Reaktor, Vol.6 No. 1, Juni 2002, Hal.: 35-39

STUDY OF SOLID PLANAR SOURCE FOR PHOSPHORUS DIFFUSION PROCESS ON SEMICONDUCTOR DEVICES FABRICATION

S Widodo *)

Abstract

The sourcing lifetimes, microstructural stability, and diffusion performance of a new solid planar phosphorus source for silicon doping were investigated in the temperature range 900^0 – 1100^0C. The source wafers were highly porous ceramic wafers containing 25 weight percentage (w/o) SiP_2O_7 as the "active" component in an inert refractory binder matrix. The microstructural stability and thermogravimetric analysis (TGA) results indicated the structural integrity and sourcing ability of this material at temperatures of at least 1050^0C. Theoretical lifetimes of 260 and 3400 hr at 1000^0 and 900^0C, respectively, have been predicted from the TGA results. Experimental data relating sheet resistance, junction depth, and diffusion coefficient for silicon wafers doped using these source wafers are presented. Special material handling procedures are also described.

Keywords : Diffusion process, solid phosphorus source, SiP_2O_5 , semiconductor devices.

Introduction

The results of previous studies concerning the diffusion performance of boron nitride as a p-type dopant source for silicon technology have shown that planar sources offer several significant adavantages over carrier gas diffusion systems using liquids and gases (1,2). The benefits of planar diffusion sources have been previously reported by Goldsmith et al. (3), and it is towards this end that the development and evaluation of the new phosphorus source was aimed. In addition to the benefits presented by Goldsmith et al., there is the added benefit of having a source material which has no toxic or corrosive by-products.

In using boron nitride as a source, the surface is oxidized (activated) to form B_2O_3, and the boron is vaporized and transported as an oxide to the silicon surface. An analogous refractory compound of phosphorus which can be fabricated into a ceramic wafer was not available to emulate the boron nitride technology. However, Murata (4) demonstrated that silicon pyrophosphate, SiP_2O_7, decomposes to SiO_2 and P_2O_5 partial pressure being adequate to effectively dope silicon in the temperature range 850^0 - 1100^0C.

In this paper the discussion is confined to a wafer composition of 25 w/o SiP_2O_7 in an inert matrix material as manufacturered by The Carborundum Company (1) and designated as Phosphorus Planar Diffusion Source Grade PH-1050.

Experimental

In order to establish that the SiP_2O_7 phase was compatible (chemical inert) wih the binder phase, the phases present after long-term annealing at temperature encompassing the projected use temperatures. To establish minimum sourcing lifetimes, the loss of P_2O_5 was monitored as a function of time at projected use temperatures using a semimicro thermogravimetric analysis (TGA) apparatus. The samples were suspended in a fused silica tube in flowing nitrogen (0.20 SLPM) and heated rapidly from 350^0C to the desired test temperature. The preheat at 350^0C was necessitated by the reversible phase transition in the wafer discussed in more detail below.

All electrical measurements and diffusion experiments were performed with silicon wafers. The silicon wafers were 3 inches, boron-doped (111) oriented substrates with resistivities of 1 – 10 ohm-cm. The phosphorus wafers were 3 inches in diameter and 381 ± 15 μm thick. The resistivity data were obtained using Allesi Four Point Probe tester, current source DC 61886C-type of Hewlett Packard with scale 0.01 – 100 mA ± 0.1% of full scale current source and 0 – 2 V ± 0.5% of full scale digital voltmeter of Voltmeter PM 2525 Phillips DMM. Sheet resistance data, ρs, were measured by probing the silicon wafer in four quadrants plus the center and then averaging; ρs indicates the average of the five readings. The junction depth was measured using Spreading Resistance System.

The surface concentration of electrically active phosphorus was determined by use of

*) Research Center for Electronics & Telecommunications
Indonesian Institute of Sciences (PPET-LIPI)
Jl. Cisitu no. 21/154 D Bandung 40135
Tel. : 62-22-2504661, fax : 62-22-2504659, e-mail : widodo@telkoma.lipi.go.id

incremental sheet resistance technique (5). All the diffusion experiments were done in an N_2 ambient with a spacing of 0.318 cm from source to silicon wafer (Fig.1).

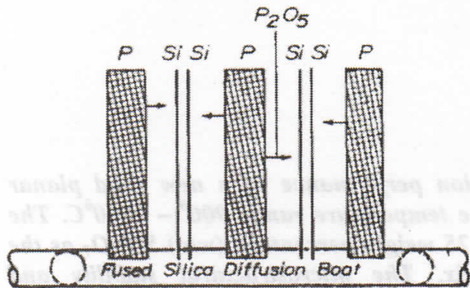

Fig. 1 Diffusion boat schematic with the solid phosphorus source

Results and Discussion

During the annealing treatments except for the SiO_2 - rich glass which resulted from the decomposition of SiP_2O_7 to yield P_2O_5 vapor. The persistence of a very small amount of the $Si_2P_2O_9$ phase until nearly all of the SiP_2O_7 had decomposed indicates that the $Si_2P_2O_9$ phase is an intermediate reaction product in the decomposition of SiP_2O_7. However, no reactions between these SiO_2 containing phases and the binder phase were observed.
The results of isothermal TGA experiments at 900^0 and 1000^0C are presented in Fig.2.

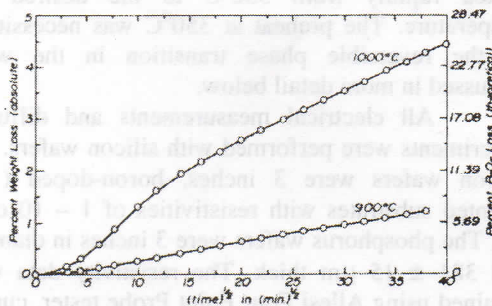

Fig.2. Weight loss vs. $(Time)^{1/2}$ for PH-1050 wafers at 900^0 and 1000^0C

In this figure the weight loss data are also plotted as percentage of available P_2O_5, the P_2O_5 combined with SiO_2 to form SiP_2O_7. After an early nonparabolic period at both temperatures, the weight loss vs. $(time)^{1/2}$ curves become linear indicating, to a first approximation, a diffusion-controlled reaction in a stable microstructure.

The main value of these TGA results is in predicting the usefulness of the wafers as sources and, specifically, to predict minimum useful lifetimes. In Fig. 3 the TGA data for a period of 100 hr for the 25 w/o SiP_2O_7 composition are presented. By fitting a straight line to the latter portion of this curve, the weight loss can be expressed as

$$W_D = 0.14\, t^{1/2} \qquad (1)$$

where W_D is the percentage weight decrease in flowing N_2, and t is time in minutes. By substituting the theoretically available P_2O_5 percentage for W_D, one arrives at a minimum lifetime of 260 hr, assuming no change in the rate constant. Doing the same exercise for the 900^0C data yields a minimum lifetime of 3400 hr. It should be pointed out that these are minimum lifetime estimates since they are based on TGA results in flowing nitrogen. They probably low compared to those experienced in a typical diffusion environment. In a diffusion system the source wafer resides in a relatively stagnant vapor environment which has a P_2O_5 partial pressure near the equilibrium P_2O_5 partial pressure of the wafer, thus reducing the driving force for dissociation. In the TGA environment the evolved P_2O_5 is continuously swept away resulting in a P_2O_5-poor vapor phase and a large driving force for dissociation. This effect has been experimentally verified by monitoring the amount of SiP_2O_7 remaining in wafers subjected to long-teerm TGA experiments and long-term diffusion heat-treatments at the same temperature.

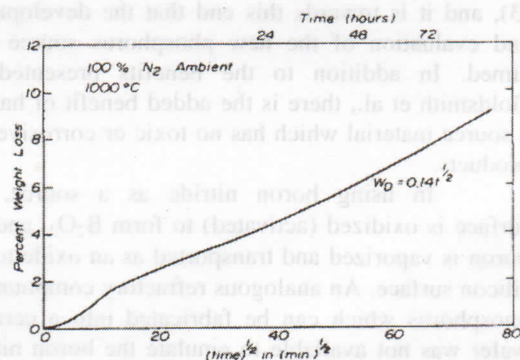

Fig 3. Weight loss vs. $(Time)^{1/2}$ for PH-1050 wafers at 1000^0C to 100 hr

The longest experiment to monitor sourcing effectiveness was for the 25 w/o SiP_2O_7 composition at 1000^0C which was still sourcing effectively after 216 hr of continuous usage.

The N_2 gas flow rate was found not to be a mojor factor in diffusion performance. The results of sheet resistance dependence on N_2 flow rate are shown in Fig. 4 for a 30 min diffusion at 1050^0C.

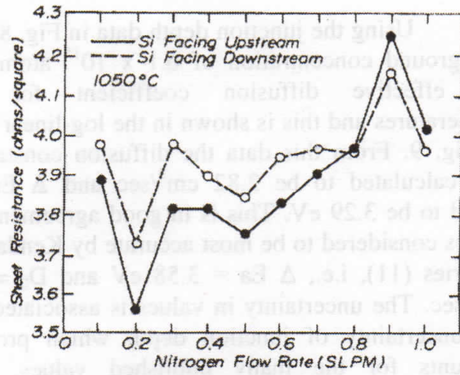

Fig. 4. Sheet resistance vs. flow rate

The sheet resistance tends to increase as flow rate increases which would seem to indicate that the dopant specie, P_2O_5, is being swept out by the N_2. Umder conditions of no N_2 flow, the sheet resistance is increased by nearly one order of magnitude. This was accompanied by an increase of phosphorus glass transfer and, consequently, could possibly be due to some Si-P surface phase (6), although no difficulty was experienced in glass removal.

Solmi et al. (7) have reported that in a $POCl_3$ system anomalous results have been observed when Si-P or SiO_2-P_2O_5 phases have been formed on or at the silicon interface. The change in sheet resistance accompanied by an increase in dopant glass suggest that Si-P or SiO_2-P_2O_5 phases have formed and are responsible for the observed anomalous behavior.

The sheet resistance data that were obtained for the range 950^0 – 1100^0C are shown in Fig. 5 . The data compare favorably with other phosphorus sources such as $POCl_3$ (8) and PH_3 (9).

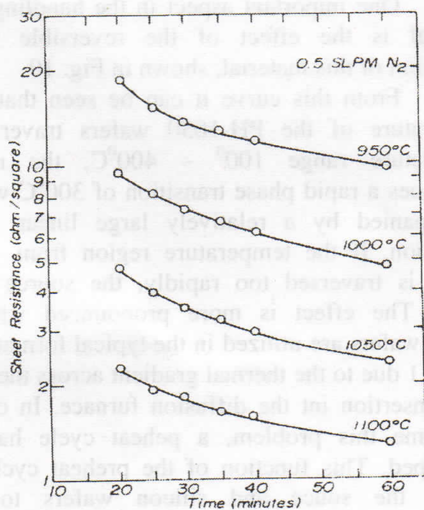

Fig. 5. Sheet resistance vs. time and temperature using 25/75 source

Figure 6 shows sheet resistance as a function of $(t)^{1/2}$ at 1050^0C. The graph is a straight line, as expected, and, hence, ρs as a function of $(t)^{1/2}$ at 1050^0C. The graph is a straightline, as expected, and, and, hence , ρ_S α $1/(t)_{1/2}$, except at lower sheet resistance where ρ_S increases with $(t)^{1/2}$ which might be attributed to the Si-P phase formation. The junction depth, X_j can be shown to be $(t)^{½}$ dependent for a one-step process

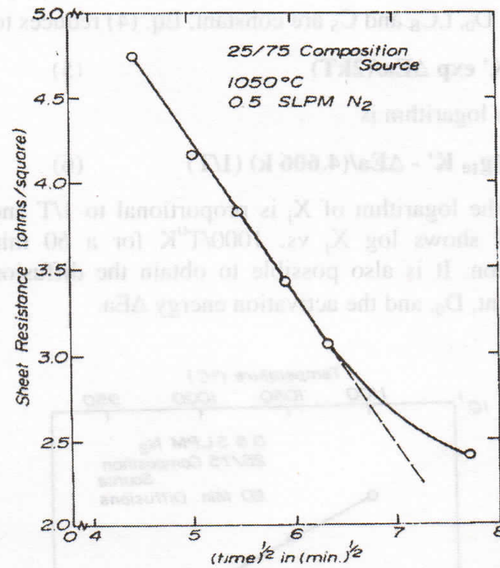

Fig. 6. Sheet resistance vs. $(time)^{1/2}$ for constant source diffusion

$$X_j = 2\,(Dt)^{1/2}\ \mathrm{erfc}^{-1}\,(C_B/C_S) \qquad (2)$$

where D is the diffusion coefficient (cm^2/sec), t is time (seconds), C_B is background concentration (atoms/cm^3), and C_S is surface concentration (atoms/cm^3). The graph of X_j vs. $(t)^{1/2}$ for 1000^0C is shown in Fig. 7.

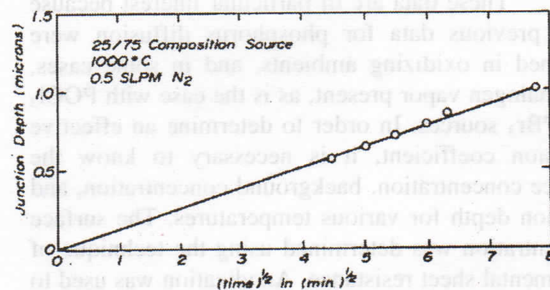

Fig.7. Junction depth vs. $(time)^{1/2}$ for constant source diffusion.

The straight line relationship indicates that phosphorus obeys the complementary error function distribution. It is also possible to obtain information on the temperature dependence of X_j as well as the

diffusion coefficient D. The diffusion coefficient, D, can be expressed in the Arrhenius form (10, 13, 14).

$$D = D_0 exp - \Delta Ea/(kT) \quad (3)$$

where D_0 is diffusion constant ($T=\infty$) (cm^2/sec), ΔEa is the activation energy (ev), k is Boltzmann's constant ($eV/^0K$), and T is absolute temperature (^0K). The substitution for D in Eq. (2) results in

$$X_j=2(D_0t)^{1/2} erfc^{-1}C_B/C_S exp - \Delta Ea/(2kT) \quad (4)$$

When D_0, t, C_B and C_S are constant, Eq. (4) reduces to

$$X_j = K' exp \Delta Ea/(2kT) \quad (5)$$

and its logarithm is

$$X_j = \log_{10} K' - \Delta Ea/(4.606 k) (1/T) \quad (6)$$

Thus the logarithm of X_j is proportional to 1/T and Fig. 8 shows log X_j vs. $1000/T^0K$ for a 60 min diffusion. It is also possible to obtain the diffusion constant, D_0, and the activation energy ΔEa.

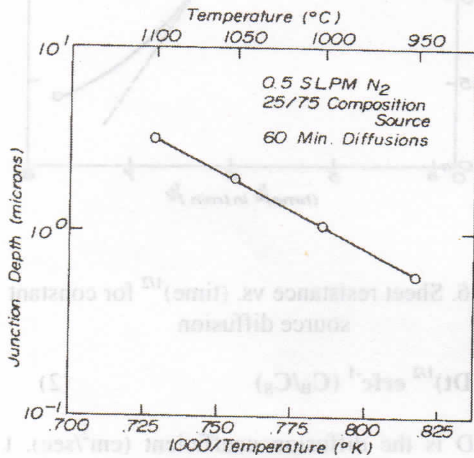

Fig. 8. Junction depth vs. reciprocal temperature for constant source diffusion

These data are of particular interest because most previous data for phosphorus diffusion were obtained in oxidizing ambients, and in some cases, with halogen vapor present, as is the case with $POCl_3$ and PBr_3 sources. In order to determine an effective diffusion coefficient, it is necessary to know the surface concentration, background concentration, and junction depth for various temperatures. The surface concentration was determined using the technique of incremental sheet resistance. Anodization was used to remove about 525 Å. An avarage lamina resistivity was calculated to be 3.08×10^{-4} Ω-cm which corresponds to a surface concentration of approximately 7.5×10^{20} atoms/cm^3. This result is in excellent agreement with the minimum resistivity, 3×10^{-4} Ω-cm, associated with the phosphorus-doped silicon reported by Kooi (6).

Using the junction depth data in Fig. 8 and a background concentration of 6.1×10^{15} atoms/cm^3, the effective diffusion coefficient for four temperatures and this is shown in the log-linear graph of Fig. 9. From this data the diffusion constant D_0 was calculated to be 2.82 cm^2/sec and Δ Ea was found to be 3.29 eV. This is in good agreement with values considered to be most accurate by Kendall and DeVries (11), i.e., Δ Ea = 3.58 eV and D_0 = 2.73 cm^2/sec. The uncertainty in values is associated with the uncertainty of junction depth which probably accounts for the many published values. Also, Masetti et al. (12) have recently reported that activation energy also depends on diffusion ambient which accounts for the observed differenced in inert and oxidizing ambient diffusions.

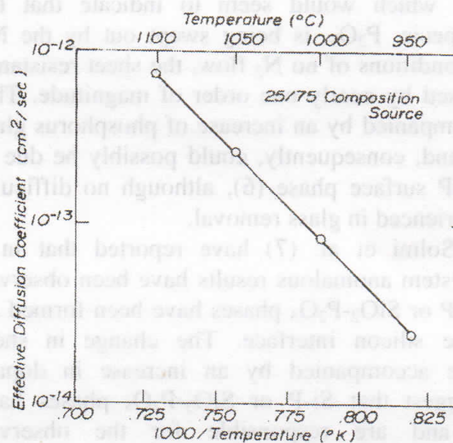

Fig.9. Junction diffusion coefficient vs. reciprocal temperature for constant source diffusion.

Special Handling Procedures

One important aspect in the handling of the material is the effect of the reversible thermal expansion of this material, shown in Fig. 10.

From this curve it can be seen that as the temperature of the PH-1050 wafers traverses the temperature range 100^0 – 400^0C, the material undergoes a rapid phase transition of 300^0C which is accompanied by a relatively large linear thermal expansion. If the temperature region from 100^0 to 400^0C is traversed too rapidly, the source wafers break. The effect is more pronounced when the source wafers are utilized in the typical format shown in Fig. 1 due to the thermal gradient across the wafers upon insertion int the diffusion furnace. In order to overcome this problem, a peheat cycle has been developed. This function of the preheat cycle is to enable the souce and silicon wafers to reach equilibrium at 350^0C prior to insertion into the furnace. This can be accomplished by a preheated extension to the diffusion tube. Once the diffusion carrier reaches equilibrium, 350^0C, the rate of

insertion is not critical, so long as the temperature does not drop below 300^{0}C, because the thermal expansion above 400^{0}C is approximately that of fused silica.

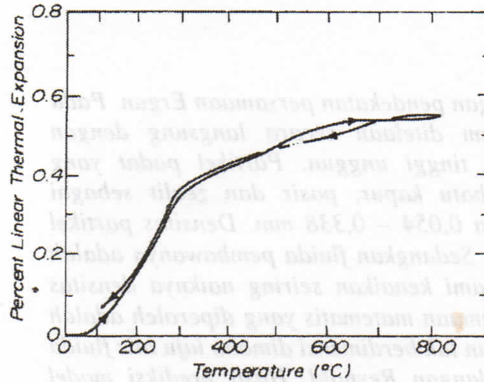

Fig.10. Percentage linear thermal expansion vs. temperature for PH-1050 wafers

Table I. PH-1050 preheat cycle

1. Insert diffusion carrier (boat) with phosphorus and silicon wafers into preheat zone at 350^{0}C.
2. Allow the load to equilibrate at 3500C, time depends on mass and thermal capacity of heat heating tape.
3. Insert carrier into hot flat zone for desired sheet resistance.
4. Remove carrier from hot zone to preheat zone.
5. Pull carrier from preheat zone into a closed end "white elephant" and allow to cool.
6. Insert next load into preheat zone making sure that the temperature has been stabilized to 350^{0}C.

Summary

The evaluation of a new solid planar source for phosphorus diffusion using SiP_2O_7 as the "active" compound in conjunction with an inert matrix phase has been described. From TGA results and assessment of the microstructural stability, the 25 w/o SiP_2O_7 composition appears to fulfill structural and sourcing requirements for use to at least 1050^{0}C. Lifetimes of ~ 260 and 3400 hr at 1000^0 and 900^{0}C, respectively, have been predicted from the TGA results assuming all of the P_2O_5 in SiP_2O_7 can be vaporized. Sourcing effectiveness in diffusion runs has been verified for times as long as 216 hr at 1000^{0}C

The experimental in-service performance of the solid planar phosphorus diffusion source over the temperature range 950^0 – 1100^{0}C has been presented with data for sheet resistance and junction depth. The test results were achieved in a nitrogen ambient. Because the P_2O_5 generated for the diffusion is the result of a solid-state chemical decomposition, there are no unspent gaseous by-products.

References

[1]. J. Stach and D. Rupprecht, *J. Electrochem.Soc.:Solid–State Science and Technology*, 120, 1266, (1973).

[2]. J. Stach and A. Turley, *ibid*., 121, 722, (1974).

[3]. N. Goldsmith, J. Olmstead, and J. Scott, Jr. , *RCA Rev.*, 28, 344, (1967).

[4]. M.Muljono, Private communication.

[5]. J. C. Irvin, NBS Special Publication, 337, p. 101 (1970).

[6]. E. Kooi, *J. Electrochem. Soc.:Solid –State Science and Technology*, 111, 1383 (1964).

[7]. S. Solmi, G. Celotti, D. Nobili, and P. Negrini, Abstract 172, p. 449, The Electrochemical Society Extended Abstract, Fall Meeting, Dallas, Texas, October 5-10, 1975.

[8]. J. S. R. Heynes andJ. T. Wilkerson, *Electrochem.Technol.*, 5, 464, (1967).

[9]. J. S. Kesperis, *J. Electrochem. Soc.:Solid –State Science and Technology*, 117, 554, (1970).

[10]. S. K. Gandhi, "TheTheory and Practice of Microelectronics", p. 67, John Wiley & Sons, Inc., New York, (1968).

[11]. D. L. Kendall and D. B. DeVries, in "Semiconductor Silicon," R. R. Haberecht and E. L. Kern, Editors, p. 358, The Electrochemical Society Softbound Symposium Series, New York, (1969).

[12].G. Masetti, S. Solmi, and G. Soncini, *Solid-State Electron.*, 16, 1419 (1973).

[13].O.D.Trapp, Semiconductor Technology Handbook, Technology Associates, (1982).

[14].W.E., Beadle, Quick Reference Manual for Silicon Integrated Circuit Technology, John Willey and Sons, (1985).