

Impurity Redistribution and Junction Formation in Silicon by Thermal Oxidation

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In the process of growing an oxide on doped silicon, electrically active impurities near the silicon/silicon dioxide interface are redistributed according to the diffusion coefficients and the distribution coefficient of the impurity between the oxide and the semiconductor. An analysis of the phenomenon predicts that single-junction or two-junction material can be obtained by oxidation of the surface of a compensated silicon crystal. For parabolic growth of the oxide, the surface concentration is independent of time, and the junction depth, gradient and sheet resistivity vary with $t^{1/2}$. This has been demonstrated experimentally by oxidation of a compensated p-type silicon crystal doped with gallium and antimony.

I. INTRODUCTION

During the growth of an oxide on a semiconductor surface, the doping impurities of the crystal may undergo a redistribution in the semiconductor in a region near the surface. The extent of the redistribution, which may range from a pile-up region to a depletion region, depends on the segregation coefficient of the impurity at the semiconductor-oxide interface, on its diffusion coefficients in both the semiconductor and the oxide and on the rate and time of oxidation.

To illustrate, consider the case where an impurity is completely rejected by the oxide; i.e., its segregation coefficient k is zero. The resulting concentration gradient will cause diffusion of the impurities back into the body of the semiconductor. This is a nonequilibrium problem, where the resulting impurity concentration profile will change continuously with time. Fig. 1 shows schematically two redistribution profiles for two extreme cases of pile-up ($k < 1$) and depletion ($k > 1$).

It is evident that, with more than one impurity in the semiconductor,

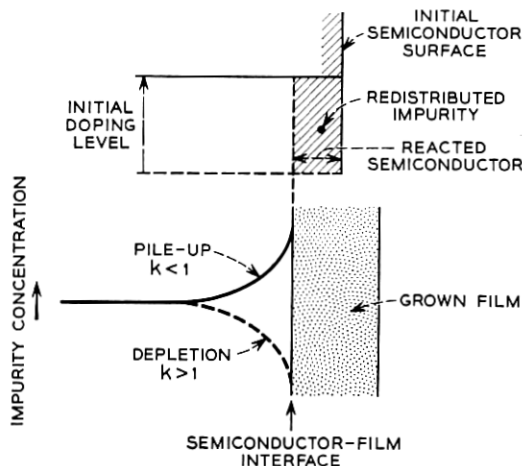


Fig. 1 — Schematic diagram of the redistribution of an impurity, originally uniformly distributed, produced by thermal oxidation of semiconductor surface.

this process may produce various distribution profiles with single or multiple junctions. Fig. 2 illustrates two such possibilities.

In this paper we will present: (a) an analysis of the impurity redistribution phenomenon and its application to junction formation, and (b) experimental data for the system silicon-silicon dioxide with gallium and antimony as impurities.

II. THEORY

In Section 2.1 the pertinent equations and boundary conditions of a model of the redistribution process is presented. In Section 2.2, an ap-

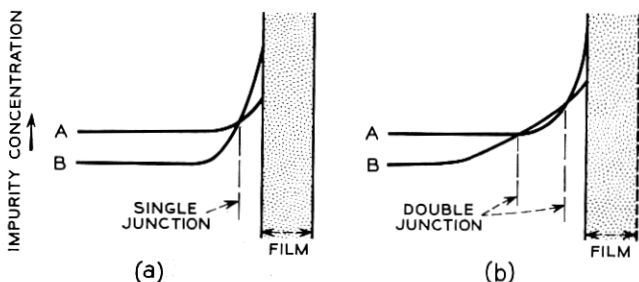


Fig. 2 — Schematic diagram of the concentration profiles of two impurities produced by thermal oxidation: (a) single junction formation; (b) double junction formation.

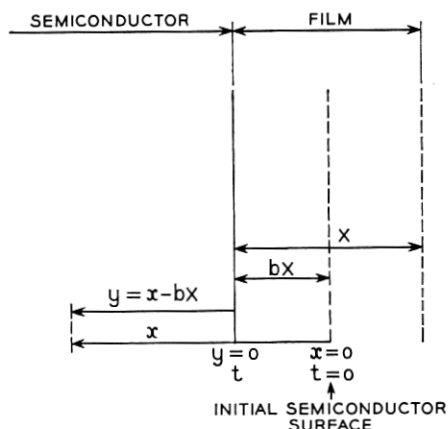


Fig. 3 — Coordinates and notations used in the analysis of the impurity redistribution phenomenon.

proximate solution is given for an important practical case where the segregation coefficient of the impurity at the semiconductor-film interface is negligibly small. In Section 2.3 an approximate solution is given for the case of parabolic growth of film thickness with time and for any segregation coefficient. In Section III, the above solutions are applied to determine some junction characteristics.

2.1 Model of Redistribution Process

Fig. 3 shows the coordinates and some of the terminology used below. At time $t = 0$, the semiconductor boundary corresponds to the plane $x = 0$ when the film growth process is started. At any time t let the film thickness be X . The corresponding thickness of semiconductor material used in producing this film is bX , where b is a constant. For the system silicon-silicon dioxide, b is about 0.44 for the amorphous oxide. Using the moving coordinate $y = x - bX$, where $y = 0$ corresponds to the instantaneous location of the semiconductor-film interface, the diffusion equation for any point within the semiconductor takes the form

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial y^2} + b \frac{dX}{dt} \frac{\partial n}{\partial y}, \quad (1)$$

where n is the impurity concentration and D is the diffusion coefficient of the impurity in the semiconductor. The term dX/dt is the rate of film growth that must be obtained from experimental data. The boundary conditions that must be satisfied are:

- i. At $t = 0$,

$$n = n_0 \quad \text{for all values of } y, \quad (2)$$

where n_0 is the initial uniform concentration of impurity in the semiconductor.

ii. At $y = \infty$,

$$n = n_0 \quad \text{for all values of } t, \quad (3)$$

for a semi-infinite semiconductor.

iii. At the moving boundary between semiconductor and film, conservation of impurity must be satisfied. The rate of impurity diffusion into the semiconductor is

$$-D \left(\frac{\partial n}{\partial y} \right)_0,$$

For a segregation coefficient k , the rate at which impurities are admitted into the oxide is

$$kn_s \left(\frac{dX}{dt} \right),$$

where n_s is the instantaneous surface concentration of the impurity in the semiconductor.* For conservation of impurity, the sum of the above terms must be equal to the impurities in the reacted semiconductor $n_s[b(dX/dt)]$:

$$D \left(\frac{\partial n}{\partial y} \right)_0 + n_s(b - k) \frac{dX}{dt} = 0. \quad (4)$$

Measurements by Ligenza³ of the kinetics of oxidation of silicon under various conditions have shown that the relation between film thickness and time can be represented by the following power expression:

$$X^m = Kt, \quad (5)$$

where K is the oxidation constant that is dependent on the pressure of the reacting gas and on temperature. The temperature dependence is exponential.

The activation energy as well as the exponent m are dependent on the

* This implicitly assumes that the film growth takes place at the semiconductor-film interface. Evidence for such a process has been shown for the oxidation of silicon under various conditions.^{1,2} Furthermore, if a film grows at the film gas interface, i.e., by migration of the semiconductor atoms or ions through the film, and if the diffusion coefficient of the impurity in the film is negligibly small, one obtains the case of effectively complete rejection of the impurity by the film. If, on the other hand, the impurity diffusion in the film cannot be neglected, one must include an additional diffusion equation for the impurity in the film and solve it simultaneously with (1). Such a case was not considered in this paper.

oxidation conditions. For oxidation in oxygen or water vapor at pressures of one atmosphere or less, the activation energy is 1.7 ev and m is 2. For oxidation in water vapor at high pressures, the activation energy is 1.0 ev and m is 1.0.

Now one desires a solution of the diffusion equation, (1), that satisfies the three boundary conditions given, (2), (3) and (4), with the oxidation process as described by (5). Such a general solution was not obtained. Approximate solutions, however, were derived based on discarding the diffusion equation, (1), and assuming a time-dependent exponential impurity distribution in the semiconductor. Such a solution satisfies all the boundary conditions, (2), (3) and (4), as well as the condition of conservation of all redistributed impurities.*

2.2 Impurity Redistribution by a Film Growth $X^m = Kt$ with a Segregation Coefficient $k = 0$.

At any time during the process, it is assumed that the impurity distribution in the semiconductor follows the following exponential form:

$$n - n_0 = (n_s - n_0)e^{-y/A}, \quad (6)$$

where n_s and A are in general time-dependent. This equation already satisfies our second boundary condition, (3). To satisfy the third boundary condition, (4), one substitutes (6) in (4) and obtains

$$1 - \frac{n_0}{n_s} = \frac{A}{D} \left(\frac{dX}{dt} \right) b. \quad (7)$$

Furthermore, for the conservation of impurity,

$$\int_0^\infty (n - n_0) dy = n_0 b X.$$

Substituting in (6) and integrating, one obtains:

$$\frac{n_s}{n_0} - 1 = \left(\frac{b}{A} \right) X. \quad (8)$$

From (7) and (8) one solves for n_s and A , which are obtained as functions of time. It is evident that the first boundary condition, (2), is also satisfied:

$$\frac{n_s}{n_0} = P + (P^2 - 1)^{\frac{1}{2}} \quad (9)$$

* More recently, Doucette et al., have obtained a rigorous solution for the special case of parabolic film growth ($m = 2$). Concentration profiles based on the above approximate solution deviate by less than 10 per cent from exact profiles.

and

$$A = \frac{bX}{\frac{n_s}{n_0} - 1},$$

where

$$P = 1 + \frac{b^2}{4D} \frac{d(X^2)}{dt} = 1 + \frac{b^2}{4D} \left[\frac{2}{m} K^{2/m} t^{2/(m-1)} \right]. \quad (10)$$

From the above equations and the distribution equation, (5), one obtains the desired distribution of impurities in the semiconductor as a function of time. It is of interest to note that both the surface concentration n_s and the penetration A/X , where X is the film thickness, are determined by the single parameter P , as defined by (10). Except for a parabolic growth of the film, where $m = 2$, the parameter P is generally dependent on time; i.e., the surface concentration n_s and the penetration A/X are time-dependent. For parabolic growth, however, the surface concentration n_s is independent of time and the penetration A/X is also independent of time; i.e., the penetration of the redistribution A is directly proportional to the film thickness X . For the two practical cases of parabolic and linear growth one, therefore, obtains

$$P = 1 + \frac{b^2 K}{4D} \quad (\text{parabolic growth}) \quad (11)$$

and

$$P = 1 + \frac{b^2 K^2}{2D} t \quad (\text{linear growth}). \quad (12)$$

The temperature dependence of the process appears in the ratio K/D for parabolic growth. Since both K and D are exponentially dependent on temperature, the process of impurity distribution is also exponentially dependent on temperature, with an activation energy equal to the difference between the activation energies of the impurity diffusion in the semiconductor and the film growth process.

For illustration, the above equations were used to calculate the surface concentration of redistributed impurities in silicon when it is thermally oxidized in oxygen. The oxidation in this case is parabolic ($m = 2$) and the oxidation constant K is best fitted in the temperature range of 900 to 1200°C and atmospheric pressure* by the following expression:

* The oxidation constant K , according to Ligenza,³ is proportional to $p^{0.8}$, where p is the oxygen pressure.

$$K = 8.3 \times 10^{-8} e^{-1.75q/kT} \text{ cm}^2/\text{second}, \quad (13)$$

where q is the electronic charge, k is Boltzman's constant and T is the absolute temperature (kT/q in this expression is in volts). Using (9), (11) and (13), n_s/n_0 was calculated for different values of D , the impurity diffusion coefficient in silicon, at various temperatures. The results are shown in Fig. 4.* On the 1100°C line, points corresponding to various impurities are indicated, using the diffusion coefficients at 1100°C reported by Fuller and Ditzemberger.⁵ The broken line shown passing through the antimony point corresponds to the effect of temperature on surface concentration. It corresponds to an activation energy of 4.0 ev for the diffusion coefficient. In general, for a diffusion activation energy greater than the oxidation activation energy of 1.75 ev, lowering the temperature will raise the surface concentration of the redistributed impurity. Only when the activation energy of diffusion of an impurity equals that of the film growth process does the surface concentration become independent of temperature.

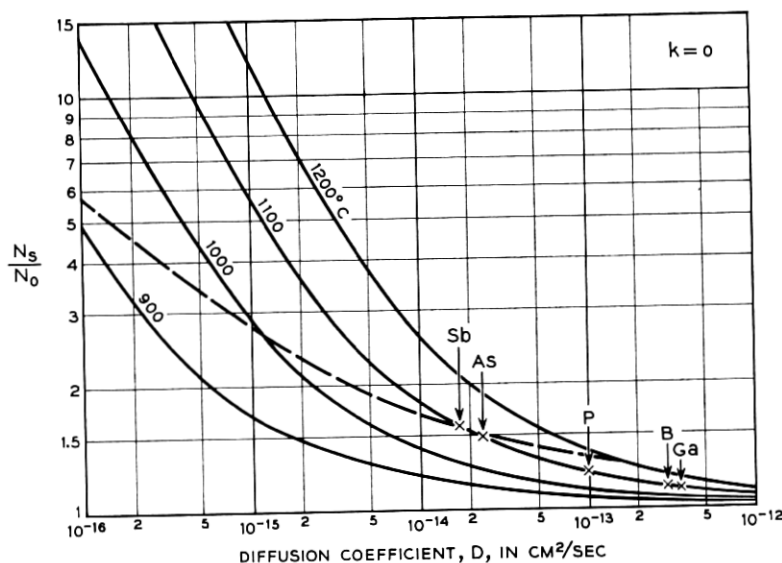


Fig. 4 — Calculated ratios of impurity surface concentration to body concentration (N_s/N_0) produced by parabolic oxidation of silicon with zero segregation coefficient. The arrows indicate the surface concentrations predicted for the impurities indicated at 1100°C. The dashed line corresponds to the surface concentrations predicted for antimony at various temperatures.

* For amorphous silica, $b = 0.44$.

2.3 Effect of Segregation Coefficient ($k \neq 0$) on Impurity Redistribution for Parabolic Film Growth ($m = 2$)

Based on thermodynamic considerations, Thurmond⁶ has calculated the segregation coefficient of various impurities at the interface between silicon and amorphous silicon dioxide. His results are summarized in Table I.

This table indicates that, for most impurities commonly used for doping of silicon, the segregation coefficient is small and should produce pile-up upon oxidation. Furthermore, for these impurities, the assumption of complete rejection by the oxide appears reasonable. For aluminum as an impurity, however, one should obtain depletion near the silicon surface upon oxidation.

TABLE I — SEGREGATION COEFFICIENTS OF VARIOUS IMPURITIES IN THE SYSTEM SILICON-SILICON DIOXIDE

Segregation Coefficient	Impurities
$k > 10^3$	aluminum (Al_2O_3)
$k = 10^3$ to 10^{-3}	boron (B_2O_3)
$k < 10^{-3}$	gallium (Ga_2O_3)
$k < 10^{-3}$	indium (In_2O_3)
$k < 10^{-3}$	arsenic (As_2O_3)
$k < 10^{-3}$	phosphorus (P_4O_{10})
$k < 10^{-3}$	antimony (Sb_2O_3)

No detailed measurements are as yet available of the segregation coefficient of the various impurities in the system silicon-silicon dioxide. There is some experimental evidence, however, that supports some of Thurmond's predictions. Tracer measurements by E. Tannenbaum on silicon doped with radioactive phosphorus have shown that, upon oxidation, more than 95 per cent of the phosphorus in the reacted silicon remains in the silicon. Measurements on junction formation by the oxidation of compensated silicon crystals, as discussed in Section III, give evidence for the pile-up of antimony. Similar measurements by Doucette indicate the depletion of aluminum.

For cases where $k \neq 0$, a solution of the impurity distribution is readily obtained for the case of parabolic film growth following the same analysis of Section 2.2. The results are as follows:

$$\frac{n_s}{n_0} = \frac{P'}{1 + 2k(P' - 1)} \left\{ 1 + \left[1 - \frac{1 + 2k(P' - 1)}{P'^2} \right]^{\frac{1}{2}} \right\}$$

and

$$\frac{A}{bX} = \frac{1 - k \frac{n_s}{n_0}}{\frac{n_s}{n_0} - 1}, \quad (14)$$

where

$$P' = 1 + (1 - k) \frac{b^2 K}{4D}.$$

It is evident that, by setting $k = 0$, these expressions reduce to those of (9), which is the case of extreme pile-up. For the case of extreme depletion, one sets $k = \infty$ and obtains:

$$\frac{n_s}{n_0} = 0 \quad (15)$$

and

$$\frac{A}{bX} = 2 \left[\left(\frac{P+1}{P-1} \right)^{\frac{1}{2}} - 1 \right],$$

where P is as defined by (11).

III. JUNCTION FORMATION BY THERMAL OXIDATION

3.1 *System with Two Impurities; Junction Formation*

We have shown that by growing a film on a semiconductor surface one may obtain, under certain conditions, pile-up or depletion of an impurity near the surface. By proper choice of two impurities, one being a donor-type impurity and the other an acceptor-type impurity, it is evident that various junction configurations may be obtained.

In this section we will discuss the conditions under which such junctions may be obtained, and will determine some of their characteristics. Use will be made of the results obtained in the previous sections. Hence, it is implicitly assumed that there are no interactions between the impurities.

In general, the choice of the impurities is based on differences in their segregation coefficient or on differences in diffusion coefficients or on both. In the silicon-silicon dioxide system, for instance, two interesting pairs of impurities are gallium-antimony and phosphorus-aluminum. In the gallium-antimony system, both impurities will pile up with nearly zero segregation coefficient. Due to the smaller diffusion coefficient of antimony, however, it will produce larger pile-up. If this difference exceeds

the initial excess of gallium over antimony in the silicon crystal, a junction is obtained (see Fig. 4). In the phosphorus-aluminum system,⁴ on the other hand, phosphorus will pile up while aluminum will be depleted. Here, again, with proper initial compensation of the silicon crystal, a junction may be obtained.

Consider the case of a crystal uniformly doped with a donor-type impurity n_d and an acceptor-type impurity n_a , both with zero segregation coefficient at the semiconductor-film surface. If the crystal is initially p-type (i.e., $n_a > n_d$) the condition for the formation of a *single* junction upon film growth is that $(n_d)_s > (n_a)_s$ and, from (9), this sets the following condition on the initial crystal compensation:

$$\frac{n_d}{n_a} > \frac{P_a + (P_a^2 - 1)^{\frac{1}{2}}}{P_d + (P_d^2 - 1)^{\frac{1}{2}}} \quad (16)$$

The resulting distribution profiles will be as shown in Fig. 2(a). In a similar fashion, one may set the condition of crystal compensation to obtain two junctions as shown in Fig. 2(b).

To demonstrate some typical characteristics of the obtained junction, we will consider only the simple case where the pile-up of one impurity can be ignored with respect to the pile-up of the other impurity. If n_1 is the impurity that piles up and n_2 is the other, the compensation of the crystal must be such that $n_2 > n_1$, and to obtain a junction one must satisfy the following requirement:

$$\frac{n_2}{n_1} < P_1 + (P_1^2 - 1)^{\frac{1}{2}} \quad (17)$$

Now an expression will be given for the resulting junction depth y_j , gradient a , and sheet resistance ρ_s by using (6), which describes the distribution profile of the impurity n_1 :

$$\frac{y_j}{X} = \frac{bn_1}{n_{1s} - n_1} \ln \left(\frac{n_{1s} - n_1}{n_2 - n_1} \right), \quad (18)$$

$$aX = -\frac{1}{b} (n_2 - n_1) \left(\frac{n_{1s}}{n_1} - 1 \right), \quad (19)$$

and

$$\frac{1}{\rho_s X} = \mu q \frac{b}{\frac{n_{1s}}{n_1} - 1} \left[(n_{1s} - n_2) - (n_2 - n_1) \ln \left(\frac{n_{1s} - n_1}{n_2 - n_1} \right) \right], \quad (20)$$

where n_{1s} is the surface concentration of the impurity n_1 , and is obtained from (9); μ is the mobility of the carrier of interest; and q is the

electron charge. The right-hand sides of the above equations are independent of time but dependent on temperature alone. For the parabolic film growth, therefore, the junction depth is directly proportional to film thickness, and both junction gradient and sheet resistance are inversely proportional to film thickness. The constants of proportionality, which are the right-hand sides of the above equations, are determined by a single parameter K/D , which is the ratio of the oxidation constant to the diffusion coefficient of the impurity in the semiconductor.

A point of interest that may be mentioned here is that, for a film growth process with well-defined kinetics, it is possible from measurements of resulting junction characteristics (such as junction depth and sheet resistivity) to obtain directly the impurity diffusion constant and its activation energy, and also the carrier mobility in the semiconductor. This is demonstrated in the following section on experimental measurements in the system silicon-silicon dioxide with gallium and antimony as the two impurities.

3.2 *Experimental Results*

All measurements reported here were obtained on silicon with gallium and antimony as the doping impurities. The choice of these two impurities was made for the following reasons. According to Thurmond's calculations (Table I) both impurities should be rejected by the oxide, and hence both should pile up when the silicon surface is oxidized. Furthermore, the diffusion coefficient of antimony is smaller by about two orders of magnitude than that of gallium, and hence should produce stronger pile-up at the surface. Also, the diffusion coefficient of gallium is sufficiently high compared to the oxidation constant that its redistribution can be neglected (see Fig. 4).

We have therefore chosen a silicon crystal that was doped with antimony to a concentration of 4×10^{18} atoms/cm³ and compensated with gallium to a higher concentration, making the crystal p-type. The crystal was not uniform in resistivity, and small slices with different resistivities, but uniform within a slice, could be obtained from different regions of the crystal. Two sets of slices were used. The first consisted of only one slice with a resistivity of 21 ohm-cm. This was used for the experiment at 1050°C, with the sample being oxidized in oxygen at one atmosphere pressure for the periods of 2, 18 and 90 hours. After each run, the junction depth and sheet resistivity were measured. The surface was then etched off to remove the junction, the sample resistivity was measured and the second oxidation run was carried out. This was repeated until three sets of measurements were made. The second set of slices con-

sisted of two slices of 4 ohm-cm resistivity. These were treated at 1210°C also in oxygen at one atmosphere pressure, one for 1 hour and the other for 16 hours. For each slice, the junction depth and sheet resistance were measured. Furthermore, small mesas were etched out of each slice and the junction breakdown voltage was measured. Using Miller's relations⁷ between breakdown voltage and junction gradient, the junction gradient was obtained. Table II gives a summary of the results.

Fig. 5 is a plot of the above data, with the oxide film thickness, junction depth and sheet resistivity for each temperature being plotted versus time of oxidation. The straight lines shown indicate, as predicted, a satisfactory fit of the data to a square root time dependence. In Table II it is also seen that the junction gradient has approximately the same time dependence. According to (18), (19) and (20), the parameters y_j/X , aX and $\rho_s X$ should be functions of the single ratio K/D , which is only dependent on temperature.

In Table III, the experimental values are given for the parameters y_j/X , aX , $\rho_s X$ and $X^2/t = K$ at the two temperatures of 1210 and 1050°C. Using (18), (19) and (20), it is now possible to substitute the experimental values of the above parameters to obtain the ratio K/D and the diffusion coefficient D for the two temperatures and compare with published data. In principle, the same value of the ratio K/D should be obtained at any one temperature from all three measurements of y_j/X , aX and $\rho_s X$. Such calculations were carried out and the results are also shown in Table III. At 1210°C, K/D was found to be 0.18 and 0.14, from the junction depth and the junction gradient measurements respectively. To obtain K/D from (20) and the measured sheet resistance parameter, $\rho_s X$, one finds a strong dependence of K/D on the value assigned to the mobility μ_n . We have instead substituted the values of K/D of 0.18 and 0.14, obtained from junction depth and junction gradient measurements, in (20) and obtained values of μ_n corresponding to the measured parameter $\rho_s X$. The values of μ_n ob-

TABLE II—JUNCTION CHARACTERISTICS OF OXIDIZED P-TYPE COMPENSATED SILICON WITH GALLIUM-ANTIMONY AS IMPURITIES*

$T, ^\circ\text{C}$	t , hours	ρ_s , ohm-cm	X, A°	Y_j, A°	ρ_s , ohm/sq	V_B , volts	a , cm ⁻⁴
1050	2	21	1250	2800	2480	—	—
1050	18	21	3800	10300	880	—	—
1050	90	21	10500	26400	414	—	—
1210	1	3.65	2100	15200	2000	55	5.5×10^{20}
1210	16	3.65	8400	73700	520	85	1.55×10^{20}

* Antimony concentration $\sim 4 \times 10^{18}$ atoms/cc.

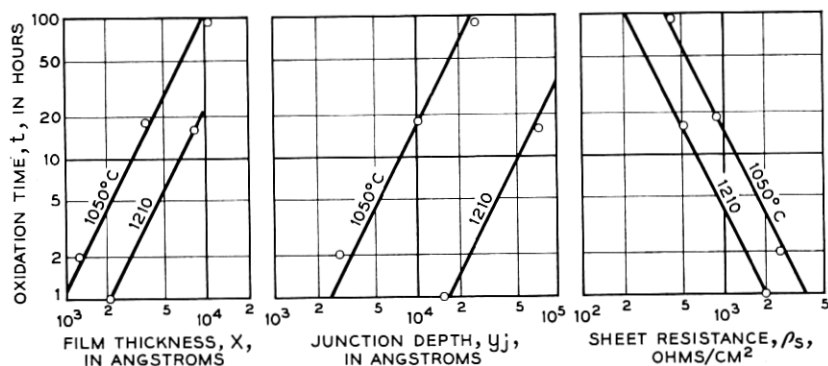


Fig. 5 — Experimental data showing the variations with time of the oxide film thickness, the junction depth and the sheet resistance, for gallium-antimony doped silicon. The straight lines correspond to $t^{\pm 1/2}$ dependence.

tained were 120 and 115 cm²/volt-seconds respectively. Similarly, the data were analyzed and the results are given in Table III. It is to be noted that the obtained values of electron mobility μ_n of 97–120 cm²/volt-second at 4×10^{18} /cm³ concentration are in satisfactory agreement with published data (see, for instance, Conwell's review article⁸). From the calculated values of K/D and the measured $K = X^2/t$, the diffusion coefficients of antimony in silicon at 1050 and 1210°C were obtained and are given in Table III. Corresponding values from the literature⁵ are also given for comparison.

The self-consistency of the above results and their fair agreement with published data are quite satisfactory considering the many simplifying assumptions on which the analysis was based.

TABLE III — CONSTANTS CALCULATED FROM MEASURED PARAMETERS

Measured					Calculated		
$T, ^\circ\text{C}$	y_j/X	aX, cm^{-1}	$\rho_s X, \text{ohm-cm}$	$K, \text{cm}^2/\text{sec}$	K/D	$\frac{\mu_n}{\text{cm}^2/\text{volt-sec}}$	$D, \text{cm}^2/\text{sec}$
1210	8.0	1.2×10^{16}	0.042	1.2×10^{-13}	0.18 0.14	115 120	(a) 7×10^{-13} *
1050	2.6	—	0.037	2.6×10^{-14}	5.8	97	(b) 4.5×10^{-15} *

* Published values (Fuller and Ditzenger⁵): (a) 2.5×10^{-13} ; (b) 5×10^{-15} .

$\mu_p = 40 \text{ cm}^2/\text{volt-sec}$.

$C_{sb} = 4 \times 10^{18} \text{ atoms/cc}$.

IV. CONCLUSIONS

A model has been presented for the phenomenon of impurity redistribution in a semiconductor during the thermal growth of a surface film. It has been demonstrated experimentally for the silicon-silicon dioxide system and satisfactory agreement with the model was obtained.

The following are some implications of this phenomenon: (a) Under certain conditions it may have significant effect on other processes such as conventional diffusion in oxidizing atmospheres. (b) In processes involving thermal film growth on junctions, such as thermal oxidation of silicon junctions for stabilization purposes, impurity redistribution effects can be significant under certain conditions and must be taken into consideration. (c) The redistribution phenomenon provides an experimental tool for determinations of some physical constants such as segregation coefficients, diffusion constants and mobilities. (d) One can make junctions by this method. However, heavily compensated starting materials are needed, which often poses a control problem.

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