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Hetero- and low-dimensional structures

Clusters of nickel atoms and controlling their state in silicon lattice

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Abstract. The paper reports that using IR-spectroscopy technique, it has been revealed that nickel atoms in the silicon lattice are gathered in clusters, i.e., the phenomenon of self-assembly takes place. The concentration and dimension of the clusters are mainly defined by the temperature of diffusion and the cooling rate. The composition of clusters of nickel impurity atoms was determined. It was shown that in the process of thermal annealing within the temperature range 650…900 °C there is a significant change in the state, concentration and size of clusters. Thermal annealing at the above temperatures 650…900 °C leads to ordering the clusters that is, self-assembly of cluster blocks, as well as clusters of a loop shape that includes several dozens of clusters. A diffusion technique to form and order clusters of nickel atoms in silicon has been suggested.

Keywords: silicon lattice, cluster, nickel atom, cluster loop, annealing, diffusion, self-assembly, nanostructure, bandgap, Schottky microbarriers.

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1. Introduction

Impurity clustering in the semiconductor lattice is of great scientific and practical interest. This might occur not only owing to the possibility to alter the fundamental parameters of semiconductors [1], but also to the chances of obtaining a specific variety of semiconductors, *i.e.*, bulk nanostructured semiconductor materials [2].

As compared to conventional semiconductor materials with nanostructures, the bulk nanostructured semiconductors can likely demonstrate much greater functionality [3].

From this viewpoint, nickel atoms in the silicon lattice are of great interest, because they are expected to behave differently than other impurity atoms that create deep energy levels in Si bandgap. This is primarily caused by the sufficiently high solubility ($N \sim 10^{18}$ cm^{-3}), which is 1.5…2 times higher than that of impurity atoms of II and VI groups as well as of the transition metals one. Another major difference is the anomalously high diffusion coefficient ($D \sim 10^{-5}$ cm^2/s at T = 1200 °C) of Ni in silicon [4-5]. It's worth mentioning that only a minuscule fraction of the doped nickel atoms happen to be in electrically active state, *i.e.*, only those atoms that are located at the lattice sites. Atoms of nickel create two acceptor levels in the bandgap of silicon: $E_1 = E_V + 0.2$ eV, $E_2 = E_C - 0.4$ eV [6], the concentration of which tends to be $N_S \sim 4 \cdot 10^{14}$ cm^{-3} at 1250 °C. The lion's share of the embedded atoms (99.99%) tends to be in interstitial positions in the silicon lattice and in electrically neutral state, which serve as a stimulating factor for assembly of clusters of nickel impurity atoms in the lattice [7].

Another advantage of using these impurity atoms is that the diffusion of nickel can be realized under ambient conditions in air (without vacuum), which allows the alloying of silicon wafers of various diameters. This not only creates cost-effective technological doping conditions, but also allows obtaining samples with fairly homogeneous and reproducible parameters.

2. Technology and technique of research

A single-crystalline *n*-type silicon sample with the resistivity 40…60 Ohm·cm was chosen as a starting material for diffusion of nickel atoms. The concentration of oxygen was $N_{O2} \sim 4 \cdot 10^{17}$ cm^{-3}, whereas the density of dislocations was $S \sim 4 \cdot 10^3$ cm^2. The diffusion of nickel was carried out from 1 μm-thick pure metallic layer of nickel deposited on the surface of a silicon wafer (60 mm in diameter and 1 mm thick) under conditions of a sufficiently high vacuum $P \sim 10^{-6}$ atm. Diffusion was carried out in the air within the range of T = 1050…1250 °C for t = 0.5…5 hours. After diffusion, the samples were removed from the furnace and cooled off in air. Shortly thereafter, silicon wafers doped with Ni were cut into samples with dimensions 1×4×10 mm.

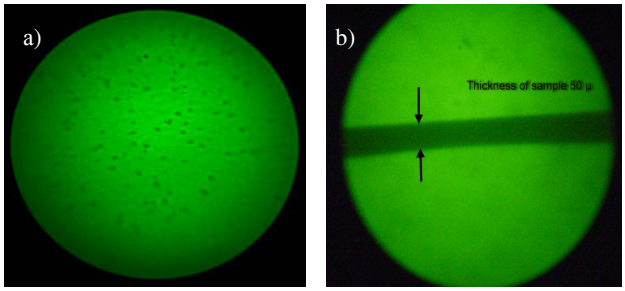

Fig. 1. (a) Homogeneous distribution of clusters. (b) Reference sample without Ni clusters.

Having done mechanical and chemical processing, the electro-physical parameters of the samples were measured by the Hall effect technique. Eventually, it was revealed that the electro-physical parameters of all the samples under investigation practically were the same and did not significantly differ from each other, which is evident of homogeneity of silicon wafer doping.

It was also revealed that the electro-physical parameters of the investigated samples were practically similar and did not depend on diffusion time (t = 0.5…5 h) but on the diffusion temperature of annealing, which confirms the sufficiently high diffusion rate of Ni atoms in silicon [4].

All the samples, after doping with nickel at the temperature T = 1250 °C, had a reversed type conductivity type, *i.e.*, became of p-type with the resistivity ρ ~ (4…5)·10^3 Ohm·cm. Being based on the temperature dependence inherent to the Hall coefficient, it was determined that the concentration of electro-active atoms of nickel turned out to be $N = (1.5…2)\cdot10^{14}$ cm^{-3}.

3. Results and discussion

The process of formation and dynamics of changes in the state of clusters from nickel atoms in silicon lattice were studied using the infrared microscope MIK-5, and also by using the X-ray diffraction analysis ("Panalytical Empyrean" diffractometer λ = 1.5418 Å (CuK (alpha) RADIATION) – copper tube.

The samples after having been mechanically and chemically treated were polished (both sides) for optical investigation under microscope, and the results were processed with a computer. The results of IR microscope studies showed that in the samples doped with nickel at the temperature T = 1250 °C and after diffusion annealing, almost uniform distribution of dark dots both on the surface and in the near-surface region may be observed, whereas the size of them was approximately d = (1…2) μm and density S = (1,5…2)·10^7 cm^2 (Fig. 1a).

Reference samples annealed under the same conditions, but without nickel atoms, were sufficiently transparent in the infra-red spectrum, and no such dark dots were found in them (Fig. 1b). The nature of dark dots in Si samples doped with nickel was further investigated by X-ray diffraction analysis.

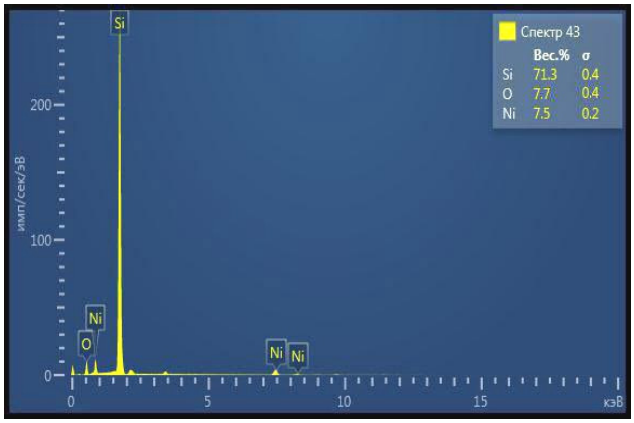

Fig. 2. Content analysis of clusters consisting of impurity nickel atoms (picture depict. SEM EVO-MA10).

As the results of our investigations show (Fig. 2), the dots consists of nickel (7-8%), oxygen (8%), silicon (71-72%), which means the clusters represent array of solid solutions containing both Ni and oxygen atoms, and every tenth atom is either atom of nickel or oxygen. The approximate dimension of such clusters is about V = 2·2·2 μm^3 = 8·10^{-12} cm^3, they can contain about 2·10^9 atoms, of which about 2·10^8 are atoms of Ni, whereas the bulk of the atoms in them is represented by silicon atoms located in crystal lattice sites.

The Ni atoms are mainly in the form of electrically neutral atoms ($3d^{10}4s^0$), and the distance between them is d = 5…6 nm. Therefore, it can be assumed that in the clusters, nickel atoms can form a face-centered cubic sublattice [1].

Thus, based on these results, one can assume that the dark dots represent microclusters enriched with atoms of nickel. To confirm the idea that such clusters occur over the entire bulk crystal, and not only at the surface, we polished the investigated samples and remove 50 μm of layer from both sides, until the samples were reduced to half in size. After the each grinding step, the samples were polished and examined under IR microscope in identical technological conditions. The results of the study apparently confirmed that the clusters appear to be practically uniformly distributed throughout the entire crystal bulk, and their dimensions and densities also did not differ significantly.

The concentration of clusters was about N = 5·10^{11}…10^{12} cm^{-3}, which means that the clusters were practically uniformly distributed throughout the entire bulk of material. The results of the study showed that if conditions of cooling of the samples after the diffusion annealing are maintained at T = 1250…1100 °C, then, depending on the diffusion temperature, their concentration would vary within the range N = 4.5·10^{12} cm^{-3} down to 6.5·10^{11} cm^{-3}. It was revealed that the size and concentration of clusters essentially depend on the cooling rate of the samples after the diffusion annealing has ended. One can reasonably assume that by varying the diffusion and cooling rates, one can create nickel clusters of different sizes in the wide range.

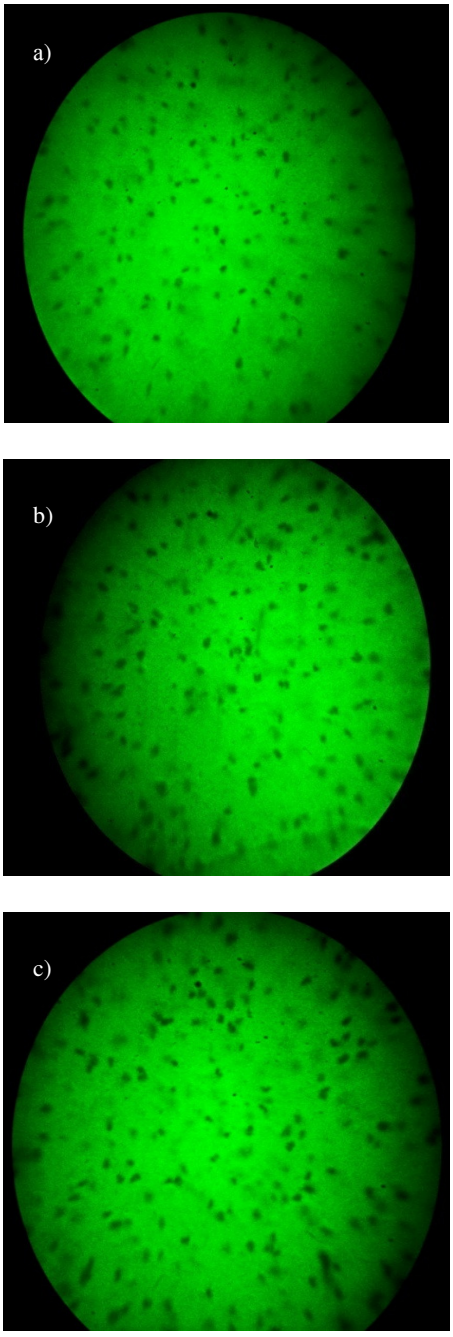

Fig. 3. Dynamics of changes in the size of clusters after thermal annealing at: 1000 (a), 900 (b), and 800 °C (c).

The samples were afterwards annealed in the temperature range of 1100…650 °C for 2 to 5 hours. The prime concern behind this procedure was to determine first of all the stability of clusters at lower annealing temperatures, and secondly to establish the functional correlation between the parameters of the clusters as a function of temperature and duration of thermal annealing, since the temperature of thermal annealing changes the super saturation of the Si-Ni solid solution.

The results of the research showed that the thermal annealing causes enlargement of clusters, *i.e.*, their size increases, and their density decreases accordingly. This process persist to temperature annealing at T = 750 °C. The dynamics of changes in clusters' dimensions is shown in Fig. 3. As can be seen, in this case clusters' sizes reach 3…5 μm, and the uniform distribution is well preserved still. The increase in the size of clusters, as well as the appearance of transparent areas in the samples during thermal annealing, suggests that it witnesses the reunion of small clusters with each other.

As a result, in the course of thermal annealing of these samples at T = 750 °C for t = 2…5 hours, very interesting physical phenomena were observed, that is, the clusters started to assemble in order, *i.e.*, chain of ordered clusters of nickel impurity atoms is formed in silicon lattice (Fig. 4a). It is established that the effect of ordering the clusters occurs throughout the bulk across different crystallographic directions. As the time of thermal annealing increases, this process goes on, and the length of the chain of clusters increases substantially. The dynamics of ordering of clusters is shown in Figs. 4a–4d.

As the annealing time at T = 750 °C increases, more and more clusters participate in the process of chain formation, and even larger transparent areas appear in the samples. The annealing for more than t > 9 hours did not lead to a significant change in ordering the clusters. This proves that almost all clusters somehow manage to participate in the ordering process.

It was ascertained that the length of cluster chains can reach from 150…200 up to 350…400 μm, and the number of clusters in the chain varies from 20 to 50, the distance between clusters in these chains can be from 0.5 to 1.5 μm. The different sharpness of the cluster chains found in the samples (Fig. 4d) suggests that the cluster chains are located in different depth profiles of the sample.

These results enabled us to assume that ordering the clusters occurs throughout the entire bulk of the crystal.

The second even more interesting phenomenon is formation of the so-called "cluster loops", in some samples during thermal annealing at T = 75…700 °C. As the time of annealing increases, the growth of the cluster loops becomes more and more transparent, and more and more clusters seem to participate in this process (Fig. 5).

As the time of thermal annealing increases, the number of clusters in the loop remains practically unchanged, but the density of the loop grows. It was found that the shape of the cluster loops is basically close to hexahedrons with a diameter d = 10…20 μm, whereas the number of clusters in them ranges from 5 to 10.

The results of this investigation give sufficient ground to assert that in the silicon lattice the so-called "self-assembly" of the clustering of nickel atoms takes place. Meanwhile, the size and density of the clusters depend mainly on the cooling rate and the diffusion temperature. It can be assumed that rapid cooling leads to formation of clusters that are several nanometers in size, and their concentrations can reach $N \sim 10^{13} \div 10^{14}$ cm^{-3}, whereas the number of atoms in these clusters can reach $n = 10^3 \div 10^4$.

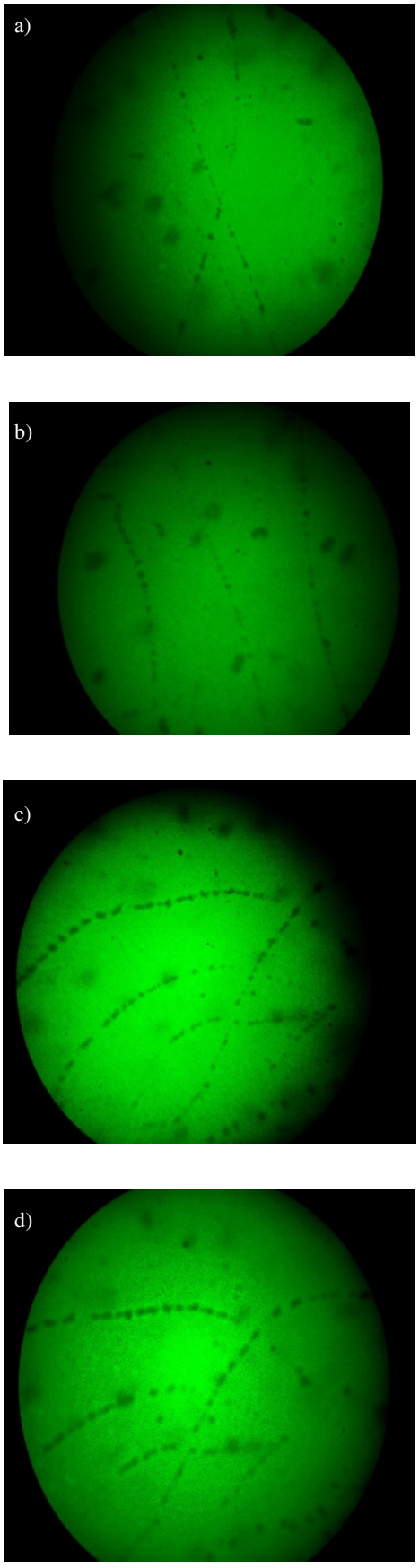

Fig. 4. Dynamics of ordering the clusters of nickel atoms in the silicon lattice at 750 °C: a) t = 3 hours, b) 5, c) 7, and d) 9.

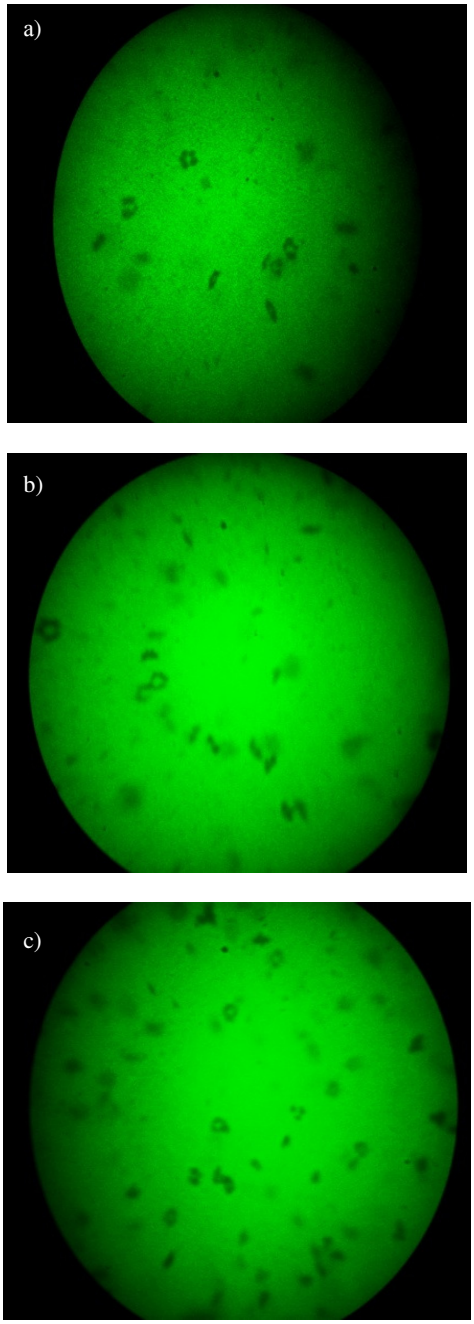

Fig. 5. Dynamics of formation of a cluster loop in the samples after thermal annealing at the temperature T = 750 °C: a) t = 3 hours, b) 6 hours, and c) 9 hours.

The availability of more advanced equipment could allow us to observe evolution of nanoscale clusters and establish the law of change in their sizes and concentration as functions of the cooling rate after diffusion annealing. The investigative results obtained make it possible to assert that by varying the temperature of diffusion and cooling rate, it would be possible to obtain bulk nano- and microstructured silicon with nano- and microclusters of nickel atoms with pre-determined dimensions and concentrations.

The temperature variation and the additional annealing time variation at lower temperatures allows to

control the state of clusters, that is, formation of cluster chains and loops with the required parameters. Formation of clustered chains and cluster loops is practically a new phenomenon and its physical nature is yet to be understood.

Formation of cluster chains and loops substantially increase the functionality of materials. One could develop nano- and microscale superlattices and ideal nano- and microbarriers of Schottky as well as surface state-free heterojunctions, as well as nano- and microdimensional variband structures, and finally, such materials could be availed in creation of more efficient solar cells with a wider spectral range.

A few words about the strengthening and formation of cluster chains and cluster loops. The obtained results allow us to assume that in this case the diffusion of whole clusters takes place practically at the same diffusion rate as that of nickel atoms in silicon, and the process of lump diffusion is well synchronized.

This process can only happen, if the nickel atoms participating in the clusters are in interstitial sites and create a certain type of sublattice inside the basic silicon matrix. These assumptions require more careful investigations, and further experimental studies are to be done using modern research methods. The study of electrical, optical, photoelectric, as well as deformation properties of silicon with clusters of nickel atoms, allows us to discover new physical features of a new material.

4. Conclusion

In conclusion, it can be said that silicon doped with nickel atoms could be of great interest, as it represents a novel material characterized by boosted functionality that, in turn, would allow enhancing the modern optoelectronics, photonics and photovoltaics, as well as nanoelectronics. And most importantly, based on a fairly simple and cheap technology, it would be possible to obtain bulk nano- and microstructured materials based on the basic material of modern electronics [8-9].

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