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Influence of electrically neutral nickel atoms on electrical and recombination parameters of silicon

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Abstract. The results of this study show that creation of clusters from impurity nickel atoms almost completely suppresses generation of thermal donors within the temperature range 450 to 1200 °C. The composition of these clusters was determined using the technique of energy dispersive X-ray spectroscopy, which revealed that the typical cluster consists of silicon atoms (65%), nickel atoms (15%) and oxygen atoms (19%). Based on the experimental results, the authors have suggested that the nickel atoms intensively perform the role of getter for oxygen atoms in the course of clusterization. It was shown that the additional doping of silicon with nickel at T = 1100…1200 °C enables to ensure a sufficiently high thermal stability of its electrical parameters within a wide temperature range.

Keywords: clusters of nickel atoms, lifetime, diffusion, thermal donors, thermal stability, electrical parameters, gettering.

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1. Introduction

Nickel, unlike other elements of transition groups, has not only the largest diffusion coefficient in silicon, but also the high solubility level (10^{18} cm^{-3}) [1, 2]. However, the maximum concentration of electroactive atoms occurred to be less than 0.1% of the total solubility of atoms at a given temperature, which implies that the majority of Ni atoms in silicon must be in the electrically neutral state.

As it has been shown in [3, 4], this fraction of atoms located in interstitial sites can form impurity clusters in the silicon lattice. Their structure, size and distribution are mainly determined by doping conditions and cooling rate immediately after diffusion annealing, as well as by the temperature and duration of further thermal annealing.

Thus, these studies aimed at determining the law of how creation of electrically neutral clusters from nickel atoms in silicon lattice influences on electro-physical parameters of the silicon material, and it is of particular interest, especially when formulating the task to obtain the silicon wafer with stable parameters, which, in turn, during the technological process are always subjected to various temperature influences.

2. Experimental results and discussion

Monocrystalline silicon ingots obtained using the Czochralski technique of both *n*- and *p*-type conductivity with the concentrations of boron and phosphorus within the range $2\cdot10^{15}…5\cdot10^{14}$ cm^{-3} were chosen as starting materials. The oxygen concentration in the studied samples was $(6…7)\cdot10^{17}$ cm^{-3}, the dislocation density was 10^3 cm^{-2}.

Diffusion doping in the diffusion furnace from a metallic nickel film both in air and in silica ampoules (pressure P~10^{-6} bar) was performed at the temperatures T = 1000…1200 °C. The duration of diffusion was chosen so as to ensure uniform distribution of atoms of nickel throughout the entire bulk of samples. The geometric size of the samples was 0.8×4×8 mm.

In separate ampoules under reference conditions, silicon samples containing no nickel atoms were annealed in order to evaluate the effect of diffusion annealing on their electro-physical parameters. After diffusion annealing, 30 μm were removed from all sides of the silicon samples in order to study the bulk properties of material. The mechanical and chemical treatment of all samples was carried out under identical conditions.

The electrical parameters of the samples were measured using the Hall technique, whereas the lifetime of minority charge carriers was measured using the technique of conduction modulation with a pin contact.

In Table, the electrical parameters and lifetime of minority charge carriers in the samples before and after diffusion of nickel atoms at various temperatures and duration are shown. Meanwhile, the authors chose only those samples, where the concentrations of initial impurities (boron, phosphorus) were always higher than the concentration of electroactive nickel atoms at a given diffusion temperature. That was done in order to exclude the influence of the concentration of electroactive nickel atoms on electro-physical parameters of the initial silicon material.

As it can be seen from the experimental results in the course of diffusion of nickel atoms at the temperature $T = 1200$ °C in the *p*-type samples with $\rho = 10\,\Omega\cdot$cm ($N_B = 2\cdot10^{15}$ cm^{-3}), both their initial electrical parameters and the lifetime practically did not change. At the same time, the resistivity in the reference samples increased by almost 30 times ($\rho = 285\,\Omega\cdot$cm), while the lifetime decreased by 5-6 times.

These experimental results prove that at such annealing temperatures, a sufficient number of thermal donors is generated ($N > 1.9\cdot10^{15}$ cm^{-3}), which is confirmed by the results of authors reported in [5–7]. At the same time, in the samples doped with nickel, neither thermal donors nor recombination centers are being generated. To verify this suggestion, we carried out the diffusion of nickel at lower temperatures of $T = 1100\ldots1150$ °C, whereas at the same temperatures, under the same conditions, the reference samples were subjected to thermal annealing without nickel.

As can be seen from Table, with a decrease in the annealing temperature, the resistivity of the reference samples significantly increases by 3 and 4 orders of magnitude and reaches $9\cdot10^4$ and $2.9\cdot10^5\ \Omega\cdot$cm, while the lifetime of minority charge carriers is 10–30-fold decreased. At the same time, in the samples doped with nickel, their initial electrical and recombination parameters do not practically change at all. These experimental results indicate that the presence of nickel atoms in silicon does indeed completely suppress generation of thermal donors.

Table. Electrical parameters and lifetime of minority charge carriers in reference and nickel-doped samples at various diffusion temperatures.

No	Before annealing			Annealing conditions			After annealing		
	Type	ρ, Ω·cm	τ, μs	*T*, °C	Hour	Impurity / Control	Type	ρ, Ω·cm	τ, μs
C-1	*p*	9.7	(25–40)	1200	2	Ni	*p*	10.9	
	p	10.1	–	–	–	Ni	*p*	11.6	(15–20)
	p	11.2	–	–	–	Control	*n*	285	(2–4)
C-2	*p*	9.7	–	1150	2	Ni	*p*	10.9	
	p	11.3	–	–	–	Ni	*p*	10.9	(20–30)
	p	10.6	–	–	–	Control	*n*	$9\cdot10^4$	4
C-3	*p*	11	–	1100	2	Ni	*p*	11.2	
	p	11.3	–	–	–	Ni	*p*	10.9	(15–20)
	p	11.4	–	–	–	Control	*i*	$2.9\cdot10^5$	1
C-4	*p*	11.2	–	1050	2	Ni	*p*	10.9	
	p	12.2	–	–	–	Ni	*p*	12.3	(20–35)
	p	7.2	–	–	–	Control	*p*	13.6	(15–40)
C-5	*p*	41		1150	2	Ni	*p*	42.5	(10–30)
	p	40		–	–	Control	*n*	$1.1\cdot10^3$	$\tau < 1$
C-6	*n*	11.9	(40–50)	1150	2	Ni	*n*	11.4	(50–70)
	n	10.2		–	–	Control	*n*	12.8	(15–30)
C-7	*n*	43		1100	2	Ni	*n*	42.7	
	n	41		–	–	Control	*n*	40.5	

Note. Ni – nickel-doped samples, Control – undoped control samples.

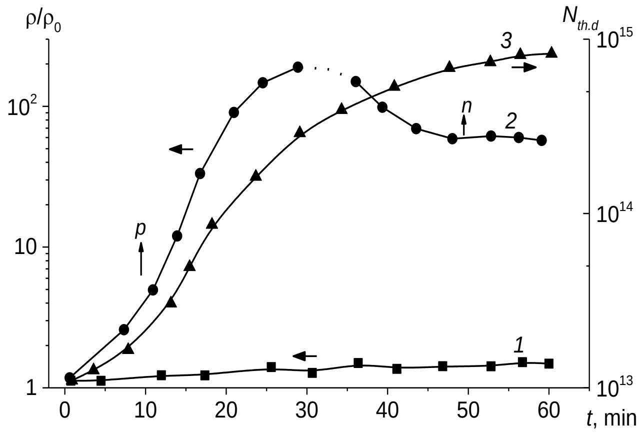


Fig. 1. Conductivity and concentration of thermal donors in Si (Ni) and in reference samples as a function of thermal annealing duration at T = 450 °C. *1* – Si (Ni) samples, *2*, *3* – reference samples.

The parameters of nickel-doped and reference samples at the annealing temperature of T = 1050 °C do not differ significantly. This may be due to the fact that the concentration of thermal donors at such annealing temperatures is less than the concentration of holes in the initial samples. In this regard, at the next stage, we used *p*-type Si with a specific resistance of ρ ~ 40 Ω·cm ($p \approx 5\cdot10^{14}$ cm^{-3}) as a starting material.

Research results in Table have shown that reference samples change their type of conductivity, that is, they become of *n*-type with the resistivity ρ ~ 10^3 Ω·cm, and the lifetime becomes τ < 1 μs. The samples doped with Ni practically retain their initial parameters. So does the lifetime of minority charge carriers. Similar results were obtained when doping *n*-type silicon with ρ = 10…60 Ω·cm.

As well known, thermal donors are more actively generated in silicon at T=450 °C [8, 9]. Therefore, it is of particular interest being able to study the effect of thermal annealing at T = 450 °C for t = 10…40 min on the resistivity of samples doped with nickel at T = 1150 °C and reference samples of *p*-type conductivity without nickel with ρ = 10 Ω·cm.

Fig. 1 shows the relative change in the resistivity of the samples preliminary doped with nickel at 1150 °C and the reference samples of *p*-type conductivity with ρ = 10 Ω·cm from the thermal annealing time at T = 450 °C. As one can see there, the electrical parameters of the samples pre-doped with nickel, practically do not change.

Meanwhile, the specific resistance of the reference samples increases with the thermal annealing time increases and reaches its maximum value at t = 30…40 min, then the type of conductivity changes.

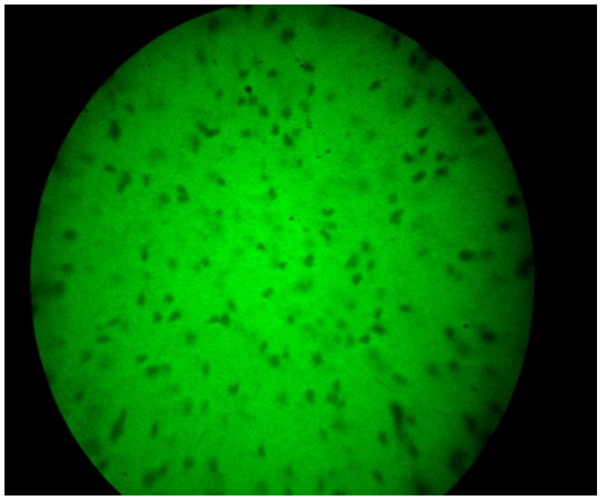
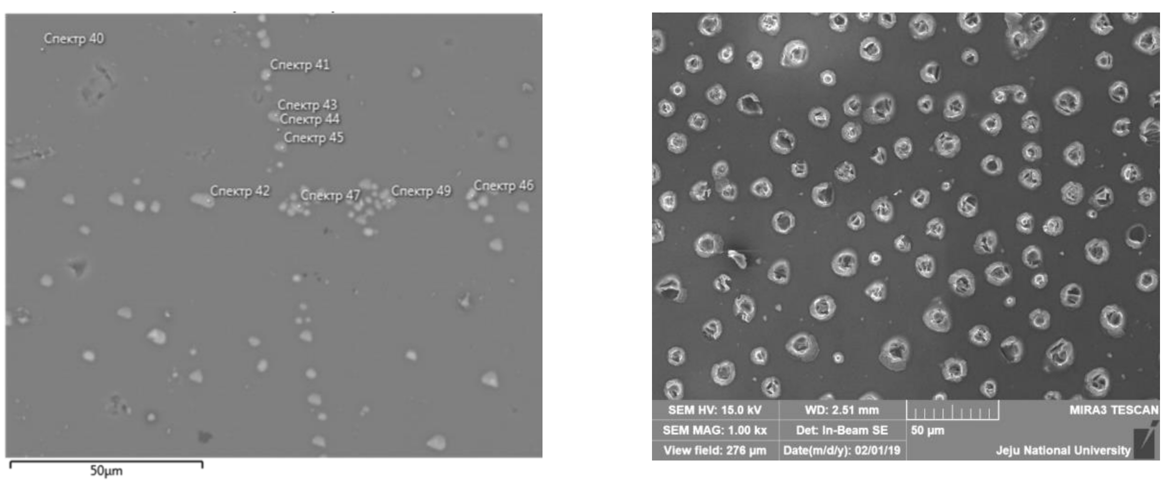


Fig. 2. Distribution of clusters from nickel atoms in silicon samples doped at T = 1200 °C.



a) b)

Fig. 3. Distribution of clusters on the surface of silicon (photographic image using a scanning electron microscope MIRA 3 TESCAN (Field-Emission Scanning Electron Microscope (FE-SEM)).

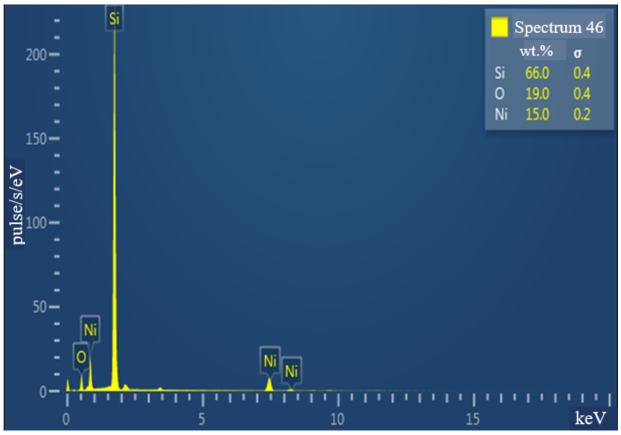


Fig. 4. Elemental analysis of clusters of impurity nickel atoms with "Spectrum 46", determined using the energy dispersive method of X-ray spectroscopy.

Meanwhile, the specific resistance of the reference samples increases with the thermal annealing time increases and reaches its maximum value at t = 30…40 min, then the type of conductivity changes.

These results once again confirm that the presence of impurity nickel atoms (*i.e.*, their electrically neutral part) almost completely suppresses generation of thermal donors in a wide temperature range T = 450…1200 °C.

To further investigate the experimental results, we studied the state of electrically neutral nickel atoms in the Si lattice by using IR microscopy with an INFRAM-I microscope. As it can be seen, the majority of electro-neutral atoms of nickel in the lattice are positioned in the form of clusters uniformly distributed throughout the entire crystal bulk (Fig. 2), which is confirmed by the results described in [2-4].

In Figs 3a and 3b the arrangement of clusters of nickel atoms on a silicon surface are shown as obtained using a MIRA 3 TESCAN scanning electron microscope (Field-Emission Scanning Electron Microscope (FE-SEM)). To verify the image and the suggestions that the observed clusters are clusters of nickel atoms, we studied their composition using the technique of energy dispersive X-ray spectroscopy. In Fig. 4, the results of these studies are presented.

As one can clearly see, the investigated clusters typically consist of silicon, nickel and oxygen atoms, the fractions of these elements are as follows: silicon – 65%, nickel – 15%, oxygen – 19%. Based on these results, it can be argued that nickel atoms significantly getter oxygen atoms in the course of buildup of clusters. Thus, one can argue that the clusters represent areas of silicon enriched with nickel and oxygen atoms.

As well known, oxygen in silicon is a source of thermal donors [10, 11], which also act as recombination centers. This behavior has clearly manifested itself in the reference samples without nickel. Therefore, it can be assumed that electrically neutral nickel atoms form clusters that practically getter and capture the significant concentration of oxygen atoms in the silicon lattice and, thus, substantially suppress generation of thermal donors, which in turn, ensures the stability of electrical and recombination parameters during various heat treatment processes.

3. Conclusions

Being based on the above experimental results, the authors propose:

1. Electrically neutral nickel atoms in the silicon lattice are mainly positioned in electroneutral clusters.
2. Clusters of nickel atoms represent micro- and nano-size areas of silicon enriched with nickel and oxygen atoms.
3. Clusters of atoms of nickel can act as active centers that getter oxygen and other uncontrolled impurity atoms in the silicon lattice; thus substantially suppressing generation of thermal donors and other recombination centers in the lattice.
4. The experiment clear indicates that in order to stabilize the initial parameters of silicon (regardless of its type of conductivity and the concentration of initial impurity atoms) within a wide temperature range T = 400…1200 °C, pre-doping with nickel at T = 1100…1200 °C for t = 30…60 min should be done.
5. The proposed technique of gettering undesirable impurity atoms could be availed of when manufacturing various electronic devices, especially in the development of effective silicon-based solar cells.
6. The process of diffusion can be carried out in air from deposited metal layers of nickel onto the surface of silicon wafers of various diameter.

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Вплив електрично нейтральних атомів нікелю на електричні та рекомбінаційні параметри кремнію

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Анотація. За результатами цього дослідження показано, що створення кластерів з домішкових атомів нікелю майже повністю пригнічує генерацію теплових донорів у діапазоні температур 450–1200 °C. Склад цих кластерів визначали за допомогою методу енергетично-дисперсійної рентгенівської спектроскопії. Виявлено, що типовий кластер складається з атомів кремнію (65%), нікелю (15%) та кисню (19%). На основі експериментальних результатів автори припустили, що атоми нікелю інтенсивно виконують роль геттера для атомів кисню в процесі кластеризації. Показано, що додаткове легування кремнію нікелем при T = 1100–1200 °C дозволяє забезпечити досить високу термостабільність його електричних параметрів у широкому діапазоні температур.

Ключові слова: кластери атомів нікелю, час життя, дифузія, теплові донори, термостійкість, електричні параметри, геттерінг.