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Technology of Silicon *p-i-n* Photodiodes with a Reduced Number of Thermal Operations

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ABSTRACT The main parameters of the *p-i-n* photodiodes (PD) are responsivity, dark current and capacity of responsive elements (RE). To ensure the maximum values of the specified parameters, it is necessary to use defect-free silicon with the maximum values of resistivity and life time of minor charge carriers. These characteristics of the starting material degrade during high-temperature thermal operations. Therefore, it is worth using a technology that allows you to avoid the degradation of silicon characteristics. This can be implemented by reducing the temperature of diffusion and oxidation operations, as well as by reducing the number of actual thermal operations. The samples were made according to two versions of the technology: diffusion-planar using two-stage diffusion of phosphorus from planar sources, and mesotechnology using one-stage diffusion of phosphorus using liquid PCl_3 diffusant. After manufacturing, the PD parameters were compared. The use of mesotechnology with one-stage diffusion of phosphorus made it possible to reduce the number of thermal operations by two times compared to serial technology. The experimental samples had a pulse responsivity at a wavelength of 1.064 µm of 0.47-0.50 A/W, and the serial ones had a responsivity of 0.45-0.48 A/W. The difference in responsivity is caused by the difference in the life time of minor charge carriers, since in the case of the proposed technology, the degree of degradation of the life time of minor charge carriers during the manufacturing process is smaller. After selective etching, it was seen that when using a liquid diffusant, the density of dislocations on the crystal surface is much higher than when using planar sources of phosphorus. Due to the higher density of dislocations, the experimental samples had higher dark currents, but when using a low bias voltage, the difference in dark currents is insignificant. The RE capacity of the experimental samples was slightly lower than that of the serial ones. This can be explained by the difference in the resistivity of the *i*-region of the final crystals.

KEYWORDS silicon, photodiode, resistivity, responsivity, mesostructure.

I. INTRODUCTION

With the development of optoelectronics and photoelectronics, the requirements for their element base are increasing. In particular, the development and production of detectors of near-IR radiation, which will have high photosensitivity with minimal noise levels, is becoming more and more relevant. Silicon p-i-n photodiodes (PD) are widely used representatives of photodetectors of IR radiation. Sensitive crystals of PD with a *p-i-n* structure are two thin low-ohmic n^+- and p^+-regions, between which there is a sufficiently long high resistance *i*-layer depleted of free carriers. If no external voltage is applied to such a structure, the field in the *i*-layer is small and generated in it charge carriers will move as a result of diffusion. With the reverse bias of the *p-i-n* structure, all the voltage will drop in the high-resistance region and the generated carriers under the action of a strong electric field will fly through the *i*-layer without having time to rebind [1].

The main parameters of the described PDs are resposivity (S), dark current (I_d, or dark current density - J_d) and capacity of responsive elements (RE) (C_{RE}). Note that each of the specified parameters depends on the life of minor charge carriers (τ) and resistivity (ρ) of the silicon used. In particular, the responsevity and dark current of the detector depends on the structural perfection and purity of the high-resistance *i*-region [2]. Accordingly, to ensure the maximum values of the specified parameters, it is necessary to use defect-free silicon with the maximum values of τ and ρ. Note that these parameters of the starting material degrade during high-temperature thermal operations due to the diffusion of uncontrolled metal impurities into the substrate volume and the formation of defects caused by various technological factors [3, 4]. Minimizing the degradation of the electrophysical characteristics of silicon is an urgent scientific and technical task, for the implementation of which various methods of heterogenization are used. They make it possible to create a near-surface region free of structural defects and contaminating metal impurities in the silicon wafer, in which active and passive elements of the detector regions are formed [5, 6]. Gettering itself is a process of dissolving unwanted impurities followed by their diffusion and precipitation in specially created zones of substrates - getters, where they do not have a harmful effect on the operation of the device or can be removed (by etching, cutting, etc.).

It is worth noting that the process of heterogenization often requires the introduction of additional operations into the technological route, which complicates the design or topology of the product, as well as the cost. Therefore, it is worth using a technology that allows you to avoid the degradation of silicon characteristics. This can be implemented by reducing the temperature of diffusion and oxidation operations, as well as by reducing the number of actual thermal operations. This can be implemented using mesa technology [7, 8], as well as diffusion from liquid diffusants in contrast to classical planar technology [2, 6]. Accordingly, the goal of this work is the development and manufacture of silicon *p-i-n* PDs with a reduced number of thermal operations, compared to classical technology, which will minimize the degradation of the electro-physical characteristics of silicon and improve the parameters of the PDs.

II. EXPERIMENTAL

The research was carried out on silicon four-element *p-i-n* PDs with a guard ring (GR). The samples were produced according to two versions of the technology: diffusion-planar technology using two-stage diffusion of phosphorus from planar sources (Fig. 1) (commercial photodiodes - PD-C), and mesotechnology using one-stage diffusion of phosphorus using liquid diffusant PCl_3 (experimental photodiodes - PD-E). After manufacturing, the PDs parameters were compared. Single-crystal *p*-type silicon with [111] orientation, resistivity ρ=16-20 kΩ and life time of minor charge carriers τ=1.6-2 ms was used.

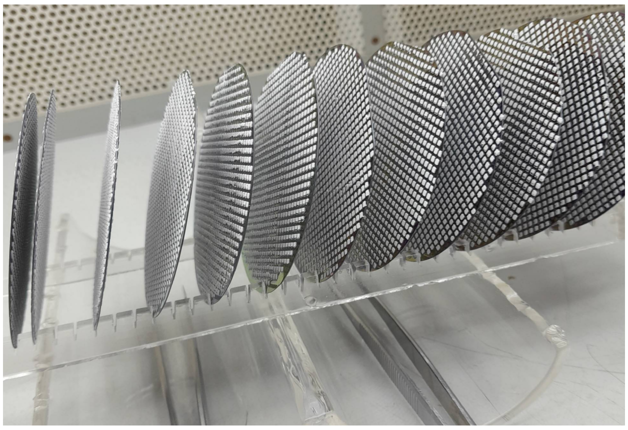


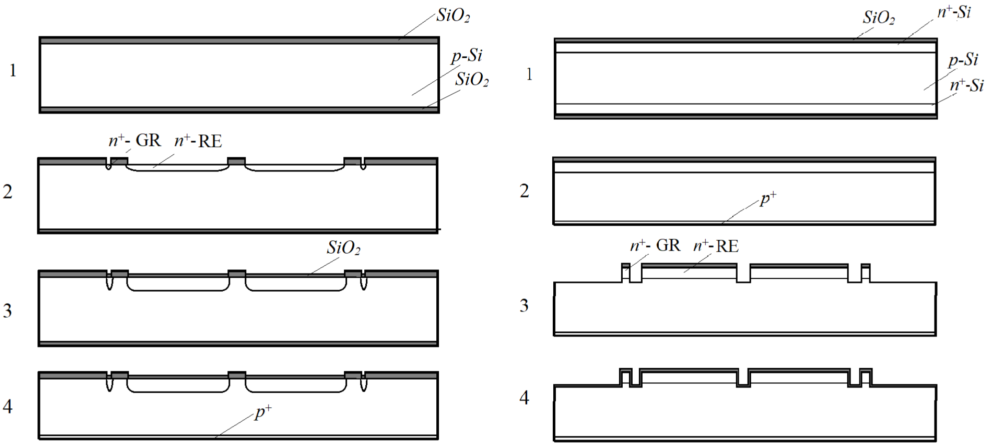
FIG. 1. Planar sources of phosphorus.

The PD-C technological route consisted of a complex of four thermal operations and three photolithographies: semiconductor substrates were oxidized (Fig. 2-a1); photolithography was carried out to create windows for phosphorus diffusion; diffusion of phosphorus (predeposition) to the front side to create n^+-type REs and GR (Fig. 2-a2); drive-in of phosphorus to redistribute the alloying impurity and increase the depth of the n^+-p-transition (Fig. 2-a3); diffusion of boron to the reverse side of the substrate to create a p^+-type ohmic contact (Fig. 2-a4); photolithography for creating contact windows; sputtering of Cr-Au on the front and back sides. The PD-C crystal can be seen in Fig. 3-a.

The PD-E technological route consisted of a complex of two thermal operations and three photolithographies: one-stage diffusion of phosphorus in an oxidizing medium was carried out according to the regimes given in [9], during which an n^+-layer was formed on both sides of the substrate covered with a SiO_2 film (Fig. 2-b1); further, after chemical dynamic polishing (CDP) of the reverse side of substrate, boron diffusion in the same side to create a p^+-type ohmic contact (Fig. 2-b2); photolithography for the formation of windows for etching the mesoprofile and actual etching of the mesostructure by the CDP method (Fig. 2-b3). Note that the film formed on the surface of the silicon substrate during the diffusion of phosphorus is a mixture of SiO_2 and phosorosilicate glass with a thickness of 0.27-0.33 microns, so it was etched, and the anti-reflective oxide was applied by cathode magnetron sputtering (Fig. 2-b4). The creation of contacts to the REs and GR was carried out by the same method as in the PD-C. The PD-E crystal is shown in Fig. 3-b.

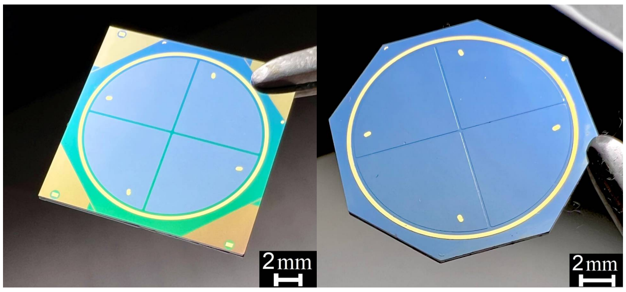
The surface concentration of phosphorus in both versions of the technology reached $N_0=3.8\cdot10^{20}$-$4.1\cdot10^{20}$ cm^{-2} ($R_s\approx2.7$ Ohm/□), boron – $N_0=4.3\cdot10^{20}$-$4.35\cdot10^{20}$ cm^{-2} ($R_s\approx18$ Ohm /□).

To study the defective structure of the surface of the finished crystals, selective etching was carried out in Sirtle's etchant [10].



a) b)

FIG. 2. Schematic section of a PD crystals of two variants of technology at various stages of production: a) diffusion-planar technology (PD-C); b) mesotechnology (PD-E).



a) b)

FIG. 3. Image of photodiode crystals: a) PD-C; b) PD-E

III. RESEARCH RESULTS AND DISCUSSION

A. Responsivity of the photodiodes. To evaluate the responsivity in the near-IR range of wavelengths, the spectral characteristics of the responsivity of experimental and commercial PDs were obtained (Fig. 4).

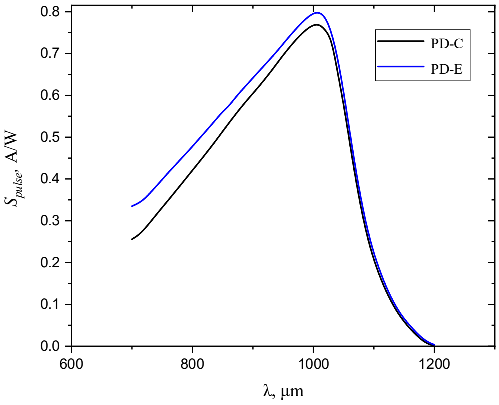


FIG. 4. Spectral characteristics of the responsivity of PD-C and PD-E.

As can be seen from fig. 4 PD-E have higher responsivity than PD-C in the entire range of investigated wavelength. At a wavelength of λ=1.064 μm, U_{bias}=120 V and pulse duration 500 ns, the PD-C had an impulse responsivity of S_{pulse} =0.45-0.48 A/W, and the PD-E had S_{pulse}=0.47-0.5 A/W. And responsivity on the modulated signal at U_{bias}=2 V for PD-C was S_λ=0.35-0.38 A/W, and for PD-E - S_λ=0.36-0.4 A/W. The difference in responsivity can be explained by the difference in the life time of minor charge carriers, since responsivity is directly proportional to τ (Eq. (1)) [9]. Although the PDs were made of the same silicon, but in the case of PD-E, the degree of degradation of τ during the manufacturing process is smaller due to the reduction in the number of thermal operations

$$S = e\beta\alpha\left(\tau_n\mu_n + \tau_p\mu_p\right), \qquad (1)$$

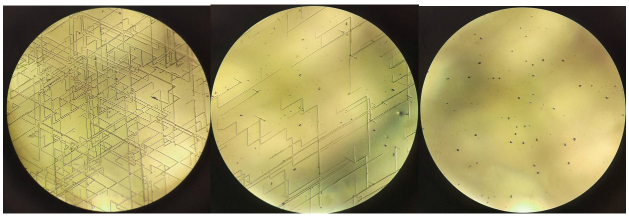
where e is the electron charge; β is the quantum yield; α is the absorption coefficient; τ_n, τ_p – life time of electrons and holes, respectively; μ_n, μ_p - mobility of electrons and holes, respectively.

Note that in the case of PD-E, two operations with a temperature of 1423 K, during which the diffusion of uncontrolled impurities is the most, are excluded from the technological route.

B. Surface of the samples. After selective etching of photodiode crystals, dislocation lines and grids of different densities were found on their surface. For comparison, selective etching of samples made by planar technology using diffusion of phosphorus from PCl_3 was also carried out [9]. From Fig. 5a, it can be seen that the density of dislocations during diffusion from the liquid-phase diffusant after the oxidation operation is the highest (N_{dis}=6·10^7-8·10^7 cm^{-2}). This can be explained by the fact that вuring diffusion from a liquid diffusant, a significant amount of the impurity is placed in the interstices of the crystal lattice and is not electrically active, unlike diffusion from planar sources of phosphorus. Accordingly, these impurities introduce significant mechanical stresses due to the difference in the diameters of phosphorus and silicon atoms, which leads to the formation of dislocations.

In Fig. 5b shows the surface of PD-E after selective etching. It can be seen from the figure that the density of dislocations in this case is lower than in the previous one (N_{dis}=2·10^6-4·10^6 cm^{-2}), although the diffusant concentration was the same. The decrease in the density of dislocations is caused by the exclusion of oxidation operations from the PD-E technological route, since during thermal oxidation point defects are formed on the surface of the substrates, which are clusters of Si atoms formed as a result of oxygen diffusion. Accumulations of these point defects are places of generation of dislocations during the diffusion of phosphorus [11]. Accordingly, the number of dislocations can be reduced by reducing the density of oxidation defects.

PD-C had the lowest density of dislocations (N_{dis}=2·10^3-4·10^3 cm^{-2}) (Fig. 5c).



a) b) c)

FIG. 5. Surface of PD crystals after selective etching: a) crystal with diffusion from the liquid-phase diffusant after the oxidation; b) PD-E; c) PD-C.

C. Dark currents of the photodiodes. When measuring dark currents, it was seen that PD-E had slightly higher values of dark current than PD-C. The increase in the dark current of PD-E is caused by the increased number of dislocations compared to serial samples, which contribute to the growth of the surface and volume generation components of the dark current [2]. At U_{bias} =120 V PD-C had $J_d\approx$80 nA/cm^2, and PD-E - $J_d\approx$250 nA/cm^2. But note that at U_{bias}=2 V PD-C had $J_d\approx$15-25 nA/cm^2, and PD-E - $J_d\approx$25-30 nA/cm^2. Accordingly, at low bias voltages, the difference in dark currents is insignificant, so the proposed PDs should be used at low bias voltages.

D. Capacity of responsive elements. The capacity of the responsive elements of the studied photodiodes differed slightly (Fig. 6).

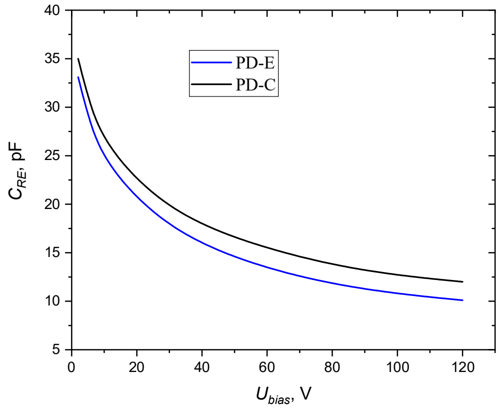


FIG. 6. Dependence of capacity of responsive elements of photodiodes on the bias voltage.

At U_{bias}=120 V C_{RE} ≈10 pF in PD-E, and C_{RE} ≈12 pF in PD-C. This can be explained by the difference in the resistivity of the *i*-region of the final crystals. After all, the capacity is inversely proportional to the resistivity (Eq. (2)) [12], and in PD-E the degree of its degradation is much lower due to the decrease in the number of dungeon operations, in particular high-temperature ones

$$C_{RE} = \frac{326 A_{RE}}{\sqrt{\rho \cdot (\varphi_k - U_{bias})}}, \qquad (2)$$

where A_{RE} is effective area of RE; φ_k is contact potential difference.

IV. CONCLUSION

Silicon *p-i-n* photodiodes with a reduced number of thermal operations were manufactured and investigated. The samples were made by mesotechnology and using PCl_3 liquid diffusant and one-stage phosphorus diffusion. This made it possible to avoid high-temperature thermal oxidation operations, and to reduce the number of thermal operations by two times compared to photodiodes manufactured by classical planar technology. As a result of the decrease in the rate of degradation of the life time of minor charge carriers and resistivity of silicon, the experimental samples had a higher responsivity and a lower capacity than the serial products. However, the proposed samples had slightly higher dark currents due to the increased number of dislocations, but when they are used at low bias voltages, the difference in dark currents is minimal. The described photodiodes are manufactured according to a much shorter technological route, which reduces their cost.

COMPETING INTERESTS

The authors declare no competing interests.

REFERENCES

[1] Aliane, A., Ouvrier-Buffet, J. L., Ludurczak, W., André, L., Kaya, H., Vialle, C., ... & Hartmann, J. M. Fabrication and characterization of sensitive vertical PiN germanium photodiodes as infrared detectors. Semiconductor Science and Technology, vol. 35(3), 035013, 2020. DOI: https://doi.org/10.1088/1361-6641/ab6bf7

[2] Kukurudziak M.S. Formation of Dislocations During Phosphorus Doping in the Technology of Silicon p-i-n Photodiodes and their Influence on Dark Currents. Journal of nano- and electronic physics. Vol. 14 No 4, 04015(6cc) ,2022. DOI: https://doi.org/10.21272/jnep.14(4).04015

[3] Peculiarities of changes in the structure and electrophysical characteristics of n-Si under the influence of various heat treatment regimes / H.P. Gaidar // Reports of the National Academy of Sciences of Ukraine. No. 5, pp. 42-51, 2020. DOI: https://doi.org/10.15407/dopovidi2020.05.042 [Ukr]

[4] Bakhrushin V. E. The influence of high-temperature treatments on the physical properties of single crystals and single crystal layers of silicon. Complex systems and processes, No. 1, pp. 32-46, 2005. [Rus]

[5] Lytvynenko V. M., & Bogach M. V. Modeling of heterization processes of fast-diffusing impurities in Schottky diode technology. Bulletin of the Kherson National Technical University. Vol. 68(1), pp. 25-33, 2019. [Rus]

[6] Kukurudziak M. S., & Maistruk E. V. Features of Diffusion Doping and Boron Gettering of Silicon pin Photodiodes. In 2022 IEEE 3rd KhPI Week on Advanced Technology (KhPIWeek). Pp. 1-6, 2022, October. IEEE. DOI: https://doi.org/10.1109/KhPIWeek57572.2022.9916420

[7] Boltar K.O., Chinareva I.V., Lopukhin A.A., Yakovleva N.I. Matrix planar and mesa-structures based on heteroepitaxial InGaAs layers. Applied Physics. No. 5, pp. 10-15, 2013.

[8] Fedorenko A.V. Spectral responsivity of diffused Ge p-i-n photodiodes. Tekhnologiya i Konstruirovanie v Elektronnoi Apparature. No. 3–4, pp. 17 – 23, 2020. http://dx.doi.org/10.15222/ TKEA2020.3-4.17 [Ukr].

[9] Kukurudziak, M. S. Diffusion of phosphorus in technology for manufacturing silicon pin photodiodes. Semiconductor Physics, Quantum Electronics & Optoelectronics. Vol. 25(4), pp. 385-393, 2022. DOI: https://doi.org/10.15407/spqeo25.04.385

[10] Sirtl E. Adler. A. Flubsaure als sperifishes system zur atzgrubenentwicklang auf silizium//Z. Metallk. Vol.119(6), pp. 529-531, 1961. [Ger].

[11] K. Ravey, Defects and impurities in semiconductor silicon. (S.N. Gorina, Trans.) (M.: Mir: 1984) [Rus].

[12] M. S. Kukurudziak, Yu.G. Dobrovolsky, Silicon p – i – n photodiode of increased pulse responsivity, Technology and design in electronic equipment, Vol. 61(1-2), 2021. DOI: http://dx.doi.org/10.15222/TKEA2021.1-2.61 [Ukr].

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Технологія кремнієвих *p-i-n* фотодіодів зі зменшеною кількістю термічних операцій

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АНОТАЦІЯ Основними параметрами *p-i-n* фотодіодів (ФД) є чутливість, темновий струм та ємність фоточутливих елементів (ФЧЕ). Для забезпечення максимальних значень вказаних параметрів потрібно використовувати бездефектний кремній із максимальними значеннями питомого опору та часу життя неосновних носіїв заряду. Дані характеристики вихідного матеріалу деградують під час проведення високотемпературних термічних операцій. Тому варто застосовувати технологію, яка дозволяє уникати деградації характеристик кремнію. Це можна втілити зниженням температури дифузійних та окислювальних операцій, а також зниженням кількості власне термічних операцій. Зразки виготовлялись за двома варіантами технології: за дифузійно-планарною із використанням двостадійної дифузії фосфору з планарних джерел, та за мезотехнологію із використанням одностадійної дифузії фосфору з використанням рідкого дифузанту PCl_3. Після виготовлення параметри ФД порівнювались. Використання мезотехнології з одностадійною дифузію фосфору дозволило скоротити кількість термічних операцій в двічі відносно серійної технології. Експериментальні зразки володіли імпульсною чутливістю на довжині хвилі 1,064 мкм 0,47-0,50 А/Вт, а серійні 0,45-0,48 А/Вт. Відмінність чутливості спричинена відмінністю часу життя неосновних носіїв заряду ,оскільки в випадку запропонованої технології, міра деградації часу життя неосновних носіїв заряду в процесі виготовлення менша. Після селективного травлення, побачено, що при використанні рідкого дифузанту густина дислокацій на поверхні кристалів значно більша, ніж при використанні планарних джерел фосфору. Внаслідок вищої густини дислокацій експериментальні зразки володіли вищими темновими струмами, але при використанні низької напруги зміщення різниця в темнових струмах несуттєва. Ємність ФЧЕ експериментальних зразків була дещо нижчою, ніж серійних. Це можна пояснити різницею питомого опору *i*-області кінцевих кристалів.

КЛЮЧОВІ СЛОВА кремній, фотодіод, питомий опір, чутливість, мезоструктура.