

## Diffusion of phosphorus in technology for manufacturing silicon *p-i-n* photodiodes

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**Abstract.** Comparative characterization of phosphorus diffusion from planar sources and liquid-phase diffusion by using  $\text{PCl}_3$  in technology for manufacturing silicon *p-i-n* photodiodes was carried out. The quantitative analysis of dislocations formed when using different variants and modes of diffusion has been performed. The influence of dislocation number on the dark current density and responsivity of photodetectors has been studied. A table has been given for estimation of surface resistance with account of colour inherent to phosphorosilicate glass after doping phosphorus into the surface layer.

**Keywords:** photodiode, phosphorus diffusion, dislocation, dark current, sensitivity.

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### 1. Introduction

In production of silicon devices, in particular photodetectors, planar technologies where diffusion is their defining process are widely used. In semiconductor crystals, this process is a directed movement of impurity atoms along the direction of their reducing concentration. Elements of Periodical Table from the third and fifth groups are mainly used as doping impurities. Most often, phosphorus and boron are employed to create  $n^+$  and  $p^+$  layers, respectively.

Phosphorus diffusion in planar technology is carried out using gas-phase ion implantation, most often with phosphine  $\text{PH}_3$ , or liquid-phase one with  $\text{PCl}_3$  or  $\text{POCl}_3$ , and with solid sources (often phosphorus oxide,  $\text{P}_2\text{O}_5$ ). Also, one of the options for solid-phase diffusion is that from planar phosphorus sources (PPS).

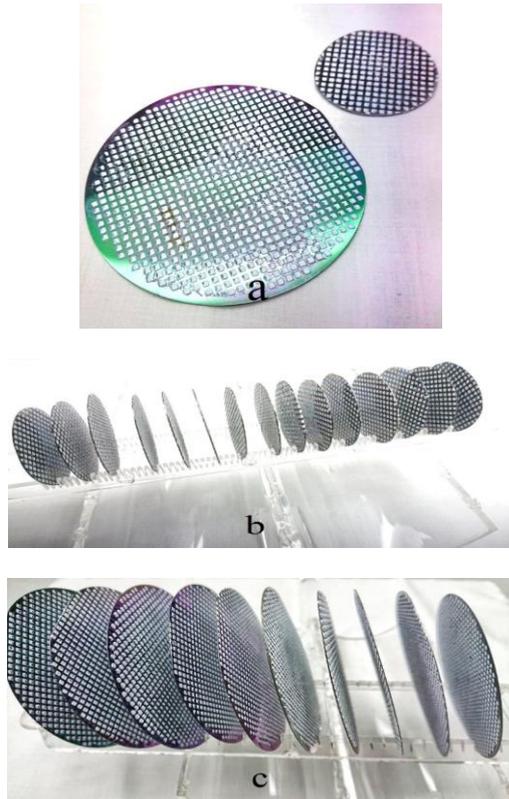
Ion doping (ID) is now becoming the main technical process used to modify electrophysical properties of materials surface layers. This method is based on monitored introduction of electrostatically accelerated ionized atoms and molecules into material. ID has a number of advantages over other diffusion methods, in particular: low process temperatures, the possibility of strict dosing of impurities, high purity of the introduced impurities, low dark currents of photodetectors, etc. But significant disadvantage of ion implantation is creation of radiation defects that reduce the lifetime of minority charge carriers ( $\tau$ ), and the need to apply annealing of doped layers [1]. It is fact that the lifetime of minority charge

carriers in the manufacture photodiodes (PD) is one of the key parameters, since the responsivity of PDs depends on it. In practice, it was seen that silicon *p-i-n* photodiodes of the same type, made using ID, have a lower responsivity than PDs made using thermal diffusion.

Diffusion by using  $\text{PH}_3$  [2] is mainly used in a closed volume, because when heated above 100...140 °C it ignites, and phosphine is also an extremely dangerous substance. It affects primarily the nervous system, disrupts metabolism; acts on blood vessels, respiratory organs, liver, kidneys. The smell of phosphine is felt at the concentration of 2...4 mg/m<sup>3</sup>, long-duration inhalation at the concentration of 10 mg/m<sup>3</sup> can cause fatal poisoning. MPC is 0.1 mg/m<sup>3</sup> [3].

Given the above facts, we do not use ion implantation and diffusion using phosphine when manufacturing the photodetectors.

Diffusion from the liquid phase by using  $\text{PCl}_3$  or  $\text{POCl}_3$  [4, 6] and from solid phosphorus sources [5, 7] is most commonly used in planar technology, and we used it in the manufacture of photodiodes. But in the case of doping from the solid phase, we use planar sources of phosphorus. After all, phosphoric anhydride ( $\text{P}_2\text{O}_5$ ) needs frequent replacement due to rapid depletion and is very sensitive to the presence of moisture. PPSs made by Lviv scientists were used in the production of PD (Fig. 1), in which  $\text{Al}(\text{PO}_3)_3$  is the main source material. Doping from the liquid phase was carried out within one thermal operation, and from the solid one – within two ones, i.e., in two stages.



**Fig. 1.** Planar sources of phosphorus: a) individual sources; b), c) sources on a silica substrate.

Many scientific works devoted to the issue of diffusion have been published, and theoretical models have been developed for the preliminary calculation of the main parameters that characterize this process. Thus, it was found in [6] that a pre-treatment consisting in an oxidation at 1050 °C followed by  $\text{POCl}_3$  diffusion at 900 °C can improve the lifetime by deactivating or eliminating grown-in defects.

In [7], plasma-assisted atomic layer deposition was carried out for growing thin phosphorus oxide films onto flat and high-aspect ratio substrates. The applicability of these films as dopant sources for shallow phosphorus doping by using different rapid thermal annealing methods, such as conventional rapid thermal annealing and flash lamp anneal, was investigated.

But it should be noted that scientific papers and publications describe doping processes mainly for silicon integrated circuits or transistors, and for the technology of *p-i-n* photodiodes manufacture many other criteria, which need to be taken into consideration in the process, are introduced. These include: high controllability and reproducibility of results; the ability to create an antireflecting coating of the desired thickness; uniformity of impurity distribution, and accordingly, the minimum scatter in dark current values  $I_d$  across responsive elements (RE); minimal surface damage during the diffusion process, minimal degradation of the lifetime of minority charge carriers, ensuring maximum responsivity, etc.

With account of the mentioned above, the purpose of this work was to create silicon *p-i-n* PDs by using liquid-phase diffusion of phosphorus and diffusion from planar sources with minimization of structural surface defects and minimal scattering of  $I_d$  across RE; to carry out a comparative analysis of these doping methods; to evaluate the possibility of obtaining maximum responsivity by using each diffusion method.

## 2. Experimental procedure

Thermal processes, diffusion in particular, were carried out using a diffusion system such as SDO-125/3-12.

Control of current monochromatic pulse responsivity  $S_{pulse}$  was performed at the pulse duration  $\tau_i = 500$  ns,  $U_{bias} = 120$  V and  $\lambda_{op} = 1.064$   $\mu\text{m}$ .

Control of dark currents  $I_d$  was performed at  $U_{bias} = 120$  V. Dark currents were measured according to the diagram shown in Fig. 2. Below, the current density  $J_d$  in  $\text{nA}/\text{cm}^2$  calculated using the formula (1) will be indicated:

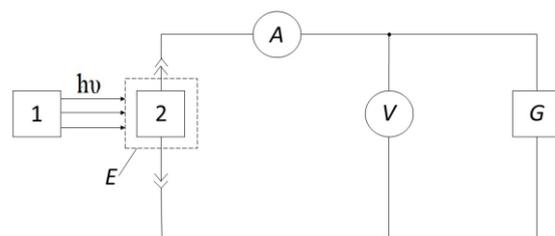
$$J_d = \frac{I_d}{A_{RE}}, \quad (1)$$

where  $A_{RE}$  is the area of the responsive element (RE).

## 3. Experimental details

Phosphorus diffusion was performed using two methods – one-stage and two-stage ones.

One-stage diffusion was carried out from  $\text{PCl}_3$  liquid diffusant. A series of wafers were loaded into the reactor at  $T = 1050$  °C in the atmosphere of nitrogen and were kept for 5 to 10 min. The nitrogen was then blocked and dry oxygen was applied for a few minutes to form a thin layer of  $\text{SiO}_2$  to reduce bombardment by the diffusant the surface of silicon and to decrease the surface resistance. Then, an oxide of the order of several nanometers in thickness is grown. The next stage is the doping process itself – oxygen is blocked, and the diffusant is fed into the reactor again in the atmosphere of nitrogen. It should be noted that as the diffusant is very volatile, the ampoule of  $\text{PCl}_3$  is placed in a thermostat of a temperature below the room one for better controlling the process. The diffusant is fed through a stream of nitrogen, the flow rate being 3...6 l/min. The process of supplying the diffusant

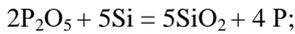
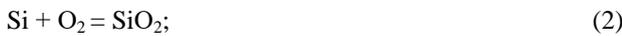
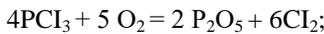


**Fig. 2.** Scheme for measuring dark currents: 1 – radiation source, 2 – PD investigated, A – ammeter, V – voltmeter, G – power supply, E – light protection screen.

**Table 1.** Estimation table for the correlation between the PSG color and surface resistance.

PSG colour	$R_s$ , Ohm/□
Bright blue	3.0...3.2
Blue	3.2...3.5
Blue-violet	3.5...3.7
Violet	3.7...4.2
Violet-brown	4.2...4.4
Brown	4.4...6.0
Brown-grey	6.0...7.0
Grey dark to transparent	7.0...12.0
Transparent	$\geq 12.0$

lasts from 1 to 5 min, depending on the specified surface resistance  $\rho_s$  and the flow rate of the carrier gas. At the end of the  $\text{PCl}_3$  supply, the nitrogen is blocked and dry oxygen is supplied to create an antireflecting oxide, and phosphorosilicate glass (PSG), which was formed by the supply of phosphorus (III) chloride, is diffused into the silicon wafer itself. The final stage of this thermal process lasts 150...200 min depending on the specified depth of the  $p$ - $n$  junction. Note that, taking into account the fact that oxygen is fed before and after supplying the diffusant, the presence of  $\text{O}_2$  in the carrier gas is of fundamental importance, because it causes formation of impurity oxides. During the described processes the following chemical reactions take place:



$m\text{P}_2\text{O}_5 n\text{SiO}_2$  – phosphorosilicate glass, where  $m$  and  $n$  are some coefficients.

The two-stage method consisted in two separate thermal operations – the so-called “driving-in” – diffusion from an unlimited source, during which phosphorus diffuses to the depth approximately 1  $\mu\text{m}$  and forms PSG on the surface of the wafers, and “start-up” – redistribution of impurities, which provides the set depth of  $p$ - $n$  junction. Phosphorus start-up was performed from PPS in the atmosphere of nitrogen  $T = 1050 \text{ }^\circ\text{C}$ . The duration of process ranged from 20 to 50 min, depending on the specified surface resistance. On completion of the driving-in, the wafers are unloaded, PSG is removed in a solution of hydrofluoric acid  $\text{HF}:\text{H}_2\text{O} = 1:10$ , and  $R_s$  monitoring by using the four-probe method was carried out [8]. It should be noted that the surface resistance of silicon wafers after phosphorus driving-in can be estimated with account of the color inherent to PSG, which changes when the thickness of the glass changes. For this purpose, an estimation Table 1 for the correlation between PSG colors and the surface resistance, when observing the samples in the day light, was experimentally ascertained and formed.

**Table 2.** Statistical parameters of silicon  $p$ - $i$ - $n$  PDs made using diffusion with  $\text{PCl}_3$  and diffusion from PPS at  $\rho_s = 2.5...2.7 \text{ Ohm}/\square$ .

Parameter	Parameter value	
	Diffusion with $\text{PCl}_3$	Diffusion with PPS
$J_d$ , nA/cm <sup>2</sup>	390...1000	50...150
$S_{pulse}$ , A/W	0.40...0.45	0.44...0.48

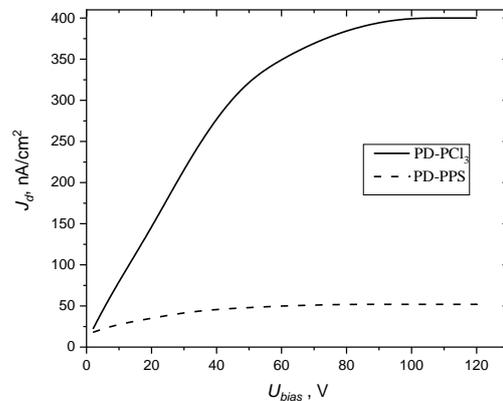
Next, the wafers were washed in a bath with solution of  $\text{HNO}_3:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 5:1:1$  and loaded into another reactor for start-up. This thermal process was carried out at  $T = 1150 \text{ }^\circ\text{C}$  first 5...10 min in the atmosphere of nitrogen, and then – 60...90 min in the atmosphere of dry oxygen, depending on the specified thickness of the antireflecting oxide and the depth of the  $p$ - $n$  junction.

#### 4. Results and discussion

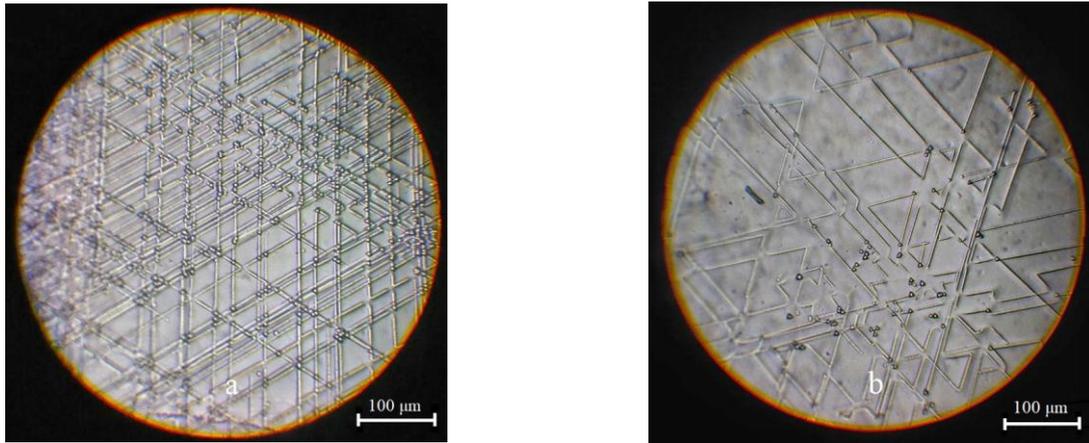
For comparative analysis of two diffusion techniques, silicon  $p$ - $i$ - $n$  photodiodes were fabricated according to two routes that included different variants of  $n^+$  layer formation. Dark currents and pulse responsivity of photodiodes were measured (see Table 2).

It was observed that the yield of suitable PDs, when using diffusion with  $\text{PCl}_3$ , is much lower than after diffusion from planar sources. Some products were rejected at the stage of controlling  $J_d$  in photoresponsive crystals. About 40...50% of the crystals were rejected because of elevated  $J_d$  levels, in particular, a significant part of the crystals were not suitable, since the scattering of dark current levels over the pads was high. After all, the two-fold scattering of currents was considered as a reason to reject. The values of dark currents inherent to individual pads were observed to be 5...10-fold and higher than the typical ones. Similar phenomena in a two-stage diffusion of phosphorus were observed much less frequently.

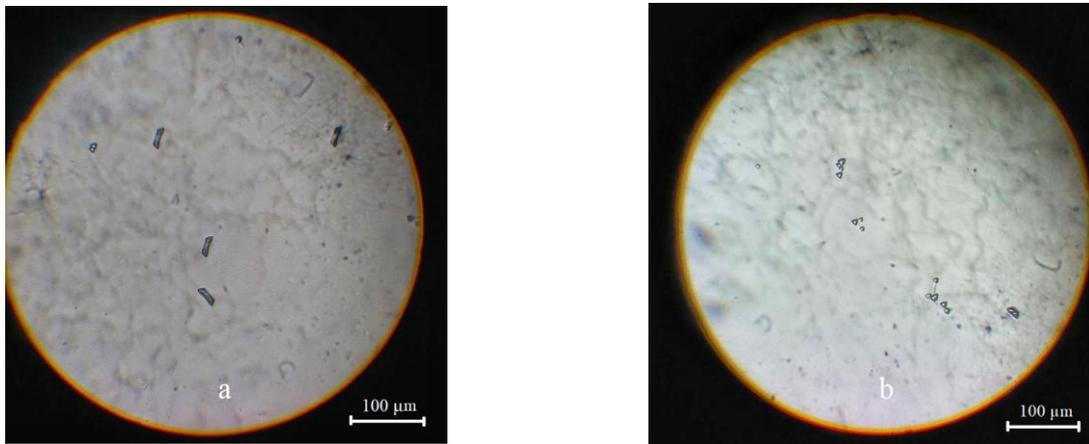
For a clearer assessment of the  $J_d$  levels, the current-voltage characteristics ( $I$ - $V$ ) of suitable PDs produced using both technological approaches within the range of 2...120 V were obtained (Fig. 3).



**Fig. 3.**  $I$ - $V$  characteristics for PDs made using phosphorus diffusion from  $\text{PCl}_3$  and PPS.



**Fig. 4.** Representation of the dislocation grids of RE after diffusion with  $\text{PCl}_3$  at 200-fold magnification: a)  $\rho_s = 2.5 \text{ Ohm}/\square$ , b)  $\rho_s = 2.7 \text{ Ohm}/\square$ .



**Fig. 5.** Representation of RE dislocations after diffusion from planar phosphorus sources at 200-fold magnification: a)  $\rho_s = 2.5 \text{ Ohm}/\square$ , b)  $\rho_s = 2.7 \text{ Ohm}/\square$ .

Also, it can be seen from Table 2 and Fig. 3 that PDs made using diffusion from  $\text{PCl}_3$  have much higher values of  $J_d$ . To study the described effects, it was decided to investigate the surface of photoresponsive crystals after different diffusion techniques. For this purpose, silicon wafers with formed crystals were treated in a selective Sirtl etchant. Previously, the oxide was stripped from the wafers washed in a mixture of Caro and ammonia-peroxide solution.

After etching for 2...5 min, both single dislocations and their grids were found on the surface of the wafers. Figs 4 and 5 illustrate the surfaces of PPGs formed using  $\text{PCl}_3$  diffusion and diffusion from solid planar phosphorus sources, respectively, at 200-fold magnification after selective etching.

The surface concentration of dislocations over the photoresponsive crystal after diffusion with  $\text{PCl}_3$  is  $N_{dis} = (2.2...2.7) \cdot 10^9 \text{ cm}^{-2}$  (Fig. 4a), and  $N_{dis} = (3.3...3.8) \cdot 10^8 \text{ cm}^{-2}$  (Fig. 4b).

The surface concentration of dislocations over the photosensitive crystal after diffusion from planar phosphorus sources: Fig. 5a –  $N_{dis} = (7...9) \cdot 10^2 \text{ cm}^{-2}$  and Fig. 5b –  $N_{dis} = (3...4) \cdot 10^2 \text{ cm}^{-2}$ .

Diffusion was performed using two ways to obtain the final surface resistance  $\rho_s = 2.5 \text{ Ohm}/\square$  and  $\rho_s = 2.7 \text{ Ohm}/\square$ . After all, we demonstrated in [9] that the optimal values of surface resistance for obtaining the maximum responsivity are  $2.7 \geq \rho_s \geq 2.5 \text{ Ohm}/\square$ .

As it was doubly noted in Figs 4 and 5, since the concentration of doping impurity grows, the number of dislocations increases, too. In the case of liquid-phase diffusion, a significant decrease in the surface resistance (increase in phosphorus concentration) causes a considerable increase in the number of dislocations over the surface of RE.

In the case of diffusion from solid sources, with increasing the phosphorus concentration, dislocations begin to form dislocation “lines”, i.e., the emergence of

dislocation grids begins. But it should be noted that in this variant of diffusion, the number of formed dislocations is much smaller than that after doping with a liquid diffusant. You can also see that when duration of the driving-in increases, the concentration of impurities does the same, the number of dislocations grows to a lesser extent in comparison with that in other methods.

It should be noted that *p-i-n* photodiodes of the operating wavelength of  $\lambda_{op} = 1064$  nm for technological reasons must have the *p-n*<sup>+</sup> junction of 4...5  $\mu\text{m}$  in depth. Also, according to the condition of minimum reflection, the antireflecting oxide should have a thickness of  $d_{\text{SiO}_2} = 0.187$   $\mu\text{m}$  [10]. This thickness is obtained by start-up of phosphorus lasting 75 min. Note that in the diffusion of phosphorus with  $\text{PCl}_3$ , the specified depth of the heterojunction is reached in 180 min, because the process temperature is 100 °C lower than in the actual start-up. With this duration of operation, an oxide with the thickness close to  $d_{\text{SiO}_2} = 0.31...0.33$   $\mu\text{m}$  is grown, which is much higher than that specified. Therefore, there is a need to etch the resulting oxide to the desired thickness in slow etchants, such as  $\text{HF}:\text{H}_2\text{O} = 1:10$ , and this introduces additional technological operations in the route of manufacturing PD, which increases its cost.

There are several reasons for dislocations to be formed during liquid-phase diffusion. In the course of diffusion from the liquid phase, a significant amount of impurities is placed into the interstices of the crystal lattice, and they are not electrically active, unlike diffusion from planar sources of phosphorus. Accordingly, these impurities introduce significant mechanical stresses caused by the difference in the sizes of phosphorus and silicon atoms, which leads to formation of dislocations. Secondly, as it was mentioned above, the antireflecting oxide is grown much thicker at liquid-phase diffusion than at diffusion from planar sources, which contributes to the appearance of more packaged defects and higher mechanical stresses, which are one of the key factors in occurrence of dislocations. Also, a small contribution to the increase in the number of dislocations is probably caused by the fact that the wafer surface already has mechanical stresses related to the presence of a thin oxide layer with the thickness several nanometers, although it is grown to reduce phosphorus bombardment and decrease surface resistance. Accordingly, the reason for the higher level of dark currents in PD made by diffusion from the liquid phase is the higher concentration of dislocations. There are several ways to explain the effect of these defects and their number on  $J_d$ . First, the presence of dislocations can cause creation of levels in the band gap due to the fields of elastic stresses associated with the dislocations, these structural defects can serve as charge carriers recombination regions. The presence of recombination centers in the depletion region of the *p-n* junction will be manifested in an increase in generation currents ( $I_d^G$ ) with a reverse bias across PD. Secondly, due to their elastic fields, dislocations can accumulate impurities. Decorated dislocations that cross the *p-n* junction give rise to high density of generation-recombination centers

in the space charge region. This again causes an increase in generation currents at the reverse bias.

The value of the generation component of dark currents can be estimated using the formula (3) [11, p. 264]:

$$I_d^G = e \frac{n_i}{2\langle\tau\rangle} W_i A_{RE}, \quad (3)$$

where  $e$  is the electron charge,  $n_i$  is the intrinsic concentration of charge carriers in the substrate,  $\langle\tau\rangle$  is the average value of lifetime inherent to the charge carriers,  $W_i$  is the width of space charge region (SCR).

When manufacturing PDs, usually used is monocrystalline silicon of *p*-type with the resistivity  $\rho \approx 18$  kOhm·cm, which corresponds to the concentration of charge carriers in the substrate  $n_i \approx 7.7 \cdot 10^{11}$  cm<sup>-3</sup>.

The width of SCR can be determined using the formula [12]:

$$W_i = \left( \frac{2\epsilon\epsilon_0(\varphi_c - U_{bias})}{eN_A} \right)^{\frac{1}{2}}, \quad (4)$$

where  $\epsilon$  is the dielectric permittivity of silicon,  $\epsilon_0$  – electric constant of vacuum,  $\varphi_c$  – contact potential difference,  $U_{bias}$  – bias voltage,  $N_A$  – concentration of acceptors in the substrate (if assuming that at room temperature all impurities are ionized, then  $n_i = N_A$ ).

At  $U_{bias} = 120$  V,  $W_i \approx 490$   $\mu\text{m}$ . But in this case, substrates with a thickness of about 440  $\mu\text{m}$  were used, so taking into account the width of the *n*<sup>+</sup>-*p* and *p*<sup>+</sup>-*p* junctions ( $x_{n^+-p} \approx 4...6$   $\mu\text{m}$  [12],  $x_{p^+-p} \approx 1...2$   $\mu\text{m}$  [13])  $W_i \approx 430$   $\mu\text{m}$ .

With an increase in the number of generation-recombination centers,  $\langle\tau\rangle$  decreases, the value of which can be estimated using the formula (5) [14]:

$$\langle\tau\rangle = \frac{3}{8R_0N_{dis}v}, \quad (5)$$

where  $R_0$  is the radius of SCR near the dislocation;  $v$  is the average relative (relative to the center of recombination) velocity of thermal charge carriers,  $v = 1.56 \cdot 10^5$  m/s.

The radius of SCR around the dislocation according to [11, p. 243] is defined as:

$$R_0 = \left( \frac{f_0}{\pi c(N_D - N_A)} \right)^{\frac{1}{2}}, \quad (6)$$

where  $f_0$  is the Fermi distribution function,  $\pi$  – mathematical constant,  $c$  – distance between the broken valence bonds ( $c = 3.34 \cdot 10^{-10}$  m for edge dislocations in silicon [11]),  $N_d$  – concentration of donors ( $N_d = 3.89 \cdot 10^{20}$  cm<sup>-3</sup> for  $R_s = 2.7$  Ohm/□).

The function  $f_0$  can be determined using the equation [11, p. 243]:

$$f_0 = \frac{1}{1 + \exp\left(\frac{E_D - E_F}{kT}\right)}, \quad (7)$$



**Fig. 6.** Dislocations at the depth 24  $\mu\text{m}$  in the silicon wafer.

where  $E_D$  is the energy level of dislocation,  $E_F$  – Fermi level,  $k$  – Boltzmann constant,  $T$  – temperature.

If we calculate  $\langle\tau\rangle$  for the samples made using diffusion with PPS ( $N_{dis} = 4 \cdot 10^2 \text{ cm}^{-2}$ ) and  $\text{PCl}_3$  ( $N_{dis} = 3.8 \cdot 10^8 \text{ cm}^{-2}$ ), we will see that  $\langle\tau\rangle$  for the first reaches  $1.7 \cdot 10^{-3} \text{ s}$  and for the second –  $1.8 \cdot 10^{-9} \text{ s}$ .

When calculating the generation component of the dark current, it was seen that  $I_d^G = 0.06 \cdot 10^{-9} \text{ A}$  for PDs made applying diffusion with PPS and  $I_d^G = 5.67 \cdot 10^{-5} \text{ A}$  for PDs prepared by diffusion with  $\text{PCl}_3$ .

In reality, the value of the lifetime of minority carriers and the generation component of the dark current differs from the calculated ones, because the calculations described above were performed in the approximation that the dislocations are uniformly distributed in the high resistance  $i$ -region, and not only in the  $n^+$  layer. In real crystals, structural defects caused by diffusion of impurities are located in the doped or adjacent areas. Although we studied the depth of dislocations for the layer-by-layer etching of plates with subsequent selective treatment, we found the presence of dislocations at the depth 20...30  $\mu\text{m}$  at the thickness of the diffusion layer of phosphorus 4...5  $\mu\text{m}$  (further etching was not performed) (Fig. 6). Note that the number of dislocations is decreased with increasing the etching depth.

From Table 2, it can be also seen that the pulse responsivity in the case of PDs created using liquid-phase diffusion is slightly less than when using PPS. In order to evaluate the responsivity of the produced PDs not only at the operation wavelength, the relative spectral responsivity characteristics for both types of the samples were obtained (Fig. 7).

As we can see from the figure, the sensitivity of PDs produced using two-stage diffusion is 10% higher in the studied range of wavelengths. This can be explained by the fact that the lifetime of charge carriers, as indicated in the formula (5), is in inverse proportion to the concentration of recombination centers, and accordingly the concentration of dislocations.

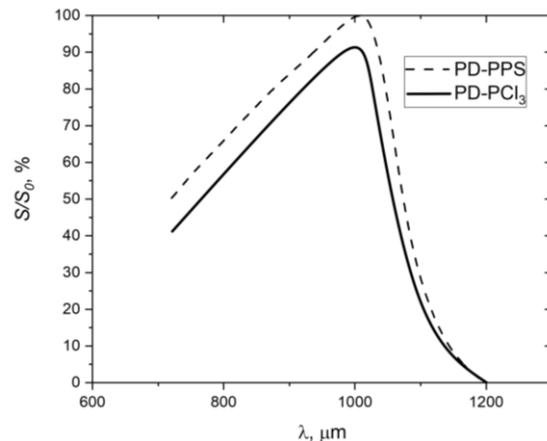
In turn, the responsivity of PDs, as seen from the formula (8), is in direct proportion to  $\tau$  [15]:

$$S = e\beta\alpha(\tau_n\mu_n + \tau_p\mu_p), \quad (8)$$

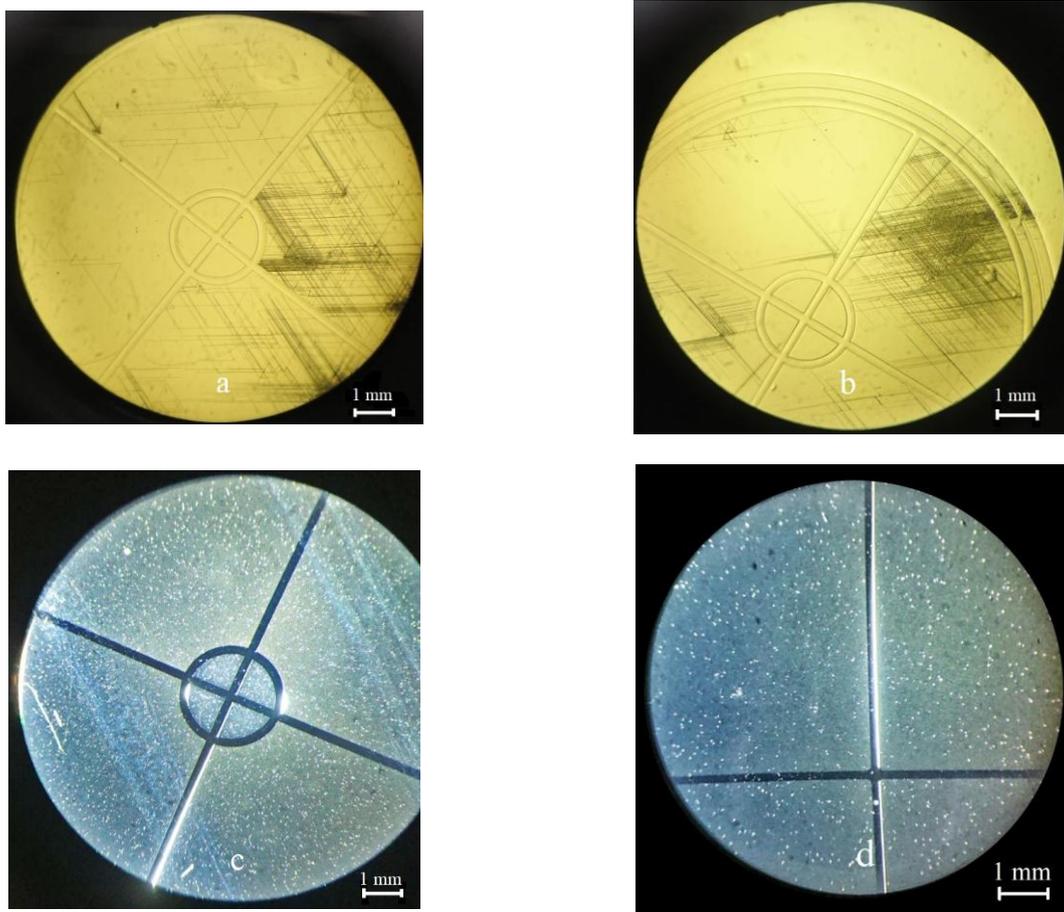
where  $e$  is the electron charge,  $\beta$  – quantum yield,  $\tau_n$ ,  $\tau_p$  – lifetimes of electrons and holes, respectively;  $\mu_n$ ,  $\mu_p$  – mobilities of electrons and holes, respectively.

That is, with increasing the number of recombination centers, the lifetime of charge carriers and, accordingly, the responsivity decrease. And given that in the PD made using liquid-phase diffusion  $N_{dis}$  is higher, then accordingly, these samples have a lower  $S_{pulse}$ .

As carrier gas low rate grew, and the wafer increased in diameter, non-uniformity of diffusion across the wafer during diffusion from phosphorus chloride was observed. These phenomena also affect the uneven distribution of dislocations over the surface of crystals (Fig. 8). The described phenomena contribute to the scattering of dark currents of PD across the pads, as well as a significant scattering of dark currents and the responsivity of the crystals of one wafer. After all, there is often an increased concentration of phosphorus at the edges of the wafer, in comparison with its central part.



**Fig. 7.** Relative spectral responsivity characteristics.



**Fig. 8.** Representation of dislocations distribution across the wafer at 16-fold magnification: a-b) by diffusion from the liquid phase; c-d) by diffusion from planar sources (dark field).

Fig. 8 shows the distribution of dislocations over the surface of silicon substrates at 16-fold magnification after diffusion from phosphorus chloride (a, b) and diffusion from planar sources (c, d). Figs 8c and 8d were obtained by observing defects in a dark field, because at this magnification, packaging defects are not clearly visualized, but “glow” in a dark field mode. It can be assumed that uneven distribution of dislocations across the surface is caused by existing defects in the starting wafers, or those acquired during previous operations. But in this case, these factors are unlikely capable to affect, because the wafers before thermal processes are subjected to chemical-dynamic polishing in a solution of  $\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH} = 9:2:4$  and undergo appearance control after each operation, respectively; thus, defective silicon substrates are not put in operation or are rejected in the production process. Accordingly, the probability of transferring wafers with defects to subsequent technological operations is minimal.

Despite the negative phenomena described above, diffusion from phosphorus chloride has several significant advantages over diffusion from PPS. First, chemical reactions during diffusion with  $\text{PCl}_3$  (2) are accompanied by formation of halogens, in particular  $\text{Cl}_2$ ,

which in turn decompose into  $\text{Cl}^-$  ions. Due to their high chemical activity, these ions interact with positively charged metal ions present on the surface of the substrates and in the reactor atmosphere, which reduces the density of surface states and the amount of fixed charge in silicon oxide. But the disadvantage is that the sources and products of the reaction are toxic substances. It should be also noted that silica reactors, in which phosphorus chloride diffusion takes place, are saturated with a diffusant much faster than reactors for diffusion with PPS. Accordingly, there is a need for frequent etching of reactors in hydrofluoric acid or their replacement.

Another advantage of liquid-phase diffusion is that it is performed in one thermal operation, while diffusion using PPS requires two thermal operations. As the number of chargings/dischargings of silicon wafers in high temperature zones increases, the influence of mechanical stresses caused by thermal shocks on photoelectric parameters of PD grows largely, it is the lifetime of charge carriers and, accordingly, responsivity. But we observe that the negative impact of structural defects formed during diffusion from phosphorus chloride does not allow one to take full advantage of this method for  $p-n$  junctions formation.

## 5. Conclusions

Silicon *p-i-n* photodiodes were manufactured using various methods of impurities to create a *p-n<sup>+</sup>* junction. Being based on the obtained parameters, a comparative analysis of phosphorus diffusion methods by using phosphorus trichloride and planar phosphorus sources was made. It has been ascertained that in the case of liquid-phase diffusion, more dislocations are formed over the responsive elements than in the case of solid-state diffusion; the concentration of structural defects is about 6 orders of magnitude higher. This factor causes a decrease in the responsivity of the devices and an increase in dark currents, and consequently a decrease in the percentage of suitable devices. In the samples made using  $\text{PCl}_3$ , an uneven distribution of dislocations across the surface of crystals contributing to the scattering of the level of dark currents over the pads was revealed. In the case of diffusion from planar sources, this phenomenon is minimal.

Being based on these facts, it can be concluded that the method of diffusion of phosphorus using PPS in the technology of manufacturing silicon *p-i-n* photodiodes provides a better yield of suitable devices than that after liquid-phase diffusion. To reduce the cost of products and to simplify the technological route, the latter method should be used in the manufacture of low-voltage photodetectors, where the impact of structural defects on the characteristics of the devices is much smaller.

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### **Дифузія фосфору в технології виготовлення кремнієвих *p-i-n* фотодіодів**

**М.С. Кукурудзяк**

**Анотація.** Проведено порівняльну характеристику дифузії фосфору з планарних джерел та рідиннофазної дифузії з використанням  $\text{PCl}_3$  у технології виготовлення кремнієвих *p-i-n* фотодіодів. Зроблено кількісний аналіз дислокацій, утворених при різних варіантах та режимах дифузії. Досліджено вплив кількості дислокацій на густину темного струму та фоточутливість фотоприймачів. Наведено таблицю для оцінки поверхневого опору за кольором фосфоросилікатного скла після легування фосфором.

**Ключові слова:** фотодіод, дифузія фосфору, дислокація, темновий струм, чутливість.