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INFLUENCE OF TIN IMPURITY ON DEGRADATION OF CONDUCTIVITY IN ELECTRON-IRRADIATED *n*-Si

The influence of an isovalent tin impurity on the electron concentration in Cz n-Si irradiated with 1-MeV electrons has been studied both experimentally and theoretically. It is found that the Sn impurity leads to the acceleration of the conductivity degradation in electron-irradiated nSi. The effect is more pronounced in high-resistance samples, whereas the rates of electron removal from low-resistance ones are almost identical in both materials. This fact can be explained by the difference between the formation efficiency of main compensating radiation-induced defects in n-Si doped with Sn (SnV and VP complexes) and undoped n-Si (mainly, VP complexes), which depends of the concentration of phosphorus in the samples.

K e y w o r d s: silicon, electron irradiation, tin-vacancy complex

1. Introduction

This work continues our researches concerning the influence of an isovalent tin impurity on the integrated parameters of irradiated n-Si, which were started in work [1]. This issue remained almost overlooked against the background of intense researches dealing with the radiation-induced defect formation in n- Si doped with Sn (see the references in work [1]). The most sensitive parameters in silicon with respect to irradiation are the lifetime of nonequilibrium charge carriers and the concentration of majority charge carriers. In the previous work [1], the results of researches concerning the influence of Sn on the lifetime of nonequilibrium charge carriers in γ-irradiated (^{60}Co) n-Si were reported. This work aimed at studying the influence of Sn on the radiation-induced degradation of the conductivity (change in the free electron concentration) in n-silicon irradiated with 1-MeV electrons. This information is important for both the search of a method to enhance the radiation resistance of silicon-based devices and the improvement of the radiation technology at their manufacture.

2. Experiment

Specimens of n-silicon doped with tin in the course of their growing from a melt (Cz n-Si$\langle$Sn$\rangle$), as well as reference Cz n-Si samples with similar concentrations of oxygen [O], carbon [C], and phosphorus [P], were used in the experiment (see Table 1). The samples were irradiated with 1-MeV electrons at room temperature on a pulsed electron accelerator (the pulse duration $t_p = 3.3$ μs, the duty cycle $s = 10^3$, and the average intensity of the electron flux $J_e \approx 3 \times 10^{12}$ electron/(cm^{2}s)).

The initial (linear) sections in the dependences of the free electron concentration on the electron irradiation dose were used to determine the conductivity degradation constant by the formula

$$n = n_0 - k_n \Phi, \tag{1}$$

where n_0 and n are the concentrations of free electrons before and after irradiation, respectively; and Φ is the exposure dose. The k_n-values were used to compare and to analyze the influence of Sn on the

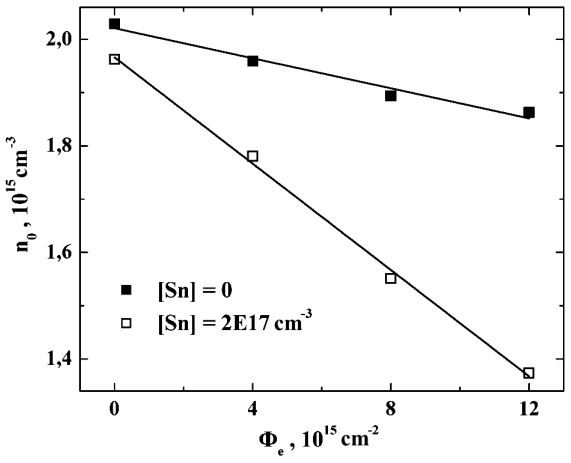

Fig. 1. Dependences of the free electron concentration in n-Si samples on the dose of irradiation with 1-MeV electrons

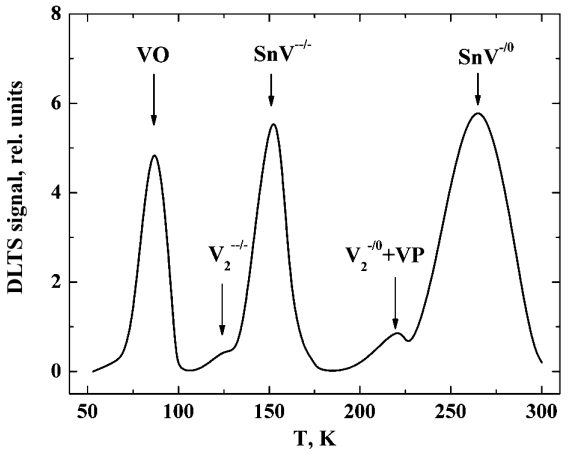

Fig. 2. DLTS spectrum for n-Si⟨Sn⟩ irradiated with 1-MeV electrons ($\Phi_e = 1 \times 10^{16}$ cm^{-2})

efficiency of free electron removal in irradiated n-Si. The concentration of free electrons in the samples was determined before and after every irradiation stage with the help of the Hall effect. The spectrum of radiation-induced defects that are responsible for a degradation of the conductivity and the efficiency of their formation were determined with the help of the DLTS method.

Table 1

Specimens	[Sn], 10^{17} cm^{-3}	[O], 10^{17} cm^{-3}	[C], 10^{16} cm^{-3}	[P], 10^{15} cm^{-3}
n-Si⟨Sn⟩	2	∼6	∼7	∼2
n-Si	0	∼7	<7	∼2

3. Results and Their Discussion

3.1. Experimental results

In Fig. 1, the dependences of the free electron concentration on the electron-irradiation dose obtained for the n-Si⟨Sn⟩ specimen and the reference n-Si one at room temperature are depicted. One can see that the charge carriers are removed from the irradiated n-Si⟨Sn⟩ much more rapidly than those from the reference one. The experimental values of degradation constant for the concentration of free electrons, $k_n = \Delta n/\Phi$, determined from the dependences exhibited in Fig. 1, equal $(5.3 \pm 0.5) \times 10^{-2}$ cm^{-1} for n-Si⟨Sn⟩ and $(1.3 \pm 0.2) \times 10^{-2}$ cm^{-1} for Sn-free n-Si. Such a substantial difference between the k_n-values for both materials has to be associated with the difference in the compositions and/or the efficiencies of formation of radiation-induced defects responsible for the conductivity degradation.

In Fig. 2, the DLTS spectrum for n-Si⟨Sn⟩ irradiated with 1-MeV electrons is shown. The notation for the defects that induced peaks in Fig. 2, their recharge activation energies, E_a, and the formation efficiencies, η, are quoted in Table 2. The presented spectrum is typical of irradiated n-Si samples doped with Sn [2–4]. First, the spectrum demonstrates the peaks characteristic of well-known acceptor radiation-induced defects that are available in Sn-free n-Si, such as the VO centers, two-, $V_2^{-/-}$, and single-charged, $V_2^{-/0}$ (plus VP centers), states of divacancies. Second – this is important – the spectrum of irradiated n-Si⟨Sn⟩ contains two additional levels belonging to the double acceptor center SnV. For the electrons to be captured on those levels, there exist energy barriers of about 0.08 eV in n-Si, and, therefore, SnV has electron levels with the energies $E_c - 0.214$ eV for SnV$^{-/-}$ and $E_c - 0.501$ eV for SnV$^{-/0}$ [2, 3]. In addition, as is seen from Table 2, the presence of tin with a concentration of 2×10^{17} cm^{-3} in silicon reduces the formation efficiency of main vacancy defects, VO and VP centers, by two times in comparison with the reference material owing to the formation of SnV.

Hence, a reduction of the free electron concentration in n-Si⟨Sn⟩ at the electron irradiation of the lat-

Table 2

Specimens	Defect	E_a, eV	η, 10^{-2} cm^{-1}	k_n, 10^{-2} cm^{-1} (calculation)	k_n, 10^{-2} cm^{-1} (calculation)	k_n, 10^{-2} cm^{-1} (experiment)
n-Si	VO	0.17	8	0.2	∼1.2	1.3±0.2
	$V_2^{--/-}$	0.23	0.1	0.02		
	$V_2^{-/0}$	0.42	0.1	0.1		
	VP	0.42	0.43	0.86		
n-Si⟨Sn⟩	VO	0.17	4.1	0.1	∼5.4	5.3±0.5
	$V_2^{--/-}$	0.23	0.1	0.02		
	$SnV^{--/-}$	0.29	4.1	0.5		
	$V_2^{-/0}$	0.42	0.1	0.1		
	VP	0.42	0.27	0.55		
	$SnV^{-/0}$	0.58	4.1	4.1		

ter (Fig. 1) occurs owing to the electron capture by acceptor VO, VP, V_2, and SnV centers. In this case, the expression to estimate the degradation constant for the free electron concentration looks like

$$k_n = \frac{\Delta n}{\Phi} = \frac{d[\mathrm{VO}]}{d\Phi} f_{\mathrm{VO}^{-/0}} + \frac{d[\mathrm{SnV}]}{d\Phi}(f_{\mathrm{SnV}^{-/0}} + \\ + f_{\mathrm{SnV}^{--/-}}) + \frac{d[\mathrm{V_2}]}{d\Phi}(f_{\mathrm{V_2}^{-/0}} + f_{\mathrm{V_2}^{--/-}}) + \\ + 2\frac{d[\mathrm{VP}]}{d\Phi} f_{\mathrm{VP}^{-/0}}, \quad (2)$$

where f is the function describing the filling of centers by electrons, and the multiplier 2 takes into account that every VP center removes two electrons from the conduction band. In n-Si with $n_0 = 2 \times 10^{15}$ cm^{-3}, the Fermi level is located at $E_c - 0.25$ eV at room temperature. Therefore, in essence, the electron filling has to be taken into consideration only for VO, two-charge states of V_2, and SnV.

With the use of Eq. (2) and experimental data from Table 2, we calculated the degradation constant of free electrons separately for each defect, as well as their total contribution, in both n-Si⟨Sn⟩ and the reference n-Si. The corresponding results are also quoted in Table 2. One can see that

– the experimentally obtained values of k_n satisfactorily coincide with the calculated ones;

– in n-Si without Sn, the main compensating radiation-induced defects are VP complexes;

– in n-Si⟨Sn⟩, the main compensating radiation-induced defects are SnV complexes; in this case, the main contribution (of about 80–90%) to a change of the electron concentration in n-Si⟨Sn⟩ is made by $SnV^{-/0}$ owing to a deep arrangement of its level in the silicon energy gap;

– the Sn impurity accelerates the conductivity degradation in irradiated n-Si, because the formation efficiency of main compensating radiation-induced defects in n-Si⟨Sn⟩ (these are SnV complexes) is by an order of magnitude higher than those in n-Si without Sn (VP complexes).

3.2. Analysis of the influence of Sn on the removal rate of equilibrium charge carriers in irradiated n-Si⟨Sn⟩

In work [1], we showed that, depending on the n_0-value, the degradation of a lifetime in γ-irradiated n-Si⟨Sn⟩ can occur both quicker and slower in comparison with the reference n-Si. Let us analyze and compare the behavior of k_n in n-Si and n-Si⟨Sn⟩ in the same interval of the free electron concentration, $n_0 \approx 10^{13} \div 10^{16}$ cm^{-3} as was studied in work [1]. By changing n_0, we change the degree of level filling in radiation-induced defects by electrons and, respectively, the relative contribution of those defects to the process of charge carrier removal. The value of n_0 is determined by the degree of doping with phosphorus; therefore, the variation in the phosphorus concentration also affects the processes of vacancy capture by oxygen, phosphorus, and tin atoms. Expressions for the formation kinetics of VO, VP, and SnV complexes in irradiated Cz n-Si⟨Sn⟩ were obtained in work [1].

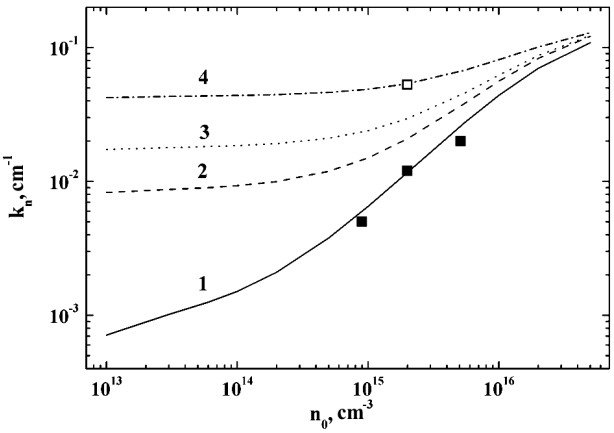

Fig. 3. Dependences $k_n(n_0)$ for n-Si with various Sn concentrations of 0 (*1*), 2×10^{16} (*2*), 5×10^{16} (*3*), and 2×10^{17} cm^{-3} irradiated with 1-MeV electrons. Solid curves correspond to calculation results, and points to experimental data

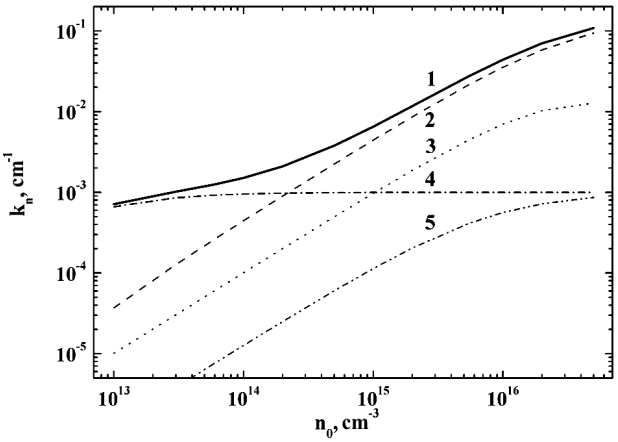

Fig. 4. Calculated dependences $k_n(n_0)$ for n-Si irradiated with 1-MeV electrons: cumulative contribution (*1*) and contributions of components VP (*2*), VO (*3*), $V_2^{-/0}$ (*4*), and $V_2^{--/-}$ (*5*)

Now, for the calculations to be proper, let us take into account that the stationary concentration of vacancies is also determined by phosphorus rather than only by reactions between vacancies and oxygen and tin atoms, the concentrations of which are higher. Then, the expressions for the formation kinetics of VO, VP, and SnV complexes in irradiated Cz n-Si⟨Sn⟩ read

$$\frac{d[\mathrm{VO}]}{dt} = \lambda_\mathrm{V}\left(1+\frac{\chi_\mathrm{SnV}[\mathrm{Sn}]}{\chi_\mathrm{VO}[\mathrm{O}]}+\frac{\chi_\mathrm{VP}[\mathrm{P}]}{\chi_\mathrm{VO}[\mathrm{O}]}\right)^{-1}, \qquad (3)$$

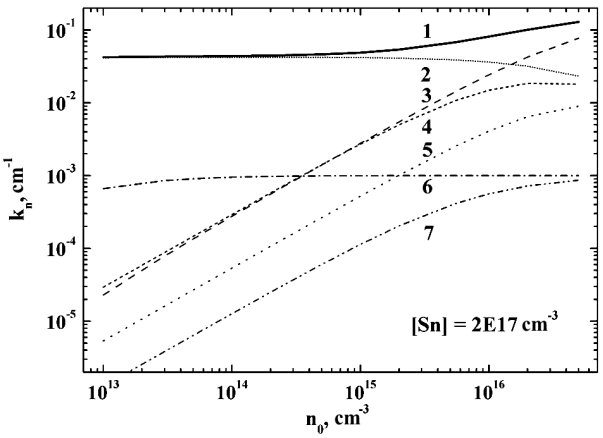

Fig. 5. Calculated dependences $k_n(n_0)$ for n-Si⟨Sn⟩ irradiated with 1-MeV electrons: cumulative contribution (*1*) and contributions of components $\mathrm{SnV}^{-/0}$ (*2*), VP (*3*), $\mathrm{SnV}^{--/-}$ (*4*), VO (*5*), $V_2^{-/0}$ (*6*), and $V_2^{--/-}$ (*7*)

$$\frac{d[\mathrm{VP}]}{dt} = \lambda_\mathrm{V}\left(1+\frac{\chi_\mathrm{VO}[\mathrm{O}]}{\chi_\mathrm{VP}[\mathrm{P}]}+\frac{\chi_\mathrm{SnV}[\mathrm{Sn}]}{\chi_\mathrm{VP}[\mathrm{P}]}\right)^{-1}, \qquad (4)$$

$$\frac{d[\mathrm{SnV}]}{dt} = \lambda_\mathrm{V}\left(1+\frac{\chi_\mathrm{VO}[\mathrm{O}]}{\chi_\mathrm{SnV}[\mathrm{Sn}]}+\frac{\chi_\mathrm{VP}[\mathrm{P}]}{\chi_\mathrm{SnV}[\mathrm{Sn}]}\right)^{-1}, \qquad (5)$$

where λ_V is the rate of vacancy generation at irradiation, and χ_VO, χ_VP, and χ_SnV are the reaction constants for the formation of complexes VO, VP, and SnV, respectively.

The dependences $k_n(n_0)$ for irradiated n-Si and n-Si⟨Sn⟩ are exhibited in Fig. 3. Figures 4 and 5 demonstrate the contribution of each defect to the conductivity degradation in those materials. The calculated dependences shown in Figs. 3 to 5 were obtained using expression (2), where the formation efficiencies for specific types of defects were determined from expressions (3)–(5). The following parameters were determined experimentally (Table 2): the ratios between the reaction constants of defect formation $\chi_\mathrm{SnV}/\chi_\mathrm{VO}\approx3$ and $\chi_\mathrm{VP}/\chi_\mathrm{VO}\approx20$, and the efficiency of free vacancy generation $\lambda_V\approx(8\div8.5)\times10^{-2}$ cm^{-1}. Figure 3 testifies the following.

1. In the examined interval of concentrations n_0, the conductivity degradation constant k_n changes much stronger in n-Si without Sn (by more than two orders of magnitude, curve *1*) in comparison with the corresponding change in n-Si⟨Sn⟩ (in particular, by approximately half as much in n-Si with the Sn concentration equal to 2×10^{17}, curve *4*). Moreover, the

dependences for n-Si⟨Sn⟩ contain sections, where k_n is practically independent of n_0 (i.e. $k_n \approx$ const). The length of those sections is determined by the tin concentration. For example, $k_n \approx$ const at $n_0 < 2\times10^{15}$ cm^{-3} for n-Si with [Sn] $= 2\times10^{17}$ cm^{-3} (curve *4*) and at $n_0 < 2\times10^{14}$ cm^{-3} for n-Si with [Sn] $= 2\times10^{16}$ cm^{-3} (curve *1*).

2. In n-Si⟨Sn⟩, the conductivity degradation at the electron irradiation occurs more rapidly than in n-Si without of Sn. This difference is considerable for high-resistance samples. If the concentration of free electrons $n_0 > 1\times10^{16}$ cm^{-3}, the rates of free electron removal come closer in both materials, with this effect happening earlier in samples with lower tin concentrations.

The features of the conductivity degradation in undoped and tin-doped n-Si, which were described above, can be explained if we analyze the relative contribution of each radiation-induced defect that compensates the conductivity in the materials (Figs. 4 and 5). From Fig. 4, it is evident that the main compensating radiation-induced defects in n-Si without Sn are VP complexes in almost the whole interval of variation of n_0, except for the values $n_0 < 1\times10^{14}$ cm^{-3}, where the contribution of the single-charged state of divacancies $V_2^{-/0}$ dominates. From Eq. (2), we obtain that, in n-Si with a phosphorus concentration higher than 1×10^{14} cm^{-3} and irradiated with electrons, the rate of free electron removal is determined as follows:

$$k_n \approx 2\frac{d[\mathrm{VP}]}{d\Phi}. \tag{6}$$

In n-Si⟨Sn⟩, the main compensating radiation-induced defects are SnV complexes (Fig. 5). At the Sn concentration [Sn] $= 2\times10^{17}$ cm^{-3} (when $n_0 < 2\times10^{15}$ cm^{-3}), the contribution of $\mathrm{SnV}^{-/0}$ to the variation of the electron concentration is not less than 90% (curve *2*). This is so because the level of $\mathrm{SnV}^{-/0}$ is arranged practically in the middle of the energy gap in silicon and is completely filled with electrons. For this case, from expression (2), we obtain

$$k_n \approx \frac{d[\mathrm{SnV}]}{d\Phi}. \tag{7}$$

When $n_0 > 2\times10^{15}$ cm^{-3}, the relative contribution of $\mathrm{SnV}^{-/0}$ diminishes against the growth of contributions made by VP (curve *3*) and $\mathrm{SnV}^{--/-}$ (curve *4*) complexes.

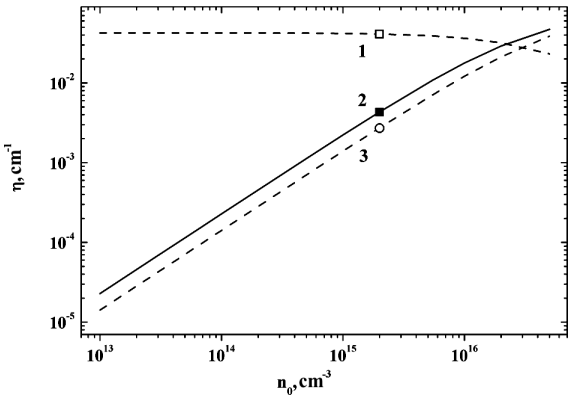

Fig. 6. Dependences of the formation efficiency η on the concentration n_0 for main compensating radiation-induced defects in n-Si⟨Sn⟩ with [Sn] $= 2\times10^{17}$ cm^{-3} (curve *1* for SnV and curve *3* for VP) and reference n-Si (curve *2* for VP). Solid curves correspond to the results of calculation by formulas (4) and (5), and points to experimental data

This means (see expressions (6) and (7)) that the formation efficiencies of the corresponding radiation-induced defect govern the behavior of the dependences $k_n(n_0)$ for irradiated textitn-Si and n-Si⟨Sn⟩. Figure 6 illustrates how the formation efficiencies η for main compensating radiation-induced defects change with the concentration of free electrons n_0 in irradiated n-Si⟨Sn⟩ with [Sn] $= 2\times10^{17}$ cm^{-3} (curve *1* for SnV and curve *3* for VP) and n-Si (curve *2* for VP). While comparing Fig. 6 with Figs. 4 and 5, we see that, in the high-resistance region, the following inequalities hold true: $(\eta_{\mathrm{SnV}} + \eta_{\mathrm{VP}})_{\mathrm{Sn}} \gg (\eta_{\mathrm{VP}})_{\mathrm{Sn}=0}$ and $(\eta_{\mathrm{SnV}})_{\mathrm{Sn}} \gg (\eta_{\mathrm{VP}})_{\mathrm{Sn}}$. Therefore, the conductivity degrades under electron irradiation much more rapidly in n-Si⟨Sn⟩. In the low-resistance material ($n_0 > 1\times10^{16}$ cm^{-3}), η_{VP} sharply increases in both doped with tin (Fig. 6, curve *3*) and reference (Fig. 6, curve *2*) n-Si owing to the high concentration of phosphorus. In this case, $(\eta_{\mathrm{SnV}}+\eta_{\mathrm{VP}})_{\mathrm{Sn}} \approx (\eta_{\mathrm{VP}})_{\mathrm{Sn}=0}$ and $(\eta_{\mathrm{SnV}})_{\mathrm{Sn}} \le (\eta_{\mathrm{VP}})_{\mathrm{Sn}}$, and the k_n-values in both materials come closer. It is clear that the variation of the Sn concentration in n-Si gives rise to a change of η_{SnV} (see expression (5)) and to the corresponding change in the contribution of SnV complexes to the conductivity degradation at irradiation.

4. Conclusion

In this work, the influence of the isovalent Sn impurity on the change of the free electron concentration

in Cz n-Si irradiated with 1-MeV electrons was experimentally studied and analyzed. It is found that the Sn impurity leads to the acceleration of the conductivity degradation in irradiated n-Si. This difference is considerable for high-resistance samples, whereas, in low-resistance samples, the rates of free electron removal become almost equal in both materials. This phenomenon is related to the fact that, in the high-resistance substance ($n_0 < 2\times10^{15}$ cm^{-3}), the formation efficiency for the main compensating radiation-induced defects in n-Si doped with Sn (SnV complexes) is much larger than that in n-Si without Sn (mainly, VP complexes). In the low-resistance material ($n_0 > 1\times10^{16}$ cm^{-3}), the presence of phosphorus in high concentrations gives rise to a drastic growth of the formation efficiency for VP complexes (and, as a result, of their relative contribution to the conductivity degradation) in both doped with tin and reference n-Si. This fact explains why the values of k_n in both materials come closer to each other.

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ВПЛИВ ДОМІШКИ ОЛОВА
НА ДЕГРАДАЦІЮ ПРОВІДНОСТІ В n-КРЕМНІЇ
ПРИ ЕЛЕКТРОННОМУ ОПРОМІНЕННІ

Р е з ю м е

Експериментально досліджено та проаналізовано вплив ізовалентної домішки олова на зміну концентрації вільних електронів у n-Si, вирощеному за методом Чохральського (Cz), опроміненому електронами з енергією 1 МеВ. Встановлено, що домішка олова прискорює деградацію провідності в опроміненому n-Si. Показано, що це прискорення є значним у більш високоомних зразках, а у низькоомних зразках швидкості видалення вільних електронів в обох матеріалах майже зрівнюються. Цей факт пояснюється відмінністю у ефективностях утворення основних компенсуючих радіаційних дефектів у n-Si з Sn (комплексів SnV і VP) та n-Si без Sn (головним чином комплексів VP) залежно від концентрації фосфору в зразках.