INFLUENCE OF TIN IMPURITY ON RECOMBINATION CHARACTERISTICS IN $\gamma$-IRRADIATED $n$-Si

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The influence of the isovalent tin impurity on the lifetime of nonequilibrium charge carriers in Cz $n$-Si irradiated with $\gamma$-quanta from $^{60}$Co has been studied experimentally and analyzed. The behavior of the lifetime in $\gamma$-irradiated tin-doped $n$-Si was shown to be governed by the initial concentration of free electrons, $n_0$. The lifetime degradation factor $k_\tau$ is demonstrated to decrease in the low-resistance and to increase in the high-resistance $n$-Si samples, as the tin concentration in them grows. This fact can be explained by a competition of the main recombination centers in $n$-Si with Sn-complexes VO and SnV. The ratio between the reaction constants for the formation of VO and SnV defects is determined, as well as the cross-sections of hole capture by single- and double-charged acceptor states of SnV.

1. Introduction

The isovalent tin impurity in silicon became a subject of intensive researches owing to its ability to affect the generation of secondary thermally and radiation-induced defects. As early as in 1972, Brelot [1] carried out one of the first studies concerning the influence of tin on the processes of radiation-induced defect formation in silicon. Since then, there has been a permanent interest in this subject (see, e.g., works [2–11]), and the researches on this topic remain challenging as in the last years [12, 13]. In review [14], we carried out a detailed analysis of the results obtained for the influence of tin on the thermally and radiation-induced defect formation in silicon. In irradiated silicon, tin can affect the generation of radiation-induced defects of the interstitial type; in particular, the processes of generation of radiation-induced carbon defects [10–13]. However, the majority of researches deal with the tin influence on the generation of radiation-induced vacancy defects, VO centers and divacancies V2, which are responsible to a great extent for the degradation of parameters of silicon and silicon-based devices at their irradiation. Tin intercepts free vacancies generated in silicon subjected to high-energy irradiation and, in such a manner, reduces the efficiency of generation of other radiation-induced defects of the vacancy type. In the course of those processes, complexes SnV are formed, which are stable up to about 150 °C. They are amphoteric defects and can exist in five charged states ($++$, $+$, $0$, $-$, $---$) inserting four electron levels into the energy gap of silicon. Two donor levels, $E_e + 0.07$ eV ($++/+$) and $E_e + 0.32$ eV ($+/0$) were found in the lower half of the energy gap [3,15]. In addition, according to the data of deep level transient spectroscopy (DLTS), two SnV acceptor levels with activation energies of 0.29 ($---/-$) and 0.58 eV ($-/0$) were revealed [6,7,15]. As was shown in works [7,15], there are energy barriers of about 0.08 eV in $n$-Si for electrons to be captured on those levels. Therefore, SnV has two acceptor electron levels in the upper half of the energy gap with the energies $E_c - 0.214$ eV for SnV$--/-$ and $E_c - 0.501$ eV for SnV$--/0$.

All those researches were mostly directed at studying the properties of SnV complexes themselves and the influence of tin on the generation of other radiation-induced defects. The issue how the integrated parameters of irradiated tin-doped silicon (in particular, the lifetime of nonequilibrium charge carriers) change in this case has practically not been studied. In works [4,16], the influence of electron irradiation on the lifetime of nonequilibrium charge carriers in silicon was examined. It was found that, at tin concentrations of $(2 \div 4) \times 10^{17}$ cm$^{-3}$, the effect on the irradiation-induced lifetime variation depends on the type of crystal doping. In $p$-Si, the presence of tin accelerates the process of irradiation-induced lifetime reduction [4] and slows it.

down in n-Si [16]. On the other hand, it was observed in work [17] that the growth in the tin concentration from \(1.7 \times 10^{18}\) to \(6.5 \times 10^{18}\) cm\(^{-3}\) also accelerates the charge-carrier lifetime degradation in n-Si.

This work is aimed at elucidating the influence of the tin impurity on a variation of the lifetime of nonequilibrium charge carriers in n-Si irradiated with \(\gamma\)-quanta of \(^{60}\)Co.

### 2. Experimental Part

In our research, silicon samples of the n type, which were doped with tin in the course of their growing from the melt following the Czochralski method (Cz n-Si(Sn)), are used. In Table 1, the main characteristics of the examined samples – the tin, \([\text{Sn}]\), oxygen, \([\text{O}]\), carbon, \([\text{C}]\), and phosphorus, \([\text{P}]\), concentrations – are quoted. As reference samples, we used undoped Cz n-Si samples with similar characteristics.

Tin concentrations, which can be found in the literature while studying the radiation-induced defect formation in Si(Sn), lie in the interval \(10^{17} \div 10^{19}\) cm\(^{-3}\). The tin concentrations in the samples, the characteristics of which are listed in Table 1, practically covered the whole concentration range presented in the literature. Moreover, the concentration of free electrons in those samples changed in wide limits, which allowed us to have both high- and low-resistance Si(Sn) samples.

In the experiment, we used irradiation by \(\gamma\)-quanta of \(^{60}\)Co with the flux intensity \(J_\gamma \sim 10^{11}\) \(\gamma\)-quantum/cm\(^2\)/s. The concentrations of free electrons in the samples were determined with the use of the Hall effect, and the lifetime of nonequilibrium charge carriers from the relaxation characteristics of nonequilibrium photoconductivity under the condition of low excitation level (\(\leq 5\%\)). Irradiation and measurements were carried out at room temperature.

The influence of irradiation on the recombination of nonequilibrium charge carriers in silicon was estimated using the well-known relation

\[
\frac{1}{\tau} = \frac{1}{\tau_0} + k_\tau \Phi,
\]

where \(\tau_0\) and \(\tau\) are the lifetimes of nonequilibrium charge carriers before and after irradiation, respectively; \(\Phi\) is the irradiation dose; and \(k_\tau\) is the lifetime degradation factor, which is a quantitative characteristic of the silicon sensitivity to the radiation action. The experimental \(k_\tau\)-value for the investigated samples was determined from the linear sections in the dose dependences of the quantity \(\Delta(1/\tau) = (1/\tau - 1/\tau_0)\). It is eligible if the concentration of radiation-induced defects, which are responsible for the variation of \(k_\tau\), linearly depends on the irradiation dose, i.e. provided that the concentration of radiation-induced defects is low in comparison with the concentration of impurity atoms that participate in the generation of defects. In our experiment, this condition was satisfied.

### 3. Results and Their Discussion

#### 3.1. Experimental results

The results of our research concerning the influence of the Sn impurity on the lifetime variation for nonequilibrium charge carriers in \(\gamma\)-irradiated n-Si are shown in Fig. 1. Here, the dose dependences of the quantity \(\Delta(1/\tau)\) for tin-doped and reference crystals are depicted. The values of lifetime degradation factor \(k_\tau = \Delta(1/\tau)/\Phi\) calculated from the experimental dependences in Fig. 1 and the \(\tau_0\)- and \(\tau\)-values obtained for the same samples are listed in Table 2.

From Fig. 1 and Table 2, one can see that the Sn-doped n-Si samples demonstrate two qualitatively different types of \(k_\tau\)-behavior in comparison with the reference material. In particular, the value of \(k_\tau\) in the n-Si(Sn-1) sample is lower, whereas, in the n-Si(Sn-2) and n-Si(Sn-3) ones, on the contrary, it is higher than that in the undoped n-Si. Such behavior of \(k_\tau\) can be not so much connected with different tin concentrations in those samples as with (or together with) the difference between the initial free electron concentrations, \(\tau_0\).

### Table 1

<table>
<thead>
<tr>
<th>Specimens</th>
<th>([\text{Sn}]) (10^{18}) cm(^{-3})</th>
<th>([\text{O}]) (10^{17}) cm(^{-3})</th>
<th>([\text{C}]) (10^{16}) cm(^{-3})</th>
<th>([\text{P}]) (10^{15}) cm(^{-3})</th>
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<tbody>
<tr>
<td>n-Si(Sn-1)</td>
<td>0.2</td>
<td>7.5</td>
<td>(~7–8)</td>
<td>(~2)</td>
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<td>n-Si(Sn-2)</td>
<td>1.7</td>
<td>6.5</td>
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<td>(~0.1)</td>
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<tr>
<td>n-Si(Sn-3)</td>
<td>6.5</td>
<td>6.0</td>
<td>(&lt;5)</td>
<td>(~0.1)</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Specimens</th>
<th>(n_0), (10^{13}) cm(^{-3})</th>
<th>(\tau_0, \mu) s</th>
<th>(k_\tau, 10^{-12}) cm(^2)/s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Si(Sn-1)</td>
<td>(~200)</td>
<td>70–80</td>
<td>43.1</td>
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<tr>
<td>n-Si-1</td>
<td>100–130</td>
<td>79.8</td>
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<tr>
<td>n-Si(Sn-2)</td>
<td>6.0</td>
<td>100–130</td>
<td>4.4</td>
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<td>n-Si-2</td>
<td>60–70</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>n-Si(Sn-3)</td>
<td>7.7</td>
<td>50–60</td>
<td>6.1</td>
</tr>
<tr>
<td>n-Si-3</td>
<td>70–90</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>
3. Dependences of $\Delta(1/\tau)$ on the dose of irradiation with $\gamma$-quanta of $^{60}\text{Co}$ for Sn-doped n-Si samples. Symbols correspond to experimental data and curves show their linear approximations.

3.2. Generation kinetics for main secondary radiation-induced defects in irradiated n-Si($\text{Sn}$)

The main secondary radiation-induced defects that are generated in irradiated Cz n-Si(Sn) are vacancy complexes VO, VP, and SnV. Therefore, the variation kinetics for the vacancy concentrations in irradiated n-Si(Sn) is governed by the generation rate of free vacancies and the processes of vacancy capture by oxygen, phosphorus, and tin atoms,

$$\frac{d[V]}{dt} = \lambda_V - \chi_{VO}[O] - \chi_{VP}[P] - \chi_{SnV}[Sn], \quad (2)$$

where $\lambda_V$ is the rate of vacancy generation under irradiation; and $\chi_{VO}$, $\chi_{VP}$, and $\chi_{SnV}$ are the reaction constants describing the formation of VO, VP, and SnV complexes, respectively. The stationary concentration of vacancies is mainly determined by reactions between vacancies and oxygen and tin atoms, the concentrations of which are much higher than that of phosphorus. Then

$$[V]_{st} \approx \frac{\lambda_V}{\chi_{VO}[O] + \chi_{SnV}[Sn]]. \quad (3)$$

Accordingly, for the generation kinetics of specific vacancy defect types, we obtain

$$\frac{d[VO]}{dt} \approx \lambda_V \left(1 + \frac{\chi_{SnV}[Sn]}{\chi_{VO}[O]}\right)^{-1}, \quad (4)$$

$$\frac{d[VP]}{dt} \approx \lambda_V \left(\frac{\chi_{VO}[O]}{\chi_{VP}[P]} + \frac{\chi_{SnV}[Sn]}{\chi_{VP}[P]}\right)^{-1}, \quad (5)$$

$$\frac{d[SnV]}{dt} \approx \lambda_V \left(1 + \frac{\chi_{VO}[O]}{\chi_{SnV}[Sn]}\right)^{-1}. \quad (6)$$

One can see that the generation efficiencies for and, accordingly, the concentrations of specific defects depend on the concentrations of corresponding impurities and the constants of vacancy capture by them. Let us estimate how effectively tin captures vacancies in silicon in the background of the four-fold increase in the tin concentration.

Therefore, the influence of tin on the lifetime of nonequilibrium charge carriers in $\gamma$-irradiated n-Si will be analyzed with regard for not only different tin concentrations, but also different initial concentrations of free electrons.

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Fig. 1. Dependences of $\Delta(1/\tau)$ on the dose of irradiation with $\gamma$-quanta of $^{60}\text{Co}$ for Sn-doped n-Si samples. Symbols correspond to experimental data and curves show their linear approximations.
comparison with other impurities (oxygen and phosphorus). Earlier, just such samples were studied using the DLTS method in works [6, 14, 17, 18] dealing with the influence of tin on the spectrum, generation efficiency, and properties at a thermal treatment of electrically active radiation-induced defects. Substituting the concentrations of the corresponding impurities from Table 1 and the experimentally measured generation efficiencies for radiation-induced defects (taken from work [6] for \( n\)-Si(Sn-2) and \( n\)-Si(Sn-3) and from work [18] for \( n\)-Si(Sn-1)) into expressions (4)–(6), we calculated the ratios between the reaction constants for defect generation (see Table 3).

The tabulated data testify that tin has no substantial advantage over oxygen at the vacancy capture. To some extent, it is clear, because oxygen and tin impurities in silicon are electrically neutral in the dispersed state and characterized by almost identical magnitudes of deformation charge \( A \) with the same sign (the parameter \( A \), which characterizes the variation of silicon crystal volume owing to the action of elastic stresses that arise in silicon at impurity insertion, equals \((1.1 \pm 0.1) \times 10^{-24} \text{ cm}^3\) for oxygen and \((8 \pm 1) \times 10^{-25} \text{ cm}^3\) for tin [19]). The tin impurity captures vacancies in \( n\)-Si(Sn-1) up to three times more efficiently than the oxygen does. This fact coincides with the data of works [4, 16], which were obtained for silicon with a close tin concentration. At first sight (see Table 3), an increase of the tin concentration gives rise to a reduction of the tin ability to capture vacancies. If this tendency really takes place, it can testify to a nonuniform distribution of tin at its high concentrations, because some tin atoms, which can be aggregated, do not capture vacancies. It should be noted that the ratio between the reaction constants for the generation of VP and VO centers is evaluated as \( \chi_{\text{VP}}/\chi_{\text{VO}} \approx 20 \), similarly to the results obtained in our previous [20] and other [21] researches.

3.3. Influence of tin impurity on recombinational characteristics

In \( n\)-Si doped with \( \gamma \)-quanta, the main recombinational centers at room temperature are VO centers [20, 21]. Therefore, for the lifetime of nonequilibrium charge carriers, we may write down

\[
\frac{1}{\tau} - \frac{1}{\tau_0} = \frac{1}{\tau_{\text{VO}}} - \frac{1}{\tau_{\text{VP}}} = \frac{1}{\tau_{\text{SnV}}},
\]

where \( \tau_{\text{VP}} \) is the lifetime of nonequilibrium charge carriers associated with the presence of VP centers. The generation of SnV defects in irradiated \( n\)-Si doped with Sn affects the lifetime decrease for nonequilibrium charge carriers both owing to a reduction of the generation efficiency of VO centers and due to the contribution of SnV’s themselves,

\[
\frac{1}{\tau} - \frac{1}{\tau_0} = \frac{1}{\tau_{\text{VO}}} + \frac{1}{\tau_{\text{SnV}^{-/0}}} + \frac{1}{\tau_{\text{SnV}^{-/-}}},
\]

where \( \tau_{\text{VO}}, \tau_{\text{SnV}^{-/0}}, \) and \( \tau_{\text{SnV}^{-/-}} \) are the lifetimes of nonequilibrium charge carriers determined by VO centers in \( n\)-Si(Sn) and one- and two-charged acceptor states of the SnV defect, respectively. In our case, namely \( n\)-Si, a low excitation level \((\Delta n \ll n_0)\) and the recombination levels VO \((E_c - 0.17 \text{ eV}), \) SnV\(^{-/-}\) \((E_c - 0.21 \text{ eV}), \) and SnV\(^{-/0}\) \((E_c - 0.50 \text{ eV})\) are located in the upper half of the energy gap. Hence, the lifetime of nonequilibrium charge carriers is determined by the lifetime of holes, and the following expression is valid for each of recombination centers:

\[
\tau_i = \left( \sigma_i v_p n_i \right)^{-1} \left[ 1 + \frac{N_c \exp(-E_i/kT)}{n_0} \right],
\]

where \( \sigma_i \) is the transverse cross-section of hole capture by the \( i \)-th recombinational center, \( v_p \) the thermal hole velocity, \( N_c \) the concentration of the \( i \)-th center, \( E_i \) the electron level depth at the \( i \)-th recombinational center reckoned from the conduction band bottom, and \( N_c \) the effective density of states in the conduction band. From Eq. (1), taking Eqs. (7)–(9) into account, we obtain

\[
k_{\tau} = \sum_i \sigma_i v_p n_i \left[ 1 + \frac{N_c \exp(-E_i/kT)}{n_0} \right]^{-1},
\]

where \( n_i = N_i/\Phi \) are the center generation efficiencies.

In expression (10), the only unknown parameters, which we must know to analyze the tin influence on the change of hole lifetime in irradiated \( n\)-Si, are the transverse cross-sections \( \sigma_\text{Sn} \) of hole capture at SnV\(^{-/0}\)

<table>
<thead>
<tr>
<th>Table 3</th>
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<tbody>
<tr>
<td>Specimens</td>
</tr>
<tr>
<td>( n)-Si(Sn-1)</td>
</tr>
<tr>
<td>( n)-Si(Sn-2)</td>
</tr>
<tr>
<td>( n)-Si(Sn-3)</td>
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</tbody>
</table>
3.3.2. Analysis of the Sn influence on the lifetime of nonequilibrium charge carriers in \(\gamma\)-irradiated \(n\)-Si(Sn)

With the help of expression (10) and applying the values \(\sigma_p\) and \(n_i\) obtained for defects, we calculated the dependence of \(k_\tau\) on the free electron concentration for each material. In Fig. 2, the dependences \(k_\tau(n_0)\) for the \(\gamma\)-irradiated \(n\)-Si and \(n\)-Si(Sn-3) samples are exhibited. We took into account that the main recombination centers in \(n\)-Si are VO centers and that the lifetime degradation in Sn-doped \(n\)-Si is determined by the cumulative contribution of SnV\(^{-/0}\), SnV\(^{-/-}\), and VO. From Fig. 2, one can see that the relative variation of \(k_\tau\) in the tin-doped and reference \(n\)-Si samples depends on the initial concentration of free electrons. In the high-resistance section (\(n_0 < 2 \times 10^{14}\) cm\(^{-3}\)), the \(k_\tau\)-values are larger for the Sn-doped \(n\)-Si sample in comparison with the reference one. In the low-resistance section (\(n_0 > 2 \times 10^{14}\) cm\(^{-3}\)), the inverse situation is observed. Therefore, let us consider the influence of different tin concentrations on the lifetime degradation factor for the maximum (\(n_0 = 2 \times 10^{15}\) cm\(^{-3}\)) and minimum (\(n_0 = 6 \times 10^{13}\) cm\(^{-3}\)) values of free electron concentration. The corresponding results are depicted in Figs. 3 and 4, respectively. One can see that the tin impurity reduces the lifetime degradation in the low-resistance \(n\)-Si sample (Fig. 3, curve 1) and increases it in the high-resistance one (Fig. 4, curve 1). Moreover, those processes run more efficiently in samples with higher tin concentrations. Let us analyze the results presented in Figs. 2 to 4 from the viewpoint of the tin-related effect.

### A. High-resistance \(n\)-Si(Sn)

As is seen from Fig. 2 (curve 1) and Fig. 4 (curve 4), the main recombination center in the high-resistance Sn-doped \(n\)-Si sample is SnV\(^{-/0}\). Then, from Eq. (10), we obtain

\[
k_\tau \approx \frac{\sigma_p \Delta \rho \tau}{\tau_p \overline{\tau}_{\text{SnV}^{-/0}}}. \tag{11}
\]

In this case, tin can affect \(k_\tau\) owing to a change in the efficiency of the SnV defect generation. Namely, the in-

| Table 4 |
|-----------------|-----------------|-----------------|
| Specimens       | Defect          | \(\sigma_p\), cm\(^2\) |
| \(n\)-Si        | VO\(^{-/0}\)    | \(\sim 2.5 \times 10^{-13}\) |
| \(n\)-Si        | VO\(^{-/-}\)    | \(\sim 2.5 \times 10^{-13}\) |
| \(n\)-Si(Sn)    | SnV\(^{-/0}\)   | \(\sim 5 \times 10^{-15}\) |
|                 | SnV\(^{-/-}\)   | \(\sim 1 \times 10^{-15}\) |
crease in the tin concentration stimulates the growth of the SnV generation efficiency (see expression (6)) and, accordingly, the increase of $k_\tau$, which is demonstrated in Fig. 4 (curve 1). Comparing the absolute values of $k_\tau$ for the reference and tin-doped $n$-Si samples ($n_0 = 6 \times 10^{13} \text{ cm}^{-3}$ for both of them), we see that the corresponding values are close to each other, although the lifetime degradation in the Sn-doped $n$-Si develops a bit quicker (Figs. 1, b, 2, and 4). This result can be explained by the fact that, owing to a deeper level location in the silicon energy gap, the electron population of the SnV $-\cdots-0$ level (the main recombination center in Sn-doped $n$-Si) at room temperature is approximately by two orders of magnitude higher than that of the VO one (the main recombination center in Sn-undoped $n$-Si), the latter being characterized by an equivalently larger cross-section of hole capture (Table 4). At $n_0 < 6 \times 10^{13} \text{ cm}^{-3}$, the ratio between $k_\tau$-values in the tin-doped and reference $n$-Si samples has to grow, because the electron population of the SnV $-\cdots/0$ level remains constant, whereas that of the VO level decreases. In Fig. 2, this tendency is already observable.

B. Low-resistance $n$-Si As the concentration of free electrons, $n_0$, grows, the electron populations of SnV $-\cdots/$ and VO levels increase, as well as their relative contributions to the hole recombination process (Fig. 2). Accordingly, the $k_\tau$-value in Sn-doped $n$-Si turns out smaller than that in Sn-undoped $n$-Si, irrespective which of defects, SnV or VO, plays the role of main recombination center. It is so, because tin and oxygen atoms are competing vacancy sinks at the vacancy generation, and, in addition, the both levels of the SnV defect have smaller hole capture cross-sections. The above is illustrated in Fig. 3, where the influence of tin on $k_\tau$ in the $\gamma$-irradiated $n$-Si (Sn) sample with the free electron concentration $n_0 = 2 \times 10^{15} \text{ cm}^{-3}$ is shown. In this case, the main recombination defects are VO centers. Therefore, from Eq. (9), we obtain

$$k_\tau \approx \sigma_{pV} \nu_p \eta_{VO} \left[1 + \frac{N_c \exp(-E_{VO}/kT)}{n_0}\right]^{-1}.$$  
(12)

From Eq. (12), one can see that the behavior of $k_\tau$ is governed only by the efficiency of VO center formation. The increase in the tin concentration reduces the efficiency of VO center generation (see expression (4)) and, as a result, $k_\tau$ (Fig. 3, curve 1).

4. Conclusions

Having studied the influence of the isovalent tin impurity within the concentration interval $(0.2 \div 6.5) \times 10^{18} \text{ cm}^{-3}$ on the lifetime variation of nonequilibrium charge carriers in $\gamma$-irradiated $n$-Si, the following results were obtained and the following facts were established.

1) The behavior of the lifetime in Sn-doped $n$-Si irradiated with $\gamma$-quanta of $60^\circ$Co depends on the initial concentration of free electrons. As the tin concentration grows, the lifetime degradation factor was shown to decrease in low-resistance and increase in high-resistance $n$-
Si samples. This fact can be explained by a competition between the main recombination centers in Sn-doped n-Si, namely, VO and SnV complexes. The transverse cross-sections of hole capture by one- and two-charged states of SnV defect are determined. The cross-section of hole capture equals about $1 \times 10^{-15}$ cm$^{-2}$ for SnV$^{-}/0$ and $5 \times 10^{-15}$ cm$^{-2}$ for SnV$^{−−}/−−$.

2) The ratio between the reaction constants for the generation of SnV and VO defects is evaluated to equal $\chi_{\text{SnV}}/\chi_{\text{VO}} \approx 0.8 \div 3$. A tendency is observed that an increase in the tin concentration gives rise to a reduction of the tin ability to capture vacancies. It may testify to a nonuniform distribution of tin at high concentrations.