Interaction of Mg with oxygen and carbon in silicon

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Received February 14, 2024
Revised February 27, 2024
Accepted February 29, 2024

A method for determining the solubility of magnesium (Mg) in silicon with oxygen content greater than $3 \cdot 10^{17}\,\mathrm{cm}^{-3}$ is proposed. The method is based on the study the intensity of oxygen absorption band $1106\,\mathrm{cm}^{-1}$ during long-time diffusion annealing of silicon. As a result of optically inactive complex MgO formation, absorption and concentration of O decreases. The difference between O concentration before and after diffusion corresponds to concentration of Mg in the crystal. The Mg solubility in dislociation-free Si at 1250°C equal to $(2.5 \pm 0.19) \cdot 10^{17}\,\mathrm{cm}^{-3}$ is determined. This value coincides with the result obtained earlier by secondary ion mass spectrometry in oxygen-free Si.

Keywords: silicon doping, diffusion, impurity centers.

DOI: 10.61011/SC.2024.02.58359.6028

1. Introduction

The magnesium impurity in silicon forms a double donor center with energy levels E_C — 0.107 eV for neutral Mg_i^0 and E_C — 0.256 eV for a single ionized state Mg_i^+ respectively [1,2]. Such values of the electron binding energy make Si : Mg a promising semiconductor material for creating radiation sources in the middle-wavelength range of the spectrum [3,4]. Recently, a number of new data have also been obtained on the structure of the excited states of Mg_i^0 and on the interaction of Mg atoms with impurities contained in the crystal [4–6].

Electrically active magnesium atoms Mg_i occupy an interstitial position in the silicon lattice. Their concentration reaches $\sim 1.5{-}2 \cdot 10^{15}\,\mathrm{cm}^{-3}$. However, the main part of the atoms of „is neutral“ [7] and it has not yet been definitively established in what state the electrically inactive Mg in Si is.

The maximum solubility value is one of the main characteristics of an impurity in a semiconductor. However, the study of the solubility of magnesium in silicon is complicated by the fact that it excludes the use of electrical methods for determining the concentration of impurities.

The temperature dependence of Mg solubility was studied in Ref. [7]. According to the provided data, the maximum value was reached at a temperature of $T = 1200$°C and was $1.5 \cdot 10^{19}\,\mathrm{cm}^{-3}$. The maximum solubility value at $T = 1287$°C was an order of magnitude less in later paper [8] —$10^{18}\,\mathrm{cm}^{-3}$.

„Metallurgical“ methods for obtaining and analyzing samples of Si : Mg were used in the studies [7,8] — thin films of solid solution were grown by liquid-phase epitaxy (LPE); Mg content was determined by atomic absorption spectroscopy and electron probe microanalysis (EPMA).

The temperature dependence of the solubility of magnesium in silicon during doping by diffusion was studied in Ref. [9] in the range of $T = 1100{-}1300$°C. The Mg concentration was determined by secondary ion mass spectrometry (SIMS). As a result, the maximum solubility value was $2.3 \cdot 10^{17}\,\mathrm{cm}^{-3}$ at 1300°C.

The discussion of the reasons for such a strong (by 2 orders of magnitude) discrepancy in the solubility values of Mg in Si is outside the scope of a brief report. Therefore, the „solubility“ will be understood as the value of the equilibrium concentration of magnesium, which is achieved in the crystal as a result of diffusion by the sandwich method [6,9].

The chemical activity of magnesium and the high mobility of the interstitial Mg atoms suggest its ability to bind to various chemical elements and defects in the silicon lattice [6]. In particular, the interaction of Mg with oxygen results in the formation of the MgO complex. At the same time, the introduction of magnesium by diffusion into silicon containing $3 \cdot 10^{17}\,\mathrm{cm}^{-3}$ oxygen at $T = 1200$°C for 20 h as shown in the experiment in Ref. [10] results in the disappearance of the characteristic absorption band $1106\,\mathrm{cm}^{-1}$, which corresponds to the absorption of atomic oxygen dissolved in the Si lattice.

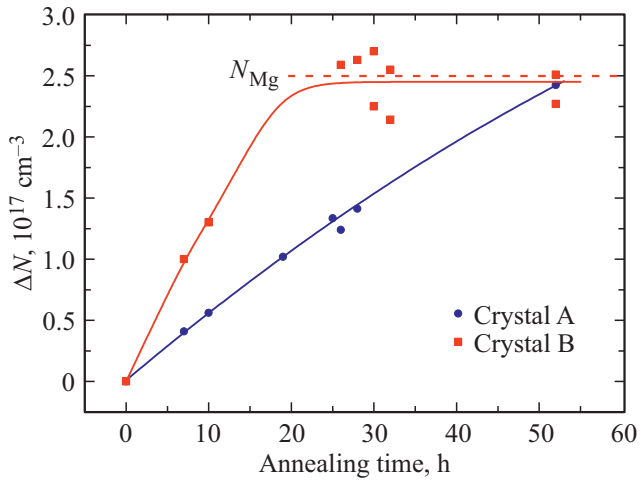
It can be assumed that the interaction of magnesium with oxygen is described by the reaction of formation of an optically inactive complex MgO:

$$\mathrm{Mg} + \mathrm{O} = \mathrm{MgO}. \quad (1)$$

Thus, if silicon with an oxygen concentration higher than the equilibrium magnesium concentration at a given temperature is used for Mg diffusion, then the difference between the initial (N_{ini}) and the residual oxygen concentration (N_{fin}) can be used to determine the concentration of reacted magnesium N_{Mg}

$$N_{\mathrm{Mg}} = N_{\mathrm{ini}} - N_{\mathrm{fin}}. \quad (2)$$

This effect can be used as the basis for the method of determining the magnesium content in a crystal. As far as



Change of the difference concentration of optically active oxygen $\Delta N = N_{ini} - N_{fin}$ depending on the diffusion annealing time.

we know, no studies have been carried out to date related to the study of the conditions of MgO formation, and there is no data on the temperature dependence of the reaction rate (1).

The purpose of this study is to investigate the change of the concentration of optically active oxygen during the diffusion of Mg into Si containing oxygen. Such data will allow evaluating the possibility of using the proposed method to determine the solubility of magnesium in Si at a given temperature.

2. Experimental methods and measurement results

Dislocation-free Si crystals with different oxygen and carbon concentrations were used in these experiments. The crystal A was of the *p*-type with a resistivity of $\rho \approx 20$ Ohms $\cdot$ cm, oxygen concentration of $\sim 3 \cdot 10^{17}$ cm^{-3} and carbon concentration of $\sim 5.7-7.5 \cdot 10^{16}$ cm^{-3}. This crystal had a high uniformity of oxygen concentration over the area of the plates. The crystal B was of *n*-type, $\rho \approx 30$ Ohm $\cdot$ cm, with oxygen concentration of $5.5-6.4 \cdot 10^{17}$ cm^{-3} (about twice as much than in the crystal A) and carbon concentration of $\sim 1.6-3.3 \cdot 10^{16}$ cm^{-3}.

High-purity magnesium (99.995%) was introduced into silicon wafers with a diameter of 30 mm and a thickness of 2 mm by the sandwich method [6,9]. The heat treatment was performed at $T = 1250^\circ$C with a duration of 3–52 h. The ampoules were rapidly cooled in a stream of compressed air after the end of the diffusion process. Control samples of Si (A and B) without Mg were heat treated at the same temperature in a separate ampoule for 26 hours. The temperature of the experiments was chosen in accordance with the values at which the maximum solubility of Mg in Si was observed in the studies in Ref. [7–9].

The concentration of oxygen and carbon was determined at room temperature by the absorption peaks of atomic oxygen 1106 cm^{-1} and carbon 605 cm^{-1} using a Fourier spectrophotometer FSM2201. The spectral resolution of the device was 1 cm^{-1}. The concentration of oxygen and carbon in the Si plates before and after heat treatment was measured in five sites on each plate. The concentration of optically active oxygen and carbon in the control samples did not change after heat treatment.

The results of measurements of the difference concentration of optically active oxygen $\Delta N = N_{ini} - N_{fin}$ as the annealing time increases are shown in the figure. The value ΔN determines the concentrations of magnesium and oxygen that took part in the formation of the MgO complex in accordance with the reaction (1). At the initial stage, the reaction rate for the crystal B is approximately twice as fast as for the crystal A, in which the oxygen concentration is half as low, i. e., the reaction rate linearly depends on the oxygen concentration, in accordance with the formula (1). One of the components (Mg) in the reaction (1) is depleted with an increase of the annealing time, and the value ΔN tends to saturation. This happens after about 20–25 h for crystal B, after about ≥ 50 h for crystal A. The observed saturation takes place when almost all Mg introduced into the crystal has reacted with oxygen. This suggests that the reaction (1) involves all Mg contained in the crystal, and the presence of oxygen does not affect the solubility of Mg in Si.

It should be noted that the carbon concentration after heat treatment did not change in any of the samples, while the carbon absorption band after annealing at $T = 1200^\circ$C disappeared according to [10].

Thus, the average value of the difference oxygen concentration in the saturation region $\Delta N = (2.5 \pm 0.19) \cdot 10^{17}$ cm^{-3}, in accordance with the methodology proposed in this work, can be considered the solubility of magnesium in silicon at a temperature of $T = 1250^\circ$C. This value is in good agreement with the data on the solubility of Mg in Si, which were obtained in Ref. [9]. The solubility value N_{Mg} is marked with a dotted line on the chart.

3. Conclusion

It should be noted that the method used in the work for determining the magnesium content in silicon when it interacts with another optically active impurity (in this case, oxygen) is methodically similar to the study in Ref. [11], where a low concentration of phosphorus was found as a result of the influence of magnesium diffusion on the optical absorption of samples.

This paper studied the kinetics of the interaction of oxygen with magnesium during long-time diffusion annealing of samples and the solubility of Mg in dislocation-free silicon $N_{Mg} = (2.5 \pm 0.19) \cdot 10^{17}$ cm^{-3} at a temperature of $T = 1250^\circ$C. Has been determined this value is in good agreement with the results obtained by introducing Mg by diffusion into oxygen-free Si. The fact that the solubility values measured in oxygen-free silicon and in Si containing

$\sim 7 \cdot 10^{17}\,\mathrm{cm}^{-3}$ of oxygen coincide indicates that oxygen does not affect the solubility of Mg. It is also shown that Mg does not interact with carbon in the crystal.

Acknowledgments

The authors thank L.M. Golovanova for her help in conducting experiments.

Funding

This study has been performed under state assignment 0040-2019-0016.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov