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Diffusion of Phosphorus in Silicon*

(Received June 22, 1966)

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Abstract

The diffusivity of phosphorus into (111) plane of silicon has been measured by means of radioactivated elemental phosphorus and electro-polishing method. The diffusion coefficient has been determined as $D=0.12\times \exp{(-2.9 \text{ eV/kT}) \text{ cm}^2/\text{sec.}}$ By comparing the activation energy values for diffusion of various atomic species in silicon, it has been found empirically that enthalpy of migration is proportional to square of radius of solute atom.

I. Introduction

The activation energy values Q for diffusion of various solutes in silicon have been recently reported by several workers. Since these investigations have been carried out on high purity silicon it is expected to deduce a correlation between Q and some parameters of diffusing element in silicon. However, as shown in Table 1, it seems that discrepancy exists in the values of Q for phosphorus

Q, eV	Solute Source	Experimental Method	Reference
2.5	Р	<i>p-n</i> junction	(1)
3.6	P_2O_5	sheet conductivity	(2)
3.4		p- n junction	(3)
4.4	—		(4)
	Р	tracer, grinding	(5)
2.9	Р	tracer, electro-polishing	present work

Table 1.	The	activation	energy	values	for	diffusion	of	phosphorus	into	silicon.
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in silicon. It has been shown by X-ray, electron diffraction, and infra-red absorption measurements⁶⁾ that the surface of silicon is gradually oxidized by P_2O_5 used as a solute source, and that released oxygen atoms diffuse into silicon. The discrepancy in the Q values should be attributed to the chemical form of solute source.

In this paper, the diffusion coefficients D have been measured by using elemental phosphorus, and then the activation energy has been evaluated in the temperature range from 1453° to 1603°K. A correlation between Q and radius of solute atomic species has been investigated.

II. Experimental methods

Disks with the diameter of 15 mm and the thickness of 3 mm were cut from approximately 20 ohm-cm *p*-type single crystal silicon. The diffusing plane was parallel to the (111) crystallographic plane. They were then brought to a mirror finish by hand-lapping and electropolishing technique. The flattness of the samples, measured optically, was at least $\pm 1\mu$. The solute source was red phosphorus irradiated by neutron flux $(4\sim 3\times 10^{11} \text{ neutrons/sec. cm}^2)$ for 72 hrs. in JRR-1. It was checked by half-life measurement that impurities in the phosphorus source did not influence the radioactivity measurement when it was made two days later after irradiation.

The diffusion process was carried out in an evacuated and closed silica ampoule with the silicon sample at one end and a small amount of phosphorus at the other end. The amount of phosphorus was estimated from the equilibrium relation⁷) of P_4-P_2 to yield a vapor pressure of 1 atm in the ampoule. Heat treatment was carried out in a silicon carbide furnace at the temperatures from 1453° to 1603°K for 600 or 540 min. Temperature was held constant within limits of $\pm 5^{\circ}$ C over the period of diffusion annealing.

After the heat treatment the deposit of phosphorus was removed from the surface of sample by washing in benzene and successively in hydrofluoric acid. The edges



Fig. 1. Schematic diagram of the arrangement for micro-lapping of sample by electropolishing method.

- (a) Diffused layer (n-type)
- (b) p-n junction
- (c) Original silicon (p-type)
- (d) Nickel contact
- (e) Copper electrode
- (f) Solder
- (g) Polystylene cover
- (h) Electrolyte (3.5 % HF)

and one of the faces were ground off to a depth far below that at which no radioactivity change was observed. The samples were weighed on a microbalance, and a surface radioactivity was measured. A layer was then removed by electro-polishing technique⁸⁾ with the arrangement shown in Fig. 1. The process of weighing, counting and polishing was successively repeated. Penetration distance was determined by difference in weight. The diffused phosphorus concentrations in layers were determined by comparing the radioactivity in layers with the specific radioactivity of standard red phosphorus.

Under the experimental condition, the distribution of phosphorus concentration in silicon is expected to be given by the complementary error function⁹:

$$C_x = C_0 \operatorname{erfc} \left[x/2(Dt)^{1/2} \right], \tag{1}$$

where x is penetration distance, C_x concentration of diffused phosphorus at x, and t diffusion time. The surface concentrations C_0 and diffusion coefficients D were graphically obtained by trial-and-error method from the C_x vs. x curves.

III. Results

A thin glassy film with the thickness of $\sim 0.1 \,\mu$ was observed on the surface of sample diffusion-annealed. The thickness of the film does not depend on annealing time between 10 and 600 min. The quantity of phosphorus absorbed in the silica ampoule is very small $(3 \times 10^{17} \text{ atoms/cm}^2)$ at 1570°K for 600 min. It is considered to be satisfied the boundary conditions giving the equation (1).

The penetration distances and the relative concentrations C_x/C_0 of diffused phosphorus are shown in Fig. 2. The surface concentrations and diffusion coefficients obtained are listed in Table 2. Any correlation could not be observed



PENETRATION DISTANCE, μ

Fig. 2. Diffusion profiles of phosphorus into silicon at various temperatures. Closed circles represent the data at 1453°K, triangle signs, at 1493°K, open circles, at 1533°K, box signs, at 1573°K for 600 min., and inverse triangle signs, at 1603°K for 540 min.

Annealing Temperature	Diffusion Time	C₀, atoms/cm³	D, cm ² /sec.		
1453°K	600 min.	7.5×1019	0.6×10 ⁻¹¹		
1493	600	$5.5 imes 10^{19}$	1.0×10 ⁻¹¹		
1533	600	$2.7\! imes\!10^{19}$	2.0×10^{-11}		
1573	600	9.1×1019	3.5×10 ⁻¹¹		
1603	540	$2.1 imes 10^{19}$	5.5×10 ⁻¹¹		

Table 2. Surface concentrations, C_0 and diffusion coefficients, D of phosphorus into (111) plane of silicon at various temperatures.



Fig. 3. Temperature dependence of the diffusion coefficient of phosphorus into silicon.

on C_0 and T. As shown in Fig. 3, an Arrhenius type of temperature dependence of D is observed. The diffusion coefficient can be expressed as:

$$D=0.12\times\exp\left(68\,\text{kcal/RT}\right)\,\text{cm}^2/\text{sec.}$$
(2)

The activation energy is found to be 2.9 eV for the diffusion of elemental phosphorus in silicon. It is closer to the value (2.5 eV) obtained for phosphorus vapor¹) rather than that (3.6 eV) for phosphorus pentoxide²).

IV. Discussion

In the previous paper⁶, it has been revealed by X-ray diffraction and radioactivation

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analysis that a thick scale like film is produced from P_2O_5 on silicon surface, and the thickness of the film $(0.5 \sim 2.0 \,\mu)$ depends on the annealing time. Furthermore, oxygen atoms from P_2O_5 diffuse into silicon because the enhancement of absorption band due to Si-O bond at 9μ is observed. These facts are considered to be a few evidences of difference in diffusion mechanism for phosphorus pentoxide and elemental phosphorus as source. The values of D, which have been measured by Tannenbaum¹⁰ for $C_x < 10^{20}$ atoms/cm³ by using P₂O₅ at the temperatures between 1170 to 1320°K, are fitting the relation obtained in present work. Therefore, the difference in Q, shown in Table 1, may be observed only when C_x is fairly high. On the basis of the discussions given above, the activation energy values obtained from oxide sources will be rejected on consideration of correlation between Q and radius R.

It has been confirmed by measuring the change in interplanner spacings for Por B-doped silicon¹¹) that phosphorus or boron solute atoms form substitutional solid solutions with the tetrahedral covalent bonding in silicon. The elements of III and or V group are considered to form substitutional solid solutions¹²⁾ in silicon, and H¹³), He¹³), Li¹³), Fe¹⁴), Au¹⁴) and O¹⁵), to form interstitial solutions.^{13),12),16}) The activation energy values for solute atom in silicon are listed in Table 3.

Table 3. The activation energy values for solute atom in silicon from elemental or chloride sources reported by various workers. The signs (tet), (2-), (+) and (3+) represent the tetrahedralatomic, divalent anion, monovalent and trivalent cation radii, respectively.

Solute	Radius, Å	Source	Q, eV
В	0.88 (tet) (20)	BCl ₃	2.5 (1)
Al	1.26 (tet) (20)	Al	3.5 (2)
Ga	1.26 (tet) (20)	Ga	4.1 (21)
Р	1.10 (tet) (20)	Р	2.9
0	1.40 (2-) (40)	O_2	3.5 (15)
Н	0.53 (13)	H ₂	0.5 (13)
He	0.93 (13)	He	1.2 (13)
Li	0.63(+)(13)	Li	0.6 (13)
Fe	0.67(3+)(20)	FeCl ₃	0.9 (14)
Au	1.37 (+) (20)	Au	1.1 (14)

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According to LeClaire's theory¹⁷⁾ the activation energy for substitutional diffusion is given by the equation:

$$Q = \mathcal{J}H_v + \mathcal{J}H_m \ . \tag{3}$$

The term $\mathcal{A}H_v$ is the enthalpy associated with the free energy on forming a vacancy. $\mathcal{A}H_m$ is the enthalpy in the isothermal work done in migration of diffusing atom from an equilibrium position to the top of the potential barrier separating it from the next equilibrium position. The activation energy for interstitial diffusion is given by

$$Q = \varDelta H_m$$
 . (4)

Provided that $\Delta H_v = 1 \text{ eV}$, the values of ΔH_m are plotted for square of radius R^2 . As shown in Fig. 4, a linear correlation is observed for the diffusing atomic species



Fig. 4. An empirical correlation between enthalpy of migration ΔH_m and square of radius R^2 of diffusing atomic species in silicon. Open circles represent the value for chrolide sources, and closed, for elemental sources.

from elemental sources, although only the $\mathcal{I}H_m$ for Au is anomalous. The values for chloride sources also satisfy the linear relation. Thus, it may be deduced that the value of $\mathcal{I}H_v$ is assigned to be about 1 eV and that $\mathcal{I}H_m$ is proportional to the square of radius for solute atom.

Such a correlation is also observed in the case of the diffusion of rare gases (A, Kr and Xe) in $Ag^{18,19}$.

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