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Gettering properties of nickel in silicon photocells

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The effect of doping with nickel on the parameters of silicon photocells, in which the $p-n$- junction was created by impurities of III (B, Ga) and V (P, Sb) groups, has been studied. It is shown that the positive effect of nickel on the photocell efficiency does not depend on the type of initial silicon and on the nature of impurities used to obtain the $p-n$- junction, but is mainly determined by the gettering properties of the near-surface nickel-enriched layer

Keywords: photocell, silicon, nickel, thermal annealing, clusters, lifetime, gettering, recombination centers.

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Introduction

In the studies [1,2] it was shown that the formation of a nickel-enriched layer in the near-surface region of silicon photocells leads to an improvement in their parameters. In these studies, the $p-n$ junction was obtained by the technique of phosphorus diffusion into p-type silicon wafers.

With diffusion doping, nickel has a sufficiently high volume solubility $N_S \sim 10^{18}\,\text{cm}^{-3}$, and a nickel-enriched layer with a thickness of $2-3\,\mu$m is formed in the near-surface region, in which the concentration can reach $N_S \sim\ 10^{20}-10^{21}\,\text{cm}^{-3}$ [3].

Most of the dissolved nickel atoms are in the electroneutral state in the internodes and can form clusters [4,5]. Nickel clusters are easily formed both during diffusion and during further heat treatment, but they practically do not affect the electrical parameters of the material due to the low $(N \sim 4\cdot 10^{14}\,\text{cm}^{-3})$ concentration of electroactive nickel. The concentration, size and composition of clusters are mainly determined by the temperature of additional annealing and the total concentration of nickel atoms introduced into silicon [6,7].

The above-mentioned clusters located in defective near-surface layers, on the front and back sides of the photocells, can act as effective gettering centers for uncontrolled recombination of impurity atoms and oxygen [8,9]. They can also, due to their „metallic" conductivity, effectively reduce the surface resistance of the front n photocell layer, which leads to a decrease in the series resistance. In addition, it is known that nickel films deposited on silicon have good gettering properties [10,11].

If nickel clusters have gettering properties and purify crystals from harmful impurities, then the positive effect of nickel on the photocells? efficiency should not depend on the type of initial silicon and on the nature of the impurities used to produce the $p-n$ junction.

In connection with the above, the purpose of this study was to study the effect of nickel on the parameters of silicon photocells, in which the $p-n$ junction was created by impurities of the III (B, Ga) and V (P, Sb) groups, as well as to show the presence of gettering properties of the nickel-enriched near-surface layer.

1. Research technology and methodology

For the diffusion of group V elements, p-type silicon wafers with a resistivity of $0.5\,\Omega\cdot$cm (thickness $380\,\mu$m and diameter $d \sim 76$ mm) were used, and for group III elements —n-type with a resistivity of $0.3\,\Omega\cdot$cm (thickness $300\,\mu$m and diameter d 45 mm).

Nickel diffusion was carried out prior to the creation of the $p-n$ junction similarly to [2]. A thin layer of pure nickel with a thickness of $1,\mu$m was sprayed on the front side o fphotocells in vacuum, then diffusion was carried out in the atmosphere of air. Nickel diffusion was carried out under the conditions $T_{diff} = 850^\circ$C for $t = 30$ min.

After nickel diffusion, all the plates were cut into separate samples of the size of 1×1 cm.

Taking into account the diffusion coefficient P, B, Ga, Sb into silicon, the optimal diffusion time for each temperature [12,13] was calculated.

Phosphorus diffusion was carried out from a deposited layer of ammonium phosphate in air at $T_{diff} = 1000^\circ$C for $t = 30$ min (depth of $p-n$-junction $x_{p-n} = 0.5-0.7\,\mu$m).

Antimony diffusion — from the gas phase, in vacuumed ampoules at $T_{diff} = 1200^\circ$C for $t = 20$ min ($x_{p-n} = 1-1.2\ mu$m).

Boron diffusion was carried out in air at $T_{diff} = 1050^\circ$C for $t = 30$ min ($x_{p-n} = 1-1.2$ mum), boron nitride was used as a source.

Gallium diffusion was carried out from the gas phase, in sealed ampoules at $T_{diff} = 1170^\circ$C for $t = 5$ min($x_{p-n} = 1.5-1.7$ mum).

Control samples were made using the same technology, only the nickel film was not applied.

After receiving the $p-n$ junction, all photocell samples underwent additional thermal annealing at $T_{ann} = 700-800^\circ$C for $t = 30$ min in order to activate the recombination impurities gettering process [14,15].

After each technological stage, chemical treatment was carried out to remove the remnants of nickel, silicon oxide and glasses from the surface of the samples (10% HCl, then 10% HF) and cleaning the surface in an ammonia peroxide solution.

Ohmic contacts were created by vacuum spraying a nickel film at a temperature of 350°C with a thickness of about 1 μm followed by tinning with solder POSK-18. 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 antireflection coating on the surface of the elements.

The volt-ampere characteristic (VAC) of photocells was measured when illuminated by 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 at 25°C was maintained by a passive water thermostat with an accuracy of ± 1 degrees. To reduce the temperature change during the measurement, the samples were illuminated by pulses with a period of 15 s and a duration of 1 s.

The parameters — the no-load voltage V_{oc} and the short-circuit current density J_{sc}, the maximum output power $P_{\max}$ and the fill factor of the VAC ξ are determined from the VAC photocells.

The lifetime of the nonequilibrium charge carriers - NCC(τ) was measured in the obtained structures by the [16] technique. The lifetime in the photocell structures corresponds to the recovery time of the reverse conductivity of the $p-n$ junction, which was measured using damped oscillations of the resonant LC-contour, the measurement error did not exceed 10%.

2. The results obtained

Table 1 presents the main parameters of the samples of photocells in which the $p-n$ junction was formed by phosphorus diffusion.

In nickel-doped samples, there is a noticeable improvement in the parameters. At the same time, the average Voc value in relation to the control increases by 2.5%, and J_{sc} increases by 20.3%. $P_{\max}$ increases by 29.1%.

Table 2 presents the main photocell parameters, in which the $p-n$ junction was formed by the diffusion of another element of the V group — antimony. And in this case, nickel doping of photocells leads to a noticeable improvement in parameters. At the same time, the average value of V_{oc} in relation to the control increases by 3.8%, J_{sc} increases by 19.4%, and $P_{\max}$ increases by 29.8%.

The main photocell parameters, in which the $p-n$ junction was formed by boron diffusion, are presented in Table 3. In nickel-doped photocells, the average value of V_{oc} in relation to the control increases by 3.44%, J_{sc} — by 16.92%, and $P_{\max}$ increases by 28.5%.

Table 1. Average values of photocell parameters obtained by phosphorus diffusion

Photocell parameters	Control	Nickel-doped
J_{sc}, mA/cm^2	32	38.5
V_{oc}, mV	590	605
ξ	0.64	0.67
$P_{\max}$, mW/cm^2	12.08	15.61
$\Delta P_{\max}/P_{\max}$	–	+29.15%

Table 2. Average values of photocell parameters obtained by antimony diffusion

Photocell parameters	Control	Nickel-doped
J_{sc}, mA/cm^2	18.0	21.5
V_{oc}, mV	530	550
ξ	0.63	0.66
$P_{\max}$, mW/cm^2	6.01	7.80
$\delta P_{\max}/P_{\max}$	–	+29.85%

Table 3. Average values of photocell parameters obtained by boron diffusion

Photocell parameters	Control	Nickel-doped
J_{sc}, mA/cm^2	32.5	38
V_{oc},mV	580	600
ξ	0.64	0.68
$P_{\max}$, mW/cm^2	12.06	15.50
$\Delta P_{\max}/P_{\max}$	–	+28.51%

Table 4. Average values of photocell parameters obtained by gallium diffusion

Photocell parameters	Control	Nickel-doped
J_{sc}, mA/cm^2	30	36
V_{oc}, mV	565	585
ξ	0.64	0.67
$P_{\max}$, mW/cm^2	10.85	14.11
$\Delta P_{\max}/P_{\max}$	–	+30.07%

Table 5. Lifetimes of NCC of photocells

Type FE	I_P	II_{Ni+P}	I_{Sb}	II_{Ni+Sb}	I_B	II_{Ni+B}	I_{Ga}	II_{Ni+Ga}
τ, μc	14−16	30−32	4−5	7−8	12−14	26−28	5−6	8−10

Note: I group — control, II group — nickel-doped.

Studies have shown that in nickel-doped photocells, in which the $p-n$ junction was formed by gallium diffusion, there is also an improvement in the parameters relative to the control photocells.

These data are presented in Table 4. The average value of V_{oc} in relation to the control increases by 3.54%, J_{sc} increases by 20%. $P_{\max}$ increases by 30%.

In all samples of nickel-doped photocells, there is an increase in the filling factor of the VAC by about 4.5−5% relative to the control photocells.

Thus, we can assume that nickel doping of photocells leads to a noticeable improvement in parameters regardless of the nature of the impurity forming the $p-n$ junction. We associate this effect with the influence of the nickel-enriched layer in the near-surface area of photocells.

The obtained data allow us to assert that the improvement of the photocells parameters is not related to the peculiarities of the interaction of nickel atoms with the studied alloying impurities — phosphorus, antimony, boron and gallium.

3. Discussion of results

It is known [2,3], that the nickel concentration in the near-surface regions of the sample during diffusion in silicon is very high ($N_S \sim 10^{21}\,\text{cm}^{-3}$). In volume, the concentration is almost constant and relatively small ($N \sim 10^{17}\,\text{cm}^{-3}$). After the formation of the $p-n$ junction, as well as additional thermal ignition at $T_{ann} = 700-800^\circ$C, the nature of nickel distribution changes little. The introduced nickel atoms easily form clusters both in the near-surface region and in the volume of [1]. These clusters act as gettering centers of [17,18] for various uncontrolled impurities (O, Cu, Fe, Au) and other defects of various nature. The gettering properties of clusters in the near-surface region will be very noticeable due to the high concentration of nickel atoms.

Measurements have shown that doping with nickel atoms with the formation of clusters allows to increase the lifetime of the NCC in the photocells base up to 2 times (Table 5). We attribute the increase in the lifetime of photocells? NCC to the gettering properties of clusters of nickel atoms.

Thus, it is shown that additional nickel doping of silicon wafers, regardless of their type of conductivity and the nature of the impurity forming the $p-n$ junction, is a very affordable and technologically advanced solution to increase the efficiency of silicon photocells. The presence of the gettering properties of nickel clusters allows the use of nickel doping technology to improve the technological stability of almost any silicon materials during heat treatment.

The convenience and accessibility of the proposed technology lies in the fact that:

— the application of a nickel metal layer to the silicon surface can be carried out by chemical means [19,20] (simultaneously on dozens of plates with different diameters);

— nickel diffusion can be carried out in air at a sufficiently low temperature ($T_{diff} = 850^\circ$C for 30 min);

– 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.

Conclusion

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

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

1. The technique of gettering recombination impurities with nickel clusters is an effective, technological and cheap method.

2. The introduction of nickel makes it possible to achieve an increase in the efficiency of silicon photocells by 20−25%.

3. – 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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