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Effect of nickel on the lifetime of charge carriers in silicon solar cells

© M.K. Bakhadyrkhanov[1], Z.T. Kenzhaev[2,¶], S.V. Koveshnikov[1], K.S. Ayupov[1], E.Zh. Kosbergenov[2]

[1] Tashkent State Technical University,
100095 Tashkent, Uzbekistan
[2] Karakalpak State University,
230112 Nukus, Uzbekistan
¶ E-mail: zoir1991@bk.ru

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It has been shown experimentally that nickel clusters on the surface of a silicon sample contain a large amount of oxygen and recombination impurities — Cu, Fe, Cr, and so shows good gettering properties of clusters. The optimum temperature of nickel diffusion into silicon is determined as 800–850°C. Doping with impurity nickel atoms with the formation of clusters makes it possible to increase the lifetime of nonequilibrium charge carriers in the base of a solar cell by up to 2 times, while the formation of a nickel-enriched region in the face layer is more efficient. It is shown that the effect of additional doping with nickel weakly depends on the sequence of the processes of nickel diffusion and the creation of a working $p{-}n$-junction.

Keywords: silicon solar cells, nickel diffusion, nonequilibrium charge carriers, gettering, $p{-}n$ junction.

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1. Introduction

Quality of silicon monocrystals for solar cells is defined by the value of a lifetime of charge carriers (τ). During solar cells manufacturing (mainly by using high-temperature processing above 1000°C) τ can decrease due to activization of non-controlled (phonon) impurity atoms of transition metals (Fe, Cu, etc.) [1,2].

Therefore, the increase of nonequilibrium charge carriers (NCC) lifetime is the main criteria for solar cells (SC) technology optimization. With lifetime increase the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) also increase due to reverse saturation current decrease [3,4].

The main way to increase lifetime in SC structures is gettering. Impurity atoms gettering allows not only to increase NCC lifetime, but also provides stability of electrical and recombination parameters of material, that is repeatedly heat treated during SC manufacturing [5].

Gettering is usually performed by adding the various impurity atoms [6,7] into the volume with laser treatment [8], as well as by formation of porous or amorphous layer in silicon surface using ion implantation [9].

It is known [10,11], that nickel in silicon has sufficiently high volumetric solubility (to concentrations $N \sim 10^{18}\,\text{cm}^{-3}$), and at near-surface area ($d = 2{-}3\,\mu\text{m}$) its concentration can reach $N_S \sim (10^{20}{-}10^{21})\,\text{cm}^{-3}$. The large part of atoms dissolved in volume, 99.999%, and even more at near-surface area, is in electroneutral state in interstices and at certain heat treatment conditions can create clusters [12,13]. Nickel clusters form easily both during diffusion and the following heat treatment, but they have very small influence on electrical parameters of the material itself during heat treatment within temperature range $T = 400{-}1000^\circ\text{C}$ [14].

Sizes, concentration, structure and composition of clusters are mainly defined by the additional annealing temperature and general concentration of nickel atoms added to silicon [15]. Also, it is known, that nickel films, deposited on silicon, have a gettering effect [16].

In this article we analyze the efficiency of the non-controlled impurity atoms gettering with nickel atoms clusters and their influence on SC parameters. Gettering efficiency defines NCC lifetime within SC base.

Therefore. we set the following tasks: to demonstrate the presence of gettering properties of nickel clusters; to experimentally demonstrate nickel influence on NCC lifetime within SC base; to define the patterns of τ variation within SC base depending on nickel diffusion temperature; to evaluate a possibility of silicon doping with nickel before creation of $p{-}n$-transition; to study the influence of nickel-enriched layer parameters on NCC lifetime.

2. Technology and method of study

For studying the nickel influence on NCC lifetime we made SC, in which $p{-}n$-transition was created by phosphor diffusion to silicon plates of p-type of conductivity, grown with Czochralski method with resistivity of $0.5\,\text{Ohm}\cdot\text{cm}$ (KDB-0.5), thickness of $380\,\mu\text{m}$ and diameter of $d \approx 76\,\text{mm}$ at $T_{\text{diff}} = 1000^\circ\text{C}$ for $t = 0.5\,\text{h}$.

After creation of $p{-}n$-transition the plates were cut into separate samples with size of $1 \times 1\,\text{cm}$. Some samples were left for control. All other samples were vacuum-deposited with a thin layer of pure nickel with thickness of $1\,\mu\text{m}$ and diffusion was performed at various temperatures (according to experiment goals). After nickel diffusion all samples were subject to additional thermal annealing at

$T_{\text{ann}} = 750-800^\circ$C for $t = 30$ min to activate the process of gettering [17,18] of non-controlled recombination impurities. After nickel diffusion and thermal annealing the samples were cooled on air.

After each process stage the surface cleaning and chemical processing were performed to remove residual nickel and silicon oxide from the surface (10% HCl, 10% HF).

Ohmic contacts were made using nickel deposition. Flush contact was deposited on the back side, while on the face side it was created through a template with a strip width of 0.5 mm and step of 2 mm. There was no antireflective coating on the elements surface.

NCC lifetime was measured at the resulting structure using the method [19]. Lifetime in SC structures corresponds to the reverse conductance recovery time of $p-n$-transition, that was measured using decreasing vibrations of resonance LC-circuit, measurement error did not exceed 10%.

3. Experimental results

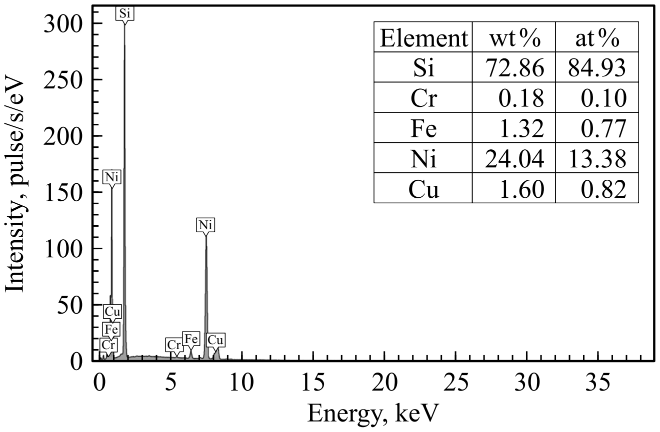
3.1. Gettering properties of nickel atoms clusters

Based on the technology described in [14,15] we made samples of monocrystalline silicon doped with nickel (without $p-n$-transition). Elementary composition of nickel clusters on silicon sample surface was measured using scanning election microscope TESCAN MIRA 3.

It was observed that clusters are formed from nickel atoms, nickel atoms clusters composition is presented in the figure. Clusters on the silicon sample surface mainly consist of atoms of silicon (84.93 at%) and nickel (13.38 at%), and also include Cu, Fe, Cr.

Thus, we can assume, that nickel atoms clusters getter fast-diffusing impurities, that act as recombination centers.

Also we studied the nickel influence on oxygen content in silicon. Based on the technology described in study [18] we made samples of solar cells, doped with nickel after formation of $p-n$-transition on the face side. Oxygen concentration was determined using the infrared spectrometry method both after nickel diffusion (at $T_{\text{diff}} = 1200^\circ$C) and after additional thermal annealing (at $T_{\text{ann}} = 800^\circ$C).



Element	wt%	at%
Si	72.86	84.93
Cr	0.18	0.10
Fe	1.32	0.77
Ni	24.04	13.38
Cu	1.60	0.82

Impurity atoms clusters composition observed through probe elementary analysis using the scanning election microscope TESCAN MIRA 3.

Table 1. Oxygen concentration (in cm^{-3}) in SC

SC type	Control	Doped with nickel
After nickel diffusion	$6.8 \cdot 10^{18}$	$3.2 \cdot 10^{18}$
After additional thermal annealing	$2.74 \cdot 10^{18}$	$7.2 \cdot 10^{17}$

Table 2. NCC lifetime

Group	I	II	III
τ, μs	5–7	7–9	10–12

As shown in Table 1, oxygen concentration in samples with nickel is 2 times less than in control samples. After additional thermal annealing the oxygen concentration in the samples doped with nickel is reduced in 4.44 times.

This means that nickel adding is not just an efficient method of gettering the various harmful impurities, but it also reduces oxygen concentration in silicon volume, i.e. it getters the oxygen.

Nickel atoms clusters contain significant amount of silicon and oxygen and act as efficient drains (gettering centers) for various harmful non-controlled impurity atoms. This can result in significant reduction of concentration of various recombination centers and increase of NCC lifetime, mainly due to formation of nano- and micro-clusters of nickel atoms in near-surface layers with high nickel concentration. This is confirmed with studies [13,14], where nickel atoms getter oxygen atoms dissolved in silicon with formation of clusters, containing, aside from nickel, significant concentrations of oxygen, silicon and various recombination impurities.

3.2. Nickel influence on nonequilibrium charge carriers lifetime within solar cell base

Three different SC groups were made after formation of $p-n$-transition: group I is the control group, group II, where after phosphor diffusion the nickel was deposited to the back side, and group III, where it was deposited on the face side. Nickel diffusion was performed at $T_{\text{diff}} = 1200^\circ$C for $t = 30$ min, and then the additional thermal annealing was performed at $T_{\text{ann}} = 800^\circ$C for $t = 1$ h. At the same time, in all groups of samples due to phosphor dissipation the depth of $p-n$-transition was increased to $x_{p-n} = 4.5-5\,\mu$m.

After that NCC lifetime was measured at the resulting structures (Table 2).

It is shown that NCC lifetime of control SC is $\tau = 5-7\,\mu$s, that corresponds to the typical values of a lifetime for such structures [20–22]. τ in groups II and

Table 3. At diffusion $T_{\text{diff}} = 1100^\circ\text{C}$ the value of NCC lifetime in SC doped with nickel is $14-16\,\mu\text{s}$

T_{diff}, °C	t_{diff}, min	T_{ann}, °C	t_{ann}, min	x_{p-n}, μm	Group	τ, μs
1250	3	800	30	2.0–2.5	III I	10–12 5–7
1200	3	800	30	1.5–2	III I	10–14 5–7
1150	5	800	30	1–1.5	III I	10–14 5–7
1100	5	800	30	0.9–1.2	III I	414–16 8–10
1050	7	800	30	0.8–0.9	III I	16–18 10–12
1000	10	800	30	0.7–0.8	III I	18–20 10–14
950	15	800	30	0.6–0.7	III I	22–26 12–14
900	20	800	30	0.6–0.7	III I	26–30 12–15
850	30	750	30	0.5–0.7	III I	30–32 14–16
800	30	750	30	0.5–0.7	III I	30–32 14–16
750	45	750	30	0.5–0.7	III I	22–26 14–16

Note. T_{diff} is the nickel diffusion temperature, t_{diff} is the diffusion time, T_{ann} is the additional annealing temperature, t_{ann} is the annealing time, x_{p-n} is the calculated depth of $p-n$-transition.

III increased in 1.5 and 2 times. Thus, we can state that: doping with impurity atoms of nickel results in increase of NCC lifetime τ within SC base; formation of nickel-enriched region in the face layer additionally increases τ of SC.

In this study the silicon doping with nickel was performed at sufficiently high temperature ($T_{\text{diff}} = 1200^\circ\text{C}$) and after formation of $p-n$-transition, that can decrease the solar cell efficiency due to phosphor dissipation.

3.3. Variation of τ within the solar cell base depending on nickel diffusion temperature

The following task was a selection of optimum nickel diffusion temperature for NCC lifetime increase.

Table 3 includes NCC lifetime within SC base, doped with nickel after creation of $p-n$-transition at temperature T_{diff} within a range of 750–1250°C. The observed experimental results show that with nickel diffusion temperature decrease the NCC lifetime increases and reaches the maximum value at $T_{\text{diff}} = 800-850^\circ\text{C}$.

Nickel diffusion, performed at lower temperatures, $T_{\text{diff}} = 750-700^\circ\text{C}$, resulted in insignificant degradation of solar cells parameters relating to samples produced at $T_{\text{diff}} = 800^\circ\text{C}$.

3.4. Possibilities of nickel-enriched layer formation before creation of $p-n$-transition of solar cell

The abovementioned results were observed when nickel-enriched area in SC was created after $p-n$-transition forming. However, this is inconvenient in terms of technology. Therefore, the possibility of nickel-enriched layer formation before creation of $p-n$-transition is of interest.

For this study we made SC of monocrystalline silicon plates with resistivity of $0.5\,\text{Ohm}\cdot\text{cm}$. Three groups of samples were created: group I — control group, group IIIa — samples, in which nickel impurity atoms diffusion was performed after creation of $p-n$-transition; group IIIb — samples, in which nickel impurity atoms diffusion was performed before creation of $p-n$-transition.

Conditions of phosphor and nickel diffusion in samples of groups IIIA and IIIb should be the same. Phosphor diffusion was performed at $T_{\text{diff}} = 1000^\circ\text{C}$ for $t = 30\,\text{min}$, nickel diffusion was performed at $T_{\text{diff}} = 800^\circ\text{C}$ for $t = 30\,\text{min}$. For all SC structures the additional thermal annealing was

Table 4. Average values of SC parameters observed at nickel diffusion temperatures $T_{\text{diff}} = 800^\circ$C

Group	I (control)	IIIa (nickel diffusion after creation of $p-n$-transition)	IIIb (nickel diffusion before creation of $p-n$-transition)
J_{sc}, mA/cm^2	32	37.5	38.5
V_{oc}, mV	590	600	605
ξ	0.640	0.68	0.67
$P_{\max}$, mW/cm^2	12.08	15.30	15.61
τ, μs	14–16	30–32	30–32
$\Delta P_{\max}/P_{\max}$	–	26.65%	29.22%

Note. J_{sc} is the short circuit current density, ξ is the volt-ampere characteristic charge coefficient, $P_{\max}$ is the maximum output power, $\Delta P_{\max}/P_{\max}$ is the relative variation of maximum power in relation to control sample.

performed at $T_{\text{ann}} = 750^\circ$C for $t = 30$ min. Then the main SC parameters and NCC lifetime were measured (Table 4).

It can be seen that the technology of doping with nickel before formation of $p-n$-transition additionally improves solar cells parameters. Adding the stage of doping with nickel before formation of $p-n$-transition complicates the SC manufacturing technology only slightly, but increases efficiency.

Thus, based on the observed results we can conclude that the effect of influence of additional doping with nickel only slightly depends on the method of its introduction, while presence of nickel-enriched layer on the face side of silicon solar cell (group III) results in parameters improving.

3.5. Nickel-enriched layer influence on nonequilibrium charge carriers lifetime within solar cell base

It is known that nickel atoms distribution at diffusion has a sufficient inhomogenuity — high, quickly reducing concentration near surface and relatively constant in volume [23]. After additional annealing the nature of distribution hardly changes, but the clusters, gettering impurities, appear. Due to high surface concentration of nickel and surface defects, „surface“ clusters have high concentration and, consequently, have a bigger influence on NCC lifetime. Relative contribution of „surface“ and „volumetric“ nickel atoms can be observed, if the surface layer, highly doped with nickel, is removed.

Samples of solar cells were made as per abovementioned technology, nickel diffusion was performed before formation of $p-n$-transition at $T_{\text{diff}} = 800^\circ$C for $t = 30$ min. Under these conditions the thickness nickel-enriched layer is evaluated at $2-2.5\,\mu$m [11].

After nickel diffusion the surface layer Δx with thickness range of $0-5\,\mu$m was removed from the samples surface by polishing. After creation of $p-n$-transition and additional thermal annealing at $T_{\text{ann}} = 750^\circ$C for $t = 30$ min the ohmic contacts were created. Then the volt-ampere characteristics (VAC) of SC and lifetime τ were measured (Table 5).

Table 5. Variation of maximum power and lifetime of NCC of SC depending on thickness of removed face surface (nickel-enriched) layer

Δx, μm	0	0.5	1	1.5	2	5
$P_{\max}$, mW/cm^2	15.40	14.97	14.37	13.64	12.74	12.00
τ, μs	30–32	28–30	26–28	24–26	24–26	24–26

As shown from the table, with increase of thickness of removed face surface (nickel-enriched) layer the SC parameters degrade, and after $\Delta x = 5\,\mu$m the maximum power drops by $\sim 30\%$ relating to the values for samples with $\Delta x = 0\,\mu$m. NCC lifetime measurement results also showed, that with increase of thickness of the removed face layer, τ slowly decreases, and hardly changes after removal of $1.5\,\mu$m. Therefore we can conclude that improvement of solar cell parameters is related to influence of surface layer with nickel concentration $N_S \sim (10^{20}-10^{21})\,\text{cm}^{-3}$ [10] and thickness of several micrometers, produced during diffusion.

4. Discussion of results

All observed data allow to conclude that doping with nickel increases NCC lifetime within SC base, increasing coefficient of performance. It was also observed that removal of nickel-enriched layer deteriorates the solar cell parameters.

We think that increase of SC NCC lifetime is related to formation of nickel atoms clusters in silicon lattice, that are in interstitial states, and presence of gettering properties.

In near-surface layers the nickel concentration is $2.5-3$ times higher than in crystal volume. Nickel clusters formation centers are oxygen atoms and other defects of silicon lattice, largely located near surface, as well as formed in diffusion layer of n-type of conductivity. Thus, nickel clusters are mainly located in near-surface layers of SC, where they can efficiently getter the recombination impurities. This is confirmed with experiments on removal of surface, nickel-enriched layer.

With nickel diffusion temperature decrease the NCC lifetime increases and reaches the maximum value at

$T_{\text{diff}} = 800-850^\circ$C, while lower diffusion temperatures degrade SC parameters. This can be related to decrease of nickel-enriched region, as well as with nickel atoms concentration decrease at such diffusion temperatures.

5. Conclusion

Thus, based on the observed results we can conclude that nickel atoms adding is an efficient method of gettering the recombination centers in silicon.

Compared with other existing methods, this one has the following advantages:

– method of gettering the recombination impurities with nickel clusters is an efficient, advanced and inexpensive method;

– nickel adding opens the possibility of silicon SC efficiency increase by 20−25%;

– when doping with nickel, there are almost no changes of electrical parameters of material, thus allowing to use it for all types of electronic devices based on silicon.

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Conflict of interest

The authors declare that they have no conflict of interest.

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