East European Journal of Physics. 1. 327-331 (2024)
DOI:10.26565/2312-4334-2024-1-30 ISSN 2312-4334

INFLUENCE OF DOPING CONDITIONS ON THE PROPERTIES OF NICKEL ATOMIC CLUSTERS

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Received October 23, 2023; revised January 22, 2024; accepted January 25, 2024

It is shown that the dynamics of changes in the state of nickel clusters depends on the temperature of the diffusion maximum and the cooling rate. It was found that with increasing annealing temperature and cooling rate, an increase in density and a decrease in cluster size are observed. In this case, the main attention was paid to the determination of the laws governing the change in the density, size, and structure of clusters from temperature and cooling. The process and dynamics of the interaction of clusters depends on the diffusion coefficient of impurity atoms in the lattice and the level of supersaturation of the solid solution. It has been established that with a change in the annealing temperature from T = 1100°C to 1250°C, the cluster density increases by almost 1-1.5 orders of magnitude, and their size decreases by a factor of 5–6. It seems to us that to obtain clusters with stable parameters, the optimal cooling rate is 200–300°C.

Keywords: *Silicon; Impurity cluster; Doping; Diffusion; Cooling rate; Nanostructure; Diffusion coefficient; Cluster density*
PACS: 78.30.Am

INTRODUCTION

The study of the influence of doping conditions on the properties of nickel atom clusters is of great scientific and practical interest. Since the study of the properties of clusters, their stability and degradation processes in them, makes it possible to create the necessary micro-and nanostructures of cluster-silicon, cluster-silicon-cluster, etc. [1; 2].

The formation of a cluster leads the system to a more equilibrium state with minimal internal energy [1, 10]. Therefore, for the formation of clusters of impurity atoms, the following conditions must be fulfilled:

- Impurity atoms must have a high diffusion coefficient and sufficient solubility in the studied semiconductor materials.
- They must not form silicides or other solid solutions.
- Bond energy of impurity atoms in a cluster should be sufficient so that such clusters do not decay when exposed to external influences or with time.

Let us analyze which impurity atoms in semiconductors and under what conditions can satisfy the above conditions.

Almost all the elements of the transition group in silicon have sufficiently large diffusion coefficients ($D \sim 10^{-5} \div 10^{-8}$ cm^2/s), but they have a low solubility ($N \sim 10^{15} \div 10^{18}$ cm^{-3}).

It should also be noted that these elements create several deep levels in the band gap, but the majority of the introduced atoms are in the electrically neutral state (90-99.99%). Under conditions of high-temperature diffusion doping, almost all elements of transition groups form silicide with silicon atoms with different compositions [3], therefore, it can be assumed that doping of silicon with elements of transition groups using high-temperature diffusion does not allow the formation of atomic clusters.

In this regard, we are studying and developing a new method of doping silicon with nickel atoms, the so-called low-temperature and step doping.

The essence of this doping method is to carry out diffusion of the impurity with a gradual and phased increase in the diffusion temperature from room temperature to a certain value, with a certain speed and holding the samples for a certain time at each diffusion stage [4,11].

The question is, what might be the result of such doping technique? It gives the following:

1. At low temperatures, the concentration of equilibrium vacancies is negligent and there is practically no capture of impurity atoms by vacancies.

2. In the region of low temperatures, the impurity is forced to diffuse only along the interstitial locations, which provides not only a high diffusion coefficient, but also significantly increases the probability of the interaction of impurity atoms with each other.

3. Under conditions of low-temperature alloying, the formation of silicides and other hard alloys is almost completely absent, since the concentration of impurity atoms will be insufficient for the formation of silicide [1, 5].

Cite as: K.A. Ismailov, Z.M. Saparniyazova, G.T. Kudeshova, G.A. Seytimbetova, F.A. Saparov, East Eur. J. Phys. 1, 327 (2024), https://doi.org/10.26565/2312-4334-2024-1-30

4. For impurities diffusing from the gas phase (Mn, Zn, S, Se, Te) erosion of the surface of the sample is excluded [6, 7].

Thus, we can say that the new doping method can create optimal conditions for the formation of clusters of impurity atoms. This allows us to create sensitive detectors and use them as implants in humans in the future.

MATERIALS AND METHODS

To study the effect of the maximum diffusion temperature on the state of clusters, samples were made based on n-type silicon with c 40 Ω·cm, with an oxygen concentration of $N \sim 7 \cdot 10^{17}$ cm^{-3}. The maximum temperatures were T = 1100℃, 1150℃, 1200℃ and 1250℃, other doping conditions and cooling conditions were the same.

In this case, the main attention was paid to determining the laws of changes in the density, size, and structure of clusters as a function of temperature. The cluster size was determined by comparing with a calibration standard with a width of 75 μm with a maximum increase of INFRAM-I, the average density was determined by counting the number of clusters in a certain area. In this case, the standard error of the measurements was 10–12%.

RESULTS AND DISCUSSION

In Figure 1 it is shown the dynamics of changes in the state of nickel clusters depending on the temperature of the diffusion maximum. As can be seen from the figure, with an increase in the annealing temperature, an increase in density and a decrease in cluster sizes are observed.

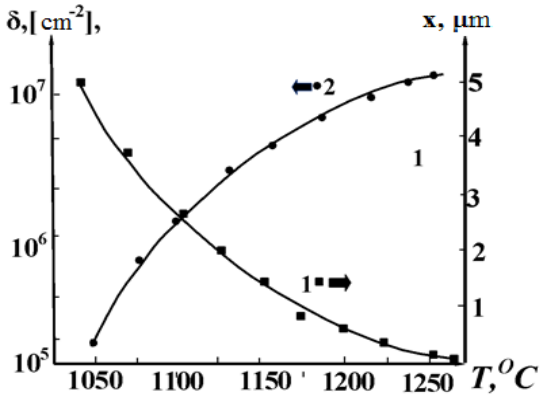

Figure 1. Change in the parameters of nickel clusters depending on temperature at the end of diffusion

Thus, it was found that with annealing temperature changing from T = 1100℃ to 1250℃, the cluster density increases by almost 1-1.5 orders of magnitude, and their size decreases by 5–6 times. To study the effect of the cooling rate, 3 parties of samples were prepared in three ampoules with the same geometric parameters. They were alloyed at T = 1200℃; the first party of samples was cooled by dropping the ampoule directly into the oil (T = 25℃) [3,12,18]. The calculation shows that in this case, the cooling rate is about v = 300℃/s. The second party of samples was cooled on a massive metal plate. In this case, the cooling rate is ~100℃/s. The third one of samples was left in the furnace, after it was turned off, and which was cooled for a very long time for approximately 160-180 minutes to a temperature of T = 200℃. The state of clusters in samples cooled at different rates is shown in Figure 2.

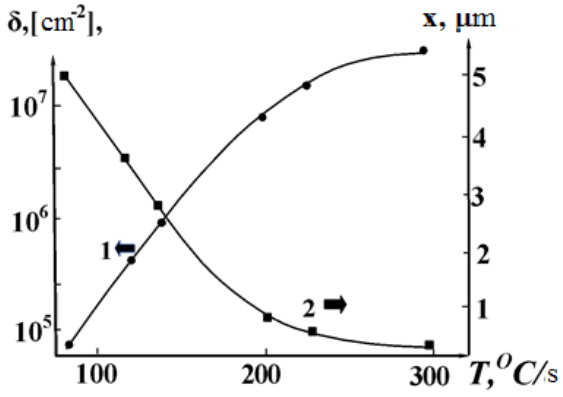

Figure 2. The effect of cooling rate on the parameters of nickel clusters

As can be seen in the samples cooled at a rate of $\vartheta_1 = 200$℃/s, a significant decrease in the cluster size and a noticeable increase in their density are observed. At the maximum cooling rate, the INFRAM-I microscope did not allow observing the presence of any clusters not only on the surface, but throughout the volume. At the same time, in samples cooled in the furnace, a noticeable increase in cluster sizes is observed. Thus, it turned out that by changing the doping

conditions, one can control the density and size of clusters. It seems to us that to obtain clusters with reproducible parameters, the optimal cooling rate is 200–300°C/s. By changing the diffusion temperature (1100–1250°C), one can obtain the necessary density and size of clusters.

The physical nature of the interaction of clusters of impurity atoms in semiconductors does consist in the tendency of the system to a state with minimum free energy [8], i.e., to the gradual restoration of the equilibrium state of the system. Under ordinary conditions (T~300 K), the introduced impurity atoms in the lattice, regardless of the doping method, create a locally deformation or electric potential. The magnitude of this potential is mainly determined by the size, electronic structure, charge state and concentration of impurity atoms. Consequently, we can assume that semiconductor materials supersaturated with impurity atoms are in a nonequilibrium state. Therefore, under the presence of appropriate thermodynamic conditions, the interaction of clusters of impurity atoms occurs, i.e., the process of restoring the equilibrium state of the system occurs due to the formation of stable complexes i.e. clusters. The process and dynamics of cluster interaction depends on the diffusion coefficient of impurity atoms in the lattice under the conditions under consideration, and the level of saturation of the solid solution. It follows that the interaction of clusters of impurity atoms with a small diffusion coefficient (i.e., an impurity forming a substitutional solid solution) occurs very slowly, almost not noticeably. However, for such impurity atoms with a high concentration ($N\sim10^{21}\div10^{22}$ cm^{-3}), the cluster interaction process is significantly accelerated [4]. In this regard, impurity atoms having a sufficiently large diffusion coefficient are of interest, i.e., impurities forming solid interstitial solutions. Thus, it can be argued that from the point of view of thermodynamics, cluster formation of impurity atoms is a natural process. But the speed of this process, as mentioned above, is mainly determined by the diffusion coefficient and the level of saturation of the solid solution.

The kinetics of the formation of clusters of impurity atoms in the crystal lattice of a semiconductor can be described by the following model. In the process, after diffusion thermal annealing, impurity atoms are in an extremely nonequilibrium state and must go to their centers of equilibrium (nuclei) of future clusters in their equilibrium positions. This process provides the system with the acquisition of minimum free energy. The kinetics of the process is determined by the following factors:

1. The coefficient of supersaturation K, which is determined by the ratio of the solubility of impurity atoms at diffusion temperature to solubility at thermal annealing temperature. The larger the K value, the more the system is in a nonequilibrium state. Therefore, we can assume that K is the main driving factor in the formation of clusters.

2. The formation of impurity atom clusters at the lattice sites is limited not only by the diffusion coefficient, but also by the formation of a sufficiently large concentration of vacancies. When impurity atoms are in internodes, the process is significantly accelerated due to the large diffusion coefficient and the possibility of cluster formation in internodes with certain states and structures, which does not require significant rearrangement of the crystal lattice and energy. The diffusion coefficient of impurity atoms at the thermal annealing temperature is determined by the ratio.

$$D_t = D_0 \exp\left(-\frac{E_g}{kT_t}\right)$$

where E_g is the diffusion activation energy; k is the Boltzmann constant. It can be seen from this relation that, with increasing temperature, the diffusion coefficient increases, but the coefficient *K* decreases accordingly.

3. The nuclei of clusters can be all kinds of defects - dislocations, vacancies, impurity atoms, etc. An analysis of experimental works [9, 10] shows that the density of clusters does not depend on the density of dislocations and exceeds their density by several orders of magnitude. Therefore, we can assume that the contribution of dislocations to the quality of the nucleus of clusters is not basic. Calculations show that the concentration of equilibrium vacancies in silicon, which are determined by the ratio:

$$N_v = N_0 \exp\left(-\frac{E_g}{kT}\right) = 5\cdot10^{22} \exp\left(-\frac{E_g}{kT}\right)$$

and the low-temperature annealing region is much lower than the concentration of impurity atom clusters in the lattice, which allows us to conclude that although vacancies can be cluster nuclei, their contribution is negligible. Therefore, we assume that the nuclei of the clusters are impurity atoms that are in equilibrium at the annealing temperature. In this regard, in a simplified model, we can assume that the concentration of impurity atoms that are in equilibrium at the annealing temperature can serve as the concentration of clusters.

4. The number of atoms in the clusters is mainly determined by the value of the supersaturation coefficient *K*. Therefore, it can be assumed that, by controlling the value of *K*, one can obtain both molecules consisting of several atoms and nanoclusters and clusters with sizes from 0.1 to 10 μm. The number of atoms in the clusters will be equal

$$N_v = \frac{N_0 - N_t}{N_t} = \frac{N_0}{N_t} - 1$$

Based on the results of studies with an INFRAM-I microscope, it was found that the cluster size varies within 0.1-3 μm. It seems to us that this is the size of the deformed region of the silicon lattice in which the clusters are located. Therefore, it can be assumed that the true cluster size is 0.05–1.5 μm.

Regarding the concentration and distribution of clusters in the lattice one can assume that if we take into account that for each elementary face-centered cubic lattice created by nickel atoms inside a silicon crystal, n=4 $\left(n = A/8 + C/2\right)$, and determining the average volume of each cluster (~ 10^7Å) and the volume of the elementary lattice of nickel atoms (~ 20Å), then we can calculate on average how many unit cells are in each cluster. As the calculation shows, the average number of unit cells in each cluster is ~ 10^5, and the number of nickel atoms in each cluster is N ~ $4 \cdot 10^5$ atoms. If we assume that almost all nickel atoms participate in cluster formation, then the cluster concentration is $N = N_i/n \sim 10^{12}$ cm^{-3}, (where N_{Ni} is the concentration of nickel atoms in silicon ~ 10^{18} cm^{-3}).

Now we determine the concentration of clusters based on experimental data. The cluster density determined on the basis of INFRAM-I results is ~ (4÷5) 10^6 cm^{-2}, the average diameter of each cluster is ~ 0.5 μm, therefore there should be about 1011 clusters in one 1 cm^{-3}. This experimental data is quite close to the calculated data. Thus, it can be undoubtedly stated that the nickel atoms in silicon (at T=1200°C) create clusters with a concentration of ~10^{12} cm^{-3}. The results of microprobe analysis on the Jeol JXA-8800R and the electrical properties of the clusters showed that the clusters of nickel atoms have a conductivity close to metallic. Then it can be assumed that each cluster-silicon structure is a Schottky barrier, i.e., Schottky diode. The features of such a Schottky diode, unlike ordinary Schottky diodes, are, firstly, the absence of surface states in the metal-semiconductor contact region, this is an ideal Schottky barrier, secondly, "buried" Schottky diodes can be created, and thirdly, a cluster-silicon structure can be created -cluster or silicon-cluster-silicon with an ideal contact region; in the fourth, it is possible to control the area of such structures with a radius of ~ 0.05÷1 μm.

CONCLUSION

By studying the various external influences and comparing the works of other authors, we made a conclusion that the sensitivity of the resulting samples demonstrates hundred times more magnitude to radial pressure in compare to results demonstrated by other authors [13-21]. And they demonstrate the results that met the parameters we needed. Based on the above, it can be assumed that the experimentally observed non-monotonicity of the dependences $\rho=f(P)$ is a consequence of two conflicting processes: the first is a decrease in the band gap and the associated change in the ionization energy of deep *Ni* levels, which leads to an increase in conductivity and the second is the decay of precipitates impurities with an increase in the concentration of electrically active centers, which, under the influence of pressure, are displaced from the volume of the semiconductor and change the spectrum of the surface charge distribution at the metal-semiconductor interface. Mechanical stresses that stimulate the gettering of defects from the bulk of the semiconductor, or impurities localized in the metal-semiconductor transition layer and interacting with surface states, may be responsible for changes in the properties of the interface under the influence of pressure [15, 16]. All these features show very interesting new functionalities of silicon with clusters of nickel atoms. For example, the abilities to create almost perfect Schottky barriers with gigantic frequency properties and to create photodetectors with a response time of the order of several picoseconds, as well as possibility to create integrated circuits with an ultrahigh degree of integration, etc.

Acknowledgment

The authors are grateful to the Director of the Research Institute of Semiconductor Physics and Microelectronics, Doctor of Physical and Mathematical Sciences, Prof. Sh.B. Utamuradova for assistance in conducting experiments and discussing the results.

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ВПЛИВ УМОВ ЛЕГУВАННЯ НА ВЛАСТИВОСТІ КЛАСТЕРІВ АТОМІВ НІКЕЛЮ

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Показано, що динаміка зміни стану кластерів нікелю залежить від максимальної температури дифузії та швидкості охолодження. Встановлено, що зі збільшенням температури відпалу та швидкості охолодження спостерігається збільшення щільності та зменшення розміру кластерів. При цьому основна увага приділялася визначенню закономірностей зміни щільності, розмірів і структури кластерів від температури та охолодження. Процес і динаміка взаємодії кластерів залежить від коефіцієнта дифузії домішкових атомів у ґратці та рівня перенасичення твердого розчину. Встановлено, що при зміні температури відпалу від T = 1100°C до 1250°C щільність кластерів зростає майже на 1-1,5 порядків, а їх розмір зменшується в 5-6 разів. Вірогідно, що для отримання кластерів з відтворюваними параметрами оптимальна швидкість охолодження становить 200–300°C.

Ключові слова: *кремній; кластер домішок; допінг; дифузія; швидкість охолодження; наноструктура; коефіцієнт дифузії; щільність кластерів*