
NONELECTRONIC PROPERTIES OF SEMICONDUCTORS
(ATOMIC STRUCTURE, DIFFUSION)

Diffusion of Interstitial Magnesium in Dislocation-Free Silicon

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Submitted May 10, 2016; accepted for publication May 18, 2016

Abstract—The diffusion of magnesium impurity in the temperature range $T = 600\text{--}800^\circ\text{C}$ in dislocation-free single-crystal silicon wafers of p -type conductivity is studied. The surface layer of the wafer doped with magnesium by the ion implantation technique serves as the diffusion source. Implantation is carried out at an ion energy of 150 keV at doses of 5×10^{14} and $2 \times 10^{15} \text{ cm}^{-2}$. The diffusion coefficient of interstitial magnesium donor centers (D_i) is determined by measuring the depth of the p - n junction, which is formed in the sample due to annealing during the time t at a given T . As a result of the study, the dependence $D_i(T)$ is found for the first time. The data show that the diffusion process occurs mainly by the interstitial mechanism.

DOI: 10.1134/S1063782617010237

Single-crystal silicon doped with a deep donor impurity of magnesium (Si:Mg) has been studied in view of the development of detectors for the IR (infrared) spectral range [1]. It is known that silicon containing shallow donors can serve as a source of emission in the long-wavelength spectral range [2]. Therefore, of interest are the prospects of also using an admixture of magnesium for this purpose [3]. Si:Mg has been obtained by various methods: growth of crystals from a melt [4], diffusion from the gas phase in a hermetically sealed cell [5], liquid-phase epitaxy [6], the so-called sandwich diffusion technique [7–9], and also ion implantation [10]. In [11], silicon was doped by the deposition of a magnesium film onto the surface of the sample and its subsequent exposure to pulsed laser light and high-temperature heating. At the same time, data on certain parameters important for the technology of Si:Mg are not available. In particular, the diffusion coefficient of magnesium in silicon has not been determined thus far.

Studies of electron paramagnetic resonance (EPR) in Si:Mg and data furnished by absorption spectroscopy in the IR spectral range [7, 8] have shown that the impurity in interstitial positions (Mg_i states) is a double donor with the energy levels $E_c - 0.11$ and $E_c - 0.25$ eV. As follows from the conductivity measurements, Mg_i has a very low solubility ($\sim 10^{15} \text{ cm}^{-3}$). At the same time, the total concentration of Mg in silicon crystals, determined by the atomic-absorption method, can reach a value of 10^{19} cm^{-3} at 1200°C [6]. The authors of [6, 10] suggested that the large difference between the total concentration of magnesium and the concentration of electrically active Mg_i be explained as follows: a magnesium atom at a site (Mg_s) must be a double acceptor (by analogy with Zn in Si),

and, therefore, isoelectronic pairs $\text{Mg}_i + \text{Mg}_s$, making no contribution to the conductivity can be formed.

In [10], Si with implanted Mg was isothermally annealed in the temperature range $450\text{--}950^\circ\text{C}$. The implanted layers were examined by the method of differential conductivity [12] and by secondary-ion mass spectroscopy (SIMS). The first of these made it possible to determine the spatial distribution of electrically active Mg_i centers, whereas the second could find the total concentration of the element. It has been shown that, with increasing annealing duration and temperature, the number of conductivity electrons per centimeter squared in the implanted layer rapidly decreases (whereas for implanted admixtures of Group-III and -V elements, this quantity is known to grow [13]). The study [10] was only concerned with the implanted layer of the semiconductor. The diffusion from this layer has not been studied, presumably because the SIMS installation could not record magnesium concentrations $\lesssim 10^{17} \text{ cm}^{-3}$.

The goal of our study was to examine the diffusion of Mg from the implanted layer and determine the diffusion coefficient of Mg, in the temperature range $T = 600\text{--}800^\circ\text{C}$. We used in our experiments 0.8-mm-thick Si (100) plates cut from dislocation-free p -Si with a resistivity of $450 \Omega \text{ cm}$ (boron concentration of $\sim 3 \times 10^{13} \text{ cm}^{-3}$), grown by the floating-zone method. Mg ions with energies of 150 keV were implanted into the plates at room temperature. We fabricated two sets of samples at irradiation doses of $F = 5.0 \times 10^{14}$ and $2.0 \times 10^{15} \text{ cm}^{-2}$, sufficient for the implanted layer to be amorphized. The samples were annealed in argon or in air in the temperature range of $600\text{--}800^\circ\text{C}$, with heat-treatment durations of 5 min to 5 h.

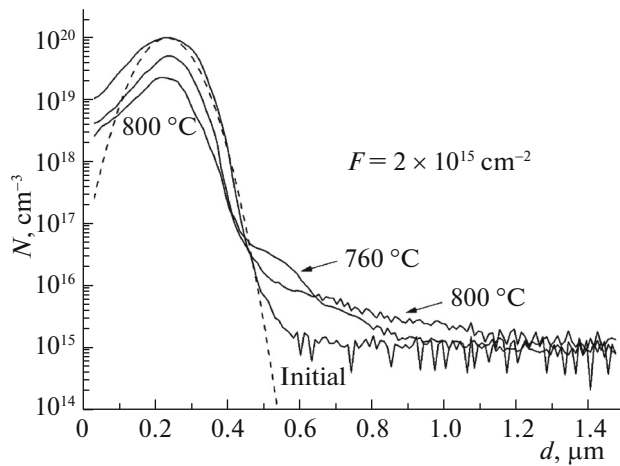


Fig. 1. Mg distribution profiles across the sample thickness at annealing durations of 1 h and annealing temperatures of 760 and 800°C. The dashed line is the Gaussian distribution best describing the initial impurity distribution.

Figure 1 shows the Mg concentration distribution profiles $N(d)$ in the ion-implanted samples. The measurements were made by secondary-ion mass spectroscopy. 9.5-keV O_2^+ ions at a beam current of 600 nA served as probes. The primary beam was scanned to give a $500 \times 500 \mu\text{m}$ raster, with ions entering the analyzer from the center of the crater being sputtered, delimited by a region with a diameter of $120 \mu\text{m}$ to eliminate the contribution of ions sputtered from the crater walls. The intensity of signals associated with positive atomic ions was recorded. The measurements were made in the layer-by-layer analysis mode, i.e., the variation in the ion current corresponding to the given mass of the element was recorded during sample sputtering. The concentration of magnesium was determined by comparison with an implanted reference. The minimum Mg concentration that could be recorded by the installation was $\sim 10^{15} \text{ cm}^{-3}$.

The Mg distribution profile measured in the implanted sample prior to heat treatment is characterized by an average projected range of $R_p \approx 230 \text{ nm}$ and is well described by a Gaussian distribution (Fig. 1). The same figure shows the Mg distributions in the samples annealed for 1 h in an atmosphere of argon at temperatures of $T = 760$ and 800°C .

In the course of annealing, there occurs the recrystallization (solid-phase epitaxial regrowth) of the amorphized region of silicon and the Mg impurity is activated. As a result, Mg atoms diffuse from the surface region into the crystal. It can be seen in Fig. 1 that the maximum impurity concentration in the diffusion-profile region is $N \approx (6-8) \times 10^{16} \text{ cm}^{-3}$.

It is known that the recrystallization of the amorphous layer results in that a region with increased content of structural defects is formed at the interface between amorphous and crystalline silicon: clusters of

interstitial silicon atoms, dislocation loops, and other kinds of defects [13]. These defects can serve as Mg precipitation centers. In addition, the diffusion of magnesium occurs under conditions of an increased concentration of intrinsic silicon defects. Therefore, the diffusion coefficient of magnesium in this region may be significantly different from the values this parameter takes in the bulk of the crystal.

Taking this circumstance into account, we examined in the present study the diffusion coefficient of the Mg_i impurity deep in the crystal. This was possible due to the fact that the implanted layer and the lower lying region of the sample were n -type after annealing, whereas the deeper region remains p -type. The depth of the p - n junctions was determined by the photo-probe method. This was done with samples fabricated as a wedge with an angle of 4° to the implanted surface. The thus measured junction depth was 45 to $220 \mu\text{m}$, depending on the annealing mode.

According to [10], the distribution of the electron concentration within the implanted layer upon annealing is bell-shaped with a maximum that is 3–4 orders of magnitude lower than the total concentration of Mg. In addition, it was mentioned above that the number of electrons in the implanted layer decreases with increasing temperature and annealing duration. This circumstance qualitatively coincides with our measurements of the sheet resistance, made by the four-probe method on the n -type layer formed. According to these data, the conductivity in the layer decreases after heat treatment of the samples. The surface concentration in the diffusion source falls in this process to values of $N_0 \leq 10^{16} \text{ cm}^{-3}$. We believe that the Mg_i distribution in the diffusion layer is close to Gaussian and the diffusion coefficient is given by the expression [12]:

$$D_i = \frac{x_{p-n}^2}{4t \ln[N_0(t)/N_{p-n}]} \quad (1)$$

Here, t is the diffusion time; x_{p-n} is the depth of the p - n junction; $N_{p-n} = 3 \times 10^{13} \text{ cm}^{-3}$ is the concentration of interstitial Mg_i at the interface of the p - n junction.

Figure 2 shows the values of the Mg_i diffusion coefficient, found for various annealing temperatures in the range $T = 600$ – 800°C for samples at irradiation doses of $F = 2.0 \times 10^{15}$ and $5.0 \times 10^{14} \text{ cm}^{-2}$. The straight line represents the analytical dependence obtained by fitting the Arrhenius equation to the experimental data:

$$D_i = 32.0 \exp(-1.98/k_B T), \quad (2)$$

where k_B is the Boltzmann constant and T is temperature (in kelvins).

Thus, we determined in the present study the dependence of the diffusion coefficient of the electrically active magnesium impurity in silicon in the tem-

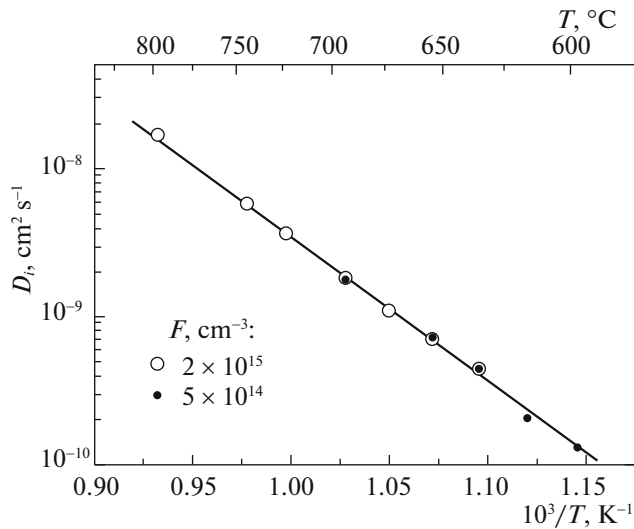


Fig. 2. Temperature dependence of the Mg_i diffusion coefficient in dislocation-free Si. The points represent the experimental data, and the solid line is dependence (2) obtained by fitting the Arrhenius equation to the experimental data.

perature range of 600–800°C. The high diffusion rate of the impurity indicates that the process mostly occurs by the interstitial mechanism. It is noteworthy that the data we obtained refer to propagation of the impurity in the bulk of the dislocation-free crystal. The diffusion rate is substantially lower in the surface region of the semiconductor.

ACKNOWLEDGMENTS

We are grateful to G.Ya. Moskalev (Experimental Design Bureau Planeta, Velikii Novgorod) for performing ion doping.

The study was in part supported by the Russian Foundation for Basic Research, grant no. 14-02-00638.

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Translated by M. Tagirdzhanov