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Annealing of Radiation Defects in Silicon Single Crystals

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N-type floating zone silicon single crystals containing phosphorus were irradiated with Co^{60} gamma rays at room temperature or bombarded with electrons of 2 Mev. Resistivity and Hall coefficient were measured as a function of temperature before and after irradiation. The results indicate the existence of two net acceptor levels, 0.17ev and 0.4 ev below the conduction band respectively. The introduction rate of the deep level increased with increasing phosphorus concentration. Activation energy associated with the annealing of this level was found to be 0.94 ev in a temperature range of 120-180°C. On the other hand the introduction rate for the shallow level was independent of impurity concentration and this level was stable in this temperature range. Temperature dependence of Hall coefficient and Hall mobility after annealing suggest that a change has occurred in the nature of charge scattering center.

1. Introduction

Considerable effort has gone into the study of radiation damage in silicon over the past five years[1)-10)]. However, until recently most of the work has been done on pulled crystals grown from quartz crucibles. Such crystals are known to contain as much as 10^{18} atoms of oxygen per cubic centimeter.[11)] Spin resonance studies on pulled silicon have been reported by Watkins, Corbett *et al.*[12),13)] They have confirmed that Si-*A* center and Si-*E* center are association of vacancy with oxygen and phosphorus atoms and these centers are required for the formation of $E_c-0.17$ ev and $E_c-0.4$ ev levels respectively.

The reports on the annealing studies of radiation defects in silicon rare. Wertheim[6)] has observed an annealing effect in oxygen free silicon crystals bombarded with 1 Mev electrons after heating the specimens at 427°K. Bemski and Augstyniak[14)] have studied the high temperature annealing process between 200 and 400°C, by measuring minority carrier life time. The annealing was found to proceed with an activation energy of 1.3 ev and the kinetics of the annealing was found to be identical in both *n* and *p* type crystals. They have fitted the annealing curves with a sum of first and second order processes. By infrared absorption techniques, Fan and Ramdas[2)] have examined the change of *a* band at 1.8 μ with the annealing. They found that the intensity of the 1.8 μ band diminishes at about 145°C and concluded that the annealing kinetics is a first order process. The activation energy for this annealing process was 0.8 ev.

2. Experimental Procedure

The bridge shaped samples used in our experiments were cut from *n* type floating zone silicon single crystals. The oxygen concentration was about 10^{16} atoms/cc and the initial carrier concentration of these samples was distributed over a range 10^{13}-10^{15} electrons/cc. Electric contacts were made by soldering with an alloy containing 75% of Sn, 20% of Zn, and 5% of Bi. Samples were irradiated with Co^{60} gamma rays or bombarded with electrons of 2 Mev at room temperature.

Hall coefficient and resistivity were measured as a function of temperature by a vibrating reed electrometer. The flux density of the magnetic field was about 1300 gauss.

The sample was mounted in a double walled glass tube for transferring the cooling gas from a Dewar's bottle containing liquid nitrogen. Temperature of the samples was measured by a chromel constantan thermocouple.

The annealing experiments were performed in an oil bath, its temperature being controlled within ±0.1°C. Hall coefficient and resistivity were measured at the triple point of water (0.01°C). Conductivity of the samples was determined by the four electrode method.

3. Results

1) *Radiation Induced Energy Levels in Silicon*

Temperature dependence of carrier concentration and Hall mobility before and after bombardment and also after annealing at 160°C or 175°C are shown in Figs. 1, 2 and 3.

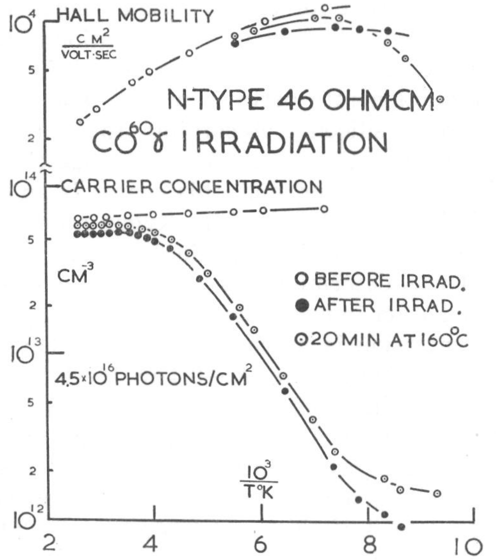

Fig. 1. Carrier concentration and Hall mobility of sample B before and after irradiation, and also after anneal at 160°C.

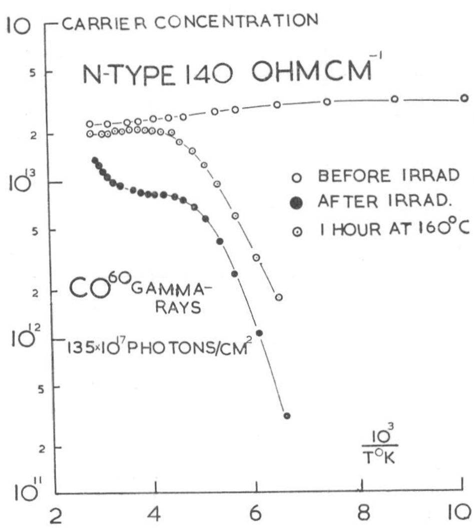

Fig. 2. Carrier concentration of sample C as a function of temperature. The different curves were obtained after irradiation and anneal.

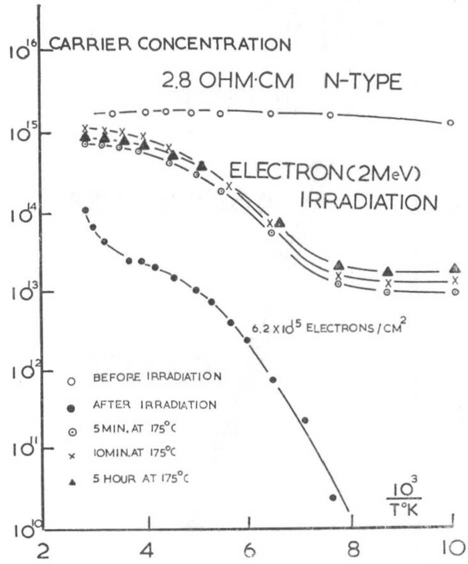

Fig. 3. Carrier concentration of sample D irradiated with electrons of 2 Mev as a function of temperature. The different curves were obtained after successive annealings.

The following conclusions can be drawn from Figs. 1 and 2: Two net acceptor levels were introduced by irradiation, 0.17 ev and 0.4 ev below the conduction band respectively. The $E_c-0.4$ ev level began to anneal at 160°C, on the other hand the $E_c-0.17$ ev level was stable in the vicinity of 160°C. The depth of this level was calculated by the following procedures.

The Fermi function of the trap level is given by

$$N_t^-/N_t=[1+\gamma\exp(E_t-E_f)/kT]^{-1}, \qquad (1)$$

where, γ, the degeneracy ratio between empty and full trapping state

N_t^-, number of negatively charged traps/cc

N_t, number of traps/cc

$N_t^0=N_t-N_t^-$, number of empty traps/cc (2)

$E_f=E_c+kT\cdot\ln(n/N_c)$, Fermi level (3)

n, number of conduction electrons/cc

N_c, state density of the conduction band. (4)

From (2), (3), and (4), Eq. (1) can be rewritten in the form:

$$N_t^0 n/N_t^-=\gamma N_c\exp[-(E_c-E_t)/kT], \qquad (5)$$

where E_c-E_t is the position of the trap level with respect to the conduction band edge. From the slope of the $N_t^0 n/N_t^- T^{-3/2}$ plotted against reciprocal temperature, the

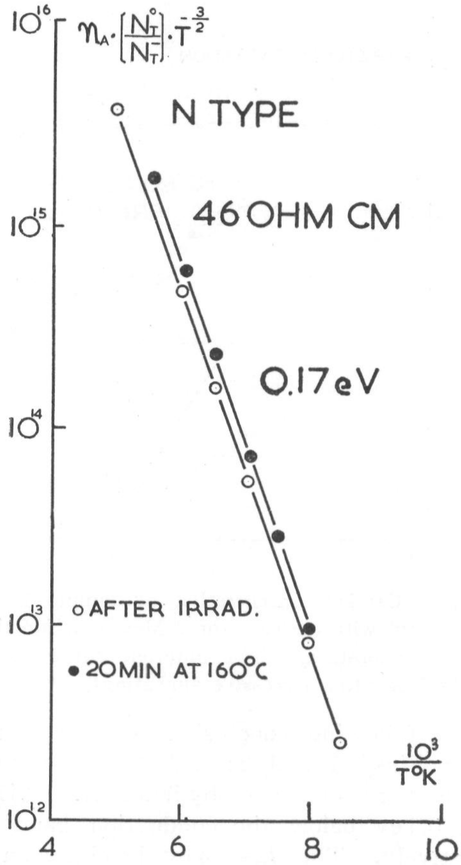

Fig. 4. The depth of the $E_c-0.17$ ev level was determined from the slope.

value, 0.17 ev was obtained as the depth of the trap level (Fig. 4). The depth of the $E_c-0.4$ ev level was obtained from the measurement of the Fermi level at the positions where carrier concentration rapidly decreases at about 300°K in Figs. 2 and 3.

It is to be noted here that the introduction rate for the $E_c-0.4$ ev level increases with increasing initial carrier concentration (nearly equal to the phosphorus concentration) and that for the $E_c-0.17$ ev level was independent of impurity concentration of the sample. No difference was found in the introduction rate between pulled[8] and floating zone silicon. According to Watkins' model the $E_c-0.17$ ev level is associated with Si-*A* center and this center is an association of vacancy with oxygen atom. It seems that the introduction rate for this level was determined by the generation rate of radiation induced vacancies, when oxygen concentration is much larger than that of the vacancies. The $E_c-0.4$ ev level is associated with Si-*E* center formed by a combination of vacancy and phosphorus atom. The dependence of introduction rate for Si-*E* center upon phosphorus concentration can be explained, if this model is adopted. The results are summarized in Table I.

Table I. The introduction rates for Si-*A* and Si-*E* centers

Author		Initial carrier concentration per cm³	Total dose photons or electrons per cm²	Introduction rate $\frac{\text{traps/cc}}{\text{photons/cm}^2}$ or $\frac{\text{traps/cc}}{\text{electrons/cm}^2}$	
				E_c-0.4 ev level	E_c-0.17 ev level
Sonder and Templeton	Pulled Si	2×10^{15}	Co^{60} γ-rays 1.7×10^{18}	2×10^{-5}	1.15×10^{-3}
	Pulled Si	7.4×10^{13}	Co^{60} γ-rays 1.5×10^{17}	2×10^{-5}	0.6×10^{-3}
Wertheim	Floating zone Si	4.6×10^{14}	1 Mev electrons 9.5×10^{14}	0.26	0.07
Authors	Floating zone Si−A	1.5×10^{15}	Co^{60} γ-rays 1.8×10^{17}	3×10^{-3}	0.85×10^{-3}
	Floating zone Si−B	7.6×10^{13}	Co^{60} γ-rays 4.5×10^{16}	1.3×10^{-4}	1.5×10^{-3}
	Floating zone Si−C	2.5×10^{13}	Co^{60} γ-rays 1.35×10^{17}	0.9×10^{-4}	—
	Floating zone Si−D	1.5×10^{15}	2 Mev electrons 6.2×10^{15}	0.27	0.14
	Floating zone Si−E	3×10^{13}	2 Mev electrons 3.1×10^{14}	0.006	—

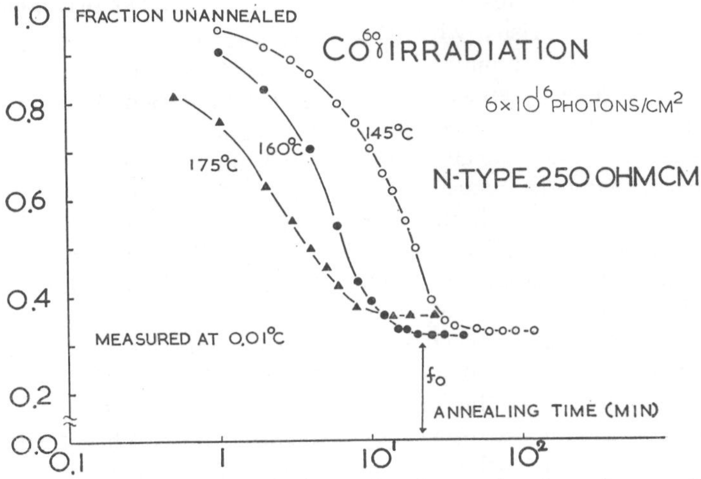

Fig. 5. The isothermal annealing of three phosphorus doped specimens. The recovery was determined from conductivity measurements.

2) *Annealing of Radiation Defects in Silicon*

Annealing of silicon crystals irradiated with Co^{60} gamma rays was studied at a temperature range of 120–180°C. The variation of carrier concentration and conductance with time was measured. During the course of annealing no change was found in Hall mobility of the samples at the triple point of water. Annealing curves of fraction unannealed against time are shown in Fig. 5. Fraction unannealed was calculated by using the following formula:

$$f \text{ (fraction unannealed)} = \frac{\sigma_b - \sigma_t}{\sigma_b - \sigma_{ab}} \text{ or } \frac{n_b - n_t}{n_b - n_{ab}}$$

where σ_b, n_b: conductivity and carrier concentration before bombardment

σ_{ab}, n_{ab}: conductivity and carrier concentration after bombardment

σ_t, n_t: conductivity and carrier concentration after anneal for time t.

The unannealed fraction decreased asymptotically to a value f_0 ranging from 30 to 40%. These annealing curves were found to be approximately represented by exponential function except at an early stage. The time constants can be estimated by graphical method. The analysis of the curves in Fig. 5 gives an activation energy of 0.94 ev.

At 0.01°C, where the carrier concentration and conductance were measured, the $E_c-0.17$ ev level is empty, while the $E_c-0.4$ ev level is filled. Therefore the decrease in unannealed fraction was considered to be

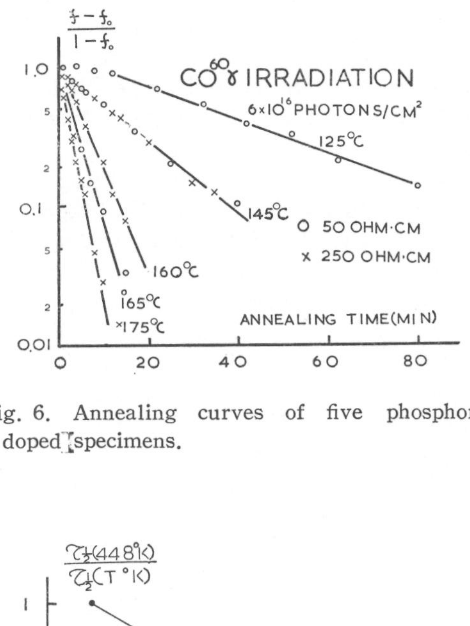

Fig. 6. Annealing curves of five phosphorus doped specimens.

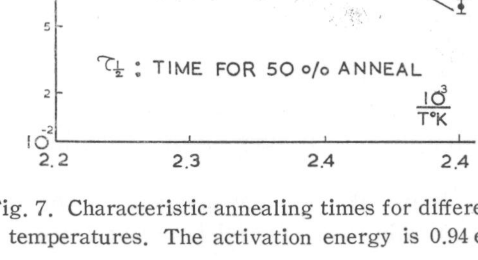

Fig. 7. Characteristic annealing times for different temperatures. The activation energy is 0.94 ev.

caused by an annealing of the $E_c-0.4$ ev level. Now the question arises why the rest of the fraction, 30–40%, remained unannealed. In Fig. 1 a reverse annealing of Hall mobility at low temperature was found. This fact suggests that the charge on the scattering center has changed. Some of the scattering centers associated with the $E_c-0.4$ ev level was considered to be changed into the other associated with deeper level. Transformation into the same level from the $E_c-0.17$ ev level was also observed with the very slow annealing of Si-A center. (Fig. 3). This conversion may be due to the formation of such a defect as divacancy by association of vacancies dissociated from Si-E or Si-A center.

4. Summary

1) Two net acceptor levels were observed in phosphorus doped silicon crystals irradiated with Co^{60} gamma rays or electrons of 2 Mev. A shallow level is located 0.17 ev below the conduction band and a deep one line 0.4 ev below the conduction band.

2) Watkins' model for Si-A and Si-E center was employed to explain the experimental results that the introduction rate for the $E_c-0.4$ ev level increased with increasing phosphorus concentration and that for the $E_c-0.17$ ev level seemed to be limited by generation rate of radiation induced primary vacancies, which mostly associate with oxygen atoms.

3) The density of the $E_c-0.4$ ev level diminishes after anneal at a temperature range of 120–180°C, on the other hand that of the $E_c-0.17$ ev level does not change at this temperature range. The annealing of the $E_c-0.4$ ev level was considered to be a dissociation of Si-E center and the activation energy for this annealing was found to be 0.94 ev.

Acknowledgement

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DISCUSSION

Watkins, G.: We have studied the anneal of the E center and we also find its disappearance in the same temperature region that you see for the 0.4 ev level. This would appear to add confirmation on the annealing of the (E_c-0.17 ev) level?

Saito, H.: From the difference in carrier concentration between 300° and 110°K in Fig. 1 or 3, we could estimate the concentration of Si–A center. This concentration decreased very slowly with increasing annealing time.

Inuishi, Y.: Did you find any annealing of A-center at 200°C or at 180°C?

Saito, H.: A few per cent of the concentration of the A-center decreased after annealing for several hours at 175°C.