Characteristic features of the accumulation of vacancy- and interstitial-type radiation defects in dislocation-free silicon with different oxygen contents

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(Submitted March 20, 1996; accepted for publication May 22, 1996)
Fiz. Tekh. Poluprovodn. **31**, 405–409 (April 1997)

The formation of the main radiation defects in silicon (A and E centers, C_i-C_s and C_i-O_i complexes) in dislocation-free crystals and crystals with a low dislocation density ($N_D \simeq 1\times10^4$ cm^{-2}) have been investigated as a function of the oxygen density N_O. The characteristic features of the accumulation and annealing of radiation defects observed in dislocation-free silicon are interpreted taking into account the presence of interstitial inclusions in the volume of such crystals. It has been determined that the gettering properties of the inclusions depend in a complicated manner on the oxygen concentration and are most obvious when $N_O \simeq 3\times10^{16}$ cm^{-3}. © *1997 American Institute of Physics.* [S1063-7826(97)00504-8]

1. INTRODUCTION

The efficiency of the formation of radiation defects (RDs) in silicon depends on the content of not only dopants, but also background impurities, primarily oxygen, which is a constituent of RDs of the vacancy type (A centers) and the interstitial type (complexes $C_i - O_i$), in the crystals.[1–3] In addition to oxygen, the effect of not previously monitored factors on the RD accumulation has been observed recently.[4–7] Analysis of available data shows that in order to gain a deeper understanding of radiation defect formation processes in silicon, it is necessary to study the effect of structural imperfections, which appear as a result of the absence of growth dislocations and the presence of oxygen impurity at definite concentrations.

We have accordingly performed a comparative study of the processes leading to the accumulation of the main RDs in dislocation-free and low-dislocation-density silicon crystals as a function of the oxygen content in the crystals.

2. EXPERIMENTAL PROCEDURE

The study was performed on n- and p-type silicon single crystals with no dislocations and with a low dislocation density ($N_D \simeq 1\times10^4$ cm^{-2}) with resistivity $\rho \simeq 100$ Ω·cm, grown by zone melting method in vacuum or an argon atmosphere, as well as by pulling from melt following Czochralski. The oxygen and carbon background impurity contents were determined from infrared (IR) absorption on ~5-mm-thick plates cut from different parts of the ingots. The degree of structural perfection of the crystals was checked by the metallographic method after selective etching of the surface. Samples with dimensions of $12\times2\times2.5$ mm with approximately the same carbon density ($N_C \simeq 2\times10^{16}$ cm^{-3}) and different oxygen contents ($N_O \leqslant 1\times10^{16}-1\times10^{18}$ cm^{-3}) were employed for the experiments. The samples were irradiated with ^{60}Co γ rays at temperature $T_{irr} \simeq 50$ °C and 15-min isochronous annealing was conducted in the temperature range $T_{ann} = 50-450$ °C. The experimental results were obtained from measurements performed at different stages of irradiation and subsequent annealing of the temperature dependences of the conductivity, Hall coefficient, and charge carrier lifetime, measured by the method of conductivity modulation in a point contact. The temperatures dependences of the Hall coefficient were analyzed according to the electroneutrality equation by the least-squares method or differential method.[8] The RD formation rates ($\eta = N/\Phi$) were found on the linear sections of the curves of the defect density N versus the irradiation flux Φ by averaging the data on η obtained on five samples.

3. EXPERIMENTAL RESULTS AND DISCUSSION

It was determined from an analysis of the temperature dependences of the Hall coefficient of the irradiated samples and data on the annealing of the defects formed that in all investigated crystals irradiation produces both vacancy- and interstitial-type radiation defects. Vacancies of the first type are A and E centers, which contribute levels $E_c-0.18$ eV and $E_c-0.42$ eV, respectively, in the band gap and the interstitial-type RDs are the complexes ⟨interstitial carbon⟩–⟨site carbon⟩ (C_i-C_s, levels $E_c-0.16$ eV and $\sim E_v+0.1$ eV) and ⟨interstitial carbon⟩–⟨interstitial oxygen⟩ (C_i-O_i, level $\sim E_v+0.35$ eV).[1–3] Under the conditions of our experiments the defects mentioned above form in appreciable quantities and the other defects form in negligible small quantities.

Figure 1 shows the rate of formation of vacancy-type (Fig. 1a) and interstitial-type (Fig. 1b) RDs versus the oxygen concentration in crystals with no dislocations and with a low dislocation density. One can see that in all crystals studied the rates of formation of A centers and C_i-O_i complexes tend to increase with increasing oxygen concentration and at the same time the rates of formation of E centers and C_i-C_scomplexes decreases. A detailed analysis of the data presented makes it possible to identify the following character-

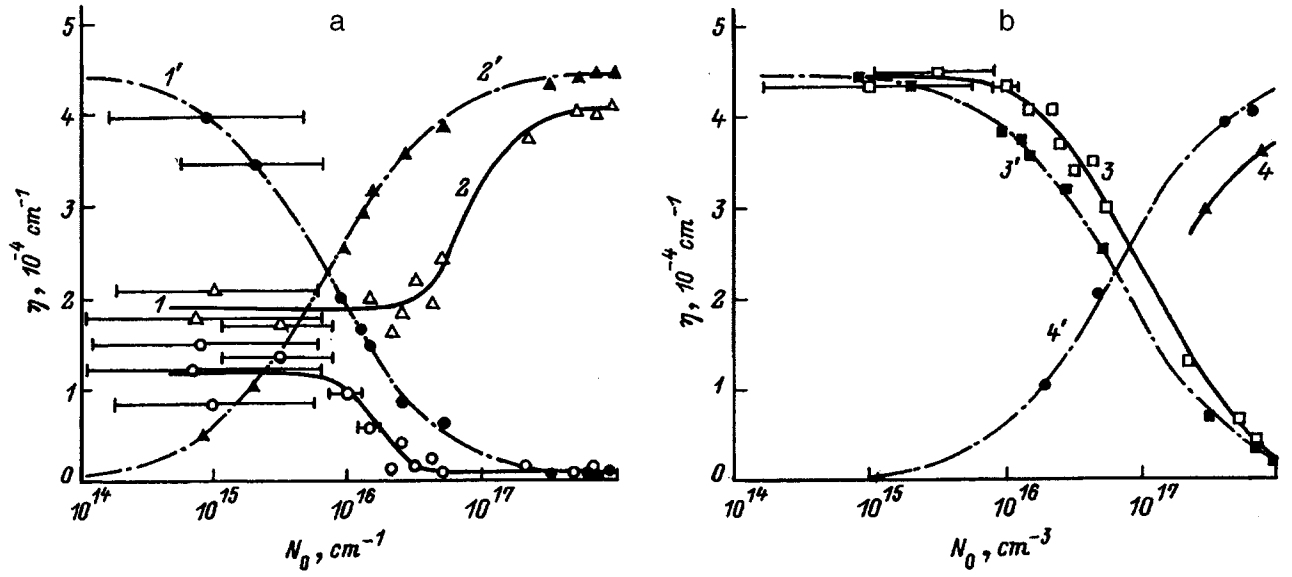

FIG. 1. Formation rates of radiation defects of the vacancy (a) and interstitial (b) types versus oxygen density. Crystals: *1–4* — dislocation free, *1′–4′* — low-dislocation density. Defects: *1, 1′* — *E* centers, *2, 2′* — *A* centers, *3, 3′* — C_i-C_scomplexes, *4, 4′* — C_i-O_i complexes.

istic features of the accumulation of RDs in the dislocation-free material:

1) The values of η are different (especially for low densities N_O) for vacancy RDs in dislocation-free silicon and in silicon with a low density of dislocations;

2) the variance in the values of η from ingot to ingot in the dislocation-free crystals is large compared with the low-dislocation-density crystals;

3) the total rate of formation of RDs does not remain constant in the dislocation-free crystal as the oxygen density changes.

The observed behavior of the dependence $\eta=f(N_O)$ in the materials investigated can be explained qualitatively on the basis of the theory of quasichemical reactions between primary RDs (vacancies and interstitial atoms) generated in the volume of the crystal and uniformly distributed impurities (oxygen, phosphorus, carbon). Since the main sinks for vacancies are phosphorus and oxygen atoms, the relative formation efficiency of *A* and *E* centers is proportional to the ratio of the oxygen and phosphorus densities. For this reason, as the oxygen density in the crystal increases, *A* centers will be introduced in greater numbers and the efficiency of introduction of *E* centers will decrease.

The situation is similar for the interstitial channel of defect formation, when the radiation-generated characteristic interstitial atoms (I) displace carbon atoms from the lattice sites ($C_s+I\rightarrow C_i$). Since O_i also acts as a sink for C_i, together with C_s,[3] the relative efficiency of formation of C_i-O_i and C_i-C_s complexes is determined by the competition with respect to the capture of C_i between interstitial oxygen atoms and site carbon: $O_i+C_i\rightarrow C_i-O_i$, $C_s+C_i\rightarrow C_i-C_s$. As a result, as N_O increases, the efficiency of formation of C_i-O_i complexes increases and that of C_i-C_s complexes, conversely, decreases.

In the quantitative analysis, the experimental data (Fig. 1) were compared with the results of calculations performed on the basis of the system of equations presented below, describing in the stationary approximation the accumulation of *A* and *E* centers at the initial stages of irradiation:[9]

$$\begin{cases} N_A=\sigma_V N_{\mathrm{Si}}\Phi\varkappa_{VO}N_O/(\varkappa_{VO}N_O+\varkappa_{VP}N_P), \\ N_E=\sigma_V N_{\mathrm{Si}}\Phi\varkappa_{VP}N_P/(\varkappa_{VO}N_O+\varkappa_{VP}N_P), \\ N_V=\sigma_V N_{\mathrm{Si}}\Phi/(\varkappa_{VO}N_O+\varkappa_{VP}N_P), \end{cases} \tag{1}$$

where σ_V is the effective cross section for the formation of vacancies and silicon as a result of γ irradiation, N_{Si} and N_P are the densities of silicon and phosphorus atoms, N_A and N_E are the densities of *A* and *E* centers, N_V is the stationary density of vacancies, $\varkappa_{VO}$ and $\varkappa_{VP}$ are the vacancy–oxygen and vacancy–phosphorous interaction constants, and Φ is the γ-ray flux.

A similar system of equations, in which σ_V, N_V, N_P, $\varkappa_{VO}$, and $\varkappa_{VP}$ were replaced by σ_{C_i}, N_{C_s}, N_{C_i}, $\varkappa_{C_iO_i}$, and $\varkappa_{C_iC_s}$, respectively (the types of defects are indicated in the subscripts), was used to describe the accumulation of interstitial-type RDs (C_i-O_i; and C_i-C_s).

It was found that the results of calculation (dot-dashed lines) are in satisfactory agreement with the experiment in a wide range of variation of the oxygen concentration for the following values of the phenomenological parameters $\sigma_V=9\times10^{-26}\ \mathrm{cm}^{-2}$, $\varkappa_{VP}/\varkappa_{VO}=135$, and $\varkappa_{C_iO_i}/\varkappa_{C_iC_s}=3$ and only for slightly dislocated crystals.

We note in this connection that the method, which is well known in the literature[10] and employed in practice, for determining low densities of oxygen (not observed by IR absorption) in *n*-silicon crystals based on measurements of the formation rates of *A* and *E* centers is, in general, correct only for low-dislocation-density crystals. It has not been ruled out, however, that the application of this method without regard for the structural perfection of the crystal can give oxygen densities which are too low [at the level ($\leqslant10^{13}\ \mathrm{cm}^{-3}$ (Ref. 11)]. In the different low-dislocation-

density crystals which we investigated and which were grown by the method of zone melting in vacuum, the oxygen density determined from the measured values of the formation rate η_E of E centers using as a calibration curve $\eta_E = f(N_O)$ calculated with the parameters indicated above was in the range $N_O = 8\times10^{14} - 5\times10^{15}$ cm^{-3}, which agrees with the data of Refs. 12 and 13.

A similar approach can also be used to determine low oxygen densities in crystals.

In the case of dislocation-free crystals it is impossible to describe satisfactorily in the model considered here the change in the RD formation rates in the experimental range of oxygen densities. This probably stems from the assumption made in the calculations that the impurity distribution is uniform and (or) that only point trapping centers (oxygen, phosphorus, and carbon) of primary RDs are present. The fact that in the experimental dislocation-free crystals the charge carrier mobility at liquid-nitrogen temperatures is, as a rule, lower than in the low-dislocation-density crystals indicates the presence of complicated structural imperfections in the bulk. These imperfections, as suggested in Refs. 7 and 14, impurity–defect clusters (IDCs) which form during growth of dislocation-free crystals, are not removed by selective etching, and consist of interstitial-type inclusions surrounded by an atmosphere of background impurities. Taking into account this circumstance, the features observed above in the accumulation of RDs in dislocation-free crystals with different oxygen density can be explained on the basis of model-based ideas developed in Refs. 7 and 14–16.

Under the action of the deformation fields produced by the clusters, the irradiation-induced free vacancies migrate toward the clusters. The effect of vacancy redistribution between the crystal matrix and interstitial-type IDCs is determined by the gettering properties of the latter. As the oxygen content in the crystal increases, this effect will weaken, since the oxygen atoms, which are effective sinks for vacancies, decrease their mean-free path length. The presence of IDCs is therefore most obvious in dislocation-free crystals with a low oxygen concentration ($N_O < 10^{15}$ cm^{-3}) and it gives rise to a sharp decrease in the rate of formation of E centers in the crystal matrix. In contrast, vacancy-type defects accumulate more efficiently in the region of IDCs. Since the local density of oxygen atoms in IDCs is high, the predominant formation is that of A centers. Their formation rate η_A, just as in the matrix, is determined by the ratio of the oxygen density and the density of other vacancy sinks localized in the IDCs (phosphorus atoms, other impurities, and inclusion–matrix interfaces, where annihilation and ''freezing'' of trapped vacancies are possible[16]). As a result, it is quite sensitive to the structure and impurity composition of IDCs.

Thus, the first of the above-noted features is due to the redistribution of free vacancies between the crystal matrix and IDCs. As a result, the ratio η_E/η_A in dislocation-free crystals changes compared with the low-dislocation density crystals.

Changing the conditions of crystal growth (growth rate, temperature gradient on the axis, growth atmosphere, etc.) changes the density of the IDCs which are formed, changes their gettering properties, and changes the composition and density of the impurity atmosphere. For this reason, the variance of η_E, η_A, and η_E/η_A (second feature), which is observed in the dislocation-free crystals, is a consequence of the differences in their structural perfection as a result of the fact that the growth conditions are not identical.

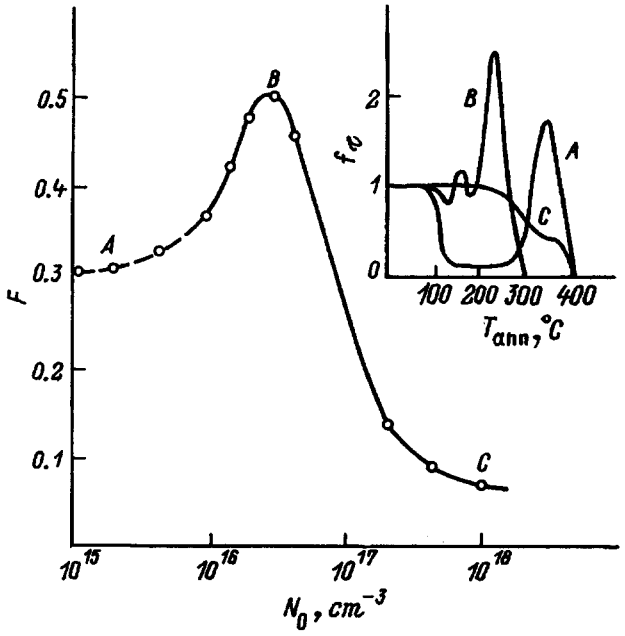

FIG. 2. Fraction F of ''unreacted'' vacancies versus oxygen density. Inset: Annealing of recombination centers.

Since the elastic stress fields produced by the inclusions are anisotropic, a qualitatively similar picture is also possible for interstitial-type defects.

The third of the above-noted features, which is connected with the fact that the total rate of formation of RDs in dislocation-free crystals does not remain constant, attests to the fact that in IDCs not all vacancies participate in the formation of electrically active defects. The N_O-dependence of the parameter $F = (\eta^c - \eta^e)/\eta^c$ (where $\eta^c = \eta^c_A + \eta^c_E$ and $\eta^e = \eta^e_A + \eta^e_E$ are, respectively, the computed and experimentally determined total rates of formation of vacancy-type RDs with fixed oxygen density), which reflects the fraction of ''unreacted'' (trapped IDCs) vacancies, is shown in Fig. 2. As one can see, as N_O increases from 10^{15} cm^{-3} to 10^{18} cm^{-3}, F at first increases, reaching a maximum value for $N_O = 3\times10^{16}$ cm^{-3} (point B), and then decreases, becoming at $N_O = 10^{18}$ cm^{-3} three times smaller (point C) than at the initial oxygen density $N_O = 10^{15}$ cm^{-3} (point A).

The most likely reason for the increase in F with increasing oxygen density in the interval from $N_O \leqslant 10^{15}$ cm^{-3} to $N_O \simeq 3\times10^{16}$ cm^{-3} is an increase in the volume and (or) density of IDCs, which formed during crystallization, and thereby also the inclusion–crystal matrix interface area, which increases the capability of trapping of free vacancies. Moreover, with an increase in N_O, so-called nuclei, whose interaction with the vacancies results in the formation of electrically inactive complexes, can form near the IDCs.

For oxygen densities $N_O > 3\times10^{17}$ cm^{-3}, the gradient of the magnitude of the elastic fields which are produced by IDCs in the crystal matrix decreases as a result of the accommodation of clusters and the presence of high densities of point sources (oxygen atoms) whose elastic stress fields are of the same sign as those of IDCs in the crystal matrix. As a result, the effect of vacancy redistribution between the crystal matrix and the IDCs becomes weaker and therefore decreases for vacancies trapped by IDCs.

The data on the annealing of recombination centers in irradiated dislocation-free material (see the inset in Fig. 2, the curves *A*, *B*, and *C* correspond to the points *A*, *B*, and *C* on the curve of *F* versus N_O) attest to the effect of oxygen on the gettering properties of IDCs. It is obvious that the change in the fraction of unannealed recombination centers $f_\tau=(\tau^{-1}-\tau_0^{-1})/(\tau_\Phi^{-1}-\tau_0^{-1})$ (τ_0, τ_ϕ, and τ are the lifetimes of the nonequilibrium charge carries before irradiation, after irradiation, and at different stages of annealing) with increasing annealed temperature T_{ann} depends on N_O and correlates with the dependence $F=f(N_O)$. The curve *A* is similar to the curve of f_τ versus T_{ann} for the vacuum, low-dislocation-density, *n*-silicon,[14] with the exception of the peak near $T_{ann}=300-400$ °C, which, in our opinion, indicates the presence of IDCs in the crystals. The curve *B* is characteristic of crystals with oxygen density $N_O \simeq 3\times10^{16}$ cm^{-3}, where the gettering properties of IDCs are most pronounced. The extremely nonmonotonic form of this curve attests to the fact that the fraction of vacancies trapped by IDCs, all of which by no means participate near IDCs in the formation of *A* centers, increases; some of them are ''frozen'' in the composition of less-stable electrically neutral complexes or enter a quasistable state on the increasing inclusion–⟨crystal matrix⟩ boundary. Freeing of vacancies by some method starts at $T_{ann} > 100$ °C and is accompanied by additional formation (maxima in f_τ) and subsequent decomposition (minima in f_τ) of a number of new recombination-active defects.

Curve *C* shows that although IDCs are present in the crystal, their gettering properties are weaker than in the preceding case (curve *C* is more even and passes below the peaks on curves *B* and *A*).

In conclusion, we note that the results which we obtained give us a reason to believe that one of the main factors responsible for the variance of the ratio $\varkappa_{VP}/\varkappa_{VO}$ in the range from 10 to 250, observed by different authors,[4,10,17–19] is the presence in dislocation-free crystals, in contrast to low-dislocation-density crystals, of impurity-defect clusters, whose gettering properties are determined by the growth conditions.

4. CONCLUSIONS

Accordingly, the observed characteristic features of the formation of RDs in dislocation-free silicon with different oxygen contents are due to the presence of interstitial-type impurity–defect clusters in the crystals. The elastic fields of these clusters give rise to a redistribution and trapping of the radiation-generated vacancies. It was found that the gettering properties of the impurity-defect clusters depend nonmonotonically on the oxygen density, reaching maximum strength at $N_O \simeq 1\times10^{16}-1\times10^{17}$ cm^{-3}.

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Translated by M. E. Alferieff