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On Defects Introduced into Silicon by Fast Electron and Neutron Irradiation

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Photoconductivity measurements on Si single crystals irradiated by electrons and neutrons show that the deep energy levels system in both cases is similar. Centers with deep levels are generated as a result of a primary process, presumably Frenkel pairs generation, and subsequent point defects migration. New energy levels not resolved by other methods were observed.

1. Introduction

A. The explanation of the nature and energy level spectra of local centers generated in silicon by fast electrons, neutrons and other particles attracted the many workers. As a result of their investigations it was found that the irradiation of silicon by electrons[1),2)] deuterons[3),4)] and neutrons[5),6)] generates centers both of donor and acceptor type. D.Hill has shown[2)] that as a result of electron bombardment, centres with shallow levels near to E_c-0.03 ev and $E_v+0.05$ ev are generated in a largest number. The effectivities* of their introduction are nearly equal to the numbers of displaced atoms calculated theoretically[8)]. According to this fact, Hill suggested that these shallow levels belong to Frenkel defects, *i.e.* vacancy-interstitial pairs. Simultaneously with the centers mentioned above are generated the centers with deep levels influencing strongly the recombination of holes and electrons, infrared absorption and the spectra and kinetics of photoconductivity. Wertheim[10)], Hill[2)] and Longo[11)] found in the irradiated silicon energy levels at $E_c-0.16$ ev, $E_c-0.4$ ev and $E_v+0.27(0.30)$ ev. Using spin electron resonance method, Bemski[12)] and Watkins, Corbett and Walker made a conclusion that the level at $E_c-0.16$ ev belongs to the association of a vacancy and oxygen atom, and the level at $E_c-0.4$ ev to the association of a point defect introduced by irradiation and a donor impurity of the 5th group (phosphorus). The investigation of the recombination capture in silicon bomdarded by electrons conducted in P. N. Lebedev Institute[14)] is in agreement with the above-mentioned conclusions concerning the nature of the center with $E_c-0.16$ ev level. In[15)] it was suggested that the level at $E_v+0.27$ ev belongs to the association of an oxygen atoms and an interstitial silicon atom.

B. The exploration of the spectra and kinetics of photoconductivity combined with Hall effect measurements in silicon single crystals irradiated by neutrons, conducted at the P.N. Lebedev Institute of Physics[16),17),18)] gave new data about the system of energy levels of radiation induced defects and the carriers capture cross sections for some of the levels. The results mentioned were discussed not long ago at the International Photoconductivity Conference at Cornell University[18)]. Present report contains new results of the investigation of defects with deep energy levels in silicon bombarded by fast electrons and neutrons.

The technique of photoconductivity measurements used in our work is given in detail in a separate paper[19)]. Special attention was paid to the selection of volume effects and to the exclusion of the shortwave background radiation in the monochromator, which might lead to complicated effects of "quenching". The shortwave background was excluded by use of thick silicon or germanium filters. The temperature of samples during the measurements was near to 100°K. The Hall effect and conductivity measurements between 100°K and 300°K were made by conventional methods. The 1 Mev electron irradiation was effected by a Van de Graaff generator.

2. The Photoconductivity Spectra of *P*-Type Silicon Irradiated by Electrons at 300°K

Fig. 1 (curve 1) shows a typical photo-

* The effectivity of centers (levels) introduction is equal to the relation of the centers concentration to the flux of radiation generating them.

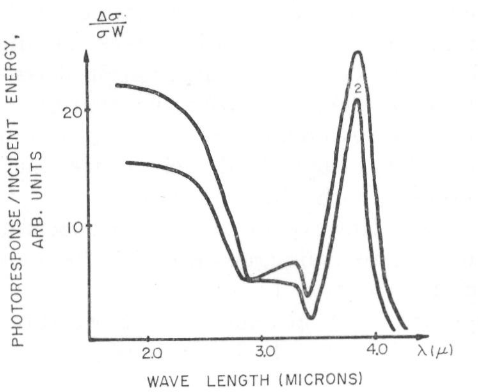

Fig. 1. The photoconductivity spectra of identical p-type silicon crystals with initial resistivity $\rho \sim 100$ ohm. cm irradiated at 300°K by a flux of $3.6.10^{14}$ electrons/cm^2 (energy 1 Mev) (curve 1) and by neutrons (curve 2). At the temperature of the experiment, 100°K, Fermi level lies at $E_v+0.20$ ev.

conductivity spectrum of a p-type crystal with an initial resistivity of 100 ohm. cm irradiated at 300°K by 1 Mev electrons (flux $3.6.10^{14}$cm^{-2}). The curve 2 of the same figure gives a spectrum of an initially identical sample irradiated by neutrons in a reactor. In both cases the Fermi level at the temperature of the experiment (100°K) was near to $E_v+0.20$ ev. The structure of both spectra is similar. This makes us to believe that the nature of local centers to which belong the levels corresponding to the spectra, is also similar. In Fig. 2a, taken from our previous paper[18] there is presented a set of photoconductivity spectra corresponding to increasing neutron fluxes. In Fig. 2b are shown similar spectra for increasing electron fluxes. The curve 1 corresponds to $2.5.10^{17}$ electrons per cm^2. Beginning from the electron flux for which the Fermi level goes up over $E_v+0.29$ ev at 100°K, the spectrum changes considerably. The curve 2 corresponds to $2.9.10^{17}$ electrons per cm^2, curve 3 to $3.2.10^{17}$ electrons per cm^2 and, finally, curve 4 to $3.6.10^{17}$ electrons per cm^2. In the last case, the Fermi level position is $E_v+0.32$ ev. For larger electron fluxes and higher Fermi level positions, the structure of photoconductivity spectrum is gradually cut off and disappears beginning from the long wave part. This fact, corresponding to the expectation and found by us for neutron irradiated silicon also,[18] means, of course, that the photoconductivity spectrum is determined by the levels'' system and their equilibrium occupation in the volume of crystal.

Another series of measurements was made with samples irradiated by small electron

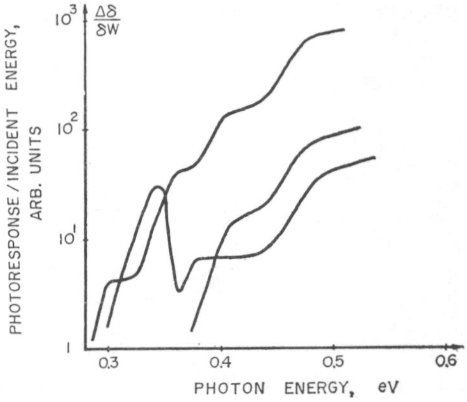

Fig. 2a. The photoconductivity spectra of p-type silicon corresponding to the increasing fluxes of neutrons.

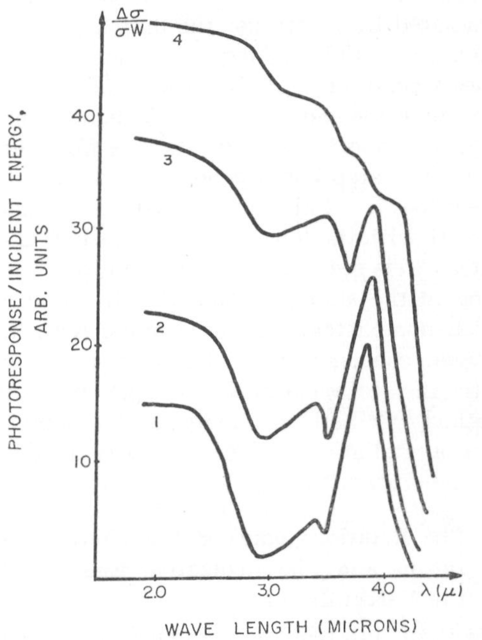

Fig. 2b. The photoconductivity spectra, obtained at 100°K for p-type silicon irradiated by 1 Mev electrons at 300°K.

Curve 1 - electron flux $2.5.10^{17}$cm^{-2}
Curve 2 - 〃 $2.9.10^{17}$cm^{-2}
Curve 3 - 〃 $3.2.10^{17}$cm^{-2}
Curve 4 - 〃 $3.6.10^{17}$cm^{-2}

In the last case, Fermi level at 100°K is at $E_v+0.32$ ev.

fluxes. In this case Fermi level position was determined by the acceptor impurity (boron) concentration. The results of the photoconductivity measurements have shown again that the spectrum observed is given by the defects levels system and the occupation of these levels. Fig. 3 shows the photoconductivity spectra in the photon energy region between 0.25 and 1 ev for two silicon samples irradiated by electrons; the first sample contains about 10^{18} cm^{-3} oxygen atoms (curve 1). The second crystal is grown by vacuum zone melting and contains less than 10^{17} cm^{-3} oxygen atoms, (curve 2). On the first curve there is a step corresponding to the level at $E_c-0.16$ev*. This level exists also in the crystal with the lower oxygen concentration, but as it is seen on curve 2, simultaneously, appears the step corresponding to $E_c-0.4$ ev level, nonexistent in the sample with high oxygen concentration. These results agree with the data obtained by spin resonance method[12),13)] and the analysis of recombination on radiation induced defects made at our laboratory[14)].

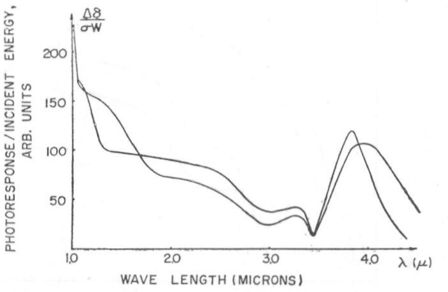

Fig. 3. The photoconductivity spectra of p-type silicon containing $10^{18}cm^{-3}$ oxygen atoms (curve 1) and less than $10^{17}cm^{-3}$ oxygen atoms (curve 2).

3. The Relations between the Thermal Ionization and Photoionization Energies for the Defect Levels

It is of interest to compare the thermal ionization energies, usually determined by the Hall effect method, with the photoionization energies. To do this we used the considerable difference between the thermal stabilities of two kinds of centers introduced into silicon by electron irradiation. It was found[5)] that the irradiation of p-type silicon with low oxygen concentration leads to the formation of centers with the thermal ionization energy equal to 0.21 ev. These centers are rather instable and their concentrations decreases with time even at a room temperature. However, after their disappearance, after the annealing, centers with the thermal ionization energy of 0.19 ev remain intact; they are stable at annealing temperatures up to 500°K. Fig. 4 shows the spectra of a p-type sample irradiated by electrons before annealing (curve 1) and after a ten minute annealing at 500°K (curve 2). In the latter case there is no step at 4.8μ, which corresponds to the thermal ionization energy 0.21 ev; however, the step at 5.5μ does not disappear. We made a conclusion that this step corresponds to the thermal ionization energy 0.19 ev. In the table in Fig. 5 there are presented the thermal ionization and photoionization energies for three defect energy levels in silicon and the effectivities of their introduction by 1 Mev electrons.

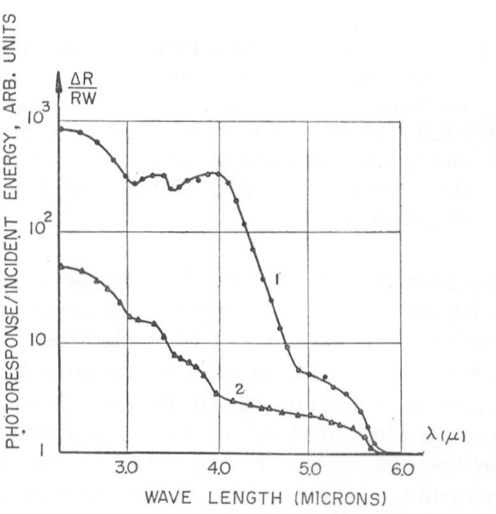

Fig. 4. The photoconductivity spectra of p-type silicon bombarded by electrons. Oxygen concentration less than $10^{16}cm^{-3}$. Curve 1-before annealing; curve 2-after annealing at 500°K.

4. The Photoconductivity in P-Type Silicon Irradiated by Fast Electrons at 100°K

The results obtained in[1),9),13)] and recent ideas concerning the process of radiation damage stabilization as a result of point

* In our work the threshold photoionization energies were determined as corresponding to the half-height of the step.

Fig. 5. The energies of thermal ionization and photoionization for radiation-induced defects in p-type silicon

Silicon p-type	Energy level (ev)		Effectivity of centers introduction
	Photoconductivity 100°K	Hall effect 250−300°K	
Oxygen $>10^{17}cm^{-3}$	$E_v+0.30\pm0.01$	$E_v+0.27\pm0.01$	$5.2\times10^{-2}cm^{-1}$
Oxygen $<5\times10^{16}cm^{-3}$	$E_v+0.25\pm0.01$	$E_v+0.21\pm0.01$	$3.4\times10^{-2}cm^{-1}$
	$E_v+0.21\pm0.01$	$E_v+0.19\pm0.01$	$7.3\times10^{-3}cm^{-1}$

defects migration in the crystal after their generation made by several authors, particularly by Wertheim, lead us to the thought that the photoconductivity spectra method might permit the observation of the changes taking place as a result of the point defects migration in crystal after the bombardment. For the investigation of these processes it is natural to follow the properties of crystals irradiated at low temperatures. This method gave already important results in the case of germanium.

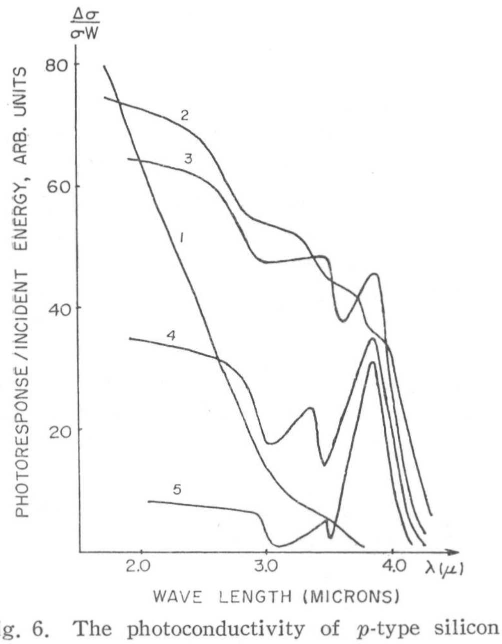

Fig. 6. The photoconductivity of p-type silicon bombarded by electrons at 100°K. Curve 1 taken 30 min. after the bombardment; during this time the sample temperature 100°K; curve 2–3 hours after the bombardment, temperature of the sample 100°K. Curve 3–16 hours after the bombardment; temperature of the sample near to 300°K. Curves 4 and 5–20 and 40 days after the bombardment; temperature of the sample 300°K.

In our experiments with p-type silicon the temperature of samples during the irradiation did not exceed 100°K. Some of the results are shown in Fig. 6. The curve 1 was obtained after 30 minutes since the end of the electron irradiation. No structure is seen except a weak bend near 3μ. The curve 2 was obtained after 3 hours after the irradiation; during this time the temperature of the sample was kept at 100°K. The spectrum shows structure of the same type as for samples irradiated at 300°K. After 16 hours at 300°K some further changes were observed (curve 3): the spectrum "stabilizes" and a maximum appears near 3.9μ. Curves 4 and 5 were obtained after 20 and 40 days, respectively.

We explain these results in a following way; the radiation induced defects usually present in irradiated silicon crystals have a nature of complexes of point defects and other imperfections of lattice, including chemical impurities. In the case of low temperature bombardment the migration velocities of point defects and impurities are low and the rate of the association is also low. Immediately after low temperature bombardment, the spectrum of photoconductivity may be due to the existence of Frenkel pairs. The binding energy of an electron to a Frenkel pair must depend on the vacancy-interstitial separation. The bombardment generates pairs with different (mostly the least possible) separations. One can suggest that the spectrum of electrons binding energies must contain a number of values near to each other which could not be resolved in our experiments. Gradually, the vacancies and interstitials are captured by impurities or other lattice imperfections.

The usual photoconductivity spectrum of crystals irradiated at room temperature corresponds to the set of the most stable complexes.

5. The Photoconductivity Spectra of *N*-Type Silicon Bombarded by Electrons

Fig.7 shows the photoconductivity spectrum of an n-type crystal bombarded by electrons;

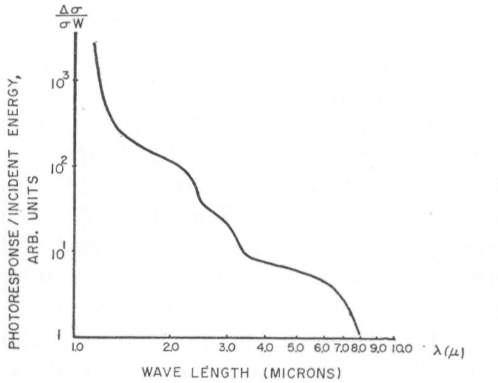

Fig. 7. The photoconductivity spectrum of n-type silicon bombarded by electrons; at 100°K Fermi level near to $E_c-0.16$ ev. Initial resistivity 7 ohm. cm; donor impurity-phosphorus; electron flux 10^{17}cm^{-2}.

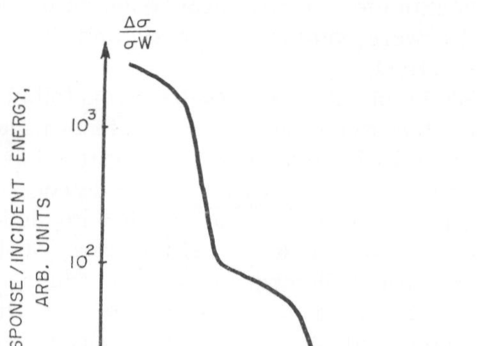

Fig. 8. The photoconductivity spectrum of n-type silicon bombarded by electrons. Donor impurity-phosphorus; Fermi level at 100°K near to $E_c-0.4$ ev.

at 100°K, the Fermi level is near to $E_c-0.16$ ev. The initial resistivity of this sample was 7 ohm. cm, the electron flux was equal to 10^{17} cm^{-2}. The spectrum has three "steps" corresponding to the photo-ionization energies 0.16 ev, 0.4 ev and 0.5 ev. For some of the samples we observed a distinctly expressed step near 8μ. In these cases the Fermi level was much lower than $E_c-0.16$ ev and the long wave part of the spectrum corresponding to electron transitions from the level $E_c-0.16$ ev was not observed. The observation of the 1.8μ step in the photoconductivity spectrum contradicts to the results reported by H. Fan and A. Ramdas.

The spectra shown in Fig. 7 and 8 were observed in samples with donor impurity concentrations exceeding 10^{15} cm^{-3}. In high-resistivity n-type silicon irradiated by electrons the photoconductivity in the impurity region increased steadily with photon energy and no structure was seen. The results obtained for n-type silicon thus also show that the impurity atoms are essential for the formation of radiation-induced centers with deep levels.

6. Discussion

The observation of photoconductivity spectra of silicon single crystals containing radiation induced defects and the analysis of the connection between the spectra, impurity concentration and Fermi level position gives the same energy levels system as other experimental methods in respect to the centers introduced with higher probability. Our results are in agreement with the conclusions about the nature of centers with levels at $E_c-0.16$ ev and $E_c-0.4$ ev made by the authors[12),13)].

In addition, we found new centers with different photoionization energies. The generation of these centers requires both the initial displacement of a lattice atoms by the radiation and the point defect migration stimulated by thermal excitation. The rates of introduction of these centers are relatively low which hinders their detection by other methods.

It was found that with the increase of defects' concentration, the discrete levels system gradually disappears. From the other side, for low defect concentrations, the sys-

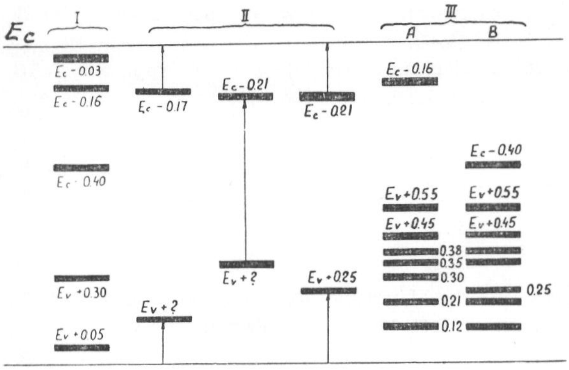

Fig. 9. The energy levels of defects in silicon bombarded by electrons.

I - The data of electrical measurements (Hall effect and resistivity; analysis of the recombination of excess carriers).

II - The data of infrared absorption measurements, interpreted by H. Fan and A. Ramdas.

III - The data obtained by photoconductivity measurements.

A - silicon crystals grown from silica crucibles (oxygen concentration over $10^{17}cm^{-3}$).

B - silicon crystals grown by zone melting in vacuum.

tems of levels of defects generated by electrons or neutrons pracitically coincide; thus the "group effects" which can appear in the latter case, play a negligible part in silicon. According to our data, shown in Fig.9, the thermal ionization and photoionization energies of the centers with deep levels are near to each other. More precisely, for three levels in the lower half of the band gap it was found that the photoionization energies are just slightly higher. These conclusions do not agree with the interpretation of infrared absorption data given by H. Fan and A. Ramdas[7].

The centers introduced by irradiation and determining the stable photoconductivity spectrum between 2μ and 6μ are not the simple point defects. Their introduction rates and stability depend upon impurities present in the crystal. The introduction rates of centers with levels at $E_c-0.4$ ev in n-type silicon and $E_v+0.45$ ev in p-type silicon depend both on the concentration of dominant donor or acceptor impurity and the oxygen concentration. It is most probable that they belong to the associations of defects with donor or acceptor impurity atoms. The annealing of the irradiated crystals at moderate temperatures (up to 600°K) shows an initial increase of the concentration of centers mentioned above. Wertheim[9] found that the rate of introduction of centers with energy levels at $E_c-0.4$ ev increased with the decrease of oxygen concentration in n-type silicon. We observed a similar correlation for $E_v+0.45$ ev centers in p-type silicon. We found also that the introduction rate of centers with $E_v+0.38$ ev level increases in samples with small excess carrier lifetime. It may be suggested that this level belongs to the association of a point defect and a "recombination center", for instance Au or Cu atom.

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On Defects Introduced by Fast Electrons into Silicon Doped by Lithium

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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