acta phys. slov. 42 (1992), No. 4, 217–227

DEFECTS FORMATION IN BORON IMPLANTED SILICON DURING RAPID ISOTHERMAL ANNEALING

LENHARD, R.[1]), Rožnov pod Radhoštěm, LUBY, Š.[2]), Bratislava

A simple model of secondary defect formation in implanted layers is presented. It describes the precipitation of postimplantation non- equilibrium silicon interstitials, the growth of stable disc agglomerates and their transformation to dislocation loops. The influence of the heating rate on the precipitation phenomena is studied and it is shown that using a sufficiently rapid annealing, the secondary defect formation can be avoided.

The model is experimentally verified using boron implanted silicon processed by furnace rapid isothermal annealing. The rate of temperature increase was 1 – 1000 °C/s. Secondary defects were visualized by reoxidation and chemical etching of silicon. Defect formation was dependent on the implantation dose N_d and at higher doses a faster temperature rise α was necessary in order to achieve defectfree structure. (E.g. $\alpha = 100\,°C/s$ was sufficient for $N_d = 10^{14}\,cm^{-2}$, but not for $N_d = 5 \times 10^{14}\,cm^{-2}$.) For the activation energy of the migration of interstitials the value of 1.7 eV was estimated. The times of the outdiffusion of defects at various doses and temperatures were calculated as well. The experimental results are in agreement with the proposed model.

I. INTRODUCTION

Due to collisions of implanted atoms in the semiconductor lattice primary point defects, e.g. vacancies, divacancies and interstitials, are created. Already during the implantation process, which is performed at the temperature of $\geq 300\,K$ as a rule, point defects partly recombine or they agglomerate into complexes. For the agglomerate formation the content of impurities, like boron, phosphorus, carbon or oxygen in the case of silicon is also important.

In the subsequent thermal processing of the implanted material the primary defects continue to recombine. However, in the case when their concentration is high, not only recombination but also agglomeration into energetically more favourable configurations occurs. The agglomerates may then transform into secondary defects — rod like defects, dislocation loops or stacking faults.

The implantation caused radiation damage and the corresponding primary defect behaviour was studied in many papers, e.g. [1, 2, 3] including our previous

[1]) TESLA Sezam, ROŽNOV POD RADHOŠTĚM, CSFR
[2]) Slovak Academy of Sciences, Institute of Physics, BRATISLAVA, CSFR

work [4]. In the present paper our attention extends to the secondary defects. A simple model for the defect formation in boron implanted silicon is presented. Using this model, the influence of the implanted dose and the heating rate on the secondary defect formation is studied.

II. MODEL OF SECONDARY DEFECT FORMATION IN IMPLANTED LAYERS

The role of post-implantation annealing is twofold: to activate the implanted dopants and to restore the damaged crystal lattice. With regard to the second part it is important to reduce the implantation caused point defects and to prevent or at least suppress their transformation into stable secondary configurations.

The thermodynamic system is in equilibrium at the minimum of the free enthalpy. Nonequilibrium defects involved by implantation increase this enthalpy, which can be again decreased by the defect recombination but also by the formation of energetically more favourable precipitates or interstitial planes inside the dislocation loops.

Let us consider a certain spherical region of the crystal containing N_i nonequilibrium silicon interstitials. Vacancies are not considered here, because the secondary defects formed from vacancies are observed rarely in silicon. Let N_a of interstitials be incorporated in an agglomerate, whereas the remaining $N_i - N_a$ interstitials are distributed randomly. The volume of the mentioned region is expressed as

$$V(t) = \frac{4}{3}\pi \left[2(D_i t)^{1/2}\right]^3, \tag{1}$$

where $R = 2(D_i t)^{1/2}$ is the diffusion length of interstitials, t is time and D_i is the diffusion coefficient of interstitial atoms [7].

We shall consider now the free enthalpy decrease via the formation of a disc agglomerates in the silicon (111) plane. (Spherical agglomerates as well as dislocation loops have a higher energy for the same number of interstitials.) The free enthalpy of the system is

$$G = G_a - G_{i-a}, \tag{2}$$

where G_a, G_{i-a} relates to the agglomerate and to the rest of the region, respectively. We can write [5]

$$G_{i-a} = kT\left\{N_i \ln\left(\frac{N_i - N_a}{N_i}\right) - N_a\left[\ln\left(\frac{N_i - N_a}{N_{eq}}\right) - 1\right]\right\}. \tag{3}$$

Here, N_{eq} is the number of interstitials which are in thermodynamic equilibrium in the volume $V(t)$ and kT has the usual meaning.

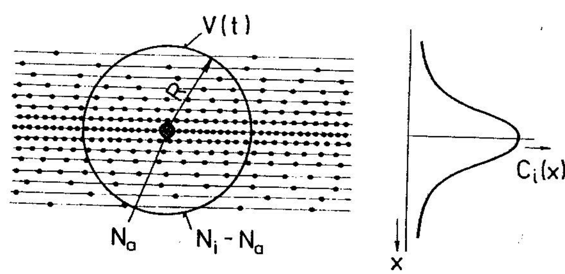

Fig. 1. Spherical region of the crystal with diameter $R = 2(D_i t)^{1/2}$ containing N_a interstitials incorporated into the energetically more favourable defect and $N_i - N_a$ interstitials distributed randomly in the rest of the spherical volume. $C_i(x)$ represents the depth distribution of the implantation caused nonequilibrium silicon interstitials

The number of nonequilibrium interstitials N_i in $V(t)$ (cf. Fig. 1) can be obtained by integration of the Gaussian distribution of interstitials (see [4]). Further, we assume a nonamorphized implanted layer.

The quantity G_a for a disc agglomerate in silicon is given by [6]

$$G_a = \left[\frac{2N_a}{K_s} + \left(\frac{4\pi N_a}{3K_s}\right)^{1/2} \cdot A_0\right]\sigma, \tag{4}$$

where $K_s = 8 \times 10^{14}\,\mathrm{cm}^{-2}$ is the density of atoms in the silicon (111) plane, A_0 is the silicon lattice constant and σ is the density of energy at the boundary of the precipitate and the surrounding crystal: $\sigma = 2H_{if}/\pi A_0^2$ [eV/cm^2], $H_{if} = 4.13 \times 10^{-4}(T - T_0) + 2.59$ [eV] for $T > T_0$, $T_0 = 570\,\mathrm{K}$ [7].

The dependence of the free enthalpy on the number of interstitials in the agglomerate in silicon is shown in Fig. 2 (curve G_a). The maximum is reached at $N_a = N_{ac}$.

Now two possibilities are to be considered:

a) For $N_a < N_{ac}$ the free enthalpy is decreasing by the decrease of N_a, i.e. by the dissolution of the agglomerate.

b) For $N_a > N_{ac}$ the decrease of free enthalpy is taking place by the further growth of the stable agglomerate.

From the condition $\mathrm{d}G/\mathrm{d}N_a = 0$, assuming $N_i \gg N_a$ and using eqs. (2, 3, 4), N_{ac} can be expressed as follows:

$$N_{ac} = \frac{\frac{4\pi}{3K_s} A_0^2}{\left[\frac{kT}{\sigma}\ln\left(\frac{N_i}{N_{eq}}\right) - \frac{2}{K_s}\right]^2}. \tag{5}$$

The temperature dependence of N_{ac} (Fig. 3) shows that at a higher temperature only larger agglomerates are stable and, therefore, the probability of formation of stable agglomerates decreases with increasing temperature.

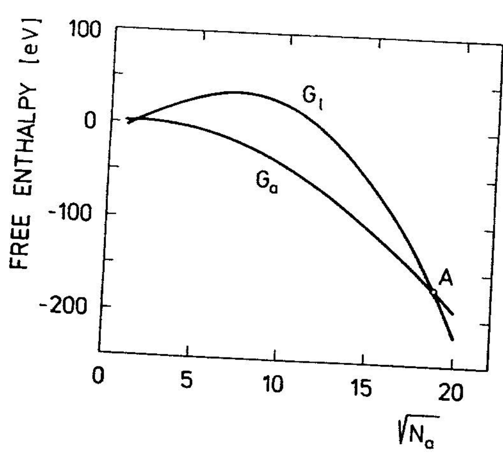

Fig. 2. Free enthalpy of disc agglomerate (G_a) and of dislocation loop G_l vs. the number of interstitials in the defect. Boron dose implanted into silicon is $N_d = 10^{14}\,\mathrm{cm}^{-2}$, $V(t) = 2 \times 10^{-12}\,\mathrm{cm}^3$

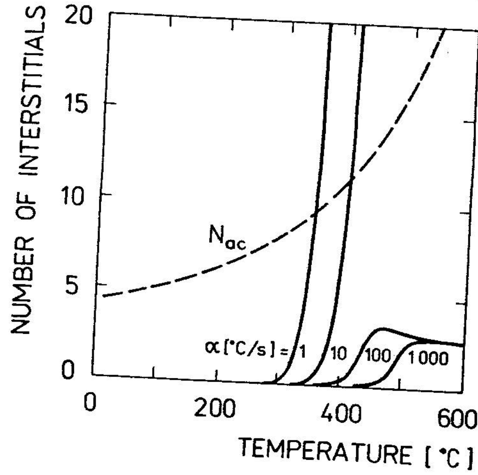

Fig. 3. Temperature dependence of the critical number N_{ac} of interstitials in the agglomerate (dashed line) and of the numbers of interstitials in the agglomerates of the maximum size that can be formed at various heating rates α (full lines). Boron dose implanted into silicon is $N_d = 10^{14}\,\mathrm{cm}^{-2}$

Now let us discuss the free enthalpy of the dislocation loop G_l. The number of interstitials in the loop again will be denoted N_a, b will be the absolute value of the Burgers vector and φ the angle between the Burgers vector and the normal to

the plane of the loop. Following [8] we can write

$$G_l = A_1(N_a)^{1/2}\left\{\ln[A_2(N_a)^{1/2}] - A_3\right\}, \tag{6}$$

where

$$A_1 = \frac{\mu b^2}{2(1-\nu)(\pi K_s)^{1/2}}(\cos^2\varphi + \frac{2-\nu}{2}\sin^2\varphi),$$
$$A_2 = \frac{4}{b(\pi K_s)^{1/2}}(2\cos\varphi + \sin\varphi),$$
$$A_3 = \cos\varphi + 2\sin\varphi.$$

Here μ is the shear modulus of silicon and ν is the Poison ratio. For the evaluation of energy the values $\varphi = 30\,°$, $\nu = 1/3$ and $\mu = 7.5 \times 10^6\,\mathrm{N/cm}^2$, $b = A_0/2\,\langle 110\rangle$ are used. The result is shown in Fig. 2, curve G_l.

From the results it follows that the system will decrease its energy up to the point A (Fig. 2) by the growth of the agglomerates. At point A the agglomerates will transform to dislocation loops. The energy of dislocation loop with critical size is too high, therefore in the implanted layer the loops do not form directly but via disc agglomerates.

Using the described model the influence of annealing and implantation conditions on the growth of agglomerates will be studied experimentally.

III. THE INFLUENCE OF THE HEATING RATE ON THE GROWTH OF AGGLOMERATES

As it was shown in the previous chapter, smaller agglomerates ($N_a < N_{ac}$) are not stable; they form and dissolve concurrently and their equilibrium concentration is given by the vant'Hoff isotherm

$$C_a = \frac{N_i}{V(t)}\exp(-\frac{G_a}{kT}). \tag{7}$$

Here, C_a is the concentration of agglomerates containing N_a interstitials in the system with the concentration of interstitials $C_i = N_i/V(t)$. If the concentration of the agglomerates with the critical number of interstitials N_{ac} is lower than a certain minimum value $C_{a\,\min}$, we shall assume for simplicity that in the implanted layer the conditions are not appropriate for agglomerate growth.

In Fig. 3 there are shown the numbers of interstitials in the largest agglomerates that can be formed at various rates of temperature increase (full lines). For the growth of the agglomerates it is decisive whether stable configurations are formed. If the temperature increases slowly ($\alpha = 1$ and $10\,°\mathrm{C/s}$), $N_a > N_{ac}$ at $C_a > C_{a\,\min}$.

At $\alpha = 100$ and $1000\,°C/s$ the situation is quite different. The inequality $C_a < C_{a\,min}$ holds before $N_a > N_{ac}$ is fulfilled. Therefore, stable agglomerates are not formed and in this case the full lines in Fig. 3 denote the numbers of interstitials in the agglomerates with the concentration $C_{a\,min}$.

From the discussed model it follows that at a rapid increase of the temperature, the volume $V(t)$, which is limited by the diffusion length of the interstitials, is not able to reach the size which is favourable for the growth of agglomerates.

For the experimental verification of the analysed phenomena the various types of RIA (rapid isothermal annealing) can be used. In our case the annealing in a diffusion furnace (FURIA [9]) was employed. Experimental samples were prepared using P-type 3-inch ⟨111⟩ silicon wafers a resistivity of 10 Ohm cm. Wafers were implanted by various doses of boron at an energy of 100 keV.

The boat with the samples was inserted into the zone of the furnace where the temperature was 1100 °C in such a way as to achieve a heating rate of 1, 10, 100 and 1000 °C/s, respectively. In the last case, however, the accuracy of this process was limited and the actual temperature rise was a little slower. The annealing time was 30 s. After the annealing the samples cooled spontaneously.

It was observed that the secondary defects are very small after these procedures and it was difficult to evaluate their density. Therefore the annealed wafers were oxidized in steam at 1000 °C up to an oxide thickness of 240 nm. During the oxidation additional interstitials are injected from the Si/SiO_2 interface into the bulk and, consequently, agglomerates and dislocation loops grow. On the other hand, reoxidation does not create new secondary defects. The enlarged defects were made visible using the Sirtl etch.

The micrographs of some of our samples are in Fig. 4. At $\alpha = 1000$ and $100\,°C/s$ only individual defects are observed. On the other hand, at slower heating rates the densities of defects are very high. Thus, the results are in correlation with the model.

IV. THE INFLUENCE OF THE IMPLANTATION DOSE ON THE GROWTH OF AGGLOMERATES

With an increasing boron dose the number of nonequilibrium interstitials increases as well [4] and, consequently, agglomerates are formed at a smaller value of $V(t)$. The situation is shown in Fig. 5 for two doses. It is evident that at the higher dose defects are formed even at $\alpha = 100\,°C/s$. This means that the increasing of the heating rate does not principally prevent the formation of secondary defects. But there is the important mutual relation — the higher the heating rate is, the higher may be the ion dose which can be annealed out without secondary defects formation during heating up.

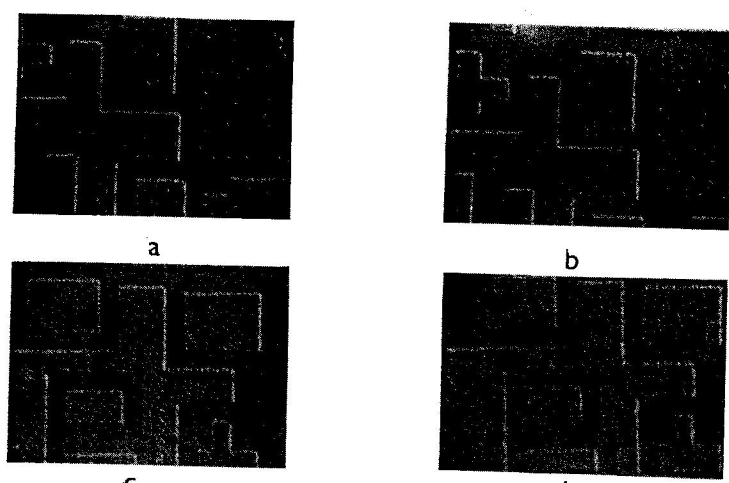

Fig. 4. The density of defects after annealing at various heating rates: a) 1000 °C/s, b) 100 °C/s, c) 10 °C/s, d) 1 °C/s. Annealing conditions are 1100 °C/30 s, boron dose was $10^{14}\ cm^{-2}$

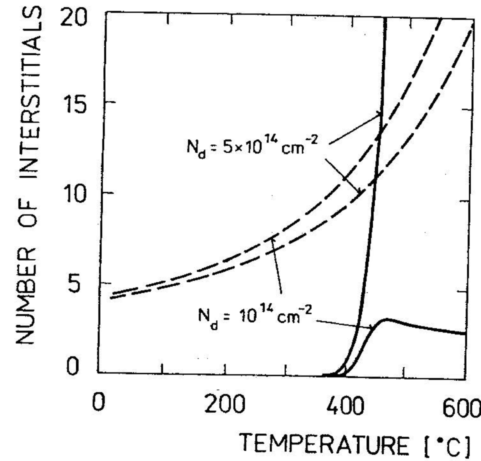

Fig. 5. Temperature dependences of the critical numbers N_{ac} of interstitials in the agglomerate (dashed lines) and the numbers of the interstitials in the agglomerates of the maximum size (full lines) for $\alpha = 100\,°C/s$ and two boron doses

In further experiments the maximum doses that can be annealed out at various temperatures were studied. The results are in Fig. 6. Using the roughly drawn boundary it can be calculated that the maximum concentration of interstitials after the out-diffusion process (at t = const.) has a limiting value of $C_{max} = 5.7 \times 10^{16}\ cm^{-3}$, which is temperature independent. The slope of the line in Fig. 6

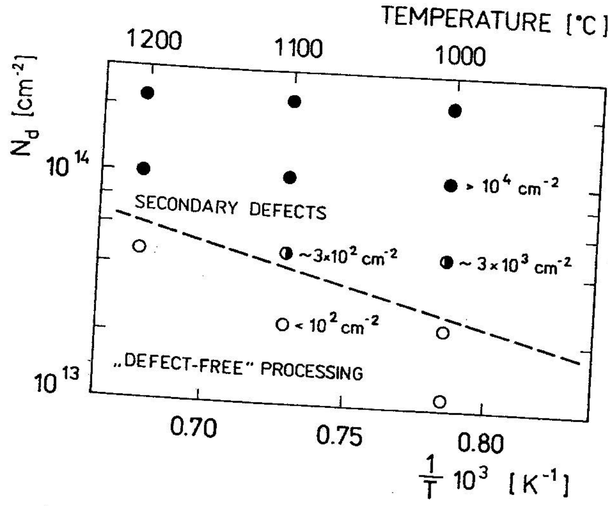

Fig. 6. The dependence of the implanted dose necessary for secondary defect formation vs. annealing temperature for the heating rate $\alpha = 100\,°C/s$ and annealing time $t = 30\,s$. The density of defects is shown by various symbols

is proportional to the activation energy of the migration of interstitials, which has a value of $H_{im} \approx 1.7\,eV$. This is in an approximate agreement with the value of the migration enthalpy 1.86 eV obtained by Seeger [7] for 1047 °C. These results confirm the assumption that the decrease of the concentration of nonequilibrium interstitials is governed by their outdiffusion.

Providing that secondary defects were not formed during heating up, from the formerly mentioned results follows the second requirement for defect-free annealing and this is the outdiffusion of interstitials below the maximum acceptable nonequilibrium concentration. It means that in a crystal containing less than C_{max} interstitials secondary defects cannot be formed even during the temperature decrease or the subsequent temperature processing. Therefore the whole annealing cycle is to be taken into account.

Using the values of H_{im} [7], C_{max} and that of the maximum concentration of primary defects after ion implantation [4], the time of outdiffusion of the primary defect (t_{min}) at various doses and temperatures can be calculated at least approximately. The results are shown in Fig. 7. Of course, these calculations are reasonable only if secondary defects are not formed during the temperature increase.

Let us now comment on Fig. 4 again. The annealing at 1100 °Cwas performed during 30 s. From Fig. 7 it follows, however, that for $N_d = 10^{14}\,cm^{-2}$ the time of outdiffusion is 200 s. Therefore the concentration of interstitials did not decrease

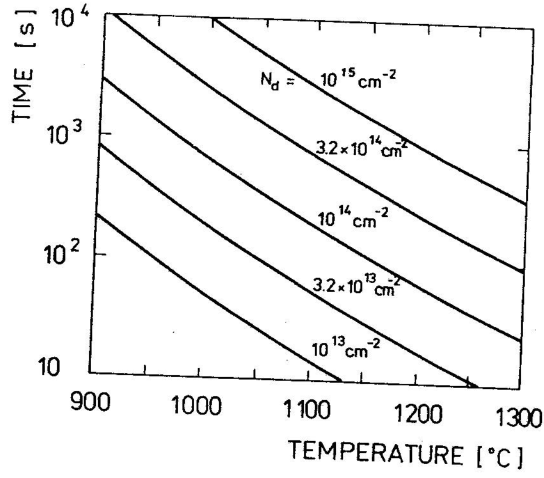

Fig. 7. The time of the outdiffusion of primary defects to the concentration below the value C_{max} vs. temperature for various boron doses

up to C_{max} and during cooling or the subsequent reoxidation secondary defects with small densities could be created. Perhaps in this way the small density of defects in samples a, b (Fig. 4) could be explained.

The calculated and experimental results are schematically summarized in Fig. 8.

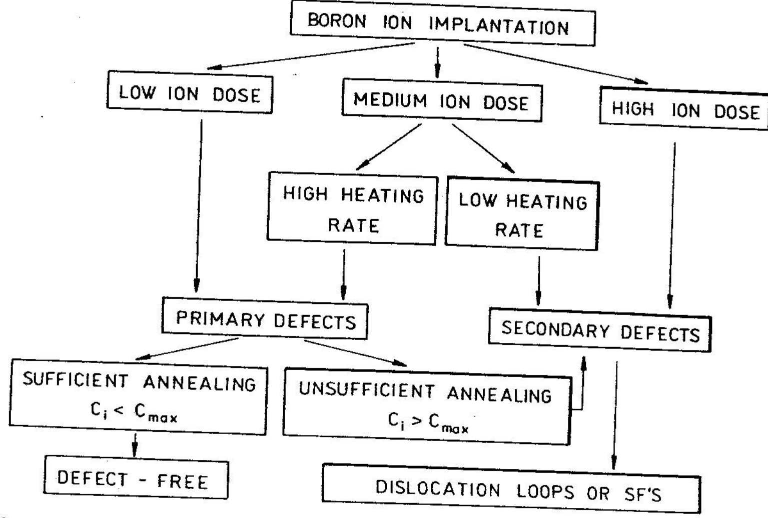

Fig. 8. Summarization of defect-formation in boron implanted silicon

V. CONCLUSIONS

a) Disc-like agglomerates of silicon interstitials precede dislocation loop formation.

b) Under certain circumstances during a fast heat up, favourable conditions for the growth of agglomerates are not created. This theoretically predicted phenomenon has been observed after boron implantation and rapid isothermal annealing.

c) There is an important mutual relation — the higher the heating rate is, the higher is the ion dose which can be annealed out without secondary defects formation during heating up. This means that for defect-free annealing of implanted layers a rapid thermal processing equipment with an as high as possible heating rate is recommended.

d) In case that secondary defects were not formed during up it is necessary for the outdiffusion of interstitials to use a certain minimum time at a given temperature and ion dose.

ACKNOWLEDGEMENTS

The authors would like to thank to Prof. H. Frank and Prof. F. Kroupa for comments and remarks concerning the manuscript.

REFERENCES

[1] Troxell, J.R.: Solid St. Electron. *26* (1983), 539.
[2] Corbet, J.W. *Proc. 1st. Int. Conf. on Ion Implantation*, (eds. Chaderton, L. and Eisen, F.), Gordon and Breach Sci. Publ., New York 1971:.
[3] Brice, D.K.: Radiat. Eff. *6* (1970), 77.
[4] Lenhard, R., Luby, Š.: Vacuum *41* (1990), 856.
[5] Foll, H., Gosele, J.: J. Cryst. Growth *10* (1977), 90.
[6] Jackson, K.A.: Phil. Mag. *7* (1962), 1117.
[7] Seeger, A., Foll, H., Frank, W. *Inst. Phys. Conf. Ser. 31*, Chap. 1. Inst. of Phys., Bristol, London 1977:.
[8] Kroupa, F. *Theory of Crystal Defects*. Proc. Sum. School in Hrazany. Academia, Prague 1964, 257:.
[9] Lenhard, R. *Proc. of Energy Pulse Modif. of Silicon and Related Mater.* Acad. Wiss. DDR, Dresden 1984, 312:.

Received August 6th, 1991
Accepted for publication January 24th, 1992

ФОРМИРОВАНИЕ ДЕФЕКТОВ В КРЕМНИИ ИМПЛАНТИРОВАНОМ БОРОМ ПРИ БЫСТРОМ ИЗОТЕРМИЧЕСКОМ ОТЖИГЕ.

Приводится простая модель формирования вторичных дефектов в имплантированых слоях, нарастание стабыльных дисковых агломератови их трансфôрмирование в дислокационные ловушки. Влияние скорости отогрева на эфект прецитипации изучается и показано, что очень быстрый отжиг наводить формирование вторичных дефектов. Модель проверяется в експерименте, где применен кремний имплантированый бором который прошел быстрый изотермический отжиг. Скорость изменения температуры нарастала с 1 по 1000°C/сек. Вторичные дефекты выявлялись с применением реоксидации и химического травления кремния. Формирование дефектов зависит на дозе имплантации N_d, но при высоких дозах требуется для получения бездефектной структуры увеличение скорости нарастания температуры α. (напр. α = 100°C/сек достаточно для N_d = 10^{14} см$^{-2}$ но уже не для $N_d = 5 \times 10^{14}$ см$^{-2}$.) Энергии активации интерстициал оценена на 1,7 эВ. Расчитано также время дифузионного удаления дефектов при разных дозах и температурах. Экспериментальные результаты находятся в хорошем согласии с предлагаемой моделью.