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

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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 deeply 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

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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 фотодетекторов с глубокозалегающим 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 фотодетектора, 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 ~ 76 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 = 29–30 μm.

Next, the resulting p-n structure was cut into separate samples of 1×0.5 cm², 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: $J_{sc}$ ~ 2.8-2.9 mA / cm², $U_{OC}$ ~ 370 380 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](image)

1) - group I - a) - n-type diffusion layer, thickness $x = 32 \pm 2 \mu m$, phosphorus concentration - $N_P$ - from $10^{15}$ to $4 \times 10^{16}$ cm⁻³; b) - p-type base, boron concentration - $N_B$ - $4 \times 10^{16}$ cm⁻³.

2) - group II - a) - nickel-enriched n-type near-surface region, $x \sim 3 \mu m$, nickel concentration - $N_{Ni}$ - from $10^6$ to $10^8$ cm⁻³, phosphorus concentration - $N_P$ - from $10^{21}$ to $10^{19}$ cm⁻³; b) - n-type diffusion layer, thickness $x = 29 \div 30 \mu m$, nickel concentration - $N_{Ni}$ - $10^{17}$ to $10^{18}$ cm⁻³, phosphorus concentration - $N_P$ - from $10^9$ to $4 \times 10^{16}$ cm⁻³. c) - p-type base, nickel concentration - $N_{Ni}$ - $10^{17}$ to $10^{18}$ cm⁻³, boron concentration - $N_B$ - $4 \times 10^{16}$ cm⁻³.
All samples were subjected to diffusion thermal annealing under the same conditions at \( T = 1200^\circ C \) 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 \( 4 \times 10^{21} \) cm\(^{-3} \) [4].

It should be noted that, in this case, in all samples, due to distillation (thermal annealing at \( T = 1200^\circ C \)), the depth of the p-n transition increased to \( L = 32 \pm 2 \) \( \mu m \). 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 \( T = 1200^\circ C \)). 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/cm\(^2\)). The peak power (Ppeak) increases by 126% (from 1.026 to 2.320 mW/cm\(^2\)).

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 \( T = 700–1100^\circ C \).

To test the effect of clustering, samples of groups I and II were heat treated at \( T = 700, 800, 900, 1000, \) and \( 1100^\circ C \) 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 \( T = 700 \div 1100^\circ C \). In the samples of group I, upon annealing at \( T = 700–900^\circ C \), 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 \( T = 900^\circ C \) and \( 1000^\circ C \), 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 \( T = 700–800^\circ C \) - the value of \( J_{SC} \) after annealing at \( T = 700^\circ C \) increases by 98.4% compared to the value before annealing, and the value of \( U_{OC} \) grows by 13.18%. Similarly, after annealing at \( T = 800^\circ C \), the value of \( J_{SC} \) increases by 86.27%, and \( U_{IK} \) by 14.28%. Thus, for the II group of samples, thermal annealing at \( T = 700^\circ C \) and \( T = 800^\circ C \) leads to a significant change in \( U_{OC} \) and \( J_{SC} \). At a higher annealing temperature \( T = 1100^\circ C \), 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 
\( T = 700 \div 1100 \, ^\circ\, C \) relative to the parameters before annealing

<table>
<thead>
<tr>
<th>Температура отжига, ( ^\circ, C )</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J ) (mA/cm²)</td>
<td>10,12</td>
<td>9,5</td>
<td>8,76</td>
<td>8,33</td>
<td>5,1</td>
</tr>
<tr>
<td>( \Delta J / J )</td>
<td>+98,4%</td>
<td>+86,27%</td>
<td>+72,35%</td>
<td>+63,30%</td>
<td>0%</td>
</tr>
<tr>
<td>( U ), (mV)</td>
<td>515</td>
<td>520</td>
<td>470</td>
<td>460</td>
<td>415</td>
</tr>
<tr>
<td>( \Delta U / U )</td>
<td>+13,18 %</td>
<td>+14,28%</td>
<td>+3,30%</td>
<td>+1,10%</td>
<td>-8,80%</td>
</tr>
<tr>
<td>( P ), (mW/cm²)</td>
<td>5,212</td>
<td>4,940</td>
<td>4,117</td>
<td>3,831</td>
<td>2,116</td>
</tr>
<tr>
<td>( \Delta P / P )</td>
<td>+129,0%</td>
<td>+113,0%</td>
<td>+77,45%</td>
<td>+65,13%</td>
<td>-8,80%</td>
</tr>
</tbody>
</table>

Note: \( \Delta J / J \) - change in short-circuit current density (in percent) relative to the values before heat treatment; \( \Delta U / U \) - change in open-circuit voltage (in percent) relative to values before heat treatment; \( P \) - specific peak power (calculated as the product of \( J \) by \( U \)); \( \Delta P / P \) - 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 \( T = 750 \div 800 \, ^\circ\, C \). This allows us to assume that the formation of nickel clusters due to thermal annealing at \( T = 750 \div 800 \, ^\circ\, C \) 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 \( T = 750 \div 800 \, ^\circ\, C \) 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 \( U \) and \( J \), but a longer annealing (\( t > 3 \) hours) leads to a deterioration of \( U \) and \( J \) 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 °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 ° C is required. The open circuit voltage of the solar cell is determined by the formula [9]:

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

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:
\[ i_{sb} \approx n_i^2 d / N_a \tau \]  \hspace{1cm} (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.

![Graph showing dark I-V characteristics of group II samples after annealing at different temperatures.](image)

**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 $T = 800 \, ^\circ C$, 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*

<table>
<thead>
<tr>
<th>Element</th>
<th>After nickel diffusion at $T = 1200 , ^\circ C$, 1 hour</th>
<th>After additional heat treatment at $T = 800 , ^\circ C$, 1 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The weight, %</td>
<td>Standard deviation (Weight, %)</td>
</tr>
<tr>
<td>C</td>
<td>37.24</td>
<td>0.63</td>
</tr>
<tr>
<td>O</td>
<td>3.93</td>
<td>0.24</td>
</tr>
<tr>
<td>Si</td>
<td>58.61</td>
<td>0.60</td>
</tr>
<tr>
<td>P</td>
<td>0.22</td>
<td>0.10</td>
</tr>
<tr>
<td>Ni</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>Amount:</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

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