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Solubility of magnesium in silicon

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The solubility of impurity magnesium, which was introduced by diffusion in the temperature range of 1100−1300°C in silicon, is studied by secondary-ion mass spectrometry. It is demonstrated that, with the electrically inactive impurity component taken into account, the maximum solubility of magnesium in silicon is 1−2 orders of magnitude lower (and the diffusion coefficient is higher) than the values reported earlier.

Keywords: silicon, doping, magnesium impurity, solubility.

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1. Introduction

It is typical of certain impurities in silicon (Zn, Cu, etc.) to combine a high diffusion coefficient with low solubility. Magnesium, which behaves in a rather complex way in silicon, also belongs to this group of impurities, and it is of practical and academic interest to determine the indicated parameters in silicon. One could expect Mg, which is a group 2 element, to be positioned at Si lattice sites in silicon and act as a double acceptor (just as Be or Zn). However, it was found in [1] that magnesium is a double donor (with ionization energies of 0.1068 and 0.2534 eV), is positioned at interstitial sites, and features a very low solubility of $\sim 10^{15}\,\mathrm{cm}^{-3}$. Only two studies [2,3] into the solubility of Mg in Si have been published to date. The results reported in them differ by almost an order of magnitude. The procedure of preparation of samples containing Mg in Si in these studies was essentially the same: a magnesium layer was deposited between two silicon wafers, and a liquid section with a thickness of $\sim 0.2\,\mu$m, which formed in the region of temperature gradient after magnesium melting, moved toward the wafer with a higher temperature.

The experiments in [2] were performed in the temperature interval of 940−1200°C. Epitaxial films of a Si:Mg solid solution with a thickness of $\sim 10\,\mu$m were obtained. They were examined by sequential etching of ~ 1-μm-thick layers, which had their composition analyzed by atomic absorption spectroscopy (AAS). The results of this analysis revealed that the limit of solubility of Mg in Si is $\sim 10^{19}\,\mathrm{cm}^{-3}$ at 1200°C; it was also demonstrated that the concentration of magnesium in layers is nonuniform. It was noted that the concentration of electrically active magnesium in these layers did not exceed $10^{15}\,\mathrm{cm}^{-3}$, which is in line with the data from [1]. It should be stressed that the state of electrically inactive Mg in Si was not determined.

The authors of [3] prepared layers of a Si:Mg solid solution with a thickness of $165\,\mu$m in the 1100−1350°C temperature interval. Their composition was examined by electron probe microanalysis (EPMA), and the maximum solubility of Mg in Si was found to be on the order of $10^{18}\,\mathrm{cm}^{-3}$ (i.e., an order of magnitude lower than the one in [2]). This discrepancy was attributed in [3] to the presence of magnesium clusters in layers of the solid solution in [2]; presumably, these clusters affected the detected amount of magnesium and thus led to an erroneously high solubility value. However, micrometer-scale inclusions, which are probably attributable to the use of insufficiently pure (99%) magnesium, are also seen in Fig. 2 in [3]. This indicates that the results reported in [3] may be inaccurate as well.

The aim of the present study is to determine the temperature dependence of solubility of Mg in Si. Following [4], we introduced magnesium into silicon by diffusion doping using the sandwich method [1]. The regime of prolonged diffusion with subsequent rapid cooling of samples was set. In our view, doping performed this way eliminates the possibility of formation of magnesium clusters in samples. It is worth noting that the solubility of an impurity in a crystal in equilibrium at a certain temperature does not depend on the method of preparation of a solid solution. This is the reason why the diffusion doping technique was used to determine the solubility of a number of impurities in silicon.

2. Experimental procedure

The time to an equilibrium magnesium distribution in a sample depends on the impurity diffusion coefficient at the temperature of the experiment. The majority of experiments were performed (as in [4]) with the use of flow-zone (FZ) dislocation-free *n*- and *p*-type silicon with a resistivity of $(8-10) \cdot 10^3\,\Omega \cdot \mathrm{cm}$ and an oxygen and carbon

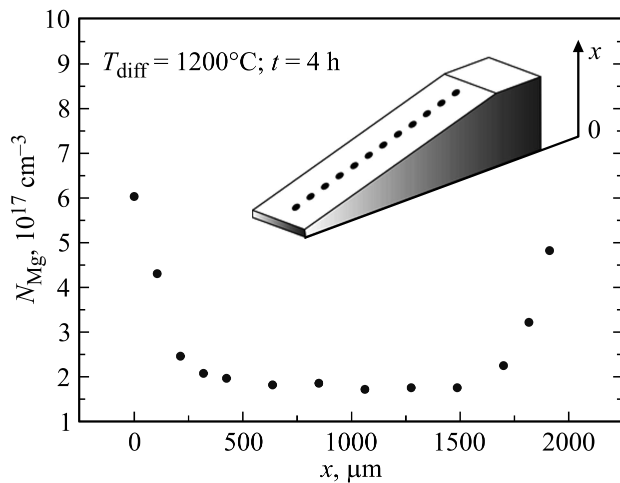

Figure 1. Depth distribution of the total magnesium concentration within a doped silicon wafer. These data were obtained using a wedge-shaped sample (see the inset).

concentration of $\leq 1 \cdot 10^{15}$ cm^{-3}. It was noted in [5] that the coefficient of diffusion of electrically active magnesium in dislocated silicon is considerably higher than the one corresponding to dislocation-free silicon. Therefore, crucibleless silicon with a dislocation density of $(3-4) \cdot 10^4$ cm^{-2} was also used in the present study.

High-purity (99.99–99.995%) magnesium was introduced into silicon wafers with a diameter of 30 mm and a thickness of 1.6–2 mm. Wafers coated with magnesium were held securely between two auxiliary silicon wafers and subjected to thermal processing in sealed quartz ampoules filled with an inert gas. This thermal processing was performed at 1100–1300°C over a long-term period of time; upon its completion, the ampoules were removed from a furnace and cooled by a compressed air flow. Auxiliary silicon wafers were then removed by grinding.

In order to measure depth distribution $N_{Mg}(x)$ of the total magnesium concentration, rectangular samples were cut out from wafers and shaped into wedges with a slope angle of 12° with respect to the initial plane. The wedge surface was polished. Total concentration N_{Mg} of electrically active and inactive magnesium in samples was determined by secondary-ion mass spectrometry (SIMS). To obtain $N_{Mg}(x)$ dependences, a series of concentration measurements with pitch $\Delta d \sim 1$ mm were performed at different points on the wedge surface (see the inset of Fig. 1, which shows the diagram of experiments).

The probing beam was formed by O_2^+ ions with an energy of 9.5 keV; the beam current was 600 nA. The flux of primary ions was expanded into a raster pattern $500 \times 500\,\mu$m^2 in size on the sample surface. Secondary ions entered the analyzer from the center of a sputtered crater bounded by a region 120 μm in diameter. The intensity of the signal of positively charged Mg ions was recorded. The magnesium concentration was determined by comparing the measurement results to the data for a reference sample prepared by implantation. The minimum concentration of magnesium in silicon detected by the setup was $\leq 10^{16}$ cm^{-3}.

3. Experimental results and their analysis

Figure 1 presents the typical distribution of magnesium concentration over the thickness of a sample prepared by diffusion doping of dislocated Si with magnesium within 4 h at 1200°C. According to the obtained data, the profiles of total concentration of magnesium in the examined samples are U-shaped (this profile shape is also typical of Au and Zn in silicon; see, e.g., [6,7]). The profiles of electrically active interstitial magnesium measured using the differential conductivity method are characterized by the complementary error function. This provided an opportunity to determine [4,5,8] the diffusion coefficient of electrically active magnesium in the temperature interval of 600–1200°C.

The magnesium concentration is $\geq 10^{18}$ cm^{-3} in layers adjacent to the wafer surface and decreases rapidly, forming an impurity distribution that is uniform over the sample thickness in the central section of the profile (plateau). The depth distribution of magnesium was examined in the present study in more than 50 samples; i.e., the net analyzed area was ≥ 5 mm^2. None of these experiments revealed any nonuniformities of the magnesium distribution at the „plateau“ (e.g., concentration spikes of at least 10%). This implies that no significant magnesium precipitates (clusters) are present even in dislocated silicon. U-shaped profiles were established in less than 1 h even at a relatively low temperature of 1000°C. This is indictive of the fact that, with the electrically inactive component taken into account, the coefficient of magnesium diffusion in silicon is much higher than the „effective“ diffusion coefficient of electrically active interstitial magnesium [4,5,8] and is probably close to the diffusion coefficient of lithium in silicon. Magnesium diffuses from the surface over interstitial sites deeper into the wafer and forms electrically inactive complexes in the process.

With this high diffusion coefficient of magnesium taken into account, the duration of thermal processing of the samples was set to 22 h for dislocation-free silicon and 1–7 h for dislocated silicon. Note that the concentration at the „plateau“ inside the sample (see Fig. 1) does not change if the duration of thermal processing is increased further. Therefore, this value was assumed to be the solubility at a given temperature.

The magnesium solubility data obtained for a number of silicon doping temperatures are denoted by squares in Fig. 2. The experimental data from [2,3] are presented in the same figure. It can be seen that the solubility values in the present study are 1–2 orders of magnitude lower than the ones reported in [2,3]. In our view, this is attributable to the use of a doping technique that does not produce a noticeable amount of magnesium (or magnesium silicide)

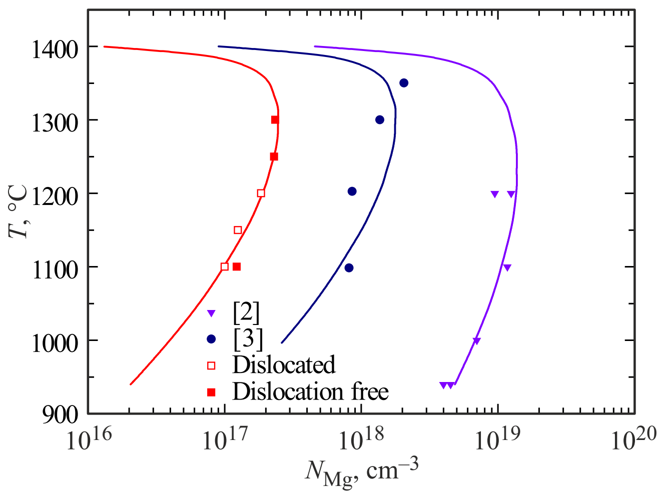

Figure 2. Solubility of magnesium in dislocation and dislocation-free silicon (data from the present study) and the results reported in [2,3]. Symbols dente experimental data. Solid curves represent the temperature dependences of solubility of Mg in Si obtained by processing the experimental data (see text).

clusters in the bulk of samples. The lack of inclusions, which could potentially distort the results of determination of the magnesium solubility, in the bulk of samples is evidenced by the fact that the SIMS signal does not deviate in any significant way from smooth spatial distributions observed in the examination of dozens of samples. Note also that the values of impurity solubility in dislocated and dislocation-free silicon agree with each other.

In a binary system, the solubility curve of an impurity in a wide temperature range may be obtained based on the experimentally determined solubility values in a certain region of T and data on the equilibrium diagram of the system. The equilibrium impurity concentration in a crystal at a given T may be characterized by distribution coefficient k, which is the ratio of impurity concentration N_S in the solid phase to concentration N_L of this element in the liquid phase at the same temperature.

The first experimental data on magnesium concentration N_{Mg} in silicon at different T have been obtained in [2]. Using the known equilibrium diagram of the Mg–Si system and the experimental N_{Mg} values, the author of this study calculated k in the 900–1200°C temperature range. It was demonstrated in [9,10] that the temperature dependence of the distribution coefficient may be written as

$$\ln k = \Delta S^{ex}/k_B - \Delta H/k_B T,$$

where ΔH is enthalpy of solution, ΔS^{ex} is the entropy of mixing, T is temperature, and k_B is the Boltzmann constant.

Thus,

$$k = \frac{N_S}{N_L} = C\exp(-\Delta H/k_B T), \quad (1)$$

where $C = \exp(\Delta S^{ex}/k_B)$.

Parameters of temperature dependences (1) for distribution coefficient k of magnesium in silicon that were determined by linear approximation of $\ln k$ values as functions of reciprocal temperature

According to study	C	ΔH, eV	k_m	N_{max}, cm^{-3}
[2]	1.16	0.9	$2.3 \cdot 10^{-3}$	$1.25 \cdot 10^{19}$
[3]	56.8 ± 15	1.69 ± 0.05	$4.9 \cdot 10^{-4}$	$2.06 \cdot 10^{18}$
This study	6.3 ± 0.6	1.66 ± 0.01	$6.9 \cdot 10^{-5}$	$2.35 \cdot 10^{17}$

Figure 3 presents temperature dependences k $(1000/T)$ of the distribution coefficient calculated with the use of experimental N_{Mg} values from [2,3] and the data from the present study. The equilibrium diagram of the Mg–Si system [11] was used to determine concentration N_L of magnesium atoms in the liquid phase.

Straight lines correspond to the k $(1000/T)$ dependences calculated in accordance with formula (1). The values of C and ΔH, which were used to characterize the experiments [3] and our results, were determined by linear approximation of experimental values of $\ln k$ as functions of $(k_B T)^{-1}$. Such an approximation for experiments [2] was performed with the use of the ΔH value indicated in the paper, and the value of C was determined in accordance with the best fit between the experimental data and the calculated dependence for coefficient k. The corresponding parameters used in approximation of the temperature dependence of the distribution coefficient are listed in the table. Distribution coefficients k_m, which correspond to the melting point of silicon ($T_m = 1408$°C), and the maximum values of impurity concentration N_{max} are also given there.

The temperature dependence of solid solubility of magnesium in silicon may be calculated with the use of formula (1) with the corresponding parameters C, ΔH

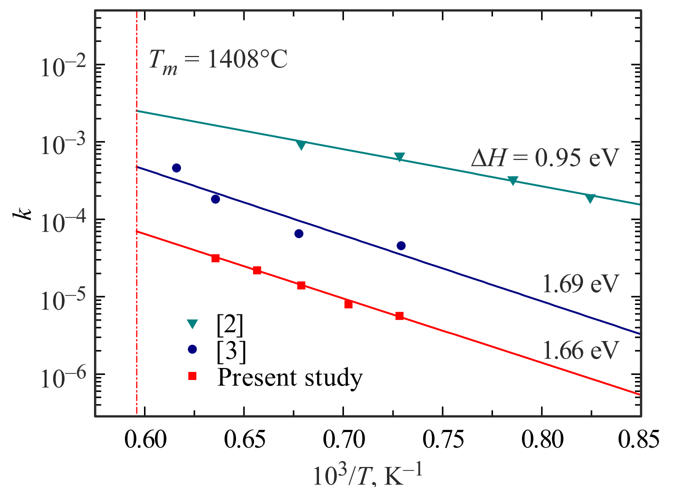

Figure 3. Temperature dependences of the distribution coefficient of Mg in Si determined in the present study and in [2,3].

and the equilibrium diagram of the Mg−Si system [11]. Therefore, relation $N_{\mathrm{Mg}}(T) = N_L(T)k(T)$ characterizes the concentration of dissolved magnesium. The results of these calculations for all three data sets are represented by solid curves in Fig. 2.

The obtained results suggest that the values corresponding to the temperature dependence of solubility of calcium in silicon in [2,3], which were obtained using the same doping technique, are also significantly overestimated.

4. Conclusion

1. The temperature dependence of solubility of magnesium in a silicon sample, which was prepared by introducing Mg in such a way that prevents the formation of magnesium clusters, was determined experimentally. The obtained solubility values are $\sim 1{-}2$ orders of magnitude lower than the available literature data.

2. The coefficient of diffusion of magnesium in silicon determined with the electrically inactive component taken into account is several orders of magnitude higher than the „effective" coefficient of diffusion of the electrically active component.

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Conflict of interest

The authors declare that they have no conflict of interest.

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