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Effect of the diffusion temperature on interaction of clusters with impurity atoms in silicon

Z.M. Saparniyazova, K.A. Ismailov, A.K. Uteniyazov, Kh.U. Kamalov

Karakalpak State University named after Berdakh,
Uzbekistan, Republic of Karakalpakstan, 230012 Nukus, Abdirov str., 1
E-mail: mzlixa@mail.ru

Abstract. In this paper, the results of studies of the effect of the diffusion temperature on interaction of clusters of manganese atoms with the sulfur ones have been presented. It has been shown that the electrical parameters of the samples simultaneously doped with sulfur and manganese completely coincide with the parameters of the initial material, *i.e.* as if they do not contain not only sulfur and manganese, but also thermodonors are not formed. The obtained results make it possible to exclude the possibility of gettering of impurity atoms or formation of some kind of solid solutions, if taking into account the impurity atoms of manganese and sulfur, which complicates their diffusion in the crystal bulk. It has been established that for the initial *p*-type silicon with the resistivity close to $\rho \sim 10\ \Omega\cdot$cm, the diffusion temperature of 1100 °C is the most optimal one to form clusters with the maximum participation of the introduced sulfur and manganese atoms.

Keywords: silicon, impurity, diffusion temperature, sulfur and manganese atoms.

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1. Introduction

As known [1–4], the elements of Group VI (S, Se) in silicon play the role of donor impurities. In the lattice, they can exist in different states S, S_2 (S^+, S^{++}) Se, $(Se)_2$, $(Se)_4$ and $(Se)_6$, Te_2, *i.e.*, these elements can create nanoclusters. According to the work [3], when silicon is doped with these impurities, practically all the types of states inherent to S and Se atoms take place, but depending on conditions of doping and subsequent heat treatment, contribution of individual states becomes predominant. In addition, it is known that these elements are quite reactive and actively interact with various defects. In this regard, it is of scientific and practical interest to study interaction of clusters of manganese atoms with atoms of Group VI elements. Such studies are of interest, since on the one hand, there is a possibility to form various types of clusters with different nature and to study their effect on the properties of materials, and on the other hand, there are practically no data in the literature on interaction of positively charged clusters of impurity manganese atoms with charged sulfur atoms (S^+, S^{++}) and selenium (Se^+, Se^{++}). This type of interaction can be called a new type of interaction of impurity atoms in semiconductors, which makes it possible to form clusters consisting of various impurity atoms. These clusters in the silicon lattice, in contrast to monoatomic electrically neutral nickel clusters or multiply charged nanoclusters of manganese atoms, allow formation of nanoscale "buried" heterostructures practically without surface states and with ideal parameters that cannot be created by the existing methods suitable to form nanoscale structures.

2. Theoretical analysis

Samples Si⟨B, S⟩ become *n*-type, *i.e.*, they are overcompensated at the position of the Fermi level $F = E_C - 0.28$ eV. In these samples, most of the sulfur atoms are in the S^+ state that dominates over the S^{++} ones. These results completely coincide with those of the samples doped with the same impurities under the same conditions, which was observed by other authors [1, 2].

The results of studying the parameters of samples Si ⟨B, Mn, S⟩ are of interest.

In these samples, donor impurities of manganese and sulfur act simultaneously, which should lead to production of a lower-resistance *n*-type material than Si ⟨B, S⟩, since the concentration of electroactive manganese atoms in it is $N_{Mn} \sim 1.9 \cdot 10^{15}$ cm^{-3} and sulfur atoms about $N_S \sim 8 \cdot 10^{15}$ cm^{-3}. The total concentration of electrons created by these atoms is $n \sim 8 \cdot 10^{15}$ cm^{-3}.

3. Experimental results

In [5], we investigated interaction of manganese nanoclusters with sulfur atoms in silicon. The starting material was monocrystalline silicon of *p*-type conductivity with the resistivity $\rho \sim 5$ Ω·cm and the oxygen concentration close to $7 \cdot 10^{17}$ cm^{-3}. It was shown that upon simultaneous and sequential doping of silicon with manganese and sulfur, the electrical parameters of the initial sample (electrical resistivity, mobility of carriers, type of conductivity) practically do not change. It was also found that to form clusters with maximum participation of introduced manganese atoms, the optimum temperature is the diffusion temperature of 1100 °C. Therefore, it is of great interest to study interaction at different temperatures, since in this case not all manganese atoms are involved in formation of clusters, the concentration of clusters decreases both with an increase in temperature and with a decrease in temperature relatively to T = 1100 °C. The diffusion temperature in this case was T = 1050 °C, 1150 °C, 1200 °C. The diffusion time varied accordingly from 80 down to 36 hours. In all the cases, 3 batches of Si samples doped with manganese, sulfur and sulfur simultaneously with manganese were prepared. These three batches of the samples in separate evacuated silica ampoules were annealed under absolutely the same conditions and had the same cooling rates. In this case, *p*-type silicon with $\rho \sim 10$ Ω·cm was used as a starting material. It was chosen to achieve noticeable compensation in the range of low temperatures T = 1050 °C. After diffusion treatment, the electrical parameters of all the samples obtained at different annealing temperatures were measured in the same way as in the case of diffusion at T = 1100 °C.

Table 1. Basic electrical parameters of three batches of samples after alloying at T = 1100 °C, t = 56 hours.

Samples	ρ, Ω·cm	Type	μ, cm^2/V·s	N^*, cm^{-3}
Original material	5.1	*p*	245	$5 \cdot 10^{15}$
Si ⟨B, Mn⟩	$6.1 \cdot 10^3$	*p*	100	$1.83 \cdot 10^{15}$
Si ⟨B, Mn⟩	$6.6 \cdot 10^3$	*p*	105	$1.9 \cdot 10^{15}$
Si ⟨B, S⟩	10.2	*n*	1270	$8 \cdot 10^{15}$
Si ⟨B, S⟩	10.5	*n*	1255	$8.1 \cdot 10^{15}$
Si ⟨B, Mn, S⟩	20	*p*	260	$<10^{14}$
Si ⟨B, S, Mn⟩	10	*p*	270	$<10^{14}$

N^* designates the concentration of electroactive atoms of sulfur, manganese and thermal donors in the corresponding samples.

Shown in Table 2 are the average values of the electrical parameters of samples of all types obtained at different temperatures.

As it follows from Table 2, when diffusion takes place at the temperature T = 1050 °C, the samples Si ⟨B, Mn, S⟩ should also be *n*-type with the resistance close to or less than that of the samples Si ⟨B, S⟩. However, as seen from the obtained results, the samples Si ⟨B, Mn, S⟩ remained to be of *p*-type, but their resistivity became significantly higher than that of the original material. It is obvious that, in this case, the concentration of electroactive atoms of manganese and sulfur in the samples Si ⟨B, Mn, S⟩ is significantly lower than that in the samples Si ⟨B, Mn⟩ and Si ⟨B, S⟩, *i.e.*, again, most of the atoms is in the electrically neutral state.

Shown in Table 2 are the parameters of the samples annealed at the temperatures higher than 1100 °C, *i.e.* at T = 1150 °C. Comparison of the parameters inherent to the samples Si ⟨B, S⟩ and Si ⟨B, Mn, S⟩ shows how considerably they differ from each other. When the samples Si ⟨B, S⟩ have the *n*-type conductivity

Table 2. Electrical parameters of the samples doped at different diffusion temperatures.

Samples	1050 °C			1150 °C			1200 °C		
	ρ, Ω·cm	μ, cm^2/V·s	*n*, cm^{-3}	ρ, Ω·cm	μ, cm^2/V·s	*n*, cm^{-3}	ρ, Ω·cm	μ, cm^2/V·s	*n*, cm^{-3}
Si ⟨B, Mn⟩	$7.7 \cdot 10^2$	950	$3.6 \cdot 10^{12}$	$1.46 \cdot 10^2$	1120	$3.82 \cdot 10^{13}$	$4.76 \cdot 10^2$	1200	$1.1 \cdot 10^{13}$
Si ⟨B, S⟩	40	1070	$1 \cdot 10^{14}$	3.2	1008	$1.94 \cdot 10^{15}$	1.33	1034	$4.54 \cdot 10^{15}$
Si ⟨B, Mn⟩	$4 \cdot 10^3$	245	$6.3 \cdot 10^{12}$	$4.6 \cdot 10^4$	108	$1.25 \cdot 10^{12}$	11	1062	$5.35 \cdot 10^{14}$

with $\rho \sim 3.2\ \Omega\cdot$cm, the electron concentration in the conduction band is $n \sim 2\cdot10^{15}$ cm^{-3}. The samples Si ⟨B, Mn, S⟩ have the *p*-type conductivity with the specific resistance $\rho \sim 4.6\cdot10^{4}\ \Omega\cdot$cm ($p = 1.25\cdot10^{11}$ cm^{-3}).

Although the silicon samples doped with manganese without sulfur are overcompensated (*n*-type), *i.e*., the concentration of electroactive manganese atoms in them is much higher than the concentration of boron atoms.

Thus, in the samples Si ⟨B, Mn, S⟩, the total concentration of electroactive manganese and sulfur atoms decreased so much that it was not even enough to completely compensate the initial boron. These data demonstrate very clear evidence of the combined effect of manganese and sulfur atoms on the electrical properties of silicon.

The electrical parameters of the samples doped at $T = 1200$ °C show (Table 1) that in this case, in contrast to diffusion at $T = 1050$ °C, 1100 °C and 1150 °C, the samples Si ⟨B, Mn⟩, Si ⟨B, S⟩, and Si ⟨B, Mn, S⟩ samples acquire the *n*-type conductivity, however, the resistivity of Si ⟨S⟩ and Si ⟨B, Mn, S⟩ samples differs by a factor of 10, respectively in Si ⟨B, Mn, S⟩ the concentration of electroactive sulfur atoms became almost an order of magnitude less than in Si ⟨B, S⟩. It follows thereof that although this strong interaction is not observed like to the case of diffusion at $T = 1100$ °C and 1150 °C, the result of interaction of manganese and sulfur atoms clearly exists. Therefore, it can be argued that the optimal temperature of interaction of clusters of manganese atoms with sulfur atoms is $T = 1100$ °C [5, 6].

4. Discussion of the results

Being based on these results, it can be assumed that the presence of sulfur atoms in silicon doped with manganese does not allow formation of magnetic clusters of manganese atoms, *i.e*., sulfur atoms significantly change the state of manganese atoms in the lattice.

To make sure that the obtained results are not typical only for the samples doped with sulfur and manganese simultaneously, we prepared samples doped sequentially with sulfur and manganese. The *p*-type silicon samples were first doped with sulfur and then doped with manganese. The temperature and diffusion conditions were the same as for simultaneous diffusion. The difference in this case was that the samples doped only with sulfur were repeatedly doped with manganese under the same conditions, and in another ampoule the samples Si ⟨B, S⟩ were annealed again under the same conditions without manganese. The electrical, photoelectric and magnetic properties of these samples were investigated, as well as the state of impurities by activation analysis. The results of these studies, with some experimental error, practically took place like to those in the case of simultaneous doping. Thus, it can be argued that, regardless of the doping conditions, sequentially or simultaneously in the Si ⟨B, Mn, S⟩ samples, all the introduced impurity atoms are in the electrically neutral state, and clusters of manganese atoms are not formed.

5. Conclusion

The electrical parameters of the Si samples simultaneously doped with S and Mn completely coincide with those of the starting material, *i.e*., as if they do not contain not only S and Mn, but also do not form thermal donors. The results make it possible to exclude the possibility of gettering of impurity atoms or formation of some kind of solid solutions, taking into account the impurity Mn and S atoms, which hinders their diffusion in the crystal bulk. Thus, the samples Si ⟨B, Mn, S⟩ contain both S atoms and Mn atoms, with the same concentration as in the samples Si ⟨B, Mn⟩ and Si ⟨B, S⟩, respectively.

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Authors and CV

Saparniyazova Zlikha Maxsetbayevna. PhD in Physics and Mathematics, Associate Professor at the Department of Semiconductor Physics of Karakalpak State University, Uzbekistan, Nukus. Author of more than 30 scientific papers.

Ismailov Kanatbay Abdreymovich. Doctor of Physical-and-Mathematical Sciences, Professor, Head of Semiconductor Physics Department of Karakalpak State University, Uzbekistan, Nukus. Author of more than 320 works, and among them: 4 patents, 1 monograph, 12 textbooks and educational-methodological manuals.

Uteniyazov Abatbay Kurbaniyazovich. PhD in Physics and Mathematics, Associate Professor at the Department of Semiconductor Physics of Karakalpak State University, Nukus, Uzbekistan. Author of more than 60 scientific papers.

Kamalov Khayratdin Usnatdinovich. PhD in Physics and Mathematics, Associate Professor at the Department of Semiconductor Physics of Karakalpak State University, Uzbekistan, Nukus. Author of more than 30 scientific papers.

Вплив температури дифузії на взаємодію кластерів з домішковими атомами в кремнії

З.М. Сапарніязова, К.А. Ісмайлов, А.К. Утеніязов, Х.У. Камалов

Анотація. Наведено результати досліджень впливу температури дифузії на взаємодію кластерів атомів марганцю з атомами сірки. Показано, що електричні параметри зразків, одночасно легованих сіркою і марганцем, повністю збігаються з параметрами вихідного матеріалу, тобто якщо б вони не містили не тільки сірку і марганець, але й не утворювали термодонори. Отримані результати дозволяють виключити можливість гетерування домішкових атомів або утворення певного виду твердих розчинів з урахуванням домішкових атомів марганцю і сірки, що ускладнює їх дифузію в об'єм кристала. Встановлено, що для вихідного кремнію *p*-типу з питомим опором $\rho \sim 10\ \Omega$·см, температура дифузії 1100 °С є найбільш оптимальною для формування кластерів з максимальною участю введених атомів сірки та марганцю.

Ключові слова: кремній, домішки, температура дифузії, атоми сірки та марганцю.