INFLUENCE OF DOPING BY THE ISOVALENT LEAD IMPURITY ON THE PARAMETERS OF n-SILICON

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The influence of the doping by an isovalent Pb impurity on the structural, electric, and recombination parameters of n-Si has been studied. The Pb-doping of Si has been revealed to result in the following: it brings the main part of the C impurity out of an optically active state, reduces the density of growth microdefects, does not influence the concentration of dislocations, increases the lifetime of nonequilibrium current carriers, does not create additional electrically active structural defects, and does not affect the mobility of the majority current carriers. The reason of the observable effects can be a reduction of internal deformation-involved stresses in the crystal owing to the correlated distribution of Pb and C atoms during the Si crystallization at the drawing of the crystal from the melt.

1. Introduction

An interest of researchers to impurities that are isovalent with respect to silicon is caused by their ability to affect essentially the radiation- and heat-induced creation of defects in silicon, practically without modifying its apparent characteristics. The mechanism of this influence is connected with internal mechanical stresses that arise in the crystal owing to a discrepancy between the covalent radius of impurity atoms and that of Si ones. In this aspect, the impurities of carbon, germanium, and tin are the best studied [1]. As concerning the Pb-impurity, whose atoms possess the largest covalent radius among isovalent impurities, its influence on the property of Si has not practically been studied till now.

This work aims at studying the influence of doping by a lead impurity at its maximal concentration on the structural, electric, and recombination parameters of n-Si.

2. Experiment

The doping of silicon by a Pb-impurity was carried out during its growth from a melt according to a special technology based on the Czochralski method. The concentration of Pb atoms in silicon was measured by the method of secondary ionic mass spectroscopy (SIMS) with the help of a SIMS (IMS-4f, "Cameca") analyzer. The specimens of n-Si grown from the same initial raw material and under similar conditions were used as reference ones. The concentrations of oxygen and carbon were determined from the spectra of IR absorption. The content of carbon was monitored, additionally, by the SIMS method. The concentration of free electrons and the Hall mobility were determined from the Hall effect and electroconductivity measurements in the temperature range of 30—300 K. The lifetime of nonequilibrium current carriers was determined from the kinetics of the non-stationary photoconductivity attenuation provided the low level of excitation. The structural perfection of crystals was monitored with the help of an optical microscope after the developing etching of the surface in the $\langle 111 \rangle$ plane. The temperature dependences of the concentration of free electrons were measured with the help of the Hall effect. The measurements of the Hall effect were carried out using the crosslike specimens in a constant magnetic field with a strength of 2000 Oe, at a current of 0.5 mA, and in a temperature interval of 30—300 K. Aluminum contacts deposited by the spark method were used.

The variation and stabilization of the temperature of researched specimens were carried out with the help of a K-25V automatic helium cryostat system. The accuracy of temperature measurements amounted to ±0.05 K.

3. Results and Their Discussion

The parameters of crystals under investigation at room temperature are listed in Table 1, where n_0 is the concentration of free electrons; N_O, N_C, and N_Pb are the concentrations of oxygen, carbon, and lead impurities, respectively; τ_0 is the lifetime of nonequilibrium current carriers.

It is of interest to compare of the results of measurements of the carbon impurity concentration by the IR absorption (IRA) and SIMS methods. The total contents of carbon in the doped and reference specimens, which were determined by the SIMS method, are almost identical in both cases and equal with a satisfactory accuracy to the concentration of dispersed optically active carbon in substitution positions determined by the IRA method. As to the crystal doped by lead, the concentration of optically active carbon is 5–7 times smaller than that in the reference specimen and the total carbon concentration in both crystals. This means that, owing to the doping by lead, the main portion of carbon leaves the optically active state. The available data do not make it possible to determine the way it occurs, either through a correlated distribution of C and Pb in the form of atomic pairs or through the formation of mixed aggregates of C and Pb atoms. It is obvious that any form of the correlated distribution of C and Pb atoms must be energetically favorable for the crystal since it reduces internal mechanical stresses due to the mutual compensation of squeezing and stretching deformations created by Pb and C atoms, respectively.

Such a point of view is supported by the influence of doping by lead upon the density of growth microdefects, which are revealed by the chemical etching of the crystal surface and by optical microscopy. Such defects originate from dislocation microloops and packing defects created by the precipitation of excessive interstitial Si atoms during the processes of growth and initial cooling of the crystal. The formation of dislocation loops and packing defects is connected to the relaxation of internal mechanical stresses in the crystal [2,3]. Therefore, the density of growth microdefects may serve, to some extent, as an indicator of such stresses.

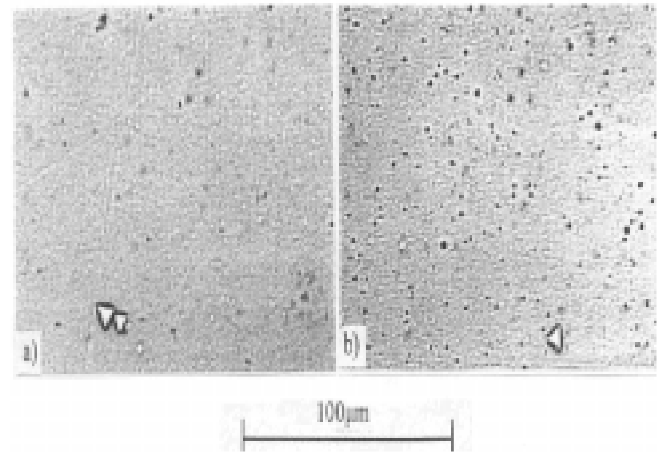

Fig. 1. Etching patterns of the surface in the ⟨111⟩ plane for the Pb-doped (a) and the reference (b) specimens

In Fig. 1, the characteristic patterns produced by etching the Pd-doped (a) and reference (b) specimens are presented. One can see that the density of growth microdefects in the doped crystal is substantially smaller than that in the reference one. This may indicate the reduction of internal stresses due to the doping by lead.

The concentrations of the etching pits of linear dislocations in both crystals are approximately equal, being of the order of 10^3 cm^{-2}. This testifies to the absence of basic differences in the distributions of macroscale deformational stresses in the Pb-doped and reference crystals. Such a result is somewhat unexpected because the doping of Si by an impurity at a concentration which exceeds the limit of solubility has to lead to the formation of precipitates, i.e. aggregates, of impurity atoms that are capable to squeeze out dislocations due to the fact that their thermal expansion characteristics considerably differ from those of the crystal matrix. The availability of such aggregates of Pb atoms was revealed by the SIMS method with the help of microprobe scanning by oxygen ions. In Fig. 2, two typical photos of such aggregates obtained on the SIMS analyzer are presented. The dimensions of aggregates of Pb atoms is about 10 μm, and their concentration is about 10^3 cm^{-3}. The availability of such microaggre-

Table 1

Material	n_0, 10^{15} cm^{-3}	N_O, 10^{17} cm^{-3} (IRA)	N_C, 10^{17} cm^{-3} (IRA)	N_C, 10^{17} cm^{-3} (SIMS)	N_Pb, 10^{18} cm^{-3} (SIMS)	τ_0, μs
n-Si	1.9	8.0—8.5	2.6	3.0	0	100
n-Si⟨Pb⟩	2.0	7.5—8.0	0.57	3.0	1—5	200
KEP-4.5	0.94	8.0—8.5	≤ 0.4	≤ 0.4	0	80

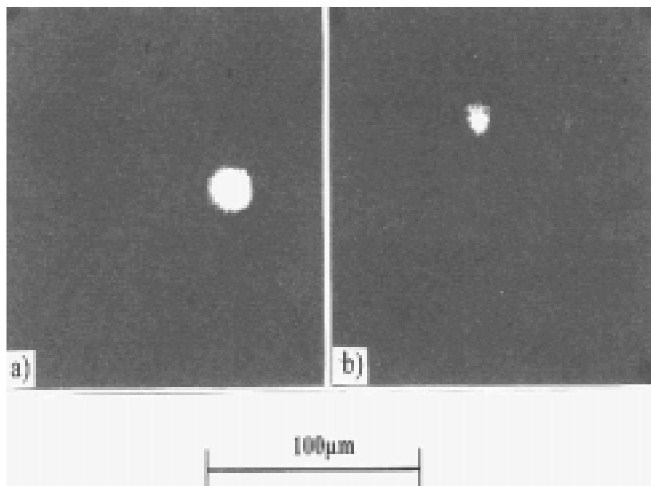

Fig. 2. Photos of aggregations of Pb atoms obtained at the SIMS analyzer

gates may indicate that the concentration of dispersed Pb atoms in the crystal matrix is close to the maximal solubility at the temperature of crystallization.

Attention is attracted by the fact that the lifetime of nonequilibrium current carriers in the Pb-doped material is twice more than that in the reference one. Which is the role of lead in all that? The lifetime of nonequilibrium carriers in Si crystals grown by the Czochralski method is known to be governed by two main types of recombination centers, namely, growth microdefects and impurities which create deep energy levels within the energy gap of silicon. These are mainly the dispersed atoms of quickly diffusing impurities Au, Cu, and Fe [4]. A probable mechanism of the influence of Pb-doping on the concentration of growth microdefects has already been considered by us above. The main mechanism of the concentration reduction of the "deep" impurities (DIs) in a recombinationally active state lies in creating additional centers for their precipitation (the getters). The precipitates of electrically neutral impurities belong to the most effective getters of DIs [5, 6]. In our opinion, it is the precipitates of Pb atoms shown in Fig. 2 that play a role of internal getters for DIs, which results in prolonging the lifetime of nonequilibrium current carriers.

In Fig. 3, the temperature dependences of the concentration of free electrons in the specimens of n-silicon doped by lead and in the reference crystals are shown. One can see that the slopes of the low-temperature sections of the curves for the doped and reference crystals differ substantially. It may be connected both to the variation of the effective energy of ionization of shallow donors and to the different

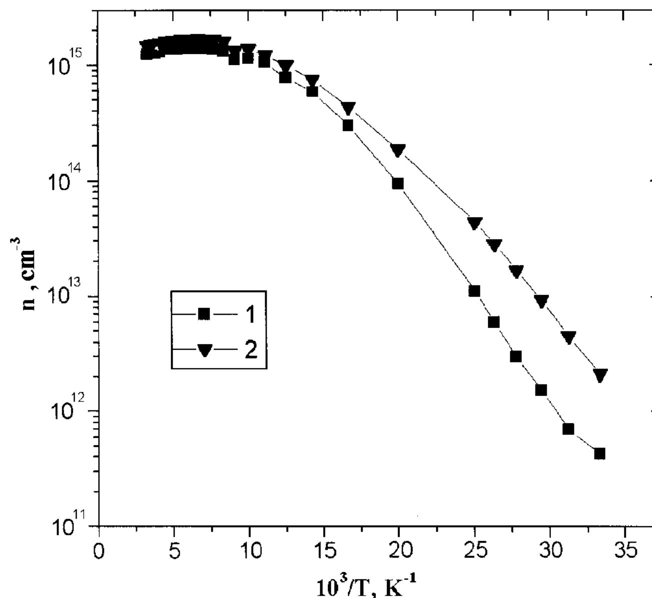

Fig. 3. Temperature dependences of the free electron concentration in the n-Si⟨C⟩ (*1*) and the n-Si⟨C+Pb⟩ (*2*) specimens

degrees of compensation by acceptors. A comparison of the experimental curve $n(T)$ for the concentration of electrons in the conduction band, measured in a wide interval of temperatures, with the theoretical expression [7]

$$n = 2\left(N_\mathrm{d} - N_\mathrm{a}\right) / \left[1 + 2\frac{N_\mathrm{a}}{N_c} e^{\frac{E_\mathrm{d}}{kT}}\right] +$$

$$+\left\{\left[1 + 2\frac{N_\mathrm{a}}{N_c} e^{\frac{E_\mathrm{d}}{kT}}\right] + 8\left(N_\mathrm{d} - N_\mathrm{a}\right)\frac{N_\mathrm{a}}{N_c} e^{\frac{E_\mathrm{d}}{kT}}\right\}^{1/2}, \qquad (1)$$

where N_d and N_a are the concentrations of donors and acceptors, respectively, E_d is the energy of the donor level, k is the Bolzmann constant, T is the temperature, and

$$N_c = 2,7310^{19}\left(\frac{T}{300}\right)^{3/2}$$

is the effective density of states in the conduction band, allows one to determine the concentrations of donors N_d and acceptors N_a separately, which is one of the important technological problems. We carried out a computer fitting of this equation to the experimental dependence. In so doing, the energy of donor ionization was assumed to be constant and equal to the energy of ionization of a P impurity, which was used for doping those crystals. The obtained results are presented in Table 2.

One can see that the degree of compensation in the Pb-doped crystals is smaller than that in the reference ones by a factor of 1.5. This does explain a smaller slope of the temperature dependence of the current carrier concentration. The concentration of acceptors in the Pb-doped crystals is half as large. This brings us to an idea of that the boron impurity, as well as the carbon one, possessing a small covalent radius, also takes part in the process of correlated distribution with Pb atoms by leaving the electrically active state.

For examining the influence of the Pb impurity and the nonhomogeneities of its distribution on the scattering of current carriers, we studied the temperature dependences of the Hall mobility $\mu(T)$.

Fig. 4 displays the temperature dependences of the Hall mobility $\mu(T)$ in the specimens of n-silicon doped by Pb and in the corresponding reference specimens, as well as in the KEP-4,5 commercial crystals, for which $\mu(T)$ is described, in the considered range of temperatures, by the dependence $\mu_f \propto T^{-3/2}$ which corresponds to the scattering by phonons. From this figure, one can see that the temperature dependences of the electron mobility in the Pb-doped and reference crystals differ from their counterparts in the KEP-4,5 crystals only in the temperature range of the scattering by point defects. Therefore, the electron mobility in n-silicon doped by Pb, μ(Pb), can be described as a result of their scattering by phonons and point defects:

$$\frac{1}{\mu_{\rm ph}} + \frac{1}{\Delta\mu} = \frac{1}{\mu\,({\rm Pb})}, \quad \Delta\mu = \frac{\mu_{\rm ph}\mu\,({\rm Pb})}{\mu_{\rm ph} - \mu\,({\rm Pb})},$$

where μ_{ph} is the mobility conditioned by thermal oscillations of the crystal lattice of Si and $\Delta\mu$ is the variation of the mobility caused by the scattering of current carriers by charged point centers.

A linear approximation of the experimental dependences $\Delta\mu(T)$ for Pb-doped and corresponding reference specimens in the range of low temperatures testifies to that $\Delta\mu$ changes with the temperature according to the law $T^{3/2}$. This means that the variation of the mobility in the specimens concerned is caused by the scattering of current carriers by ionized point centers. The experimental dependences $\Delta\mu(T)$ and the theoretical expression [8]

$$\Delta\mu = \frac{8\sqrt{2}k^{3/2}\varepsilon^2}{\pi^{3/2}e^3Z^2\Delta N_{\rm i}m^{*1/2}} \quad \frac{T^{3/2}}{\ln\left[1+\left(\frac{3\varepsilon kT}{\Delta N_{\rm i}^{1/3}Ze^2}\right)^2\right]},$$

where ε is the dielectric permittivity of Si, $Z = 1$, e is the electron charge, m^* is the effective electron mass in

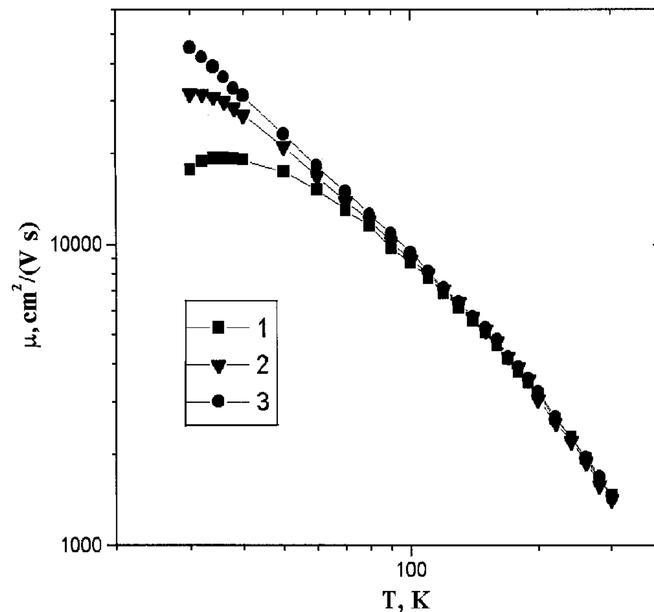

Fig. 4. Temperature dependences of the Hall mobility in the n-Si⟨C⟩ (*1*), n-Si⟨C+Pb⟩ (*2*), and n-Si (*3*) specimens

Si, and $\Delta N_{\rm i}$ is the concentration of ions, are in a good agreement with one another for the following values of $\Delta N_{\rm i}$: for the reference specimens, $\Delta N_{\rm i}$(n-Si)$=2.7\times10^{15}$ cm^3; for the Pb-doped specimens, $\Delta N_{\rm i}$(n-Si⟨Pb⟩) $= 9.1 \times 10^{14}$ cm^3.

At helium temperatures, all acceptors in n-Si and the same quantity of donors compensated by the former are ionized, i.e. $N_{\rm d}^+ = N_{\rm a}^- = N_{\rm a}$. Accordingly, $\Delta N_{\rm i}$(n-Si) $=$ $2N_{\rm a}$(n-Si)$-2N_{\rm a}$(KEP-4,5) and $\Delta N_{\rm i}$(n-Si⟨Pb⟩) $= 2N_{\rm a}$(n-Si⟨Pb⟩) $-$ $2N_{\rm a}$(KEP-4,5). Taking those relations into account, the values of $N_{\rm a}$ estimated from the behavior of the mobility are seen to agree satisfactory with the corresponding values obtained from the temperature dependences of the free electron concentration given in Table 2.

Thus, the features of the Hall mobility behavior observed experimentally in Pb-doped and reference crystals in the range of low temperatures are explained by the extra scattering by ionized B and P atoms. The Pb impurity does not affect appreciably the mobility of electrons.

T a b l e 2

Material	$N_{\rm d}$, 10^{15} cm^{-3}	$N_{\rm a}$, 10^{15} cm^{-3}	Compensation degree, %
n-Si	3.81	1.85	47—49
n-Si⟨Pb⟩	2.96	0.93	30—31
KEP-4.5	1.33	0.39	30—31

4. Conclusions

Doping of silicon by lead:
— brings the main portion of a C impurity out of an optically active state,
— diminishes the density of growth microdefects,
— increases the lifetime of nonequilibrium current carriers,
— does not create additional electrically active structural defects,
— does not affect the concentration of dislocations,
— does not affect the mobility of the majority current carriers.

The reason of the observed effects can be a reduction of internal deformational stresses in the crystal owing to the correlated distribution of Pb and C atoms during the Si crystallization at the drawing of the latter from the melt.

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ВПЛИВ ЛЕГУВАННЯ ІЗОВАЛЕНТНОЮ ДОМІШКОЮ СВИНЦЮ НА ПАРАМЕТРИ n-КРЕМНІЮ

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Р е з ю м е

Досліджено вплив легування ізовалентною домішкою Pb на структурні, електричні та рекомбінаційні параметри n-Si. Виявлено, що легування Si домішкою Pb має такі наслідки: виводить основну частину домішки C із оптично активного стану, зменшує щільність ростових мікродефектів і не впливає на концентрацію дислокацій, збільшує час життя нерівноважних носіїв струму, не створює додаткових електрично активних структурних дефектів і не впливає на рухливість основних носіїв струму. Причиною спостережуваних ефектів може бути зменшення внутрішніх деформаційних напружень у кристалі внаслідок корельованого розподілу атомів Pb і C в процесі кристалізації Si при витягуванні із розплаву.