TEMPERATURE INFLUENCE ON THE FORMATION OF DEFECTS IN n-Si IRRADIATED WITH ELECTRONS

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The kinetics of formation and annealing of A-centers in silicon with n-type conductivity grown by the Czochralski method (Cz n-Si) under irradiation with 1-MeV electrons have been studied. The irradiation was carried out either at room temperature, with the following annealing at 360 °C, or immediately at 360 °C. The revealed difference between the corresponding kinetics of A-centers was demonstrated to be associated with the difference between the conditions of defect accumulation and annealing. Irradiation does not affect the mechanism of A-center annealing. The reason may be an insufficient excitation degree of the crystal electron subsystem for the given concentration of equilibrium charge carriers. It has been found that the increase of the irradiation temperature within the interval from room temperature to 360 °C practically does not influence the generation rate of free vacancies λ_V, in contrast to the interval from 100 K to room temperature, where λ_V grows with the temperature.

1. Introduction

Irradiation, as well as heat treatment, is a convenient tool for a controllable modification of semiconductor crystal parameters in rather a wide range. Nowadays, the processes occurring at such irradiation temperatures, when either primary or secondary radiation-induced defects (RIDs) are stable, have been studied well enough. Concerning the processes that run at the irradiation temperatures equal or higher than the annealing temperature for secondary RIDs (hot-irradiation (HI) temperature), they have been studied to a much lesser extent. Under such conditions, owing to the annealing of secondary RIDs, other – the so-called tertiary – defects can be formed [1], which are more thermally stable; this is important for radiation-based technologies of instrument making. Another way to generate tertiary RIDs comprises the irradiation at room temperature and the subsequent annealing. In work [2], it was demonstrated that those two methods can be nonequivalent to each other. Moreover, the researches carried out earlier showed that the RID generation rate increases with the temperature in the temperature interval from 100 to 300 K [3]. On the other hand, ionization of the crystal at HI can give rise to different defect annealings [4].

The aim of this work was to make a comparative research of the processes of RID formation and annealing for two n-Si treatment routines: (i) irradiation of the specimens at room temperature followed by their annealing at 360 °C and (ii) hot irradiation of the specimens at 360 °C. The treatment temperature was chosen to provide the intense annealing of A-centers (the complexes of a vacancy and interstitial oxygen), the main RIDs in n-Si.

2. Experimental Part

The first group of specimens was irradiated at a high temperature equal to the intense annealing temperature of A-centers (360 °C). The specimens of the second group were irradiated to the same exposure dose at room temperature and then annealed at the HI temperature. The periods of annealing and irradiation were identical and equal to the HI time. In order to study the kinetics of defect accumulation, the dose dependences of the defect concentration were investigated at the same HI temperature.

In our researches, we used Cz n-Si specimens with the concentration of free carriers $n \approx 10^{15}$ cm^{-3} (KEF-4.5). The concentrations of oxygen and carbon were $N_O = 6 \times 10^{17}$ cm^{-3} and $N_C \leq 5 \times 10^{16}$ cm^{-3}, respectively. Specimens were irradiated with 1-MeV electrons ($j = 0.5$ μA/(cm$^2 \times$ s)). The defect concentration was determined from the temperature dependences of the Hall effect and in the approximation of the electroneutrality equation validity. The fitting parameters were the defect concentration and the defect level energy in the energy gap.

3. Results and Their Discussion

The results of measurements for the exposure dose $\Phi = 1 \times 10^{16}$ cm^{-2} are depicted in Fig. 1. A characteristic

step in the temperature interval from 120 to 270 K is observed in the temperature dependence of charge carrier concentration n after irradiation. In the specimens irradiated at room temperature (curve *2*), the variation of n is caused, as a rule, by the recharge of the acceptor level of A-centers (E_c − 0.17 eV). Hot irradiation at 360 °C (curve *4*) does not bring about qualitative changes in the behavior of $n(1/T)$-dependences. A computer-assisted approximation of Hall dependences gave the best agreement of calculation results with experimental ones just for the A-center level value. The values of the A-center concentration in both groups of specimens are quoted in Table. The determination error for the concentration was 10%.

It is evident that the concentration of A-centers after HI at $T = 360$ °C is lower than the corresponding value after specimen irradiation at room temperature. In the course of HI, some portion of A-centers undoubtedly had enough time to be annealed. But their remaining part was still larger than that after specimen irradiation at 20 °C and their consecutive annealing at 360 °C for the same time interval as in the HI case.

As the exposure dose of high-temperature irradiation increases (see Table), the gain of the A-center concentration diminishes, which evidences for a nonlinear dependence of the concentration of those defects on the irradiation dose, in contrast to irradiation at room temperature, where this dependence is linear. The non-linearity in the accumulation kinetics of A-centers is caused by the simultaneous formation and annealing of the latter. At the initial stage, when the A-center concentration is still low, the influence of annealing on the process of A-center accumulation is small. At further stages, the rate of annealing and, correspondingly, its contribution to the process of accumulation increases. At high exposure doses, the A-center concentration must achieve saturation. Small changes of the concentration, which are observed in experiment as the irradiation dose grows, testify that the value $N_{V\mathrm{O}} = 3.9 \times 10^{14}$ cm^{-3} is close to the saturation one.

In work [1], it was shown that, after the irradiation at 450 °C, an unidentified acceptor level at $E_c - 0.19$ eV

Φ, 10^{16} cm^{-2}	N_A, 10^{14} cm^{-3}		
	T_{irr}=20 °C	T_{irr}=20 °C + annealing at 360 °C	T_{irr}=360 °C
0.5	2.4	1.4	2.1
1	5.1	1.7	3.2
1.5	–	1.4	–
2	–	–	3.9

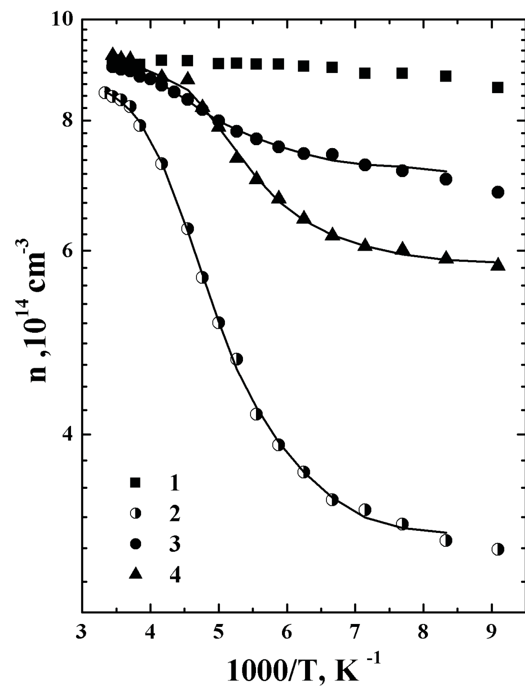

Fig. 1. Dependences of the charge carrier concentration n on the reciprocal treatment temperature for various treatment routines: initial specimen (*1*), irradiation at 20 °C at the exposure dose $\Phi = 1 \times 10^{16}$ cm^{-2} (*2*), irradiation at 20 °C at the exposure dose $\Phi = 1 \times 10^{16}$ cm^{-2} followed by annealing at 360 °C for 53 min (*3*), and irradiation at 360 °C at the dose $\Phi = 1 \times 10^{16}$ cm^{-2} (*4*)

was observed near the A-center level in deep-level transient spectra. In the temperature dependences of the Hall effect, it is difficult to distinguish between this level and the A-center one. In order to elucidate whether A-centers or other electrically active and more thermally stable defects are formed in the course of irradiation at 360 °C, specimens subjected to HI were annealed at $T =$ 360 °C for 2 h. At such a treatment, the temperature dependence of the charge carrier concentration restored to the initial one. That is, at 360 °C, A-centers remain dominant RIDs, while defects with the level at E_c − 0.19 eV are not formed.

Now consider the variation kinetics of the A-center concentration at (I) irradiation at 20 °C followed by annealing at 360 °C and (II) high-temperature irradiation at 360 °C.

I. For irradiation at room temperature, we obtain the system of two equations

$$\begin{cases} \frac{dN_V(t)}{dt} = \lambda_V^I - \chi_{V\mathrm{O}} N_V(t) N_{\mathrm{O}}, \\ \frac{dN_A(t)}{dt} = \chi_{V\mathrm{O}} N_V(t) N_{\mathrm{O}} \end{cases} \quad (1)$$

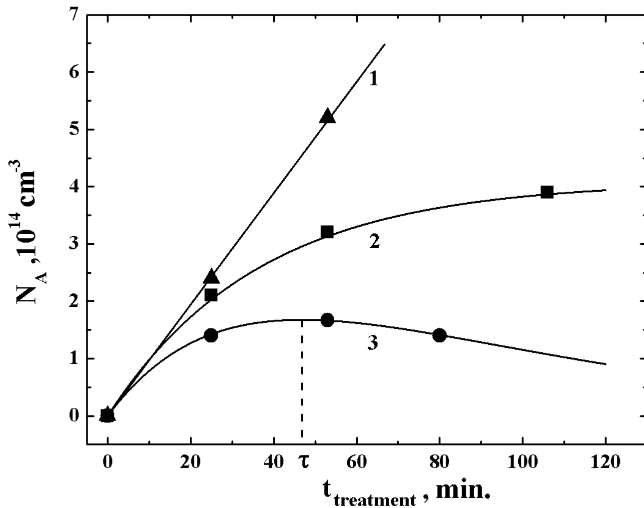

Fig. 2. Dependences of the A-center concentration on treatment time: irradiation at room temperature (*1*); HI at 360 °C (see Eq. (4)) (*2*); and irradiation at 20 °C and successive annealing at 360 °C (see Eq. (6)) (*3*). Points correspond to experimental values

for vacancies and A-centers, respectively, where λ_V^I is the vacancy generation rate, and χ_{VO} is the constant of vacancy capture by oxygen. Since the lifetime of vacancies is much shorter than the irradiation time, the vacancy concentration can be considered constant, whence we have

$$N_A(t) = \lambda_V^I t. \tag{2}$$

For annealing, we consider a general model, not specifying the mechanism:

$$\frac{dN_A(t)}{dt} = -\frac{N_A(t)}{\tau^I}. \tag{3}$$

Here, τ^I is the annealing constant. The final solution of this equation is

$$N_A = \lambda_V^I t_{\mathrm{irr}} \times \exp\left(-\frac{t_{\mathrm{ann}}}{\tau^I}\right). \tag{4}$$

Therefore, the ultimate concentration of A-centers after irradiation and annealing is determined by formula (4).

II. For irradiation at $T = 360$ °C, the system of equations is somewhat different, because the formation of A-centers is accompanied by their annealing:

$$\begin{cases} \frac{dN_V(t)}{dt} = \lambda_V^{II} - \chi_{V\mathrm{O}} N_V(t) N_{\mathrm{O}}, \\ \frac{dN_A(t)}{dt} = \chi_{V\mathrm{O}} N_V(t) N_{\mathrm{O}} - \frac{N_A(t)}{\tau^{II}}. \end{cases} \tag{5}$$

The experimental conditions differ from those in the previous case, so that the values of the vacancy generation rate λ_V and the annealing constant τ may be not identical.

Similarly to the previous case, the vacancy concentration is constant. Basing on this fact, we obtain the following dependence for the A-center concentration:

$$N_A(t) = \lambda_V^{II} \tau^{II} \times \left(1 - \exp\left(-\frac{t}{\tau^{II}}\right)\right). \tag{6}$$

It is easy to see that, in this case, the concentration of A-centers cannot exceed the value of $\lambda_V^{II}\tau^{II}$, i.e. it becomes saturated as the irradiation time grows.

Using the experimentally determined values for the A-center concentration (see Table) and solutions (4) and (6) of the kinetic equations, we obtained the following values for the annealing constant and the vacancy generation rate: case I – $\tau = 2.8 \times 10^{-3}$ s and $\lambda_V = 1.6 \times 10^{-11}$ cm^{-3}s^{-1}; case II – $\tau = 2.2 \times 10^{-3}$ s and $\lambda_V = 1.9 \times 10^{-11}$ cm^{-3}s^{-1}.

In Fig. 2, the plots of the A-center concentration kinetics calculated by formulas (4) and (6) are depicted for the cases of irradiation and consecutive annealing (curve *3*) and HI (curve *2*), provided that the durations of HI, preliminary irradiation, and following annealing are equal. The points correspond to experimental results. Figure 2 demonstrates that the concentration of A-centers is always higher at hot irradiation. This circumstance is associated with the fact that, in the course of HI simultaneously with the defect annealing, additional defects are permanently generated. Since the annealing cannot be instant, a certain portion of defects always remains unannealed. On the other hand, the rate of defect annealing depends on their initial concentration. At HI, the concentration of defects is low at the initial stage, so that annealing is slower. In the case of the combined treatment (irradiation followed by annealing), all defects, which were accumulated at the irradiation stage (curve *1*) and having therefore the maximal concentration, are annealed simultaneously, and the annealing is more rapid. In contrast to HI, at the consecutive irradiation/annealing treatment, the resulting concentration of A-centers (formula (4)) possesses a maximum at $t_{\mathrm{treat}} = \tau^I$. The maximum position is determined by the annealing constant only and does not depend on the irradiation intensity.

As we see, the annealing constants τ^I and τ^{II} differ insignificantly, which evidences for identical mechanisms of A-center annealing in those two cases. It is, however, known (see, e.g., work [4]) that crystal ionization can enhance RID annealing. The maximum

possible concentration of nonequilibrium charge carriers generated by irradiation with $j = 0.5\ \mu\text{A}/(\text{cm}^2 \times \text{s})$ is about 1×10^{16} electron-hole pairs per cubic centimeter. At a temperature of 360 °C, the concentrations of thermal electrons and holes are the same. This fact can probably explain the reason why there is no appreciable influence of irradiation on the A-center annealing.

The concentration of vacancies, which make a contribution to the formation of secondary defects (in our case, these are A-centers), is governed by the decay of genetic (formed at the same crystal site) Frenkel pairs [3]:

$$N_V \sim \int_{r_{\text{cr}}}^{r_{\max}} 4\pi r^2 f(r) dr, \tag{7}$$

where $f(r)$ is the Frenkel pair distribution function over the distance between the components (a vacancy and an interstitial atom) at the moment when the knocked out atom becomes thermalized. The capture radius r_c is determined by the condition that the electrostatic energy of attraction between a negatively charged vacancy and a positively charged interstitial atom is equal to the thermal energy:

$$\frac{e^2}{4\pi\varepsilon\varepsilon_0 r_{\text{cr}}} = k_{\text{B}}T. \tag{8}$$

Here, e is the elementary charge, ε the dielectric constant, ε_0 the dielectric permittivity of vacuum, and k_{B} the Boltzmann constant. In this case, the rate of free vacancy generation per one electron is

$$\lambda_V = \frac{dN_V}{d\Phi} \approx \lambda_{\text{FP}} e^{-r_{\text{cr}}/r_0}, \tag{9}$$

where λ_{FP} is the number of Frenkel pairs created by a 1-MeV electron along its 1-cm path, and r_0 is the parameter of $f(r)$-function. The experimental value $\lambda_V = 1.9 \times 10^{-11}\ \text{cm}^{-3}\text{s}^{-1}$ measured at $T = 360$ °C is almost five times smaller than that calculated from model [3]. At first glance, this result substantially contradicts the traditional ideas concerning the role of temperature in the processes of primary radiation-induced defect formation in semiconductors. For attaining a consensus in this issue, more detailed additional researches are necessary.

Knowing the factor of vacancy generation allows one to evaluate the total concentration of vacancy defects at HI. This quantity corresponds to the introduced vacancy concentration, which is equal to $12 \times 10^{14}\ \text{cm}^{-3}$ for the exposure dose $\Phi = 2 \times 10^{16}\ \text{cm}^{-2}$. At the same time, the concentration of electrically active defects, which are observed in experiment, is approximately $4 \times 10^{14}\ \text{cm}^{-3}$. It is known that the A-center can be annealed by its migration as a whole, with its capture by oxygen and the formation of a VO_2-complex which is electrically inactive under the conditions of our experiment [5]. Therefore, we may expect that it is the VO_2-complex that is responsible for the difference between the total concentrations of vacancy defects determined theoretically and measured experimentally.

4. Conclusions

– The kinetics of A-center accumulation in silicon at the simultaneous or consecutive action of electron irradiation and high temperatures (360 °C) are substantially different owing to the difference between the conditions of defect accumulation and their annealing.
– The parameter τ of A-center annealing is practically the same for the annealing of preliminarily irradiated specimens (equilibrium conditions) and their annealing under the conditions of the electron subsystem perturbation by ionizing irradiation. This can testify that either the mechanism of annealing of those defects does not depend on crystal ionization or the excitation degree of the crystal electron subsystem is insufficient for the given concentration of equilibrium charge carriers.
– The elevation of the temperature, at which the specimens are irradiated with electrons, from 20 to 360 °C does not affect the rate of free vacancy generation λ_V in silicon. This result contradicts the traditional ideas on the role of temperature in the processes of primary radiation-induced defect formation in semiconductors. The more detailed researches of this phenomenon are required.

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ВПЛИВ ТЕМПЕРАТУРИ НА ДЕФЕКТОУТВОРЕННЯ В n-Si ПРИ ЕЛЕКТРОННОМУ ОПРОМІНЕННІ

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Р е з ю м е

Досліджено кінетику утворення та відпалу A-центрів у зразках кремнію n-типу провідності, вирощеного за методом Чохральського (Cz n-Si), які опромінювались електронами з енергією 1 МеВ, у двох серіях експериментів: 1) опромінення при кімнатній температурі (КТ) з наступним відпалом при 360 °C; 2) опромінення при 360 °C. Показано, що відмінність у кінетиці A-центрів пов'язана з різницею умов накопичення та відпалу дефектів. Механізм відпалу A-центрів не змінюється під дією опромінення. Причиною цього може бути недостатній ступінь збудження електронної підсистеми кристала в порівнянні з концентрацією рівноважних носіїв заряду. Встановлено, що зі збільшенням температури опромінення від КТ до 360 °C швидкість генерації вільних вакансій λ_V практично не змінюється на відміну від діапазону 100 К – КТ, в якому λ_V зростає зі збільшенням температури.