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.

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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,

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

Table I

Sample No.	Resistivity	Dopant	Type	Dislocation density	Oxygen concentration	Remarks
FZ-1	20 Ω-cm		N type	1×10^5cm^{-2}	nearly oxygen free	
FZ-2	80	P	N	1×10^5	〃	
FZ-3	230	P	N		〃	$\sim3\times10^{13}$(cm^{-3}) Ni contaminated to Sample FZ-2
PU-1	40	Sb	N	3×10^4	7.2×10^{17}cm^{-3}	
PU-2	70	Al	P	1×10^5	8.5×10^{17}	
PU-3	3000	Al	P	$\sim5\times10^6$	8.5×10^{17}	Bent Si cystal of PU-2
PU-4	7500	Al	P	$\sim3\times10^7$	8.5×10^{17}	〃
PU-5	250	P	N	1×10^5	6.0×10^{17}	

where N_r, E_r, E_f, T, n and p are recombination center density, depth, Fermi level, temperature, electron and hole density respectively. Suffix 1 and 0 denote the density when Fermi level is on the recombination center and at thermal equilibrium respectively. τ_{p0} and τ_{n0} are the life times in strongly n and p type sample respectively. If the change of Fermi level is small as in our case of γ irradiation, inverse life time at a given temperature is a good measure of recombination center density N_r as seen from Eq. (1).

2. Experimentals

The Si samples investigated were vacuum floating zoned (FZ) Si and pulled (PU) Si both of n and p type as summarized in Table 1. Oxygen content from 9 μ infrared absorption and dislocation density from etch pits were also obtained. Ni doping in FZ Si was carried out by heating Ni plated sample at 300°C for 1 hr in H_2 gas flow. γ irradiation from CO^{60} were done at room temperature with the dose rate of 10^5 γ/hr. Pile neutron irradiation were done in "JRR-1" pile with the dose rate of 3×10^{11} neutron/cm$^2\cdot$sec. The carrier life time was measured by the change of microwave[1),2)] absorption due to decay of the carriers following 0.5 μs Xe light pulse thinning with a sample crystal inserted into wave guide. Hall effect and resistivities were also measured for some crystals. Inverse life time $1/\tau$ were taken as a measure of the defects through this paper from the reason stated previously. In our case of neutron irradiation where Fermi level moved appreciably, proper attention should be paid to the interpretation of $1/\tau$. Fig. 1 shows the defects

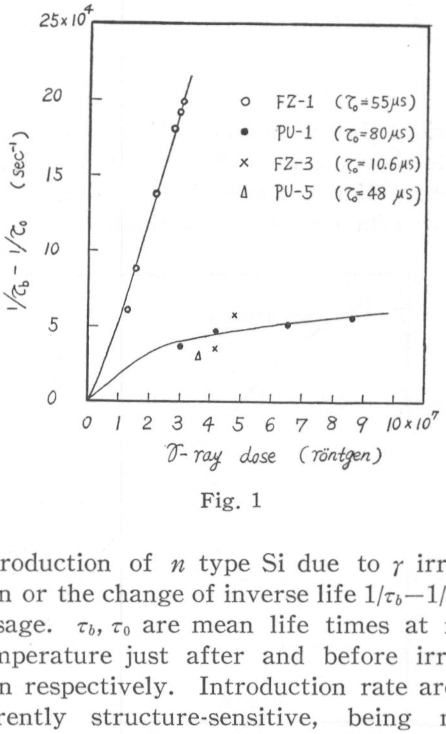

Fig. 1

introduction of n type Si due to γ irradiation or the change of inverse life $1/\tau_b - 1/\tau_0$ *vs.* dosage. τ_b, τ_0 are mean life times at room temperature just after and before irradiation respectively. Introduction rate are apparently structure-sensitive, being much larger for FZ Si than for pulled and for Ni doped Si. Since the same amount of Frenkel defects primarly should have been introduced at the same dosage, the recombination cross sections in pulled Si seems to have decreased from that in FZ Si possibly due to complex formation as will be mentioned later. Ten minutes isochronal annealing of the inverse life time $1/\tau - 1/\tau_0$ are shown in Fig. 2 for the same samples where τ means life time at room temperature after each annealing stage. Although n type FZ Si shows monotonous annealing, pulled n and p type Si containing larger amount of oxygen show remarkable "reverse annealing" peak at 200°C irrespective of doping

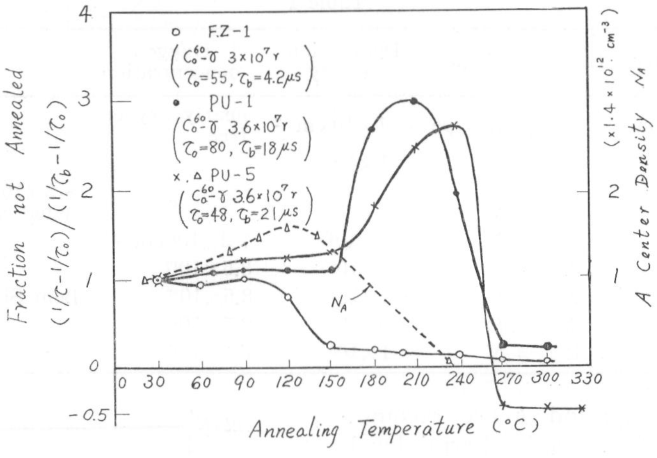

Fig. 2

impurity. Isothermal annealing of the same sample shows similar behaviour as Fig. 3, where fraction not annealed $(1/\tau-1/\tau_0)/(1/\tau_b-1/\tau_0)$ was taken as the ordinate. Reverse annealing in pulled Si is evidently associated with oxygen and can be explained by the formation and the dissociation of the vacancy-oxygen complex (like A center[3]) as will be discussed.

The occurrence of reverse peak by the introduction of oxygen into FZ Si which showed monotonous annealing was also observed. Hall mobility of irradiated pulled Si at lower temperature show monotonous annealing behaving differently from the life times.

The Ni doped n-type Si also shows similar reverse annealing possibly due to vacancy (or interstitial)-Ni complex as shown in Fig. 4. Fig. 4, 5→Fig. 5 shows ten minutes isochronal annealing of 10^{25} nvt neutron irradiated pulled and FZ n-type Si. Appearance of thermal release time τ_t following recombination in photodecay curve, and absence of reverse annealing is characteristic in this case. The latter phenomena may be due to much shorter duration of neutron irradiation than in γ irradiation which does not allow complex formation by defect dif-

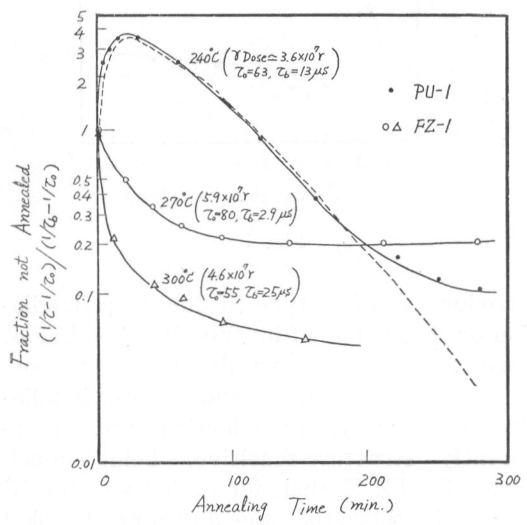

Fig. 3

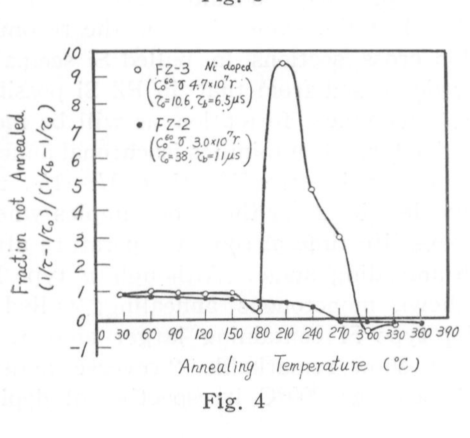

Fig. 4

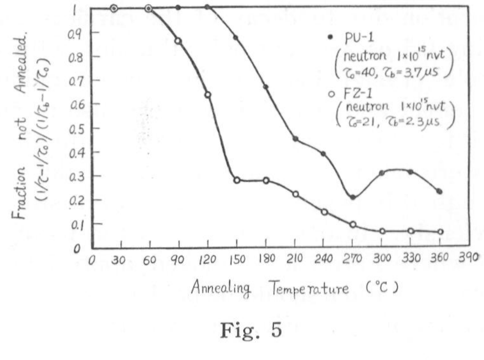

Fig. 5

fusion.

Inspection of the annealing curves of FZ Si reveals that at least two stages of annealing exist at around 150°C and 300°C and that isothermal curves can not be expressed by a simple exponential decay with single activation energy. The activation energy of annealing for γ irradiated Si around 300°C is estimated to be 1.2 ev from isothermal curve in agreement with Bemski's values[5].

The annealing mechanism of radiation induced defect may be (i) direct recombination of close Frenkel pairs, (ii) diffusion into sinks such as dislocations or surfaces. To clarify these situations, dislocations were introduced into p-type pulled Si cut from the same host crystal by plastic bending at 950°C with various bending radius. The isochronal annealing curves of these sample in Fig. 6 show that lower recovery stage is favoured markedly with increasing dislocation density and that oxygen reverse annealing still remains.

Accordingly the lower annealing stage (150°C) is considered to be the diffusion of free vacancies or interstitials (not trapped by impurities) into dislocations. Activation energy of this process was estimated to be 0.7~0.8 ev as will be discussed later. Small reverse annealing peak at 330°C in Fig. 6 may be speculated to be the dissociation of Al-vacancy (or interstitial) complex.

To determine the depth of recombination and trap levels, temperature dependence of life time (Fig. 7~Fig. 9), thermal release time, and sometimes Hall coefficient were obtained. Although unirradiated Si shows decrease of life time with decreasing temperature in accordance qualitatively with S-R theory, irradiated high resistivity Si

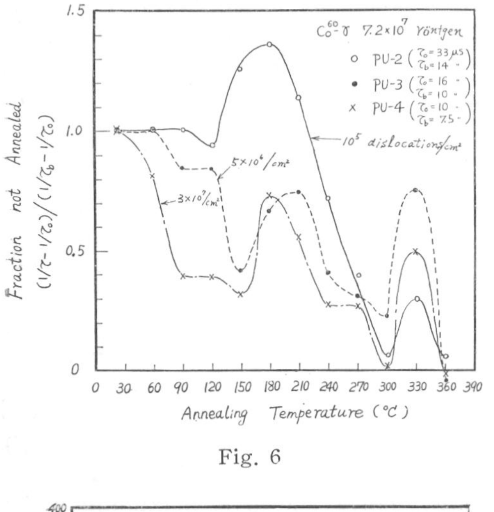

Fig. 6

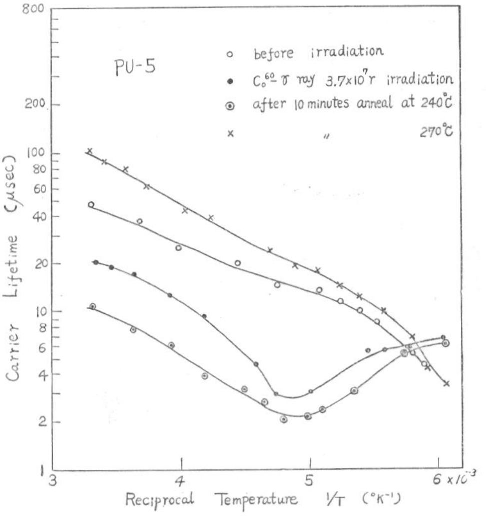

Fig. 8

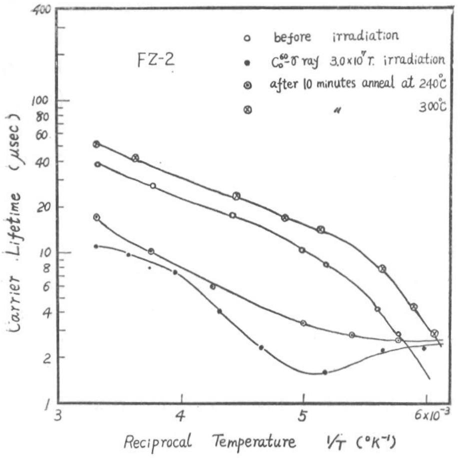

Fig. 7

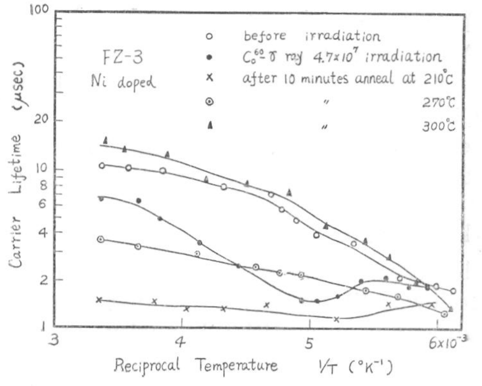

Fig. 9

shows V shaped curve like Fig. 7 and Fig. 8 which may be explained by the effect of temporary minority carrier traps as was suggested by Wertheim and Crawford[6]. It should be noticed that the temperature dependency of life time at the top of reverse annealing peak was much different from the rest of the curves in Ni doped n-type Si. Temperature dependence of thermal release time τ_t in neutron irradiated n-type Si gave trap levels at $E_v+0.28$ ev, $E_v+0.4$ ev. Hall coefficient gave $E_v+0.4$ ev and $E_c-0.3$ ev. From the temperature dependence of life time, with physical consideration based on S-R statistics taking temporary traps into account as Wertheim formula[6], the level of recombination center was tentatively evaluated as in Fig. 10 where trap levels stated above are also shown with the trap level for bent Si[7].

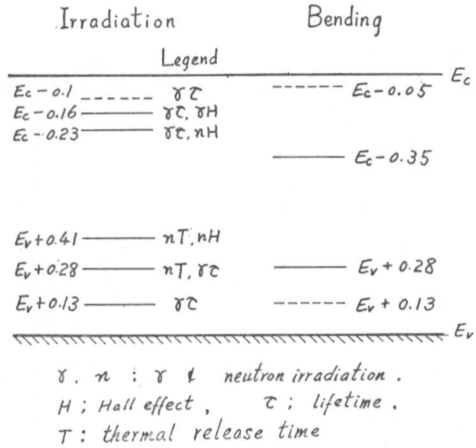

Fig. 10

In the case of γ irradiation, temperature dependence of carrier density from Hall coefficient suggests that $E_c-0.16$ ev center or A center is the most effective net acceptor for carrier removal in n-type pulled Si and that the density of A center N_A determined from carrier removal anneals at lower temperature like dotted line in Fig. 2.

3. Discussions

The reverse annealing can be explained as follows; (i) formation and dissociation of vacancy (or interstitial)-impurity complex. (ii) much larger cross section as recombination center for free vacancy (or interstitial) than for complex. (iii) annihilation of Frenkel defect through diffusion into sinks (dislocation, surfaces). The kinetic equation of the annealing of free vacancy density N_v and of complex density N_A can be given as

$$\frac{dN_A}{dt}=-\alpha N_A+\beta N_v\,,\quad \frac{dN_v}{dt}=-\frac{dN_A}{dt}-\gamma N_v\,, \tag{2}$$

where α, β and γ are rate constants for complex dissociation, complex formation and free vacancy annihilation into sinks. As is well known

$$\alpha=\nu_A \exp(-E_D/kT),\quad \gamma=\pi^2 D(T)/\Lambda^2,$$
$$\beta=\beta_0 D(T)N_t,$$
$$D(T)=\nu a^2 \exp(-E_M/kT),$$

where ν_A, ν, E_D, E_M $D(T)$, N_t, Λ and a mean vibration frequency for complex, for free vacancy, activation energy for complex dissociation, for free vacancy migration, diffusion constant at T°K, impurity density, characteristic distance between sinks (dislocation etc.), and lattice constant respectively. The solution of (2) is obtained as,

$$N_v(t)=N_v(0)\exp(-P_1t)$$
$$+\frac{[\alpha N_A(0)+(\beta+\gamma-P_1)N_v(0)]}{P_2-P_1}[\exp(-P_2t)$$
$$-\exp(-P_1t)] \tag{3}$$

and

$$P_1,\,P_2=\frac{(\alpha+\gamma+\beta)\pm\sqrt{(\alpha+\gamma+\beta)^2-4\alpha\gamma}}{2}\,.$$
$$P_2\geq P_1 \tag{4}$$

A similar solution is obtained for $N_A(t)$. The second term of Eq. (3) in suitable condition evidently shows a maximum which corresponds to reverse annealing peak. For example the isothermal curve at 240°C for pulled Si in Fig. 3 well fits with Eq. (3) like dotted line by choosing P_1, P_2 to be 2.5×10^{-4}/sec and 10^{-3}/sec respectively. Provided $\alpha\gg\beta$ in this temperature, Eq. (4) gives $P_1\simeq\gamma$, $P_2\simeq\alpha$.

This, combined with the experimental values of P_1 and P_2, gives $E_D\simeq 1.8$ ev and $E_M\simeq 1.0$ ev respectively, provided $\nu=\nu_A=10^{13}$/sec. In the case of dislocation enhanced recovery at low temperature shown in Fig. 6, we may put β, $\gamma\gg\alpha$. Then Eq. (3) becomes

$$N_v(t)=N_v(0)\exp(-P_2t)\simeq N_v(0)\exp[-(\gamma+\beta)t]. \tag{5}$$

Provided that the characteristic length for A is equal to dislocation line distance, experimental results of Fig. 6 on lower temperature recovery seems to be explained from Eq. (5) by taking $E_M \simeq 0.7 \sim 0.8$ ev and $\nu \simeq 10^{13}$/sec.

The Authors wish to express their gratitude to Dr. Ryuzen, Mr. Edgawa, Mr. Tanaka and Mr. Nakano who have helped our experiment.

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DISCUSSION

Watkins, G.: The annealing you attribute to the $E_c - 0.17$ ev level appears to be occurring at a lower temperature than for the A center which we observed both by spin resonance and the corresponding 12μ absorption band. You have any comments on this?

Inuishi, Y.: To this respect I would suggest that the A center density (10^{13}/cc) in our experiment is much smaller than the density which would be necessary to observe the absorption. We observed that the reverse annealing peak broadens and shifts to higher temperature with increasing A center concentration.

Ramdas, A. K.: The "inverse annealing" observed by you $\sim 200°C$ cannot be, in my opinion, associated with dissociation of Si-A center (single vacancy oxygen) as it is stable $\simeq 35°C$. Could this be associated with divacancy moving to oxygen site, forming a "divacancy-oxygen" center, as divacancies may become mobile at this temperature?

Inuishi, Y.: No, as was replied to Dr. Watkins question, we observed the shift of reverse annealing peak edge to higher temperature. Namely, it shifts from 340°C to 330°C with increasing A center density from 10^{13}/cc to 10^{14}/cc. Concerning with divacancy mechanism, nothing conclusive can be said in the lack of direct evidence.

Crawford, J. H.: In studies of the introduction of recombination centers in n-type Ge, Baruch observed a decrease in the rate of defect introduction in deformed crystals. Did you observe a similar effect in the deformed specimens that you studied?

Inuishi, Y.: Yes, there is a slight decrease in introduction rate with increasing dislocation density. However, the change is as small as several 10% for the change of dislocation density from $10^5/cm^2$ to $5 \times 10^6/cm^2$.