EFFICIENCY OF INTERACTION OF INTERSTITIAL CARBON WITH OXYGEN, TIN, AND SUBSTITUTION CARBON IN IRRADIATED SILICON

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The infrared Fourier spectroscopy technique is used for the investigation of the efficiency of interaction of interstitial carbon with the basic technological impurities in silicon, oxygen and substitution carbon, as well as with an isoelectronic impurity, tin. It is shown that the probabilities of the interaction of interstitial carbon with interstitial oxygen and substitution carbon are close. It is found that interstitial carbon in tin-doped Si is less thermostable than that in Si, and the temperature of its complete annealing gradually decreases with increasing the tin concentration. It is shown that the probability of the interaction of interstitial carbon with tin exceeds the probability of its interaction with oxygen and on-site carbon by a factor of $\sim$2.3.

1. Introduction

Carbon in silicon represents a technological electrically inactive isoelectronic impurity. However, under various technological treatments (thermal treatment, irradiation), carbon effectively interacts with structural defects forming electrically active complexes that considerably affect the parameters of materials and devices produced on their basis. The properties of carbon in silicon both in grown crystals and after thermal and radiation treatments have been widely investigated during several decades [1–13]. But, in spite of intensive studies, there still remain a lot of unsolved problems concerning the influence of carbon on the processes of thermal and radiation-induced defect formation. The obtaining of new information on properties of carbon is important both from the fundamental viewpoint and from the practical one, as carbon doping is widely used today in nanotechnologies, for example for the production of Si:Ge relaxed layers on Si.

Under irradiation, self-interstitials push carbon from sites to interstices according to the Watkins exchange mechanism [3], which results in the formation of a stable defect (C_i). It is annealed out by diffusion at temperatures close to room one ($T \approx 310$ K). In the course of diffusion in the lattice, interstitial carbon effectively interacts with impurities forming a large variety of electrically active defects of the interstitial kind. In silicon grown by the Czochralski method, the defect C_i effectively interacts with interstitial oxygen (O_i), substitution carbon (C_s), self-interstitials (Si_i), and impurities of groups III or V, which results in the formation of C_iO_i, C_iC_s, C_iSi_i, and C_i+(III, V)$_s$ complexes, respectively [4–6,12,13]. It was recently found out that C_i in silicon effectively interacts with atoms of isoelectronic tin and germanium impurities with formation of C_iSn_s and C_iGe_s stable complexes [14–19], though C_i, Sn, and Ge form deformations of the same sign in the silicon lattice.

The possibility of interaction of interstitial carbon with various sinks in the silicon lattice was widely discussed in literature, though the available data are ambiguous. For example, according to [6], the ratio of the radii of capture of C_i by interstitial oxygen and on-site carbon that determine the possibilities of interaction amounts to 0.3, whereas in [8] this ratio is equal to 3. There are no data on the efficiency of interaction of C_i with atoms of Sn and Ge isoelectronic impurities in silicon attracting heightened interest due to the development of materials for producing fast acting devices. This work is devoted to the study of the comparative efficiency of interaction of interstitial carbon with substitution carbon, oxygen, and tin atoms.

Investigations of the efficiency of interaction of interstitial carbon with various sinks are important for the development of the control influence on the defect composition of a material, as defects formed with participation of C_i atoms are electrically active and substantially affect the electrophysical properties of silicon.

2. Samples and Experimental Technique

We investigated single-crystal samples of n-type (phosphorus-doped) silicon grown using the Czochralski method. The phosphorus concentration was determined measuring the Hall effect and equaled $(2–3)\times10^{14}$ cm^{-3}. The tin content in Si:Sn was determined by means of the neutron-activation analysis as well as with the help of a JCXA-733 X-ray microanalyzer. The concentrations of oxygen and carbon were found based on the intensities of the 1107-cm^{-1} and 607-cm^{-1} absorption lines, respectively [11, 20]. The parameters of the investigated samples are given in Table.

The samples were irradiated by 5-MeV electrons at a temperature close to 90 K using an M-30 microtron. The irradiation dose amounted to 6×10^{17} - 10^{18} cm^{-2}. The efficiencies of interaction of interstitial carbon with impurities were determined based on the isochronous (20-minute) annealing of the irradiated samples in the temperature range 240–380 K at a step of 10 K. The absorption spectra of the samples were investigated with the help of an IFS-113v Fourier spectrometer. The measurements were performed at a temperature of 10 K with a 0.5-cm^{-1} resolution.

3. Experimental Results and Their Analysis

3.1. Interaction of C_i with interstitial oxygen and substitution carbon

As is known, the main sinks for interstitial carbon diffusing under annealing in Czochralski silicon are interstitial oxygen and substitutional carbon resulting in the formation of C_iO_i and C_iC_s complexes, respectively. The efficiency of formation of these complexes is proportional to the concentrations of the interacting components. Therefore, if the oxygen concentration (N_O) considerably exceeds that of carbon (N_C), the main trap for C_i will be oxygen; while, under the condition $N_C \gg N_O$, interstitial carbon will interact more effectively with C_s. The oxygen concentration in Czochralski silicon is often
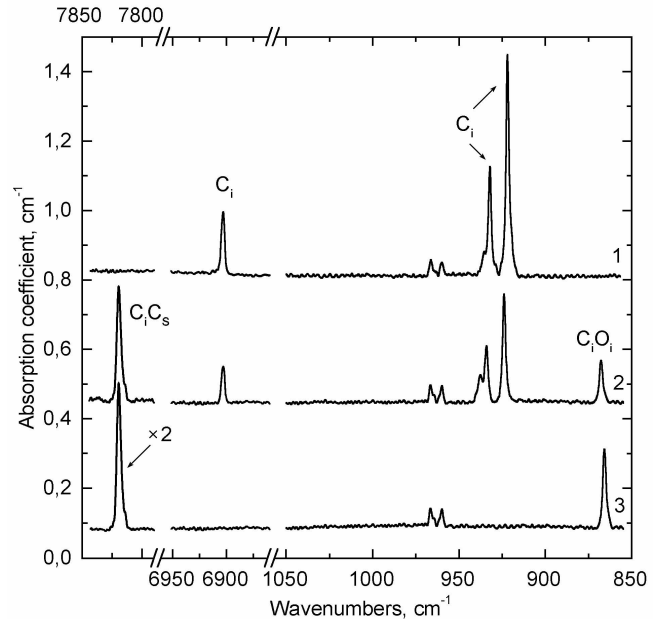

Fig. 1. Transformation of the absorption spectrum under annealing of electron-irradiated Si at $T_{ann} = 250$ (*1*), 287 (*2*), and 305 K (*3*). $\Phi_e=1\times10^{18}$cm^{-2}, $N_O=6.9\times10^{17}$cm^{-3}, $N_C=6.6\times10^{17}$cm^{-3}

either larger than the content of carbon or close to it. In the latter case, there occurs the competitive interaction of C_i with the both impurities. In order to estimate the probabilities of the interaction of C_i with O_i and C_s, we used samples with close initial concentrations of oxygen and carbon (see Table). Figure 1 shows the absorption spectrum registered at 10 K for a sample irradiated at $T\approx90$ K by the dose $\Phi_e=1\times10^{18}$ cm^{-2} and annealed to 250 K, as well as its transformation after the following annealing of interstitial carbon. As one can see from Fig. 1, the spectrum at $T_{ann}=250$ K (curve *1*) contains intense absorption lines with frequencies of 922, 932, and 6903 cm^{-1} corresponding to interstitial carbon [6]. Less intense lines with frequencies equal to 960 and 966 cm^{-1} correspond to C_iSi_i centers [12]. Under the annealing of C_i(curves *2* and *3*), there synchronously appear the lines corresponding to C_iO_i (865.9 cm^{-1}) and C_iC_s (7819.2 cm^{-1}) complexes [4–6]. The temperature of the complete annealing of C_i is close to 305 K.

Based on the obtained data on the intensities of the absorption lines corresponding to C_iO_i and C_iC_s complexes (865.9 and 7819.2cm^{-1}), we determined their concentrations using the coefficients 5.6×10^{16} and 1.47×10^{16}cm^{-2}, respectively [6,21]. Our estimates show that the concentration of C_iO_i is equal to 1.22×10^{16} cm^{-3}, whereas that of C_iC_s amounts to 1.27×10^{16} cm^{-3}.

Concentrations of tin, oxygen, and carbon in the samples

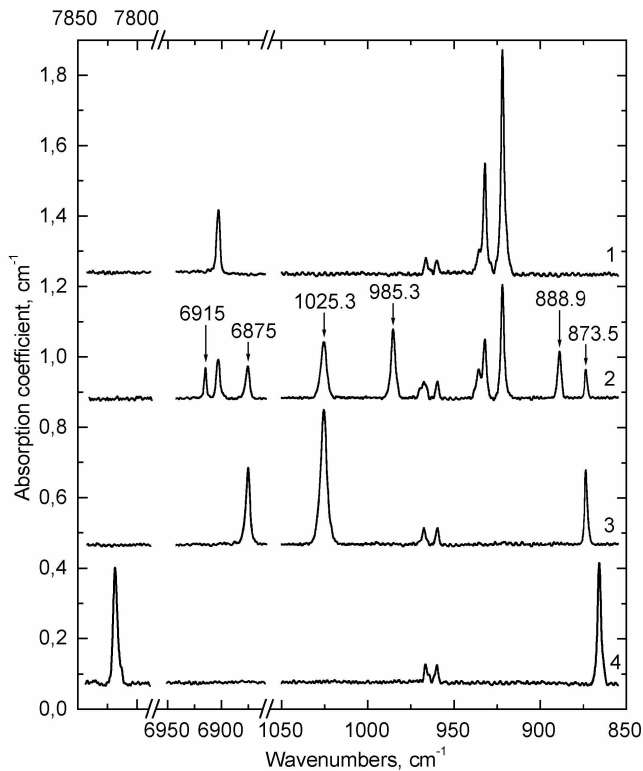| Sample	N_{Sn}, 10^{18} cm^{-3}	N_O, 10^{17} cm^{-3}	N_C, 10^{17} cm^{-3}
Si	–	6.9	6.6
Si:Sn-1	2	8.5	0.3
Si:Sn-2	3	6.4	0.47
Si:Sn-3	6	6.5	1.4
Si:Sn-4	18	5.5	2.7

Fig. 2. Transformation of the absorption spectrum under the annealing of electron-irradiated Si:Sn at T_{ann} = 240 (1), 260 (2), 305 (3), and 380 K (4). Φ_e=6×10^{17}cm^{-2}. N_{Sn}=1.8×10^{19}cm^{-3}, N_C=2.7×10^{17}cm^{-3}

Fig. 3. Relative change of the concentration of interstitial carbon under the isochronous annealing of irradiated Si:Sn crystals. N_{Sn} = 0 (1), 2×10^{18} (2), 3×10^{18} (3), 6×10^{18} (4), and 18×10^{18} cm^{-3} (5)

Thus, the obtained results testify to the fact that the concentrations of the both centers are comparable, i.e. the ratio of the probabilities of their formation is close to 1, rather than to 0.3 as in [6] or 3 as in [8].

It is worth noting that the concentrations of C_iO_i and C_iC_s complexes available in the literature were usually estimated at room annealing temperature after the complete vanishing of interstitial carbon. In [22], it was shown that, in the case of the complete annealing of C_i centers, the concentration of C_iO_i complexes did not reach a maximum, as a considerable portion of C_i was a part of the so-called "precursors" of C_iO_i that transformed into a stable C_iO_i configuration as the temperature increased to ∼340 K. The ratio of the C_iO_i and C_iC_s concentrations estimated from the obtained experimental data for the samples annealed to T_{ann} = 340 K amounts to 1.3.

3.2. Interaction of C_i with tin

Another effective sink for interstitial carbon in silicon is tin [14–18], though its covalent radius (1.44 Å) is larger
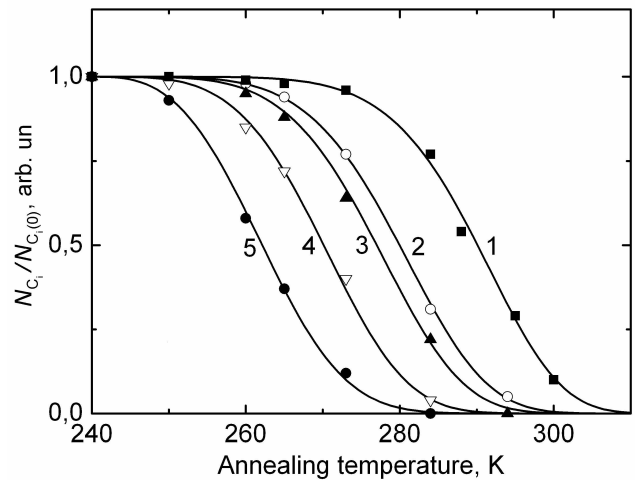
than the radius of the matrix (1.17 Å), and it effectively interacts with vacancies [2]. Figure 2 presents the transformation of the absorption spectrum for Si:Sn (curve 1) under the isochronous annealing in the temperature range 240–380 K. As one can see from Fig. 2, in the case of the annealing of interstitial carbon (T_{ann} > 250 K) in Si:Sn, one does not observe the absorption lines corresponding to C_iO_i and C_iC_s that were registered in Si. Instead, there appear six absorption lines corresponding to C_iSn complexes. According to [16–18], the lines with frequencies of 888.9, 985.3, and 6915 cm^{-1} correspond to a less stable configuration of the given centers and are annealed at T_{ann} ≈ 280 K, whereas the lines at 873.5, 1025.3, and 6875 cm^{-1} correlate with a more stable configuration and are annealed at T_{ann} ≈ 380 K. A considerable intensification of the lines corresponding to C_iO_i and C_iC_s centers in Si:Sn is observed only in the case of the annealing of C_iSn complexes in the temperature range T_{ann} = 325–380 K.

Figure 3 shows the intensities of the absorption lines corresponding to C_i versus the annealing temperature for Si (curve 1) and Si:Sn (curves 2–5) plotted with the use of the results obtained in the course of isochronous annealing of the irradiated samples. As one can see from the figure, interstitial carbon in tin-doped Si is less thermostable than that in Si. The larger the content of Sn in the samples, the lower the initial annealing temperature of C_i. For example, at N_{Sn} = 2×10^{18} cm^{-3}, the annealing begins at T_{ann} ≈ 255 K, while at N_{Sn}= 1.8 ×10^{19} cm^{-3} – at T_{ann} ≈ 245 K. The figure also demonstrates that, as compared to silicon, the tem-

perature of the complete annealing of C_i considerably decreases with increasing the tin content.

We estimated the efficiency of the capture of diffusing C_i by Sn impurity atoms as compared to the probabilities of the capture by such sinks as O_i and C_s. The results of measurements could not be directly used for such estimations, as the investigated Si:Sn samples contained different concentrations of carbon, whereas the formation of C_iO_i and C_iC_s complexes under the annealing of C_i was registered only in one sample with the minimal Sn content. That is why the efficiency of the capture of C_i by Sn atoms was estimated using the approximation of quasichemical reactions [23]. As is known, the annealing of interstitial carbon in silicon can be described by the following reactions [4–6]:

$$C_i + O_i \rightarrow C_iO_i, \qquad (1)$$

$$C_i + C_s \rightarrow C_iC_s. \qquad (2)$$

In the presence of tin, the following reaction also takes place:

$$C_i + Sn_s \rightarrow C_iSn. \qquad (3)$$

With regard for reactions (1)–(3), the process of annealing of C_i in Si:Sn crystals can be described by the kinetic equation

$$\frac{dN_{C_i}}{dt} = -\chi_{C_i,\,O_i} N_{C_i} N_{O_i} - \chi_{C_i,\,C_s} N_{C_i} N_{C_s} -$$

$$-\chi_{C_i,\,Sn} N_{C_i} N_{Sn}, \qquad (4)$$

where N denote the concentrations of the interacting defects, and χ are the probabilities of reactions between the corresponding components.

In [23, 24], it was shown that, under the annealing of defects by means of diffusion to immovable sinks, the probabilities of reactions χ can be presented in the form

$$\chi = 4\pi D_0 \exp\left(-\frac{E_a}{kT}\right) r, \qquad (5)$$

where E_a is the diffusion activation energy, k is the Boltzmann constant, T is the absolute temperature, r is the effective radius of capture of a diffusing component by a sink, and $D_0 = z\nu_0 l^2$, where z is an integer depending on the type of the crystal lattice, ν_0 is the frequency of thermal oscillations, and l is the interatomic distance.

In view of (5), Eq. (4) can be presented in the form

$$\frac{dN_{C_i}}{dt} = -4\pi D_0 \exp\left(-\frac{E_a}{kT}\right) N_{C_i} \sum_m r_{C_i,\,m} N_m, \qquad (6)$$

where N_m are the concentrations of the corresponding sinks.

In order to perform the further analysis of Eq. (6), it is necessary to establish the explicit time dependence of the annealing temperature $T = f(t)$. As the temperature changes stepwise, it is appropriate to use the linear approximation [25]

$$T = T_0 + at, \qquad (7)$$

where $a = \Delta T / \Delta t$ is the mean rate of increase of the annealing temperature.

According to [25], approximation (7) practically has no effect on the final result if the rate a remains constant in the annealing process. Integrating Eq. (6) after the change of variables (7), we obtain

$$\ln \frac{N_{C_i}}{N_{C_i(0)}} = -\frac{4\pi D_0 k}{aE_a} T^2 \exp\left(-\frac{E_a}{kT}\right) \sum_m r_{C_i,\,m} N_m, \qquad (8)$$

where $N_{C_i(0)}$ is the initial concentration of C_i, and N_{C_i} is the concentration of C_i after the annealing to some temperature T.

In what follows, the annealing temperature of interstitial carbon T_a will mean such a temperature, at which the concentration of the given centers decreases by a factor of e with respect to the initial value. Under the condition $T = T_a$, we obtain the equality $N_{C_i}/N_{C_i(0)} = e^{-1}$. As a result, Eq. (8) yields

$$\frac{T_a^2}{E_a} \exp\left(-\frac{E_a}{kT_a}\right) \sum_m r_{C_i,\,m} N_m = \frac{a}{4\pi D_0 k}. \qquad (9)$$

Equation (9) establishes the relationship between such parameters as the annealing temperature of C_i, the diffusion activation energy of a given center E_a, and the sink concentration N_m with regard for the corresponding capture radii.

Using the results of isochronous annealing of the investigated crystals, we estimated the diffusion activation energy of C_i in samples with various tin contents according to the technique described in [25]. Our estimates demonstrate that, at the considered concentrations of tin in Si, the activation energy takes the value $E_a = (0.75\pm0.02)$ eV which insignificantly differs from the known annealing activation energy of C_i in Si that amounts to 0.77 eV [10].

Estimating the efficiencies of the interaction of interstitial carbon with Sn impurity atoms, we allowed for the fact that the probabilities of their capture by such sinks as O_i and C_s are equal, as was demonstrated above. Then, with regard for the concentrations of the impurities and the experimentally determined annealing temperatures of C_i in Si:Sn samples, using Eq. (9) and the energy E_a, we derived the following relation for the radii of capture of C_i by O_i, C_s, and Sn sinks:

$$r_{C_i, O_i} : r_{C_i, C_s} : r_{C_i, Sn_s} \approx 1 : 1 : 2.3. \tag{10}$$

In view of (5), the same relation can be written for the corresponding probabilities of the reactions:

$$\chi_{C_i, O_i} : \chi_{C_i, C_s} : \chi_{C_i, Sn_s} \approx 1 : 1 : 2.3. \tag{11}$$

Using relation (11) and taking values of the contents of the tin, oxygen, and carbon impurities from Table, we estimated the concentrations of C_iSn, C_iO_i, and C_iC_s complexes formed at the annealing of C_i in the investigated samples. It was found that, in the sample with the minimal tin content $N_{Sn} = 2 \times 10^{18}$ cm^{-3} at the corresponding concentrations of oxygen and carbon, the resulting concentration of C_iSn centers exceeded that of C_iO_i and C_iC_s complexes more than by a factor of five. In the sample with the maximal tin concentration $N_{Sn} = 1.8 \times 10^{19}$ cm^{-3}, this ratio already reaches fifty. These estimates give a possibility to explain the fact that, after the annealing of C_i in samples with a large tin content, the absorption spectra practically do not contain bands corresponding to C_iO_i and C_iC_s complexes.

4. Conclusions

We studied the efficiencies of the interaction of interstitial carbon with the basic technological impurities in silicon, oxygen and substitutional carbon, as well as with an isoelectronic impurity, tin. It is shown that the probabilities of the interaction of interstitial carbon with interstitial oxygen and substitution carbon in the silicon lattice are close.

It is found that interstitial carbon in tin-doped Si is less thermostable as compared with silicon, and the temperature of its complete annealing gradually decreases with increasing the tin concentration. The probabilities of the capture of diffusing C_i atoms by O_i, C_s, and Sn impurity atoms are quantitatively estimated. It is shown that the probability of the interaction of C_i with tin is higher than the probability of its interaction with oxygen and substitution carbon by a factor of ~ 2.3. We also

estimated the concentrations of C_iSn, C_iO_i, and C_iC_s complexes formed in the investigated samples under the annealing of C_i with regard for the content of oxygen, carbon, and tin in the initial samples (see Table). Our estimates demonstrate that the concentration of C_iSn centers in the Si:Sn-1 sample with the minimal tin concentration ($N_{Sn} = 2 \times 10^{18}$ cm^{-3}) is higher than that of C_iO_i and C_iC_s centers by a factor of five, whereas, for the Si:Sn-4 sample ($N_{Sn} = 1.8 \times 10^{19}$) cm^{-3}, this ratio reaches fifty.

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ЕФЕКТИВНІСТЬ ВЗАЄМОДІЇ МІЖВУЗЛОВИННОГО
ВУГЛЕЦЮ З КИСНЕМ, ОЛОВОМ І ВУГЛЕЦЕМ
ЗАМІЩЕННЯ В ОПРОМІНЕНОМУ КРЕМНІЇ

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Р е з ю м е

У роботі методом інфрачервоної фур'є-спектроскопії проведено дослідження ефективності взаємодії міжвузловинного вуглецю з основними технологічними домішками кремнію – киснем та вуглецем заміщення, а також з ізоелектронною домішкою – оловом. Показано, що ймовірності взаємодії міжвузловинного вуглецю з міжвузловинним киснем та вузловим вуглецем є близькими за величиною. Виявлено, що міжвузловинний вуглець у Si, легованому оловом, має меншу термічну стабільність, ніж у кремнії, і температура його остаточного відпалу поступово знижується при зростанні концентрації олова. Показано, що ймовірність взаємодії міжвузловинного вуглецю з оловом у ~2,3 раза перевищує ймовірність його взаємодії з киснем та вузловим вуглецем.