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## Magnesium diffusion in silicon grown by the Czochralskii method

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Magnesium diffusion in dislocation-free Czochralski silicon (CzSi) with oxygen concentration  $\sim (1.2-1.6) \cdot 10^{17} \text{ cm}^{-3}$  was studied. The temperature dependence of the magnesium diffusion coefficient was compared with the data obtained earlier in Cz-Si with a higher oxygen concentration  $\sim (3-4) \cdot 10^{17} \text{ cm}^{-3}$ . Diffusion coefficient values measured at temperatures  $T = 1100-1250^\circ\text{C}$  were found to be larger in silicon with lower oxygen concentration. The experimental data were processed in the frame of the trap-limited diffusion model, in which diffusion retardation occurs as a result of trapping of interstitial Mg atoms by oxygen-related centers. The trap binding energy was determined to be  $\sim 2.2 \text{ eV}$ .

**Keywords:** Czochralskii silicon, magnesium, diffusion, deep donors.

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### 1. Introduction

Interest to deep donors in silicon is due to both quantum structure of these centers, and possible their use as active mediums for laser generation in intracenter optical transitions [1]. Use of deep impurities opens prospects for development of the radiation sources in medium-wave spectrum, and silicon doped by magnesium Si:Mg is one of such materials [2–5].

Electrically-active magnesium atoms  $\text{Mg}_i$  occupy interstitial position in silicon lattice and form double donor center with energy levels  $E_C - 0.107 \text{ eV}$  of neutral  $\text{Mg}_i^0$  and  $E_C - 0.256 \text{ eV}$  singly ionized state  $\text{Mg}_i^+$ , respectively [6,7]. Centers concentration  $N_{\text{Mg}_i}$  is  $\sim (1.0-1.5) \cdot 10^{15} \text{ cm}^{-3}$ . Due to interaction with other impurities the magnesium forms in the forbidden gap of silicon different donor levels. These complexes Mg with substitutional acceptors B, Al, Ga, In, interstitial Li, and many other donor centers (see review [8]). The interaction of Mg with oxygen results in the formation of the complex Mg-O [9,10]. Like Mg, this complex is of interest for use in IR-photonics.

The paper [11] studied diffusion of Mg into dislocation-free silicon of *n*-type, grown by Czochralski method (Cz-Si), with concentration of oxygen  $\sim (3-4) \cdot 10^{17} \text{ cm}^{-3}$ . The choice of such material was related to the assumed possibility to obtain high concentration of complex Mg-O. Dependence of diffusion constant of magnesium on temperature  $D_{\text{Mg}}(T)$  in range  $T = 1100-1250^\circ\text{C}$  was determined. Significant decrease in  $D_{\text{Mg}}(T)$  by 2–3 orders of magnitude in Cz-Si as compared to appropriate values in oxygen-free silicon grown by floating zone method was detected (Fz-Si). It was suggested that diffusion in Cz-Si is slowed down by the capture of interstitial Mg atoms by oxygen-related traps. The experimental results were analyzed in the frame of the

trap-limited diffusion model. Binding energy of trapping centers  $\sim 2.3 \text{ eV}$  was determined.

The present paper is continuation of study performed in [11] and directed for further study of the diffusion of interstitial magnesium atoms in silicon containing trapping centers.

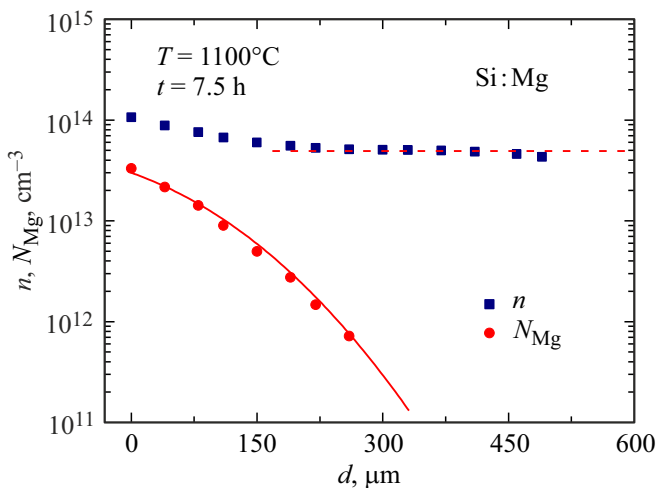
To carry out Mg diffusion Cz-Si with oxygen concentration lower than in above referred paper was chosen as initial material. The diffusion constant was determined from profile of concentration of electrically active centers of magnesium  $N_{\text{Mg}}$  in samples obtained as result of execution at temperatures  $T = 1100-1250^\circ\text{C}$ .

Comparison of the present paper results with the trapping center parameters determined in [11] allowed us to verify the concept of Mg diffusion in the presence of trapping centers and the applicability of the model used for data processing.

### 2. Experimental procedure

Silicon doping was performed by „sandwich“-method of diffusion [8,12]. The plates Cz-Si of *n*-type (KEF) with resistivity  $\rho \sim 100-120 \Omega \cdot \text{cm}$  were used as initial material. The concentration of oxygen and carbon in the initial silicon was determined at room temperature by the absorption peaks of atomic oxygen  $1106 \text{ cm}^{-1}$  and carbon  $605 \text{ cm}^{-1}$  using a Fourier spectrophotometer FSM2201. The concentration of oxygen was  $\sim (1.2-1.6) \cdot 10^{17} \text{ cm}^{-3}$  and of carbon was  $\sim (1.2-1.5) \cdot 10^{17} \text{ cm}^{-3}$ , respectively.

Impurity was introduced into Si by two stages. At first stage all preliminary operations required for „sandwich“-method of diffusion were executed [12]. On one side of plate of the initial silicon with diameter  $\sim 30 \text{ mm}$  and thickness  $d \approx 1.2-2.0 \text{ mm}$  a magnesium film with purity



**Figure 1.** Profiles of electron concentration  $n$  and centers of magnesium  $N_{\text{Mg}}$  in sample obtained by diffusion at temperature  $T = 1100^\circ\text{C}$  for 7.5 h. The horizontal dashed line corresponds to electron concentration in initial  $n$ -Si with resistivity  $\rho \approx 100 \Omega \cdot \text{cm}$ . Solid curve shows the profile of theoretical dependence of diffusion  $N_{\text{Mg}}$  with factor  $D_{\text{Mg}} = 2.5 \cdot 10^9 \text{ cm}^2 \text{ s}^{-1}$ .

$\sim 99.995\%$  is sputtered. Then the plane of the sample with the deposited magnesium was covered with an auxiliary silicon wafer  $\sim 0.4\text{--}0.5 \text{ mm}$  thick. Such „sandwich“ was placed in quartz ampoule, which was filled with argon and soldered. The ampoule was heated for 30 min at temperature  $1100^\circ\text{C}$ , this resulted in welding of sample material and auxiliary wafer via the magnesium layer.

The „sandwich“ was taken from the ampoule, and samples were prepared from it with dimensions  $10 \times 10 \text{ mm}$ . Such samples were loaded in thin-wall quartz ampoules of low diameter  $15\text{--}16 \text{ mm}$ , filled with argon and soldered. The magnesium diffusion was performed at temperature  $T = 1100\text{--}1250^\circ\text{C}$  for 7.5 h. At the end of the process the doped sample was quenched by dropping the ampoule into mineral oil. High cooling rate was ensured by use of thin-wall ampoule and small size of samples. After quenching the auxiliary silicon wafer was removed by grinding.

The diffusion constant of interstitial magnesium  $D_{\text{Mg}}$  was determined by profile measurement of electrons concentration by method of differential conductivity [12]. For this distribution of specific conductivity along the thickness of sample was determined using successive removal of silicon layers  $\sim 20 \mu\text{m}$ . The surface conductivity of the sample was measured by the four-probe method before and after layer removal. The conductivity distribution was approximated by an analytical function, which was used to calculate the electron concentration profile  $n$ .

Figure 1 shows example of profile  $n$  in sample Si:Mg, doped at  $T = 1100^\circ\text{C}$  for 7.5 h. Electrons concentration decreases with sample depth and at  $d > 300 \mu\text{m}$  nearly constant value  $n_p \approx 4.9 \cdot 10^{13} \text{ cm}^{-3}$  is observed. This value corresponds to electron concentration of completely

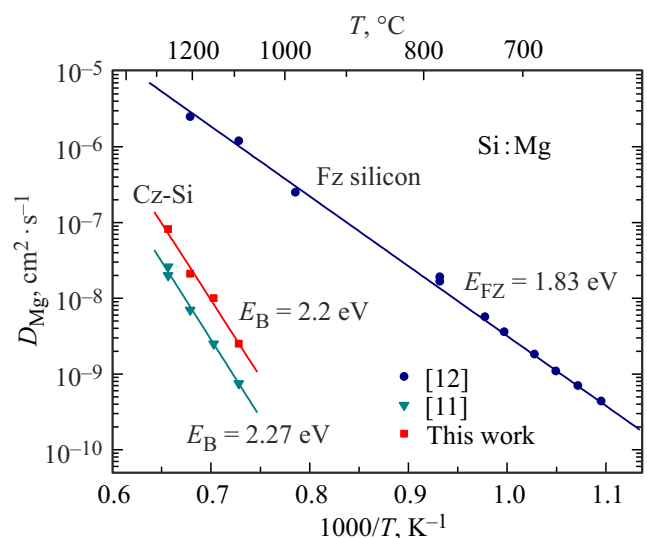
ionized impurity of phosphorous in the initial silicon with  $\rho \approx 100 \Omega \cdot \text{cm}$ , and is marked in graph by dashed line.

Electron concentration due to ionization of donor centers Mg can be obtained by value  $n_p$  subtraction from  $n$ . Concentration distribution of magnesium atoms  $N_{\text{Mg}}$  through depth of sample was determined from profile of corrected value of electron concentration using the calibrated dependence  $N_{\text{Mg}}(n)$ .

This dependence was determined by numerical solution of charge-balance equation for silicon containing double donor center Mg, compensated by shallow acceptor. Energies  $\text{Mg}^{0/+}$  of states corresponded to values specified in Introduction, and impurity charge was determined by statistics of filling by electrons of center states at room temperature (see. Suppl. Material to article [13]). Values  $N_{\text{Mg}}$  are marked in graph with symbols. Solid curve in Figure — results of fitting the complementary error-function distribution, to set of experimental points. Such procedure ensured value evaluation of diffusion constant —  $D_{\text{Mg}} = 2.5 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ .

### 3. Measurement results and discussion

To determine temperature dependence of diffusion constant of magnesium  $D_{\text{Mg}}(T)$  the processes were performed at temperatures  $1100, 1150, 1200$  and  $1250^\circ\text{C}$ . The graph in Figure 2 shows values  $D_{\text{Mg}}(T)$ , obtained as result of processing the experimental data according to the above procedure. As noted, oxygen concentration in the initial Cz-Si was  $\sim (1.2\text{--}1.6) \cdot 10^{17} \text{ cm}^{-3}$ . For comparison the graph shows the temperature dependence of diffusion



**Figure 2.** Temperature dependences of diffusion constant of magnesium in silicon. Symbols correspond to experimental values  $D_{\text{Mg}}(T)$  in Fz-Si [12], in Cz-Si with oxygen concentration  $\sim (3\text{--}4) \cdot 10^{17} \text{ cm}^{-3}$  [11] and  $\sim 1.4 \cdot 10^{17} \text{ cm}^{-3}$  — data of present paper. Solid lines — results of calculation  $D_{\text{Mg}}(T)$  in Fz-Si by formula (1), in Cz-Si by formula (3) with parameters specified in text.

constant of magnesium  $D_{CZ}(T)$  in Cz-Si with oxygen concentration  $\sim (3-4) \cdot 10^{17} \text{ cm}^{-3}$  [11]. Also temperature dependence of diffusion constant of Mg  $D_{FZ}(T)$  in oxygen-free silicon grown by method of floating zone of (Fz-Si) is plotted [12]. The comparison of the experimental data shows that values of diffusion constant in Cz-Si is by several order of magnitude lower than in oxygen-free Fz-silicon. The oxygen concentration decreasing in the initial silicon results in increase in diffusion constant of Mg.

Temperature dependence  $D_{FZ}(T)$  in Fz-Si was determined in [12] as

$$D_{FZ}(T) = D_{0FZ} \exp(-E_{FZ}/k_B T), \quad (1)$$

where  $D_{0FZ} = 5.3 \text{ cm}^2 \text{ s}^{-1}$  — pre-exponential factor,  $E_{FZ} = 1.83 \text{ eV}$  — activation energy of diffusion,  $k_B$  — Boltzmann constant. In paper [11] the parameters of Arrhenius dependence  $D_{CZ}(T)$  in Cz-Si were obtained:  $D_{0CZ} = 7.7 \cdot 10^5 \text{ cm}^2 \text{ s}^{-1}$ , and  $E_{CZ} = 4.1 \text{ eV}$ . Processing of experimental data  $D_{Mg}(T)$  of present paper gives the following values of pre-exponential factor:  $D_0 = 1.7 \cdot 10^6 \text{ cm}^2 \text{ s}^{-1}$  and activation energy of diffusion  $E_m = 4.03 \text{ eV}$ .

Introduction noted that the experimental results of paper [11] were analyzed within the trap-limited diffusion model. The terms „trapping center“ or „trap“ are used to refer a region in crystal, where the potential energy of atoms is lower as compared to energy in the lattice interstitials. Decrease in potential energy in this region can be due lattice distortion by structural defects or interaction with impurities having high affinity for interstitial atoms. For movement in crystal atoms shall overcome the energy barrier  $E_m$  — activation energy of diffusion. For trapping — barrier is same as for movement, but to get free the atoms shall overcome the energy barrier  $E_m + E_B$ , where  $E_B$  — binding energy, additional energy required to escape of the trap.

The traditional approach to describing the diffusion of interstitial impurity atoms in the crystal containing trapping centers is based on solving a system of equations of reaction–diffusion. Under conditions of thermodynamic equilibrium between the trapped and diffusing atoms the system of equations can be reduced to the classical form of diffusion equation with the effective coefficient  $D^*$  [14–16]. The atomic model of diffusion of interstitial atoms in the presence of traps (atomic model of trapping) was developed in [17]. Both these models provide formally same expression for the effective diffusion constant. In the notations of [17] the temperature dependence  $D^*(T)$  can be represented as

$$D^*(T) = \frac{D(T)}{1 + \alpha C \exp(E_B/k_B T)}, \quad (2)$$

where  $D(T)$  — diffusion constant, in crystal without traps.  $\alpha$  — configuration factor.  $C$  — atomic fraction of trapping centers. In some papers, which used dependence (2) to determine  $D^*(T)$ , value  $\alpha \approx 1$  was taken close to unity [18,19].

The exponential term in denominator of formula (2) in model of reaction-diffusion corresponds to ratio of

concentration of atoms captured by traps, to equilibrium concentration of interstitial atoms. In atomic model — to ratio of averaged time of atoms staying on traps to time of free movement in crystal.

From graph in Figure 2 we see the ratio of diffusion constant of Mg in Fz and Cz-Si is several orders of magnitude. So, we can neglect the unity on denominator (2). Then after (1) substitution into (2) the temperature dependence of the diffusion constant of Mg in Cz-Si is expressed as

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

Thus, the binding energy of trapping centers  $E_B$  is equal to the difference in the activation energies of magnesium diffusion in Cz-Si ( $E_m$ ) and in silicon without traps Fz-Si ( $E_{FZ}$ ):  $E_B = E_m - E_{FZ} = 2.2 \text{ eV}$ . Value of atomic fraction of trapping centers is  $\alpha C = D_{0FZ}/D_0 = 3.1 \cdot 10^{-6}$ . In silicon with high concentration of oxygen, which was used in experiments [11] —  $\alpha \cdot C = 6.9 \cdot 10^{-6}$ . Solid lines in graph in Figure 2, passing through points of experimental data, correspond to dependence  $D_{Mg}(T)$  calculated according to formula (3) with above specified parameters.

Concentration of trapping centers in crystal  $N_{TR}$  can be evaluated multiplying value of atomic fraction by number of silicon atoms  $N_{TR} = \alpha \cdot C \times 5.0 \cdot 10^{22} \text{ cm}^{-3}$ . So, for silicon, used in [11],  $N_{TR} \approx 3.5 \cdot 10^{17} \text{ cm}^{-3}$ , and for KEF silicon of this paper  $N_{TR} \approx 1.5 \cdot 10^{17} \text{ cm}^{-3}$ . These values by order of magnitude correspond to oxygen concentrations determined by absorption spectra in different crystals.

As it was noted in [11], value of binding energy  $\sim 2.2 \text{ eV}$  is significantly higher the appropriate energies observed in experiments on slowing down the diffusion of interstitial atoms of other impurities in silicon. Thus, upon formation of donor-acceptor pairs (B-Cu) the binding energy is about  $\sim 0.5 \text{ eV}$  [20]. Value  $E_B \approx 0.9 \text{ eV}$  corresponds to trapping of diffusing interstitial atoms Pb by structural defects in amorphous Si [18].

The trapping centers with binding energy  $\sim 2.3 \text{ eV}$  and concentration  $\sim 1.5 \cdot 10^{17} \text{ cm}^{-3}$  were identified when studying diffusion of interstitial atoms Si in doped by boron superlattices grown by method of molecular-beam epitaxy [19]. By author's opinion such traps can be associated with impurities of oxygen O or carbon C, dissolved in crystal.

## 4. Conclusion

During experiments the temperature dependence of diffusion constant of magnesium  $D_{Mg}(T)$  in Cz-Si with oxygen concentration  $\sim (1.2-1.6) \cdot 10^{17} \text{ cm}^{-3}$  and carbon concentration  $\sim (1.2-1.5) \cdot 10^{17} \text{ cm}^{-3}$  is determined. The results of the present study are compared with the results of paper [11], in which the diffusion of Mg in Cz-Si with oxygen concentration  $\sim (3-4) \cdot 10^{17} \text{ cm}^{-3}$  higher than in this paper is studied. It is shown that the oxygen concentration decreasing in the initial silicon results in increase in value

$D_{\text{Mg}}(T)$ . Concentration of trapping centers determined from experimental value of pre-exponential factors of Arrhenius function for Cz-Si and Fz-Si insignificantly differs from oxygen concentration in materials initial for diffusion. The binding energy of trapping centers is  $\sim 2.2$  eV and coincides within error of measurements with value determined in paper [11]. These factors confirm the assumption that trapping centers of Mg atoms are associated with oxygen dissolved in crystal.

### Conflict of interest

The authors declare that they have no conflict of interest.

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