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Halmurat Mijitovich Iliiev

Tashkent State Technical University, Tashkent, Uzbekistan, xolmurod.iliev@tdtu.uz

Zoir Tohir ugli Kenjaev

Karakalpak State University, Nukus, Karakalpakstan, zoir1991@bk.ru

Babir Alimdjanovich Isakov

Tashkent State Technical University, Tashkent, Uzbekistan, Bobur.isakov@tdtu.uz

Nigmat Narkulov

University of Uzbekistan, Tashkent, bahazeb@yandex.com

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EFFECT OF TEMPERATURE ANNEALING ON THE EFFICIENCY OF NICKEL-DOPED SILICON SOLAR CELLS

Iliev Halmurat Mijitovich, Dr. of Phys. and Math. Sc., Professor, Head of the Department of Tashkent State Technical University, Tashkent, Uzbekistan. E-mail: xolmurod.iliev@tdtu.uz

*Kenjaev Zoir Tohir ugli**, Basic Doctoral Student of Karakalpak State University, Nukus, Karakalpakstan. E-mail: zoir1991@bk.ru

Isakov Babir Alimdjanovich, Assistant of Tashkent State Technical University, Tashkent, Uzbekistan. e-mail: Bobur.isakov@tdtu.uz

Narkulov Nigmat, Cand. of Phys. and Math. Sc., Docent of National University of Uzbekistan, Tashkent, Uzbekistan. e-mail: bahazeb@yandex.com

Abstract. *Si <B, P> and Si <B, P+Ni> structures with a deep p-n-junctions (30 microns) were obtained by diffusion doping. It is shown that the parameters of silicon solar cells with a deep-lying p-n junction are improved by Nickel doping. Influence of additional temperature annealing at different temperatures of samples with clusters of Nickel atoms in the silicon lattice was investigated and optimal conditions for cluster formation were determined.*

Keywords: *silicon, solar cell efficiency, Nickel doping, Nickel clusters, temperature annealing, gettering, lifetime, saturation current.*

ВЛИЯНИЕ ТЕМПЕРАТУРНОГО ОТЖИГА НА ЭФФЕКТИВНОСТЬ КРЕМНИЕВЫХ ФОТОЭЛЕМЕНТОВ, ЛЕГИРОВАННЫХ НИКЕЛЕМ

Илиев Халмурат Миджитович, д.ф.-м.н., профессор, заведующий кафедрой Ташкентского государственного технического университета, Ташкент, Узбекистан. e-mail: xolmurod.iliev@tdtu.uz

*Кенжаев Зоир Тохир угли**, базовый докторант Каракалпакского государственного университета, Нукус, Каракалпакстан. e-mail: zoir1991@bk.ru

Исаков Бобир Олимжонович, ассистент Ташкентского государственного технического университета, Ташкент, Узбекистан. e-mail: Bobur.isakov@tdtu.uz

Наркулов Немат, к.ф.-м.н., доцент Национального университета Узбекистана, Ташкент, Узбекистан. e-mail: bahazeb@yandex.com

Аннотация. *Диффузионным способом легирования получены структуры Si <B, P> и Si <B, P+Ni> с глубоким p-n-переходом (30 мкм). Показано, что параметры кремниевых фотоэлементов с глубоководящим p-n-переходом улучшаются за счет легирования никелем. Исследовано влияние дополнительного температурного отжига при разных температурах образцов на формирование кластеров атомов никеля в решетке кремния и определены оптимальные условия для кластерообразования.*

Ключевые слова: *кремний, эффективность фотоэлемента, легирование никелем, кластеры никеля, температурный отжиг, геттерирование, время жизни, ток насыщения.*

1. Introduction

Expansion of the spectral range of sensitivity of solar cells, especially in the infrared (IR) range, is one of the ways to increase their efficiency [1, 2]. Therefore, it is of particular interest to study the effect of additional low-temperature annealing on the main parameters and characteristics of solar cells made on the basis of single-crystal silicon containing clusters of impurity nickel atoms in its volume. As well as to determine the stability and binding energy of nickel atoms in these clusters and the possibility of controlling their concentration and ordering in the crystal lattice of silicon [3].

The paper presents the results of studying the doping of silicon photocells with a deep p-n junction with nickel atoms and the results of studying the change in their parameters upon additional temperature annealing.

2. Experimental technique

p-n structures of photocells were formed based on single-crystal silicon wafers (KDB-0.5) with a thickness of 380 μm and a diameter of $d \sim 76 \text{ mm}$. The depth of the p-n-junction was determined by layer-by-layer grinding and determination of the type of conductivity with a thermal probe. In the structures obtained, the depth was $L = 29\text{--}30 \mu\text{m}$.

Next, the resulting p-n structure was cut into separate samples of $1 \times 0.5 \text{ cm}^2$, which were subjected to appropriate mechanical treatment and chemical cleaning. For all samples (without antireflection layers and with indium-gallium contacts) under the same conditions, the open-circuit voltage U_{oc} and the short-circuit current density J_{sc} were determined. The average values of the parameters of the samples corresponded to a large depth of the p – n junction and were: $J_{sc} \sim 2.8\text{--}2.9 \text{ mA} / \text{cm}^2$, $U_{oc} \sim 370\text{--}380 \text{ mV}$.

The resulting samples were divided into two groups of 10 samples to create the structures shown in Fig. 1. Group I - control samples (Si <B, P>). Group II - samples (Si <B, P + Ni>), in which a thin layer of pure nickel 1 μm thick was deposited on the surface of the n-type diffusion layer (on the front side of the photocell) in vacuum, and then diffusion annealing was performed.

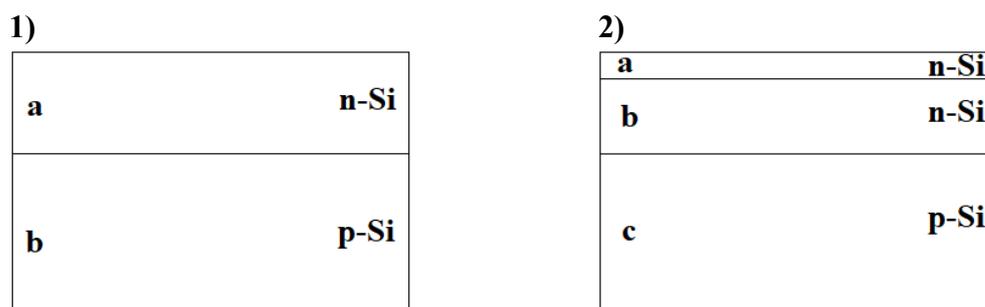


Fig. 1. Varieties of structures

- 1) - group I - a) - n-type diffusion layer, thickness $x = 32 \pm 2 \mu\text{m}$, phosphorus concentration - N_P - from 10^{21} to $4 \times 10^{16} \text{ cm}^{-3}$; b) - p-type base, boron concentration - $N_B - 4 \times 10^{16} \text{ cm}^{-3}$.
- 2) - group II - a) - nickel-enriched n-type near-surface region, $x \sim 3 \mu\text{m}$, nickel concentration - N_{Ni} - from 10^{21} to 10^{18} cm^{-3} , phosphorus concentration - N_P - from 10^{21} to 10^{19} cm^{-3} . b) - n-type diffusion layer, thickness $x = 29 \div 30 \mu\text{m}$, nickel concentration - $N_{Ni} - 10^{17} \div 10^{18} \text{ cm}^{-3}$, phosphorus concentration - N_P - from 10^{19} to $4 \times 10^{16} \text{ cm}^{-3}$. c) - p-type base, nickel concentration - $N^{Ni} - 10^{17} \div 10^{18} \text{ cm}^{-3}$, boron concentration - $N_B - 4 \times 10^{16} \text{ cm}^{-3}$

All samples were subjected to diffusion thermal annealing under the same conditions at $T = 1200^{\circ}\text{C}$ for $t = 1$ hour. This annealing time is sufficient for uniform alloying of samples with nickel throughout the entire volume with a concentration of about 10^{18} cm^{-3} , as well as for the formation of a near-surface region enriched with nickel atoms, the nickel concentration in which can reach $4 \times 10^{21}\text{ cm}^{-3}$ [4].

It should be noted that, in this case, in all samples, due to distillation (thermal annealing at $T = 1200^{\circ}\text{C}$), the depth of the p-n transition increased to $L = 32 \pm 2\ \mu\text{m}$. Then, under the same conditions, the values of U_{IK} and J_{SC} were measured in all samples.

Since a very deep-lying p – n junction was used in the solar cell, the effect of doping with nickel only on the sensitivity of the photocell in the IR spectral region was actually investigated [5].

2. Results and discussion

The average values of U_{IK} and J_{SC} of control samples (group I) practically did not change (their values are very close to the values before thermal annealing at $T = 1200^{\circ}\text{C}$). In all samples of group II, a rather noticeable improvement in parameters is observed. In this case, the average value of U_{OC} in the samples of group II increases by 19.7% (from 380 to 455 mV) in relation to group I, J_{SC} - increases by 89% (from 2.7 to 5.1 mA/cm²). The peak power (P_{peak}) increases by 126% (from 1.026 to 2.320 mW/cm²).

The data obtained allow us to assert that additional doping with impurity nickel atoms leads to an improvement in the efficiency of photocells with a deep p – n junction.

As is known [6, 8], electrically neutral interstitial nickel atoms in the silicon lattice can form nano- and microclusters upon additional thermal annealing at temperatures $T = 700\text{--}1100^{\circ}\text{C}$.

To test the effect of clustering, samples of groups I and II were heat treated at $T = 700, 800, 900, 1000,$ and 1100°C for 1 hour. After additional heat treatment, the samples were also subjected to mechanical and chemical treatment similar to the treatment after nickel diffusion. The parameters (J_{SC} and U_{IK}) were measured in the same way.

Table 1 shows the results for samples of group II annealed at $T = 700 \div 1100^{\circ}\text{C}$. In the samples of group I, upon annealing at $T = 700\text{--}900^{\circ}\text{C}$, a slight improvement in the parameters is observed (within a few percent), therefore, their changes after thermal annealing are not given in the table.

As can be seen from Table 1, the parameters of the II group of samples with additional annealing changed towards improvement. At annealing temperature $T = 900^{\circ}\text{C}$ and 1000°C , the value of J_{SC} increases (+ 72.35% and + 63.3%) compared to the value before annealing, and the value of U_{xx} increases slightly (within a few percent). Very good results were obtained in the temperature range $T = 700\text{--}800^{\circ}\text{C}$ - the value of J_{SC} after annealing at $T = 700^{\circ}\text{C}$ increases by 98.4% compared to the value before annealing, and the value of U_{OC} grows by 13.18%. Similarly, after annealing at $T = 800^{\circ}\text{C}$, the value of J_{cr} increases by 86.27%, and U_{IK} by 14.28%. Thus, for the II group of samples, thermal annealing at $T = 700^{\circ}\text{C}$ and $T = 800^{\circ}\text{C}$ leads to a significant change in U_{OC} and J_{SC} . At a higher annealing temperature $T = 1100^{\circ}\text{C}$, the value of J_{SC} almost does not change, and the value of U_{IK} decreases (by 8.8%).

Table 1

**Average values of the parameters of samples of group II after additional heat treatment at
 $T = 700 \div 1100 \text{ } ^\circ\text{C}$ relative to the parameters before annealing**

Температура отжига.	700°C	800°C	900°C	1000°C	1100°C
$J_{кз}$, (mA/cm ²)	10,12	9,5	8,76	8,33	5,1
$\Delta J_{кз} / J_{кз}$	+98,4%	+86,27%	+72,35%	+63,30%	0%
U_{xx} , (mV)	515	520	470	460	415
$\Delta U_{xx} / U_{Ixx}$	+13,18 %	+14,28 %	+3,30 %	+1,10 %	-8,80%
$P_{пик}$, (mW/cm ²)	5,212	4,940	4,117	3,831	2,116
$\Delta P_{пик} / P_{Iпик}$	+129,0%	+113,0%	+77,45%	+65,13%	-8,80%

Note: $\Delta J_{SC} / J_{ISC}$ - change in short-circuit current density (in percent) relative to the values before heat treatment; $\Delta U_{OC} / U_{IOC}$ - change in open-circuit voltage (in percent) relative to values before heat treatment; $P_{пик}$, (mW / cm²) - specific peak power (calculated as the product of J_{SC} by U_{OC}); $\Delta P_{peak} / P_{Ipeak}$ - change in specific peak power (in percent) relative to the values before heat treatment.

As a result, studies have established that the parameters of the II group of samples change most significantly during thermal annealing in the temperature range $T = 750\text{--}800^\circ\text{C}$. This allows us to assume that the formation of nickel clusters due to thermal annealing at $T = 750\text{--}800^\circ\text{C}$ significantly affects (increases) the main parameters of a photocell with a deep p-n junction.

To establish the optimal parameters of additional heat treatment, thermal annealing was carried out at $T = 750 \div 800^\circ\text{C}$ for $t = 2, 3$ and 5 hours. As shown by the experimental results, an increase in the thermal annealing time at the beginning practically does not affect the parameters U_{OC} and J_{SC} , but a longer annealing ($t > 3$ hours) leads to a deterioration of U_{OC} and J_{SC} in all samples.

In fig. 2 shows the dark current - voltage characteristics (CVC) of samples II after additional thermal annealing at temperatures $T = 700, 800, 900,$ and $1000 \text{ } ^\circ\text{C}$.

As can be seen from the figure, the slope of the I - V characteristic in the region of high forward currents does not change, that is, upon annealing, the volume resistance of the base of the photocell does not change. The change in the values of the forward voltage drop and reverse current can be explained by a change in the saturation current. To change the parameters of the p-n junction, annealing at a temperature of at least $900 \text{ } ^\circ\text{C}$ is required. The open circuit voltage of the solar cell is determined by the formula [9]:

$$U_{OC} = \frac{kT}{e} \ln \left(\frac{I_{ph}}{I_s} + 1 \right) \quad (1)$$

From expression (1) it follows that U_{xx} of samples of group II can increase due to an increase in the ratio I_{ph}/I_s (I_{ph} is the photocurrent, I_s is the saturation current). This can occur due to a decrease in I_s as a result of an increase in the doping level of the p - n regions or an increase in the lifetime of nonequilibrium carriers. Thus, it is known [10] that the saturation current density i_{sb} , in a sharply asymmetric p - n junction, is determined by the lifetime of nonequilibrium charge carriers and the base doping level:

$$i_{sb} \approx en_i^2 d / N_a \tau \quad (2)$$

where n_i is the intrinsic concentration of carriers, N_a is the concentration of acceptors in the base, d is the thickness of the base.

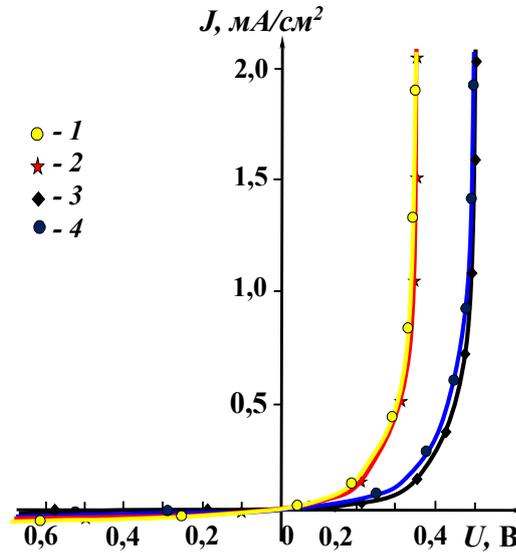


Fig. 2. Dark I - V characteristic of group II samples after annealing at different temperatures. 1- at $T = 1000^\circ\text{C}$ (sample No. 2), 2- at $T = 900^\circ\text{C}$ (sample No. 3), 3- at $T = 800^\circ\text{C}$ (sample No. 1), 4- at $T = 700^\circ\text{C}$ (sample no. 2)

Thus, due to a decrease in the saturation current, U_{OC} and the efficiency of the solar cell increase, especially with a simultaneous increase in the lifetime of nonequilibrium carriers in all regions of the solar cell, which actually increases I_{ph} . (by increasing the collection rate).

Since nickel clusters are easily formed both during diffusion and during further heat treatment, their effect on the properties of the base volume should be more significant than that of isolated interstitial nickel atoms. It is possible that an increase in the oxygen concentration in the initial silicon will lead to an even more significant effect of nickel on the lifetime of nonequilibrium charge carriers.

Also measured, light I - V characteristics of photocells after additional annealing at $T = 750 \div 800^\circ\text{C}$. In samples with a nickel-enriched region on the front side of the p-n junction (group II), an increase in the fill factor of the current-voltage characteristic is observed. This growth (relative to group I) was 30% (from $\xi_I = 0.45$ to $\xi_{II} = 0.59$).

We associate such an increase with a decrease in the layer resistance of the surface layers of the solar cell emitter due to the formation of microclusters of nickel atoms located in the interstitial voids of the silicon lattice. The centers of formation of nickel clusters are silicon lattice defects, which are in large numbers near the surface. Direct measurement of the surface resistance of the emitter (n-layer) after additional thermal annealing shows its decrease by 25%, which is quite consistent with an increase in the fill factor.

Additionally, the elemental composition of the front surface of the samples was investigated in a scanning electron microscope (SEM) - EVO MA 10, in the mode of X-ray microanalysis.

As can be seen from Table 2, after nickel diffusion, the oxygen content in the cluster is 3.93 at.%, And after additional thermal annealing at $T = 800^\circ\text{C}$, only 1.5 at.% is recorded. After thermal annealing, the oxygen concentration decreases by 2.62 times, possibly due to the gettering of oxygen by nickel clusters.

Table 2
Elemental composition of the front surface of structure II before and after thermal annealing

Element	After nickel diffusion at $T = 1200^\circ\text{C}$, 1 hour		After additional heat treatment at $T = 800^\circ\text{C}$, 1 hour	
	The weight, %	Standard deviation (Weight,%)	The weight, %	Standard deviation (Weight,%)
C	37,24	0,63	9,30	1,08
O	3,93	0,24	1,50	0,26
Si	58,61	0,60	88,67	1,11
P	0,22	0,10	0,23	0,11
Ni	0,24	0,20	0,30	0,25
Amount:	100,00		100,00	

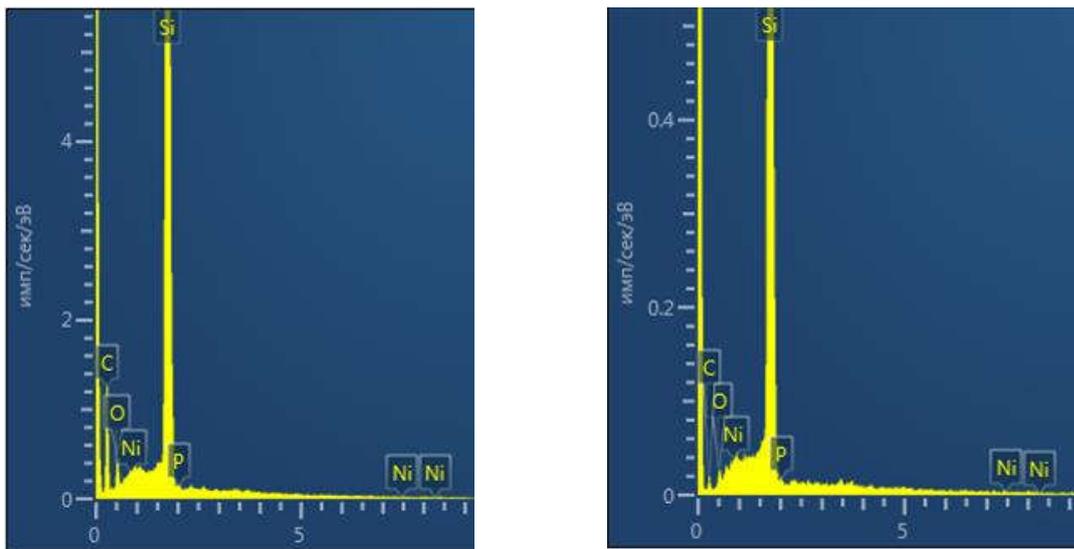


Figure: 3. Results of X-ray microanalysis of clusters on surface of structure II after nickel diffusion - (a), and after additional thermal annealing at $T = 800^\circ\text{C}$ - (b)

In addition, it is known that nickel films deposited on silicon have gettering properties. Therefore, we believe that the clusters of nickel atoms formed in the sample volume getter recombination impurities and oxygen. This effect can increase the lifetime of minority charge carriers and, accordingly, lead to a significant increase in the collection coefficient of a photocell with a deep p – n junction.

The sizes, concentration, structure, and composition of clusters are mainly determined by the additional annealing temperature and the total concentration of nickel atoms introduced into silicon.

This can lead to a significant decrease in the concentration of various recombination centers and an increase in the lifetime of minority charge carriers, primarily due to the formation of nano- and microclusters of nickel atoms in the surface layers with a high concentration of nickel and oxygen and other defects that affect surface recombination. The deposition of nickel atoms on surface defects with the formation of clusters screens the effect of defects on surface recombination. An increase in the lifetime of minority charge carriers in the base and on the surface of the solar cell can explain the increase in the parameters of group II samples after thermal annealing.

4. Conclusion

Thus, it has been experimentally established that for solar cells with a sufficiently deep p n junction, doping with impurity nickel atoms with further additional heat treatment makes it possible to improve their basic parameters. Nickel doping provides new opportunities for the creation of silicon photocells with increased efficiency due to an increase in the filling factor of the I - V characteristic, an increase in the lifetime of nonequilibrium carriers, and, possibly, an increase in the sensitivity in the infrared region of the solar spectrum.

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