excessive gate oxide leakage currents.⁵⁾ Therefore, it is necessary to investigate the diffusion of phosphorus into ultra-thin oxides from phosphorus-doped polysilicon sources. In this study, the diffusivity and segregation coefficient of phosphorus were determined in ultra-thin oxides and the dependence of the diffusivity on oxide thickness and drive-in ambients was also investigated.

2. Experimental

The substrates used for the present study were p-type Czochralski (CZ)-Si(100) wafers of 10–20 Ω·cm resistivity. The gate oxides with a thicknesses of 27, 32 and 42 Å were thermally oxidized at 800°C in dry O₂ followed by deposition of 3000 Å phosphorus-doped polysilicon films (P concentration: 1.8×10^{20} cm⁻³) from Si₂H₆/PH₃/He mixture gas at 515°C. Diffusion was carried out in dry N₂, dry O₂, and wet O₂ ambients at 1000–1100°C. To avoid out-diffusion of phosphorus from the polysilicon into the annealing ambient, the polysilicon surface was covered with chemical vapor deposition (CVD) SiO₂ (1000 Å) before annealing.

The SiO₂ thickness was determined using an ellipsometer. The oxide thickness on the polysilicon after diffusion in dry O₂ and wet O₂ ambients was determined by DEKTAK. The junction depth was measured by staining after angle lapping. The concentration profiles of phosphorus were obtained in silicon using a spreading resistance profiler (SRP).

3. Results and Discussion

The two-boundary diffusion model⁶⁾ was applied to this study. The model is expressed with two Fick's diffusion equations and the following boundary and initial conditions.

$$\frac{\partial C_{\text{SiO}_2}}{\partial t} = D_{\text{SiO}_2} \frac{\partial^2 C_{\text{SiO}_2}}{\partial x^2} \quad (-d_{\text{ox}} < x < 0) \quad (1)$$

$$\frac{\partial C_{\text{Si}}}{\partial t} = D_{\text{Si}} \frac{\partial^2 C_{\text{Si}}}{\partial x^2} \quad (0 < x < \infty) \quad (2)$$

$$C_{\text{SiO}_2} = C_{\text{Si}} = 0 \quad (t \leq 0) \quad (3)$$

$$C_{\text{SiO}_2}(-d_{\text{ox}}, t) \equiv C_{\text{poly}}/m \quad (t > 0) \quad (4)$$

$$mC_{\text{SiO}_2}(0, t) = C_{\text{Si}}(0, t) \quad (t > 0) \quad (5)$$

$$D_{\text{SiO}_2} \frac{\partial C_{\text{SiO}_2}}{\partial x} = D_{\text{Si}} \frac{\partial C_{\text{Si}}}{\partial x} \quad (\text{at } x = 0, \text{ for } t > 0) \quad (6)$$

$$C_{\text{Si}}(x, t) \rightarrow 0 \quad (\text{as } x \rightarrow \infty), \quad (7)$$

where x is the distance from the SiO₂/Si substrate interface, t the diffusion time, and d_{ox} the oxide thickness. D and C are the phosphorus diffusivity and concentration, and the subscript SiO₂ and Si denote the region of oxide and silicon, respectively. The phosphorus concentration in the polysilicon, C_{poly} , is assumed to be constant because of a large diffusivity along grain boundaries in the polysilicon.⁷⁾ The constant m is the segregation coefficient of phosphorus at the SiO₂/Si substrate interface. Here, m at the polysilicon/SiO₂ interface is assumed to be equal to that at the SiO₂/Si substrate interface. The solution in silicon is⁶⁾

$$C_{\text{Si}} = m(1 - \alpha) \frac{C_{\text{poly}}}{m} \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc} \left[\frac{(2n+1)d_{\text{ox}}}{2\sqrt{D_{\text{SiO}_2}t}} + \frac{x}{2\sqrt{D_{\text{Si}}t}} \right]. \quad (8)$$

Here, $\alpha \equiv (m - r)/(m + r)$ and $r \equiv \sqrt{D_{\text{SiO}_2}/D_{\text{Si}}}$. For $d_{\text{ox}}/2\sqrt{D_{\text{SiO}_2}t} > 0.7$ and $d_{\text{ox}} > rx$, eq. (8) can be approxi-

* Author to whom all correspondence should be addressed. E-mail address: matumoto@elec.keio.ac.jp

mated only by the first term of the series.⁷⁾ The constant r can be estimated by varying the diffusion time and measuring the change in the junction depth, with the other factors being kept constant. In addition, eq. (8) reduces to⁸⁾

$$\frac{d_{\text{ox}}}{\sqrt{t}} + r \frac{x_j}{\sqrt{t}} = \text{constant}. \quad (9)$$

The value r at each temperature can be obtained from the gradient in the relationship between $d_{\text{ox}}/\sqrt{t}$ vs $x_j/\sqrt{t}$. The segregation coefficient can be derived from eq. (8) by calculation using the obtained D_{SiO_2} since x_j is the junction depth and C_{Si} is the substrate concentration. In the above procedure, the values of D_{Si} were used from published data.⁹⁾

Prior to using the two-boundary diffusion model, it was necessary to ascertain that the model can also be applied to the diffusion of phosphorus in ultra-thin oxides (<50 Å). Figure 1 shows the relationship between junction depth and the square root of diffusion time in N_2 at 1075°C. It was found that the parabolic law was satisfied at each oxide thickness and that the diffusion of phosphorus in ultra-thin oxides from the doped polysilicon was accounted for based on the two-boundary diffusion model. In Fig. 1, all of the lines had the same slope, which means that either the diffusivities for the three different thicknesses of oxides used were the same at this temperature, or the diffusivity is independent of oxide thickness. For other annealing temperatures, results similar to those shown in Fig. 1 were obtained.

The diffusivity and segregation coefficient were estimated using the two-boundary diffusion model. Figures 2 and 3 show the temperature dependence of the diffusivities and segregation coefficients of phosphorus in SiO_2 in N_2 ambient, respectively. In these figures, data for thicker oxides (200–400 Å) from Matsuura *et al.*⁷⁾ are also shown. In Fig. 2, the activation energy of diffusion is closer to their result. It

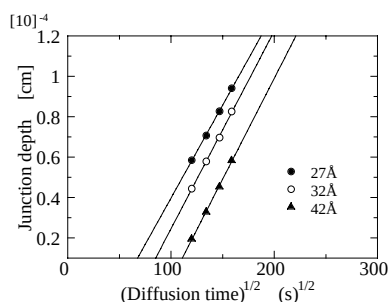


Fig. 1. Relationship between junction depth and the square root of diffusion time in N_2 ambient at 1075°C.

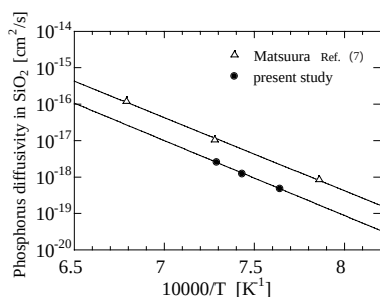


Fig. 2. Temperature dependence of phosphorus diffusivities in SiO_2 in N_2 ambient.

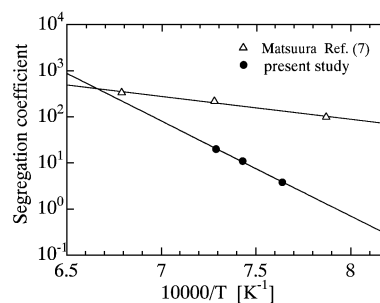


Fig. 3. Temperature dependence of segregation coefficients.

is considered that the reaction of phosphorus and oxide in thicker oxides is the same as that in ultra-thin oxides. In contrast to the case of boron diffusion, where enhancement of diffusion is observed with decrease in oxide thickness, no enhancement in phosphorus diffusion was observed in the present results.

Regarding the segregation coefficient, different activation energies were obtained as shown in Fig. 3. The present data of ultra-thin oxides are lower than those of thicker oxides below 1100°C. It seems that a compositionally graded interface with a Si-rich region influences segregation because of the presence of ultra-thin oxides. The resulting phosphorus diffusivity and segregation coefficient can be expressed by

$$D_{\text{SiO}_2} = 2.46 \times 10^{-3} \exp(-4.08 \text{ eV}/kT) \quad (10)$$

$$m = 2.39 \times 10^{16} \exp(-4.10 \text{ eV}/kT). \quad (11)$$

The diffusion model of phosphorus diffusion in ultra-thin oxides from phosphorus-doped polysilicon will be discussed briefly. If only phosphorus atoms diffuse in SiO_2 via peroxy linkage defect (PLD) as in boron diffusion, enhanced diffusion of phosphorus in ultra-thin oxides with numerous PLDs must be observed. However, the phosphorus diffusion was slightly influenced by the quality of the ultra-thin oxides, enhancement was not observed, and the quality of ultra-thin oxides affected segregation. Therefore, the diffusion model of boron in SiO_2 can not account for the phosphorus diffusion in SiO_2 .

Ghoshtagore identified two diffusing species in SiO_2 .¹⁰⁾ One is a solid P_2O_5 and the other is a fixed composition liquid ($x\text{P}_2\text{O}_5 \cdot y\text{SiO}_2$). The activation energies of the diffusion of these species are 4.44 ± 0.23 (eV) and 1.62 ± 0.03 (eV), respectively. Considering only the diffusion activation energy, the diffusing species in this study is suggested to be P_2O_5 . If we assume that P_2O_5 diffuses in SiO_2 , this species may be slightly influenced by the Si-rich region in ultra-thin oxides during diffusion.

Figure 4 shows the relationship between junction depth and the square root of diffusion time in dry N_2 , dry O_2 and wet O_2 ambients. In dry O_2 and wet O_2 ambients, the significantly enhanced phosphorus diffusion into SiO_2 was observed, but the parabolic law was not satisfied. Figure 5 shows the carrier concentration profiles from the surfaces of these samples to Si substrates by SRP. Even with a short diffusion time in dry O_2 and wet O_2 ambients, very high carrier concentration profiles in silicon substrate were obtained. The two-boundary diffusion model could not predict the profiles in silicon after the diffusion in dry O_2 and wet O_2 ambients as shown Fig. 5.

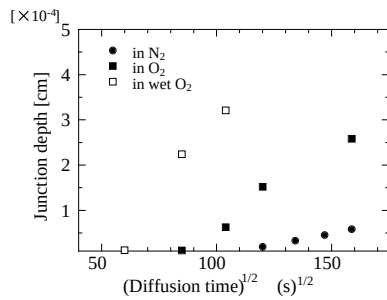


Fig. 4. Relationship between junction depth and the square root of diffusion time in dry N_2 , dry O_2 and wet O_2 ambients at 1075°C for oxide thickness of $42\text{ \AA}$.

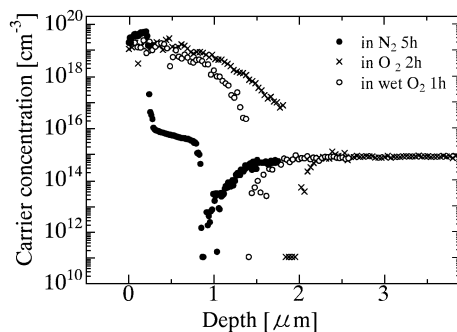


Fig. 5. Carrier concentration profiles from sample surfaces to Si substrates in dry N_2 , dry O_2 , wet O_2 ambients at 1075°C by SRP.

This enhancement seems to be attributed to the melt-through diffusion that results from the formation of glassy compounds by a reaction of phosphorus with SiO_2 due to high phosphorus concentration in the polysilicon.⁸⁾ These samples formed very thick oxides on the polysilicon (or Si substrates) after the diffusion in dry O_2 and wet O_2 ambients. Polysilicon was consumed to form the oxides resulting in a very high phos-

phorus concentration in the polysilicon.¹¹⁾

4. Conclusions

The two-boundary diffusion model can be applied to the diffusion of phosphorus in ultra-thin oxides from a doped polysilicon. The enhanced diffusion, which has been seen in boron diffusion in ultra-thin oxides, was not observed for the phosphorus diffusion. This means that the diffusion model based on peroxy linkage defects cannot be applied to the phosphorus diffusion in SiO_2 . For the diffusion in dry O_2 and wet O_2 ambients, an enhanced diffusion due to high phosphorus concentration in the polysilicon was observed.

Acknowledgements

The authors would like to thank Professor T. Matsuura for many valuable discussions.

- 1) H. P. Wong: *ULSI Devices*, eds. C. Y. Chang and S. M. Sze (John Wiley & Sons, New York, 2000) Chap. 3.
- 2) T. Aoyama, K. Suzuki, H. Tashiro, Y. Toda, T. Yamazaki, Y. Arimoto and T. Ito: *J. Electrochem. Soc.* **140** (1993) 3624.
- 3) R. B. Fair: *J. Electrochem. Soc.* **144** (1997) 708.
- 4) Y. Tkachev, V. S. Lysenko and V. I. Turchanikov: *Phys. Status Solidi (a)* **140** (1993) 163.
- 5) M. K. Khan, F. Zdancewicz and A. Bhalla: *Semicond. Int.* **97/98** (1997) 100.
- 6) C. T. Sah, H. Sello and D. A. Tremere: *J. Phys. Chem. Solids* **11** (1959) 288.
- 7) T. Matsuura, J. Murota, N. Mikoshiba, I. Kawashima and T. Sawai: *J. Electrochem. Soc.* **138** (1991) 3474.
- 8) K. Shimakura, T. Suzuki and Y. Yadoiwa: *Solid-State Electron.* **18** (1975) 991.
- 9) W. E. Beadle, J. C. C. Tsai and R. D. Plummer: *Quick Reference Manual for Silicon Integrated Circuit Technology* (John Wiley & Sons, New York, 1985) pp. 6–31.
- 10) R. N. Ghoshtagore: *Thin Solid Films* **25** (1975) 501.
- 11) T. Kamins: *Polycrystalline Silicon for Integrated Circuit Applications* (Kluwer Academic Publishers, London, 1988) p. 128.