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Low-Temperature Diffusion of Implanted Sodium in Silicon

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Abstract—We have studied the low-temperature diffusion of sodium atoms implanted (at primary ion energy E = 300 keV to total doses within $\Phi = 5 \times 10^{14}$–3×10^{15} cm^{-2}) in single-crystalline silicon grown by the method of float-zone melting (fz-Si) with low oxygen concentration N_O and by the Czochralski method in the presence of magnetic field (mCz-n-Si and mCz-p-Si) with $N_O \approx 5 \times 10^{17}$ cm^{-3}. The diffusion was studied at annealing temperatures within T_{ann} = 500–420°C for periods of time t_{ann} = 72–1000 h. It is established that the temperature dependence of the diffusion coefficient $D(10^3/T)$ of sodium in fz-Si in a broad range of T_{ann} = 900–420°C obeys the Arrhenius law with E_{fz} = 1.28 eV and $D_0 = 1.4 \times 10^{-2}$ cm^2/s. The same parameters are valid for the implanted sodium diffusion in mCz-Si in the interval of T_{ann} = 900–700°C. However, at lower temperatures, the values of D in mCz-Si are lower than to those in fz-Si, which is related to the formation of more complicated Na–O$_n$ (n > 1) complexes in the former case. Estimation of the diffusion activation energy of these complexes yields $\Delta E \approx 2.3$ eV.

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The first experiments on ion implantation of sodium into silicon, which were performed in the second half of the 20th century, already showed that a small fraction of embedded Na atoms exhibited the properties of mobile shallow donors. In contrast, sodium introduced by thermal diffusion did not exhibit such behavior. The unusual behavior of impurity dependent on the method of introduction prompted investigations of the properties of this system (see, e.g., review [1] covering publications until 1985). Later, this problem has also continuously drawn the attention of researchers [2–10].

Until recently, the diffusion of implanted sodium in silicon was studied at annealing temperatures T_{ann} above 500°C [1, 5–7, 10]. It was recently proposed [8] to use sodium dopant for the formation of a deep donor profile in high-ohmic Si for the technology of high-power devices. Instead of the traditional doping of silicon by phosphorus diffusion (1300°C, 100 h), we have jointly introduced phosphorus and sodium into silicon by ion implantation with subsequent annealing at 750°C for 35 min. This processing ensures a sufficiently high level of doping with phosphorus and, simultaneously, creates a deep (~150 μm) n-Si layer as a result of sodium diffusion. To complete this task, it is necessary to obtain data on the thermal stability of implanted sodium in silicon at lower temperatures. The present work was aimed at partly filling this gap.

The experiments were performed on p-type silicon grown by float-zone melting (fz-Si) with low oxygen concentration N_O and a resistivity of ρ = 2–3 kΩ cm, as well as on silicon grown by the Czochralski method in the presence of magnetic field (mCz-n-Si and mCz-p-Si) with $N_O \leqslant 5 \times 10^{17}$ cm^{-3} and ρ = 0.5 and 1 kΩ cm (for n- and p-type, respectively). Sodium ions were implanted at primary energies of E = 50 and 300 keV to total doses within $\Phi = 5 \times 10^{14}$–3×10^{15} cm^{-2}. The subsequent diffusion spreading was carried out in air in a quartz tube heated to annealing temperatures within T_{ann} = 500–420°C for periods of time t_{ann} varied from several dozen hours up to ~1000 h, which provided conductivity profiles $\sigma_s(x)$ with widths (50–160 μm) convenient for measurement. Prior to diffusion spreading, the implanted samples were subjected to short-time annealing at T_1 = 590–630°C for t_1 = 5–15 min in order to form a shallow profile of implanted sodium that played the role of a diffusion source.

Concentration profiles $n(x)$ of free electrons were constructed using $\sigma_s(x)$ curves measured using the four-point-probe method with layer-by-layer removal of material by grinding. Since the donor concentration did not exceed 1×10^{16} cm^{-3}, the mobility of electrons along the diffusion layer was assumed to be μ = 1250 cm^2/(V s). The diffusion coefficient of sodium in mCz-n-Si was determined from the profiles of donor concentration expressed as $N_{Na}(x) = n(x) - N_d$, where N_d is the concentration of donor measured in the sample upon grinding. As is known, silicon annealed in

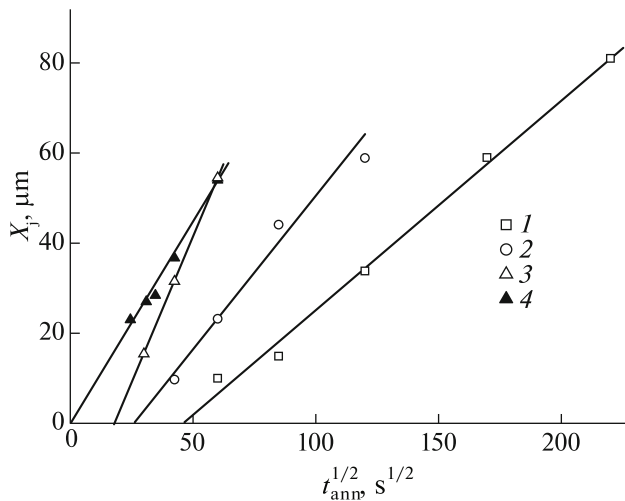

Fig. 1. Plots of n–p junction depth X_j vs. time t_{ann} of annealing at T_{ann} = (*1*, *4*) 550, (*2*) 575, and (*3*) 600°C for mCz-p-Si implanted with sodium at primary ion energies (*1*–*3*) 300 and (*4*) 50 keV.

the given interval of T_{ann} is characterized by the formation of thermal donors (TDs). In order to remove these, the samples upon long-term low-temperature diffusion annealing were additionally annealed at T_2 = 600–630°C for t_2 = 5–15 min [11]. Nevertheless, the measured value of N_d may contain a very small contribution due to retained (unannealed) TDs in addition to phosphorus. For taking into account the contribution of additional annealing to smearing of the profile of sodium dopant concentration, we used the following equation:

$$D_{eff}t_{eff} = D_1t_1 + Dt_{ann} + D_2t_2,$$

where D_{eff} is the effective diffusion coefficient of sodium in the measured donor profile and D_1, t_1 and D_2, t_2 are the diffusion coefficients and durations of the corresponding annealing, respectively. By setting $t_{eff} \approx t_{ann}$, we obtain the following formula for calculation of the diffusion coefficient of sodium:

$$D = D_{eff} - (D_1t_1 + D_2t_2)/t_{ann}. \quad (1)$$

For fz-Si samples in the given interval of T_{ann}, the D_1t_1 correction term can be ignored in view of its smallness in comparison to Dt_{ann}.

It was shown previously [8] that the diffusion of ion-implanted sodium at $T_{ann} \leqslant 600$°C is characterized by some delay (incubation period t_d) related to the presence of structural imperfections and radiation-induced complexes involving sodium atoms. For example, in mCz-p-Si implanted with sodium ions at E = 50 keV and annealed at T_{ann} = 550°C, the delay time was t_d ~ 1 h, while in fz-Si annealed at T_{ann} = 500°C this delay amounted to $t_d \approx 1.5$ h. In the present work, t_d vales were determined for fz-Si samples implanted at E = 300 keV. The results of these measurements are presented in Fig. 1 by the dependences of depth X_j of the n–p junction on annealing time t_{ann} plotted as $X_j = f(t_{ann}^{0.5})$ for the samples annealed at T_{ann} = 600, 570, and 550°C. As can be seen, these plots appear as straight lines, the intercepts of which with the abscissa axis determine the corresponding values of delay time at these annealing temperatures: t_d = 5.5, 9.5, and 36 min for curves *1*–*3*, respectively. Note that, for the sample implanted at E = 300 keV and annealed at T_{ann} = 600°C (curve *3*), the t_d value is not zero in contrast to that for a similar sample implanted at E = 50 keV (curve *4*).

Figure 2 shows the profiles sodium donor concentration in (a) mCz-n-Si and (b) fz-Si samples with characteristics listed in the table, including ion dose Φ, regime of diffusion spreading (T_{ann}, t_{ann}) and additional annealing (T_1, t_1; T_2, t_2), and the measured diffusion coefficient D (the sample numbers coincide with curve numbers on the corresponding figure). Each figure shows the sodium concentration profiles for the maximum initial annealing temperature T_1 = 630°C used in this work. The samples of fz-Si upon the annealing spreading at T_{ann} = 430 and 420°C (Fig. 2b, curves *5* and *6*, respectively) show a significant decrease in the amount of sodium atoms involved in diffusion as compared to that at higher T_{ann} (curves *2*–*4*), which can be explained as being a result of the reverse diffusion taking place at T_{ann} > 600°C [1, 3, 9].

Figure 3 presents the plot of $D(10^3/T)$ for the samples of (open circles) fz-Si, (open squares and black triangles) mCz-n-Si, and (open triangles) mCz-p-Si. The points for T_{ann} > 500°C refer to experimental data obtained previously [6, 10]. As can be seen, the temperature dependence of the diffusion coefficient of sodium in fz-Si (solid line) in a broad temperature range obeys the Arrhenius law with parameters E_{fz} = 1.28 eV and $D_0 = 1.4 \times 10^{-2}$ cm^2/s, which are in good agreement with data reported previously [7]. The $D(10^3/T)$ plot of sodium diffusion in mCz-Si coincides with that for fz-Si in the interval of T_{ann} = 900–700°C. However, with further decreasing annealing temperatures, the values of D in mCz-Si shift downward from a straight line, which is related to the interaction of diffusing Na atoms with oxygen and the resulting formation of Na–O complexes [6]. It was previously suggested [10] that these complexes, similarly to Li–O [12, 13], represent immobile shallow donors. An increase in the annealing temperature leads to their reversible decomposition via reaction $NaO^+ \rightleftarrows Na^+ + O$, and the released sodium atoms are again involved in diffusion. In the equilibrium state, the concentration of Na–O complexes and their decomposition products is characterized by the equation $(NaO^+)C = (Na^+)(O)$, where C is the temperature-dependent dissociation constant. This constant

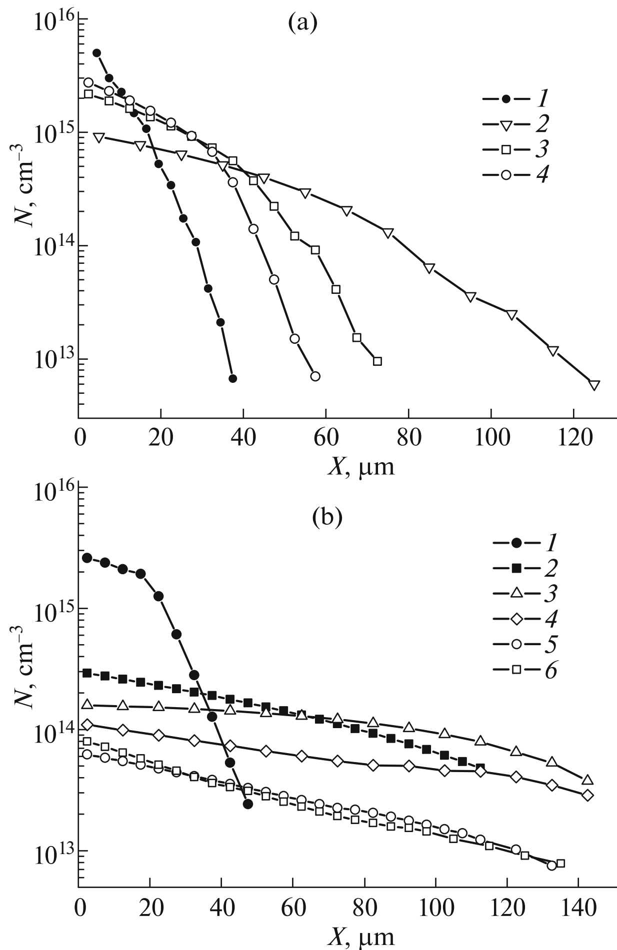

Fig. 2. Sodium donor atom concentration profiles in (a) mCz-n-Si and (b) fz-Si samples with characteristics listed in the table.

can be expressed as $C = C_0\exp(-\Delta E_{Na}/kT)$, where ΔE_{Na} is the binding energy of Na–O complexes.

The proximity of the properties of sodium and lithium impurities allows us to assume that the diffusion coefficients of sodium in mCz-Si (D_{cz}) and fz-Si (D_{fz}) at the same temperature obey a relation that was established for lithium diffusion [12]:

$$D_{cz} = D_{fz}/(1 + N_O/C), \quad (2)$$

where N_O is the oxygen concentration. This formula was also used for determining a set of C values and plotting their temperature dependence (see the inset to Fig. 3). This straight line is characterized by parameters $\Delta E_{Na} = 2.3$ eV and $C_0 = 1.9 \times 10^{32}$ cm^{-3}, which have been used to approximate the experimental D_{cz} values by the calculated $D_{cz}(10^3/T)$ dependence (dashed curve in Fig. 3). It should be noted that the obtained activation energy ΔE_{Na} is significantly greater than the value (0.82 eV) obtained previously for the T_{ann} = 600–500°C interval [10]. This difference is explained by the fact that the dependence approximating the experimental D_{cz} values has been calculated using a significantly smaller value of $C_0 = 4.5 \times 10^{22}$ cm^{-3}. A sharp decrease in D_{cz} at $T_{ann} < 500$°C (where TDs are intensively generated) suggests that the interaction of sodium and oxygen leads to the formation of involved complexes of the Na–O$_n$ type (with $n > 1$), which possess significantly higher binding energies compared to that of a simple N–O complex. As a result of this interaction, sodium atoms become much less mobile. Complexes of this type have been observed in silicon doped with nitrogen [14], where the N–O$_n$ complexes with n = 2–5 possessed a binding energy of ~2.5 eV, which is close to

Characteristics of samples (for Fig. 2)

Sample no.*	Φ, cm^{-2}	T_1, °C	t_1, min	T_{ann}, °C	t_{ann}, h	T_2, °C	t_2, min	D, cm^2/s
				mCz-n-Si (Fig. 2a)				
1	2×10^5	630	15	–	–	–	–	5.4×10^{-10}
2	3×10^{15}	625	5	500	72	–	–	3.0×10^{-11}
3	3×10^{15}	600	5	470	482	600	10	1.5×10^{-12}
4	1.5×10^{15}	615	10	430	1150	590	15	2.4×10^{-13}
				fz-Si (Fig. 2b)				
1	2×10^{15}	630	15	–	–	–	–	1.2×10^{-9}
2	3×10^{15}	630	10	500	72	–	–	7.5×10^{-11}
3	3×10^{15}	630	10	465	336	–	–	2.7×10^{-11}
4	2×10^{15}	610	10	440	670	–	–	1.5×10^{-11}
5	1.5×10^{15}	615	10	430	1030	–	–	5.9×10^{-12}
6	1.5×10^{15}	615	10	420	986	–	–	4.2×10^{-12}

*Sample numbers coincide with curve numbers on the corresponding figures.

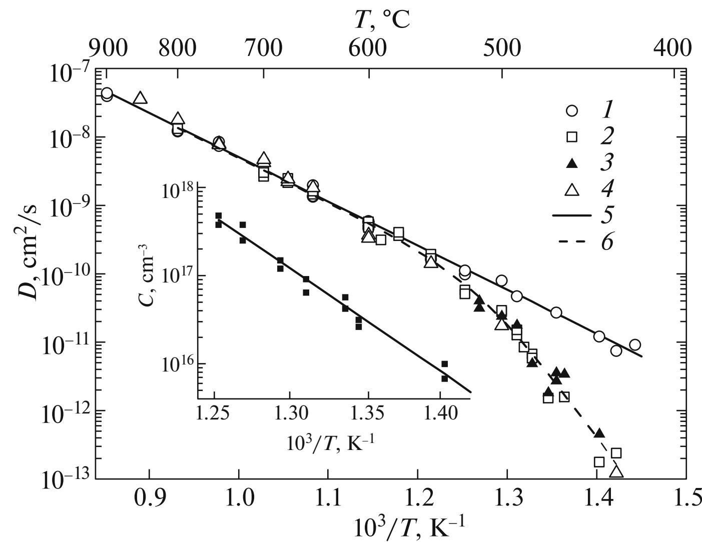

Fig. 3. Experimental temperature dependence of the coefficient D of sodium diffusion in (*1*) fz-Si, (*2*, *3*) mCz-*n*-Si implanted at $E = 300$ and 50 keV, respectively, and (*4*) mCz-*p*-Si. Solid line *5* shows the Arrhenius plot of $D_{fz}(10^3/T)$ with parameters $E_{fz} =$ 1.28 eV and $D_0 = 1.4 \times 10^{-2}$ cm²/s; dashed curve *6* presents the effective diffusion coefficient $D_{cz}(10^3/T)$ in oxygenated Si with $\Delta E_{Na} = 2.3$ eV and $C_0 = 1.9 \times 10^{32}$ cm^{-3}. The inset shows the temperature dependence of dissociation constant C.

the ΔE_{Na} value estimated above from the experimental data.

In concluding, the activation energy for implanted sodium diffusion in mCz-Si at $T_{ann} \geqslant 700$°C coincides with that for fz-Si ($E_{fz} = 1.28$ eV), while at lower temperatures its effective value increases as a result of the interaction of sodium with oxygen and the formation of both simple Na–O complexes and more involved complexes of the N–O_n type with $n > 1$. In fz-Si, the diffusion coefficient $D(10^3/T)$ in a broad temperature interval $T_{ann} = 900$–420°C obeys the Arrhenius law with parameters $E_{fz} = 1.28$ eV and $D_0 = 1.4 \times 10^{-2}$ cm²/s.

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REFERENCES

1. V. M. Korol, Phys. Status Solidi A **9**, 9 (1988).
2. W. H. Wang, W. Boles, C. Illgner, et al., Thin Solid Films **295**, 169 (1997).
3. V. M. Korol' and A. V. Zastavnoi, Poverkhnost, No. 5, 74 (2001).
4. H. Francois-Saint-Cyr, E. Anoshkina, F. Stevie, et al., J. Vac. Sci. Technol. **19**, 1769 (2001).
5. V. M. Korol', Poverkhnost, No. 1, 105 (2005).
6. V. M. Korol', S. A. Vedenyapin, A.V. Zastavnoi, and V. Ovchinnikov, Semiconductors **42** (9), 1122 (2008).
7. V. M. Korol', Yu. Kudriavtsev, A. V. Zastavnoy, and S. A. Vedenyapin, J. Surf. Invest. X-ray, Synchrotr. Neutron Tech. **3** (2), 292 (2009).
8. V. M. Korol', V. P. Astakhov, S. A. Vedenyapin, and A. V. Zastavnoi, J. Surf. Invest. X-ray, Synchrotr. Neutron Tech. **5** (2), 358 (2011).
9. E. Hvidsten Dahl, J. Madsboll, A.-K. Soiland, et al., Semicond. Sci. Technol. **28**, 105010 (2013).
10. A. V. Zastavnoi and V. M. Korol', J. Surf. Invest. X-ray, Synchrotr. Neutron Tech. **8** (6), 1174 (2014).
11. V. Cazcarra and P. Zunino, J. Appl. Phys. **51** (8), 4206 (1980).
12. E. M. Pell, Phys. Rev. **119**, 1222 (1960).
13. E. M. Pell, J. Appl. Phys. **32**, 1048 (1961).
14. H. Ch. Alta, Y. V. Gomeniuka, F. Bittersbergerb, et al., Mater. Sci. Semicond. Process. **9**, 114 (2006).

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