Diffusion of Magnesium in Czochralski Silicon

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The diffusion of magnesium in monocrystalline dislocation-free Czochralski silicon (Cz–Si) with an oxygen concentration of $(3–4) \times 10^{17}\,cm^{-3}$ is studied. Initial silicon wafers are doped with Mg by using the sandwich technique. The impurity diffusion profiles are investigated in n-Si samples by the differential conductivity method. The diffusivity of electrically active magnesium in the temperature range of 1,100–1,250 °C is two to three orders of magnitude lower than the values observed at doping high-purity silicon crystals grown by the float-zone method (Fz–Si). The diffusion in Cz–Si is retarded through the trapping of diffusing Mg atoms by oxygen-related traps. The observed high value of the activation energy of Mg diffusion in investigated samples (4.1 eV) is due—along with the migration energy of interstitial magnesium in the crystal lattice (1.83 eV) —to the significant binding energy of Mg atoms with traps (2.27 eV). A study of the temperature dependence of the Hall effect in bulk-doped samples reveals two types of deep double donors: interstitial Mg atoms and Mg–O complexes.

1. Introduction

Silicon doped with deep donors is interesting, given possible applications in infrared (IR) silicon photonics. Magnesium impurity gives many donor levels in silicon. The deep double donor formed by the interstitial Mg atom (Mg_i) is the most studied, whose ionization energy is 107 meV for the neutral Mg_i^0 and 256 meV for the singly ionized Mg_i^+ state, respectively.[1,2] The concentration of interstitial magnesium in samples reaches the value of $1.5 \times 10^{15}\,cm^{-3}$. Among other impurity atomic centers that form deep double donors in Si, such as S and Se, whose ionization energies for neutral states are 318 and 307 meV, respectively (while their second ionization energies are 614 and 593 meV),[3] Mg_i has the lowest values of these parameters. Compared to other interstitial donors in silicon—Li, Cu, and Ni—Mg_i has the highest ionization energy and the lowest diffusion coefficient.[4–6] The diffusivity of magnesium in Si is much higher than that of substitutional impurities.[7,8]

Magnesium in silicon can form electrically active complexes with other impurities (see review article[9]). Experimental data indicate that most of the magnesium in Mg-doped silicon is electrically inactive.[10,11] The structure of this "neutral" component has not yet been established. It can be in Mg_i–Mg_s isoelectron pairs,[10,12] magnesium silicide Mg_2Si, or clusters of Mg atoms. In particular, the interaction of Mg with oxygen leads to the formation of the Mg–O complex, which is also a double He-like donor. The ionization energies for the neutral and singly charged states are 124.66[13,14] and 274.90 meV,[15] respectively. The optical absorption spectroscopy of Si:Mg samples has shown that their long-term storage at room temperature is accompanied by a decrease in interstitial magnesium content, while the concentration of the Mg–O complex increases over time.[6,16] Based on these data, we can assume that the Mg–O complex is a more stable donor than Mg_i. Therefore, the donor may be of interest for use in silicon IR photonics.

In the above-cited studies, magnesium has been introduced into the floating zone (Fz) grown p- or n-Si using the so-called "sandwich" method. The residual oxygen concentration in such silicon is relatively low, typically slightly above $10^{16}\,cm^{-3}$. Based on the low-temperature absorption spectra of samples given in the previous studies,[13,14] one can estimate the ratio of concentrations $N_{Mg–O}/N_{Mgi}$. It does not exceed 0.3–0.5. Concentrations themselves were not determined in the cited works.

We can obtain an increased density of Mg–O complexes in magnesium-doped samples using initial Si with a high oxygen concentration, enabling—by analogy with studies of Mg_i centers[17] —to investigate characteristics of the He-like Mg–O deep donor, which is important for IR photonics. Among them are featured in the energy spectrum of the complex and relaxation times of its excited states.

The natural way to prepare such samples is to use Cz–Si wafers—where the oxygen content is typically above $10^{17}\,cm^{-3}$—for magnesium doping. This can be done using the sandwich diffusion method.

Magnesium diffusion in such crystals has not yet been investigated, although Cz–Si samples doped with Mg were used in some experiments (e.g., ref. [18]). In this article, we describe the results of a magnesium diffusion study in the dislocation-free Cz–Si. The oxygen concentration in the initial silicon is $(3–4) \times 10^{17}\,cm^{-3}$. During experiments, a relatively low quenching rate used earlier to cool diffused Fz–Si samples[4–6] does not allow us to obtain specimens with the parameters required (e.g., to make the Hall effect measurements).

In this work, we used a modified "sandwich" method of doping, which provides a significantly higher quenching rate

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of samples after thermal processing than the cooling mode usually applied for Fz—Si. The use of this variant of technology allowed us to determine the temperature dependence of the diffusion coefficient $D_{Mg}(T)$ in the investigated Cz—Si. We observed a significant decrease in D_{Mg} compared to high-purity Fz—Si, interpreted as being due to decreased mobility of diffusing magnesium atoms in Cz—Si compared to Fz—Si.

The data obtained in the present study and the corresponding results for high-purity Fz—Si[4–6] allowed us to estimate both the activation energy of motion of magnesium atoms over the lattice interstices and their binding energy with traps responsible for the effect of diffusion retardation.

We have attempted to determine the parameters of doped samples by studying the Hall effect's temperature dependence. We used samples with a spatial distribution of magnesium close to the uniform for these experiments. The data suggest that both deep donors, Mg_i, and Mg—O are involved in the electrical conductivity of samples at room temperature.

2. Experimental Section

We carried out the doping of Cz—Si wafers with magnesium by the "sandwich" diffusion method. Wafers of n-type Si with resistivity ρ of ≈100 and $\approx30\,\Omega\,cm$ and p-type with $\rho \approx 200\,\Omega\,cm$ were used as initial materials. The oxygen concentration in them—as determined from the absorption spectra measured by FTIR at room temperature with the FSM2201 Fourier spectrometer—was in the range of $(3–4) \times 10^{17}\,cm^{-3}$.

We doped an initial wafer with Mg in two stages. The first one was similar to that previously used in the previous studies.[4–6] We deposited a film of purity of (99.995%) magnesium onto one or both sides of an initial silicon wafer of 30 mm diameter and thickness in the 1.2–2.0 mm range done by the thermal evaporation of the metal in a vacuum chamber at a pressure of $\approx10^{-6}$ mm Hg. Experiments show that homogeneous doping over a sample area is achieved by depositing a sufficiently high specific mass of magnesium m_{Mg} on the crystal surface.[9] In the present work, the value of m_{Mg} is $\approx500\,\mu g\,cm^{-2}$. We then covered the magnesium-coated sides of the wafers with 0.4–0.5 mm-thick auxiliary silicon plates, placed a prepared sandwich in a quartz cassette, and fixed it with silicon wedges (see a schematic representation of such a setup in **Figure 1**).

We installed the cassette in a quartz ampoule, evacuated it to a high vacuum, filled it with high-purity argon to a pressure of about 0.2 atm, sealed it off, and placed it in a quartz tube. We then put the tube with the ampoule inside a heated furnace, where the entire structure was subjected to heat for 30 min at 1,100 °C. After removing the tube from the furnace, we cooled the ampoule with a stream of compressed nitrogen gas to a state where the sample temperature decreased to below the disappearance of the red glow, which took $\approx100\,s$. The described technology resulted in auxiliary plates being welded to the doped sample through the magnesium layers. As a result, the near-surface volume of the plate was enriched with magnesium up to a depth of 10–15 μ. This estimate follows from the temperature dependence of impurity diffusion (see below, Figure 4).
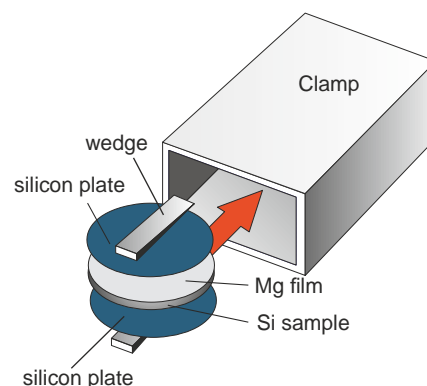
Figure 1. Schematics of the insert in an ampule prepared for diffusion.[9]

Thus prepared sandwich was cut into $10 \times 10\,mm^2$ specimens. We placed these small sandwiches in thin-walled quartz ampoules of a relatively small (15–16 mm) diameter. After evacuating the ampoules, filling them with argon, and sealing them, we further processed specimens at different temperatures and durations. At the end of the diffusion procedure, we quenched a doped sample by dropping the ampoule into mineral oil. Then we removed the auxiliary silicon wafers from the surfaces of thus prepared samples by grinding.

The key factors in determining a sample quenching rate in our case are the thermal conductivity of the quartz ampoule wall and the gas filling the ampoule volume. We ensured the high cooling rate of a sample in our experiments by its small size, use of a thin-walled ampoule, and filling the ampoule with Ar at a pressure close to 1 atm at the diffusion temperature.

Based on the study of Botha et al.'s [19] results, where quenching modes of test objects in a system close to that we use are investigated, one can estimate the quenching rate of samples studied in the present work. This estimation gives a cooling time at the high-temperature stage (where the quenching speed is essential) not exceeding 10 s.

The reason why we implemented the described two-step doping procedure in the present experiments is as follows. Preparing samples whose surface is homogeneously doped with Mg requires using initial Si wafers of considerable size. Therefore, it is necessary to use appropriately sized ampoules and cassettes. However, ensuring the rapid quenching of such massive objects heated to a high temperature is difficult.

The magnesium diffusion coefficient was determined by studying the concentration profiles of free electrons in the doped samples, which we carried out by the differential conductivity method, see our previous study.[5] We made the measurements on samples, where we performed doping from a layer of magnesium deposited on one side of a wafer. To find the concentration of donors in bulk-doped specimens with the Hall effect, we used samples diffused from both sides of a wafer, which provided a spatial distribution of impurities that were close to uniform and evaluated the concentration of donors by fitting theoretical temperature dependences of the free electron concentration, n(T), to experimental data points found through the Hall effect measurements in the temperature range 78–300 K.[20]

# 3. Results

3.1. Temperature Dependence of Mg Diffusivity

The diffusion profiles were determined using n-Si with a resistivity of ≈ 30 and $\approx 100\,\Omega\,\text{cm}$ as starting materials. **Figure 2** shows an example of the concentration profile of free electrons, n, obtained for an n-Si sample (whose initial resistivity is $\approx 30\,\Omega\,\text{cm}$) doped at $T = 1{,}250\,°\text{C}$ for 2.5 h. The electron density decreases with the sample depth, and an almost constant value, $\approx 2.9 \times 10^{14}\,\text{cm}^{-3}$, is observed at depths greater than $\approx 500\,\mu$. This value, n_P, is provided by the ionization of phosphorus impurity in the initial silicon and is shown by the dashed horizontal line. The n_P value must be subtracted from the free electron density to obtain the free electron concentration, n_Mg, provided by the ionization of magnesium donors.

We evaluated the concentration of magnesium N_Mg in different profile points using the approach that considers statistics of double-charged donors. (Such a procedure was used, in particular, to process the Hall effect data obtained for Si doped with different deep donors.[20]) The solid curve in Figure 2 results from fitting the complementary error-function distribution to the set of points for N_Mg extracted from the profile data for free electrons. Therefore, finally, the described procedure allows us to estimate the diffusion coefficient of magnesium. For the considered doping parameters, we have $D_\text{Mg} = (2.0 \pm 0.1) \times 10^{-8}\,\text{cm}^2\,\text{s}^{-1}$.

In obtaining the N_Mg profile shown in Figure 2, we assumed that the excess conductivity of silicon (i.e., additional to that provided by shallow donors) is due to the ionization of interstitial magnesium atoms. Note that the Hall effect data show that a significant contribution to the concentration of free electrons at room temperature is also due to the ionization of Mg—O donors. However, since the ionization energies of both (Mg$_i$ and Mg—O) deep donors are close, we believe that the data in Figure 2 correctly reflect the characteristics of the diffusion profile.
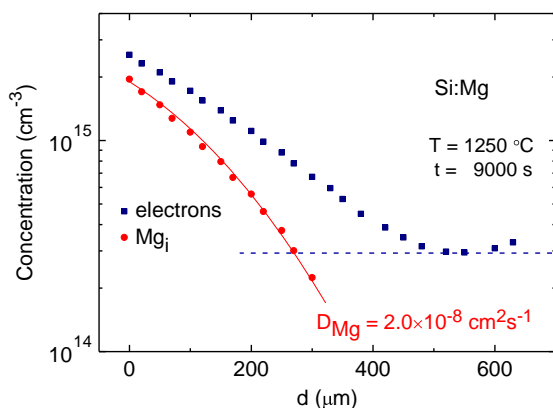
Figure 2. Profiles of concentrations of free electrons n and magnesium centers N_Mg in a sample obtained by diffusion at $T = 1{,}250\,°\text{C}$ for 2.5 h. The initial n-Si is of resistivity $\approx 30\,\Omega\,\text{cm}$, which corresponds to the electron concentration marked by the dotted horizontal line. N_Mg profile is calculated from the corrected value of n considering the degree of ionization of this deep donor at room temperature (see ref. [20]). The solid curve is the complementary-error function that best fits experimental data. It corresponds to the diffusion coefficient $D_\text{Mg} = 2.0 \times 10^{-8}\,\text{cm}^2\,\text{s}^{-1}$.
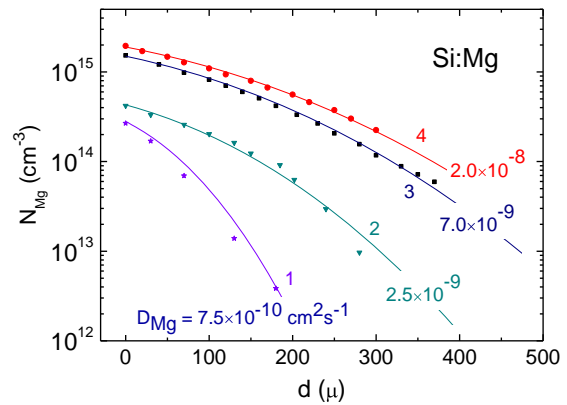

Figure 3. Profiles of magnesium concentration observed at different temperatures of doping. T, °C, 1 – 1,100; 2 – 1,150; 3 – 1,200; 4 – 1,250. For diffusion time, see Table 1.

Samples were doping at different T—see a set of N_Mg profiles in **Figure 3**—to find the temperature dependence of the diffusion coefficient of magnesium, $D_\text{CZ}(T)$, see **Figure 4** and **Table 1**. Note that data for $T = 1250\,°\text{C}$ were obtained for samples made from two n-Si ingots (≈ 30 and $\approx 100\,\Omega\,\text{cm}$) with close oxygen content. We did not observe an appreciable difference in Mg diffusion coefficients for these materials. **Figure 4** also represents the temperature dependence of D_Mg for Fz-grown silicon.[6] Clearly, the diffusivity of magnesium in Cz silicon is orders of magnitude lower than that for Fz—Si. The solid lines on the graph are approximations of dependences $D(T)$ with the exponential function[21]

$$D(T) = D_0 \exp(-E/k_\text{B}T)\ [\text{cm}^2\text{s}^{-1}] \tag{1}$$

where E is the diffusion activation energy, D_0 is the pre-exponential factor, and k_B and T are Boltzmann constant and absolute temperature, respectively.

Thus obtained, we have $E_\text{CZ} = 4.1\,\text{eV}$ and $D_\text{0CZ} = 7.7 \times 10^5\,\text{cm}^2\,\text{s}^{-1}$ for the studied Cz—Si, whereas for
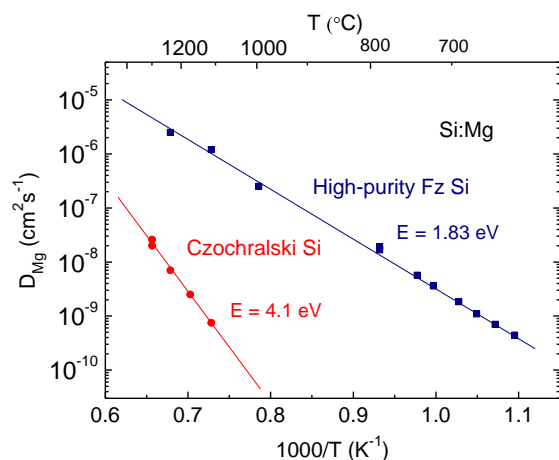
Figure 4. Temperature dependences of the magnesium diffusion coefficient in Cz-grown silicon, present work data, and dislocation-free Fz-grown silicon.[9] The diffusion activation energy E is shown for both cases.

Table 1. Diffusion coefficient of magnesium in Czochralski-grown silicon at different temperatures and diffusion time. Sample #189-1a is made of n-Si with a resistivity of $100\,\Omega\,cm$, and the others are made of n-Si with $\rho \approx 30\,\Omega\,cm$.

Sample	T [°C]	Time [h]	D_{CZ} [cm^2 s^{-1}]	$1000/T$ [K^{-1}]
188-1a	1,100	7.5	$(7.5 \pm 1.5) \times 10^{-10}$	0.73
188-1c	1,150	10	$(2.5 \pm 0.5) \times 10^{-9}$	0.70
188-1b	1,200	6	$(7.0 \pm 0.5) \times 10^{-9}$	0.68
181-1-1	1,250	2.5	$(2.0 \pm 0.2) \times 10^{-8}$	0.66
189-1a	1,250	26.5	$(2.6 \pm 0.2) \times 10^{-8}$	0.66

Fz—Si, these parameters are $E_{FZ} = 1.83\,eV$ and $D_{0FZ} = 5.3\,cm^2\,s^{-1}$, respectively.[6]

As noted above, magnesium atoms in Si are interstitial donors and diffuse via interstitial lattice sites. One can assume that atoms diffusing in oxygen-enriched (Cz—Si) crystal may be captured by oxygen-related centers, which act as traps causing a decrease in atoms' mobility compared to Fz—Si, thus reducing the magnesium diffusion coefficient.

Trap-retardation effects on the diffusivity of impurities in silicon have been considered in a number of works (see, e.g., refs. [22–28]). In particular, a decrease in the diffusivity of copper due to the formation of donor-acceptor pairs Cu—B, Cu—Ga, and Cu—Al has been studied.[29–32] At passivating acceptors in boron-doped silicon with atomic hydrogen, it was found that forming B—H pairs leads to slower hydrogen diffusion.[33] Trapping of diffusing impurity atoms by lattice defects can also decrease the diffusion coefficient. An example is the trap-retarded diffusion of interstitial transition metals in amorphous silicon.[34,35] In the study by Schachtrup et al.,[23] the reduction of the gold diffusion coefficient in plastically deformed monocrystalline silicon was investigated.

The general approach to describe the diffusion of impurity atoms in a semiconductor is based on solving the diffusion-reaction equations. To describe the trap-limited diffusion of interstitial atoms, their reaction with traps is included in the model being analyzed.[28]

A concept of an effective diffusion coefficient of interstitial atoms in the presence of traps—which we use to interpret data obtained in the present study—was proposed by Koiwa.[26] The diffusion process includes two characteristic energies: the activation energy for migration of a diffusing atom over interstices, E_m, and the energy of its binding to a trap, E_B, as shown in **Figure 5**, the corresponding potential energy curve for an interstitial atom near a trapping center. To be released from the trap, a diffusing atom has to overcome the energy barrier $E_m + E_B$. As a result, diffusing atoms spend much more time attached to defects than they do traveling through the lattice interstices, which gives a low impurity diffusivity.

According to the study of Koiwa,[26] for an impurity interacting with traps, the diffusion constant $D*$ can be expressed as

$$D* = \frac{D}{1 + \alpha C \exp(E_B/k_B T)} \tag{2}$$
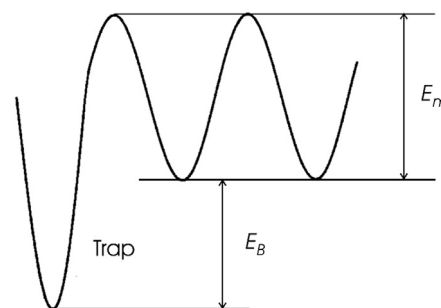
Figure 5. Potential energy curve for an interstitial impurity atom near a trapping center (schematically). E_m is the activation energy for migration over interstices, and E_B is the binding energy of the interstitial atom associated with a trap.

where D is the diffusion coefficient, which refers to a crystal without trapping centers; $\alpha = 4(\nu_0/\nu_1)$; ν_0 and ν_1 are frequency factors, which are "attempt-to-jump frequencies" for a free interstitial and trapped atom, respectively; C is the atomic fraction of trapping centers.[26] In a case, where lattice phonon vibrations control attempt-to-jump frequencies, one can assume $\nu_0/\nu_1 = 1$. For the observed large difference between the impurity diffusion coefficients in Fz— and Cz—Si, one can neglect "1" in the denominator of expression (2). Now, combining Formula (1) and (2), we get the Mg diffusion coefficient in Cz—Si

$$D_{CZ} = \frac{D_{0FZ}}{\alpha C} \exp\left(-\frac{E_{FZ} + E_B}{k_B T}\right) \tag{3}$$

This expression allows us to estimate values of E_B and C using experimental activation energies and pre-exponential factors for magnesium diffusion in both Fz and Cz silicon. We obtain the binding energy $E_B = E_{CZ} - E_{FZ} = 2.27\,eV$, which is the difference in activation energies of diffusion in two kinds of silicon; this value of E_B also follows from the data in Figure 4. In the frame of the considered model, the atomic fraction of the capture centers in Cz—Si can be estimated as $C = D_{0FZ}/(4 \cdot D_{0CZ}) \approx 1.7 \times 10^{-6}$.

We stress that the Formula (2) has similarities to the corresponding expression for the trap-limited diffusion coefficient of an interstitial impurity, which is obtained by solving diffusion-reaction equations for the state of the crystal near the thermodynamic equilibrium.

The binding energy estimated above (2.27 eV) is much higher than the corresponding energies observed in trap-retarded diffusion experiments for other impurities in silicon. Thus, for trapping of diffusing atoms by the Coulomb interaction (through the formation of donor–acceptor pairs), these are on the order of $\approx 0.5\,eV$.[8,36] For the capture of diffusing interstitial atoms by structural defects in amorphous Si, the corresponding values are ≈ 0.8–$0.9\,eV$.[34,37] An essentially higher E_B value observed in the present experiments seems to result from magnesium strong (covalent) bonding with oxygen-related defects in Cz—Si.
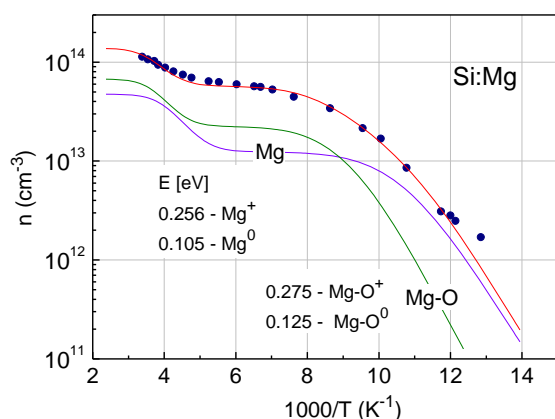
3.2. Investigation of the Hall Effect in Mg-Doped Samples

To study the results of doping Cz—Si with Mg, we measured the Hall effect on bulk-doped samples. We used a p-Si wafer of a resistivity of $\approx 200\,\Omega\,cm$ and thickness of 1.8 mm as an initial material and applied a double-side doping process ($t = 26\,h$ at $T = 1250\,°C$) to prepare a sample that would be close to uniformly doped. **Figure 6** shows the temperature dependence of the concentration of free electrons in the prepared sample, $n_{exp}(T)$, found from the Hall effect data.

We estimated concentrations of donors in the sample by fitting a calculated temperature dependence, $n_{calc}(T)$, to a set of experimental points and evaluated n_{calc} at a given temperature by a numerical solution of the charge balance equation described in the study of Pavlov et al.[20] The negative charge in a sample is the sum of concentrations of free electrons and negatively charged boron acceptors, whose concentration, $6.3 \times 10^{13}\,cm^{-3}$, corresponds to the resistivity of the initial p-Si. The positive charge is provided by ionized double-charged donors—interstitial Mg atoms and Mg—O complexes—and some density (N_{DX}) of singly charged shallow donors. When calculating a trial function $n_{calc}(T)$, it is supposed that the ionization energies of both double-charged donors are those defined by the results of optical absorption experiments.[2,13–15] Namely, for the interstitial Mg, energies for the first and second ionization are 0.107 and 0.256 eV, respectively, and for the complex Mg—O, the corresponding values are 0.125 and 0.275 eV. To obtain the correspondence of a calculated dependence $n_{calc}(T)$ to experimental data, the concentrations of interstitial magnesium and magnesium–oxygen complex and the concentration of shallow donors and their ionization energy have been fitting parameters.

We obtained a satisfactory fitting result using deep donor ionization energies corresponding to optical absorption spectroscopy data. The solid upper line in Figure 6 shows the curve $n_{calc}(T)$ that best fits the experimental point set. The found values for concentrations of donors in the sample are $N_{Mg} = 3.5 \times 10^{13}\,cm^{-3}$, $N_{Mg-O} = 4.5 \times 10^{13}\,cm^{-3}$, and $N_{DX} = 4.0 \times 10^{13}\,cm^{-3}$. As an illustration, Figure 6 also shows calculated temperature dependencies of the partial contributions of the two deep donors to the total density of free electrons. According to the result obtained, both are in the sample in comparable concentrations.

Interestingly, the partial contribution curves of the two donors to the total electron concentration at some temperature intersect. The reason for such behavior of corresponding curves is that, although concentrations of Mg_i and Mg—O double centers in the investigated sample are close, the concentration of Mg—O is slightly higher. Therefore, in the region of the high T (when both deep donors are almost completely ionized), the partial contribution of the deeper donor to the electron concentration is higher. At low T, higher is the partial contribution of the donor with lower ionization energy.

4. Discussion and Conclusion

We studied magnesium diffusion in Cz-grown silicon with an oxygen concentration higher than $10^{17}\,cm^{-3}$. We found the diffusivity of Mg in the investigated temperature range of 1,100–1,250 °C lower by 2–3 orders of magnitude compared to that in the high-purity Fz—Si. Magnesium diffusion activation energy E_{CZ} in Cz—Si (4.1 eV) significantly exceeds the corresponding values for the Cu, Ni, and Fe interstitial impurities in silicon and such impurities as Au, Zn, and Pt. At the same time, it is close to the corresponding parameters for B, P, and As in Si, which are 3.40, 3.66, and 4.05 eV, respectively.[28,38] The pre-exponential factor is closer to the value for the self-diffusion in silicon.[28,38,39]

We discussed the data regarding trap-limited diffusion, where the flow of diffusing magnesium atoms in silicon is retarded by their capture by oxygen-related traps. Concerning the considered data, it is appropriate to point out a relatively large diffusion activation energy of the electrically active magnesium (1.83 eV) observed in high-purity Fz crystals. In our opinion, this energy defines the intrinsic diffusion coefficient of interstitial Mg atoms in silicon. Thus, the activation energy of magnesium diffusion in Cz—Si is the sum of the corresponding activation energy in silicon without traps (E_{FZ}) and the binding energy of Mg atoms with oxygen-related traps, E_B. We suggest that the high E_B value in the case studied (2.27 eV) is apparently due to the chemical (covalent) bonding of magnesium atoms with oxygen-related traps in Czochralski silicon.

A hypothesis may be advanced that the strong retardation of magnesium diffusion in Cz—Si – in comparison to that in pure Fz—Si – is due to the reaction of magnesium with oxygen, which produces deep Mg—O donors. (In other words, the Mg—O donor is the product of the reaction, which controls the effect of diffusion retardation). However, the results available to date do not support this hypothesis. Two facts testify to this: 1) The analysis of the data suggests that the density of such traps in the samples studied is too low to produce the observed effect and 2) our preliminary experiments on the heat treatment of doped Cz—Si samples indicate a relatively low thermal stability of Mg—O donors, comparable to the stability of Mg_i donors in Fz—Si samples, which has been investigated in the study of Shuman et al.[40]

Figure 6. Temperature dependence of electron concentration in a Si:Mg sample obtained by doping p-Si with a resistivity of $\approx 200\,\Omega\,cm$. The doping was performed at $T = 1,250\,°C$ for 26 h from both wafer sides. Symbols denote the measured n values. The solid upper line is the calculated dependence, $n_{calc}(T)$, which fits best the experimental points. The lower curves show the estimated partial contributions of both deep donors, Mg_i and Mg-O, to the total electron concentration.

This observation is inconsistent with the experimentally found high binding energy E_B. Thus, the nature of the traps responsible for the Mg diffusion retardation in Cz—Si remains unclear at present.

The E_B value for magnesium observed in the present study significantly exceeds binding energies for other interstitial impurities that associate with traps or form donor–acceptor pairs in silicon. For example, in the well-studied trap-limited diffusion of interstitial copper, binding energies of Cu—A pairs (A = B, Al, Ga, In) do not exceed 0.5 eV, ensuring a fairly high diffusion coefficient of this impurity even at a relatively low temperature.

For the value of pre-exponential factor D_{0CZ} in the temperature dependence of diffusivity of Mg in Cz—Si, it equals—in the model discussed in this paper according to Equation (3)—the ratio $D_{0FZ}/4C$, where C is the atomic fraction of trapping centers. Therefore, we may interpret the observed large coefficient D_{0CZ} as being due to a small value of parameter C.

The IR absorption of silicon crystals in the 1,107 cm^{-1} band associated with oxygen decreases significantly after doping samples with magnesium.[18] In the cited work, the effect was attributed to the interaction of magnesium atoms with oxygen and the formation of magnesium complexes. We also observed the converting oxygen to an optically inactive state in our experiments on doping Si with Mg. We note that this effect may influence the detailed dynamics of the diffusion process. However, possible nonlinearities in the considered trap-limited diffusion require further investigation.

Earlier, we revealed the effect of pairing magnesium atoms with group-III acceptors in silicon, giving shallow donors.[41] The formation of the donor–acceptor pairs can influence the diffusivity of magnesium in such crystals; however, since the binding energy of such pairs is relatively low (according to the previous studies,[32,36] it cannot exceed $\approx$0.5 eV in silicon), and the diffusion retardation should be relatively weak compared to the case investigated in the present study.

The magnesium impurity in silicon is mainly electrically inactive, as observed in various sample preparation methods–ion implantation, epitaxial growth of Si:Mg films, and sandwich method.[9] An interesting problem for further research is whether the accumulation of electrically neutral magnesium impurities in a crystal affects the magnesium diffusion process. Within the framework of the present study, for the Cz silicon, such an influence can be caused by the interaction of neutral magnesium with oxygen, which may change the concentration of oxygen-related traps.

Samples doped with Mg at 1,250 °C have shown comparable concentrations of Mg_i and Mg—O double donors, $(4–5) \times 10^{13}$ cm^{-3}. They are produced by a prolonged (26 h) Mg diffusion into 1.8 mm thick samples. These values are averaged over the crystal volume and essentially lower than the concentration of deep donors ($\approx 10^{15}$ cm^{-3}) observed in the crystal region adjacent to the surface, from where diffusion occurs, see Figure 3. Note that, as previously established,[40] a prolonged high-temperature treatment of Si:Mg samples is accompanied by the decomposition of the solid solution of electrically active magnesium introduced into the crystal volume.

Based on the results discussed here, we can conclude that obtaining samples with a sufficiently high concentration of deep Mg—O donor ($\approx 10^{15}$ cm^{-3})—desirable for comprehensive center studies—requires optimizing the doping regime and sample geometry.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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