Semiconductor Physics, Quantum Electronics & Optoelectronics, 2021. V. 24, No 3. P. 255-260.

Semiconductor physics

Formation of complexes consisting of impurity Mn atoms and group VI elements in the crystal lattice of silicon

K.A. Ismailov[1], X.M. Iliev[2], M.O. Tursunov[3], B.K. Ismaylov[2]

[1]*Karakalpak State University, Uzbekistan, Nukus,*
E-mail: k_ismailov@karsu.uz
[2]*Tashkent State Technical University,*
100095, Uzbekistan, Tashkent, Universitetskaya str., 2,
E-mail: xolmurodov.iliev@tdtu.uz
[3]*Termez State University,*
190111, Uzbekistan, Termez, Barkamol avlod str., 43
E-mail: mtursunov@tersu.uz

Abstract. Formation of complexes of impurity Mn atoms with impurity atoms of group VI elements (S, Se, Te) in the silicon crystal lattice has been studied. It has been experimentally found that formation of electrically neutral molecules with an ionic-covalent bond between Mn atoms and group VI elements takes place, which possibly leads to formation of new $Si_2B_{VI}^{++}Mn$ binary unit cells in the silicon crystal lattice. It has been shown that in the samples Si⟨S, Mn⟩, Si⟨Se, Mn⟩ and Si⟨Te, Mn⟩, an intense complex formation occurs at the temperatures 1100, 820 and 650 °C, respectively.

Keywords: silicon, electrically neutral molecule, diffusion, thermal annealing.

https://doi.org/10.15407/spqeo24.03.255
PACS 61.72.Cc, 81.40.Ef

Manuscript received 27.05.21; revised version received 22.06.21; accepted for publication 18.08.21; published online 26.08.21.

1. Introduction

Study of interaction of impurity atoms in the Si lattice is interesting not only from the scientific viewpoint, but also allows developing the promising methods to create nanoclusters over the total crystal bulk, *i.e.*, to form nanostructured semiconductors in this bulk [1, 2]. As the investigation results have already shown [3, 4], in these materials not only the several interesting and new physical phenomena are observed but also they have great functional possibilities in development of new clusters of optoelectronic and photomagnetic devices and high effective photoelements. This situation, due to growing concentration of nanoclusters (quantum dots) inside the crystal, allows one to essentially change the fundamental parameters (E_g, μ and band structure) of the main Si material and, accordingly, to obtain new materials based on Si, which have other fundamental parameters.

Therefore, the aim of present paper is to study interaction of Mn atoms with those of VI group elements in the Si lattice.

The choice of interacting impurity atoms is dictated by the property of Mn and VI group elements (beside oxygen) in Si to act as the donor impurity atoms and to create two donor energetic levels [5, 6]. It means that studied impurity atoms can be in the single and double positively charged states (*i.e.*, in the ionic ones). It implies that electrostatic interaction between Mn ions (Mn^+, Mn^{++}) and VI group elements (S^+, S^{++}; Se^+, Se^{++}; Te^+, Te^{++}) is impossible. However, as investigation results showed in the defining thermodynamic conditions, interaction between these ions through formation of electric neutral molecules $\{Mn^{--}(B^{VI})^{++}\}$ can take place.

2. Sample preparation and research methods

As initial material, we used the industrial *p*-type Si single crystal with specific resistivity ρ = 5 Ohm·cm, oxygen concentration $N_{O_2} \sim (5\ldots7)\cdot10^{17}$ cm^{-3}, and dislocation density δ = 10^3 cm^{-2}. S, Se, Te diffusion from gas phase in the silica ampoules pumped out down to residual pressure 10^{-6} Pa under the temperature T = 1250 °C and time of diffusion 20, 60 and 80 hours, accordingly, was carried out. The pressure of gas phase in the ampoules according to calculations was 0.8 atm. To provide the uniform doping, the diffusion time was chosen to provide distribution of impurity atoms over the whole bulk. In each ampoule, there were 5 samples with the sizes 8×3×0.8 mm. To avoid erosion of the sample surface,

Table 1. The samples electric parameters reached after diffusion.

Samples	ρ, Ohm·cm	type	μ, $cm^2/V·s$	Concentration of charge carriers, cm^{-3}
Initial material	4.8	*p*	280	$4.6·10^{15}$
Si⟨B, Mn⟩	$5.8·10^3$	*p*	105	$1.02·10^{13}$
Si⟨B, S⟩	5.8	*n*	1007	$1·10^{13}$
Si⟨B, Se⟩	1.7	*n*	1280	$2.9·10^{15}$
Si⟨B, Te⟩	10.7	*n*	1150	$5.1·10^{14}$

which appears under usual conditions of S, Se and Te diffusion, the diffusion annealing was performed using a new technological approach. Diffusion through gradual increasing the temperature from 25 °C up to 600 °C with the heating speed 5...7 °C/min was carried out. Further, the samples were kept under T = 600 °C for t = 15…20 min. Finally, these samples were heated with the heating speed 15...17 °C/min up to reaching the diffusion temperature [7, 8]. As the investigation results showed, the sample surfaces did not practically exhibit any erosion. Mn diffusion under the temperature 1100 °C within period 40 min from the gas phase was performed too, but after diffusion the cooling through releasing ampoules to water was carried out.

Thus, 20 of each type samples were prepared:

- Si⟨B, S⟩,
- Si⟨B, Se⟩,
- Si⟨B, Te⟩,
- Si⟨B, Mn⟩.

3. Results and discussion

To remove the silicide surface layer appearing after doping the samples were polished out from all the sides down to the depth 50 μm. Uniformity of doping over the volume was checked using the method of layer-by-layer grinding with M-10 micropowder, removing from the surface 50 μm to halve the thickness of the sample. As the investigation results showed that in all cases the samples by volume (besides surface layer) were doped evenly. The average values of electric parameters for the samples doped with different impurities have been presented in Table 1. The obtained samples were separated by three groups.

The first group of samples (doped with S, Se and Te) were annealed with Mn in the separated ampoules within the range of temperatures T = 1050…1200 °C (with 50 °C temperature step), 40-min doping period. The aim of this procedure was to provide studying the effect of Mn atoms on S, Se and Te atoms' states in the Si lattice.

The second group of samples (doped with S, Se and Te) in silica ampoules under the same conditions as for the first group samples, but without Mn, was annealed. Thereby the re-annealing effect on S, Se and Te atoms in the Si lattice states was revealed.

The third group of Si samples, doped only with Mn, demonstrates the same effect like to that revealed in the first and second groups. In these experiments, as a result of additional annealing, we observed that the state of Mn atoms was changed in the Si lattice.

After each annealing stage, the samples were processed under identical mechanical and chemical conditions, and their electric parameters were measured using the Hall method. The photoelectric properties were investigated using the spectrophotometer "IRS-14" equipped with the special cryostat.

The average values of the samples electric parameters for all three groups are summarized in Table 2.

3.1. S and Mn in Si

S and Mn atoms in Si are donor impurities and create two energy levels ($E_1 = E_C + 0.18$ eV), ($E_2 = E_C + 0.3$ eV) and ($E_1 = E_C + 0.27$ eV), ($E_2 = E_C + 0.49$ eV), accordingly. The material obtained introducing only donor impurities should be of *n*-type conductivity and have comparatively low resistance. However, as experiments showed, after the Mn diffusion process under the temperature T = 1100 °C one obtains the material of *p*-type conductivity with specific resistivity ρ = 6 Ohm·cm, *i.e.*, the samples acquire practically proper initial parameters. Consequently, introduction of S and Mn impurities causes lost of electric activity. Wherein doping with elements from group II keeps the *n*-type conductivity, though its specific resistivity is a bit higher than before the re-annealing process. It means that here S atoms present and act as donor impurities. Si⟨Mn⟩ samples from group III after re-annealing process keep practically their own parameters obtained after Mn diffusion (*p*-type with ρ = $5·10^3$ Ohm·cm). This fact confirms keeping Mn atoms in them with donor properties.

Therefore, we assume that between S and Mn atoms there takes place the "chemical" interaction (during the Mn diffusion process). Wherein for creation of the $S^{++}Mn^{--}$ electric neutral molecules, there is an optimal temperature (about 1100 °C). Under higher heat treatment temperatures (T > 1100 °C), interaction between S and Mn atoms is broken, and they will act as usual donor impurity atoms.

Table 2. The average values of electric parameters of I, II and III group samples adduced for the different annealing temperatures.

Group I									
T, °C	Si⟨B, S, Mn⟩			Si⟨B, Se, Mn⟩			Si⟨B, Te, Mn⟩		
	type	ρ, Ohm·cm	μ, $cm^2/V·s$	type	ρ, Ohm·cm	μ, $cm^2/V·s$	type	ρ, Ohm·cm	μ, $cm^2/V·s$
1050	*p*	$4.2·10^3$	255	*p*	$1.3·10^2$	230	*p*	75	230
1100	*p*	7	267	*n*	$2.5·10^2$	970	*n*	$1.5·10^2$	1060
1150	*p*	$4.5·10^4$	118	*n*	10.7	1200	*n*	3.9	1250
1200	*n*	9.8	1070	*n*	4.3	1220	*n*	2.5	1190
Group II									
T, °C	Si⟨B, S⟩			Si⟨B, Se⟩			Si⟨B, Te⟩		
	type	ρ, Ohm·cm	μ, $cm^2/V·s$	type	ρ, Ohm·cm	μ, $cm^2/V·s$	type	ρ, Ohm·cm	μ, $cm^2/V·s$
1050	*n*	42	1080	*n*	$1.6·10^3$	1110	*n*	$3.4·10^2$	1030
1100	*n*	10.7	1250	*n*	8.7	1220	*n*	5.5	1170
1150	*n*	3.3	1010	*n*	3.1	1270	*n*	2.1	1220
1200	*n*	1.35	1040	*n*	0.97	1210	*n*	0,9	1140
Group III									
T, °C	Si⟨B, Mn⟩								
	type			ρ, Ohm·cm			μ, $cm^2/V·s$		
1050	*p*			$7.5·10^2$			264		
1100	*p*			$6.4·10^3$			95		
1150	*n*			$7.1·10^2$			1245		
1200	*n*			$4.8·10^2$			1100		

This fact means, as seen from the investigations results (Table 2), that Mn diffusion in Si⟨S⟩ under the temperature T = 1100 °C does not depend on the essential difference in the S and Mn atomic concentrations. According to representation

$$N = 2.42 \cdot 10^{20} \exp\left(\frac{-1.24}{kT}\right).$$

Mn solubility value was calculated, and under the temperature T = 1100 °C it reached up to $N \sim 7·10^{15}$ value. According to representation

$$N = 1.5 \cdot 10^{22} \exp\left(\frac{-1.65}{kT}\right).$$

S solubility value was also calculated, and under the temperature 1100 °C it reached up to $N \sim 1.3·10^{16}$ value. These samples have their own initial parameters of *p*-type with the specific resistance ρ = (5…7) Ohm·cm. These results testify that formation of the electric neutral molecules ($S^{++}Mn^{--}$) stimulates increasing the solubility of Mn atoms in Si [9, 10].

3.2. Se, Te and Mn in Si

The investigation results for the first group samples preliminarily doped with Se and Te (under the same conditions as for Si⟨S⟩ samples) and further doped with Mn showed the absence of "chemical" interaction between impurities. Interaction between Se and Mn atoms as well as Te and Mn doping the Mn diffusion process within range of temperatures T = 1050…1200 °C did not happen.

Therefore, the samples of all three groups (that is Si doped with Se and Mn, Te and Mn and also only with Se, Te or Mn) under annealing within the range of lower temperatures than the Mn diffusion one were exposed. It has been ascertained that in Si⟨Se, Mn⟩ and Si⟨Te, Mn⟩ samples the intense complex creation under the temperatures 820 °C and 650 °C, accordingly, occurs.

Naturally, the question arises: what oxygen acts in this plane which is VI group element too? The experiments with the samples containing the Se element and various oxygen concentrations were carried out. The maximal oxygen concentration was equal to $N_{O_2} \sim (5…7)·10^{17}$ cm^{-3}, and the minimal one was $N_{O_2} \sim 10^{16}$ cm^{-3}. The investigations were based on the method described above. It was ascertained that formation of molecules between oxygen and Mn atoms under the temperatures T > 1100 °C takes place, but the optimal temperature at which all Mn atoms form molecules equals T = 1300 °C.

Thus, it has been established that in the Si lattice Mn atoms form the electrically neutral molecules with VI group elements (O, S, Se and Te). Though formation of molecules occurs over all the ranges of diffusion annealing temperatures, the optimal temperatures which stimulate these molecules to form (in the case of O, S, Se and Te impurities) are 1300, 1100, 820 and 650 °C, accordingly.

Now let us talk briefly on the molecules nature consisting of Mn and VI group elements. As known

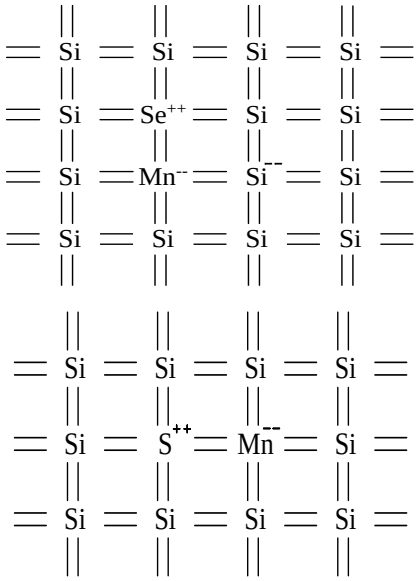

Fig. 1. The structure of $Si_2Mn^{--}Se^{++}$ and $Si_2Mn^{--}S^{++}$ complexes in the Si lattice.

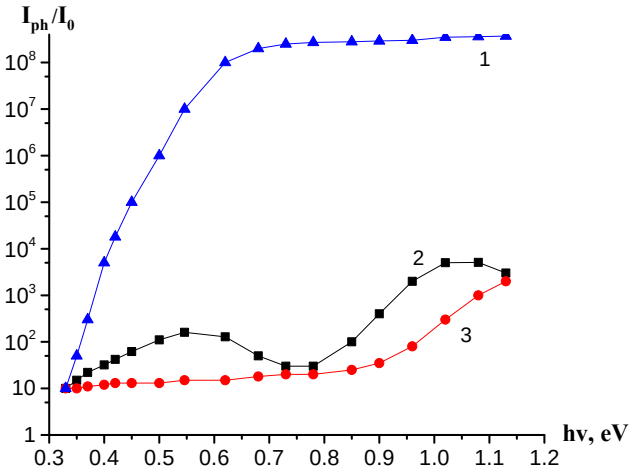

Fig. 2. Spectral dependence of photoconductivity of Si⟨B, Mn⟩, Si⟨B, S⟩, Si⟨B, Mn, S⟩ samples at the temperature 77 K (curve *1* corresponds to Si⟨B, Mn⟩ of *p*-type; *2* – to Si⟨B, S⟩ of *n*-type, and *3* – to Si⟨B, Mn, S⟩ of *p*-type).

[11, 12] that S, Se and Te atoms in Si are basically located in the lattice nodes, and they can give own two electrons to the conductivity band. In dependence on the thermodynamic conditions, they can exist in neutral, single and double charged states. Therefore, we have assumed that the molecules can be formed as a result of Mn atom transition between one node to adjacent near S, Se and Te atoms. Wherein two extra electrons from these elements transfer to Mn atoms and form electrically neutral molecule of $S^{++}Mn^{--}$ and $Se^{++}Mn^{--}$ types (see Fig. 1).

As a result, new (binary) cells of $Si_2B_{VI}{}^{++}Mn^{--}$ type are formed in the Si lattice. In this case, Mn atoms and S, Se and Te ones do not act as impurity atoms and do not form the energy levels in the Si forbidden band.

S, Se and Te atoms act as the main atoms of the new lattice, and formation of such elementary cells provides the more profitable thermodynamic state for the system:

– under formation of these new cells in the lattice (having ionic-covalent bonds) the tetrahedral bonds in the main Si lattice is not breaken;

– formation of these cells takes off the electric and deformation potential which exists when these impurities are located separately as S^{++}, Se^{++} and Te^{++} and Mn^{++} ions between cells;

– the sum covalent radius of Mn atoms and S, Se and Te ones exceeds not essentially the covalent radius of two Si atoms.

All these factors stimulate formation of these binary cells.

As the proof of this assumption, the spectral dependence of photoconductivity of Si samples doped with S and re-annealed at the temperature T = 1100 °C and Si doped with Mn as well as Si doped with S and Mn under the same conditions can serve (see Fig. 2).

As is seen from the results (curves *1* and *2*) in the Si⟨S⟩ and Si⟨Mn⟩ samples, the photoresponse related with donor energy levels of these impurities in Si is pronounced clearly. However, curve *3* shows that in the Si⟨S, Mn⟩ samples the impurity levels corresponding to S and Mn are not observed. This fact confirms formation of $S^{++}Mn^{--}$ electrically neutral molecules.

Thus, formation of the electrically neutral molecules having the ionic-covalent bonds between Mn and VI group elements has been ascertained experimentally, probably, these bonds lead to formation of the new binary elementary cells in the Si lattice.

The bond energy of atoms in these binary elementary cells will differ essentially from the atoms bond energy in the Si lattice. This fact means that, with growing the concentration of these elementary cells in the crystal, we can create the bulk nanostructured material that is a new class of materials based on Si with absolutely other fundamental parameters: width of forbidden band, mobility of electron carriers and band structure. This situation allows us expect expansion of the spectral sensitivity of photoconductivity of Si to both infrared and also ultraviolet ranges of spectrum.

4. Conclusions

The new materials that is Si enriched with binary cells of $Si_2B_{VI}{}^{++}Mn$ type allows us to create on their base the new optoelectronic and nanoelectronic devices and also highly effective photoelements based on Si having the same best parameters as expensive manycascade photoelements based on $A^{III}B^{V}$ compounds. That is why the new scientific branch requires to carry out further complex experimental and theoretical investigations.

Acknowledgements

The authors express their deep and sincere gratitude to Academician M.K. Bakhadyrkhanov for valuable advice given during performance of the work and discussion of the results obtained.

References

1. Saparniyazova Z.M., Ismailov K.A., Uteniyazov A.K., Kamalov Kh.U. Effect of the diffusion temperature on interaction of clusters with impurity atoms in silicon. *Semiconductor Physics, Quantum Electronics & Optoelectronics*. 2021. **24**, No 1. P. 22–25. https://doi.org/10.15407/spqeo24.01.22.
2. Iliev Kh.M., Saparniyazova Z.M., Ismailov K.A., and Madzhitov M.Kh. Formation of nanoclusters of gadolinium atoms in silicon. *Surf. Eng. Appl. Electrochem.* 2011. **47**, No 1. P. 1–3. https://doi.org/10.3103/S1068375511010066.
3. Klimanov, E.A. Formation of thermal defects in silicon grown by means of float zone melting. *J. Commun. Technol. Electron.* 2017. **62**, No 9. P. 1066–1073. https://doi.org/10.1134/S1064226917090121.
4. Bakhadyrkhanov M.K., Iliev Kh.M., Tachilin S.A. *et al.* Impurity photovoltaic effect in silicon with multicharge Mn clusters. *Appl. Sol. Energy.* 2008. **44**, No 2. P. 132–134. https://doi.org/10.3103/S0003701X08020151.
5. Bakhadyrkhanov M.K., Saparniyazova Z.M., Iliev Kh.M., and Ismailov K.A. Interaction of multiply charged manganese nanoclusters with selenium and tellurium atoms in silicon. *Inorg Mater*. 2015. **51**, No 8. P. 767–771. https://doi.org/10.1134/S0020168515070031.
6. Nakashima H., Hashimoto K. Deep impurity levels and diffusion coefficient of manganese in silicon. *J. Appl. Phys*. 1991. **69**, No 3. P. 1440–1445. https://doi.org/10.1063/1.347285.
7. Bakhadyrkhanov M.K., Mavlonov G.Kh., Isamov S.B. *et al.* Transport properties of silicon doped with manganese via low-temperature diffusion. *Inorg Mater*. 2011. **47**, No. 5. P. 479–483. https://doi.org/10.1134/S0020168511050062.
8. Bakhadyrkhanov M.K., Mavlyanov A.S., Sodikov U.K., Khakkulov M.K. Silicon with binary elementary cells as a novel class of materials for future photoenergetics. *Appl. Sol. Energy*. 2015. **51**, No 4. P. 258–261. https://doi.org/10.3103/S0003701X1504009X.
9. Saparniyazova Z.M., Bakhadyrkhanov M.K., Sattarov O.E. *et al.* Interaction between multiply charged manganese nanoclusters. *Inorg. mater*. 2012. **48**, No 4. P. 325–328. https://doi.org/10.1134/S0020168512030144.
10. Bakhadirkhanov M.K., Askarov Sh.I., Norkulov N. Some features of chemical interaction between a fast diffusing impurity and a group VI element in silicon. *phys. status solidi*. 1994. **142**. P. 339–346. https://doi.org/10.1002/pssa.2211420206.
11. Bakhadyrkhanov M.K., Isamov S.B., Zikrillayev N.F., Tursunov M.O. Anomalous photoelectric phenomena in silicon with nanoclusters of manganese atoms. *Fizika tekhnika poluprovodnikov*. 2021. **55**, Issue 6. P. 489–492 (in Russian). https://doi.org/10.21883/FTP.2021.06.50912.9259.
12. Mil'vidskii M.G., Chaldyshev V.V. Nanometer-size atomic clusters in semiconductors – a new approach to tailoring material properties. *Semiconductors*. 1998. **32**, Issue 5. P. 457–465. https://doi.org/10.1134/1.1187418.

Authors and CV

Ismailov Kanatbay Abdreymovich. Doctor of Phisical-and-Mathematical Sciences, Professor, Head of Semiconductor Physics Department of Karakalpak State University, Uzbekistan, Nukus. Author of more than 330 articles, 4 patents, 3 monographs, 12 textbooks and educational-methodological manuals. https://orcid.org/0000-0003-2867-0826

Iliev Khalmurod Midzhitovich. Doctor of Physical-and-Mathematical Sciences, Professor, Head of the Department of Digital Electronics and Microelectronics, Tashkent State Technical University, Uzbekistan. Author of over 300 articles, 3 patents, 1 monograph, 8 textbooks and teaching manuals. https://orcid.org/0000-0002-1309-3133

Ismaylov Bayrambay Kanatbaevich. Doctor of Philosophy in Physics and Mathematics, Senior Lecturer at the Department of Digital Electronics and Microelectronics at the Tashkent State Technical University, Uzbekistan. Author of more than 40 articles. https://orcid.org/0000-0002-5880-4568; i.bayram@karsu.uz

Tursunov Mamasobir Ochildiyevich. Currently he is a post-graduate student at the Physical-and-Mathematical faculty of Termez State University. Author of 2 articles and more than 10 theses of international and republican conferences. https://orcid.org/0000-0001-7641-4259

Формування комплексів домішкових атомів Mn з елементами VI групи в кристалічній решітці кремнію

К.А. Ісмайлов, Х.М. Ілієв, М.О. Турсунов, Б.К. Ісмайлов

Анотація. Досліджено формування комплексів домішкових атомів Mn з домішковими атомами елементів VI групи (S, Se, Te) у кристалічній решітці кремнію. Експериментально виявлено, що має місце утворення електронейтральних молекул з іонно-ковалентним зв'язком між атомами Mn та елементами VI групи, що можливо приводить до формування нових бінарних елементарних комірок $Si_2B_{VI}^{++}Mn$ у кристалічній решітці кремнію. Показано, що в зразках Si⟨S, Mn⟩, Si⟨Se, Mn⟩ and Si⟨Te, Mn⟩ відбувається інтенсивне комплексоутворення при температурах 1100, 820 та 650 °C відповідно.

Ключові слова: кремній, електронейтральні молекули, дифузія, термічний відпал.