Influence of formation conditions of silicon diodes on their reverse currents

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In this work, a study was made of the influence of silicon diode manufacturing technology on the emergence of generation and recombination centers. The electrical characteristics of $p-n$ junctions formed in different ways on n-type silicon substrates were compared: a) the p-type layer was created by the diffusion method; b) the p-type layer was formed by ion implantation into an epitaxial n-layer preliminarily grown on the substrate; c) two n- and p-type epitaxial layers were successively deposited on the substrate. It has been established that for diodes based on a double epitaxial layer, the direct and reverse current-voltage characteristics (CVC) are due to the diffusion mechanism, and the structures themselves have a low concentration of recombination centers. At the same time, in diodes based on the diffusion method and ion implantation, the CVCs are due to the generation-recombination mechanism. With reverse bias, electron-phonon processes play a significant role in the formation of the CVC, and with forward bias, carrier recombination in the region of the space charge of the $p-n$ junction. The concentrations and energies of recombination centers have been determined.

Keywords: forward and reverse current-voltage characteristic, $p-n$ junction, diffusion, ion implantation, epitaxy, recombination centers, the Poole–Frenkel effect, electron-phonon interaction.

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1. Introduction

The magnitude of the current through the $p-n$ junction under reverse bias is determined in most cases by defects that form generation-recombination centers in the space charge region. In this region processes of generation of electrons and holes take place with participation of deep levels [1]. The generation is accompanied by the Pool−Frenkel effect, and this process is also influenced by the electron-phonon interaction, which leads to a smooth increase in the reverse current with increasing voltage [2–4]. From the point of view of the diffusion theory of the $p-n$ junction current flow, the reverse current should not depend on the applied voltage [5]. The activation energy of the temperature dependence of diffusion current should be equal to the band gap energy of the semiconductor, but experimental studies show that this is not the case, and the activation energy is less than the band gap [2,6]. This is due to the fact that in most cases the reverse current is the sum of the diffusion current and the generation current [7], moreover the latter one is predominating [1–4]. The mechanism of current flow can be determined by studying its dependence on temperature. If the experimental value of the activation energy of the temperature dependence of the current is less than the band gap energy, but more than half of it, then the reverse current is determined by the process of

generation of electrons and holes through the levels of deep centers and should not depend on the bias voltage at the $p-n$ junction. The generation of electrons and holes occurs in the space charge region of the $p-n$ junction, where a sufficiently strong electric field exists, which affects the current value. In the majority of papers that investigate the reverse current-voltage characteristic (CVC) of semiconductor devices, this phenomenon is ignored, while in others — the influence of the applied voltage is explained by the Poole−Frenkel effect [8,9]. The Pool−Frenkel coefficient has a well-defined theoretical value. This value must be calculated and compared with its experimental value in order to prove the existence of this effect. However, the Poole−Frenkel coefficient calculated from the experimental results may be larger than the theoretical one, which is due to the influence of the electron-phonon interaction [2–4,10]. The electron-phonon interaction can be significant when the recombination centers are complexes of several point imperfections. The composition of the complexes depends on the production technology and the content of accompanying impurities. High synthesis temperature leads to increased concentration of vacancies [11]. Vacancies in silicon are easily captured by oxygen and form vacancy−oxygen complexes. Such complexes can contain different numbers of both vacancies and oxygen atoms [12]. They create recombination centers near the middle of the band gap in the band

gap of silicon and actively influence the value of reverse currents [2–4,13,14]. While the influence of oxygen on the magnitude of the reverse currents of $p-n$ junctions has been studied quite well, the influence of nitrogen has not been studied enough, and it affects both the formation of oxygen complexes [15] and creates deep levels itself in the band gap of silicon [12]. The purpose of this work is to study the influence of the conditions for the formation of diodes on the current-voltage characteristics of $p-n$ junctions. To achieve this purpose, the electrical properties of $p-n$ junctions obtained on single-crystal silicon substrates, including those with epitaxial silicon layers, differing in the temperature of the epitaxy process and the composition of the gas phase in the reactor, are compared.

2. Experimental results

Silicon wafers were prepared for the experiments in three different methods. The group objects „A" were created on n-type low-alloyed silicon wafers obtained by the float zone melting. The resistivity of the sample substrate „A" was $\sim 4400\,\text{Ohm}\cdot\text{cm}$. The p-type layer $0.5\,\mu\text{m}$ thick with the dopant concentration of $10^{19}\,\text{cm}^{-3}$ was created by ion implantation of the boron impurity. Diodes of the „B" group were formed on low-resistance n-type silicon wafers. The n-type epitaxial layer with a thickness of $30\,\mu\text{m}$ was sequentially grown on them at a temperature of $1050°\text{C}$ by the monosilane decomposition. The reactor was purged with nitrogen before the synthesis of samples of the „B" group. Then, by ion implantation, the p^+-layer $0.5\,\mu\text{m}$ thick with concentration of $10^{20}\,\text{cm}^{-3}$ was formed. Boron and nitrogen concentrations in epitaxial layers of „B" group diodes were measured by time-of-flight secondary ion mass-spectrometry on a ToFSIMS-5 spectrometer by IonTOF GmbH. Boron concentration was $2\cdot 10^{18}\,\text{cm}^{-3}$, and nitrogen one was $10^{21}\,\text{cm}^{-3}$. Apparently, the use of nitrogen to purge the reactor before epitaxial deposition contributed to its accumulation in the p^+-layer of „B" diode. Wafers of the „C" group were obtained on low-resistance silicon wafers by sequential deposition of two epitaxial layers of n- and p-type at temperature of $950°\text{C}$ from trichlorosilane and hydrogen. All technological processes were carried out using highly purified argon and hydrogen without trace impurities of oxygen and nitrogen. The oxygen concentration in the initial wafers of the „C" group was controlled by infrared absorption spectra and amounted to $8\cdot 10^{17}\,\text{cm}^{-3}$.

All diodes after their preparation were of the p^+-n type, had the p^+-region with high doping level, and had the sharp $p-n$ junction. To measure the current-voltage and capacity-voltage characteristics of these diodes, the automated complex based on the Keysight B1500A semiconductor device analyzer was used. The concentration of free charge carriers in the n-type low-doped region was calculated

from the results of measuring capacity-voltage characteristics. It was for samples of different groups: „A" — $(5.9 \pm 0.2)\cdot 10^{11}\,\text{cm}^{-3}$; „B" — $(3.0 \pm 0.5)\cdot 10^{16}\,\text{cm}^{-3}$; „C" — $(2.2 \pm 0.2)\cdot 10^{14}\,\text{cm}^{-3}$.

Reverse current-voltage characteristics of the diodes are shown in Fig. 1.

3. Discussion

The activation energy of the temperature dependence of the reverse current depends on the main mechanism that generates this current. Activation energy close to the band gap (E_g) corresponds to the diffusion mechanism. The activation energy, which lies in the range of $0.5 \cdot E_g < E_a < E_g$, corresponds to generation through recombination centers in the band gap of the semiconductor region, which is less doped. The activation energies were calculated using the Arrhenius coordinates from the data shown in Fig. 1 and at various electric field strengths. To plot the dependence, the maximum value of the electric field in the space charge region of the diodes was chosen, which is equal to twice the average value of the field, since the decrease in the activation energy occurs exactly at the boundary where the field is maximum. The measurement results are presented in Fig. 2.

The activation energy of the reverse current in the diodes of the „C" group approaches the energy of band gap in silicon. This indicates that the reverse current flow mechanism in them is diffusional, and the reverse diffusion current exceeds the generation current through the local electronic states of deep levels. This does not mean that defects do not affect the reverse current of diodes „C". The content of deep levels determines the lifetime of charge carriers in the corresponding regions. This time can be calculated from the saturation current [5]. Recombination occurs in the quasi-neutral n-region, where holes are minority carriers, then

$$\tau_p = D_p \left(\frac{q n_i^2 S}{n_n I_s} \right)^2, \qquad (1)$$

where D_p is hole diffusion coefficient in silicon, q is electron charge, n_i is self-carrier concentration in silicon, S is area of diode, n_n is concentration of intrinsic charge carriers in n-region of silicon, I_s is diode saturation current.

Assessment of the lifetime by formula (1) gives the value of $3 \cdot 10^{-4}\,\text{s}$ for diodes of the „C" group. The hole lifetime is quite high, which indicates a low concentration of recombination centers in the space charge region of these diodes. Indeed, a capacitive measurement of the concentration of deep centers of these diodes gave values of concentration $5\cdot 10^{10}\,\text{cm}^{-3}$ and activation energy of $0.48\,\text{eV}$. The lifetime value and the concentration of deep centers indicate the high quality of the double epitaxial diodes of the „C" group.
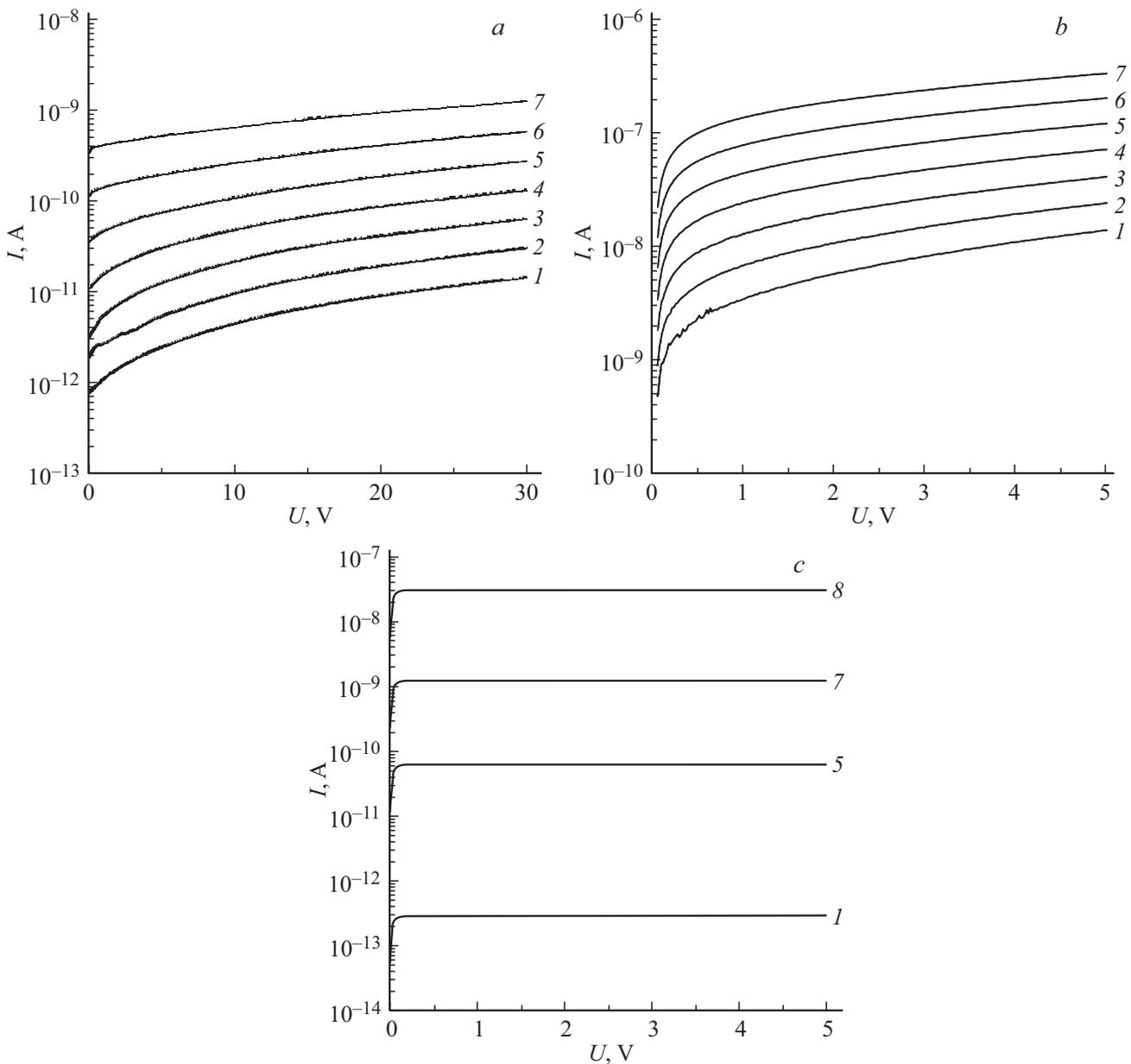
Figure 1. Reverse current-voltage characteristics of samples of groups „A" (*a*), „B" (*b*), „C" (*c*), measured at temperatures °C: *1* — 0, *2* —10, *3* — 20, *4* — 30, *5* — 40, *6* — 50, *7* — 60, *8* — 80.

As noted above, in the presence of the Poole−Frenkel effect, the activation energy of the reverse current depends on the electric field, which is associated with decrease in the height of the potential barrier near the deep center in the electric field:

$$\Delta E_t = \frac{q^{3/2}}{\sqrt{\pi \varepsilon_S}} \sqrt{F} = \beta_{\text{FT}} \sqrt{F}, \qquad (2)$$

where ε_S is static permittivity of the semiconductor; β_{FT} is theoretical value of the Poole−Frenkel constant, which for silicon is $0.00023 \, \text{eV} \cdot \text{cm}^{1/2}/\text{V}^{1/2}$.

In order to find the activation energies of recombination centers, an extrapolation procedure was carried out by the

regression. In addition, it was taken into account that the generation current is limited by the electronic transition, which has the high activation energy [2–4]. To find the activation energy of the center through which the generation occurs, it is necessary to subtract the energy value from the band gap of silicon at 0 K, which is obtained by extrapolation to zero electric field strength. For diodes of the „A" group, the energy is 0.47 eV and the Poole−Frenkel constant $(1.34 \pm 0.03) \cdot 10^{-3} \, \text{eV} \cdot \text{cm}^{1/2}/\text{V}^{1/2}$, and for the diodes of the group „B" the energy is 0.29 eV and the constant $(1.02 \pm 0.03) \cdot 10^{-3} \, \text{eV} \cdot \text{cm}^{1/2}/\text{V}^{1/2}$. In both cases, the Poole−Frenkel constant exceeds the theoretical value, which is due to the electron-phonon interaction. In
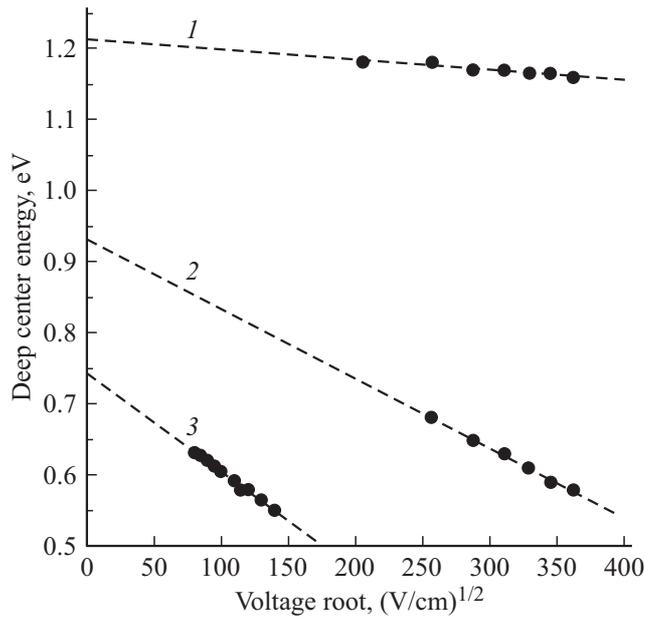
Figure 2. The dependence of the activation energy of the reverse current on the value of the maximum field strength in the space charge region of the diodes: 1 — „C", 2 — „B", 3 — „A".

Expression (3) is true when the generation of charge carriers occurs as a result of a multi-phonon process, and only one type of phonons with some effective energy takes part in it. The algorithm for calculating the parameters of the electron-phonon interaction is described in the works [2–4]. Analysis of publications on defects in silicon shows that the activation energy of $0.47-0.48$ eV can correspond to the complex $V_{Si}-O$ [12,16–18] or the divacancy [12,13,19]. The recombination center 0.25 eV is associated with the incorporation of nitrogen into the silicon lattice [16]. Thus, the recombination centers in diodes of the „A" and „B" groups are due to oxygen complexes with the silicon vacancy. In diodes prepared by the sequential double epitaxy „C", there are significantly fewer recombination centers, and they do not determine the reverse current of these diodes.

In a number of works, including works [1,2], the method of recombination spectroscopy is used, which consists in converting direct current-voltage characteristics according to certain algorithms in order to appear on the initially monotonic current-voltage characteristic of some features. These features make it possible to estimate the parameters of recombination centers. One such algorithm is to calculate the value of the reduced recombination rate $(R_{red}(U))$, which has the meaning of the inverse lifetime. This value is calculated from the experimental current-voltage characteristic by the formula

the work of S.F. Timashev [16] it was demonstrated that

$$\beta = \beta_{FT}\left(1 + \frac{E_0 - S\hbar\omega}{S\hbar\omega}\right),\quad (3)$$

where $S\hbar\omega$ is value equal to half of the heat release that accompanies the electron-phonon interaction; E_0 is energy of merely electronic transition.

$$R_{red}(U) = \frac{I_r(U)}{qSw(U)n_i\left[\exp\left(\frac{qU}{2kT}\right) - 1\right]}\frac{q(V_d - U)}{2kT},\quad (4)$$

where U is current value of the forward bias voltage, $I_r(U)$ is current value of the recombination current in the
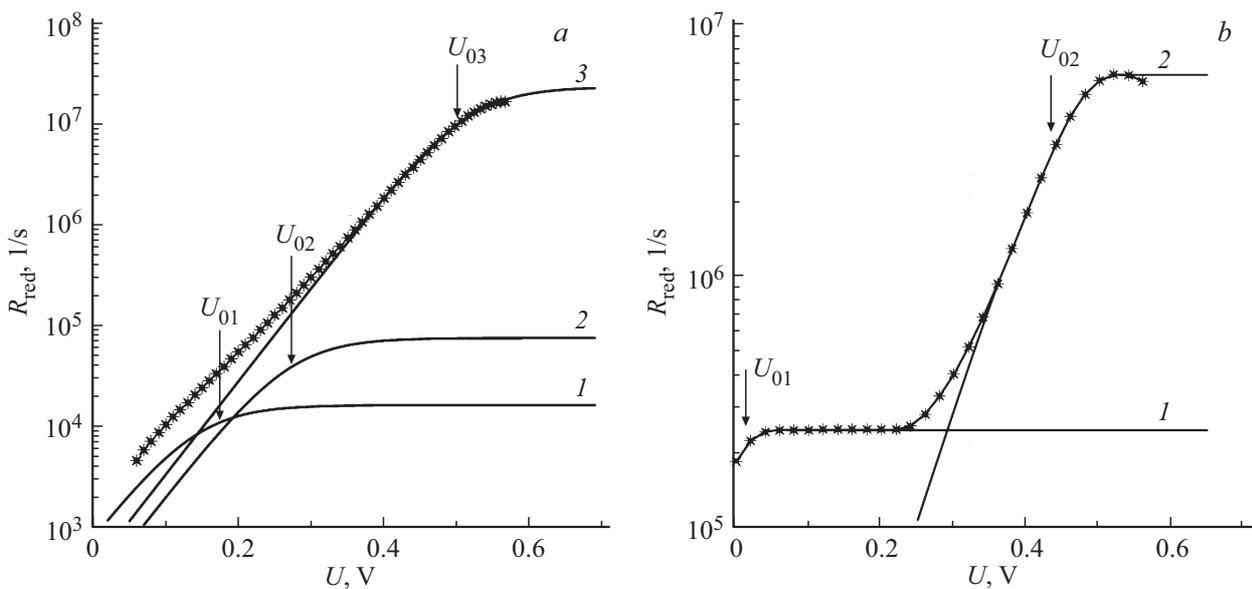

Figure 3. Reduced rate of recombination of diodes of groups „A" (a) and „B" (b) calculated at temperature 0°C. The arrows mark the voltages at which the reduced saturation recombination rate decreases by a factor of 2. The numerical symbols indicate the number of the recombination process.

space charge region, $w(U)$ is width of the space charge region, V_d is diffusion potential of the $p-n$ junction.

Reduced rates of recombination of diodes of groups „A" (a) and „B" (b) at temperature 0°C are shown in Fig. 3.

The activation energy of recombination centers can be estimated using the simple formula [1,2]

$$E_t = \frac{E_g - qU_0}{2} + \delta, \qquad (5)$$

where

$$\delta = \frac{kT}{2} \ln\left(\frac{1}{4} \frac{c_n N_c}{c_p N_v}\right). \qquad (6)$$

Here, U_0 is voltage at which the reduced saturation recombination rate decreases by a factor of 2, E_g is band gap of silicon at room temperature, c_n is electron capture coefficient per recombination center, c_p is hole capture coefficient per recombination center, N_v is effective density of electronic states of the valence band, N_c is effective density of electronic states of the conduction band.

The capture coefficients for us are unknown; nevertheless, formula (5) makes it possible to estimate the activation energy with an accuracy of 0.02 eV. The reduced rate of saturation recombination is equal to $R_{\text{red}}^{\max} = \sqrt{c_n c_p}\, N_t / 2$.

Its reciprocal value makes it possible to estimate the lifetime during recombination through a specific center. Samples of the „A" group have three such recombination centers: $E_{t1} = 0.48$, $E_{t2} = 0.44$, $E_{t3} = 0.33$ eV; the lifetimes during recombination through them are equal respectively: $5 \cdot 10^{-5}$, $1.3 \cdot 10^{-5}$, $5 \cdot 10^{-8}$ s. Samples of the „B" group have two types of recombination centers: $E_{t1} = 0.58$, $E_{t2} = 0.34$ eV; the lifetimes during recombination through them are equal respectively: $4 \cdot 10^{-6}$, $1.6 \cdot 10^{-7}$ s. On the whole, the results of estimating the activation energy of recombination centers from forward and reverse characteristics agree against each other. Energy 0.33 eV has the recombination center, which is associated with the divacancy in silicon. Therefore, the issue of the nature of this center requires further study. It is not improbable that since the activation energies of nitrogen centers and divacancies are close, the recombination processes are superimposed on each other and this method does not allow one to separate these processes.

4. Conclusion

Features of the technology for obtaining $p-n$ junctions of silicon lead to the different set of recombination centers. The creation of diodes on silicon, which is grown by the float zone melting or the Czochralski method, is carried out at temperatures close to the melting temperature of silicon, in addition, these single crystals contain a lot of oxygen. Therefore, the presence of recombination centers associated with silicon-oxygen complexes is inevitable. These centers reduce lifetime and increase leakage currents. Reverse CVCs in the presence of such centers vary smoothly. The

use of nitrogen in the technological process can create additional recombination centers. Diodes obtained by double epitaxy have few recombination centers, their CVCs are described by the diffusion mechanism of current flow with the sufficiently long lifetime so that the reverse current at room temperature is small. This is due to the fact that the relatively low temperature of epitaxy leads to the low concentration of vacancies, which decreases exponentially with decreasing silicon synthesis temperature. The use of highly pure hydrogen in the synthesis process reduces the oxygen concentration in the epitaxial layers. This overall leads to the decrease in the concentration of recombination centers.

Conflict of interest

The authors declare that they have no conflict of interest.

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