THE EFFECT OF RADIATION DEFECTS ON THE PHOTOCONDUCTIVITY OF ALLOYED MICRO-NANOCRYSTALLINE SILICON SAMPLES

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Annotation: The creation of thermos and photo sensors that are inexpensive and sensitive to external influences, which form radiation defects in silicon samples, is an urgent task in semiconductor physics and technology.

This work employs a radiation irradiation technology to obtain condensed monocrystalline silicon material by irradiating a Janine silicon monocrystal with fast neutrons. This method allows for the targeted modification of the photoelectric parameters of the sample. The use of irradiation methods for technological purposes involves, on one hand, the management of the composition of the resulting defects, and on the other hand, the search for ways to optimize the radiative technological process.

Keywords: photodetector, Fermi level, p-n-type, silicon, comparative resistance, potential barrier, deep energy level, copper, iridium, radiation defect, conduction band.

Introduction: Recently, the use of compensated micro-nanostructured silicon that forms deep energy levels for the production of photodetectors, thermal sensors, and other devices has been proposed. However, it is challenging to obtain a large quantity of compensated material with identical photoelectric and electrophysical properties for producing sensors using the thermal diffusion method.

Firstly, ensuring the required precision of compensation by introducing acceptor (or donor) dopants through high-temperature diffusion is difficult due to the small diffusion coefficient of compensatory dopants in silicon. Secondly, the complexity of the production technology for deep energy level-donating compensated silicon results in an uneven distribution of dopants in the sample after high-temperature diffusion, significantly affected by the cooling rate post-diffusion.

According to recent research, deep energy levels with acceptor-centered defects have been identified in neutron-irradiated p-type silicon. These include defects at energy levels Es-0.18 eV (vacancy + oxygen complex, a-center), Es-0.40 eV (vacancy + donor atom complex, e-center), and levels associated with divacancies at Es-0.24, Es-0.39, and Es-0.54 eV. Primarily, these defective centers serve to alter the electrophysical properties of neutron-irradiated n-type silicon.

It is known that during the irradiation and processing of silicon, radiation defects are formed throughout the sample, and the level of compensation in the crystal is determined by the concentration of charge carriers in the source material and the irradiation flux. Additionally, with an increase in the concentration of non-principal charge carriers, the neutron irradiation time also increases (assuming constant neutron flux density).

On the other hand, to minimize the activity of dopants during neutron irradiation, it is essential to use monocrystalline silicon with the lowest possible concentration of principal charge carriers. In this regard, p-n type monocrystalline silicon with a specific resistance of 70 - 150 Ω·cm was utilized, with the Fermi level positioned in the lower part of the conduction band at room temperature (Es-(0.32 ÷ 0.36) eV).

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The dimensions of the selected samples were 5x5x0.5 mm³, and the n+-n-n+ structures were formed using a thermal diffusion method with phosphorus at 1050 °C for 120 minutes. The photoelectric parameters of the compensated samples were monitored based on the change in the ratio Rt/Rs. Here, Rt is the resistance when unilluminated (in ohms), and Rs is the resistance when illuminated (in ohms). Light and illuminated resistances were measured at an energy level of E = 200 lux.

Thus, the study of samples based on neutron-irradiated silicon doped with copper and iridium indicated the possibility of creating thermal sensors with identical properties operating in the temperature range of 305–600 K, utilizing n+-n-n+ structural photodetectors and thermal sensors.

The prepared samples (n+-n-n+ structures) were placed in quartz ampoules and encapsulated. They were irradiated in a nuclear reactor channel until the principal charge carriers were fully compensated by acceptor irradiation defects, at a neutron flux intensity of $\varphi = (3–4)\cdot 10^{12}$ $cm^{-2}\cdot s^{-1}$. Dark resistance was monitored by measuring the temperature dependence from 303 K to 373 K. The obtained results are shown in Figures 1 and 2.

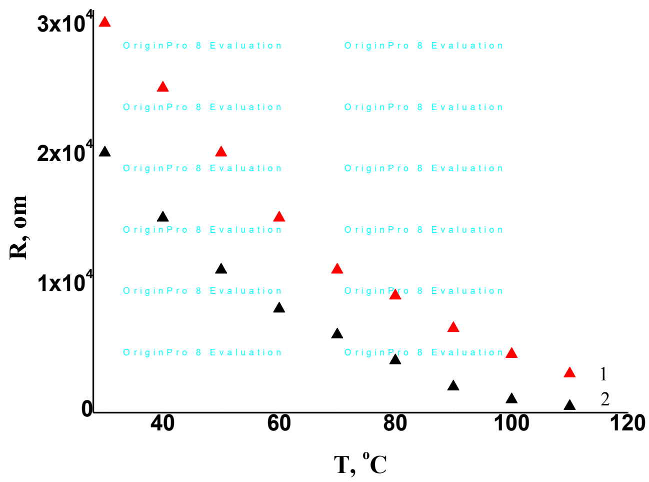

Figure 1: Temperature dependence of the resistance of photoconductors (n+-n-n+ structures) made from silicon doped with copper: 1 - in the dark; 2 - in light.

From Figure 1, it can be seen that the values of R_t reach their maximum after a time of $t = 60$ seconds. It is noteworthy that when the neutron flux density is 2 times 10^{14} cm^{-2}, the R_t values of resistors with a comparative resistance of 100 ÷ 170 Ω·sm are compared (Figure 2).

In these samples, the Fermi level is located below E_c - 0.50 eV, and the generated levels E_c - 0.18 eV and Ec - 0.39 eV are fully ionized due to the shift of the Fermi level towards the middle of the band gap, which enhances the neutron flux. The concentration of phosphorus atoms related to the vacancy (E-center) at the level Ec - 0.40 eV remains low 10^{12} sm^{-3} even after irradiation, meaning it does not significantly affect the electrical properties of silicon. Therefore, it can be assumed that the regions involving the initial phosphorus donor doping are primarily related to the Ec - 0.54 eV acceptor divacancies.

Figure 2. Graph of the resistance of photodetectors made from iridium-doped silicon (n+-n-n+ structures) as a function of temperature: 1 - in the dark; 2 - in light (E = 200 lux)

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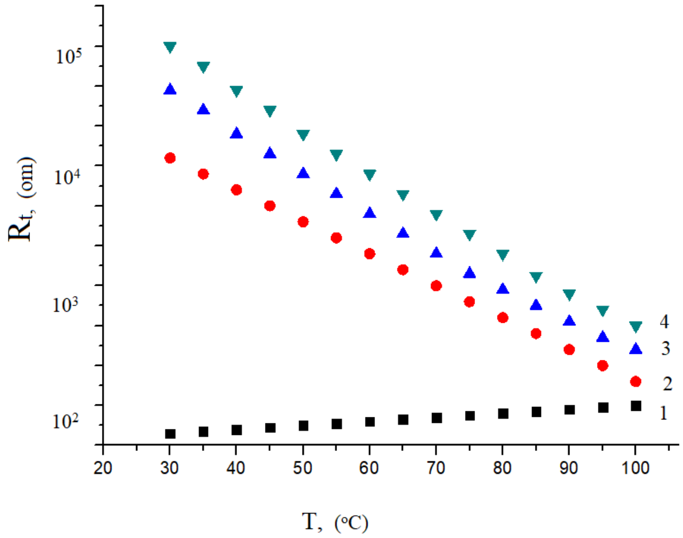

Figure 3: Dependence of the electrical resistance of the n+-n-n+ structure samples ρ= 170 Ω·sm on temperature before and after irradiation with fast neutron fluxes: 1 – before irradiation; 2 – 5 times 10^{13} cm⁻²; 3 – 8 times 10^{13} cm⁻²; 4 – 2 times 10^{14} cm⁻².

To stabilize the photoelectric parameters of the irradiated sample, thermal diffusion was performed at a temperature of 493 K for 20 minutes. The results of measuring $\frac{R_t}{R_s}$ in relation to the annealing temperature are presented in Table 1.

Table 1a

Changes in $\frac{R_t}{R_s}$ for samples doped with copper after thermal treatment, related to thermal heating.

	$\frac{R_t}{R_s}$ multiplicity of relative variation			
Before thermal purification	1,2	1,1	1,12	1,3
After thermal deformation	11,2	9,7	11,1	12

From the table, it can be observed that the change in electrical resistance increases multiplicatively after thermal treatment, with samples doped with copper showing an increase of up to 10 times.

Table 1b

Changes in $\frac{R_t}{R_s}$ for samples doped with iridium after thermal treatment, related to thermal heating.

	$\frac{R_t}{R_s}$ multiplicity of relative variation			
Before thermal purification	2	4.5	9.5	11.5
After thermal deformation	80.5	120.5	160.2	145.6

From the table, it can be observed that the change in electrical resistance increases multiplicatively after thermal treatment, with samples doped with iridium showing an increase of up to 40 times.

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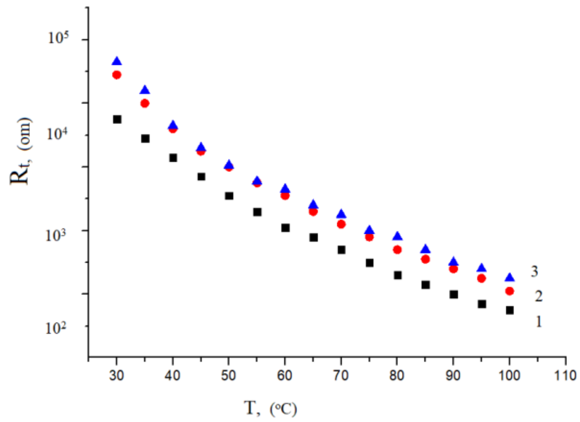

Figure 4. The temperature dependence of the electrical resistance after irradiation for n^+-n-n^+ structured silicon with different initial specific resistances: 1) ρ– 70 Ω·sm; 2) ρ– 100 Ω·sm; 3) ρ– 170 Ω·sm.

Figure 4; illustrates the relative change in electrical resistance as a function of temperature for n^+-n-n^+ structured silicon samples irradiated by a fast neutron flux (~$2\cdot10^{14}$ cm^{-2}). The samples, based on a specific resistance of 170 Ω·cm, were illuminated with a light energy of ~200 lux. The observed relationship is described by the following expressions:

$$\frac{R_t - R_S}{R_t} = exp\,(\frac{-670}{T})$$

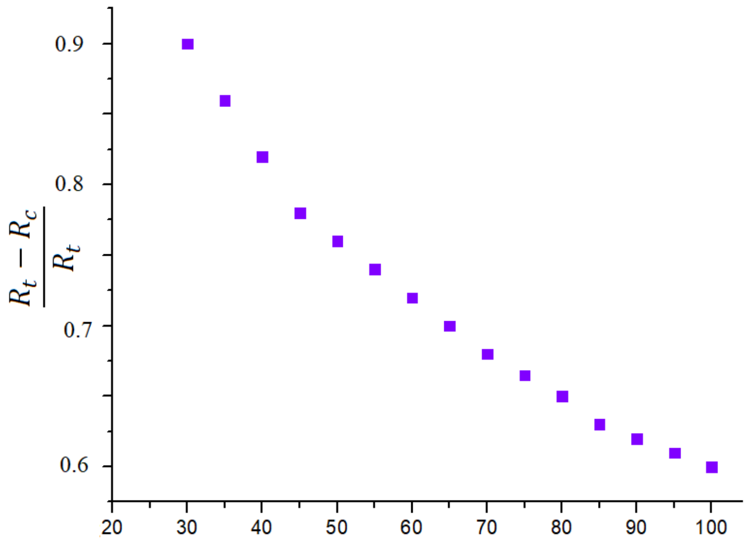

Figure 5. The relative change in electrical resistance of n^+-n-n^+ structured photodetectors as a function of temperature at E = 200 lux.

The study of radiation-compensated silicon has demonstrated the potential to create photodetectors and thermal sensors with uniform properties operating in the temperature range of 303 to 373 K. A high-quality photodetector and photo-thermal sensors based on silicon, which operates effectively at temperatures up to ~373 K, can be developed (see Figure 5).

It is well known that the accumulation of thermal and radiation defects in silicon often leads to changes in the electrophysical parameters of semiconductor samples. When the concentration of these

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defects is comparable to the initial concentration of charge carriers, the electrical properties of compensated silicon exhibit increased radiation resistance[1-2]. Many researchers believe that the defects formed after irradiation significantly affect the electrical properties of silicon samples, while others argue that this leads to an increase in the height of potential barriers (D) between high and low resistances. However, the impact of radiation-induced potential barriers on the electrical properties of silicon remains insufficiently studied.

The changes in the electrophysical parameters of radiation-doped p-type silicon (p-Si<B, P, Cu>; p-Si<B, P, Ir>) indicate that the height of the potential barrier between high and low resistances increases with radiation exposure. The initial specific resistance of the p-type silicon samples used in our research ranged from 1 to 20 Ω·sm. To obtain compensated silicon, samples doped with phosphorus (P) and boron (B) were used, which were grown using the Czochralski method. The studies involved n- and p-type samples with an oxygen concentration of (5–10)$\cdot 10^{17}$ cm^{-3}, a dislocation density of 10^4 cm^{-2}, and specific resistances of approximately 3 to 100 Ω·sm, as well as neutron-doped p-type silicon (p-Si<B, P>).

The neutron flux density from a 10 MVt BBP-CM nuclear reactor was approximately (0.002–8)$\cdot 10^{13}$ neutrons/$sm^2\cdot s$ in horizontal and vertical channels at around 320 K. The production of compensated n- and p-type silicon was based on the reaction of the Si^{30} isotope converting to P^{31} under slow neutron irradiation.

$$1430Si(n,\gamma) \rightarrow 1431Si \frac{\beta-1}{2.04} \rightarrow 1531P \qquad (2)$$

The concentration of introduced phosphorus can be calculated using the formula N_P=1.7 times 10^{-4} cdot F, where F represents the neutron flux density in neutrons$\cdot sm^{-2}\cdot s^{-1}$.

The flux of slow neutrons can be determined by measuring the concentration of charge carriers in the samples before and after irradiation. To eliminate excess defects, the samples were heated in a SUOL-0.44/12 horizontal furnace at approximately 1000 °C for 30 minutes and then cooled down to room temperature at a rate of about 5-10 °C/min.

Ohmic contacts to the silicon samples were formed using a Sn+In alloy (50% + 50%) via soldering at 120 °C. For the preparation of Schottky diodes, aluminum and indium were deposited onto the polished silicon surface by sputtering.

It is known that the energy intervals between electron-electron transitions (n^{min}–n^{max}) or hole-hole transitions (p^{min}–p^{max}) are defined by the height of the potential barrier [3].

$$\Delta = \varphi q = kT \ln \frac{n_0^{max}}{n_0^{min}}; \qquad \Delta = \varphi q = kT \ln \frac{p_0^{max}}{p_0^{min}}, \qquad \Delta = kT \ln \frac{\tau_.}{\tau_{o.}} \qquad (3)$$

Here n_0^{max}, p_0^{max} - ва n_0^{min}, p_0^{min} - Maximum and minimum concentration of charge carriers, respectively.

$$p^{max} = p_0\left(1 + \frac{p^{max} - p^{min}}{2p_o}\right) - K \quad \text{va} \quad p^{min} = p_o\left(1 - \frac{p^{max} - p^{min}}{2p_o} - K\right) \qquad (4)$$

The maximum and minimum concentrations of charge carriers are denoted as n^{max} and n^{min}, respectively. The degree of compensation K can be expressed as K=(N_P/ p), where N_P is the concentration of induced phosphorus atoms, and p_0 is the average concentration of charge carriers before irradiation. The terms t_0 and t represent the lifetimes of the main charge carriers in p-type silicon before and after neutron doping.

The electrophysical parameters of the silicon sample that was diffused at a temperature of 1050 °C were obtained, and the results are presented in Table 2.

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Table 2.

Electrophysical parameters of the silicon sample.

№	Samples	Specific Resistance, ρ (Om·sm)	Concentration of the charge carrier, N (sm^{-3})	Actionability μ (sm^2/V·s)	Potential obstacle height energy, Δ (meV)
1	*p-Si<B>*	9.8	$1.9 \cdot 10^{15}$	345	5
2	*p-Si<B,P>*	9.1	$2.3 \cdot 10^{15}$	330	23
3	*p-Si<B,P,Ir>*	1800	$1.3 \cdot 10^{15}$	280	30
4	*p-i<B,P,Cu>*	1500	$1.5 \cdot 10^{15}$	215	105.7

As can be seen from the table, the potential barrier height energy in the irradiated p-Si<B,P,Ir> and p-Si<B,P,Cu> samples was found to be higher compared to the standard sample. For example, in silicon doped with iridium, the barrier height energy increased by a factor of 6 compared to the standard sample, while in silicon doped with copper, the barrier height energy increased by 20 times. Subsequently, these samples were irradiated with neutrons in a horizontal channel of a nuclear reactor at a temperature of approximately 300 K. The efficiency of radiation defect (RD) formation was studied by measuring the Hall coefficient and resistance at room temperature. The results of the study are presented in Figure 6. As seen in the figure, the rate of removal of the main charge carriers (curves 2 and 4) in the p-Si<B,P,Ir> and p-Si<B,P,Cu> samples is higher compared to the control samples (curves 1 and 3).

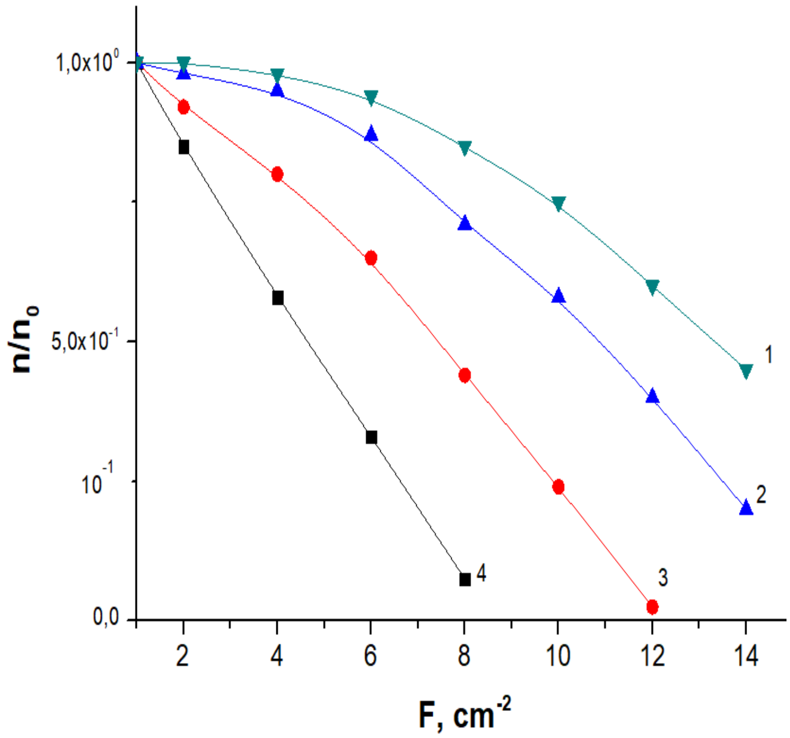

Figure 6. The dependence of the relative change in the concentration of majority charge carriers in silicon on the fast neutron flux:
1 – p-Si<B,P,Ir> (ρ = 9.8 Ω·cm);
2 – p-Si<B,P> (ρ = 8.6 Ω·cm);

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3 – p-Si<P> (ρ = 1800 Ω·cm);

4 – p-Si<B,P,Cu> (ρ = 1500 Ω·cm)

A barrier model is proposed to explain the observed effect. The essence of this model is as follows: It is known that due to the non-uniform distribution of primary boron (or phosphorus) impurities, as well as technological impurities of oxygen and carbon in the crystal mass, low-resistance (p^{max}) and high-resistance (p^{min}) conductivity zones are formed in the main part of the crystal. The presence of contacts between these regions leads to the formation of an insignificant potential barrier, Δ_o, for charge carriers (Table 2). In this case, the Fermi level (E_f) energy remains the same for both the p^{max} and p^{min} zones, and its position defines the p^{max}–p^{min} interface [4-6]. In neutron-irradiated p-type silicon samples, defects create ionization energies: E_v + 0,18 эВ , E_1= E_v + 0,28 эВ , E_2= E_v + 0,35 эВ , E_3 = E_v + 0,40 эВ.

In our case, since $E_f \geq E_V$ +0,20 эВ _ it is assumed that all the observed donor radiation defects in the p^{max} region are fully ionized. In p-Si<B>, the p^{min} region consists of partially ionized zones, whereas in p-Si<B,P,Ir> and p-Si<B,P,Cu>, they are fully ionized (for example, Figure 7b and 8b for samples 1 and 2). Furthermore, it is assumed that the concentration of majority charge carriers, holes ($p=N_V$), is higher than the concentration of radiation-induced defects RN (N_{RN}), (N_V) > (N_{RN}).

At the initial stages of neutron irradiation, the p^{min} regions of the crystal exhibit high resistance, while the p^{max} regions maintain the same low resistance without significant compensation of carriers. In this case, due to the substantial difference in compensation levels, the irradiation leads to an increase in the initial height of the potential barrier between these levels, denoted as ($\Delta_o \rightarrow \Delta$) (Figure 7b). The increase in the neutron flux leads to a rise in $\Delta_o \rightarrow \Delta$, which, in turn, increases the level of filling of the p^{min} region by the radiation-induced defects (RN), as seen through E_1. In this scenario, holes liberated from the p^{min} region move to the p^{max} region. Eventually (up to a certain neutron flux), the concentration of free holes in the valence band of the non-uniformly compensated material remains almost unchanged until it equals the concentration of electrons trapped by E_1 defects in the p^{min} region (Figure 7b). That is, it continues until there are no significant changes in the Fermi level energy in the p^{max} region. As mentioned earlier, this conductive behavior is characteristic of such a heterojunction material. A similar effect was also observed for the n-Si<P> sample [5]. Before repeated neutron irradiation, it was observed that the p-Si<B,P> samples exhibited a higher potential barrier height and conductivity compared to the p-Si<B,P,Ir> and p-Si<B,P,Cu> samples. In all the samples (p-Si<B,P>, p-Si<B>, p-Si<B,P,Ir>, and p-Si<B,P,Cu>), it was assumed that the radiation-induced defect concentration (RN) formed during irradiation was nearly identical for comparison of the rate of removal of the majority charge carriers. Under such conditions, the charge state of radiation defects in the high-resistance region significantly differs from the Fermi level, as can be seen in Figures 7(b) and 8(b).

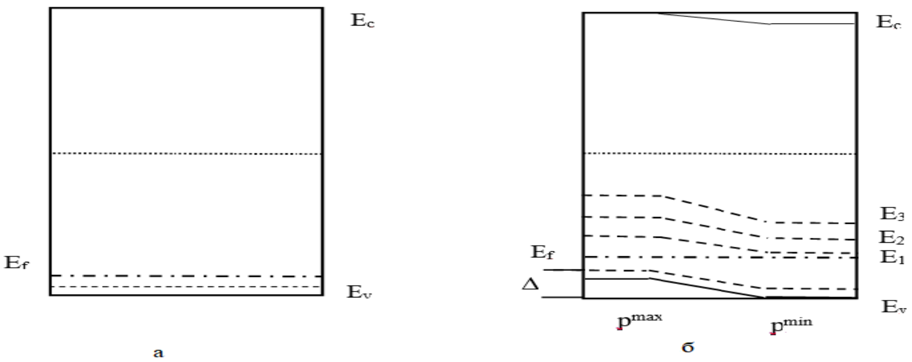

Figure 7. Models of the homogeneous non-uniform p_max and p_min regions formed in neutron-irradiated p-type samples before (a) and after (b) irradiation in compensated silicon: **E_1 =E_v + 0,28eV, E_2 =E_v + 0,35eVva E_3 =E_v + 0,40eV**

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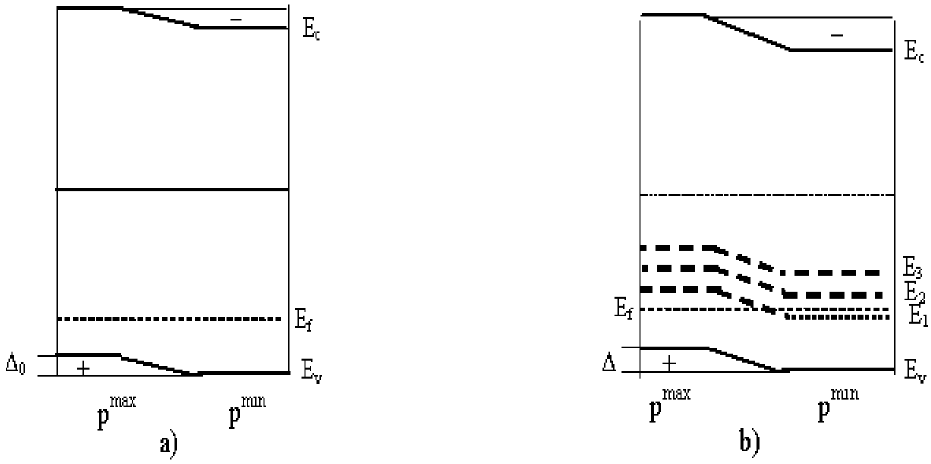

Figure 8. Models of the homogeneous non-uniform p_max and p_min regions formed in neutron-doped silicon: before (a) and after repeated neutron irradiation (b). **E1=Ev +0,28eV, E2=Ev +0,35eVva E3 =Ev +0,40eV**

Therefore, the filling of RN with electrons in the p-min region occurs faster in neutron-irradiated silicon compared to the control (p-Si<B,P,Ir>; p-Si<B,P,Cu> > p-Si<B> > p-Si<B>) (Figure 8), respectively increasing the speed of charge carriers in neutron-irradiated silicon.

Conclusion

After thermal treatment of neutron-doped silicon with copper and iridium atoms, a change in electrical resistance was observed, with a significant increase in copper-doped samples by up to 10 times and in iridium-doped samples by up to 40 times.

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