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DIFFUSION OF PHOSPHORUS IN SILICON OXIDE FILM

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Abstract—The system P_2O_5 (vapor), SiO_2 (thin film) and single-crystal silicon has been investigated by solid-state-diffusion techniques. The *p*-type silicon underneath the silicon oxide film was used as a "phosphorus detector". A rapid and complete chemical reaction apparently takes place between the SiO_2 and the diffusant, phosphorus or phosphorus oxide, forming a glass (or compound) of unknown composition $P_xSi_yO_z$ at the glass/silicon interface. A sharp boundary is found between the glass and unreacted SiO_2. The results indicate that the growth of the glass is limited by the diffusion of the phosphorus species in the glass with very little or no diffusant left to diffuse in the unreacted silicon dioxide after the complete reaction at the glass/silicon dioxide interface. The growth of this compound or glass follows the parabolic law and is experimentally given by $x_m^2/t_m = 1{\cdot}7 \times 10^{-7} \exp(-1{\cdot}46/kT_m)$ cm²/sec or $x_m/\sqrt{(t_m)} = 250 \exp(-1{\cdot}46/2kT_m)$ $\mu/\sqrt{(\text{hr})}$ over the temperature range 900–1250°C. Here x_m is the thickness of the glass, t_m the diffusion time and T_m the diffusion temperature (°K). The subscript m denotes the condition of complete masking of the silicon oxide against phosphorus, i.e. no *n*–*p* junction is formed.

Diffusion experiments in which the silicon oxide film failed to mask or only partially masked against P_2O_5, i.e. x_0^2/t_d was smaller than the value given for x_m^2/t_m, where x_0 is the original oxide thickness and t_d is the diffusion time, were also performed and could be interpreted by using a two-boundary diffusion model. In this case, a species of phosphorus or phosphorus oxide apparently diffuses through the glass with a diffusion coefficient, D_1, followed by the diffusion of phosphorus in the *p*-type silicon with a higher diffusion coefficient, D_2, to form a *n*–*p* junction underneath the glass. The segregation coefficient of phosphorus at the boundary between the glass and the silicon is apparently small. The transition region between complete masking and partial masking is well defined and occurs at a silicon oxide layer thickness < 500 Å. Such a rapid change represents the transition between the models discussed above: the model for the growth law of the glass in silicon oxide and the two-boundary diffusion model for partial masking.

1. INTRODUCTION

Silicon oxide films have been used for selective masking against impurity vapors during diffusion in silicon for semiconductor-device fabrication.(1) The completeness of masking of phosphorus, in general, can be controlled through several parameters: oxide thickness, diffusion temperature, diffusion time, impurity vapor pressure and impurity concentration (*p*-type) originally present in the silicon. Partial masking for the control of the total amount of impurity diffused into the silicon is also possible by adjusting the above parameters. A series of experiments were performed in which several of the above parameters were varied and in which phosphorus was used as the impurity atom. The results are discussed in terms of two approximate diffusion models.

2. EXPERIMENTAL APPARATUS AND TECHNIQUES

The oxide film was grown on silicon slices in a high-temperature, open-tube furnace containing a Mullite furnace tube of 45 mm inside diameter. The oxidizing atmosphere consisted of tank oxygen saturated with water at room temperature (around 25°C). The oxygen was allowed to flow over the silicon surface at a rate of 500 cc/min.

The silicon slices were *p*-type, 0·30 Ω-cm, ~ 200 μ thick, cut from a single crystal of (100) orientation. One of the surfaces of the silicon slices was mechanically polished to a mirror finish with Linde A aluminum oxide powder. The other surface was lapped with carborundum powder of 1950 grit. All experimental data were obtained on the polished surface.

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* Formerly of Shockley Transistor Corporation, where the experimental work was done.

The diffusion experiments were performed in a two-zone, open-tube furnace system similar to that described by FROSCH and DERICK[1]. The system is shown in Fig. 1. The carrier gas, N_2, was dried through a silica gel drier and a cold trap of dry ice and acetone mixture at −78·6°C. Traces of water in the carrier gas would cause the life or the constancy of the vapor pressure of the P_2O_5 source to deteriorate rapidly and tend also to build up oxide on the silicon surface during diffusion. The carrier gas flow-rate was maintained at 200 cm^3/min through a quartz furnace tube of 34 mm inside diameter. The furnace tube was thoroughly rinsed in tap and deionized water after each experiment and dried before being used again. Fresh and dry P_2O_5 powder was loaded in a cleaned and dried quartz boat and pushed into the low-temperature (source) zone of the furnace. The P_2O_5 was usually aged for 1 hr before the start of the experimental run. For all the experimental data presented, the source was held at 211°C. Fresh P_2O_5 was used every 4 or 5 hr.

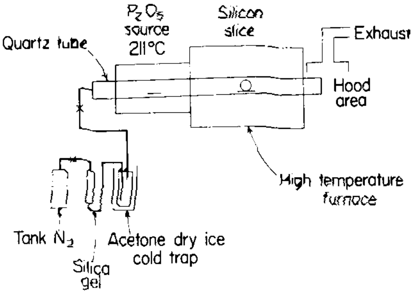

FIG. 1. Schematic of the two-zone phosphorus-diffusion furnace.

The oxidation and the diffusion-furnace temperatures were controlled to within ±1°C over the entire duration of the experimental run by a thermocouple-controlled automatic system. The silicon samples and the P_2O_5 source were placed in the flat temperature zones where temperature variation over the zone was less than 1°C.

3. EXPLORATORY EXPERIMENT

In order to design a complete set of experiments to determine the diffusion characteristics of phosphorus in silicon oxide films, exploratory experiments were performed to ascertain that the reaction of phosphorus and silicon oxide would be accounted for by a diffusion model. The solution of the diffusion equation requires that the diffusion depth, x, be proportional to the square root of the diffusion time—the parabolic law. In the exploratory experiment, this relation was verified for the condition of complete masking at a diffusion temperature $T_d = 1100°C$. Oxides of various thicknesses, x_0 were grown, and the diffusion time, t_m, required for each oxide mask to fail, i.e. just before a *n*-skin is formed, was determined. The experimental results, shown in Fig. 2, indicated that a parabolic law was satisfied.

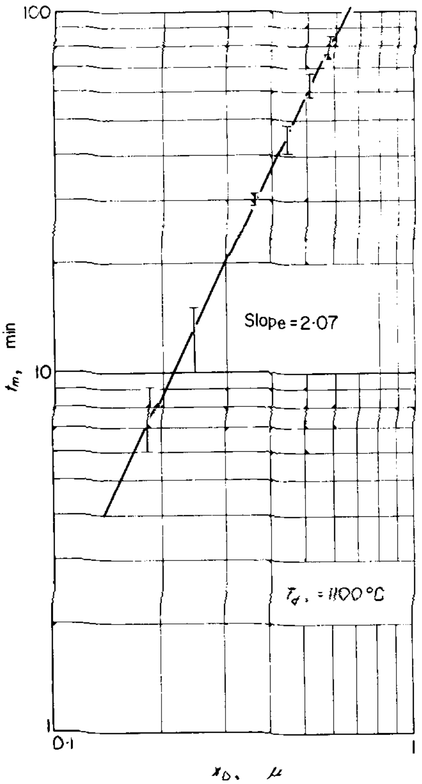

FIG. 2. Exploratory experimental results of the diffusion time, t_m, at which a silicon oxide film of a given thickness x_0 fails to mask against P_2O_5 vapor at a diffusion temperature $T_d = 1100°C$ and a P_2O_5 temperature $T_s = 211°C$. The original resistivity is 0·3-Ω-cm *p*-type.

4. EXPERIMENTAL RESULTS

In view of the confirmation of the diffusion model from the preliminary experimental data, extensive experiments were designed to determine the mask-failure condition at various temperatures. Some partial-masking experiments were also performed and are discussed below.

(a) *Oxide films on silicon*

The oxide films were grown at two temperatures: 1200 and 1300°C. Accurate oxide-thickness measurements were obtained with a Beckman DK-2 spectrophotometer modified for reflectance measurements. These reflectance measurements were accurate to better than 1 per cent and lie on a straight line. Thus, only solid lines are drawn in Fig. 3 rather than showing individual experimental points from the reflectance measurements.

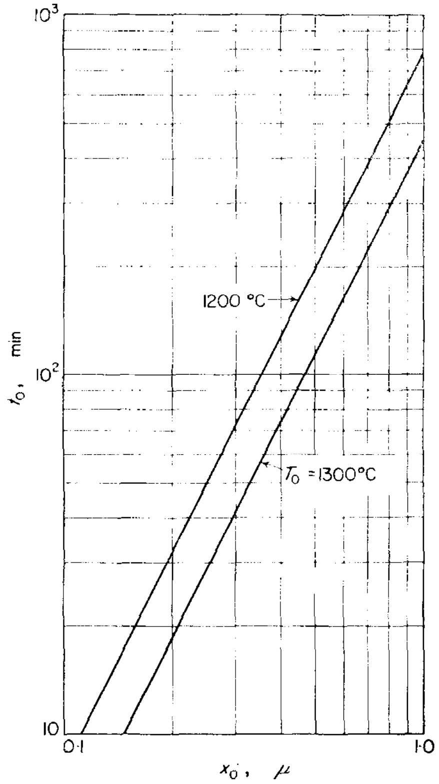

FIG. 3. The growth of the silicon oxide film on single-crystal silicon. Oxidation time, t_m, vs. oxide thickness, x_0, at oxidation temperatures T_0 = 1200 and 1300°C.

In addition, a uniform spacing was observed in the wavelengths of reflectance maxima and minima which follows the relationship $2nx_0 = m\lambda$, where $n = 1{\cdot}5$ is the index of refraction of silicon oxide, x_0 is the oxide thickness, m is the order of the reflectance maxima or minima and λ is the wavelength of light at the extremes. This suggests that the silicon oxide film had a rather uniform composition throughout the entire film.

The experimental data shown in Fig. 3 indicate a parabolic growth law for the oxide film. The activation energy of this process, estimated from the data at the two temperatures, is roughly 1·5 eV (35 kcal/g-mol). The results obtained by LIGENZA[(2)] and by LAW[(3)] on single-crystal silicon surfaces show an activation energy of 1·7 eV (40 kcal/g-mol) in the range 750–950°C. The activation energy compares favorably with that of BARRER[(4)], who obtained a value of 31·2 kcal/g-mol (1·36 eV) from permeability experiments on oxygen in fused silica.

Some published oxidation data for silicon are compared in Fig. 4. The data obtained by EVANS and CHATTERJI[(5)] on polycrystalline silicon disagree in that they obtain films about ten times thicker at the same temperatures.

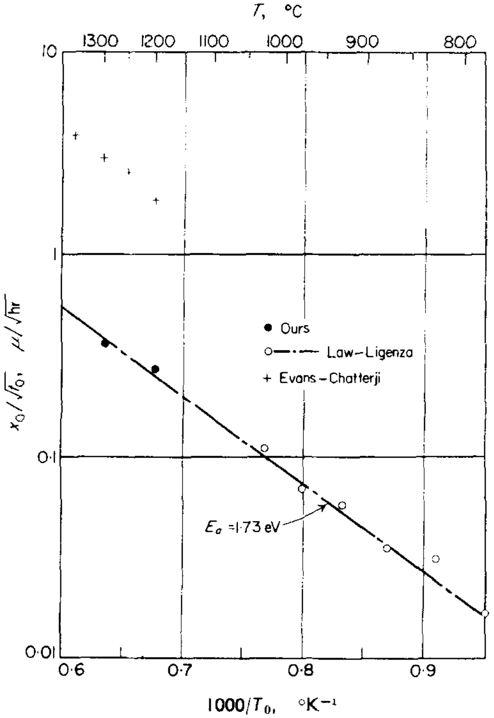

FIG. 4. The growth of the silicon oxide film on a silicon surface, $x_0/\sqrt{(t_0)}$ vs. $1/T_0$(°K), the reciprocal of the oxidation temperature.

(b) *Silicon oxide mask-failure condition*

One series of experimental results is presented in Fig. 5. In this series the diffusion time, t_m, was fixed at 30 min (the subscript m denotes the masking condition). Silicon oxide layers of various thicknesses were prepared and exposed to P_2O_5.

Diffusion was performed at several closely spaced temperatures to determine T_m, the temperature at which the oxide fails to mask against P_2O_5. Mask failure was ascertained by the presence of an n-skin underneath the glass. The n-skin was detected by a hot probe after the glass had been dissolved in hydrofluoric acid. Each point in Fig. 5 corresponds to about three to five trial $\frac{1}{2}$-hr diffusion runs.

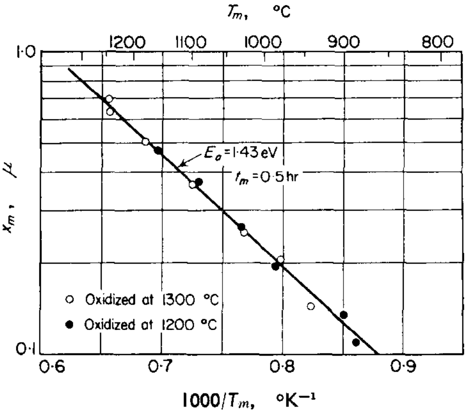

FIG. 5. The thickness at which the silicon oxide film fails completely to mask against P_2O_5 vapor at a diffusion time t_m = 30 min vs. the reciprocal of the diffusion temperature, $1/T_m$(°K).

From these data, the activation energy (E_a) of the diffusion process of phosphorus oxide in the silicon oxide film is found to be 1·43 eV.

The increase of the oxide thickness during diffusion has been neglected in the data of Fig. 5. This approximation is justified from two observations:

(1) The original oxide thickness, x_0, required for masking is considerably thicker than the additional increase during diffusion, as estimated from Fig. 4.

(2) There is no oxygen present other than that chemically combined in the P_2O_5 vapor during diffusion and that distributed and unreacted in the SiO_2 during the oxide-film growth.

Hence, it is probable that the additional oxide-film growth would be even less than anticipated from the data given in Fig. 4, since the latter correspond to a constant-surface-concentration oxygen source.

Another series of experiments was performed with a fixed oxide layer thickness $x_0 = 0{\cdot}36\ \mu$ obtained by oxidation at 1300°C for 1 hr. With several trial experiments at a given diffusion temperature, T_m, the diffusion time, t_m, at which the oxide layer failed to mask against P_2O_5, was obtained. The experimental data are presented in Fig. 6. These results indicate an activation energy of 1·47 eV, in agreement with the experiments of Fig. 5. Because of the thermal mass of the silicon slice and the sample boat, the high-temperature data at relatively short times t_m may not be accurate.

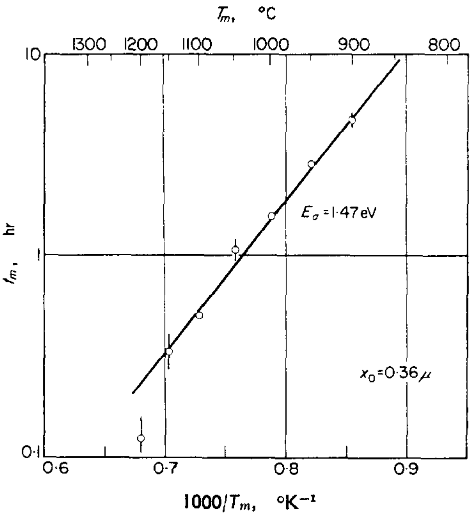

FIG. 6. The diffusion time, t_m, at which a silicon oxide film of thickness $x_0 = 0{\cdot}36\ \mu$ fails to mask against P_2O_5 vapor vs. the reciprocal diffusion temperature, $1/T_m$(°K).

The experimental results of mask failure are analyzed by using a diffusion model. Thus, it may be assumed that

$$\frac{x_m}{2\sqrt{(D_1 t_m)}} = L \tag{4.1}$$

Here L is a constant and is a function of the boundary condition at the vapor/silicon oxide interface for the limiting case of complete reaction at the glass/silicon oxide interface; $D_1 = D_0 \exp(-E_a/kT_m)$ is the diffusion coefficient of phosphorus or an oxide of phosphorus in the phosphorus silicate glass produced by this diffusion;

x_m is the silicon oxide thickness and t_m is the diffusion time. The experimental data from Figs. (2), (5) and (6) are reduced by means of equation (4.1) and presented in Fig. 7. It is seen that the results from the three sets of experiments lie on one curve and are thus consistent with equation (4.1). The data can be fitted by the relation $x_m/\sqrt{(t_m)} = 250 \exp(-1{\cdot}46/2kT)\ \mu/\sqrt{(\mathrm{hr})}$, or $x_m^2/t_m = 1{\cdot}7\times 10^{-7} \exp(-1{\cdot}46/kT)\ \mathrm{cm}^2/\mathrm{sec}$.

In Fig. 7 the calculated square root of the diffusion coefficients is also plotted from data of partial-masking experiments discussed in the following section. The diffusion coefficient D_1 is the same as that in equation (4.1), while D_2 is the diffusion coefficient of phosphorus in silicon, neglecting any concentration-dependence. The detailed calculations are discussed in a later section.*

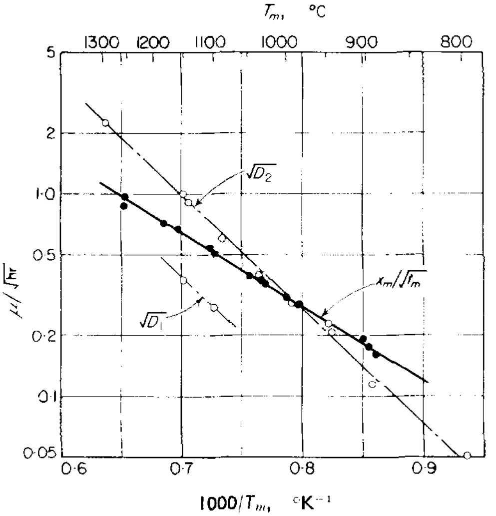

FIG. 7. The growth of the phosphorus silicate glass in a silicon oxide film on single-crystal silicon, $x_m/\sqrt{(t_m)}$ vs. the reciprocal temperature, $1/T_m$(°K).

(c) *Partial masking by silicon oxide*

The mask-failure conditions determined in the previous section, if exceeded, would result in an n–p junction in the silicon at a distance x_j beneath the silicon oxide. Several series of experiments were performed by fixing the diffusion temperature T_d and the diffusion time t_d while varying the oxide thickness. Thus, increasing amounts of phosphorus pass through the silicon oxide/silicon interface as the oxide layer gets thinner. The result of a typical experimental series is shown in Fig. 8.

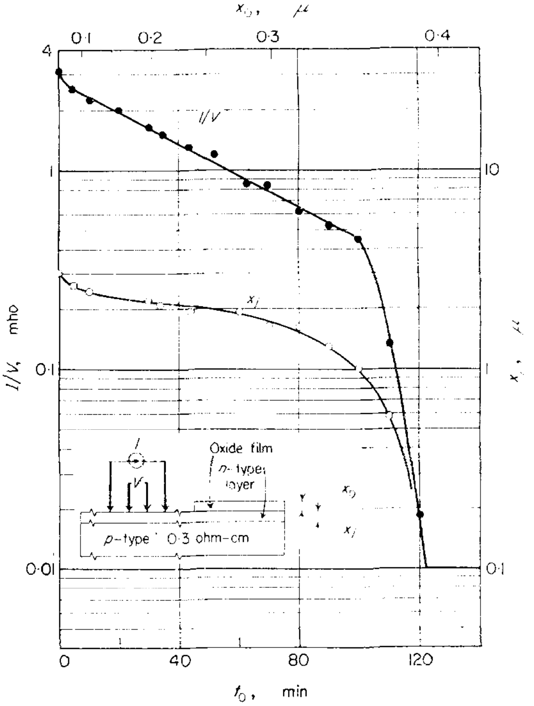

FIG. 8. The four-point probe resistance and the n–p junction depth of a n-type (phosphorus) layer formed by diffusion of phosphorus oxide through a silicon oxide film vs. the silicon oxide film thickness.

The sheet conductance (I/V) was obtained by the four-point probe technique,(6) while the n–p junction depth, x_j, was obtained by cylindrical grooving and subsequent staining with a solution of concentrated hydrofluoric acid containing 0·25 per cent nitric acid. Experimental results of junction depth in silicon vs. original oxide thickness are shown in Fig. 9. A linear region was observed for each case. However, an extremely rapid drop of junction depth occurs near the masking condition. This indicates the existence of a well-defined moving boundary or interface.

The sheet conductance measurement can be taken as an indication of the concentration of

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* Data plotted for $\sqrt{(D_2)}$ in Fig. 7 in addition to the two values shown in Table 1 were obtained under the experimental conditions described in the text but with zero initial oxide thickness.

phosphorus at the silicon oxide/silicon interface. The sheet conductance can be calculated from:⁽⁷⁾

$$\frac{I}{V} = 4{\cdot}53 \int_{0}^{x_j} q\mu(C)[C_2(x)-C_3]\,dx \qquad (4.2)$$

Here q is the electronic charge, $\mu(C)$ is the majority carrier mobility, $C_2(x)$ is the concentration of phosphorus and C_3 is the impurity concentration originally present in the bulk silicon. The experimental I/Vx_j and the $C_2(0)$ calculated from I/Vx_j are plotted in Fig. 10. The theoretical calculations of $C_2(0)$ are discussed in detail in a later section. A

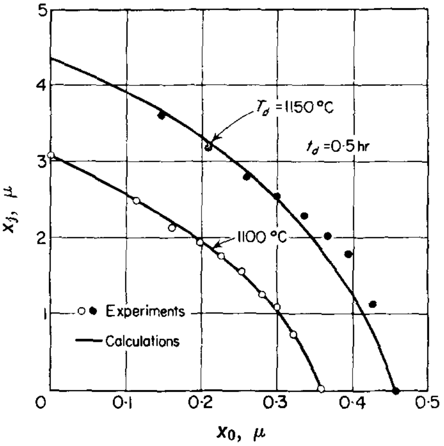

FIG. 9. The n–p junction depth, x_j, versus the oxide film thickness x_0 for a diffusion time t_d = 0·5 hr and diffusion temperatures 1100 and 1150°C.

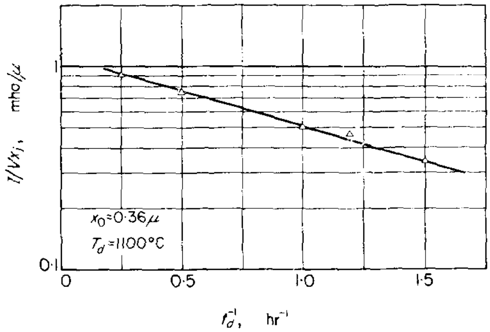

FIG. 11. The four-point probe resistance and junction depth of the n-type layer vs. the reciprocal diffusion time $1/t_d$. The n–p junction is formed by diffusion of phosphorus oxide through a silicon oxide layer of thickness x_0 = 0·36 μ at a diffusion temperature T_d = 1100°C.

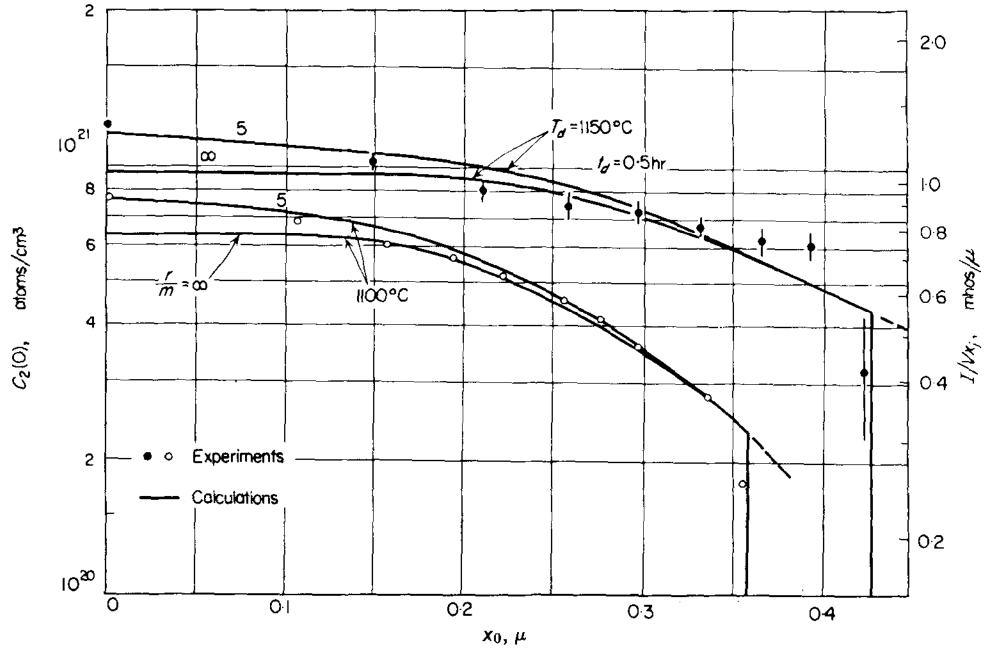

FIG. 10. $C(0)$ and I/Vx_j as a function of x_0^2. $C(0)$ is the phosphorus surface concentration or the phosphorus concentration at the interface of phosphorus silicate glass and silicon. The term x_0 is the silicon oxide thickness or phosphorus silicate glass thickness. Diffusion temperatures are 1100 and 1150°C.

rapid decrease of I/Vx_j near the mask-failure oxide thickness is again observed, giving further evidence of a well-defined moving boundary or interface.

An additional set of experiments was performed with a constant oxide-film thickness of $0{\cdot}36\ \mu$ at a diffusion temperature $T_d = 1100°C$. The diffusion time, t_d, was varied. The experimental results shown in Fig. 11 indicate that the surface concentration of phosphorus is proportional to the quantity $\exp(-\text{constant}/t_d)$. This result is consistent with a diffusion model.

5. INTERPRETATION OF THE EXPERIMENTAL RESULTS

The experimental data have indicated a parabolic law in the temperature regions examined in these studies for the growth both of the oxide film on silicon and of a phosphorus silicate compound (or glass) in silicon oxide. These films are characterized by a rather homogeneous concentration and a very sharp and advancing boundary. The parabolic growth law suggests that diffusion is the limiting process.

The sharp and advancing boundary suggests that the concentration of the diffusing species decreases rapidly from the boundary. This in turn may correspond to a very rapid chemical reaction between the diffusant and the unreacted substrate at the boundary. Thus, one interpretation of the oxide film growth may be as follows: the oxygen diffuses in the silicon oxide film previously formed; as the diffusing oxygen reaches the boundary between the silicon oxide and the silicon, it rapidly oxidizes the unreacted silicon and forms a new layer of silicon oxide. The oxidation reaction is almost instantaneous compared with the diffusion rate of oxygen in the silicon oxide film, so that the process is diffusion-limited with a sharp and advancing boundary. A second possible mechanism is the diffusion of silicon atoms in the oxide. Upon reaching the surface, the silicon atoms react rapidly with the oxygen in the ambient and form an additional layer of oxide. At present, it is not possible to distinguish these two mechanisms from our data.

The binary system involving P_2O_5 and SiO_2 can be accounted for similarly. In this case, the diffusing species is probably an oxide of phosphorus diffusing in a phosphorus silicate glassy layer of an unknown composition ($P_xSi_yO_z$) referred to as the "glass". The reaction of the oxide of phosphorus and the unreacted silicon oxide at the interface between the glass and the silicon oxide is again very rapid, so that phosphorus concentration in the unreacted silicon oxide film decreases to zero in a very short distance from the interface.

The ternary system involving phosphorus oxide, silicon oxide and silicon can be analyzed following the same line as that discussed above. For such a system, two approximate models may be considered for physical simplicity: one model for the complete-masking experiments and the other for the partial-masking experiments. The model for the binary systems discussed above, i.e. O_2–Si or P_2O_5–SiO_2, may be used to account for the results of complete masking. For partial masking, namely, phosphorus diffusion in silicon through an oxide film, a two-boundary diffusion model is useful. In this case, it is assumed that the pregrown silicon oxide has completely reacted with the phosphorus species to form a phosphorus silicate glass. Thus, no further reaction takes place, and we need consider only the diffusion of phosphorus or an oxide of phosphorus in the glass with diffusion coefficient D_1 and the diffusion of the phosphorus in silicon with a diffusion coefficient D_2. The phosphorus surface concentration may be assumed to be proportional to the concentration of the oxide of phosphorus at the glass/silicon interface. The solution of this two-boundary diffusion problem has been worked out.(8)

There may exist a second, very thin, glassy layer formed between the diffusing phosphorus oxide and the unoxidized silicon, with a composition of ($P_uSi_vO_w$) Additional experiments must be performed to investigate this point. In this discussion, this second glassy layer, if it exists, is not considered.

(a) *Mathematics*

The mathematics of the two approximate physical models discussed can be formulated and the exact solutions obtained from Fick's diffusion equation with chemical reaction for the first case and without chemical reaction for the second case. The results obtained by using standard techniques(8) are listed below.

(i) *Growth of phosphorus silicate glass or silicon oxide film (Fig. 12)*

The boundary and the initial conditions and the diffusion equations are:

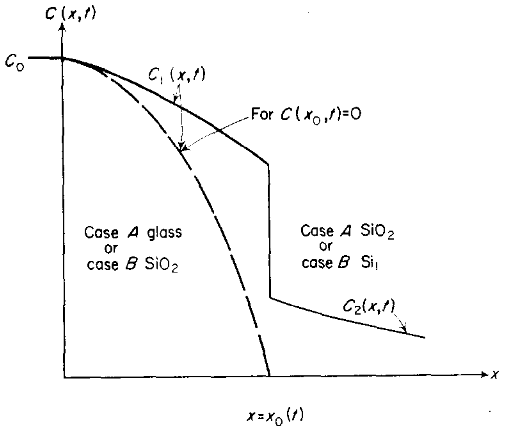

FIG. 12. The concentration profile of the film or glass-forming diffusant in the film or glass and in the unreacted silicon or silicon oxide.

$$D_1\frac{\partial^2 C_1}{\partial x^2} = \frac{\partial C_1}{\partial t} \qquad 0 < x < x_0(t) \qquad (5.1)$$

$$D_2'\frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t}+\frac{\partial S_2}{\partial t} = (1+R)\frac{\partial C_2}{\partial t}$$
$$x_0(t) < x < \infty \qquad (5.2)$$

or
$$D_2\frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t} \qquad x_0(t) < x < \infty \qquad (5.2a)$$

where
$$D_2 = D_2'/(1+R)$$

$$C_2 = mC_1 \qquad x = x_0(t), \quad t > 0 \qquad (5.3)$$

$$D_1\frac{\partial C_1}{\partial x}+C_1\frac{dx_0}{dt} = D_2\frac{\partial C_2}{\partial x}+C_2\frac{dx_0}{dt}$$
$$x = x_0(t), \quad t > 0 \qquad (5.4)$$

$$N\frac{dx_0}{dt} = -D_1\frac{\partial C_1}{\partial x}-C_1\frac{dx_0}{dt} \qquad x = x_0(t), \quad t > 0 \qquad (5.5)$$

$$C_1 = C_0 \qquad x = 0, \quad t > 0 \qquad (5.6)$$

$$C_2 = 0 \qquad x = \infty, \quad \text{all } t \qquad (5.7)$$

$$C_1 = C_2 = 0 \qquad x > 0, \quad t < 0 \qquad (5.8)$$

The subscript 1 denotes the region of the glass or the oxide film bounded by $0 < x < x_0(t)$, where $x_0(t)$ is the moving boundary. The subscript 2 denotes the region of the unreacted oxide film or the unreacted silicon. The D's are the corresponding diffusion coefficients and the C's are the concentration of the diffusants, i.e. phosphorus oxide or oxygen.

In equation (5.2) the reaction of the phosphorus oxide with silicon oxide or of oxygen with silicon is assumed to be in local equilibrium, so that the concentration of the reacted substance S_2 is directly proportional to the concentration C_2 of the substance free to diffuse. Thus, $S_2 = RC_2$.

The rate of increase of the phosphorus silicate glass or the silicon oxide layer thickness is assumed to be proportional to the net rate of the number of diffusing atoms crossing the interface $x_0(t)$. Thus, (5.5) results where N is the concentration of the *reacted* oxygen in the silicon oxide or of the *reacted* phosphorus or phosphorus oxide in the glass, assuming that the amount of the diffusant crossing the interface is completely reacted.

At the interface between the silicon oxide and the silicon, it is assumed that the unreacted oxygen concentration in the unreacted silicon is proportional to that in the silicon oxide. This boundary condition is given by (5.3), where the factor m is the segregation coefficient at the corresponding interface. A similar boundary condition may be assumed for the case of phosphorus silicate glass formation.

The solution of equation (5.1) and (5.2) satisfying the boundary and initial conditions of (5.3)–(5.8) are:

$$\frac{x_0}{2\sqrt{(D_1 t)}} = L = \text{constant} \qquad (5.9)$$

where L is obtained from

$$m\frac{(\sqrt{(\pi)}L\exp L^2 \operatorname{erf} L)N-C_0}{\sqrt{(\pi)}L\exp L^2 \operatorname{erf} L-1}$$
$$= \frac{(\sqrt{(\pi)}rL\exp r^2L^2 \operatorname{erfc} rL)N}{\sqrt{(\pi)}rL\exp r^2L^2 \operatorname{erfc} rL+1} \qquad (5.10)$$

$$C_1(x,t) = C_0-\frac{\sqrt{(\pi)}L\exp L^2}{\sqrt{(\pi)}L\exp L^2 \operatorname{erf} L-1}(C_0-N)\times$$
$$\times \operatorname{erf}\frac{x}{2\sqrt{(D_1 t)}} \qquad (5.11)$$

$$C_2(x,t) = \frac{\sqrt{(\pi)}rL\exp r^2L^2}{\sqrt{(\pi)}rL\exp r^2L^2 \operatorname{erfc} rL+1}\times$$
$$\times \operatorname{erfc}\frac{x}{2\sqrt{(D_2 t)}} \qquad (5.12)$$

Here $r = \sqrt{(D_1/D_2)}$. Thus, if the diffusant crossing the interface is completely reacted, it may be assumed that $C_2(x_0) = 0$ and a simpler solution is obtained:

$$C_1(x,t) = C_0\left(1-\frac{\operatorname{erf} x/2\sqrt{(D_1 t)}}{\operatorname{erf} L}\right) \qquad (5.13)$$

$$C_0/N = \sqrt{(\pi)}L\exp L^2 \operatorname{erf} L \qquad (5.14)$$

The parabolic law of film growth is predicted by (5.9), while (5.14) can be used to obtain the diffusion constant D_1 if C_0 and N are known.

(ii) *Diffusion through a layer into a semi-infinite region—partial masking* (*Fig.* 13)

The boundary and the initial conditions are:

$$C_1(-x_0, t) = C_0 = \text{constant} \quad t > 0 \quad (5.15)$$

$$mC_1 = C_2 \quad x = 0, \quad t > 0 \quad (5.16)$$

$$D_1\frac{\partial C_1}{\partial x} = D_2\frac{\partial C_2}{\partial x} \quad x = 0, \quad t > 0 \quad (5.17)$$

$$C_1 = C_2 = 0 \quad x > -x_0, \quad t < 0 \quad (5.18)$$

$$C_2 = 0 \quad x = \infty, \quad \text{all } t \quad (5.19)$$

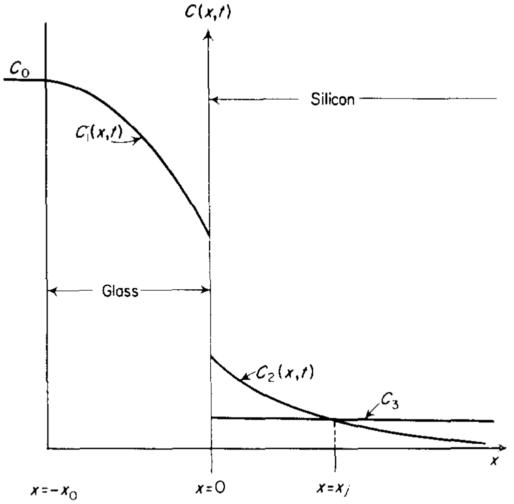

FIG. 13. The concentration profile of diffusing phosphorus oxide in phosphorus silicate glass and the concentration profile of phosphorus in silicon.

The subscript 1 denotes the region of the glass bounded by $-x_0 < x < 0$, where x_0 is the original oxide thickness and is a constant. The subscript 2 denotes the semi-infinite region of silicon. The D's and C's are the diffusion coefficients and the concentrations of the diffusant, respectively. The proportionality constant m is the "segregation coefficient" of phosphorus at the interface of silicon and phosphorus glass and has in general a different value from that given in case (i). The initial distribution of the diffusant in the glass is neglected in order to simplify the problem. Thus, (5.18) is assumed. The more exact initial condition for C_1 in place of (5.18) is given by (5.11) or (5.13), where t is replaced by $x_0^2/4D_1L^2$ given by (5.9).

The solutions of the diffusion equation satisfying equations (5.15)–(5.19) are:

$$C_1(x, t) = C_0 \sum_{n=0}^{\infty} \alpha^n \left\{ \operatorname{erfc}\frac{(2n+1)x_0+x}{2\sqrt{(D_1t)}} - \alpha \operatorname{erfc}\frac{(2n+1)x_0-x}{2\sqrt{(D_1t)}} \right\} \quad (5.20)$$

and

$$C_2(x, t) = m(1-\alpha)C_0 \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc}\frac{(2n+1)x_0+rx}{2\sqrt{(D_1t)}} \quad (5.21)$$

Here $\alpha = (m-r)/(m+r)$ and $r = \sqrt{(D_1/D_2)}$.

(b) *Analysis of experimental data at diffusion temperatures of* 1100 *and* 1150°*C*

The data from partial-masking experiments may be correlated with the theoretical calculations of the preceding section through equation (5.21).

The surface concentration of phosphorus on silicon at the glass/silicon interface may be obtained from (5.21) by setting $x = 0$;

$$C(0) = C_2(0, t) = m(1-\alpha)C_0 \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc}\frac{(2n+1)x_0}{2\sqrt{(D_1t)}} \quad (5.22)$$

This is plotted in Fig. 14. For $x_0/2\sqrt{(D_1t)} > 0{\cdot}7$, only the first term of the series in (5.22) is significant, and the concentration profiles follow the complementary error function. The match between the theory and the experimental data shown in Fig. 10 gives $\sqrt{(D_1)} = 0{\cdot}27\ \mu/\sqrt{(\text{hr})}$ at 1100°C and $\sqrt{(D_1)} = 0{\cdot}37\ \mu/\sqrt{(\text{hr})}$ at 1150°C. It is seen from Fig. 10 that the lower limit for the factor r/m seems to be approximately 5.

The condition at the n–p junction can be obtained from (5.21) by setting $x = x_j$ and $c_2(x_j, t) = C_3$:

$$C_3 = m(1-\alpha)C_0 \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc}\frac{(2n+1)x_0+rx_j}{2\sqrt{(D_1t)}} \quad (5.23)$$

If $x_0/2\sqrt{(D_1t)}$ is greater than $\sim 0{\cdot}7$, the series in

(5.23) can be approximated by the first term when x_0 and rx_j are comparable. Thus, the region of approximate proportionality between x_0 and x_j shown in Fig. 9 is expected. As x_0 becomes smaller, the first several terms in (5.23) are comparable, and the junction depth x_j would increase less rapidly. Such a trend is also observed in the experimental results in Fig. 9. The behavior near the point of complete masking is not predicted by (5.23), even if one considers that C_3 outdiffuses into the glass and D_2 is concentration-dependent. In this region, the initial distribution of the diffusant in the glass becomes important, and the more accurate initial condition discussed previously for $C_1(x, 0)$ must be used in place of (5.18).

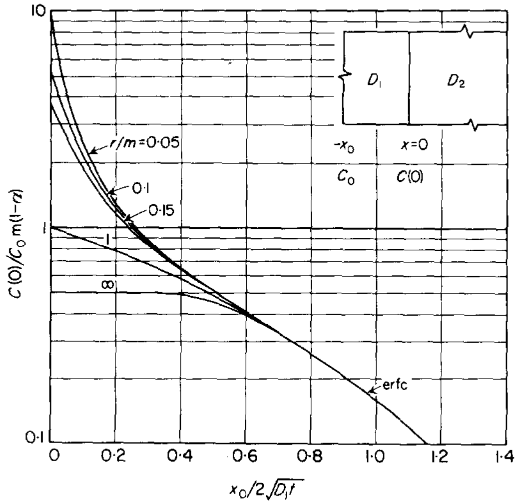

FIG. 14. The calculated phosphorus concentration at the glass/silicon interface as a function of the glass thickness (or oxide thickness) $x_0/2\sqrt{(D_1t)}$.

An approximate approach will be used in applying (5.23) to the experimental data given in Fig. 9. The result of the two-boundary diffusion model is derived on the assumption that the initial phosphorus or phosphorus oxide concentration in the glass is zero. However, it is actually not zero, being given by (5.18), with the time t replaced by $x_0^2/4D_1L^2$ as discussed before. Thus, we may make an approximation to include the initial distribution by taking the result given by (5.21) or (5.23) restricting their applicability to times greater than t_m, the time required for the diffusant to penetrate through the oxide of thickness x_0. Thus, we may replace the time t in (5.21) or (5.23) by $t_d-t_m = t_d-Ax_0^2$. We assume that $t_m = Ax_0^2$, where A depends on temperature only, since the masking condition follows the parabolic relation. Here t_d is the diffusion time. For a given diffusion condition, the argument of the complementary function in (5.23) must be a constant, so that we may write:

$$x_0+rx_j = B\sqrt{(t_d-Ax_0^2)} \qquad (5.24)$$

by taking only the term $n = 0$. The constants A and B are empirically obtained by matching (5.24) to the experimental data and cannot be explicitly related to any of the physical quantities. However, approximate values of $r = \sqrt{(D_1/D_2)}$ may be obtained. From these values of r and the values of D_1 from (5.22), the values of D_2 may then be determined.

An independent check on D_2 may be made from the data at $x_0 = 0$ by using (5.22) and (5.23). Thus,

$$C_3/C(0) = \operatorname{erfc} x_j/2\sqrt{(D_2t)} \qquad (5.25)$$

in which $C(0)$, the phosphorus surface concentration on silicon at the silicon/glass interface, is obtained from (4.2) by using BACKENSTOSS's curves.(7) The self-consistent results obtained by matching the experimental data with (5.22), (5.24) and (5.25) are tabulated in Table 1. The calculated experimental value of L and C_0/N using (5.14) are also given.

Table 1

T_d (°C)	$C(0)$ $x_0 = 0$ (atoms/cm³)	$\sqrt{(D_1)}$ ($\mu/\sqrt{(\text{hr})}$)	$\sqrt{(D_2)}$ ($\mu/\sqrt{(\text{hr})}$)	$r = \sqrt{(D_1/D_2)}$	A	$B/2\sqrt{(D_1)}$	L	C_0/N
1100	$7{\cdot}9\times10^{20}$	0·27	0·80	0·34	3·46	2·69	0·927	3·17
1150	$1{\cdot}1\times10^{21}$	0·38	1·12	0·34	2·17	2·74	0·856	2·45

It is interesting to note that the ratio of the diffusion coefficients in the glass and in the silicon is relatively insensitive to temperature. From this ratio, we may make an estimate of the upper limit of the segregation coefficient, m, by using the estimated lower limit of 5 for r/m from Fig. 10. Thus, m is probably less than $r/5 = 0{\cdot}34/5 = 0{\cdot}07$.

6. SUMMARY

Experimental investigation of the diffusion of phosphorus oxide through a silicon oxide film on silicon indicates that the diffusion process can be described by two approximate models, while the transition region between the two models occurs at an oxide thickness of less than $\sim 0{\cdot}05\ \mu$. During the first step, the oxide layer is completely effective in masking against P_2O_5, so that there is no phosphorus-rich layer in the silicon beneath the silicon oxide film. In this case an oxide of phosphorus diffuses through an apparently glassy layer of a composition ($P_xSi_yO_z$) and upon reaching the interface between the glass and the silicon oxide it reacts very rapidly with the silicon oxide to form a new layer of the glass. (Another possibility is the diffusion of a silicon oxide in the glass toward the surface; upon reaching the surface it reacts with P_2O_5 in the vapor phase to form the glass.) Thus, the glass/silicon oxide interface is well defined and advances with a velocity which is limited by the diffusion rate of an oxide of phosphorus in the glass. The growth of the glass follows a parabolic law. Experimentally, it is determined that

$$x_m^2/t_m = 6{\cdot}25\times 10^4 \exp(-1{\cdot}46/kT)\ \mu^2/\text{hr}$$
$$= 1{\cdot}7\times 10^{-7} \exp(-1{\cdot}46/kT)\ \text{cm}^2/\text{sec}$$

for the growth of the phosphorus silicate glass in silicon oxide.

During the second step, at a later time, the silicon oxide film is completely penetrated by the glass, and an n-p junction is formed beneath the glass in the silicon from the n-type phosphorus impurity. This situation can be approximated by assuming that the glass reaches a final thickness equal to the thickness of the original silicon oxide and no reaction takes place between silicon and the diffusing phosphorus oxide species. Then, the model becomes that of diffusion of an oxide of phosphorus in the glass. As the oxide of the phosphorus reaches the glass/silicon interface, phosphorus atoms enter the silicon and diffuse away. The structural detail of the glass/silicon interface is not known, but it is approximately described by a small "segregation coefficient" for phosphorus between the glass and the silicon.

REFERENCES

1. Frosch C. J. and Derick L., *J. Electrochem. Soc.* **104,** 547 (1957).
2. Ligenza J. R., Unpublished work at Bell Telephone Laboratories.
3. Law J. T., *J. Phys. Chem.* **61,** 1200 (1957).
4. Barrer R. M., *Diffusion in and through Solids* p. 126. Cambridge University Press (1951).
5. Evans J. W. and Chatterji S. K., *J. Phys. Chem.* **62,** 1064 (1958).
6. Valdes L. B., *Proc. Inst. Radio Engrs.* **42,** 420 (1954).
7. Backenstoss G., *Bell Syst. Tech. J.* **37,** 699 (1958).
8. Crank J., *The Mathematics of Diffusion.* Clarendon Press, Oxford. (1956).