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論 文
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고온에서 반도체에 인을 도핑하기 위한 새로운 고체 판상 원료에 관한 연구

A Study on the New Solid Planar Source for High-Temperature Phosphorus Doping of Semiconductors

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요 약

고온에서 실리콘에 인을 확산시키기 위한 새로운 고체 판상 원료를 개발하였다. Source Wafer는 거품 형태의 골결을 지닌 불활성 재료에 Yttrium metaphosphate가 들어있는 구조로 되어있다. 새로운 고체 판상 원료를 사용하여 고온(1050-1150℃)에서 인을 확산시켜서 재현 가능한 Sheet resistance와 깊은 Junction을 얻었다. 일련의 한 시간 도핑 결과들로부터 새로운 고체 판상 원료의 수명은 40시간 이상인 것으로 판명되었다. 1150℃에서 인의 실리콘에로의 확산에 대한 유효 확산계수와 대응되는 활성화 에너지의 값을 구하였다.

Abstract

A new solid planar source for high temperature phosphorus diffusion into silicon was developed. The source wafer consists of an "active" compound(yttrium metaphosphate) embedded in a skeletal foam-like, inert substrate. Phosphorus diffusion from the new solid planar sources at high temperatures(1050-1150℃) produced reproducible sheet resistances and deep junctions. From a series of one hour doping runs, the lifetime of the yttrium metaphosphate source was determined to be over 40 hours. The effective diffusion coefficient of phosphorus into silicon at 1150℃ and the corresponding activation energy are presented.

1. Introduction

Solid planar sources in wafer or disk form are available for boron, phosphorus, and arsenic diffusions.[1-4] The solid planar source first developed was the boron nitride source, which was introduced by Goldsmith et al. in 1965.[1] The benefits of solid planar diffusion sources include excellent uniformity and reproducibility, and the ability of processing a large number of device wafers in a batch to reduce the manufacturing cost.

Several solid planar sources have been developed for phosphorus diffusion. In 1976 Jones et al.[2] tested a solid planar source for phosphorus diffusion using silicon pyrophosphate (SiP_2O_7) as the active compound. Later versions consisted of porous ceramic wafers containing various concentrations of SiP_2O_7 in an inert skeletal, substrate wafer.[5] Solid planar sources using magnesium pyrophosphate($Mg_2P_3O_7$) and aluminum metaphosphate ($Al(PO_3)_3$) have been investigated as phosphorus sources with favorable results.[6]

Though many researchers have investigated low temperature, phosphorus planar sources, few has investigated high temperature, phosphorus planar source. Yttrium ($Y(PO_3)_3$) has been reported to decompose to yttrium orthophosphate(YPO_4) and a P_2O_5 liquid above 1100℃.[7] Based on this result, the $Y(PO_3)_3$ compound was investigated for the feasibility as a high temperature, phosphorus planar diffusion source.

2. Experiments

2-1 Synthesis of the $Y(PO_3)_3$ Powder

Yttrium metaphosphate was synthesized using the following procedure.

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(1) Y_2O_3 (99.99% purity) and $NH_4H_2PO_4$ were weighed and mixed in stoichiometric amounts.
(2) The mixed powder was ball milled under acetone in a plastic bottle with alumina media for a day.
(3) The batch was calcined at 500℃ in air for 24 hours.
(4) The calcined powder was ball milled again under acetone for a day.
(5) After the powder was dried, it was heated at 1000℃ for 50 hours in covered alumina crucible.
The synthesized compound was identified by X-ray diffraction analysis.

2-2 Thermal Analysis

Thermogravimetric analysis(TGA) was performed on powders to determine the weight loss kinetics at temperatures above 950℃ using the TGA apparatus showing in Figure 1 Equipment consisted of an Ainsworth RV-AU-1 Electrobalance, a Ainsworth AU-1 recorder, a Kanthal resistance wound clamshell tube furnace with a Eurotherm proportioning controller, and a calibriated flow system for the gases which were used as ambient. Fused silica fibers were hooked onto a platinum wire chin attached to the balance,

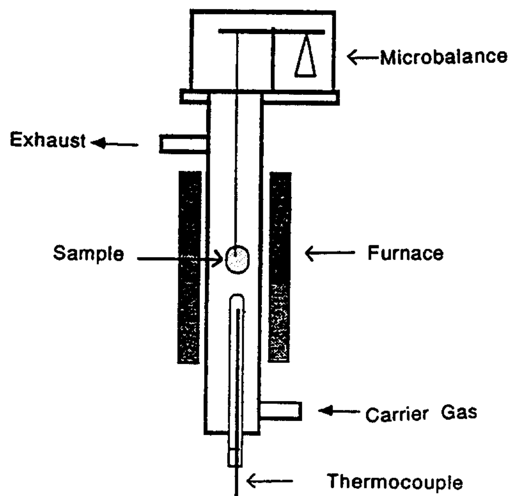


Fig. 1. Schematic diagram of the thermogravimetric analysis system.

to suspend the sample in the reaction tube.

The analysis were carried out on 0.5-1 gram samples of yttrium phosphate powder. The flow rate of the carrier gas, oxygen, was maintained at 0.2 SLPM during TGA.

2-3 Diffusion Experiments

The source wafer consists of an "active" phosphorus compound embedded in a skeletal foam-like, inert substrate which has excellent thermomechanical properties.[8] In this work, the yttrium metaphosphate powder was used as the active compound. This compound dissociates to yield phosphorus oxide vapor at the diffusion temperatures. The substrate wafer is a high purity siliconized silicon carbide with an average porosity of 85-90%. The substrate wafer was infiltrated with a slurry containing active compound powder mixed with methanol, dried and fired to produce a sintered but porous material.

The silicon wafers were 3 inches in diameter, 13-15 mils thick, (100) oriented, p-type, 10-20 ohm/cm resistivity. They were cleaned by the standard RCA cleaning procedure,[9] and dipped in dilute HF prior to diffusion. The diffusion boat used for diffusion experiment was a standard four rail, fused silica boat, with 0.04 inch slots for silicon wafers. The silicon wafers were arranged back-to-back and source wafers inserted between two silicon wafers at a surface-to surface(dopant to wafer) spacing of 0.06".

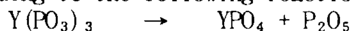
For the diffusion experiments, a 4-inch diameter fused silica tube furnace capable of maintaining a 10-inch long flat temperature zone was used. A "white elephant" fused silica tube extension was attached to the front of the diffusion tube to minimize contamination. The exit from the diffusion tube was connected to a water scrubbing system in order to remove any undesirable vapor in the exit stream before it was vented to an exhaust system. The procedure for a diffusion run consisted of the folling time cycle:
(1) Place diffusion boat in white elephant and flush for 10 minutes with nitrogen flowing at 8 SLPM.
(2) Push the boat into hot zone in about 5 minutes under above flow conditions.
(3) Flush the system for 1 minute under above flow conditions.
(4) Reduce the flow rate to 1.3 SLPM, and leave the boat in hot zone for required diffusion time.
(5) Increase the flow rate to 8 SLPM and pull out the diffusion boat for 5 minutes
(6) Allow the boat to cool for-15 minutes
Loading and unloading of the diffusion boat was carefully performed so as not to break the source and the silicon wafers by thermal shock. After a run was completed, the doped silicon wafers were taken out and

stored in a nitrogen cabinet before further analysis.

The doping performance was judged by several parameters. Glass thickness, which is the thickness of the glass phase grown from oxidation of silicon during doping, and refractive indices were determined using an automated laser ellipsometer with 6328Å wavelength. Sheet resistance data were obtained using a four point method. Junction depth measurements were made on selected wafers using a grooving-and-staining technique. A groove was cut in the silicon by rotating a diamond-grit impregnated wheel against the wafer.

3. Results and Discussion

TGA was performed on yttrium metaphosphate powder at temperatures from 950℃ to 1200℃ using a fused silica boat in flowing nitrogen. At high temperatures, yttrium metaphosphate is expected to dissociate according to the following reaction.[7]



$$Y(PO_3)_3 \rightarrow YPO_4 + P_2O_5$$

Metaphosphate Orthophosphate

The available P_2O_5 in yttrium metaphosphate was calculated from the above equation to be 43.6 weight percent.

During TGA runs, the temperature was increased successively after holding for several hours at each temperature. The weight loss was nearly linear with time at each temperature. The rate of the weight loss, listed in Table 1, is shown to increase as the temperature is increased. The X-ray diffraction analysis of the powder after TGA showed yttrium metaphosphate and yttrium orthophosphate.

Diffusion experiments were performed at

Table 1 The weight loss rates of $Y(PO_3)_3$ Powder.

Temperature (°C)	Average weight loss rate (wt%/hour)
950	0.02
1000	0.06
1050	0.12
1100	0.20
1150	0.37
1200	0.63

temperatures of 1050, 1100 and 1150℃ in nitrogen flowing at 1.3 SLPM. Glass thickness and sheet resistance as a function of temperature are plotted in Figure 2 and Figure 3, respectively. The sheet resistance decreased as the temperature increased.

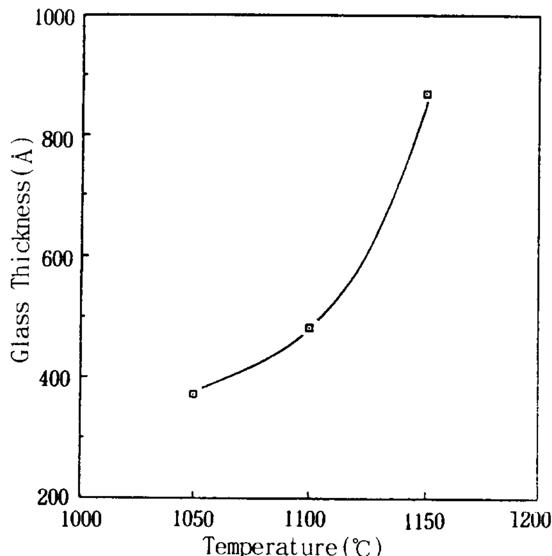


Fig. 2 Variation in glass thickness with diffusion temperature for 1 hour doping.

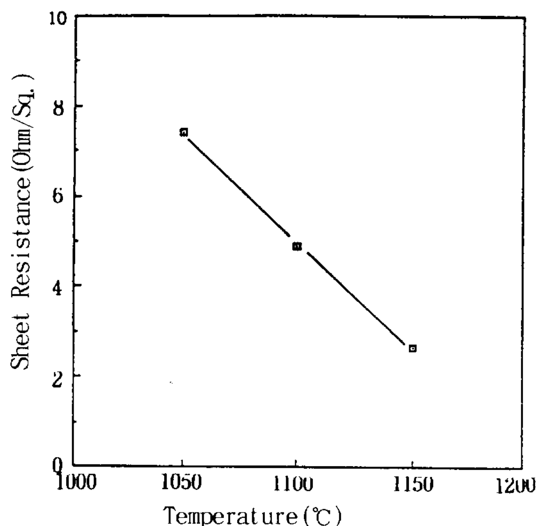


Fig. 3 Variation in sheet resistance with diffusion temperature for 1 hour doping.

The sheet conductance, or the inverse of sheet resistance, can be expressed by a simple equation as:

$$R_S^{-1} = K\mu_{eff}N_O\sqrt{Dt} \quad (1)$$

where K is a constant, μ_{eff} is the effective layer mobility, N_o is the concentration at the surface, D is the diffusion coefficient and t is the diffusion time. Equation 1 shows that the sheet conductance is a linear function of the square root of time when the surface concentration is constant. The sheet conductances of the silicon doped at 1100 and 1150℃ using the yttrium metaphosphate source are plotted against the square root of time in Figure 4. The sheet conductances are shown to be linearly proportional to the square root of time, which indicates that the surface concentration is constant.

The run-to-run reproducibility which is

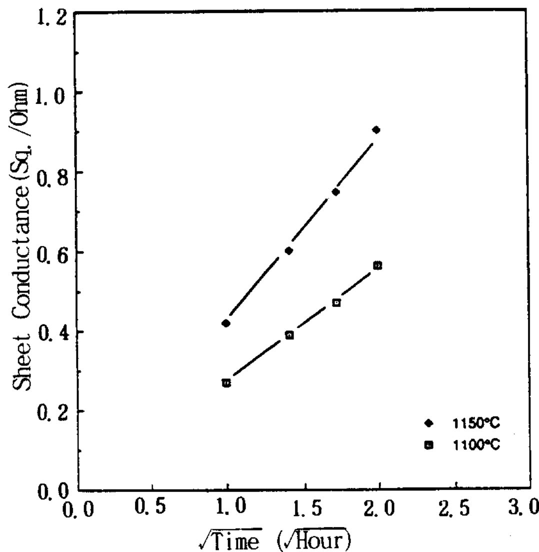


Fig. 4 Sheet conductance versus square root of diffusion time at 1100 and 1150℃.

an important factor for planar diffusion sources has been tested on the yttrium metaphosphate source. To examine the run-to-run reproducibility, a series of 1 hour diffusion runs was carried out at 1050, 1100 and 1150℃. In Figure 5 and Figure 6, the glass thickness and the sheet resistance for 1 hour diffusion runs are presented against the service time. The glass thickness and the sheet resistance from the phosphosilicate source were nearly constant over 40 hours of service time.

When the surface concentration is independent of time, the effective diffusion coefficient can be estimated from the junction depth measurement. When the surface concentration is constant, the junction

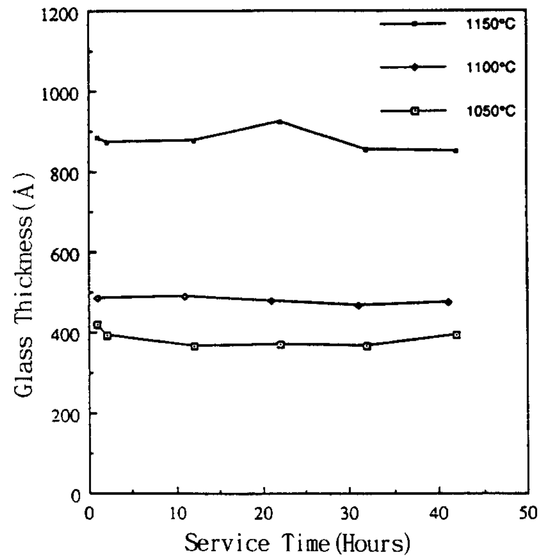


Fig. 5 Variation in glass thickness with the service time at 1050, 1100 and 1150℃

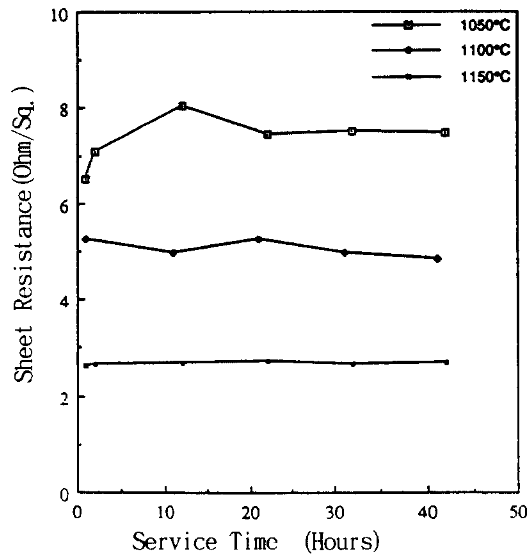


Fig. 6 Variation in sheet resistance with the service time at 1050, 1100 and 1150℃

depth, x_j, can be expressed as:

$$x_j = 2\sqrt{Dt}\,\mathrm{erfc}^{-1}\left(\frac{N_{sub}}{N_o}\right) \quad (2)$$

where N_{sub} is the substrate concentration.

From the above equation, the junction depth should be a linear function of the

square root of the diffusion time, and the slope of the straight line is the measure of the diffusivity of the dopant in silicon.

$$\sqrt{D} = \frac{\dfrac{d(x_j)}{d(\sqrt{t})}}{2\,\mathrm{erfc}^{-1}\left(\dfrac{N_{sub}}{N_o}\right)} \qquad (3)$$

The junction depth of the silicon doped at 1150℃ using the phosphosilicate source, as shown in Figure 7, appears to be a linear function of the square root of time.

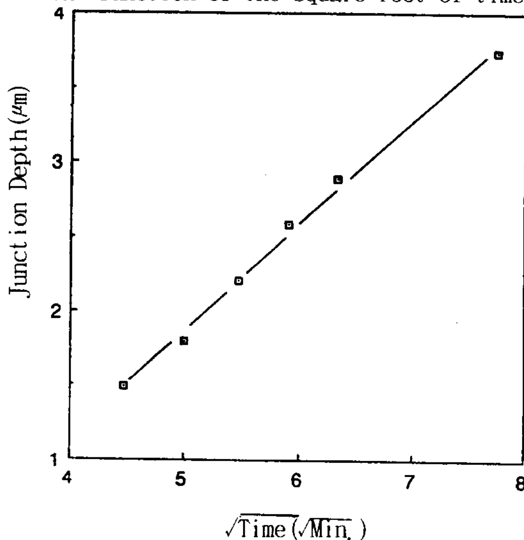


Fig. 7 Junction depth versus square root of time for doping at 1150℃

From the slope of the plot, the surface concentration, and the substrate concentration(1×10^{15} atoms/cm^3), the effective diffusion coefficient was determined to be 1.23×10^{-13}cm^2/sec. This result is in good agreement with the value reported for phosphorus diffusion under inert atmosphere by Masettti.[10]

The diffusion coefficient can be expressed in the Arrhenius form[11] as:

$$D = D_o \exp\left(-\frac{E}{KT}\right) \qquad (4)$$

where D_o is the frequency factor, E is the activation energy, k is the Boltzmann constant, and T is the temperature. From equation(2) and (4) the junction depth can be expressed as follows:

$$x_j = 2\sqrt{D_o t}\ \mathrm{erfc}^{-1}\left(\frac{N_{sub}}{N_o}\right)\exp\left(-\frac{E}{2KT}\right) \qquad (5)$$

$$\log x_j = C - \frac{E}{4.606kT} \qquad (6)$$

where $C=\log\left[2\sqrt{D_o t}\ \mathrm{erfc}^{-1}\left(\frac{N_{sub}}{N_o}\right)\right]$

From equation (6) the activation energy can be expressed as:

$$E = -4.606\,k\frac{d(\log x_j)}{d\left(\frac{1}{T}\right)} \qquad (7)$$

Equation (7) shows that the activation energy can be obtained from the slope of the Arrhenius plot of the junction depth. The Arrhenius plot of the junction depth of silicon doped with the phosphosilicate source for one hour at 1050, 1100 and 1150℃ is present in Figure 7. From the slope of plot the activation energy was obtained to be about 3.5eV. This result is in quite good agreement with the value reported for phosphorus diffusion by Masetti.[10]

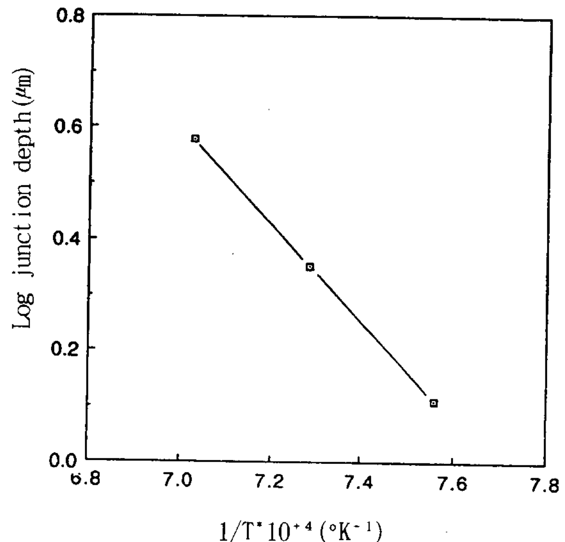


Fig. 8 Arrhenius plot of the junction depth of silicon doped for 1 hour at each temperature.

4. Summary

The evaluation of new solid planar diffusion sources for high temperature diffusion of phosphorus into silicon using yttrium metaphosphate as an active compound has been described. Preliminary diffusion experiment at 1050-1140℃ resulted in repro-ducible sheet resistances and deep junctions. The lifetime of the yttrium metaphosphate source was determined from a series of one hour doping runs to be over 40 hours These results showed that the yttrium metaphosphate compound can be used as a high temperature, phosphorus planar source.

From the junction depth data, the effective diffusion coefficient of phosphorus in silicon at 1150℃ and the corresponding activation energy were determined to be $1.23\times10^{-13}cm^2/sec$ and ~ 3.5 eV, respectively.

References

1. N. Goldsmith, J. Olmstead, and J. Scott, Jr., "Boron Nitride as a Diffusion Source for Silicon," RCA Rev., 28, 344(1967).
2. N. Jones, D. M. Metz, J. Stach, and R. E. Tressler, "A Solid Planar Source for Phosphorus Diffesion," J. Electrochem. Soc., 123, 1565(1976).
3. R. E. Tressler, H. J. Boeglin, J. Monkowski, J. Stach, G. De Munda, and C. Volk, "Present Status of Arsenic Planar Diffusion Source," Solid State Tech., 27, 165(1984).
4. D. Rupprecht and J. Stach, "Oxidized Boron Nitride Wafers as an In-Situ Boron Dopant for Silicon Diffusion," J. Electrochem Soc., 120, 1266(1973).
5. The Carborundum Company, Electronics Materials Div., Niagara Falls, New York 14302
6. R. H. Kakkad: "Study of Candidate Compounds for Phosphorus Solid Planar Diffusion Sources," M. S. Thesis, The Pennsylvania State University 1986.
7. W. R. Foster, Am. Mineral., 34, 830(1949).
8. M. O. Ten Eyck, M. R. Kasprzyk, and R. E. Tressler: "Foam Semiconductor Dopant Carriers," U. S. Patent No. 4, 526, 826(1985).
9. W. Kern and D. A. Puotinen, "Clean Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology," RCA Rev., 31, 187(1970).
10. G. Masetti, S. Solmi and G. Soneini, Solid-State Electronics, 16, 1419(1973).
11. S. K. Ghandhi: "The Theory and Practice of Microelectronics," p. 67, John Wiley & Sons, Inc., New York(1968).

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