EFFECT OF DOPING BY LEAD ON THE FORMATION OF THERMAL DEFECTS IN SILICON WITH INCREASED CARBON CONCENTRATION

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The influence of a lead ($N_{Pb}=1\cdot10^{18}$ cm^{-3}) doping on the kinetics of the generation of thermodonors (formed at 450 and 650 °C) and the oxygen precipitation (at 650 °C) in n-Si with the increased carbon impurity concentration ($N_C= (7\div8)\cdot10^{16}$ cm^{-3}) is studied. An acceleration of the low-temperature thermodonors generation and a deceleration of both the high-temperature thermodonors generation and oxygen precipitation have been found in a Pb-doped sample, as compared to the reference one. The results obtained are interpreted accounting for the interaction of Pb and C influencing the defect formation processes, namely, due to the formation of electrically neutral complexes with the participation of Pb and C. It is shown that the preliminary low-temperature annealing (450 + 510) °C eliminates the difference in the kinetics of the generation of high-temperature thermodonors and the oxygen precipitation between the Pb-doped and reference samples.

Introduction

Isovalent impurities, among which carbon, germanium, and tin are most studied, exert an essential influence on the processes of thermal defect formation in silicon single crystals grown by the Czochralski method. In the first place, such an influence is associated with a value and a sign of internal elastic stresses arising due to a difference between atom sizes of silicon and isovalent impurities. For this reason, the effect of carbon, which has small covalent radius as compared with that of the silicon ($R_C = 0.77$ Å, $R_{Si} = 1.17$ Å), on the processes of thermal defect formation is slightly different from that produced by Ge and Sn impurities ($R_{Ge} = 1.22$ Å, $R_{Sn} = 1.40$ Å). Carbon, which decreases a silicon lattice parameter, decelerates the thermodonor formation rate in the temperature range 300—500 °C (TD-I), and completely stops the process of their formation at high concentrations ($N_C > 10^{17}$cm^{-3}) [1, 2]. At the same time, carbon accelerates the dissociation of an oversaturated oxygen solid solution and the thermodonor formation process in the temperature range 600—800 °C (TD-II) [1, 3—5]. Ge and Sn impurities, which increase the Si lattice parameter, decelerate both the formation of TD-I and TD-II, as well as the dissociation of the oversaturated oxygen solid solution [6—10]. Effectiveness of the influence of Ge and Sn impurities on the thermal defect formation in Si increases with their concentration. Moreover, the effect becomes stronger with the increase of the ratio between covalent atomic radii of the impurities and Si [6, 10]. Therefore, in the series of Ge, Sn, and Pb impurities, which are isovalent to Si, the strongest influence on the thermal defect formation in Si can be expected from lead, whose covalent radius is maximal ($R_{Pb} = 1.46$ Å). The aim of our investigations was to obtain the information about the influence of Pb doping on the thermal defect formation in Si. In this paper, we have studied the kinetics of both TD-I and TD-II generation, as well as the kinetics of oxygen precipitation in silicon doped by the lead impurity.

1. Experiment

The study was carried out on the specially crucible-grown n-Si single crystals, additionally Pb-doped in the process of growth. n-Si specimens, grown from the same initial raw materials and under the same conditions, were used as reference specimens. Initial parameters of the crystals under investigation are shown in the Table (n_0 is the concentration of free electrons at room temperature, N_O , N_C, and N_{Pb} — concentrations of oxygen, carbon, and lead impurities, respectively).

The concentrations of Pb and C atoms in Si were measured by the secondary ion mass-spectroscopy method. The oxygen concentration was determined from the infrared absorption spectra, while that of free electrons was calculated from the value of the room-temperature resistivity measured by the four-point method, with the assumption of the invariability of

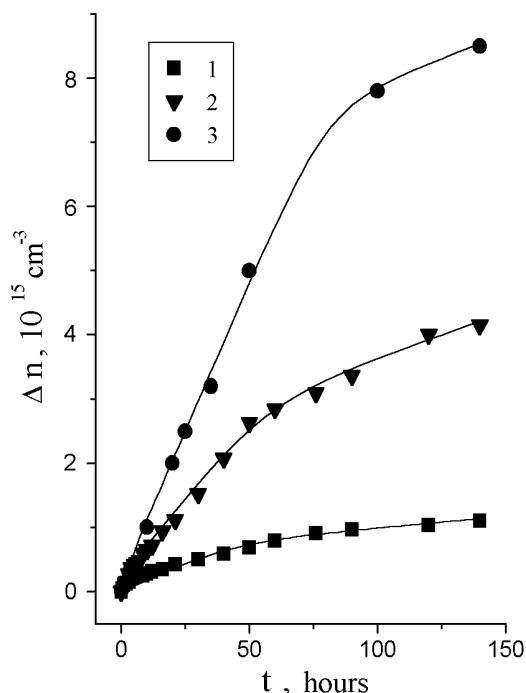| Specimens	N_{Pb}, 10^{17} cm^{-3}	N_O, 10^{17} cm^{-3}	N_C, 10^{16} cm^{-3}	n_0, 10^{15} cm^{-3}
n-Si	—	8—8.5	7—8	1.5—1.65
n-Si(Pb)	10	7.5—8	7—8	1.9—2.0

Fig. 1. Change in the room-temperature free electrons concentration as a function of the duration of HT at 450 °C for the samples: $1, 3 - n$-Si, $2 - n$-Si(Pb). $1, 2, 3 - N_O \approx 8 \cdot 10^{17}$ cm^{-3}; $1, 2 - N_C = (7 \div 8) \cdot 10^{16}$ cm^{-3}, $3 - N_C < 5 \cdot 10^{16}$ cm^{-3}

Fig. 2. Change in the room-temperature free electrons concentration as a function of the duration of HT at 650 °C for the samples: $1, 1' - n$-Si, $2, 2' - n$-Si(Pb); $1', 2' -$ subjected to preliminary HT (at 450 °C for 140 h and at 510 °C for 20 h)

electron mobility. The initial value of the mobility was determined from the Hall effect measurements (1200 cm^2/V·s).

The kinetics of TD-I and TD-II generation was studied at 450 and 650 °C, respectively. Fig. 1 shows a change in the room-temperature concentration of free electrons as a function of the duration of heat treatment (HT) at 450 °C, for both the Pb-doped and reference samples with the carbon concentration $N_C = (7 \div 8) \cdot 10^{16}$ cm^{-3}, as well as for silicon without Pb with $N_C < 5 \cdot 10^{16}$ cm^{-3}. Since at 450 °C, the primary reason for a change of the concentration of the of free electrons in silicon is the TD-I formation, it is seen from Fig. 1 that the accumulation of TD-I goes far quicker in n-Si(Pb) (curve 2) than in n-Si without Pb (curve 1). This means that, although Pb increases the silicon lattice parameter as both the Ge and Sn do, the presence of Pb in Si gives rise to the acceleration of the TD-I generation. At the same time, in the samples under study, both in n-Si without Pb and n-Si(Pb), the TD-I generation rate is lower than that in silicon with $N_C < 5 \cdot 10^{16}$ cm^{-3} (curve 3).

Fig. 2 shows a change in the room-temperature concentration of free electrons (as a result of the TD-II formation) as a function of the duration of HT at
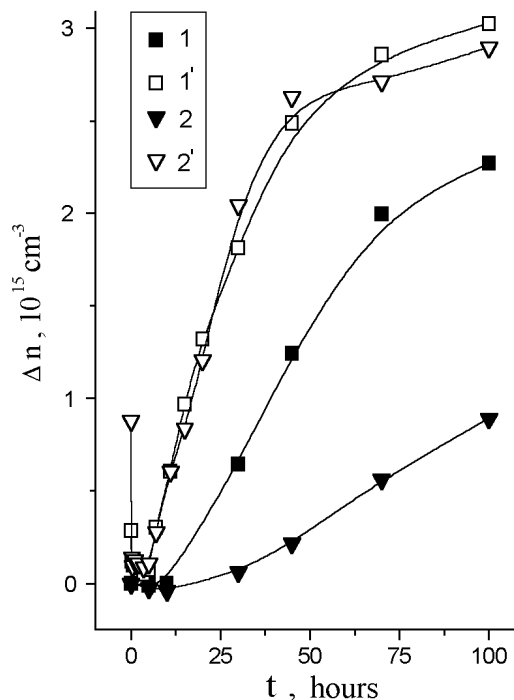
650 °C, for both the n-Si without Pb (curve 1) and n-Si(Pb) (curve 2). As can be seen from Fig. 2, the TD-II generation is sufficiently reduced in the doped material, as compared to the reference one. That is, in this case, the influence of Pb on the TD-II formation is similar to that of both Ge and Sn.

Additional information about the mechanism of such an influence may be obtained from the investigation of the TD-II generation kinetics after a preliminary low-temperature annealing of both the Pb-doped and reference samples. To do the experiment, we used the samples which had been subjected to HT at 450 °C for 140 h followed by that at 510 °C for 20 h for the annealing of TD-I. The results of the study are also shown in Fig. 2 (curves 1' and 2' for n-Si without Pb and n-Si(Pb), respectively). It is seen that the preliminary low-temperature HT not only accelerates the TD-II formation in both the samples, but also leads to the nearly complete disappearance of the difference in the kinetics of TD-II generation for these materials.

Since the processes of thermodonor formation and oxygen precipitation in Si are inseparably associated with each other, it is of interest to study the effect of Pb doping on the oxygen precipitation. Fig. 3 shows

a relative concentration of optically active oxygen as a function of the duration of HT at 650 °C, for both the Pb-doped and reference samples, as well as for those subjected to the preliminary HT according to the procedure described in the paragraph above. It is seen that, for the given samples, the kinetics of dissociation of the oversaturated oxygen solid solution follows the same tendencies as that of TD-II formation. This means that the dissociation of the oxygen solid solution goes slower in n-Si(Pb) (curve 2) than in n-Si without Pb (curve 1), and this is accompanied with a noticeable increase in the incubation period. The preliminary low-temperature HT practically eliminates the effect from the Pb impurity (see curves $1'$ and $2'$ in Fig. 3) simultaneously with the acceleration of oxygen precipitation.

2. Discussion of the Results

As follows from the above results, the presence of Pb in Si, on the one hand, accelerates the TD-I generation, but, on the other hand, it slows down both the TD-II generation and oxygen precipitation. However, by analogy with the effects of Sn and Ge, the doping by Pb should slow down the processes of both TD-I and TD-II generation as well as oxygen precipitation. Thus, in our case, it is necessary to suggest the existence of additional mechanisms which influence these processes. Let's focus attention on the data shown in the table. The crystals under investigation have the increased carbon concentration — $(7 \div 8) \times 10^{16}$ cm^{-3}. It is known that the effect of carbon on the TD-I formation is completely opposite to that produced on both the TD-II formation and oxygen precipitation: the presence of carbon slows down the former process and accelerates the latter [1—5]. In the former case, the effect may be explained by the formation of various types of electrically neutral (C—O) complexes [2] like

$$C + O \to CO \qquad (1)$$

which compete with the processes of TD-I formation

$$O_n + O \to O_{n+1}. \qquad (2)$$

Indeed, the TD-I generation rate (see Fig. 1, curve 3) is higher in Si with the carbon concentration $N_C < 5 \cdot 10^{16}$ cm^{-3} than that in the samples with the increased carbon concentration (see Fig. 1, curves 1 and 2, respectively). At HT at $T \geq 600$ °C, the carbon atoms play role of centers for heterogeneous oxygen precipitation, which results in acceleration of both the TD-II generation and oxygen precipitation [3, 5]. The additional doping of Si
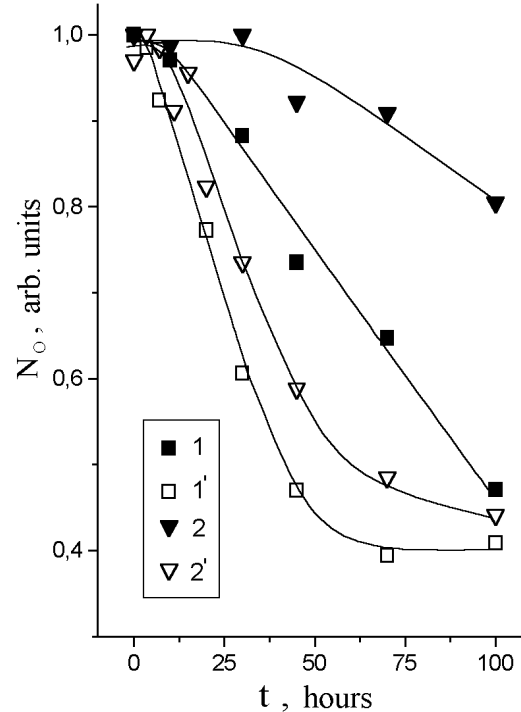

Fig. 3. The same as in Fig. 2 for the relative concentration of the oxygen impurity

by Pb slows down these processes, as can be seen from the experiment.

The obtained results may be explained, assuming that lead neutralizes the carbon influence on both the TD-I and TD-II formation. This may occur at the expense of electrically inactive complexes with the participation of Pb and C. In this case, an acceleration of the TD-I generation in n-Si(Pb) is expected, as compared with the reference sample (see Fig. 1), because the formation of Pb—C complexes competes with that of C—O complexes. At the high-temperature HT, the formation of Pb—C complexes may reduce the concentration of the centers of heterogeneous oxygen precipitation with carbon participation, that, in turn, should slow down both the TD-II generation and oxygen precipitation. It is this result that is observed in the experiment.

As can be seen from Figs. 2 and 3, the preliminary low-temperature HT accelerates the processes of both TD-II formation and oxygen precipitation. At the same time, the difference in the kinetics of both the processes in the Pb-doped and reference samples disappears. Such a low-temperature HT is considered to lead to an increase in the concentration of the centers of heterogeneous oxygen precipitation formed by the

homogeneous mechanism, and just these centers are thought to be responsible for the precipitation of oxygen at higher temperatures [5].

It should also be noted that it is unlikely to expect the formation of Pb—C complexes due to the carbon diffusion, which has very small diffusion coefficient in a nodal state (by one order smaller than that of oxygen). Rather, a correlated distribution of Pb and C is established already at the crystal growth. This may occur because the Pb and C atoms in Si give rise to the internal elastic stresses of opposite signs. The diffusion coefficient of carbon, however, may be sufficiently increased by transferring it into the interstitial state. This process is possible, when considering the generation of interstitial silicon upon the formation of O_n complexes. An interstitial silicon atom (Si_i) is known to effectively interact with a carbon atom (C_s), transferring the latter into the interstitial state (C_i) [11]:

$$Si_i + C_s \rightarrow C_i. \qquad (3)$$

In this case, the following reaction is possible:

$$C_i + Pb \rightarrow (PbC), \qquad (4)$$

which leads to the elimination of both Pb and C atoms from the process of thermodonor formation. However, the present data do not allow us to give a preference to anyone of the possible mechanisms of mutual influence of Pb and C.

Conclusions

The presence of the isovalent Pb impurity in n-Si single crystals grown by the Czochralski method and containing the enhanced carbon concentration $N_C = (7 \div 8) \times 10^{16}$ cm^{-3}, leads to:

the acceleration of the TD-I formation,

the deceleration of both the TD-II generation and oxygen precipitation.

The reason for these effects may lie in the fact that Pb neutralizes the influence of carbon on the processes of thermodonor formation due to the formation of electrically inactive complexes with the participation of Pb and C.

It is shown that the preliminary low-temperature annealing at (450 + 510) °C eliminates the difference in the kinetics of both the TD-II generation and oxygen precipitation between the Pb-doped and reference samples. This may occur due to the increase in the concentration of the centers of heterogeneous oxygen precipitation formed by the homogeneous mechanism.

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ВПЛИВ ІЗОВАЛЕНТНОЇ ДОМІШКИ СВИНЦЮ НА ТЕРМІЧНЕ ДЕФЕКТОУТВОРЕННЯ В КРЕМНІЇ З ПІДВИЩЕНИМ ВМІСТОМ ВУГЛЕЦЮ

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Р е з ю м е

Досліджено вплив свинцю ($N_{Pb} = 1 \cdot 10^{18}$ cm^{-3}) на кінетику генерації термодонорів, що утворюються при 450 і 650 °C , а також кінетику преципітації кисню при 650 °C в n-Si з підвищеною концентрацією вуглецю ($N_C = (7 \div 8) \cdot 10^{16}$ cm^{-3}). Виявлено, що в n-Si із Pb утворення низькотемпературних термодонорів відбувається значно швидше, а утворення високотемпературних термодонорів і преципітація кисню — повільніше порівняно з n-Si без Pb. Отримані результати інтерпретуються з урахуванням ролі у процесах термічного дефектоутворення міждомішкової взаємодії Pb і C внаслідок утворення електрично нейтральних комплексів з участю Pb і C. Виявлено також, що попередній низькотемпературний відпал (450+510) °C згладжує відмінності у кінетиках генерації високотемпературних термодонорів і преципітації кисню для легованого свинцем і контрольного матеріалу.