J. of Solid State Physics USSR **3** (1961) 3523.
18 V.S. Vavilov, E.N. Lotkova and A.F. Plotnikov: J. Phys. Chem. Solids **22** (1961).
19 A. F. Plotnikov, V. S. Vavilov and B. D. Kopylovsky: Review of Sci. Instr. (USSR) N3 (1962).
20 J. MacKay and E. Klontz: J. Appl. Phys. **30** (1959) 1269.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

On Defects Introduced by Fast Electrons into Silicon Doped by Lithium

V. S. VAVILOV, V. A. CHAPNIN
P. N. Lebedev Institute of Physics
Academy of Sciences of the U. S. S. R.
Moscow, U. S. S. R.
AND I. V. SMIRNOVA
Moscow State University
Moscow, U. S. S. R.

The irradiation of lithium doped silicon by fast electrons leads to the interaction of lithium with radiation-induced defects. The introduction rates and stability of radiation-induced centers with deep energy levels are considerably influenced. However the most abundant deep energy levels do not shift.

1.

It is known that atoms of lithium introduced into silicon easily migrate interstitially and actively react with other impurities. We have investigated the interaction of lithium with defects introduced by fast electron bombardment.

The ionization energy of lithium atoms occupying interstitial sites in silicon crystals is equal to 0.033 ev, and at room temperature practically all "free" lithium atoms are ionized. In silicon containing oxygen atoms, lithium has a tendency to form LiO^+ complex which has a shallow donor level and is stable at 300°K[1].

In our experiments lithium was introduced by diffusion from a tin-lithium melt at 550°-650°C into *p*-type silicon grown from quartz crucibles and containing residual boron acceptor impurity. After this treatment samples had *n*-type conductivity with electron concentrations varying between 3.10^{14} and 2.10^{17} cm^{-3}. The samples were bombarded by 0.9 Mev electrons at room temperature. The energy level positions of defects introduced by electrons and the changes taking place at the subsequent annealing were determined using the carriers concentration temperature dependence determined by Hall effect and resistivity measurements. The annealing was conducted in vacuum, in a silica tube.

2.

In the samples with initial electron concentrations under 10^{16} cm^{-3}, after the bombardment centers with a level $E_c-0.17$ ev were producted; however, the effectivity of the centers introduction was only about one third of the effectivity for other *n*-type samples containing other donor impurities, for instance, phosphorus instead of lithium. This difference was observed earlier in the work of Watkins and *et al.*[2]

In irradiated samples with lithium concentrations exceeding 10^{17} cm^{-3}, the temperature dependence of carriers concentration indicated the presence of a system of shallow levels situated between 0.06 and 0.14 ev from the conductance band. In this well-known work, Hill[3] interpreted his results

on a base of shallow levels of single depth. However, Wertheim in his experiments with irradiated silicon containing oxygen at relatively low concentrations[4] made a conclusion that there is not one, but a system of shallow levels. In our case the oxygen concentration was higher than in Wertheim's experiments. However, one has to take into account the formation of lithium-oxygen complexes mentioned above. One can suggest that in samples containing more than 10^{17} cm^{-3} lithium atoms the concentration of oxygen atoms free for interaction with vacancies resulting in E_c—0.17 ev level formation was very low.

It is thought that the shallow levels system corresponds to Frenkel pairs separated by different distances. One cannot exclude the possibility that the same system of shallow levels gives origin to the shift of the fundamental optical absorption band observed in irradiated silicon by several authors[5),6),7)].

It is possible that at higher defects concentrations, for instance, after neutron irradiation in a reactor, the system of levels finally is transformed into an impurity zone.

The data based on photoconductivity measurements do not contradict to the suggestions made above, as besides spectral components corresponding to the system of deep levels in irradiated silicon, there is always a component in the spectrum beginning right from the fundamental band and decreasing steadily at longer wavelengths.

3.

After a heating up to about 70°C the samples containing lithium and having before the irradiation the electron concentration of $1.5.10^{17}$ cm^{-3}, showed a considerable decrease of electron concentration (Fig. 1). This decrease of concentration is thought to be due to the interaction of radiation induced defects and lithium ions, *i.e.* "lithium precipitation." It is probable that the lithium ion precipitates on the defect as an atom; thus the equilibrium conductivity electron concentration decreases and after this the existence of defect associated with lithium atom does not affect the Hall effect temperature dependence. As it was mentioned by us in an earlier work[8] the decrease of electron concentration correlates with the disappearance of E_c—0.17 ev levels.

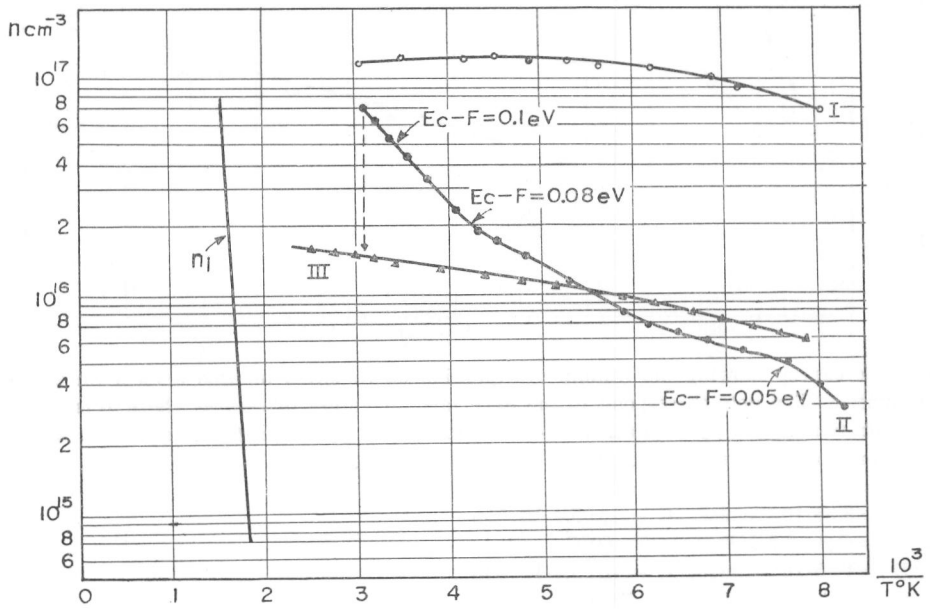

Fig. 1. The temperature dependence of electron concentration for a sample where after the lithium diffusion the room temperature electron concentration was equal to $1.5.10^{17}cm^{-3}$.
Curve I. The temperature dependence of electron concentration before irradiation.
II. After the irradiation by 0.9 Mev electrons; flux $\phi=2.4.10^{17}cm^{-2}$.
III. After the precipitation of lithium on radiation induced defects at 70°C.

Analysing the precipitation of lithium on radiation induced defects we used initially the theory of precipitation from oversaturated solution, where it is supposed that the formation of clusters of precipitate is possible[8]. However, the subsequent experiments have shown that even after the precipitation the concentration of shallow donor centers (lithium ions) remains higher than the equilibrium concentration at the temperature of the experiments, while the centers of precipitation definitely exist in the crystal. Thus one has to conclude that one point defect (most probably a vacancy) can bind only one lithium ion.

It follows that the number of the bound lithium-vacancy pairs should be determined as equal to the difference of conductance electron concentrations.* The application of the theory of the recombination of "heterogeneous" pair for lithium ions and vacancies gives a possibility of the determination of capture radius $r_{\min}$; if the separation becomes less than $r_{\min}$, the pair is bound. According to the expression given in the paper of B. Jurkov[9] the relative number of bound pairs for the time t is equal to

$$1-f(t)=\frac{1}{1+\eta\pi r_{\min}DC_A^0 t} \qquad (1)$$

where D is the sum of diffusion coefficients of reacting "particles" and C_A^0 the initial concentration. In Fig. 2 are presented the time dependences of the relative parts of

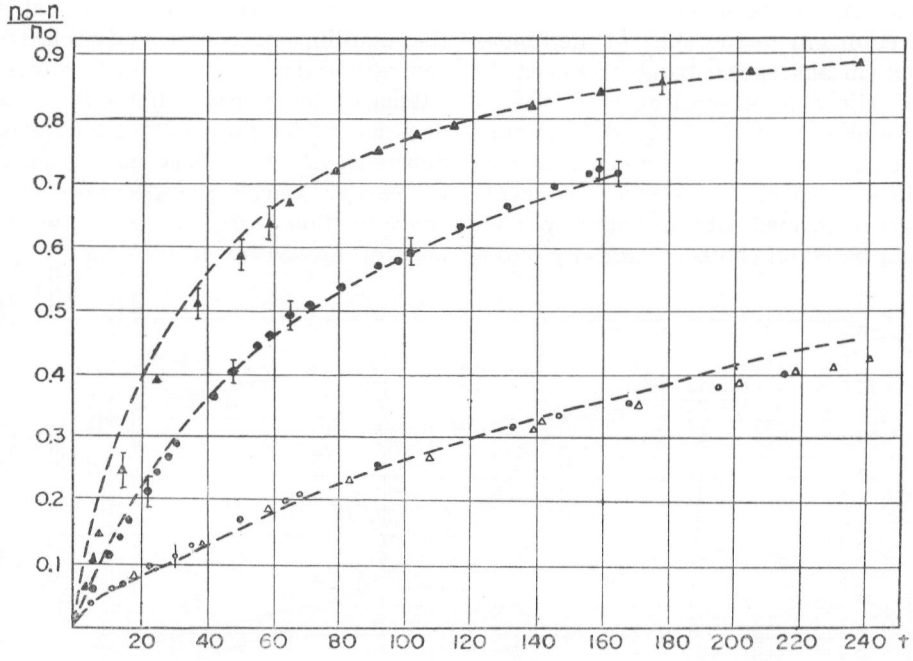

Fig. 2. The curves showing the lithium precipitation on radiation induced defects (most probably vacancies). The dots correspond to the experimental values of $1-n/n_0$ where n_0 is the electron concentration before precipitation, n-concentration at the time t. The curves are plotted according to the expression (1) at the conditions given below.

▲ $C_A^0=n_0=2.3\cdot10^{16}\mathrm{cm}^{-3}$; $T=55°\mathrm{C}$
$D=3.35\cdot10^{-14}\mathrm{cm}^2\mathrm{sec}^{-1}$; $r_{\min}=5.4\cdot10^{-8}\mathrm{cm}$

● $n_0=C_A^0=2.2\cdot10^{16}\mathrm{cm}^{-3}$; $T=60°\mathrm{C}$
$D=1.55\cdot10^{-14}\mathrm{cm}^2\mathrm{sec}^{-1}$; $r_{\min}=5.4\cdot10^{-8}\mathrm{cm}$

○ $n_0=C_A^0=2.65\cdot10^{16}\mathrm{cm}^{-3}$; $T=50°\mathrm{C}$
$D=2.55\cdot10^{-15}\mathrm{cm}^2\mathrm{sec}^{-1}$; $r_{\min}=5.4\cdot10^{-8}\mathrm{cm}$

△ $n_0=C_A^0=3.6\cdot10^{16}\mathrm{cm}^{-3}$; $T=50°\mathrm{C}$
$D=2.55\cdot10^{-15}\mathrm{cm}^2\mathrm{sec}^{-1}$; $r_{\min}=5.4\cdot10^{-8}\mathrm{cm}$

* It is not known whether the $E_c-0.17$ ev center has only this level and takes only one electron. There might be another level, and then the uncertainly of 100% follows from this calculation.

precipitated lithium ions number. Choosing an appropriate value of r_{min} one can obtain curves corresponding to experimental data; the best value of r_{min} is of the order of lattice constant $5.4.10^{-8}$ cm.

4.

In the cases when the concentration of defects is high enough, the inversion of conductivity type takes place, *i.e.* the samples doped by lithium after the electron bombardment obtain hole conductivity. The inversion takes place approximately after 20 days at room temperature or after an hour at 200°C. This inversion of conductivity type is due, probably, to the interaction of lithium ions and defects after which the donor centers disappear while the concentration of group III acceptors does not change. Using the inversion effect we obtained the data on the defect energy levels positions both for upper and lower halves of the forbidden gap on the same samples. The main conclusion from the analysis of the concentration temperature dependences is that the deep levels connected with radiation induced defects in silicon doped by lithium coincide with those in silicon containing no lithium. In both cases the well-known level $E_c-0.17$ ev and also levels at $E_v+0.21$ ev, $E_v+0.28$ ev and $E_v+0.45$ ev are seen.

It was found that defects with the level $E_v+0.28$ ev are unusually stable against high-temperature annealing. In silicon containing no lithium radiation damage anneals at 450°C after a few minutes[3),11)]. In crystals doped by lithium after such a treatment the level $E_v+0.21$ ev disappears, but the major part of centers with levels at $E_v+0.28$ ev remains. They do not disappear totally even after a many hours long annealing at 700°C. The high stability of this type of defects in silicon doped by lithium can be interpreted as follows: after a heat treatment a radiation induced defect (a Frenkel pair) usually disappears as a result of recombination of a vacancy and interstitial. In the case of our experiments the vacancies are bound to lithium atoms; if we suppose that the $E_v+0.28$ ev level corresponds to a complex of an interstitial and oxygen atom, for the final recombination, the interstitial atom after the dissociation must migrate to the crystal surface or a dislocation.

The authors express their gratitude to V. L. Bonc Bruevic and B. Ya. Jurkov for the discussion and to T. Garanina for the assistance during the experiment.

References

1 E. M. Pell: J. Appl. Phys. **32** (1961) 1048.
2 G. Watkins, J. Corbett and R. Walker: J. Appl. Phys. **30** (1959) 1198.
3 D. Hill: Phys. Rev. **14** (1959) 1414.
4 G. Wertheim and D. Buchanan: J. Appl. Phys. **30** (1959) 1232.
5 M. Becker, H. Fan and K. Lark-Horovitz: Phys. Rev. **85** (1952) 730.
6 H. Fan and A. Ramdas: J. Appl. Phys. **30** (1959) 1127.
7 V.S. Vavilov, E.M. Lotkova and A.F. Plotnikov: *Photoconductivity*, Pergamon Press, London (1962) p. 31.
8 V.S. Vavilov, I.V. Smirnova and V.A. Chapnin: J. Solid State Phys. USSR **4** (1962) 1128.
9 B. Ya. Yurkov: J. Solid State Phys. USSR **3** (1961) 3563.
10 E. M. Pell: Phys. Rev. **119** (1960) 1222.
11 G. Bemski and W. Augustiniak: Phys. Rev. **108** (1957) 645.
12 G. N. Galkin, V. M. Malovetskaya, V. S. Vavilov and A. F. Plotnikov: J. Solid State Phys. USSR **4** (1962).

DISCUSSION

Hasiguti, R. R.: 1). In your table in the preprint, there are many unidentified levels. I am interested in knowing if there is possibility that a free single vacancy or a free single interstitial corresponds to one of them. 2). According to Dr. Watkins, the migration energy of interstitials is extremely small, because he considers that the migration energy of interstitials is smaller than that of vacancies, which is already very small. Now my question is this. To make a close Frenkel pair stable, I think it may be necessary for a vacancy and a interstitial to have a repulsion. I should like to know, if you consider that this is the case.

Vavilov, V. S.: 1). The well known results of Dr. Hill and also the low-temperature irradiation experiments seem to indicate that at least the close Frenkel

pairs have only shallow energy levels that would not be observed in the spectral region where we made measurements. However, one cannot exclude that for well separated vacancies and interstitials the Johnson-Lark-Horovitz model is really applicable, and thus your suggestion may be right. 2). Additional repulsive interaction, of course, would stabilize the Frenkel pairs. Experiments show that the occupation of radiation damage center by electrons which can be influenced for instance by strong light excitation, appreciably influences the annealing processes. Unfortunately, at this moment it is not possible to say, what forces can act in the case mentioned by you, as no good model of a close Frenkel pair exists.

Fan, H. Y.: It was thought for some time that electron irradiation of silicon introduces few, discrete defect levels whereas neutron irradiation introduces a spectrum with some nearly continuous level distribution. Our work on absorption and photoconductivity some years ago showed that neutron irradiated as well as electron irradiated silicon show distinct absorption band and photoconductive thresholds. It is interesting to note that Dr. Vavilov's work revealed some additional defect levels with no significant difference between neutron irradiated and electron irradiated samples. Some definite difference between the effects of neutron irradiation and electron irradiation have been found by us, as pointed out in my comment to our paper IA-3*.

* *Proc. Int. Conf. Cryst. Latt. Def. (1962)*; J. Phys. Soc. Japan **18** Suppl. II (1963) 33.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

Radiation Damage and Annealing of Carrier Life-time in Silicon

Y. INUISHI AND K. MATSUURA

Faculty of Engineering, Osaka University, Osaka, Japan

Radiation damage (γ, neutron) and its annealing processes in various kind of Si crystals were investigated by measuring the change in minority carrier life time with microwave method. The interaction between radiation introduced Frenkel defects and various other imperfections such as impurities (O, Ni, Au) and dislocations were found both in introduction and in annealing curves. "Reverse annealing" in pulled Si was ascribed to the formation and dissociation of vacancy-oxgen complex (A center). Similar effect occurs in Ni doped Si. Activation energy of the annealing was 1.2 ev for 0.7—0.8 ev for bulk and dislocation enhanced annihilation respectively. The depth of the recombination levels and trap levels were estimated from temperature dependence of life time, thermal release time and Hall coefficient.

1. Introduction[1)]

The authors intended in the present paper to investigate the interaction of radiation induced Frenkel defects in Si with chemical impurities such as oxygen, nickel, gold and also with the dislocations. These investigations were carried out by measuring the change in minority carrier life time τ with microwave absorption method[1),2)], which avoids the troubles concerning with electrode contact and allowed high temperature heat treatment. As is well known, the life time τ in the simple cases is expressed by Shockley-Read formula,

$$\tau=\frac{\tau_{p0}(n_0+n_1)+\tau_{n0}(p_0+p_1)}{(n_0+p_0)}=\frac{1}{N_r}F(E_r, E_f, T) \quad (1)$$