FORMATION OF RADIATION-INDUCED DEFECTS IN n-Si WITH LEAD AND CARBON IMPURITIES

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The processes of formation and annealing of radiation-induced defects (RDs) in n-Si with lead and carbon impurities have been investigated. It has been established that, under the irradiation of specimens by 1-MeV electrons, the efficiency of the formation of principal RDs, i.e. vacancy—oxygen (VO) complexes, is by 30% lower in lead-doped specimens than that in reference ones. Lead has been shown to transfer a considerable proportion of carbon atoms into an optically inactive state, thus switching them off from the processes of formation of carbon RDs C_iC_s. It has been established that the concentration of dispersed lead atoms does not exceed 10^{17} cm^{-3} in the crystals under investigation with the total atomic concentration of about 10^{18} cm^{-3} which was determined with the help of secondary ionic mass-spectrometry.

1. Introduction

The enhanced attention to isovalent impurities (IVIs) in Si is stimulated by their ability to influence the generation of secondary RDs, not affecting the initial parameters of silicon. From this point of view, the most investigated objects are the IVIs of carbon, germanium, and tin [1–3]. The key-note in the majority of interpretative models is that IVI atoms interact with primary RDs by means of elastic deformation fields, which arise in the crystal as a result of the difference between the covalent radii of an IVI and a Si atom [4]. The amplitude and the sign of such elastic fields are considered to govern the efficiency of the interaction between neutral IVIs and primary RDs. The carbon impurity C_s reduces the lattice parameter of silicon. Therefore, C_s interacts effectively with intrinsic interstitial Si atoms. The atoms of Ge and Sn impurities, which increase the lattice parameter of silicon, capture free vacancies (Vs) effectively. Complexes VGe and VSn, which are stable up to approximately 200 and 500 K, respectively, are formed at that [2,3]. The cross-section of the vacancy capture by Ge and Sn atoms correlates with their covalent radii. Recognizing that the covalent radius of a lead atom is the greatest among all of the IVIs, one may expect that it would interact with Vs most strongly. Work [5] was devoted to the verification of this assumption and the search for evidences for the VPb-complex formation. In that work, the influence of the doping with lead, obtained from a melt, on the spectrum of deep levels in crucible n-Si irradiated with electrons has been studied with the use of the DLTS method. It has been found that the presence of the Pb impurity does not result in the appearance of new radiation-induced levels in the upper half of the Si energy gap. But we did not succeed to reliably establish that lead affects the generation of principal RDs because of the overlap of the DLTS peaks of two main RDs — VO- and C_iC_s-complexes. This work aimed at studying the influence of the Pb impurity on just the generation rate of those main RDs, taking into account the role of another isovalent impurity — carbon.

2. Experiment and Results

The doping of silicon with heavy IVIs creates significant internal stresses which negatively influence the structural perfection of the crystal. It can be avoided by executing the additional doping with another IVI — carbon. At that, owing to the sign difference between the elastic charges of C and Pb atoms, there occurs probably a certain compensation of internal stresses [4]. We studied the single-crystalline specimens of n-Si grown by the Czochralski method and doped with lead from the melt of the initial substance with the enhanced content of carbon. Actually, we dealt with crystalline Si doped with the mixture Pb+C. In what follows, we designate it as Si[Pb+C]. In order to elucidate the role of just the Pb impurity, a reference crystal grown from the same initial substance with the enhanced content of carbon was studied. Below, we designate it as Si[C]. The notion "with the enhanced content of carbon" has a relative meaning, and it was applied to make a difference with

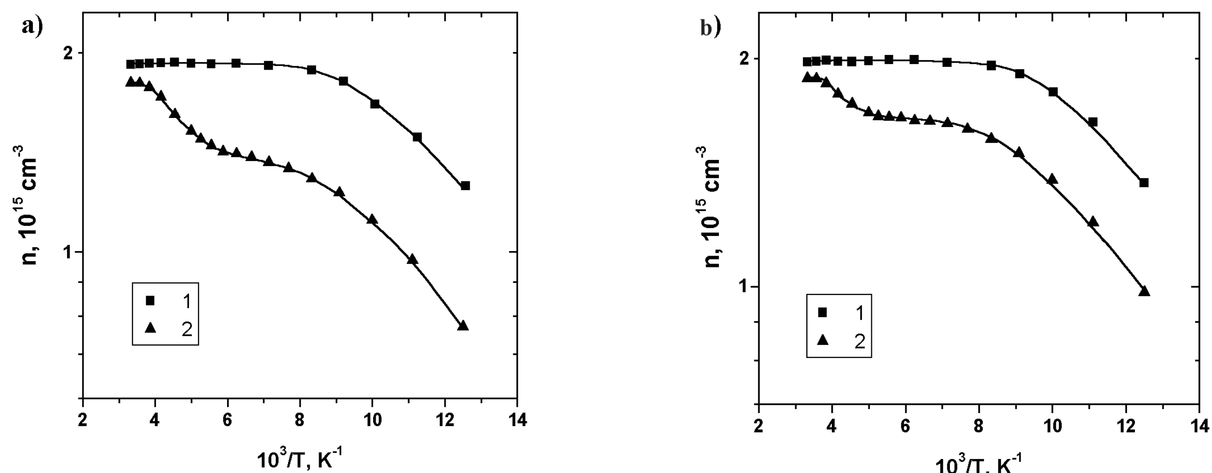

Fig. 1. Temperature dependences of the free electron concentration in the Si[C] (a) and Si[Pb+C] (b) specimens; *1* — before irradiation, *2* — after irradiation

modern industrial standards for single-crystalline silicon in the electronic instrument-making. The main initial parameters of the crystals researched are quoted in Table 1. Here, n_e is the concentration of free electrons; and $N_{\rm O}$, $N_{\rm C}$, and $N_{\rm Pb}$ are the concentrations of oxygen, carbon, and lead impurities, respectively. Two methods were used: infra-red absorption (IRA) to determine $N_{\rm O}$ and $N_{\rm C}$, and secondary ion mass-spectroscopy (SIMS) to determine $N_{\rm C}$ and $N_{\rm Pb}$. In the first case, the concentrations of oxygen and carbon were determined, provided the frequency of 1106 cm^{-1} and the constant of proportionality of 2.45×10^{17} cm^{-2} for oxygen [6] and the frequency of 609 cm^{-1} and the constant of proportionality of 1.1×10^{17} cm^{-2} for carbon [7]. In the second case, a beam of high-energy oxygen ions (O_2^+) with a current of 500 nA knocked out various atoms, including carbons and leads, from the surface of the researched crystals; the content and the concentration of atoms were determined making use of an IMS-4f "Cameca" SIMS-analyzer. Such an etching process proceeded for 6 min, after which a layer of silicon approximately 0.5 μm in thickness has been etched. The obtained results are presented in Table 1.

From the table data, one can see that the total contents of carbon in the doped and reference crystals are almost equal to each other. At the same time, the concentration of optically active (i.e. diluted dispersively in the substitution state) carbon in the Pb-doped crystal is 7 times as low as that in the reference crystal and the total carbon concentrations in both the crystals.

Such a difference may occur probably owing to the correlated distributions of C and Pb atoms (for example, as C–Pb-complexes); and it is this correlation which results in the mutual compensation of deformation stresses induced by C and Pb atoms in the crystal. In accordance, the conditions for the C atoms to vibrate under the light absorption are changed. How such a simultaneous doping with carbon and lead affects the structural, electric, and recombination characteristics of a Si crystal was investigated in work [8]; and its influence on the precipitation of oxygen and the generation of thermally induced donors was studied in work [9]. In this work, the defect formations induced by electron irradiation in Pb-doped and reference crystals are compared. The RDs were studied with the help of the Hall effect. The crystalline specimens 2.6 mm in thickness were irradiated from both sides by 1-MeV electrons up to a dose of 10^{16} cm^{-2} at room temperature.

The temperature dependences of the free electron concentration in the initial and irradiated Si[C] specimens are presented in Fig. 1,a; and the analogous dependences for the Si[Pb+C] specimens in Fig. 1,b. A

T a b l e 1. Initial parameters of the crystals under investigation

Crystal	n_e, 10^{15} cm^{-3}	$N_{\rm O}$, 10^{17} cm^{-3} (IRA)	$N_{\rm C}$, 10^{17} cm^{-3} (IRA)	$N_{\rm C}$, 10^{17} cm^{-3} (SIMS)	$N_{\rm Pb}$, 10^{18} cm^{-3} (SIMS)
Si[C]	1.9	8.0—8.5	4.1	~ 4	0
Si[Pb+C]	2.0	7.5—8.0	0.6	~ 4	~ 1

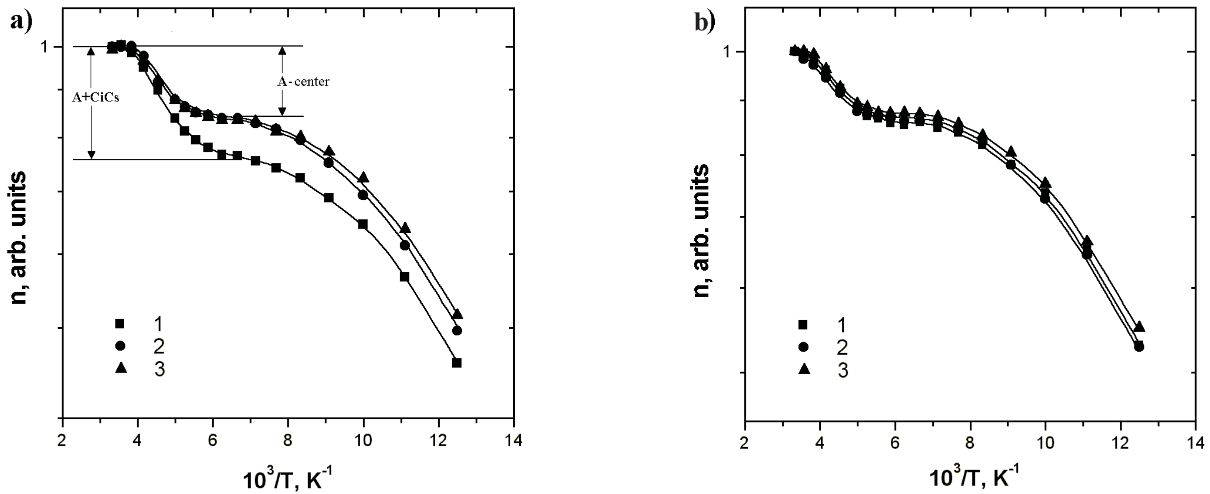

Fig. 2. Temperature dependences of the free electron concentration in the Si[C] (*a*) and Si[Pb+C] (*b*) specimens; *1* — after irradiation, *2* — after irradiation and thermal treatment at 280°C for 1 h, *3* — after thermal treatment at 280°C for 2 h

"step", which appears in the spectra of both the materials after their irradiation, corresponds to the recharging of two levels of the VO- and $\mathrm{C}_i\mathrm{C}_s$-RDs, which possess the same ionization energy (see, e.g., work [10]). The height of this "step" corresponds to the total concentration of VO- and $\mathrm{C}_i\mathrm{C}_s$-centers. One can see that, for the Pb-doped crystal, it is almost half as large as for the reference one.

The difference of the RD concentrations in the Si[Pb+C] and Si[C] specimens can be explained by both the different contributions of the $\mathrm{C}_i\mathrm{C}_s$-complex, owing to the different concentrations of C atoms, and the different contributions of the VO-complex, owing to the flow-out of vacancies which participate in the formation of the electrically neutral complex VPb. To clarify the relation between those contributions, we carried out an experiment on the annealing of $\mathrm{C}_i\mathrm{C}_s$-complexes.

The annealing temperature of the $\mathrm{C}_i\mathrm{C}_s$-complex is known to be within the interval of 200–300°C, while the annealing temperature of the A-center within the interval of 300–360°C [11, 12]. Fig. 2 displays the temperature dependences of the free electron concentration in the Si[C] and Si[Pb+C] specimens.

3. Discussion of Results

Figure 2 testifies to that, at a temperature of 280°C, the $\mathrm{C}_i\mathrm{C}_s$-complexes are annealed effectively: the height of the step corresponding to the recharging of the VO- and $\mathrm{C}_i\mathrm{C}_s$-complexes decreases. Such a reduction is more substantial for the reference specimen. This means that the content of $\mathrm{C}_i\mathrm{C}_s$-complexes in the reference material is higher. Such a result agrees with the fact of a higher C_s concentration in the Si[C] crystal (Table 1). The height of the step, which remained after the $\mathrm{C}_i\mathrm{C}_s$-complexes having been annealed, corresponds to the concentration of VO-centers.

For a more accurate quantitative definition of the concentrations of VO- and $\mathrm{C}_i\mathrm{C}_s$-complexes, we carried out a computer-assisted approximation of the experimental dependences of the free electron concentration, using the equation of electrical neutrality. In our case of the electron-irradiated specimens, the latter looks like

$$n + n_{A+\mathrm{C}_i\mathrm{C}_s} + N_{E+VV} = N_D, \tag{1}$$

where n is the concentration of electrons in the conduction band, N_{E+VV} the concentration of completely ionized acceptors (E-centers and divacancies), $n_{A+\mathrm{C}_i\mathrm{C}_s}$ the concentration of partially ionized acceptors (A-centers and $\mathrm{C}_i\mathrm{C}_s$-complexes), and N_D the concentration of ionized donors.

If the dependence of the distribution function of electrons at acceptor levels on the temperature is taken into account, Eq. (1) reads

$$n + \frac{nN_{A+\mathrm{C}_i\mathrm{C}_s}}{n + 2N_\mathrm{C}e^{-\frac{E_a}{kT}}} - (N_D - N_{E+VV}) = 0, \tag{2}$$

where E_a is the energy of the acceptor level, and N_C is the density of states.

The solution of Eq. (2) has the form

$$n = -\frac{1}{2}\Big[2N_\mathrm{C}e^{-\frac{E_a}{kT}} + N_{A+\mathrm{C}_i\mathrm{C}_s} - (N_D - N_{E+VV})\Big] +$$

$$+\left\{\frac{1}{4}\left[2N_{\mathrm{C}}e^{-\frac{E_a}{kT}}+N_{A+\mathrm{C}_i\mathrm{C}_s}-(N_D-N_{E+VV})\right]^2+\right.$$

$$\left.+2N_{\mathrm{C}}e^{-\frac{E_a}{kT}}(N_D-N_{E+VV})\right\}^{1/2}. \qquad (3)$$

Here, n and T are variables. Using the step-by-step fitting method, we approximated the experimental curves, which are presented in Fig. 2, by this dependence. This made us possible to find the concentration of (A + $\mathrm{C}_i\mathrm{C}_s$)-centers. The results obtained are quoted in Table 2.

From the table, one can see that, after the annealing of $\mathrm{C}_i\mathrm{C}_s$-centers, the Pb-doped crystal contains A-centers by 25% less, than the reference specimen does. This confirms that there exists an additional drain for vacancies in this crystal, which competes with the mechanism of vacancy capture by oxygen atoms. Taking into account the high concentration of Pb-impurity atoms, one may expect that exactly they are the drain. We may suppose that the formation of the complexes VPb takes place in the Pb-doped crystals, which reduces the probability of the formation of complexes with oxygen atoms. The absence of a manifestation of VPb-complexes in DLTS spectra means that they are electrically neutral, at least in n-Si.

The obtained experimental results allowed us to estimate the concentration of Pb atoms which have interacted with radiation-induced vacancies in Si. Really, the kinetics of variation of the vacancy concentration N_V under irradiation is governed by the generation rate of free vacancies λ_V and the processes of vacancy capture by oxygen, lead, and phosphorus atoms, as well as by other vacancies, with the formation of relevant RDs:

$$\frac{dN_V}{dt}=\lambda_V-\chi_{V\mathrm{O}}N_VN_{\mathrm{O}}-\chi_{V\mathrm{Pb}}N_VN_{\mathrm{Pb}}-$$

$$-\chi_{V\mathrm{P}}N_VN_{\mathrm{P}}-\chi_{VV}N_V^2, \qquad (4)$$

where $\chi_{V\mathrm{O}}$, $\chi_{V\mathrm{Pb}}$, $\chi_{V\mathrm{P}}$, and χ_{VV} are the reaction constants of formation of VO- (A-centers), VPb-, and VP-complexes (E-centers) and divacancies, respectively; and N_{O}, N_{Pb}, and N_{P} the concentrations of oxygen, lead, and phosphorus atoms, respectively. In a stationary state, the concentration of vacancies is determined by their capture by oxygen and lead atoms, the concentrations of which are much higher than those of phosphorus and stationary vacancies:

$$N_V^{\mathrm{st}}\approx\frac{\lambda_V}{\chi_{V\mathrm{O}}N_{\mathrm{O}}+\chi_{V\mathrm{Pb}}N_{\mathrm{Pb}}}. \qquad (5)$$

The generation rate of A-centers is equal to

$$\frac{dN_A\,(\mathrm{C})}{dt}\approx\lambda_V \qquad (6)$$

in the Si[C] specimen and to

$$\frac{dN_A\,(\mathrm{C+Pb})}{dt}\approx\frac{\lambda_V}{1+\frac{\chi_{V\mathrm{Pb}}N_{\mathrm{Pb}}}{\chi_{V\mathrm{O}}N_{\mathrm{O}}}} \qquad (7)$$

in the Si[Pb+C] one. Taking into account Eqs. (6) and (7), the ratio between the generation rates of A-centers in Si[C] and Si[C+Pb] is

$$\frac{dN_A\,(\mathrm{C})}{dt}\Big/\frac{dN_A\,(\mathrm{C+Pb})}{dt}\approx1+\frac{\chi_{V\mathrm{Pb}}N_{\mathrm{Pb}}}{\chi_{V\mathrm{O}}N_{\mathrm{O}}}. \qquad (8)$$

The atoms of the isovalent impurity Sn have the covalent radius close to that of Pb atoms. It is known that $\chi_{V\mathrm{Sn}}/\chi_{V\mathrm{O}}=3$ [13]. Therefore, we may suppose that, for Pb, the similar ratio is not less, i.e. $\chi_{V\mathrm{Pb}}/\chi_{V\mathrm{O}_i}\geq3$. The concentration of oxygen N_{O_i} in a Si[C+Pb] crystal is known. Then, from Eq. (8), we can approximately determine the concentration of Pb which is in the state suitable for the interaction with a V. Such an estimation gives the value $N_{\mathrm{Pb}}\leq10^{17}$ cm^{-3}, or about 10% of the total number of lead atoms. This means that 3.5×10^{17} Pb atoms per cm^3 (or approximately 35% of their total number), which are "engaged" in the withdrawal of carbon atoms from the optically active state, do not interact with vacancies as well. Perhaps, it is a consequence of the mutual compensation of elastic deformations created by C and Pb atoms in their complexes. A significant part of Pb atoms in such a material is included into the content of impurity precipitates [8] and also does not interact with RDs. Therefore, the results obtained can be regarded as not contradicting one another by the order of magnitude and as agreeing with the known literature data. They can be considered as an estimation of the threshold solubility

T a b l e 2. Effect of annealing on the concentration of ($A+\mathrm{C}_i\mathrm{C}_s$)-centers

Material	$N_{A+\mathrm{C}_i\mathrm{C}_s}$, 10^{14} cm^{-3}		
	Before thermal treatment	After thermal treatment (280°C), 1 h	After thermal treatment (280°C), 2 h
Si[C]	2.9	2.2	2.1
Si[Pb+C]	1.7	1.7	1.6

of lead in silicon when doping the latter from the melt. A reduction of the generation rate of the principal RDs after doping Si with Pb, without the formation of additional, electrically active RDs, where Pb takes part, opens the prospects in the enhancement of the radiation stability of silicon. A key condition for this is the increase of the share of Pb atoms in the disperse atomic state.

4. Conclusions

Our researches showed the following:

1. The doping of silicon with lead causes a significant part of carbon atoms to transfer into an optically inactive state, thus excluding it from the process of formation of C_iC_s-complexes under the action of electron irradiation.

2. The doping of silicon with lead results in a reduction of the efficiency of the generation of radiation-induced VO-complexes by approximately one third of the initial value. The origin of this fact may be a reduction of the stationary concentration of vacancies under irradiation, owing to the vacancy capture by disperse Pb atoms.

3. The threshold solubility of Pb in silicon is about 10^{17} cm^{-3}. It can be increased, at least by a factor of three, by a simultaneous doping with carbon. A probable reason for this phenomenon is the formation of C–Pb pairs, which results in the mutual compensation of elastic deformations in the crystal which are created by C and Pb atoms. This compensation substantially reduces the efficiency of the interaction between Pb atoms and radiation-induced vacancies.

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РАДІАЦІЙНЕ ДЕФЕКТОУТВОРЕННЯ В n-Si
З ДОМІШКАМИ СВИНЦЮ І ВУГЛЕЦЮ

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Р е з ю м е

Досліджено процеси утворення та відпалу радіаційних дефектів (РД) у n-Si з домішками свинцю і вуглецю. Встановлено, що під час опромінення зразків електронами з енергією 1 МеВ ефективність введення основних РД — комплексів вакансія—кисень (*VO*) — у зразках із свинцем на 30 % менша, ніж у контрольних. Показано також, що свинець переводить значну частину атомів вуглецю в оптично неактивний стан, тим самим виключаючи їх із процесу утворення вуглецевих РД C_iC_s. Встановлено, що при загальній концентрації порядку 10^{18} см$^{-3}$, яку визначено за допомогою вторинної іонної мас-спектрометрії, концентрація дисперсних атомів свинцю в даних кристалах не перевищує 10^{17} см$^{-3}$.