About the Lifetime of Auxiliary Charge Carriers in Neutron-Doped Silicon

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Abstract

The results of works aimed at mastering the technology of obtaining NTD silicon, carried out at the KEPP Corporation in collaboration with L. Ya. Karpov NIFKhI, are reported. The results include optimization of the annealing mode, for the purpose of increasing the minimal lifetime of charge carriers from the values observed (100–200 µs) to 200–400 µs, the specific resistance being about 50 Ω cm. The regimes developed as a result of the investigations allowed us to decrease the time of thermal treatment necessary for the annealing of radiation defects and, as a consequence, to increase the lifetime of auxiliary charge carriers. The analysis of the results on obtaining NTD silicon grown from the initial polycrystalline silicon of different manufacturers allows us to conclude that further routes to increase the lifetime in NTD silicon are connected mainly with mastering the technology of obtaining the initial material.

INTRODUCTION

One of the parameters characterizing the quality of single crystal silicon is the lifetime of the auxiliary charge carriers (lifetime). It is known to be the longer, the lower is the concentration of recombination-active impurities and other imperfections of the crystal structure. In the industrial technology of the crucible-free preparation of silicon for power electronics, neutron-transmutation doping (NTD) is widely used. This method includes the irradiation with reactor neutrons followed by the annealing of radiation defects, which is necessary to recover the prescribed specific resistance and lifetime. One of the technological problems is traditionally the task to select optimal conditions for thermal treatment, to provide reproducible recovery of the lifetime till values comparable to the initial ones. At present, the recognized leaders in the manufacture of high-quality silicon including NTD silicon, such as Topsil and Wacker Companies, offer material characterized by the lifetimes shown in Table 1. This Table also shows the home technical standards for lifetimes and radial non-uniformities of the specific resistance at the edges of slab (calculation was made according to ASTM F81).

As one can see in this Table, the leading manufacturers of NTD silicon provide the lifetime either at a level characteristic of undoped material (200–1000 µs) with similar specific resistance, or a comparable value, using for irradiation the initial silicon with the lifetime more than 1000 mm, while under the actual technical conditions accepted in Russia the minimal permissible lifetime for the NTD silicon is at a level of 30–100 µs [1]. High level of the radial uniformity of the distribution of specific resistance in the silicon manufactured by foreign companies should also be noted. This is due not only to high doping factor (the ratio of specific resistance in the initial single crystal to that of the doped one is 10–20), but also to high radial uniformity of the specific resistance of initial material (less than 15–18 % at the resistance of 500 Ω cm).

TABLE 1

Some characteristics of the quality of single crystal silicon

Manufacturer of silicon	Initially grown silicon (electron type of the conductivity)		NTD silicon		
	ρ, Ω cm	τ, μs	ρ, Ω см	τ, μs	$\delta\rho_{rad}$, %
Wacker	20−50	> 200	20−50	> 200	< 3
	50−150	> 500	50−150	> 500	< 3
	> 150	> 1000	> 150	> 1000	< 4 (200−600 Ω cm)
					< 5 (600−1000 Ω cm)
Topsil	20−100	> 500	20−100	> 500	< 3
	100−500	> 1000	100−600	> 600	< 5
	500−1000	> 1000	600−1000	> 750	< 7
Home-made (technical standard 48-443-83)			40−60	≥ 30	< 10
			70−200	≥ ρ/2	< 10
			210−350	≥ 100	< 14

It is evident that such a high level of the parameters is the result of perfect technology of growing the initial material; as regards the lifetime after NTD, it is also due to high degree of sterility of thermal treatment after NTD.

In the present communication we describe the results of investigations into the mastering of the technology of obtaining NTD silicon at the JSC KEPP Corp. together with the Karpov Institute NIFKhI. The problem was to optimize the conditions of thermal treatment of the material after NTD and to determine if the quality of the initial polysilicon obtained from different manufacturers has an effect on the lifetime.

For this purpose, experimental-industrial lots of silicon were grown, the diameter being 3 inches; the specific resistance was more than 800 Ω cm (n type), and more than 3 κΩ cm (p type) by means of a single-pass purification in vacuum followed by growing dislocation-free single crystals in argon atmosphere. Polycrystalline silicon manufactured by the companies: Hemlock, Wacker, ASiMi and ZTMK was used in the experiments; the samples differed from each other in electrophysical properties only slightly. The resulting single crystals were irradiated in the reactor at NIFKhI at cadmium ratio of about 20 (doping factor was more than 10) with doses of reactor neutrons about $5 \cdot 10^{17}$ cm^{-2}, then thermally treated in air in the diffusion furnace. The conditions of thermal treatment were cho-

sen so that, on the one hand, to completely remove radiational defects caused mainly by the action of fast neutrons, on the other hand, to maximally exclude the effect of uncontrollable surface contamination due to the decrease of the time of thermal treatment at the temperature point involved. Thermal treatment in chlorine-containing atmosphere at 820 °C for 2 h provided a lifetime of 100−200 μs for 90 % of slabs. The authors tried to recover the lifetime during thermal treatment to achieve the value observed for initial silicon before radiation or, at least, to increase the minimal lifetime in single crystals with the specific electrical resistance of 50 Ω cm up to 200−400 μs. The lifetimes were measured at the edges of slabs before irradiation by means of photoconductivity decay; after irradiation and thermal treatment, the lifetimes were measured by the modulation of conductivity in a point contact. To determine the temperature dependence of the minimal duration of thermal treatment providing the elimination of radiation defects, thermal treatment was carried out within the range 600−900 °C for 0.25 − 4 h. The samples of NTD silicon with the specific resistance of 25 Ω cm were repeatedly irradiated with fast neutrons, with a dose of $1 \cdot 10^{16}$ cm^{-2}, which corresponds in order to magnitude to the dose of fast neutrons in the integral flow of reactor neutrons used to dope the slabs. The completeness of the annealing of radiation defects was estimated using the degree of the
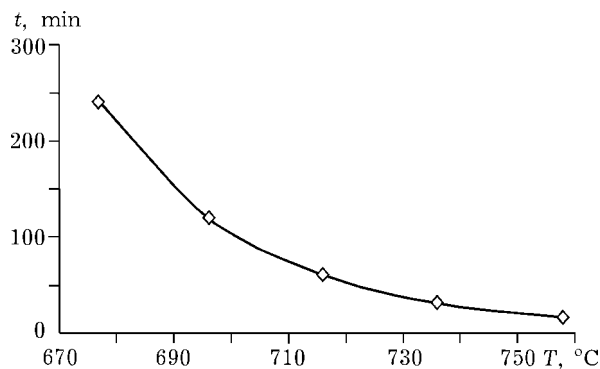
Fig. 1. Dependence of the duration of complete removal of radiation defects in NTD silicon on temperature.

recovery of specific resistance to initial value. The plot of the duration of thermal treatment till complete annealing of the radiation defects versus the treatment temperature is shown in Fig. 1. The duration of the complete annealing depends exponentially on reverse temperature of thermal treatment and is linear when plotted in the corresponding coordinates (Fig. 2). The necessary duration of thermal treatment at a given temperature sufficient for the complete annealing of the defects may be estimated from the equation obtained on the basis of the described dependence:

$$T = 3.36 \cdot 10^4 / (\ln t + 25.8) \qquad (1)$$

Here T is the treatment temperature, K; t is the duration of thermal treatment, s.

It is known that temperature not less than 750 °C is necessary to achieve complete an-
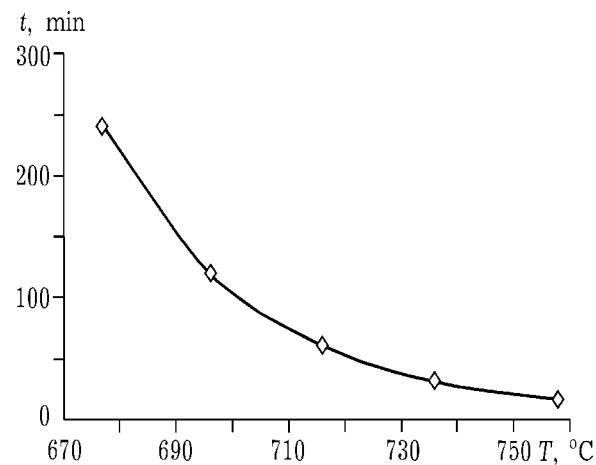

Fig. 2. Dependence of the logarithm of the duration of complete annealing on reverse temperature.
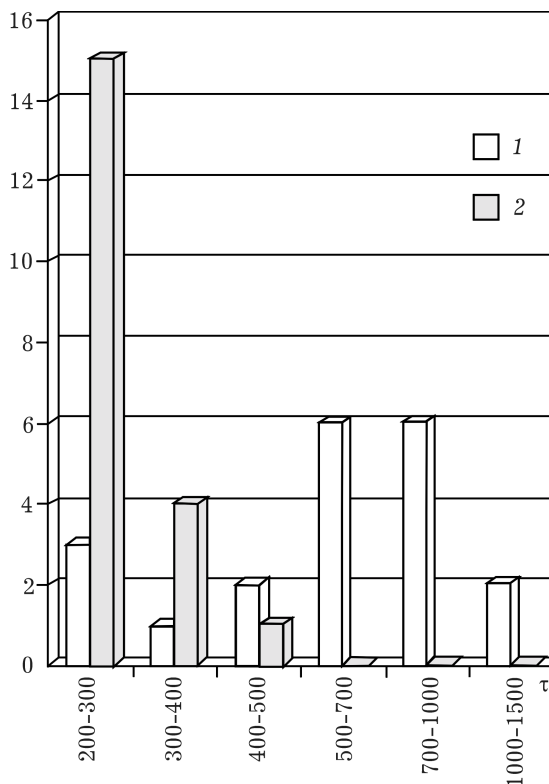

Fig. 3. The distribution of τ under new conditions of thermal treatment: 1 − initial silicon, 2 − NTD silicon.

nealing of the defects in the case if a substantial fraction of fast neutrons is present in the beam [2]. Because of this, the basic temperature for the thermal treatment of NTD silicon was chosen at 800 °C. Minimal time of thermal treatment necessary for complete annealing of radiation defects at this temperature, determined from the eq. (1), is 4.1 min. Thermal treatment of chemically polished slabs in the container placed into diffusion furnace for 5 min followed by cooling till room temperature at a rate of 1 °C/min allowed obtaining minimal lifetime in single crystals not less than 200 μs (Fig. 3). No regularities could be revealed in the investigation of the character of changes of lifetime in NTD silicon in comparison with the initial one.

However, the problem of recovering the lifetime to the values observed for initial single crystals was not solved. Because of this, we investigated the effect of the initial polycrystalline silicon on the result achieved. At the same time, an attempt was made to state the existence of correlation between lifetime in the initial silicon and in NTD silicon.
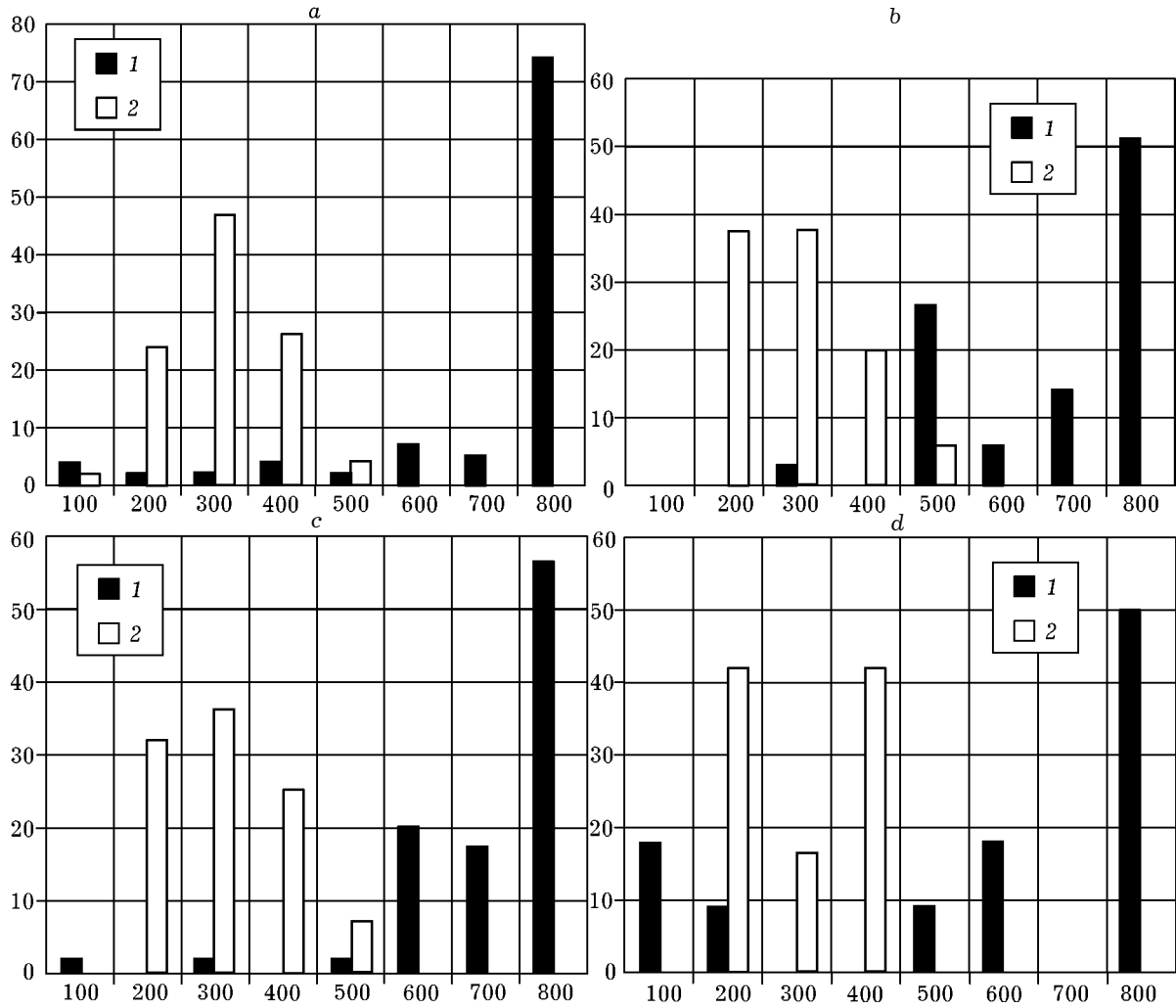
Fig. 4. Distribution of lifetime of the auxiliary charge carriers at different stages of the technological process for Si single crystals grown from Si: *a* − ASiMI, *b* − Hemlock, *c* − Wacker, *d* − ZTMK (*1* − before doping, *2* − after doping).

Figure 4 show the results of processing the data on the lifetimes of auxiliary charge carriers before and after irradiation for single crystals grown from polysilicon obtained from different manufacturers. To evaluate the quality of the initial crystals using τ characteristics, minimal levels 500 and 800 μs* were selected; they correspond to the medium and high level of the crystal quality with respect to lifetime.

As the data show, the fraction of single crystals with lifetimes above 500 and above 800 μs in initially grown single crystals was:

− for the crystals grown from polysilicon ASiMi − 90 and 73 %;

− for the crystals grown from the polysilicon of Hemlock − 97 and 51 %;

− for the crystals grown from the polysilicon of Wacker − 95 and 56 %;

− for the crystals grown from the polysilicon ZTMK − 77 and 50 %, respectively.

So, the manufacturers of polysilicon can be listed in a row according to the decrease of the fraction of initially grown slabs with the lifetime more than 800 μs: ASiMi − Wacker − Hemlock − ZTMK.

If we assume that at the other conditions of slab treatment after growing being kept identical, the final τ should correlate with the initial one, one should expect a similar distribution of

*It was impossible to investigate the τ above 1000 μs because of very small amount of the material with such characteristics.

the polysilicon-manufacturing companies according to the results of measuring lifetimes after the irradiation and thermal treatment. Besides, in this case it should be expected that the character of the histograms depicting the distribution of initial and irradiated slabs over lifetime will be similar. Minimal values characterizing the level of NTD silicon as the medium and top were selected to be 200 and 400 μs (a level close to 500 μs for the specific resistance of 50 Ω cm according to the specification of Wacker and Topsil). The results are listed.

The fractions of single crystals with lifetimes longer than 200 μs and longer than 400 μs were:

− for the crystals grown from the polysilicon ASiMi − 98 and 30 %;

− for the crystals grown from the polysilicon of Hemlock − 100 and 25 %;

− for the crystals grown from the polysilicon of Wacker − 100 and 32 %;

− for the crystals grown from the polysilicon ZTMK − 100 and 42 %, respectively.

One can see that the differences in the distribution of crystals with long lifetime grown from polysilicon of different manufacturers have got leveled as a result of radiation thermal treatment. Moreover, the fraction of slabs obtained from the ZTMK polysilicon with lifetime longer than 400 μs turned out to be larger in comparison with other crystals. This result may be explained by the influence of two independent main factors: the decisive effect of the increase in the concentration of doping impurity to similar level as a result of NTD process, and contamination of the crystals with rapidly diffusing impurities during the annealing of radiation defects.

In order to estimate the contribution from thermal treatment itself into the formation of the final lifetimes, a cycle of thermal treatment steps was carried out with the single crystals of the p type with the initial specific resistance of 5−8 kΩ and lifetime within the range 500−800 μs, compensated using NTD and intended for the production of IR radiation receivers. The practice of obtaining compensated silicon of the p type or re-compensated silicon of the n type [3] is well known and often used to obtain high-resistance material with the specific resistance of 10 to 100 kΩ cm; we also often use this practice. As a result of irradiation with small doses of the reactor neutrons followed by annealing, the crystals with the specific resistance of more than 10 kΩ cm with lifetime at a level of the initial value were obtained. This result, obtained without any increase of the concentration of the doping impurity, allows one to conclude that the annealing does not bring substantial additional contamination that would have dramatic effect on the lifetime.

It is evident that the observed absence of any correlation in the distribution of slabs over the initial and final lifetime values is conditioned by the fact that the lifetime of the auxiliary charge carriers in NTD silicon at the given level of the initial τ is defined by the doping level. The absence of slabs with lifetimes less than 200 μs and the substantial fraction (about 30 %) of slabs with high (according to our conditional classification) lifetime longer than 400 μs are the evidence of the fact that the level of contamination with rapidly diffusing metal impurities is generally low and reproducible from one process to another.

So, the investigations resulted in obtaining the dependence to determine a minimal duration of thermal treatment at a given temperature for complete removal of radiation defects. A practical goal is achieved: reproducible obtaining of single crystal silicon with the specific resistance up to 50 Ω cm and lifetime not shorter than 200 μs. It is demonstrated that the developed thermal treatment process does not lead to the decrease of lifetime in comparison with the initial single crystal silicon at small irradiation doses, which is the evidence of its sufficient sterility. No correlation has been stated between the quality of the initial polysilicon from different manufacturers and the lifetime in the initial silicon with the lifetime in the NTD silicon. In our opinion, further increase of lifetime in NTD silicon is possible due to the mastering of growing processes and irradiation of single crystals.

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