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Effect of nickel doping on the spectral sensitivity of silicon solar cells

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Abstract. In the modern industrial production of solar cells (SC), there is a growing trend to utilize "solar silicon" as the base material due to its cost-effectiveness. However, solar silicon possesses a drawback - it has a shorter lifetime of minority charge carriers (MCC), making it challenging to achieve high efficiency in solar cells. To address this limitation and improve the efficiency of solar cells based on "solar silicon," two key objectives need to be met. Firstly, it is essential to increase the lifetime of photogenerated charge carriers. Secondly, there is a need to minimize both optical and electrical energy losses. To achieve an increase in the lifetime of minority charge carriers in SCs, a process called gettering can be employed. This process involves utilizing clusters of nickel atoms to trap uncontrolled impurity atoms. The paper presents the results of a study on the additional doping of silicon solar cells with nickel atoms, for factors affecting the long-wave and short-wave efficiency. Nickel doping has been shown to increase the efficiency of solar cells. It is determined that in the visible region of the spectrum the spectral sensitivity of a silicon solar cell doped with nickel is higher up to 25÷35% due to a decrease in surface recombination. Technological recommendations for nickel doping of single-crystal silicon solar cells are proposed to be combined without significant changes with the standard technological process for manufacturing solar cells.

1. Introduction

In the modern industrial production of solar cells (SC), there is a tendency [1] to increase the share of SCs made on the basis of "solar silicon", which is explained by its cheapness. Solar silicon has a shorter lifetime of minority charge carriers (MCC), which makes it difficult to obtain a high efficiency [2].

To increase the efficiency of a solar cell based on "solar silicon", it is required to increase the lifetime of photogenerated charge carriers [3], as well as to reduce optical and electrical energy losses [4]. An increase in the lifetime of minority charge carriers in SCs is possible by gettering uncontrolled impurity atoms with clusters of nickel atoms [5, 6].

It was shown in work [7] that doping the front side of a solar cell with a deep p–n junction with nickel atoms leads to an increase in efficiency. The study of the effect of clusters of nickel impurity atoms on the parameters of silicon SCs is of great practical interest, due to the technological features of nickel doping [8].

The main part of dissolved nickel atoms, up to 99.99%, in the near-surface region are in an electrically neutral state in interstices [9] and, under certain heat treatment conditions, can form nano- and micro clusters that act as effective gettering centers for uncontrolled impurity atoms and oxygen in silicon [10-12].

One of the main parameters of valve SCs is the collection coefficient of photogenerated charge carriers, which strongly depends on the design parameters of the structure [2–4]. In modern efficient solar cells, the *p–n* transition depth is of the order of $x_{p\text{-}n} = 0.3 \div 0.5$ μm, which is optimal for the visible part of the solar spectrum [1]. However, in this case, the number of solar infrared spectrum quanta absorbed near the *p–n* junction is significantly reduced, which reduces the collection coefficient. Infrared rays are absorbed in the depth of the base, and a significant part of the generated carriers recombine. Therefore, the development of a method for creating solar cells, which will increase their efficiency in the IR spectrum [13–15], is of great interest.

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The paper presents the results of a study on additional doping of silicon SCs with deep ($x_{p\text{-}n}$=28 μm) and shallow ($x_{p\text{-}n}$=0.5÷0.75 μm) *p–n* junction with nickel atoms. In such an SC, it is possible to identify the factors that affect the long-wave and short-wave efficiency.

2. Materials and methods

For the starting material, we used p-type single-crystal silicon wafers with a resistivity of 0.5 Ω cm (KDB-0.5), 380 μm thick, grown using the Czochralski method. By controlling the temperature and diffusion time of phosphorus [16] in the range T_{diff} = 1000–1280 °C and t = 0.5–5 h in p-type silicon with 0.5 Ω cm, SCs were fabricated with different depths of the *p–n* transition $x_{p\text{–}n}$ – from 28 to 0.5÷0.75 μm. The depth of the *p–n* transition in the resulting structures was determined by layer-by-layer grinding.

Then two different groups were formed. Of these, group I - control, group II - a thin layer of pure nickel 1 μm thick was deposited in vacuum for diffusion on the front side. Diffusion of nickel impurity atoms was carried out at T_{diff} = 800–850 °C for t = 30–40 min.

After diffusion, all samples underwent additional thermal annealing at T_{ann}=750–800°C for t=30–40 min in order to activate the gettering process [7–12] of uncontrolled recombination impurities.

After each technological stage, the surface was cleaned [17] and chemically treated to remove nickel residues and silicon oxide from the surface (10% HCl, 10% HF) [18].

Nickel ohmic contacts to the samples were created by vacuum deposition of a nickel film with a thickness of about 1 μm, followed by tinning. On the back side, a solid contact was deposited, and on the front side, through a stencil. There was no antireflection coating on the surface of the elements.

After obtaining nickel contacts, the volt-ampere characteristic (VAC) of the SC was measured under illumination with a halogen incandescent lamp powered by a voltage stabilizer with a radiation power density of about 150 mW/cm^2. All measurements were carried out under almost identical conditions. The temperature of the samples was maintained by a passive water thermostat and was 25+1°C.

3. Results

It has been experimentally determined [7] that with a decrease in the depth of the $x_{p\text{-}n}$ *p–n* junction, the main parameters of the SC increase and their maximum values are observed for the SC with 0.5÷0.75 μm. These data are consistent with theory and experiment [1-4].

Fig. 1 shows the change in the value of the maximum power P_{max} of the SC of I and II groups depending on the $x_{p\text{-}n}$ of the SC.

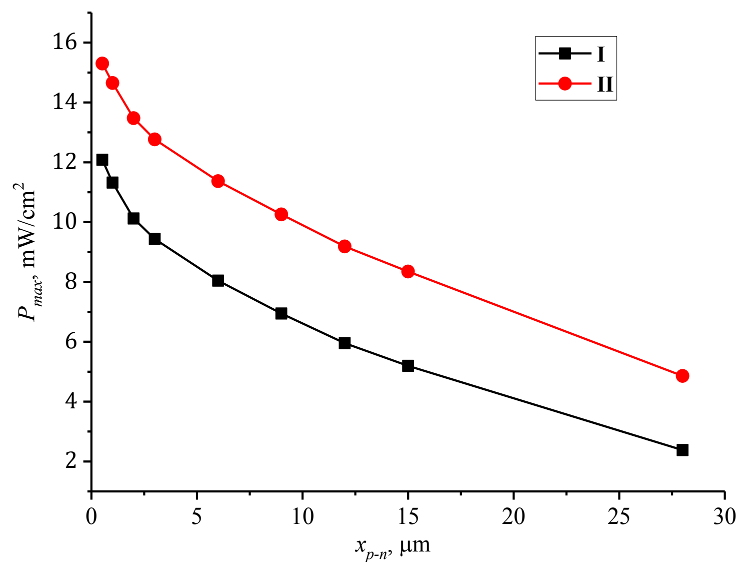

Fig. 1. Change in the maximum power P_{max} of SCs of groups I and II depending on the depth of the *p–n* junction $x_{p\text{-}n}$ SC.

As can be seen from Fig 1, doping of silicon SCs with nickel atoms gives a significant positive effect, which weakly depends on $x_{p\text{-}n}$ SCs. With a decrease in $x_{p\text{-}n}$, the nickel alloying effect is somewhat weakened, but remains quite noticeable (26.62%).

To assess the change in the spectral sensitivity, the spectral dependence of short circuit current (J_{sc}) for samples of groups I and II was measured after additional thermal annealing at T_{ann}=750÷800 °C.

Fig 2 shows the spectral dependence $J_{sc}(hv)$ of group II SC doped with nickel at a temperature T_{diff} = 850°C and control group I SC (not alloyed with nickel) measured under the same conditions.

The measurements were carried out in an IRS-12 spectrometer (λ= 0.496÷3.872 μm) at a radiation power density P=5·10^{-6} W/cm^2, at T=300 K. As can be seen from Fig. 2, in this case, a significant increase in the value of Jsc is observed, almost in the entire region of the spectrum under study. At hv>1.24 eV, an increase is observed, which reaches its maximum value at hv=1.84 eV (λ=0.67 μm). At the same time, for SC with $x_{p\text{-}n}$ =28 μm, the growth reaches 2.2 times, and for SC $x_{p\text{-}n}$ =0.5 μm, the growth is up to 1.65 times. At hv>1.84 eV, the sensitivity of nickel-doped SCs falls slowly.

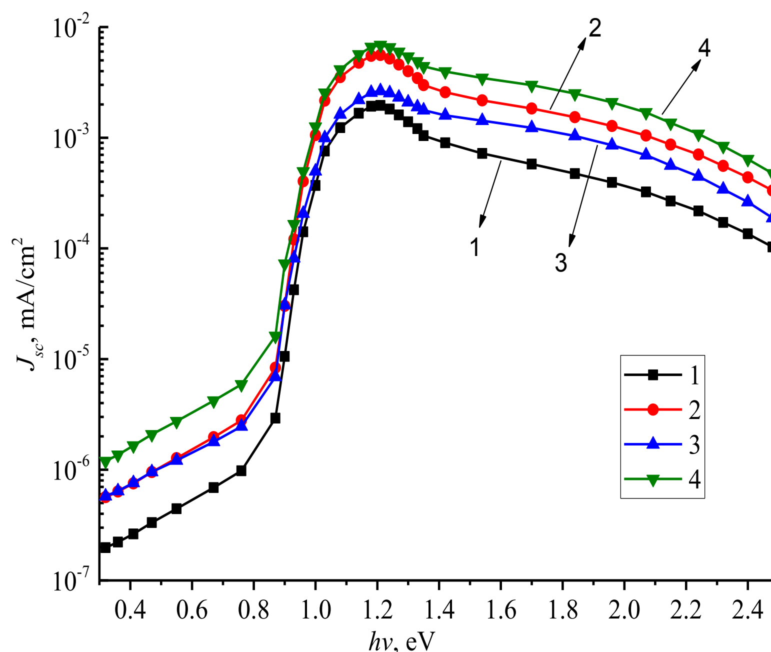

Fig 2. Spectral dependences $J_{sc}(hv)$ of SC. 1 - group I ($x_{p\text{-}n}$=28 μm), 2 - group I ($x_{p\text{-}n}$ =0.5 μm), 3 - group II ($x_{p\text{-}n}$ =28 μm), 4 - group II ($x_{p\text{-}n}$ =0.5 μm).

4. Discussion

It is difficult to explain the results obtained by the absorption of electroactive nickel atoms in the studied region of the spectrum, since their concentration is rather low. Therefore, we assume that a significant improvement in the spectral sensitivity of the SC can be associated with high concentrations of nickel clusters in the near-surface regions of the SC.

One of the possible options for the influence of clusters is to increase the absorption coefficient of "cluster" regions of solar cells in the infrared region of the spectrum due to the occurrence of plasmon resonance [19] in nickel clusters, which leads to better matching of the absorption region of IR light with the *p–n* junction. The cluster sizes depend on the concentration of silicon lattice defects, the degree of supersaturation, and heat treatment conditions; therefore, it is possible to obtain nickel clusters with a significant size spread. The plasmon resonance frequency in them will be different, which significantly expands the region of spectral sensitivity.

It is also possible that nickel clusters act as original receiving antennas in the infrared wavelength range. In this case, there is a local increase in the amplitude of the electric field of the light frequency near the edges of the cluster, which can cause both direct emission of electrons from the cluster into the semiconductor and a decrease in the band gap due to the Franz-Keldysh effect.

The improvement in sensitivity in the spectral region hv > Eg is apparently explained by the decrease in surface and (or) volume recombination due to nickel doping. Nickel clusters, which are much larger on the surface than in the

volume, have strong gettering [8, 12] and, possibly, this reduces the recombination of minority charge carriers and, accordingly, leads to surface passivation and an increase in the SC collection coefficient.
To study the effect of surface recombination, a normalization was made (each J_{sc} value was divided by the maximum $J_{sc.max}$ value of this SC). Then the $J_{sc}/J_{sc.max}$ values of groups II and I were divided by each other.
Fig 3 shows the spectral dependence of the relative change in the $J_{sc}/J_{sc.max}$ value of the SC doped with nickel atoms to the current of the control SC. From the data obtained from Fig 3, the reduction in surface recombination was calculated.
An increase in sensitivity (S) in the visible region of the spectrum or a decrease in surface recombination is defined as follows:

$$S = \frac{J_{sc(Ni)}/J_{sc.max(Ni)}}{J_{sc(K)}/J_{sc.max(K)}} \tag{1}$$

where, index Ni - corresponds to the SC doped with nickel, index K - corresponds to the control SC.
The increase in sensitivity S reaches its maximum value at $h\nu$=1.84 eV. In this case, for a silicon SC with $x_{p\text{-}n}$ = 28 µm, it is 38%, and for a SC with $x_{p\text{-}n}$ = 0.5 µm, it is 25%.
To obtain a depth of 28 microns, diffusion of phosphorus was carried out at T=1280 °C for 5 hours from the deposited layer, in this case, part of the phosphorus evaporates from the silicon surface. The decrease in the surface concentration in this case can reach an order of magnitude, which was confirmed by specially performed measurements of the doping profile.

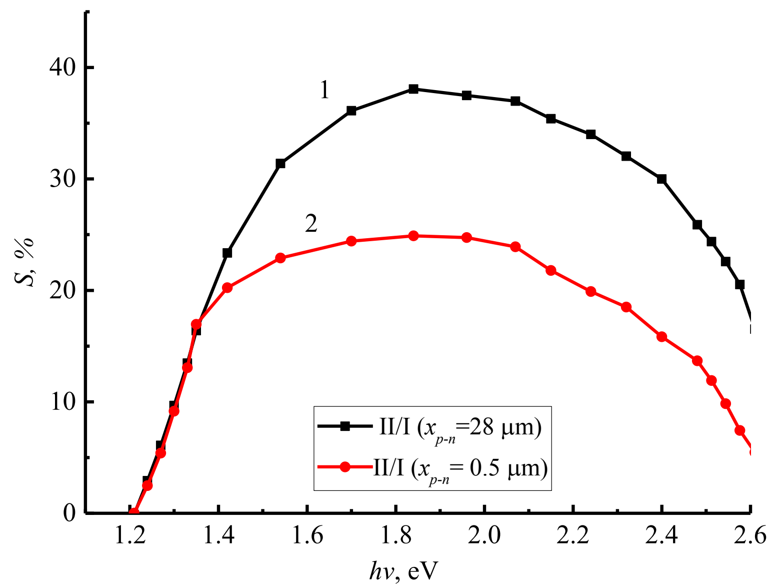

Fig 3. Spectral dependence of the ratio of $J_{sc}/J_{sc.max}$ ($h\nu$) values of SC II to Group I - 1. SC ($x_{p\text{-}n}$ =28 µm), 2. SC ($x_{p\text{-}n}$ =0.5 µm).

Nickel clusters, located in the near-surface region of silicon due to the formation of complexes of nickel-phosphorus complexes, weaken the effect of the "dead" surface layer. Accordingly, surface recombination is weakened in a SC with a deep *p–n* junction to a greater extent than in a SC with a shallow *p–n* junction. This leads to a higher short-wavelength spectral sensitivity of a SC with a deep *p–n* junction.
Thus, nickel clusters located in the near-surface region of silicon reduce the surface recombination of silicon solar cells to 25–35% due to gettering and passivating properties.
In the near-surface region, the concentration of electrically neutral nickel atoms is very high ($10^{20}\div10^{21}$ cm^{-3}) and, accordingly, the concentration of clusters is 2÷3 orders of magnitude higher than in the bulk [8]. Clusters getter quickly diffusing impurities and screen the influence of defects that cause near-surface recombination.
The surface recombination rates (S) will be calculated according to the work [20]:

$$S \approx \frac{J_{sc}}{q\Delta p_{oc}} - \frac{D}{L_{diff}} \tanh\left(\frac{W}{L_{diff}}\right) \tag{2}$$

where, Δp_{oc} is the concentration of excess charge carriers in the base, is related to open circuit voltage V_{oc}, q is the electron charge, W is the thickness of the substrate (220 μm).
It has been experimentally shown that the value of V_{oc} increased from 590 mV to 605 mV, the value of Jsc increased by 1.2 times (38.5 and 32 mA/cm^{-2}), and the value of τ increased up to 2 times [8]. Comparison of the surface recombination rate of SC doped with nickel and control SC shows that the surface recombination rate is significantly reduced in SC doped with nickel.
For direct use of the results obtained in the production of SCs, nickel doping of the initial plates can be carried out from a layer of chemically deposited nickel [21] and nickel diffusion can be performed at T_{diff} = 800–850 °C. Then, the remains of metallic nickel should be removed by etching and, further, the standard industrial technology for the manufacture of solar cells should be used. Chemical deposition is much cheaper than vacuum deposition and makes it possible to simultaneously process a large number of wafers of any size and shape [22], while uniform doping is ensured over the entire crystal surface. This does not require mechanical processing of the plates after nickel diffusion, only chemical etching and cleaning. The above features make it possible to recommend the technology of pre-alloying silicon with nickel from a chemically deposited layer for implementation in the industrial technology for the production of photovoltaic cells.
This means that the technology proposed by us makes it possible to combine it with the standard technological process without significant changes and at low cost to create more efficient photocells. If a standard antireflection coating and ohmic contacts with an optimal shape are used, then the parameters of photocells based on the proposed technology can be improved by approximately 20–25%.

5. Conclusions

It is shown that doping with nickel increases the parameters of solar cells. It has been determined that in the visible region of the spectrum the spectral sensitivity of a SC doped with nickel is higher up to 25÷35% due to a decrease in surface recombination.
Clusters getter quickly diffusing impurities and screen the influence of defects that cause near-surface recombination. Thus, doping with nickel atoms increases the efficiency of silicon solar cells by increasing the lifetime of minority charge carriers and increasing the sensitivity in the visible region of the solar spectrum.
The developed technology of doping silicon with impurity nickel atoms makes it possible to create more efficient solar cells without significant changes in the technological process and at low cost.

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