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SILICON MONOCRYSTALS FOR ALTERNATIVE ENERGY

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This paper considers features of the formation and microstructure revealing of profound n- and p-type silicon monocrystals. Influence of hole and electron conductivity in semiconductors on the pattern of anodic etching is determined. Correlation among silicon microstructure, dislocation density and minority carriers' lifetime has been studied. Influence of impurity diffusion from the surface into the space of the crystal on electrical properties' changes of the semiconductor is shown.

KEY WORDS: monocrystal, semiconductor, solar cell, dislocation, oriented crystallization, electron conductivity

МОНОКРИСТАЛИ КРЕМНІЮ В НЕТРАДИЦІЙНІЙ ЕНЕРГЕТИЦІ

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Розглянуто особливості утворення та виявлення мікроструктури досконалих монокристалів кремнію n- і p-типу. Визначено вплив діркової та електронної провідності напівпровідників на характер анодного травлення. Встановлено взаємозв'язок між мікроструктурою густини дислокацій і часом життя нерівноважних носіїв струму. Показано вплив дифузії домішок с поверхні в об'єм кристала на зміну електричних властивостей напівпровідника.

КЛЮЧОВІ СЛОВА: монокристал, напівпровідник, сонячний модуль, дислокації, спрямована кристалізація, електронна провідність

МОНОКРИСТАЛЛЫ КРЕМНИЯ В НЕТРАДИЦИОННОЙ ЭНЕРГЕТИКЕ

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Рассмотрены особенности образования и выявления микроструктуры совершенных монокристаллов кремния n- и p-типа. Определено влияние дырочной и электронной проводимости полупроводников на характер анодного травления. Установлена взаимосвязь между микроструктурой, плотностью дислокаций и временем жизни неравновесных носителей тока. Показано влияние диффузии примесей с поверхности в объем кристалла на изменение электрических свойств полупроводника.

КЛЮЧЕВЫЕ СЛОВА: монокристалл, полупроводник, солнечный модуль, дислокации, направленная кристаллизация, электронная проводимость

Modern development of scientific and technical progress conditions the necessity of creating new materials for nuclear and renewable energy search and development. The problem of economical use of natural and development of alternative energy sources becomes more acute. Among various non-traditional methods of energy production, conversion of solar radiation into electricity using semiconductor materials is the most promising one. It is a serious alternative to traditional fuel, nuclear and other forms of energy. In the vast majority of papers degradation of solar energy materials properties is being indicated [1-3]. However, structural analysis, analysis of the impact of heat treatment and radiation on the thermal stability, efficiency of solar cells, etc. is missing. The use of semiconductor materials in various fields of alternative energy conditions the need of their production in monocrystalline form with a near perfect structure [4-8].

Solar cell efficiency is defined by semiconductor materials physical-mechanical properties and phase-structural transformations that are present in them. The problem of a crystalline silicon solar cell fabrication, creation of a material based on crystalline silicon by using alloying and heat treatment techniques to achieve the maximum power output of a solar module is actual. The principal material for solar cells manufacturing is a nondirect gap semiconductor – silicon (amorphous, polycrystalline and monocrystalline). Semiconductor material that is the best for high-efficient solar cells production must be selected with the condition of obtaining the maximum output power, not the maximum short-circuit current or open-circuit voltage individually [9]. It is known that the optimal material for converting radiation of the solar spectrum into electricity are semiconductors (Si, GaAs, InP, CdTe, Ge, GaInP) with a band gap (E_g) ~1.3-1.5 eV. Light quanta with energies less than the bandgap are not absorbed by the semiconductor and are not involved in the photovoltaic process. Silicon band gap depends on temperature T the following way: $E_g \approx 1.21 - 3.6 \cdot 10^{-4} \cdot T$; while gallium arsenide has the value of E_g close to optimal. In theory, the maximum efficiency of solar cells based on it is 31% (Shockley-Queisser limit). It should be noted, however, that GaAs solar cells, lose their photoelectric properties if influenced by radiation. In space radiation, silicon solar cells have a clear advantage over other semiconductor materials [10,11]. This explains its extensive use for photoelectric converters production (Fig. 1). Apparently, change of the band

gap E_g under the influence of doping makes silicon solar cells work. The use of achievements of nanotechnology helps improving the characteristics of silicon solar cells [12]. Devices based on thin films (second generation of solar cells) and high-efficient and low-cost devices (third generation), which increase the energy extraction efficiency, are of an unquestionable interest [7]. It is worth mentioning that pure silicon is very rarely used in solar modules. Efficiency of solar cells based on amorphous poly- and monocrystalline silicon is 15, 17 and >25% respectively. Grain boundaries in multicrystalline silicon (mc-Si) create additional defect levels in the semiconductors' band gap, being the local centers of a high recombination rate, reducing the lifetime of minority current carriers. In addition, grain boundaries reduce the efficiency by preventing current flow through the system and creating a shunt path for the current flow through the p-n junction [13,14].

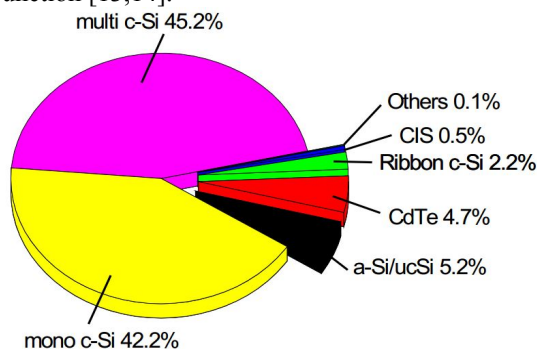


Fig. 1. Semiconductor materials used for solar modules and their portion of the total usage.

It should be noted that there is no unambiguous data considering the acceptor (boron) and donor (phosphorus) impurities solubility in silicon in the literature, which is necessary for the analysis of the impact of structural-phase transitions on the work of solar modules. It is supposed that the stability of a solar cell work, and thus their controlled structural-phase condition offsets the cost of their production substantially. Along with the purity of solar silicon (SOG-Si, solar grade, 99.999%), in order to eliminate the degradation of solar cell properties utter doped monocrystals with controlled structure and properties are needed.

The object of this work is to study the influence of impurities, linear and point defects generated during the controlled liquid-solid phase transition on the structure and properties of monocrystalline silicon.

MATERIALS AND EXPERIMENT

As a source material polycrystalline silicon was used. Its impurity composition was: B – 0.3 ppm ($1.16 \cdot 10^{-5}$ wt.%), Al – 0.1 ($9.6 \cdot 10^{-8}$), P – 0.2 ($2.2 \cdot 10^{-5}$), C – 3 ($1.29 \cdot 10^{-6}$), Fe – 0.03 ($5.98 \cdot 10^{-8}$), Ni – 0.1 ($2.1 \cdot 10^{-7}$), Zn – 0.1 ($2.34 \cdot 10^{-7}$), O – 10 ($5.71 \cdot 10^{-6}$), Cr – 0.01 ($1.86 \cdot 10^{-8}$). As a donor impurity boron was used, acceptor – phosphorus, concentration of which was 2.6 ppm (10^{-4} wt.%) and 1.4 ppm ($1.5 \cdot 10^{-4}$ wt.%) respectively. They form substitutional and interstitial solution, as their atoms have valence electrons on s- and p-orbits [15].

Silicon n- and p- type monocrystals with resistivity between about 0.001 and 200 Ohm·cm were obtained using directional crystallization (Czochralski method, vacuum of less than 10^{-4} Pa) [9]. Crystallization rate R was ~ 30 ... 100 mm/h ($8.33 \cdot 10^{-6}$... $2.78 \cdot 10^{-5}$ m/s), the temperature gradient G at the solid and liquid phases – 50 ... 100 K/cm.

Metallographic, electron microprobe and microscopic analyzes of the crystals were conducted. Microstructure of n- and p-type silicon crystals was revealed by anodic etching with preliminary polishing using boron carbide 220 and subsequent chemical polishing in a mixture of HF(48%):HNO₃(58%) = 10:15 acids solution. Longitudinal and lateral sections of the samples were examined. One side of the sample was nicked, the other one was immersed in the electrolyte, a platinum plate served as a cathode. For the n-type samples current density was 15-20 mA/cm², temperature – 5-15 °C, time of etching τ – 5-7 min, for p-type – the current density was 50-60 mA/cm², T – 5-10 °C, τ – 10-12 min.

Dislocation decoration in silicon was conducted using copper diffusion at a temperature of about 900 °C. Coating with a layer of nitrate copper followed by hydrogen heating was implemented. Upon heating copper diffuses along the interstices and segregates along the dislocation lines. Since silicon is not transparent to visible light, dislocations were observed using infrared rays.

In this paper conductivity type, resistivity (four-probe method) and nonequilibrium carriers' lifetime were determined before and after the heat treatment of p-type (vacuum $<10^{-4}$ Pa, 800 and 1200 °C) samples. Conductivity type was determined using a thermal probe and a current-voltage characteristic. The minority carriers' lifetime – using photoconductive decay method [2,9].

RESULTS AND DISCUSSION

During metallographic analysis of the samples, it was found that the nature of n- and p-type silicon crystals etching is different. This is explained by a different electrochemical behavior of studied semiconductor materials in electrolyte solutions. A relatively small concentration of free charge carriers ($\sim 10^{-8}$ wt.%) in semiconductors influences the structure of the double electrical layer formed at the semiconductor-solution interface. In metals, electric charge is concentrated in the surface layer of the depth of 10^{-8} cm. In semiconductors, volume charge layer depth depends on the carrier quantity and can be up to 10^{-5} - 10^{-4} cm. Participation of the charge carriers of the opposite sign in electrochemical reactions determines different behavior of silicon monocrystals of electron and hole conductivity type in electrolyte solutions. On the p-type silicon electrode, where major charge carriers are holes, anodic process occurs smoothly and anodic behavior of the electrode is not very different from the one of a metal. N-type silicon – holes are minority charge

carriers, their concentration in the volume is small. As a result, rate of anodic process is determined by the rate of volume charge layer generated holes' inflow to the electrode surface. It was determined that all the factors that contribute to the increase of holes in the near-electrode space concentration: surface lightning, semiconductor heating, holes injection, etc; increase the n-type silicon anodic dissolution rate. Etching developed technique is of undoubted interest in solar modules production.

It was found that during a crystal growth using Czochralski method, impurities' concentration decreases. Its impact is equivalent to one pass of a molten zone in floating-zone refining method. It should be noted that in order to suppress a movement of fluid flows in electrically conductive melt and prevent a non-uniform impurities distribution in the growing crystal, the crucible with the melt was placed in a magnetic field, which slows the movement of the conductive melt. Magnetic viscosity effect – an increase of melt viscosity in the magnetic field to a value that exceeds its own kinematic viscosity is observed. Purification efficiency is determined by the distribution coefficient (k) of impurities in solid and liquid phases, according to expression [14]

$$k = \frac{k_0}{[k_0 + (1 - k_0) \exp(-R\delta / D_1)]}, \quad (1)$$

where k_0 is equilibrium distribution coefficient; R – linear crystallization rate, cm/s; δ – diffusion layer thickness, cm; D_1 – dopant diffusion coefficient in the melt, cm^2/s . Diffusion layer thickness, which is present in (1) can be determined from an empirical relation $\delta = 1.6D_1^{1/3} \nu^{1/6} \omega^{-1/2}$, where ω – crystal rotation frequency, s^{-1} ; ν – kinematic melt viscosity, cm^2/s .

Maximum impurities' solubility in silicon is observed at temperatures of 1100-1300 °C, and is estimated using distribution coefficient between solid and molten silicon. Tetrahedral covalent radii of boron and phosphorus are 0.88 and 1.10 Å, respectively. Maximum boron solubility (at 1200 °C) is $5 \cdot 10^{20} \text{ cm}^{-3}$ (0.38 wt.%), phosphorus (at 1150 °C) – $1,3 \cdot 10^{21} \text{ cm}^{-3}$ (2,8 wt.%). It is determined that boron and phosphorus dopants diffuse in accordance with the vacancy mechanism during solar cell operation. It was also established that such impurities as Li, Cu, Au, diffuse through the crystal lattice interstices at high velocities.

It was determined that the most effective purification is observed for Zr, Mo, W, Ta, Nb, Cd, Bi, as well as a quite effective removal of such metals as Ti, V, Cr, Mn, Fe, Co, Zn, Ni, Cu, Ga, Ag.

Silicon nitride crucibles (instead of quartz ones) and tungsten heaters (instead of graphite ones) that were used in the current study allowed to significantly reduce the content of harmful impurities. This way, oxygen concentration in the product was $2 \cdot 10^{15} - 2 \cdot 10^{16} \text{ cm}^{-3}$ ($2,29 \cdot 10^{-6} - 2,29 \cdot 10^{-7}$ wt.%), carbon part – $5 \cdot 10^{16} - 5 \cdot 10^{17} \text{ cm}^{-3}$ ($4,29 \cdot 10^{-5} - 4,29 \cdot 10^{-6}$ wt.%), nitrogen portion – $< 10^{12} \text{ cm}^{-3}$ (10^{-9} wt.%).

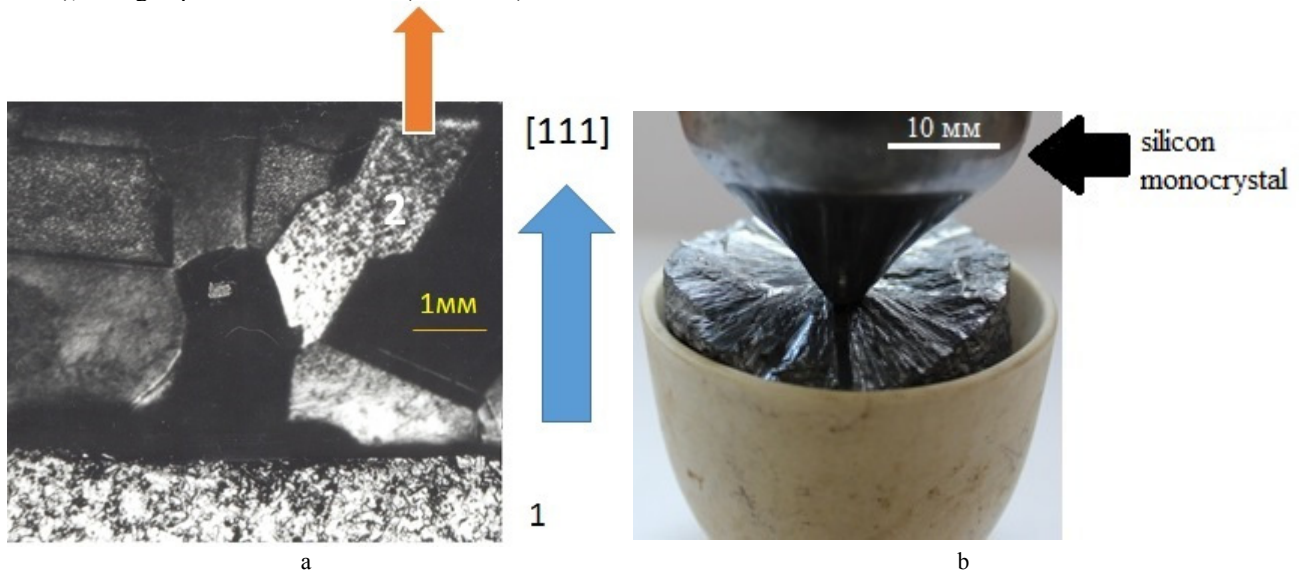


Fig. 2. Formation of monocrystal silicon structures
a - selective crystal growth (the arrow indicates direction of the growth), b - monocrystalline silicon.

A monocrystal seeds with [111], [110] and [100] orientations were used for doped silicon monocrystals grows. Fig. 2 shows the character of monocrystal structure formation.

As can be seen from the Fig., under certain conditions, grains did not have the same orientation throughout their volume. Selective growth of monocrystal grains was observed. It has been found that acceptor and donor impurities concentration of one atom per million (P – $1,1 \cdot 10^{-6}$ wt.%, B – $3,86 \cdot 10^{-7}$ wt.%) is sufficient to cover the grain boundaries that consist of pure silicon, with a layer of impurity atoms.

It has been determined that while crystal growth with the [100] and [111] orientations, significantly fewer dislocation density ($< 10^2 \text{ cm}^{-2}$) than in the [110] and [112] orientations is observed.



Fig. 3. Growth dislocations in silicon crystals.

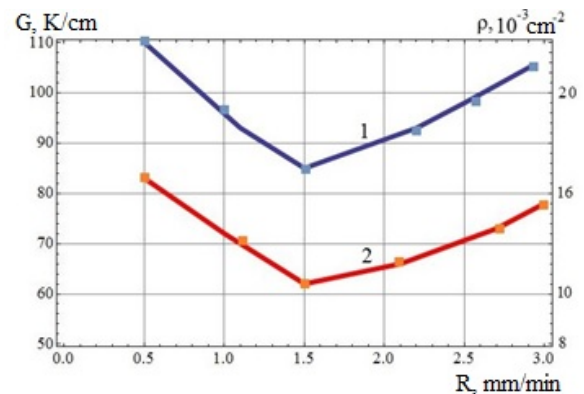


Fig. 4. The influence of the crystallization rate on the temperature gradients along the axis of the crystals (1) and the average dislocation density (2).

For silicon monocrystals with low ρ_d growth the "overclamping" method was used. It involves supersaturation with vacancies near the crystallization front of the growing crystal by increasing the crystallization rate and temperature gradient. This facilitates the dislocations inflow to the surface of the crystal and prevents dislocations from penetrating the growing crystal (Fig. 3). According to the calculations, equilibrium concentration of vacancies in silicon at room temperatures is $10^7 - 10^8 \text{ cm}^{-3}$, and that it increases to $10^{17} - 10^{18} \text{ cm}^{-3}$ when temperature is raised up to 1000 °C.

With the help of radiometal and electron microscopic analyses dislocation loops, vacancy clusters and their complexes were revealed. During the crystal growth microdefects (MD) were formed as a result of impurity complexes capturing by a growing crystal. In the post-crystallization period MD formation was observed as a result of the supersaturated solid solution decomposition.

The influence of the rate of growing silicon on the dislocation density during directional crystallization was determined (Fig. 4).

Analysis of the obtained data (Fig. 4) shows that the change in the average dislocation density of silicon monocrystals correlates with the change of the maximum radial temperature gradient value in range of studied crystallization rates. This dependence is exponential. In order to reduce the dislocation density, it is expedient to have the maximum value of G observed not at the crystallization front, but in the volume of the growing crystal. The lowest value of the maximum radial G in the crystal was observed when the phase boundary was slightly convex to the melt. It was $\sim 10-15 \text{ }^\circ\text{C}$ and corresponded to the minimum of observed values of $\rho_d = 3.4 \cdot 10^{-2} \text{ cm}^{-2}$.

Fig. 5 shows the etch pits and dislocations found in n- and p-type silicon monocrystals. Dislocation density in the most perfect crystals was less than 10^2 cm^{-2} .

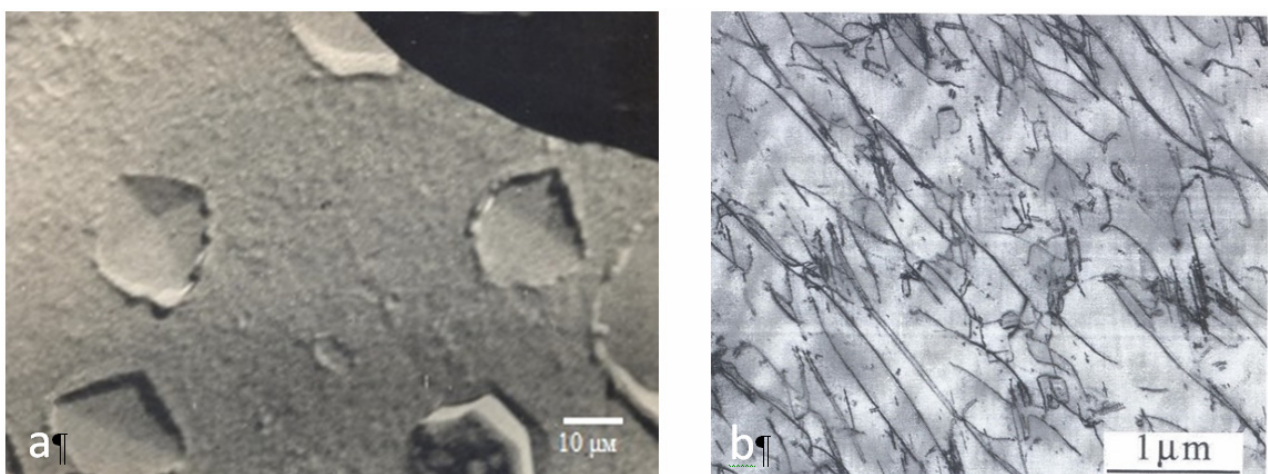


Fig. 5 Silicon microstructure
 a - etch pits, b - dislocation structure.

It is known that heat treatment of the semiconductor materials leads to a substantial change in minority carriers lifetime, however, the relationship between the magnitude of the dislocation density in doped silicon monocrystals and

thermal stability, electrical properties remains unclear. Typically, heat treatment leads to a significant reduction of carriers lifetime. In order to avoid harmful effects of heat treatment, preparatory treatment with special organic reagents of silicon monocrystals surface, annealing in chlorine containing atmosphere, coarse sanding, ion bombardment and other methods are used.

In various papers authors claim that they are studying "dislocation-free" silicon crystals, but at the same time, it is known that the most perfect monocrystals with low dislocation density are whisker crystals with the dislocation density ρ_d of $\leq 10^1$ - 10^2 cm^{-2} [17, 18].

It is also known that the rate of dopants diffusion along dislocations is 10^6 - 10^7 times greater than the rate of volume and grain boundary diffusion [19]. This is likely to be the reason why monocrystals with a high dislocation density are more sensitive to surface impurities' influence and their nonequilibrium carriers' lifetime alters more significantly after diffusion annealing.

In this paper the effect of p-type samples heat treatment (vacuum $< 10^{-4}$ Pa, 800 and 1200 °C) on the type of conductivity, resistivity and nonequilibrium charge carriers' lifetime τ is revealed (Table 1).

As can be seen from the table, when heated up to 1200 °C, the difference in the value of dislocation density has no significant effect on the τ – post-heat treatment minority carriers' lifetime. On the contrary, when heated up to 800 °C the difference in the value of dislocation density influences the change of τ heavily. In dislocation-free crystals ($\rho_d < 10^2$ cm^{-2}) the lifetime has virtually unchanged after the heat treatment, while in crystals with $\rho_d = 10^4$ cm^{-2} it was 8 times less. The findings may serve as an indirect evidence of a significant influence of impurity diffusion from the surface into the volume of a crystal on the reduction of nonequilibrium carriers' lifetime in silicon after being heated up to 800 °C.

Table 1.

Influence of dislocation density on the change of electrical properties of silicon.

At 800 °C				
Properties before heat treatment			After	
Dislocation density, cm^{-2}	ρ , Ohm·cm	τ , μs	ρ , Ohm·cm	τ , μs
$5 \cdot 10^4$	10.8	39	12.9	5
$2.3 \cdot 10^4$	11.9	37.4	13.1	4.6
$4.5 \cdot 10^4$	13.7	37	13.6	5.4
$< 10^2$	54	19	60.5	18
$< 10^2$	67	20	49	15
$< 10^2$	70	17	65.4	16
At 1200 °C				
$> 10^4$	12.3	27	12	< 3
$5 \cdot 10^4$	11.9	23	15.4	< 3
$3 \cdot 10^4$	12.4	27	13.4	< 3
$< 10^2$	51	23	66.6	< 3
$< 10^2$	68	39	64	< 3
$< 10^2$	56.5	21	70.1	< 3

CONCLUSIONS

The optimal n- and p-type silicon monocrystals formation conditions were determined. During the crystallization with high values of G and R oversaturation with vacancies of the growing crystal near the crystallization front is observed. For [111] seed orientation this helps dislocations to come to the surface of a crystal.

Distinctive features of the n- and p-type silicon monostructure revealing that are associated with the existence of the electric double layer formed at the semiconductor-solution surface, were determined. Surface lightning, semiconductor heating, injection of the holes, etc. increase the rate of anodic dissolution of n-type silicon. Interconnection of the dislocation structure of the crystals, crystallization rate and temperature gradient was revealed. The minimal silicon perfect monocrystals' dislocation density was 10^2 cm^{-2} .

High-temperature heat treatment of the n-type samples (up to 1200 °C) with different dislocation density has no significant impact on the nonequilibrium carriers' lifetime. A similar pattern is observed in the case of heat treatment with < 800 °C of crystals with low dislocation density. In doped perfect silicon monocrystals with $\rho_d < 10^2$ cm^{-2} lifetime virtually unchanged after the heat treatment. There was an evident decrease of the minority carriers' lifetime (8 times less) of the crystals with high dislocation density (heat treatment ≤ 800 °C), which is caused by the impurity (O_2) and recombination centers' diffusion from the surface into the volume of the crystal.

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