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Thermal stability of electrical parameters of silicon crystal doped with nickel during growth

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Abstract. This work shows that the introduction of nickel atoms in the process of growing silicon crystals enables to obtain a material with stable electrophysical parameters during thermal annealing in the wide temperature range 450…1050 °C and duration (t = 0.5...25 hours). This is the most cost-effective way to create material for semiconductor devices and solar cells with stable parameters.

Keywords: silicon, thermal donor, nickel, doping, thermal stability.

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1. Introduction

The manufacturing process of semiconductor devices based on silicon, which includes various thermal treatments, is accompanied by numerous changes in its electrophysical properties [1, 2]. Nevertheless, stringent requirements for the stability of their parameters are imposed on the semiconductor devices obtained.

Oxygen is an important impurity in silicon used for photovoltaic application. Particulary present in monocrystalline Czochralski Si ingots, O atoms can form several defects [3]. O atoms also participate in formation of some thermally activated defects, among which there are the so-called aged thermal donors (TDs) [4].

Introduction of various impurities can not only change the nature of TD, but also improve the thermal stability of silicon. In [5], the effect of low-temperature annealing on the electrical, optical, and structural properties of silicon doped with nickel (Si-DN) by the diffusion method was studied. It has been shown that during heat treatment in the temperature range of 300...500 °C, the electrical properties of Si-DN practically remain stable for a rather long time.

It was shown in [6, 7] that nickel atoms in silicon are mainly in an electrically neutral state and form various types of clusters. It was found that the clusters contain rather high concentration of oxygen atoms, as well as the rapidly diffusing ones (Fe, Cu, Cr …).

Oxygen-related TDs in silicon have attracted significant attention due to their detrimental effects on the fabrication process of semiconductor devices. On the basis of the results obtained, the authors of [5, 7] argued that the thermal stability of the electrophysical parameters of silicon after diffusion doping is associated with the gettering properties of clusters of nickel atoms, namely, with oxygen gettering (which leads to generation of TDs during thermal treatment of silicon in the process of manufacturing devices). This assumption is confirmed in [8], where it was found that additional doping of silicon with nickel significantly affects the efficiency of silicon photocells. The results of these and other works [5, 7] show that doping silicon with nickel by using the diffusion method is the most effective one, which provides thermal stability of the silicon electrophysical parameters during thermal treatment in a wide temperature range, as well as during a long thermal annealing time.

However, this method (diffusion doping of silicon with nickel) for improving the parameters and thermal stability of silicon requires a number of additional technological operations, such as: sputtering of nickel (or chemical deposition of nickel), high-temperature diffusion annealing, as well as mechanical treatment and chemical cleaning before and after diffusion of nickel, and most importantly, it is necessary to process each silicon wafer.

All these operations significantly complicate technology of manufacturing silicon-based devices. In this regard, it is worth paying attention to the study of silicon doped with nickel during crystal growth (Si-DNG). Doping silicon with nickel during crystal growth enables to obtain large ingots of monocrystalline silicon homogeneously doped with nickel with the required concentration throughout the entire bulk without additional operations and costs. Therefore, the purpose of this work was to study the effect of thermal treatment on the electrophysical properties of Si-DNG.

2. Sample preparation and research methods

To carry out the research, as a starting material we used monocrystalline Si obtained using the Czochralski method of *p*-type conductivity, with the resistivity $\rho \sim 70\,\Omega\cdot\text{cm}$, with the diameter close to 76 mm, doped with nickel atoms during crystal growth. The oxygen concentration in these materials was $N \sim (5\ldots6)\cdot10^{17}\ \text{cm}^{-3}$. All the given data were obtained from the passport of material, which was taken from the manufacturer plant. The purpose to use this material (of *p*-type, with the concentration $p \sim (2\ldots3)\cdot10^{14}\ \text{cm}^{-3}$) was to determine the effect of TD generated during heat treatment of silicon, the concentration of which can reach $\sim 10^{15}\ \text{cm}^{-3}$ [9, 10]. The samples of dimensions 1.3×5×10 mm were made from these ingots. The electrical parameters of the samples were measured using the Hall effect method.

To have the reference sample, we used the material without nickel with the resistivity ρ close to 40 Ω·cm (*p*-type), which was annealed using the same temperature regimes, which enabled to estimate the real rate of TD generation.

3. Results and discussion

3.1. Influence of low-temperature annealing

A huge number of works have been devoted to the kinetics of oxygen TD accumulation in silicon during the low-temperature annealing [11]. Temperature defects in silicon, depending on the kinetics of formation, concentration and nature, can be separated into several groups. One of the groups is low-temperature thermal donors, *i.e.*, silicon-oxygen complexes of the SiO_4 type, formed during low-temperature thermal treatment at $T = 300\ \ldots\ 500$ °C.

To study the effect of low-temperature thermal treatments on the properties of Si-DNG, the samples were annealed at $T = 450$ °C for various periods of time in air. Annealing was carried out in several stages (durations of these stages are shown in Table 1).

Each stage of annealing was completed with air cooling followed by chemical cleaning. After each stage of thermal annealing, the electrical parameters of the samples were determined using the Hall effect method. Table 1 shows the electrical parameters of Si-DNG samples, as well as the reference ones. The TD concentration was calculated using the formula $N_{TD} = p_0 - p_{TA}$, where N_{TD} is the concentration of thermal donors, p_{TA} – concentration of holes in the sample after thermal treatment, and p_0 – concentration of holes in the sample before thermal treatment. As shown by the research results (Table 1), regardless of the duration of this treatment, the electrical parameters of the Si-DNG samples practically retain their initial values (with a maximum deviation of approximately 5%). At the same time, the parameters of the reference samples change significantly with an increase in the thermal treatment time, and with an annealing time of more than 12 hours, the type of conductivity changes, *i.e.*, the samples acquire *n*-type conductivity with a resistivity $\rho = 6.6\cdot10^3\ \Omega\cdot\text{cm}$, which corresponds to the results described in [3, 11].

The obtained results convincingly show that Si-DNG samples indeed have high thermal stability, *i.e.*, generation of thermal donors in them is practically completely suppressed.

3.2. Influence of thermal annealing performed within the range *T* = 530 ... 1050 °C

Another type of thermal defects, which strongly affects the parameters of silicon, is called as the high-temperature or quenching one; it is formed with participation of rapidly diffusing impurities [9]. To study the effect of nickel on formation of thermal quenching defects, the samples were annealed within the temperature range $T = 530\ \ldots\ 1050$ °C. This process was completed with rapid cooling at the rate close to 200 °C/s.

Table 1. Change in electrical parameters in the reference samples and in Si-DNG after thermal treatment at 450 °C.

Annealing time, hour	Sample parameters					
	Reference			Si-DNG		
	type	ρ, Ω·cm	N_{TD}, cm^{-3}	type	ρ, Ω·cm	N_{TD}, cm^{-3}
No annealing	*p*	40	–	*p*	70	–
1	*p*	55	$1.2\cdot10^{13}$	*p*	73.6	$1.2\cdot10^{13}$
3	*p*	102	$1.58\cdot10^{13}$	*p*	70.9	$2.5\cdot10^{13}$
6	*p*	$5.5\cdot10^2$	$3.68\cdot10^{13}$	*p*	71.8	$2.9\cdot10^{13}$
9	*p*	$3.6\cdot10^3$	$1.3\cdot10^{14}$	*p*	70.3	$2.9\cdot10^{13}$
12	*p*	$7.9\cdot10^3$	$2.8\cdot10^{14}$	*p*	69.6	$3.3\cdot10^{13}$
15	*n*	$6.6\cdot10^3$	$4.7\cdot10^{14}$	*p*	68.9	$3.5\cdot10^{13}$
20	*n*	$2.5\cdot10^3$	$7.15\cdot10^{14}$	*p*	71	$3.73\cdot10^{13}$
25	*n*	$2.3\cdot10^3$	$8.36\cdot10^{14}$	*p*	74	$3.8\cdot10^{13}$

Table 2. Changes in electrical parameters of the reference sample and in Si-DNG after annealing.

Annealing time, hour	Annealing tempera-ture, °C	Studied parameters			
		Reference sample		Si-DNG	
		type	ρ, Ω·cm	type	ρ, Ω·cm
No annealing	–	*p*	40	*p*	70
1	550	*p*	60	*p*	71.1
15	550	*n*	$5.6\cdot10^3$	*p*	77
1	850	*p*	$2\cdot10^2$	*p*	73.4
1	1050	*n*	10^3	*p*	77.8

Note. After changing the conductivity type of the reference sample, the concentration of TD in it was determined using the formula $N_{TD} = p_0 + p_{TA}$.

Table 2 shows the electrical parameters of both Si-DNG samples and those of the reference sample annealed under identical conditions after annealing at temperatures of 530, 850 and 1050 °C. After each stage of thermal annealing, the samples were chemically treated, and the electrical parameters were measured using the Hall effect. As you can see from Table 2, the electrical parameters of the Si-DNG samples after each thermal annealing retain not only the type of conductivity, but also the values of electrical parameters, in contrast to the reference sample, in which the electrical parameters change significantly, reaching a change in the type of material conductivity. The obtained data allow us to conclude that even with high-temperature annealing, the presence of nickel introduced during the growth of a silicon single crystal ensures the stability of the electrical parameters of material, *i.e.*, generation of quenching defects is suppressed by the nickel impurity.

4. Conclusions

The experimental results show that doping with nickel atoms during the growth of silicon crystals enables to obtain a material with stable electrical parameters not only during low-temperature (450 °C) treatments, but also after annealing within the temperature range 530...1050 °C.

The obtained experimental results show that to obtain silicon with stable electrophysical parameters within a wide range (T = 450...1050 °C) of thermal treatment temperatures, the most effective method is doping the silicon crystals with nickel during growth at the nickel concentration $N_{\mathrm{Ni}} \geq 10^{18}$ cm^{-3}. This allows creation of devices and solar cells based on this material in a technologically affordable way, with minimal costs and with high reproducibility. It should be also noted that the bulk doped with nickel atoms (99.99%) in the silicon lattice is electrically neutral. It means that introduction of nickel atoms into silicon during crystal growth does not affect the main parameters of monocrystalline silicon, which is required for application in electronics industry and in production of silicon solar cells.

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Термічна стабільність електричних параметрів кристалів кремнію, легованих нікелем під час вирощування

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Анотація. У даній роботі показано, що легування атомами нікелю в процесі вирощування кристала кремнію дозволяє отримати матеріал зі стабільними електрофізичними параметрами в процесі термовідпалу в широкому інтервалі температур 450...1050 °C та тривалості (t = 0,5 ... 25 год). Це найбільш економічно ефективний спосіб створення матеріалу для напівпровідникових приладів і сонячних елементів зі стабільними параметрами.

Ключові слова: кремній, термодонор, нікель, легування, термостабільність.