IRSTI 29.19.16 https://doi.org/10.26577/phst.2023.v10.i1.02

Clusters of impurity nickel atoms and their migration in the crystal lattice of silicon

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(Received April 10, 2023; received in revised form April 29, 2023; accepted May 15, 2023)

The formation of clusters of impurity atoms in the crystal lattice of semiconductor materials is of great interest. The formation of nanoclusters with controlled parameters in the lattice of semiconductor materials can serve as the basis for the technology of creating and obtaining bulk nanostructured semiconductor material. This paper shows the experimental results obtained, as well as the proposed physical model of the structure of nickel atomic clusters. It is shown that the clusters move and migrate in the crystal lattice of monosilicon with an anomalously high diffusion coefficient of about c ($D \sim 10^{-9}$ cm^2/s at T = 800°C). The structural composition of clusters of impurity atoms is determined, its structure and the mechanism of migration in the crystal lattice are proposed. Thus, it was found that it is possible to control the state of impurity atom clusters in the silicon crystal lattice, obtaining a new type of semiconductor materials with unique functional and properties using the cluster migration process. This makes it possible to create a new class of photonic materials with bulk superlattices based on semiconductors with ordered clusters, which has unique functionality for creating optoelectronic, nanoelectronic, photoelectric devices and sensors of physical quantities of a new generation.

Key words: atom, cluster, nickel, temperature, diffusion, silicon, gettering.
PACS number: 61.46.+w.

1 Introduction

Of great interest is the formation of clusters of impurity nickel atoms in the crystal lattice of semiconductor materials. The formation of nanoclusters with controlled parameters in the lattice of semiconductor materials can guarantee the structure of the technology for creating and obtaining the volume of a nanostructured semiconductor material. The properties and uses of such materials are not yet well understood. The creation and control of the state of clusters of nickel impurity atoms in the silicon crystal lattice is of great practical and scientific interest. In this respect, nickel atoms are of particular interest. This is due to a rather high solubility ($N \sim 10^{18}$ cm^{-3}) and a large diffusion coefficient ($D \sim 10^{-5}$ cm^2/s at T = 1250 °C), as well as the formation of a predominantly solid ejection embedded in the silicon lattice [1-3]. The formation of clusters of nickel atoms in silicon and the effect of doping conditions, cooling rate, and additional annealing temperature on the state of clusters were sent to work [4–6]. However, this raises a very important question related to their movement, i.e. infection of clusters in the crystal lattice. This question is not only of scientific but also of very practical interest from the point of view of creating a fundamentally new class of materials with a superlattice. This paper presents a number of new, original experimental results on the diffusion of nickel atom clusters in the silicon crystal lattice.

Nickel, unlike other transition group elements, has not only an increased diffusion coefficient in silicon, but also a high solubility rate (10^{18} cm^{-3}) [6]. However, the maximum concentration of electroactive atoms turned out to be less than 0.1% of the total solubility of atoms at this temperature, which means that most of the Ni atoms in silicon should be in an electrically neutral state.

As shown in [7] this fraction of interstitial atoms can form impurity clusters in the silicon lattice. Their structure, size and situation are mainly related to the situation of legalization and the speed of cooling

immediately after diffusion ignition, as well as the temperature and duration of the onset of thermal ignition.

The prospects of this direction are also due to the possible gettering of uncontrolled impurity atoms using clusters of impurity nickel atoms in the manufacture of various electronic devices, and especially in the development of high-efficiency silicon-based solar cells [8, 9]. The gettering method makes it possible to increase the lifetime of minority charge carriers, and also ensures the stability of the electrical and recombination parameters of the source material, which is repeatedly subjected to heat treatment during the manufacture of electronic devices [10-12].

The processes of complex formation and gettering strongly depend on the mobility of impurity atoms in the lattice and their binding energy [13–15]. Therefore, an important task is to estimate the structure of nickel clusters and the binding energy of impurity atoms with clusters [16–18].

At the same time, there are no models of such clusters, and the physical mechanisms of the influence of nickel atomic clusters on the electrophysical parameters of silicon are not clear.

2 Technology for obtaining materials and research method

Samples of p-type single-crystal silicon with resistivity ρ=1 Ohm×cm and orientation (111), oxygen content N_{O2}~(4÷6) × 10^{16} cm^{-3} and dislocation density S ≤ 10^3 cm^2, were alloyed from a thin metal layer of nickel deposited in vacuum onto the surface of silicon samples [19-22].

Nickel diffusion was carried out both in evacuated ampoules and in air at T = 1200÷1250 °C, during t=60÷40 minutes. After diffusion, 50 μm were ground down from all sides of the samples in order to study the clusters in the bulk of the crystal. The electrical properties of the samples were studied by the Hall effect method. The results of the study showed that the parameters of the source material remained practically unchanged. This shows that the concentration of electroactive nickel atoms is not more than 4×10^{14} cm^{-3}, and the main part of the dissolved atoms in the lattice is in an electrically neutral state, which is confirmed by the results of works [23-27]. After polishing the surface of the samples, the state of the clusters was examined using an INFRAM-I infrared microscope. To make sure that the formation of clusters occurs over the entire volume of the crystal, the samples were subjected to stage-by-stage polishing. From the surface of the crystal, 5 μm and up to half the thickness of the crystal were ground off, and each time the samples were again polished and examined under a microscope.

3 Results and discussion

As shown by the results of IR microscopic studies, uniformly distributed dark dots with a size of d=2÷5 μm are observed in all samples (Fig. 1, a). Using energy dispersive X-ray spectroscopy (EDS), it was found that these dark dots are indeed clusters of nickel atoms.

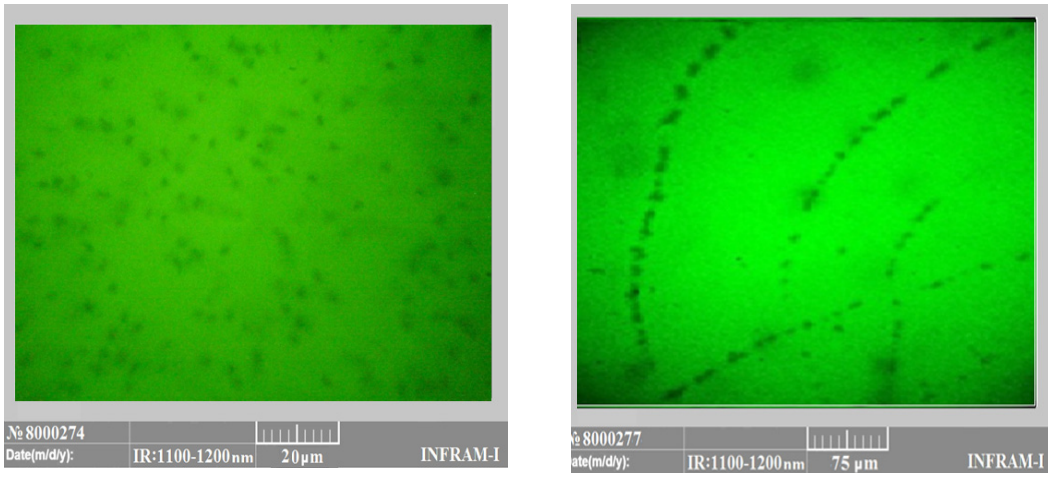
Then the samples with clusters of nickel atoms were subjected to sequential thermal annealing for 1 hour at T = 700, 800, 900, 1000 °C. After each stage of thermal annealing, the state of the clusters was examined with an IR microscope.

Interesting results were found at T = 800 °C. At the same time, the ordering of clusters occurs clearly in a certain direction, and this process ends with the formation of cluster chains 40 ÷ 45 μm long, consisting of numerous clusters (Fig. 1b). The remaining parts of the crystal, as can be seen from Figure 1.b, become completely transparent, that is, there are practically no clusters in this region of the sample.

These data show that during heat treatment in the temperature range T =700÷800 °C, the clusters are ordered. This phenomenon cannot be explained without displacement of clusters from their initial states, i.e. their diffusion in the lattice [2].

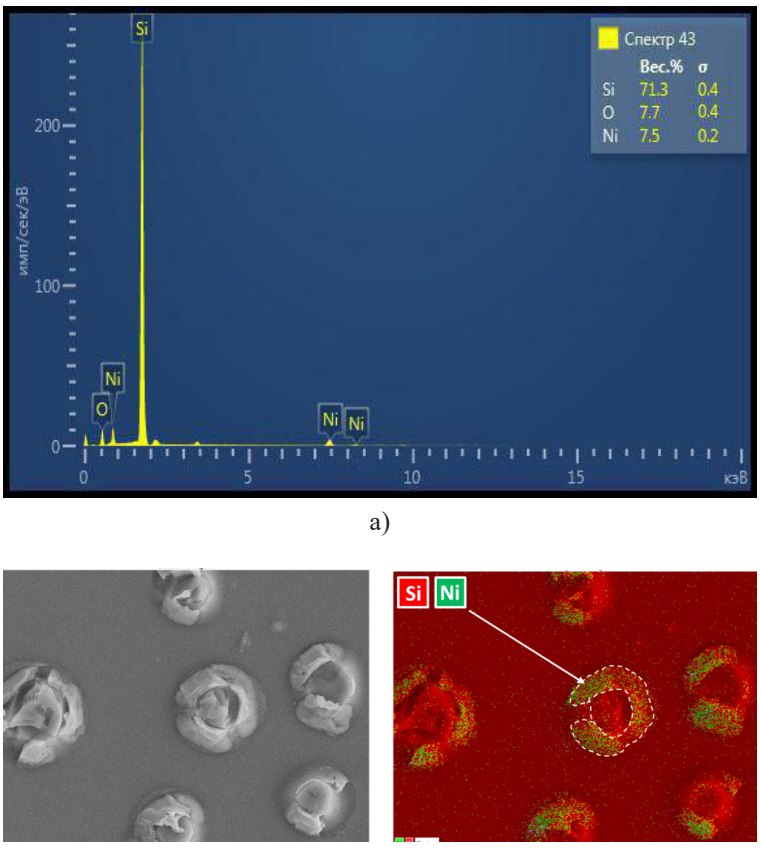
Thus, a very interesting and new phenomenon is observed – the diffusion of clusters, which makes it possible to control their state in the silicon crystal lattice. The diffusion coefficient of clusters was calculated taking into account their density (S ~ 10^6 cm^2) and the distance between them. Then, at a given temperature, the diffusion coefficient of the cluster turns out to be D≈1.1 × 10^{-9} cm^2/c, although this value is almost 1.5÷2 orders of magnitude lower than the diffusion coefficient of nickel atoms at a temperature T =800 °C [1], it shows that clusters of nickel atoms diffuse with an anomalously large diffusion coefficient.

To elucidate the mechanism of diffusion of nickel atom clusters, it was necessary to determine the composition of the clusters. The composition of such clusters was determined by energy dispersive X-ray spectroscopy (EDS) (Fig. 2a.).



a) b)

Figure 1 – Clusters of nickel atoms in the crystal lattice of silicon.
a) Clusters of impurity nickel atoms at T=1200º C;
b) ordering of clusters of nickel impurity atoms at T=800º C



a)

b) c)

Figure 2 – Composition (a), structure (b) and distribution (c) of clusters of impurity atoms of nickel on surface of silicon sample (MIRA-3 TESCAN scanning electron microscope X-ray energy dispersive microanalysis images)

This bold assumption allows us to explain the diffusion of clusters of nickel atoms with such a comparatively large diffusion coefficient. Since atoms of nickel twinned with oxygen atoms are present in clusters in interstitial positions in the crystal lattice, all cluster atoms move synchronously under the influence of external forces (temperature). This provides the thermodynamically most favorable state of clusters in the silicon lattice. The structure and distribution of clusters of impurity atoms of nickel on silicon surface are shown in Fig. 2b-c (MIRA-3 TESCAN scanning electron microscope images).

According to the proposed structure, the clusters were modeled in the Avagadro and Chem3Dvisualiser programs, where the 3D structure of the silicon cluster formed in the sublattice was studied. At the same time, based on the calculation, the distances between interstitial atoms within the cluster were determined ($R_{O\text{-}Ni}$) ~ 4 Å, ($R_{O\text{-}O}$) ~ 4.56 Å, ($R_{Ni\text{-}Ni}$) ~ 4.56 Å, ($R_{Si\text{-}Si}$) ~ 2.34 Å, ($R_{Ni\text{-}Si}$) ~ 5 Å. This model of clusters not only agrees fairly well with the experimental results obtained, but also explains the diffusion of clusters of nickel atoms in silicon.

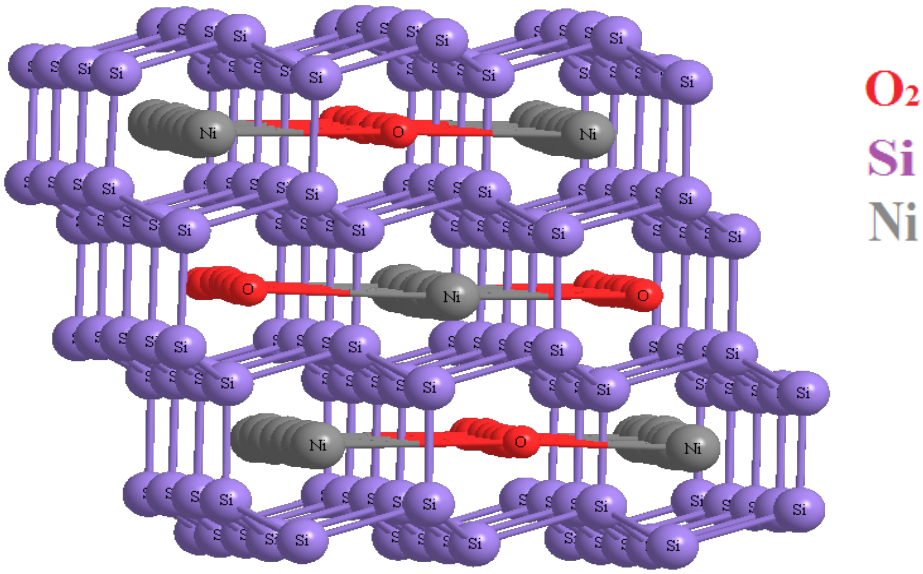


Figure 3 – Sublattice of a cluster of nickel atoms in the crystal lattice of silicon

During cooling after diffusion, nickel atoms in silicon form cluster nuclei, and additional thermal annealing activates the formation and growth of clusters. Electrically neutral nickel atoms in clusters are located in the nearest equivalent interstitial positions, forming a partially or completely filled cubic nickel sublattice.

4 Conclusions

Thus, the experimental results obtained, as well as the proposed physical model of the nickel atomic cluster structure, show that not only a new physical phenomenon has been discovered – the diffusion of impurity atomic clusters in semiconductors, but also the possibility of controlling the state of clusters in semiconductors. The coefficient of migration of clusters of impurity atoms of nickel is calculated, at a temperature of T=800 °C the migration coefficient of the cluster is D ≈ 1.2 10^{-8}÷10^{-9} cm^2/s, this value is almost 1.5÷2 orders of magnitude less than the diffusion coefficient nickel atoms at a given temperature.

This makes it possible to create a new class of photonic materials with bulk superlattices based on semiconductors with ordered clusters, which has unique functionality for creating a new generation of optoelectronic, nanoelectronic, photoelectric devices and sensors of physical quantities.

A more comprehensive study of their physical properties can reveal a number of new physical phenomena that do not exist not only in doped semiconductor materials, but also in semiconductors with impurity atom clusters.

References

1. Lindroos J., Fenning D.P., Backlund D. J, Verlage E., Gorgulla A., Estreicher S.K., Savin H., Buonassisi T. Nickel: A very fast diffuser in silicon // Journal of Applied Physics. – 2013. – Vol. 113. – P. 204906. https://doi.org/10.1063/1.4807799.

2. Bakhadyrkhanov M.K., Ismailov K.A., Ismaylov B.K., Saparniyazova Z.M., Clusters of nickel atoms and controlling their state in silicon lattice // SPQEO. – 2018. – Vol. 21. – No. 4. – P. 300–304. https://doi.org/10.15407/spqeo21.04.392

3. Milvidsky M.G., Chaldyshev V.V. Nanosized atomic clusters in semiconductors – a new approach to the formation of material properties // Physics and technology of semiconductors. – 1998. – Vol. 32. – No. 5. – P. 513-522.

4. Abdurakhmanov B.A., Bakhadirkhanov M.K., Saitov E.B. et al. // Formation of clusters of impurity atoms of nickel in silicon and controlling their parameters. // Nanoscience and Nanotechnology. – 2014. – Vol. 4. – No. 2. – P. 29-32.

5. Babich V.M., et al. Kislorod v monokristallax kremniya, Interpres LTD, Kiev, Ukraine, 1997. – 46 p. (In Russian).

6. Bakhadyrkhanov M.K., Ismaylov B.K., Tachilin S.A., Ismailov K.A., et al., Influence of electrically neutral nickel atoms on electrical and recombination parameters of silicon // SPQEO. – 2020. – Vol. 23. – No. 4. -P. 361. https://doi.org/10.15407/spqeo23.04.361

7. Astashenkov A.S., Brinkevich D.I., Petrov V.V. Svoystva kremniya, legirovannogo primesyunikelya metodom diffuzii // Dokladi BGUIR. – 2018. – Vol. 38, – No. 8, – P. 37-43. (In Russian).

8. Bakhadyrkhanov, M.K., Isamov, S.B., Kenzhaev, Z.T., Koveshnikov, S.V. Studying the effect of doping with nickel on silicon-based solar cells with a deep p–n-junction // Tech. Phys. Lett. – 2019. – Vol. 45. – No.10. – P. 959. https://doi.org/10.1134/S1063785019100031

9. Bakhadyrkhanov, M.K., Isamov, S.B., Kenzhaev, Z.T., Melebaev, D., et al., Silicon photovoltaic cells with deep p–n junction // Appl. Sol. Energy. – 2020. – Vol. 56. – No. 1. – P. 22-29.

10. Bakhadyrkhanov, M.K., Kenzhaev, Z.T., Optimal conditions for nickel doping to improve the efficiency of silicon photoelectric cells // Tech. Phys. – 2021. – Vol. 66. – No.7. – P. 851-856. https://doi.org/10.1134/S1063784221060049

11. Bakhadirkhanov M.K., Kenzhaev Z.T., Turekeev Kh.S., Isakov B.O., Usmonov A.A. Gettering properties of nickel in silicon photocells // Technical Physics. – 2021. – Vol. 11. – No. 14. – P. 2217-2220. https://doi.org/10.21883/JTF.2021.11.51529.99-21

12. Bakhadyrkhanov, M.K., Kenzhaev, Z.T., Koveshnikov, S.V., Ayupov, K.S., Kosbergenov Ye. Zh. Effect of nickel on the lifetime of charge carriers in silicon solar cells // Semiconductors. – 2022. – Vol. 56. – No. 1. – P. 128. http://dx.doi.org/10.21883/SC.2022.01.53028.9642

13. Saltas V., Chroneos A., Vallianatos F., Thermodynamic modelling of fast dopant diffusion in Si // J. Appl. Phys., – 2018. – Vol. 123. – P. 161527. https://doi.org/10.1063/1.5001755

14. Lozhkina D.A., Astrova E.V., Sokolov R.V., Kirilenko D.A., Formation of silicon nanoclusters in disproportionation of silicon monoxide // Semiconductors. – 2021. – Vol. 55. – No.4. – P. 373-387. http://dx.doi.org/10.21883/FTP.2021.04.50743.9575

15. Yakimov Yu.A., Klimanov E.A. Simulation of the processes of gettering of generation-recombination centers in silicon during the diffusion of phosphorus and boron // Applied Physics. – 2015. – No. 15. – P. 15.

16. Gafner Yu.Ya., Gafner S.L., Entel P., Formation of an icosahedral structure during the crystallization of Ni nanoclusters // Physics of the Solid State. – 2004. – Vol. 46. – No. 7. – P. 1287.

17. Bazhin I. V., Leshcheva O. A., Nikiforov I. Ya. Electronic structure of nanosized metal clusters // Physics of the Solid State. – 2006. – Vol. 48, – No. 4. – P. 726.

18. Galashev A., Vorob'ev A. Electronic properties and structure of silicene on Cu and Ni substrates // Materials, 2022, – Vol. 15. – P. 3863. https://doi.org/10.3390/ma15113863

19. Abdurahmanov B.A., Bakhadyrkhanov M.K., Ismailov K.A., Ismaylov B.K., Saparniyazova Z.M. Functional possibilities of silicon with clusters of impurity atoms // Science and Education in Karakalpakstan. – 2019. – Vol.9. – No.1. -P. 43-47.

20. Boltaks B.I., Bakhadirkhanov M.K., Gorodetsky S.M., Kulikov G.S. Compensated silicon. Nauka, Leningrad, USSR, 1972, 122 p. (In Russian).

21. Ismailov K.A., Kenzhaev Z.T., Koveshnikov S.V., Kosbergenov E.Z., Ismaylov B.K. Radiation stability of nickel doped solar cells // Physics of the Solid State. – 2022. – Vol. 64. – No.3. – P. 513–515. http://dx.doi.org/10.21883/PSS.2022.05.53509.253

22. Ismailov K.A., Iliev K.M., Tursunov M.O., Ismaylov B.K. Formation of complexes consisting of impurity Mn atoms and group VI elements in the crystal lattice of silicon // Semiconductor Physics, Quantum Electronics and Optoelectronics. – 2021. – Vol. 24. – No.3. – P. 255–260. https://doi.org/10.15407/spqeo24.03.255

23. Zainobiddinov S. Physical foundations of the formation of deep levels in silicon. Fan, Tashkent, Uzbekistan, 1984, 160 p. (In Russian).

24. Boltaks B.I., Bakhadirkhanov M.K., Gorodetsky S.M., Kulikov G.S. Compensated silicon. Nauka, Leningrad, USSR, 1972, 122 p. (In Russian).

25. Ismaylov B.K, Ismailov K.A, Kamalov Kh.U. Suppression of harmful impurity atoms with clusters of nickel impurity atoms in a silicon lattice // AIP Conference Proceedings. – 2023. – Vol. 2552. – P. 060015 (2023); https://doi.org/10.1063/5.0129486.

26. Zikrillayev N.F., Saitov E.B., Ayupov K.S., Yuldoshev I.A. Determination of the resistance of external parameters to the degradation of the parameters of silicon photocells with input nickel atoms // Physical Sciences and Technology. – 2022. Vol. 9. No. 1-2. – P. 30-36 https://doi.org/10.26577/phst.2022.v9.i1.04

27. Zikrillayev N.F., Shoabdurahimova M.M., Kamilov T., Khusanov A. Zh., Kurbonaliev K.K., Norkulov N., Saitov E.B. Obtaining manganese silicide films on a silicon substrate by the diffusion method // Physical Sciences and Technology. – 2022. – Vol. 9. – No. 3-4. – P. 89-93 https://doi.org/10.26577/phst.2022.v9.i2.011.