IMPURITY DIFFUSION INTO SEMICONDUCTORS

Yu. B. Bolkhovityanov

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A method is described by which it is possible to obtain thin diffusion layers with various impurity distributions within the layer. Calculations and graphs are given which may be used to determine the junction thickness and impurity concentration at any point of the diffusion layer when the diffusion conditions are known.

One of the main steps in developing high-frequency transistors is impurity diffusion in the semiconductor. In particular, diffusion is employed in order to obtain thin base layers. At present, the most widely used method is diffusion from the gas phase. However, this method has a number of drawbacks which limit the field of application of thin base layers. If diffusion is carried out in a quartz ampul, the quartz must be very pure, as otherwise the specimen may become contaminated. It is very difficult to calculate and control the impurity vapor pressure which is necessary in order to obtain a predetermined impurity concentration in the specimen. The impurity concentration in the surface layer of a crystal proves to be so high that the breakdown voltage at the emitter-base junction is no greater than 1.5–2 V; therefore, other methods are used for reducing the impurity concentration at the surface of the specimen.

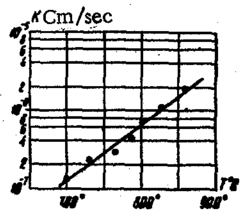

Fig. 1

A diffusion method is proposed which does not have the above mentioned drawbacks and which makes it possible to obtain base layers with a varying impurity distribution within the specimen thickness.

The semiconductor crystal is placed in an evacuated chamber in a heat-treatment furnace, the surface of the specimen on which the diffusion layer is to form remaining exposed. In order to achieve a high vacuum, the crystal is heated to the diffusion temperature, after which the impurity begins to evaporate from a special evaporator. It is possible to choose the evaporator parameters in such a way that during the evaporation process, the concentration of diffusant at the specimen surface does not exceed 10^{17}–10^{18} atoms/cm^3. After evaporation ceases the crystal is maintained at the diffusion temperature for some time, as a result of which the surface layer becomes impoverished and the depth of the junction increases. The impurity distribution within the specimen thickness will vary depending upon the evaporation time and subsequent diffusion.

THEORETICAL RELATIONSHIPS

The diffusion processes are described by the Fick equations:

$$J = -D\frac{\partial N}{\partial x}, \quad \frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial x^2}, \tag{1}$$

where J is the diffusion flaw of the material, D is the diffusion coefficient, and N is the concentration of the diffusing particles.

Equations are given for the one-dimensional case. In practice, we are usually faced with the problem of impurity diffusion into a semibounded body. For this case, a general formula for (1) is derived:

$$N(x,t) = \frac{1}{2\sqrt{\pi D t}}\int_0^\infty \left[N(\xi,0)\,e^{-\frac{(\xi-x)^2}{4Dt}} + N_1(\xi,0)\,e^{-\frac{(x+\xi)^2}{4Dt}}\right]d\xi, \tag{2}$$

where N (ξ, 0) is the initial impurity distribution in the crystal and N_1 (ξ, 0) is an unknown function which is determined from the boundary condition

$$J(x_1 t)\Big|_{x=0} = -D\frac{\partial N}{\partial x}\Big|_{x=0}. \tag{3}$$

Usually, the diffusion problem is solved for the condition that there is no flow of material across the boundary x = 0 (reflecting boundary) or that the impurity concentration at the surface is zero (connecting boundary). In actual crystals, a combination of these conditions exists, and a flow of impurities from the crystal across the surface takes place. As a result, the boundary condition takes the form of (2) and (3):

$$D\frac{\partial N(x,t)}{\partial x}\Big|_{x=0} = KN(0,t), \tag{4}$$

where N(0,t) is the concentration of material as the surface of the crystal, and K is a constant determining the rate of particles passage across the interface of the solid and the surrounding medium (in particular, a vacuum). This boundary condition does not take into account the evacuation rate of the system, but in this case the evacuation rate is quite high and the error will be so small that it can be ignored.

Substituting expression (2) into (4), we obtain

$$\int_0^\infty N\left(\frac{\xi}{2t}-K\right)e^{-\frac{\xi^2}{4Dt}}d\xi = \int_0^\infty N_1\left(\frac{\xi}{2t}+K\right)e^{-\frac{\xi^2}{4Dt}}d\xi. \tag{5}$$

The unknown function N_1 may be found from (5). To do this it is necessary to write explicitly the initial impurity distribution N. Let us denote the impurity evaporation time by t_0 and the subsequent diffusion time by t, and let us assume that in the evaporation process, the impurity concentration at the specimen surface is constant. This may be realized by constructing the evaporator in such a way that the impurity evaporates uniformly. This is a design problem. Then the concentration distribution within the specimen obtained after the impurity has evaporated will be described by

$$N(x, t_0) = N_0 \operatorname{erfc}\frac{x}{2\sqrt{Dt_0}}, \tag{6}$$

where N_0 is the concentration at the specimen surface and $\operatorname{erfc} Z = 1 - \frac{2}{\sqrt{\pi}}\int_0^z e^{-\lambda^2}d\lambda$ is an addition to the error function.

Since diffusion continues after evaporation ceases, we shall take expression (6) as giving the initial distribution of the impurity in the specimen. It is not possible to solve equation (5) by substituting the initial distribution (6) into it. Therefore we shall derive an approximation to (6):

$$\operatorname{erfc}\frac{x}{2\sqrt{Dt_0}} \approx e^{-\frac{\alpha x^2}{4Dt_0}}, \tag{7}$$

where α is an approximation factor. Such an approximation is chosen solely for convenience in integration.

Let us assume that the unknown function N_1 may be represented as

$$N_1 = N + f(x) \tag{8}$$

and let us further assume that

$$f(x) = Se^{Mx} + T. \tag{9}$$

Substituting Eqs. (7), (8), and (9) in (5) and solving, we obtain

$$f(x) = 2e^{-K\left(1+\frac{t}{t_0}\alpha\right)x} - 1. \tag{10}$$

Now it is necessary to substitute the function obtained for N_1 into the general solution (2) and solve it. As a result, we obtain

$$\frac{N(x,t)}{N_0} = \frac{e^{-\frac{\alpha t}{t_0}y^2}}{\sqrt{1+\frac{t}{t_0}\alpha}} \cdot [\operatorname{erf} y + e^{z^2+2yz}\cdot \operatorname{erfc}(y+z)], \tag{11}$$

where

$$y = \frac{x}{2\sqrt{Dt}\sqrt{1+\frac{t\alpha}{t_0}}}, \quad z = K\sqrt{\frac{\left(1+\frac{t\alpha}{t_0}\right)t}{D}}. \tag{11a}$$

ERROR ANALYSIS

The p-n junction in a crystal is known to be located at the point x_0 where the concentrations of donor and acceptor impurities are equal. Usually the impurity concentration found in the crystal before diffusion is smaller than the concentration of the diffusing impurity at the crystal surface by 2–4 orders of magnitude. Then the approximate formula (7) yields a relative error of not more than 10% in the junction region for an approximation factor $\alpha = 1.5$. During subsequent diffusion this error decreases. Thus, the accuracy of formula (11) increases with increase in the ratio of the subsequent diffusion time to the evaporation time, t/t_0.

Fig. 2

We have taken Eq. (7) as the initial impurity distribution. More exactly, diffusion from a constant source is expressed by

$$\frac{N(y,z)}{Ne} = \operatorname{erfc} y - e^{z^2+2yz}\cdot \operatorname{erfc}(y+z). \tag{12}$$

where

$$y = \frac{x}{2\sqrt{Dt_0}}, \qquad z = K\sqrt{\frac{t_0}{D}}, \tag{12a}$$

Ne is the impurity concentration in the solid phase and is in equilibrium with the impurity density in the gaseous phase.

The differences between (7) and (2) become greater with a decrease in the initial diffusion (evaporation) time t_0. As a result, the actual depth of the junction will be less than that determined by (11) for small evaporation times t_0.

EXPERIMENTAL VERIFICATION OF CONCLUSIONS

Let us assume that the initial impurity distribution in the crystal has the form $N = N_0$ (the crystal has a uniform impurity distribution over the depth).

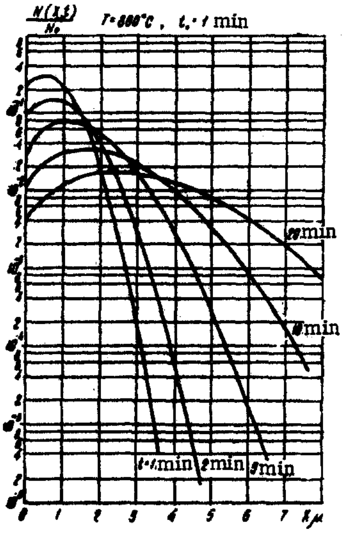

Fig. 3

We may arrive at such a distribution by setting the approximation factor equal to zero. Then (11) takes the form

$$\frac{N(x,t)}{N_0} = \operatorname{erf} y + e^{z^2+2yz}\cdot\operatorname{erfc}(y+z), \tag{13}$$

where

$$y = \frac{x}{2\sqrt{Dt}}, \qquad z = K\sqrt{\frac{t}{D}}. \tag{13a}$$

This formula was obtained by Miller and Smits [3]. If in expression (13) x is set equal to zero, we obtain an equation for the impurity concentration at the crystal surface

$$\frac{N(0,t)}{N_0} = e^{z^2}\operatorname{erfc} z. \tag{14}$$

Using this expression, we may easily determine the coefficient K experimentally. To do this, it is necessary to have a crystal with constant impurity doping which will be used for diffusion in subsequent experiments, to heat it for a predetermined time and to follow the change in concentration at the specimen surface.

In the present work, germanium doped with antimony and having a resistance of 0.005 ohm · cm was used to determine the coefficient K. As a result we have a graph of the coefficient K as a function of temperature, which is given in Fig. 1.

For the experimental verification of Eq. (11), germanium doped with gallium and having a resistance of 4 ohm · cm was used, with antimony as the diffusant.

Experimental and theoretical data are given in the table, from which it is clear that for a reduction in evaporation time t_0 the error in determining the depth of the p-n junction is greater than was previously supposed.

Direct determination of the thickness of the p-n junction $|N(x,t) = Na|$ from formula (11) is quite difficult; therefore Eq. (11) is given in the form of graphs (Figs. 2, 3, 4) for several diffusion temperatures and in inpurity evaporation times, and by using these, it is easy to determine the thickness of the p-n junction. To do this, it is necessary to know either the initial concentration at the crystal surface, the diffusion time, and diffusion temperature or the concentration at the surface of the crystal after diffusion and the corresponding diffusion time and temperature.

APPLICATION OF THE EQUATION OBTAINED TO OTHER METHODS OF IMPURITY DIFFUSION

Another method exists for reducing the impurity concentration at the surface. Diffusion is divided into two stages. The first stage is the basic diffusion, which continues as long as is necessary to obtain the predetermined depth of the p-n junction. The second stage involves maintaining the crystal in a vacuum at a definite temperature, as a result of which the specimen surface layer is impoverished in the impurity while the depth of the p-n junction remains almost constant.

Table 1

t_0, sec	x_{theor} u	x_{exp}, u	$\frac{x_{\text{theor}}-x_{\text{exp}}}{x_{\text{exp}}\%}$, %
10	4.4	3.4	29
30	3.35	2.8	20
30	4.6	3.9	18

Equation (11) obtained earlier is not suitable for determining the depth of the junction, since in our case the time of subsequent annealing in a vacuum is significantly less than the basic diffusion time. Moreover, the depth of the junction may be determined quite simply from (6) (if we assume diffusion from the gas phase). However, by modifying formula (11), we can determine the change in concentration at the specimen surface as a function of the time and temperature of annealing in a vacuum. To do this it is necessary to know the temperature and time of basic diffusion.

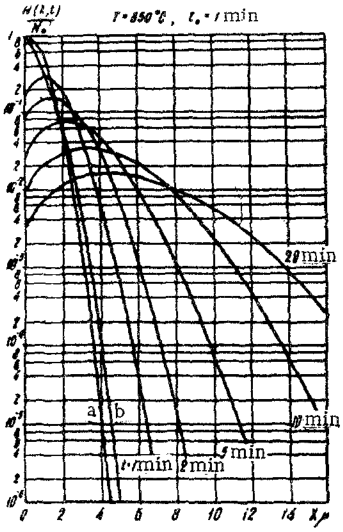

Fig. 4. a) approximation: $\operatorname{erfc}\frac{x}{2\sqrt{Dt_0}}$, b) Actual impurity distribution in the crystal after evaporation the law $e^{-\frac{1.5x^2}{4Dt_0}}$.

Let us simplify Eq. (11) with regard to determining the surface concentration:

$$\frac{N(0,t)}{N_0} = \frac{1}{\sqrt{1+\frac{Dt}{D_0 t_0}\alpha}} e^{z^2} \operatorname{erfc} z, \tag{15}$$

where $z = K\sqrt{\frac{\left(1+\frac{Dt}{D_0 t_0}\alpha\right)t}{D}}$,

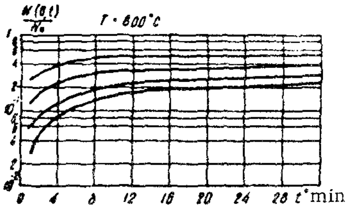

Fig. 5

where t_0 and D_0 are the time and coefficient of basic diffusion, t and D are the time and coefficient of diffusion for vacuum annealing. In order that expression $e^{-\alpha\lambda^2}$ shall not closely approximate to the function erfc λ, initially we take $\alpha\_ = 3.5$. The accuracy of this formula increases with a reduction in the ratio t/t_0, since in this case the effect of the approximation factor α decreases.

On the basis of (15) a number of graphs were constructed for different basic diffusion and annealing temperatures by using these graphs it is easy to determine the vacuum annealing time necessary for the desired reduction in impurity concentration at the specimen surface (Fig. 5: top curve—for t = 30 sec; bottom curve—t = 3 min, second from top —t = = 1 min, and second from bottom—t = 2 min).

REFERENCES

1. B. I. Boltaks, Diffusion in Semiconductors [in Russian], Fizmatgiz, 1961.

2. R. Miller and F. Smits, Phys. Rev., **107**, 1, 65, 1957.

3. F. Smits and R. Miller, Phys. Rev., **104**, 1242, 1956.

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Gor'kii Kharkov
State University