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Electrically inactive magnesium in silicon

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The dynamics of MgO complex formation during magnesium diffusion in Czochralskii-grown silicon with oxygen content of $\sim 3 \cdot 10^{17}\,\mathrm{cm}^{-3}$ has been studied. MgO complexes were found to form only at temperatures above $1100\,^\circ$C. At lower temperatures, magnesium atoms are in a bound state, presumably in the form of particles, or Mg_2Si phase. The formation of complexes occurs after the dissociation of Mg_2Si into Mg and Si at higher temperatures. Thus, the experimental results confirm the assumption that the electrically inactive component of the magnesium content in the crystal is the Mg_2Si compound.

Keywords: silicon doping, diffusion, impurity centers.

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1. Introduction

Behavior of magnesium (Mg) in silicon has certain features. As the element of the second group, Mg must have occupied a site position in a silicon lattice and been a double acceptor. It turned out that electrically-active magnesium occupies an intersite position Mg_i and is a double donor with ionization energy 107 meV for neutral Mg_i^0 and 256 meV for once ionized state Mg_i^+, accordingly [1,2]. Concentration of electrically-active magnesium in the specimens does not exceed $2 \cdot 10^{15}\,\mathrm{cm}^{-3}$. Apart from donor centers Mg_i, the crystal volume also includes an electrically-inactive component of admixture [3], besides, the full concentration of magnesium N_{Mg} considerably exceeds concentration Mg_i. Maximum equilibrium concentration of magnesium that was introduced into silicon in process of diffusion, reached the value of $N_{\mathrm{Mg}} = 2.5 \cdot 10^{17}\,\mathrm{cm}^{-3}$ at temperature $1250\,^\circ$C [4]. Concentration of magnesium in these experiments was determined by the secondary ion mass spectroscopy (SIMS).

The questions on the nature of the electrically-inactive component of magnesium admixture and physical processes, which result in its formation, were discussed in papers [5–7]. One of the potential admixture formations are the pairs (Mg_s-Mg_i), where Mg_s — magnesium atom in the lattice point [6,7]. Besides, the assumption was made on existence of electrically neutral magnesium atoms in a crystal in the form of precipitates Mg_2Si [7]. But so far there exists no clear idea of what the state of the electrically inactive magnesium is.

The objective of this paper is to identify the nature of the electrically inactive component of magnesium admixture in silicon.

To determine the full concentration of magnesium N_{Mg} in the crystall, various methods are used, such as atomic absorption spectroscopy [8] and secondary ion mass spectroscopy (SIMS) [4]. Paper [9] proposed the method to determine equilibrium concentration of Mg, based on the study of how MgO complex is formed as a result of magnesium interaction with oxygen contained in Si. This process is described by reaction

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

Concentration of optically active oxygen at the same time decreases, which results in the change to the intensity of the corresponding light absorption band $1106\,\mathrm{cm}^{-1}$. If silicon with oxygen concentration hígher 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})

$$\Delta N = N_{\mathrm{ini}} - N_{\mathrm{fin}} \quad (2)$$

corresponds to the concentration of reacted magnesium.

This paper studied the effectiveness of MgO complex formation at temperatures $T = 1000-1250\,^\circ$C in the specimens obtained by Mg diffusion into silicon grown by Czochralski method (Cz-Si). It was shown that at temperatures below $1100\,^\circ$C the MgO complexes are not formed. Mg atoms at the same time are in the bound state in the form of Mg_2Si. The assumption was made that the electrically inactive component of magnesium admixture in the crystal is the compound Mg_2Si.

2. Experimental method and measurement results

Silicon doping was performed by „sandwich"-method of diffusion [10]. The plates of non-dislocation Cz-Si

with specific resistivity $\rho \approx 30\,\Omega \cdot \text{cm}$ were used as source 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 Fourier transform spectrometer FSM2201. Oxygen concentration was $\sim 4.0 \cdot 10^{17}\,\text{cm}^3$, and carbon concentration was $\sim 3 \cdot 10^{17}\,\text{cm}^{-3}$. The accuracy of concentration measurement was $\sim 10^{15}\,\text{cm}^{-3}$.

On both sides of plate of the source silicon with diameter ~ 30 mm and thickness ~ 2.0 mm a magnesium film with purity of ~ 99.995 % is sputtered. Then the planes of the specimen with the deposited magnesium were coated with auxiliary silicon wafers $\sim 0.4{-}0.5$ mm thick. Such „sandwich" installed in a quartz cassette is loaded in a quartz tube filled with argon and soldered. Diffusion was carried out at $T = 1000{-}1250\,^{\circ}\text{C}$ for ~ 40 h. Tempering was done by specimen tube cooling in air. Auxiliary silicon wafers were removed by polishing.

To illustrate the method of detection N_{Mg}, Figure 1 shows the dependence of the difference concentration of the optically active oxygen ΔN on the time of diffusion achieved in paper [9] at $T = 1250\,^{\circ}\text{C}$. As diffusion time increases, ΔN increases. Some oxygen participates in formation of MgO and becomes optically inactive, which results in decrease of N_{fin} compared to N_{ini}. The value of the differential concentration reaches its limit value $\Delta N = N_{\text{Mg}}$, when all magnesium introduced in the crystal reacts with oxygen.

If the speed of reaction (1) is proportionate to concentration of Mg, the change ΔN with time is described by the following expression:

$$\Delta N(t) = N_{\text{Mg}}\left[1 - \exp(-t/\tau)\right], \qquad (3)$$

where t — diffusion time, τ — time constant, which defines the speed of reaction (1). In Figure 1 this dependence is shown with a solid line. $N_{\text{Mg}} = 2.5 \cdot 10^{17}\,\text{cm}^{-3}$, $\tau = 12$ h. The dotted line shows the limit value ΔN.

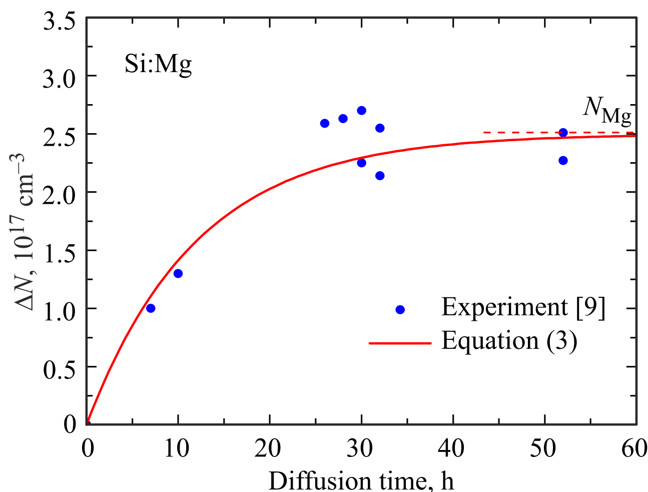

Figure 1. Change of the difference concentration of optically active oxygen ΔN depending on the diffusion time at temperature $T = 1250\,^{\circ}\text{C}$. Symbols correspond to experimental values obtained in [9]. Solid line — calculation using formula (3). Dotted line — limit value $\Delta N = N_{\text{Mg}}$.

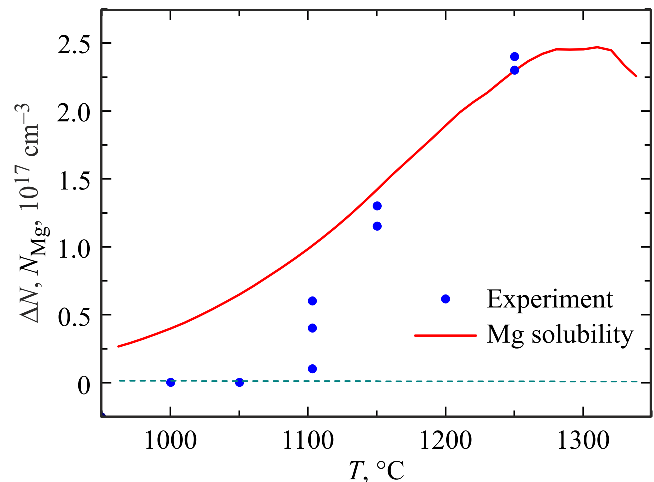

Figure 2. Differential concentration of optically active oxygen ΔN depending on diffusion temperature. The solid line indicates temperature dependence of magnesium solubility in silicon N_{Mg} [4].

Figure 2 presents the experimental values ΔN, measured at various temperatures of diffusion in the range from 1000 to $1250\,^{\circ}\text{C}$. This data corresponds to the residual concentration of oxygen N_{fin}, which was achieved by the moment of process completion. Figure 2 also shows the temperature dependence of the full concentration of magnesium in the crystal N_{Mg}, determined by SIMS method [4]. This dependence is seen as magnesium solubility in silicon — limit equilibrium concentration at this temperature.

At temperature $1250\,^{\circ}\text{C}$ the value ΔN corresponds to magnesium solubility in Si. Duration of the diffusion process in this case was sufficient to achieve the limit value of differential concentration. At $T = 1150\,^{\circ}\text{C}$ the value ΔN is slightly below solubility of Mg. Temperature decrease causes slower reaction speed (1). Therefore, more time is required to achieve the limit value ΔN. At temperatures $\sim 1000{-}1100\,^{\circ}\text{C}$ an abnormality is observed in dependence $\Delta N(T)$. Values of the differential concentration of oxygen at temperatures is lower than $T < 1100\,^{\circ}\text{C}$, are equal to zero — $\Delta N = 0$. In this region of temperatures no MgO is formed. At $T = 1100\,^{\circ}\text{C}$ the sharp increase of ΔN occurs. A significant spread of the values is probably related to sharp increase in the speed of reaction (1), and to the error in the experiment temperature detection. Process duration at $T = 1100\,^{\circ}\text{C}$ was also insufficient to achieve the limit value $\Delta N = N_{\text{Mg}}$.

3. Discussion

To explain the obtained experimental results, the assumption was made that magnesium in the region of temperatures below $1100\,^{\circ}\text{C}$ is in the bound state and does not react with oxygen. Such position may occur when magnesium

silicide is formed. An indirect confirmation of existence of either particles or phase of this substance in silicon is the value of temperature $\sim 1100\,^{\circ}$C, at which the sharp growth ΔN is observed. Only one compound may be formed in Si : Mg — Mg_2Si, liquidus in the melting point of which has a smooth maximum at temperature $1102\,^{\circ}$C [11]. At higher temperatures Mg_2Si dissociates to Mg and Si, and it becomes possible to form MgO complex as a result of reaction (1).

However, the question about formation of Mg_2Si in process of diffusion remains open. Thus, the magnesium solubility in silicon in the temperature range $1000-1100\,^{\circ}$C is $4.0 \cdot 10^{16}-1.0 \cdot 10^{17}\,\mathrm{cm}^{-3}$. If the interaction of magnesium atoms and interstitial silicon atoms forms particles Mg_2Si, the equilibrium concentration of interstitial silicon atoms $C_{\mathrm{I}}^{\mathrm{eq}}$ must be at least twice less and amount to $(2-5) \cdot 10^{16}\,\mathrm{cm}^{-3}$. However, the literature data obtained by different methods corresponds to values $C_{\mathrm{I}}^{\mathrm{eq}} \approx 10^{12}-10^{14}\,\mathrm{cm}^{-3}$ in the studied temperature range [12]. Only one publication [13] reports the value $C_{\mathrm{I}}^{\mathrm{eq}} \approx (1-5) \cdot 10^{16}\,\mathrm{cm}^{-3}$ at $T = 1000\,^{\circ}$C. Concentration of internal defects in this paper was determined by comparison of linear expansion ratios in silicon specimens determined from the difference between the macroscopic linear thermal expansion and the lattice-parameter thermal expansion.

4. Conclusion

The paper studied the dynamics of MgO complex formation in process of Mg atom interaction with oxygen dissolved in Cz-Si. It was found that in the temperature range $T = 1000-1100\,^{\circ}$C the magnesium atoms are in bound state and do not participate in the reaction (1). The assumption was made that such state occurs when magnesium silicide Mg_2Si is created. At higher temperatures $T > 1100\,^{\circ}$C Mg_2Si dissociates to Mg and Si, and it becomes possible for the reaction to take place (1).

It would be natural to assume that in oxygen-free silicon grown by the method of zone melting (Cz-Si), the same processes of Mg bound state formation take place. It means after diffusion in process of Si : Mg specimen cooling as temperature $\sim 1100\,^{\circ}$C and below is achieved, the interstitial atoms of magnesium in the crystal may form Mg_2Si compound. Depending on the speed of cooling and speed of silicide formation, móst atoms Mg will end up in the bound state. That part of atoms which failed to participate in the formation of Mg_2Si while the crystal was cooled down, will stay in the interstices and will be electrically-active at low temperatures.

Therefore, electrically inactive magnesium in silicon at $T < 1100\,^{\circ}$C is in the form of Mg_2Si. To form such compound, concentration of interstitial silicon atoms must be $(2-5) \cdot 10^{16}\,\mathrm{cm}^{-3}$.

Conflict of interest

The authors declare that they have no conflict of interest.

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