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Effect of Different Heat Treatment Regimes on Electrical Properties and Microstructure of *n*-Si

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The features of changes in the electrical properties and microstructure of *n*-type silicon single crystals, doped with phosphorus by different methods (through the melt and by the nuclear transmutation method) are revealed, depending on the heat treatment conditions, which are widely used in research with semiconductors and when creating devices based on them. The nuclear transmutation method is based on the transformations of silicon isotopes when they capture thermal neutrons. The principal difference of the transmutation doping from the metallurgical doping method is that dopants are not introduced into the initial material from the outside, but are formed during the irradiation process directly from the atoms of the doped material. Using transmutation doping, one can obtain a high homogeneity of the distribution of impurities, which is ensured by the random distribution of isotopes, neutron flux uniformity and small neutron capture cross sections, as well as one can obtain the high accuracy of doping due to proportionality of the concentration of introduced impurities (at the constant neutron flux) to the irradiation time. It was established that the degree of defectiveness of the *n*-Si annealed crystals, controlled by selective chemical etching and X-ray topography, depends not only on the time of high-temperature annealing, but also on the cooling rate of the samples from the annealing temperature to room temperature. It was revealed that the long-term high-temperature annealing of silicon samples, regardless of the phosphorus doping method, promotes the generation of deep donor centers, both at slow and fast cooling, and reduces the charge carrier concentration in the samples, doped through the melt, by 1.5-2 times, in the transmutation-doped ones by 1.5-3.5 times, and in the latter case the effect is more pronounced upon fast cooling.

Keywords: Silicon, Thermal annealing, Cooling rate, Charge carrier concentration, Charge carrier mobility, Microstructure.

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1. INTRODUCTION

Modern scientific and technological progress is largely determined by the level of development in physics and semiconductor technology. Silicon has been and remains nowadays the main material for the production of electronic devices for various purposes, namely large and ultra-large integrated circuits, power semiconductor devices, microwave devices, semiconductor lasers, photodetectors, and many others [1]. The rapid development in microprocessor technology and nanoelectronics created a demand not only for new materials, but also for the improvement of existing ones. Therefore, it is necessary to constantly expand knowledge about the properties of silicon. It is important to investigate the methods of its processing and doping in order to obtain crystals of the required degree of purity and uniformity as a result.

Silicon single crystals used in microelectronics and instrument engineering significantly change their physical characteristics under the influence of various external effects [2]. The main trend in the development of modern electronics is a constant increase in the degree of integration. Meanwhile, the properties of an individual element are increasingly determined by the local properties of the basic material. Currently, the requirements for spatial uniformity of the parameters of the initial silicon single crystals are even more stringent in connection with the development of manufacturing technologies for semiconductor devices. The perfection of crystals (uniformity of properties in volume) has a significant impact on the performance of devices and microcircuits based on them. It determines the stability of parameters to degradation under the influence of effective external effects and causes the qualitative functionality, as well as expands the scope of crystals [3].

The manufacturing technology of semiconductor devices includes heat treatment as a necessary element. Since the effect of high temperatures often leads to irreversible deterioration of the properties of crystals, the main attention is paid to the choice of annealing temperatures when developing and justifying the sequence of necessary thermal annealings. At the same time, unduly less attention is paid to the choice of optimal cooling conditions. Nevertheless, the cooling conditions have a significant effect on both the structure of the semiconductor material and the characteristics of devices based on it. The aim of this paper was to study the effect of heat treatment and cooling conditions on the electrical characteristics and microstructure of *n*-Si single crystals doped with phosphorus by different methods.

2. RESULTS AND DISCUSSION

A study was made of *n*-Si crystals doped with phosphorus, both in the traditional method during the growth process through the melt (we will call them ordinary silicon samples n-Si^{OR}) and the nuclear transmutation method (transmutation-doped samples n-Si^{TD}). The nuclear transmutation method is based on the

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transformations of silicon isotopes during the capture of thermal neutrons in accordance with a nuclear reaction $^{30}\mathrm{Si}(n,\gamma)^{31}\mathrm{Si} \xrightarrow{\beta^-} {}^{31}\mathrm{P}$ [4]. The fundamental difference between the transmutation doping and the metallurgical doping method is that dopants are not introduced into the initial material from the outside, but are formed during the irradiation process directly from the atoms of the doped material.

It should be mentioned that in comparison with traditional metallurgical methods of introducing impurities into a semiconductor material, the nuclear transmutation method has a number of significant advantages. The random distribution of isotopes, the neutron flux uniformity, and the small neutron capture cross-sections provide a high homogeneity of the distribution of impurities. This method also provides high doping accuracy due to the proportionality of the concentration of introduced impurities (at a constant neutron flux) of the irradiation time.

Transmutation-doped silicon was subjected to obligatory technological annealing at temperatures T_a = 800-850 °C for t = 1-2 h. The necessity of such annealing was discussed in [5]. We will consider silicon crystals after technological annealing as initial ones and subject them to further heat treatment.

The first stage of heat treatment was high-temperature (HT) annealing (at T_a = 1200 °C) of n-Si crystals ($\rho_{300K} \approx$ 79.5 Ohm·cm) for t = 2 and 72 h followed by fast (with the rate of $\upsilon_{cl} \approx$ 1000 °C/min) or slow ($\upsilon_{cl} \approx$ 1 °C/min) cooling from annealing temperature to room one. The sample was cooled together with the furnace at slow cooling. The annealed sample was dumped into the transformer oil at fast cooling.

The second heat treatment stage consisted of annealing at 430 °C for t = 8 h followed by cooling together with the furnace (low-temperature (LT) annealing).

The temperature dependences of the concentration, charge carrier mobility, resistivity for slowly cooled n-Si^{OR} samples after HT annealing, as well as the results of subsequent LT annealing, are shown by the corresponding curves in Fig. 1a and Fig. 2a. Similar results are shown in Fig. 1b and Fig. 2b for rapidly cooled n-Si^{OR} samples.

Regardless of the cooling conditions, the sufficiently long-term (from 2 to 72 h) HT annealing of crystals noticeably decreases (approximately 1.5-2 times) the concentration of charge carriers in the liquid nitrogen temperature range (77 K) (see Fig. 1a, Fig. 1b, curves *1-3*). These changes cannot be explained by the diffusion of foreign impurities during annealing, since the annealing was carried out under sufficiently sterile conditions. This is confirmed by the results of other experiments in which changes in concentration and mobility, depending on the prehistory of samples and the composition of the background impurities, never exceeded 6-8 %.

It can be assumed that a decrease in the concentration of charge carriers resulting from HT annealing, accompanied by an insignificant change in their mobility (Fig. 2, curves *1′-3′*), is a consequence of the decomposition at 1200 °C of both ordinary [6] and high-temperature [7, 8] thermal donors that appeared in the sample earlier. It is possible that the thermal generation of shallow acceptors makes some contribution to reducing the charge carrier concentration along with the dissociation effect of thermal donors, and only under conditions of curve *3* (Fig. 1b). Such acceptors increase the compensation level of donor centers and noticeably decrease the charge carrier mobility at low temperatures (Fig. 2b, curve *3′*).

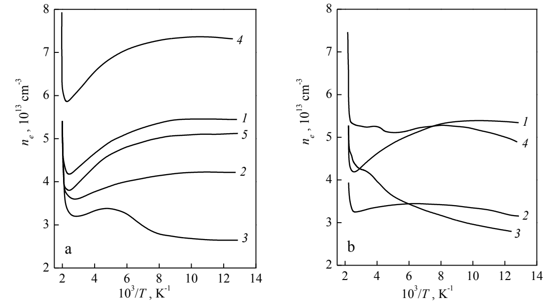

Fig. 1 – Dependences of $n_e = f(1/T)$ for n-Si^{OR} crystals after HT treatment and slow (1 °C/min) (a) or fast (1000 °C/min) (b) cooling: *1* – initial; *2* – 1200 °C, 2 h; *3* – 1200 °C, 72 h; and also after additional LT annealing: *4* – 1200 °C, 72 h + 430 °C, 8 h; *5* – annealing of the initial crystal (430 °C, 8 h)

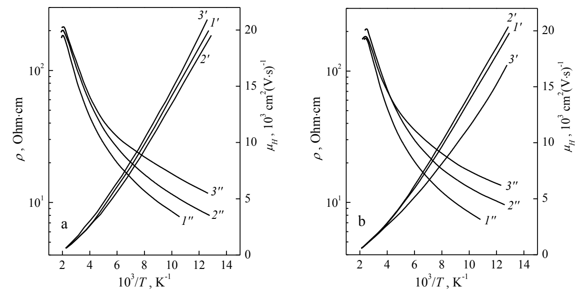

Fig. 2 – Dependences of $\mu_H = f(1/T)$ (*1′-3′*) and $\rho = f(1/T)$ (*1″-3″*) for n-Si^{OR} crystals after HT treatment and slow (1 °C/min) (a) or fast (1000 °C/min) (b) cooling: *1′*, *1″* – initial; *2′*, *2″* – 1200 °C, 2 h; *3′*, *3″* – 1200 °C, 72 h

As can be seen from Fig. 1, HT annealing for 72 h leads to the generation of deep donor centers, which are depleted in slowly cooled samples at 180 K (Fig. 1a, curve *3*), and in rapidly cooled samples at 280 K (Fig. 1b, curve *3*).

After HT annealing, depending on the cooling rate, LT annealing affects differently the sample properties. In slowly cooled samples, as a result of LT annealing, the shape of the dependence $n_e = f(1/T)$ is completely restored, and the concentration becomes even higher (1.35 times) than the initial one (Fig. 1a, curve *4*). In rapidly cooled samples, LT annealing only approximately restores the initial carrier concentration while retaining traces of the presence of deep levels in the $n_e = f(1/T)$ dependence that prevents complete recovery of its shape (Fig. 1b, curve *4*).

The comparison between curves *4* in Fig. 1a and Fig. 1b shows that fast cooling of samples after HT annealing (in contrast to their slow cooling) significantly increases the stability of deep donor centers with respect to LT annealing, and also reduces the generation efficiency of ordinary thermal donors under the LT heat treatment conditions.

It should be noted that not only slow cooling of the crystals after HT annealing, but also HT annealing

itself is a condition for increasing the efficiency of the formation of ordinary thermal donors during LT annealing (430 °C, 8 h). We have made such conclusion, since the same LT annealing in the initial crystals that have not been subjected to HT treatment causes the decrease (not an increase) (see Fig. 1a, curve *5*) in the charge carrier concentration compared to initial ones (Fig. 1a, curve *1*).

The $n_e = f(1/T)$ dependences measured on the initial samples (Fig. 1a and Fig. 1b, curves *1*) are characterized by the decrease in the charge carrier concentration with increasing temperature (up to the intrinsic conductivity) that is determined by the temperature dependence of the Hall factor in these crystals. Some straightening of indicated curves, which is already observed after HT annealing for 2 h (Fig. 1a and Fig. 1b, curves *2*), can be the result of the manifestation of not only deep centers, but also the consequence of the change in the anisotropy of the charge carrier scattering by defects. However, these reasons are not separated in the framework of the data presented here, and therefore the question of changing the scattering anisotropy as a result of HT annealing remains open in this consideration.

Information on the parameters of the initial and transmutation-doped n-Si^{TD} samples after different thermal treatment regimes has been given in Table 1. The temperature dependences of the charge carrier concentration $n_e = f(1/T)$, obtained for these samples, have been presented by the corresponding curves in Fig. 3.

Table 1 – Parameters of the investigated n-Si^{TD} samples

Parameters	Heat treatment and cooling conditions				Initial crystal
T_a, °C	1200				
t, h	2	72	2	72	
υ_{cl}, °C/min	1	1	1000	1000	
n_{e77K}, 10^{13} cm^{-3}	5.68	3.31	6.63	1.82	6.40
μ_{77K}, 10^3 cm^2/(V·s)	20.000	20.840	20.480	17.260	21.400
ρ_{77K}, Ohm·cm	5.50	9.06	4.60	19.9	4.56

As a result of heat treatment of the samples, the charge carrier mobility changes slightly; nevertheless, the concentration n_e changes 1.5-3.5 times under certain conditions (see Table 1). Let us analyze these changes in more detail. For this, we consider the dependences of the charge carrier concentration on the reciprocal temperature.

It should be noted that the reduction in curves *1* and *2* (Fig. 3) with rising temperature is defined by the Hall factor temperature dependence. The steepness of the reduction in the carrier concentration with increasing temperature (at $T > 155$ K) is general for curves *2* (Fig. 3) and slightly increases compared to the initial curve *1*. Such steepness can be considered as a result of changes in the carrier scattering conditions in heat-treated samples. Obviously, these changes in scattering conditions have non-concentration character. This effect does not depend on whether the charge carrier concentration (measured at low temperatures) increases (Fig. 3b, curve *2*) or decreases (Fig. 3a, curve *2*) after relevant heat treatment. Fig. 3 (curves *3*) shows that when annealing n-Si^{TD} samples at $T_a = 1200$ °C for 72 h, the charge carrier concentration decreases (compared to the initial one) during both slow and fast cooling. In both cases, along with a decrease in concentration, the appearance of deep donor centers was observed, as in n-Si^{OR} silicon crystals doped with phosphorus in the ordinary method (see Fig. 1, curves *3*).

Along with electrical measurements, the microstructure of silicon crystals has been investigated after different heat treatment regimes. It has been studied using 220-X-ray topograms taken by the Lang method (using $K_{\alpha 1}$-molybdenum radiation). Analysis of surface micrographs has been also provided after selective etching of samples. Samples were cut parallel to the (111) plane from the same ingot. The mechanical and chemical treatment of all samples has been carried out under the same conditions.

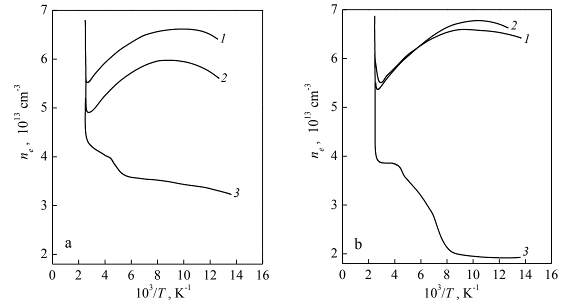

Fig. 3 – Dependences of $n_e = f(1/T)$ for n-Si^{TD} crystals after HT treatment and slow (1 °C/min) (a) or fast (1000 °C/min) (b) cooling: *1* – initial; *2* – 1200 °C, 2 h; *3* – 1200 °C, 72 h

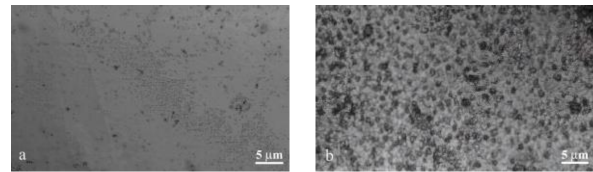

Fig. 4 – Micrographs of the surface of the initial silicon samples doped with different methods: a – n-Si^{OR}, b – n-Si^{TD}, after selective chemical etching

In the initial silicon sample doped by the ordinary method, the structural defects were not detected by either the X-ray method or selective etching (Fig. 4a). On the contrary, microstructural analysis of transmutation-doped Si showed that such samples have a large accumulation of defects, probably, small complexes of point defects (Fig. 4b).

In n-Si^{OR} samples, annealed at 1200 °C for 2 h (regardless of the cooling rate), large etching pits belonging to the outputs of dislocation loops on the crystal surface with a relatively uniform density of $\sim 1 \times 10^6$ cm^{-2} were revealed by the selective etching method. In addition, the small non-uniformly distributed hillocks, apparently belonging to the impurity pre-

cipitates, were found (Fig. 5a). In these cases, the structural defects were not detected by the X-ray topography method.

The microstructural analysis of transmutation-doped silicon showed that in such n-Si^{TD} samples after HT annealing at 1200 °C for 2 h with subsequent fast cooling the point defects and complexes have dissolved, while the dislocations have appeared (Fig. 5b).

After HT annealing for 72 h, the rapidly and slowly cooled n-Si^{OR} samples demonstrated different properties. Structural defects in the rapidly cooled samples were detected on the topograms in small quantities as separate points (Fig. 6b).

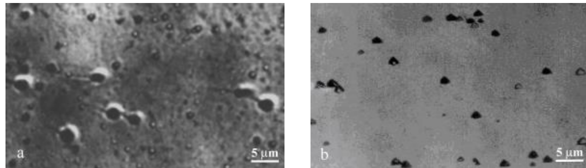

Fig. 5 – Micrographs of the surface of silicon samples heat-treated at 1200 °C for 2 h, doped with different methods: a – n-Si^{OR} (υ_{cl} = 1 and 1000 °C/min); b – n-Si^{TD} (1000 °C/min), after selective chemical etching

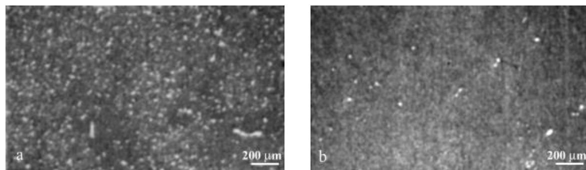

Fig. 6 – X-ray topograms of heat-treated (1200 °C, 72 h) n-Si^{OR} samples followed by slow (1 °C/min) (a) or fast (1000 °C/min) (b) cooling

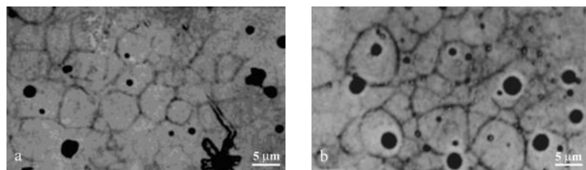

Fig. 7 – Micrographs of the surface of heat-treated (1200 °C, 72 h) n-Si^{OR} samples followed by slow (1 °C/min) (a) or fast (1000 °C/min) (b) cooling after selective chemical etching

As a result of selective etching, both dislocation loops (of the same density ~ 1×10^6 cm^{-2}) and impurity precipitates with a density of ~ 5×10^9 cm^{-2}, uniformly distributed over the bulk (Fig. 7b), were found. In this case, the sizes of the pits caused by dislocation loops were 1.5-1.7 times larger than in the case of HT annealing for 2 h, which is associated with different density of impurities surrounding the dislocations [9].

After HT annealing for 72 h in the slowly cooled n-Si^{OR} samples, structural defects were well detected both by the X-ray method (Fig. 6a) and by the selective etching method (Fig. 7a). However, after selective etching, only pits of the dislocation loops with the same density of ~ 1×10^6 cm^{-2} were found on the surface of the samples, and traces of impurity precipitates were almost absent (Fig. 7a). On the other hand, the pits associated with dislocation loops in the slowly cooled samples had the more complex structure and exceeded in size the similar pits in the rapidly cooled samples, as can be seen from the comparison of Fig. 7a and Fig. 7b.

The results presented, as well as taken into account the high migration rates of point defects in the presence of traces of rapidly diffusing impurities in the bulk of weakly doped Si crystals, do not allow us to correctly analyze the mechanisms of generation and dissociation of electrically active oxygen-impurity complexes without studying the structural perfection of these crystals subjected to one or another heat treatment. Dislocation loops arising under annealing in silicon crystals are effective sinks for impurity atoms and point defects. Dislocation loops, like impurity precipitates, can significantly affect the kinetics of the formation and annealing of electrically active oxygen-impurity complexes, and largely determine their effect on the electrophysical and degradation properties of these crystals.

The analysis of the experimental data indicates that the formation of dislocation loops and impurity precipitates during HT annealing of n-Si^{OR} crystals is accompanied by the generation of a small number of deep donor centers and the well-pronounced dissociation (inactivation) of existing thermodonors. This is demonstrated in the differential increase in n_e with increasing temperature and the noticeable decrease in the average carrier concentration in these crystals. The obtained results of HT annealing can be associated with the change in the efficiency of complex formation processes in the region of elevated temperatures. Also, these results can be explained with the partial departure of impurity atoms to effective sinks (dislocation loops and precipitate nuclei). The progressive decrease in n_e concentration with the increase in the duration of HT heat treatment (from 2 to 72 h) of n-Si^{OR} samples correlates with the increase (up to 5×10^9 cm^{-2}) in the average density of precipitates.

The time delay of the increased concentration of point defects in the n-Si^{OR} bulk, which is achieved due to the fast cooling of the samples after prolonged HT annealing, creates the prerequisites for the effective precipitation of impurity atoms (including oxygen atoms) (Fig. 7b). This circumstance makes it difficult to saturate the Cottrell atmospheres, surrounding the dislocations, to the level that could ensure their satisfactory detection by X-ray topography. In the case under consideration, this method turned out to be relatively weakly sensitive. Therefore, in Fig. 6b, traces of dislocations decorated with impurities appear to such a small degree. These experiments indicate that point defects, along with impurity carbon atoms, can act as effective precipitation nuclei.

In the case of slow cooling of the samples, which effectively depletes the crystal bulk with precipitation nuclei (through enhanced annealing of point defects), oxygen atoms and other impurities dissolved in silicon are directed by diffusion fluxes of increased density onto dislocation loops, decorating them well (Fig. 6a), and also partially remain in the crystal bulk in dissolved form. The latter fact (in contrast to the conditions of fast cooling) contributes to increasing formation of thermodonors during LT annealing, which follows HT annealing and slow cooling, which is clearly seen from the comparison of curves *4* in Fig. 1.

3. CONCLUSIONS

1. It was established that long-term high-temperature annealing (1200 °C, 72 h) of *n*-Si samples, regardless of the phosphorus doping method, promotes the generation of deep donor centers, both at slow and fast cooling. Such annealing significantly reduces the charge carrier concentration. In the samples doped through the melt, the concentration decreases by 1.5-2 times, in the transmutation-doped ones by 1.5-3.5 times. In the latter case, the effect is more pronounced upon fast cooling.

2. Using the selective chemical etching method, it was found that in transmutation-doped silicon crystals after high-temperature annealing for 2 h followed by fast cooling, the dislocations appeared instead of the point defect aggregation and their complexes.

3. It was revealed that annealing (1200 °C, 72 h), depending on the cooling conditions, has a different effect on the release of impurities in the crystal bulk, doped by the ordinary method, as well as on the change in their properties, caused by low-temperature annealing (430 °C, 8 h), which directly follows the high-temperature treatment.

4. It was shown that after annealing (1200 °C, 72 h) in rapidly cooled samples doped by the ordinary method, the sizes of etching pits caused by dislocation loops are 1.5-1.7 times larger than in the case of high-temperature annealing for 2 h, which is associated with different density of impurities around dislocations. In slowly cooled samples, the similar etching pits had not only large sizes, but also a more complicate structure.

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Вплив різних режимів термічної обробки на електричні властивості та мікроструктуру *n*-Si

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Виявлено особливості змін електричних властивостей і мікроструктури монокристалів кремнію *n*-типу, легованих домішкою фосфору різними методами (через розплав і методом ядерної трансмутації), в залежності від умов термічних обробок, які широко використовуються в дослідженнях з напівпровідниками і при створенні приладів на їх основі. Метод ядерної трансмутації базується на перетвореннях ізотопів кремнію при захопленні ними теплових нейтронів. Принципова відмінність цього методу від металургійного способу легування полягає в тому, що легуючі домішки не вводяться у вихідний матеріал ззовні, а утворюються в процесі опромінення безпосередньо з атомів матеріалу, який легують. За допомогою трансмутаційного легування можна отримувати високу однорідність розподілу домішок, що забезпечується випадковим розподілом ізотопів, рівномірністю нейтронного потоку і невеликими перерізами захоплення нейтронів, а також високу точність легування, внаслідок пропорційності концентрації введених домішок часу опромінення (при сталому нейтронному потоці). Встановлено, що ступінь дефектності відпалених кристалів *n*-Si залежить не тільки від часу високотемпературного відпалу, а й від швидкості охолодження зразків. Виявлено, що тривалий високотемпературний відпал зразків *n*-Si, незалежно від способу легування, сприяє генерації глибоких донорних центрів у разі як повільного, так і швидкого охолодження, і знижує концентрацію носіїв заряду в зразках, легованих через розплав, у 1,5-2 рази, а в трансмутаційно легованих – у 1,5-3,5 рази, причому в останньому випадку ефект сильніше виражений у разі швидкого охолодження.

Ключові слова: Кремній, Термічний відпал, Швидкість охолодження, Концентрація носіїв заряду, Рухливість носіїв заряду, Мікроструктура.