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ELECTRODIFUSION OF MANGANESE ATOMS IN SILICON

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The paper describes the research and study of the process of electrically induced diffusion of Mn atoms in silicon directly from a *Si* surface layer that was preliminarily enriched with *Mn*. To ensure the so-called electrically induced diffusion process, a constant electric field was applied to the investigated samples. It has been revealed that as a result of the diffusion of *Mn* impurity atoms into samples placed at the negative pole of the electrical diffusion unit, the proportion of *Mn* atoms was 75.4% (relative to silicon atoms), while in samples placed at the positive pole this indicator tended to be 2.7% (relative to silicon atoms). Besides that, for the first time, an experimental increase in the electro-active concentration of *Mn* impurity atoms in silicon (at $T = 900°C$) was detected under the influence of an external constant-value electric field. In this case, the maximum solubility of impurity atoms of *Mn* at a temperature of $T = 900°C$ was $N_{Mn}{\sim}2.27{\cdot}10^{14}\ cm^{-3}$, while the average concentration of electro-active *Mn* atoms diffused into silicon under the influence of an external constant electric field reached $N_{Mn}^{*}{\sim}2.62{\cdot}10^{14}\ cm^{-3}$.
Keywords: *Resistivity; Silicon; Impurity atoms; Diffusion; Mobility of charge carriers; Concentration of charge carriers; Electrically induced diffusion*
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1. INTRODUCTION

Over recently, of great interest to many researchers in the field of semiconductor physics was the issue of engineering fundamentally novel materials by modifying the functional parameters of semiconductors, especially *Si* [1,2]. One of the most promising ways appears to be the technique of engineering of binary compounds of type *III-V* and *II-VI* in the bulk matrix of *Si* material [3,4,5,6,7] and on its surface alike [8,9,10,11]. However, in times of creating compounds of type *II-VI* in the silicon crystal lattice, due to the insufficient solubility ratio of elements of groups *II* and *VI* in the *Si* material ($\sim10^{15}\div10^{18}$), it is almost impossible to prove the phenomenon of a significant change in the functional parameters of *Si* by using the existing instrumentation. In this regard, a significant increase in the solubility of impurity atoms in a *Si* crystal has both scientific and practical significance.

The authors of the study expect that using the proposed technique of electrically induced diffusion, it would be possible not only to increase the solubility of impurity atoms in silicon, but also to theoretically increase the diffusion coefficients of impurity atoms in silicon under the influence of an external electric field. This could help not only to increase the solubility of elements of groups *II* and *VI* in silicon, but also to boost diffusion coefficients of elements of groups *III* and *V* in silicon, which are traditionally characterized by comparatively low diffusion coefficients, but quite a high ($\sim10^{18}\div10^{21}$) solubility [12-15].

This paper presents the results of elemental analysis and studies of the electrical parameters of silicon samples doped with *Mn* impurity atoms under the influence of an external electric field.

2. MATERIALS AND METHODS

Silicon wafers of *p*-type conductivity ($\rho \sim 5\ \Omega{\cdot}cm$; $N_B \sim 5{\times}10^{15}\ cm^{-3}$) were the starting material. Samples sized $1{\times}5{\times}10\ mm^3$ were cut from the wafers using an *STX-402*-type diamond cutter. Surfaces of the silicon samples were chemically cleaned with *HF* acid. Manganese atoms (purity 99.999%) were deposited onto the surface of the samples using a *VUP-4* vacuum deposition unit, after which thin layers of manganese were formed on the surfaces of the samples. 2 silicon samples with thin layers of *Mn* were placed into the electrical diffusion unit with thin layer surfaces facing each other. In this case, one of the samples was placed at the positive pole side of the electrical diffusion unit, and the other - at the negative one.

The investigated samples were divided into 3 groups:

Group I consisted of silicon samples with thin layers of manganese on the surface, which were placed at the positive pole of the electrical diffusion unit;

Group II consisted of silicon samples with thin layers of manganese on the surface, which were placed at the negative pole of the electrical diffusion unit;

Group III consisted of samples with thin layers of manganese on the surface, which were placed in an evacuated quartz ampoule for diffusion in a furnace.

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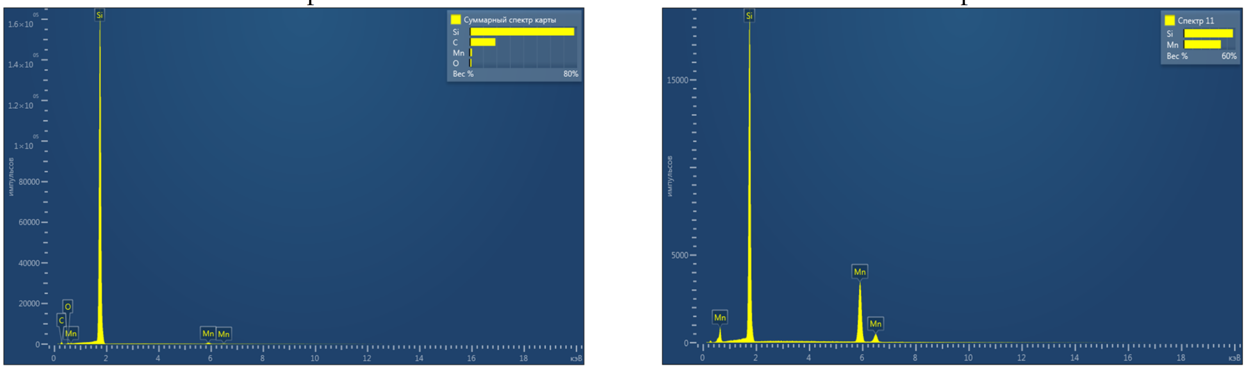
In samples of groups I and II, the process of electrically induced diffusion was carried out by ensuring the flow of a direct current with density of 50÷100 A/cm^2. Due to the presence of electrical resistance at the points of contact of the samples, the samples normally heat up. The heating temperature can be controlled by adjusting the electric current value. The temperature resulting from the flow of electric current in the samples during the experiment was T = 900°C.

In samples of group III, diffusion was carried out in a diffusion furnace at a temperature of 900°C.

After electrically induced diffusion, elemental analysis of samples of groups I and II was carried out using a *JSM-IT 200* scanning electron microscopes [16] (Fig. 1).

Group I Group II



a) *b*)

Element	Type of curve	Weight %	Sigma weight %
Si	K series	77.89	0.20
C	K series	18.95	0.20
Mn	K series	2.1	0.50
O	K series	1.06	0.50
Total:		100.00	

Element	Type of curve	Weight %	Sigma weight %
Si	K series	57.01	0.20
Mn	K series	42.99	0.20
Total:		100.00	

Figure 1. Elemental analysis of a silicon sample with Mn impurity atoms using the electrically induced diffusion method: *a*) sample belonging to the group I (sample placed at the positive pole of the electrical diffusion unit); *b*) the group II sample (sample placed at the negative pole of the electrical diffusion unit)

The profiles of distribution of impurity atoms across the depth received in the course of a layer-by-layer chemical etching of samples of groups I, II and III, were studied using the Hall effect measurement unit *HMS-3000* from ECOPIA [17] (Fig. 2).

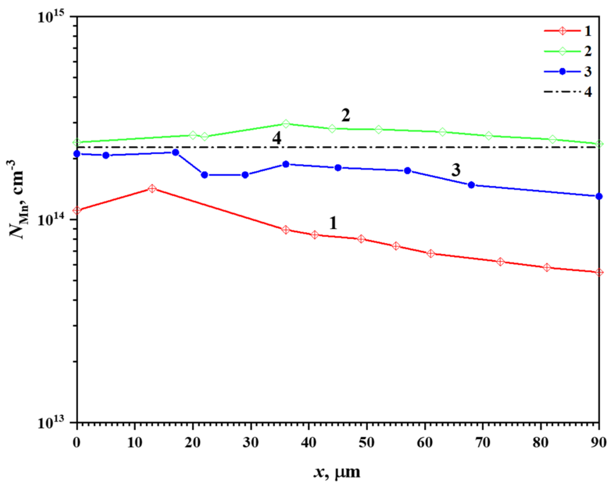


Figure 2. Distribution profile across the depth of impurity atoms of manganese in samples belonging to groups I, II and III: curve 1 - group I; curve 2 - sample of group II; curve 3 - sample of group III; curve 4 reflects the maximum solubility of manganese impurity atoms in silicon at a temperature of 900°C.

3. RESULTS AND DISCUSSION

3.1. Analysis of the SEM-investigation results

Figures 1-*a*) and 1-*b*) show elemental analyzes of samples placed at the positive and, accordingly, negative poles at a constant electric field. Tables *a*) and *b*) provide numerical elemental analysis data for the samples shown in Figures 1*a*) and 1*b*), respectively. From Figure 1 and the table it is clear that manganese atoms appear to have penetrated more towards the sample placed at the negative pole at a constant electric field. Moreover, in tables *a*) and *b*), when calculating using the formula for the weight of manganese atoms relative to silicon atoms, it was established that in silicon samples placed at the negative pole of the electrical diffusion unit, the fraction of manganese atoms appears to be 75.4%, while in silicon samples placed at the positive pole, this figure was 2.7%.

3.2. Analysis of electrophysical parameters

The Figure 2 proves that the concentration of impurity atoms of manganese in the group II sample placed at the negative pole of the electrical diffusion unit, noticeably exceeds the concentration of impurity atoms of manganese in samples belonging to groups III and I. In this case, the average concentration of electro-active manganese atoms in samples of group I was $N_{Mn}^{I}\sim 8.23\cdot 10^{13}$ cm^{-3}, the average concentration of electro-active manganese atoms in samples of group II was $N_{Mn}^{II}\sim 2.62\cdot 10^{14}$ cm^{-3}, the average concentration of electro -active manganese atoms in samples of group III was $N_{Mn}^{III}\sim 1.78\cdot 10^{14}$ cm^{-3}, and the maximum solubility of impurity Mn atoms at a temperature of $T = 900$°C was $N_{Mn}\sim 2.27\cdot 10^{14}$ cm^{-3}.

The diffusion coefficient of impurity atoms of manganese in silicon at a certain temperature is determined using the equation (1), the solubility is determined using the equation (2).

$$D_{Mn}(T) = 2.6\cdot 10^{-1}\cdot \exp\left(-\frac{1.3}{k\cdot T}\right) \tag{1}$$

$$N_{Mn}(T) = 2.5\cdot 10^{23}\cdot \exp\left(-\frac{2.1}{k\cdot T}\right) \tag{2}$$

The Table 1 proves that the maximum solubility of manganese atoms at a temperature of $T = 900$°C is $2.27\cdot 10^{14}$ cm^{-3}. However, the concept of solubility is applicable to the grand total concentration of both electro-active and non-electro-active manganese atoms.

Table 1. Diffusion coefficients and solubility of impurity atoms manganese in silicon at a given temperature

T, °C	700	750	800	850	900	950	1000
$D_{Mn}(T)$	$4.65\cdot 10^{-8}$	$9.94\cdot 10^{-8}$	$1.98\cdot 10^{-7}$	$3.7\cdot 10^{-7}$	$6.58\cdot 10^{-7}$	$1.11\cdot 10^{-6}$	$1.81\cdot 10^{-6}$
$N_{Mn}(T)$	$3.15\cdot 10^{12}$	$1.07\cdot 10^{13}$	$3.27\cdot 10^{13}$	$9.01\cdot 10^{13}$	$2.27\cdot 10^{14}$	$5.33\cdot 10^{14}$	$1.17\cdot 10^{15}$

An analysis of the reference data showed that impurity atoms of manganese in silicon normally create 3 energy levels in silicon (2 donor levels with the values $E_c = -0.12$ and $E_c = -0.41$ eV and 1 acceptor level with the value $E_v = +0.32$ eV) [18,19,20]. Impurity atoms of manganese could be present in a silicon matrix in the form of a Mn^- ion (adding one electron), a neutral Mn^0 atom without having to add or donate one electron, a singly positively charged Mn^+ ion with the transfer of one electron, and a doubly positively charged ion Mn^{++}. The total concentration of impurity atoms of manganese in silicon is determined by formula (3):

$$N_{Mn}^{total} = N_{Mn^-} + N_{Mn^0} + N_{Mn^+} + N_{Mn^{++}} \tag{3}$$

However, using the Hall measurement method, only the concentration of electro-active atoms of Mn can be determined. Therefore, in this study, provided that impurity atoms of Mn presumably have compensated impurity atoms of boron in silicon, so the authors have determined only the sum of the concentrations of Mn^+ and Mn^{++} ions (the concentration determined from Fig. 2 is equal to the sum of concentrations).

CONCLUSION

Thus, it can be assumed that the Mn^+ and M^{++} ions most probably migrate towards the negative pole of the electrical diffusion unit both under the influence of temperature and under the influence of an external constant electric field, while the Mn^- ions both under the influence of temperature and under the influence of external constant electric field seem to migrate towards the positive pole of the electrical diffusion unit. Behavior of neutral Mn^0 atoms is not affected by the external electric field, however neutral atoms appear to diffuse into the sample under the influence of temperature.

The experimental results showed that in the sample placed at the negative pole of the electrical diffusion unit, the concentration of electroactive impurity atoms of Mn tended to increase under the influence of an external constant electric field. These results were also confirmed by SEM analysis.

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ЕЛЕКТРОДИФУЗІЯ АТОМІВ МАРГАНЦЮ В КРЕМНІЇ

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У статті описано дослідження та дослідження процесу електроіндукованої дифузії атомів *Mn* у кремнії безпосередньо з поверхневого шару *Si*, попередньо збагаченого *Mn*. Для забезпечення так званого процесу електроіндукованої дифузії до досліджуваних зразків прикладали постійне електричне поле. Виявлено, що в результаті дифузії атомів домішки Mn в зразки, розміщені на негативному полюсі електродифузійної установки, частка атомів *Mn* становила 75,4% (відносно атомів кремнію), а в зразках, розташованих на позитивному полюсі полюсу цей показник мав тенденцію до 2,7% (відносно атомів кремнію). Крім того, вперше експериментально виявлено збільшення електроактивної концентрації атомів домішки *Mn* у кремнії (при $T = 900°C$) під впливом зовнішнього постійного електричного поля. При цьому максимальна розчинність домішкових атомів *Mn* при температурі $T = 900°C$ становила $N_{Mn}{\sim}2{,}27{\cdot}10^{14}$ $см^{-3}$, а середня концентрація електроактивних атомів *Mn* дифундувала в кремній під впливом зовнішнього постійне електричне поле досягло $N_{Mn^*}{\sim}2{,}62{\cdot}10^{14}$ $см^{-3}$.

Ключові слова: *питомий опір; кремній; домішкові атоми; дифузія; рухливість носіїв заряду; концентрація носіїв заряду; електрично індукована дифузія*