

TWO-CHANNEL GETTERING OF RECOMBINATION-ACTIVE IMPURITY IN POLYCRYSTALLINE SOLAR SILICON

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The features of the recombination-active impurity gettering in polycrystalline silicon have been studied. The research method included the formation of a porous silicon layer 0.5–2 μm in thickness on the backside of a silicon wafer, the deposition of aluminum layer 0.5–1 μm in thickness, and the thermal annealing at 700–950 $^{\circ}\text{C}$ during 30–60 min. The corresponding gettering model has been proposed, which includes the diffusion of iron atoms by means of two most probable independent channels: in the wafer bulk and along the grain boundaries. By comparing the theoretical results and experimental data, we established that 30% of gettered impurity atoms diffuse with a high rate along the grain boundaries, and 70% of them in the grain bulk.

1. Introduction

The influence of a thermal treatment on the lifetime of photo-induced charge carriers, τ , in single-crystalline silicon has been studied since the beginning of the 1960s [1–5]. However, such researches became recently especially challenging in connection with solar-cell problems. For typical *n* and *p* oxygen-containing specimens which were obtained at that time, their heating at even moderate temperatures (600–800 $^{\circ}\text{C}$) for 1–20 h was accompanied by a substantial (by 1–2 orders of magnitude) reduction of the charge-carrier lifetime from about 20–50 μs . At longer annealing times and higher annealing temperatures (above 800 $^{\circ}\text{C}$), a certain restoration of τ was observed, especially for specimens with higher oxygen contents, $N_{\text{O}_2} \geq 10^{16} \text{ cm}^{-3}$. Hence, the initial single-crystalline specimens subjected to the heating revealed the unstable behavior with respect to τ . As was found in works [1, 2], this phenomenon is associated with the action of oxygen defects or impurity-defect complexes bound with them; some of the complexes being recombination-active, and the others being characterized by the getter action.

It is expedient to carry out experiments with a specially created getter, the action of which would include the mechanisms of both stabilization and increase of the lifetime. Such an external getter is a combined structure

composed of a layer of porous silicon and an Al layer [10]. Under such conditions, it becomes possible not only to preserve τ (in other words, a high photosensitivity) at a heat treatment, but also to increase it considerably. The corresponding results were reported in some earlier works, in which a single-crystalline substance was dealt with. In polycrystalline Si, which is widely used in solar photoelectronics, the phenomena turned out to be a little more complicated. They are studied in this work.

The impurities of heavy metals in crystalline silicon are known to reduce the lifetime and the diffusion length of minority charge carriers. The impurities create deep levels in the forbidden gap of a semiconductor, thus promoting the recombination processes. One of those basic “harmful” metals is iron [1–12]. Interstitial Fe atoms combine with atoms of boron, a typical doping impurity in *p*-type silicon, to create complexes FeB, which are even more recombination-active than individual Fe and B atoms. In addition, Fe atoms create stable inactive complexes FeSi₂ in silicon during the cooling in the temperature range 900–200 $^{\circ}\text{C}$ [1]. Such precipitates generate mobile interstitial Fe atoms at a subsequent thermal treatment of a wafer.

The well-known method to remove metallic impurities from crystalline silicon wafers is gettering, in particular, with the use of an aluminum layer. The physical basis of this process consists in the segregation of impurities in the metallic Al layer. In our previous work [13], we studied the kinetics of gettering processes related to the behavior of precipitated iron in single-crystalline silicon wafers. In this work, we carried out similar researches of the effect of gettering of recombination-active impurities in polycrystalline solar silicon, which is widely used in solar power engineering.

2. Experimental Technique

2.1. Getter fabrication

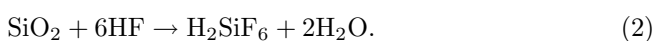
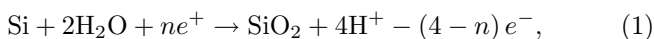
In early works [6, 7], the method of gettering with a damaged layer obtained by grinding the wafer backside

was proposed. The optimum dimension of the abrasive fraction for grinding was $60\ \mu\text{m}$. The thickness of a damaged layer obtained under those conditions amounted to about $20\ \mu\text{m}$. Then the layer was ground to a thickness of $10\ \mu\text{m}$. The wafer was annealed in an inert environment at a temperature of $1070\text{--}1470\ \text{K}$ for $1\text{--}4\ \text{h}$. As a result, a network of dislocations with a concentration of $10^8\text{--}10^{10}\ \text{cm}^{-2}$ was formed in the gettering layer. This network has the accumulation effect. In the course of annealing, the harmful impurities move in the specimen bulk until they are captured at dislocations in the damaged layer. In such a manner, the wafer bulk is purified of recombination-active impurities. Substantial shortcomings of this method are the necessity of a slow cooling after a thermal treatment, a bad reproducibility because of the imperfect control over the structure and the thickness of a damaged layer, considerable mechanical stresses, *etc.*

In the proposed technology, instead of a mechanical treatment, we use a porous layer with a deposited thin layer of aluminum. The surface of single- and polycrystalline silicon wafers is preliminarily purified of recombination-active impurities. The application of porous silicon in solar cells as an antireflecting, reemitting, and passivating layer is well-known [14, 15]. In this work, we propose to use porous silicon as a getter. The corresponding thermal treatment results in a decay of impurity-defect recombination complexes and a subsequent removal of recombination-active impurities. The latter is evidenced by an increase of the diffusion length for minority charge carriers. The getter is formed at the backside of the wafer, oppositely to the face with the collector $p\text{--}n$ -junction.

The initial procedure is aimed at removing the damaged layer formed as a result of the cutting of wafers. In order to remove the damaged layer, the wafer was treated in a polishing etching solution $\text{HF}:\text{HNO}_3:\text{CH}_3\text{COOH} = 1:4:5$ for $2\ \text{h}$. The thickness of the etched layer was about $5\ \mu\text{m}$ at both wafer faces.

A layer of porous silicon on the surface of single- and polycrystalline wafers of the p -type with a specific resistance of $0.5\text{--}1\ \Omega \times \text{cm}$ was obtained by applying the chemical etching in a decorating etching solution $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$. Silicon is dissolved according to the reactions



In a solution with an excess of HNO_3 or HF , the parameter $n = 4$ or 2 , respectively.

While forming a porous layer on the polycrystalline silicon surface, the important factor is the uniformity of the porous silicon over the surface, because the wafer includes domains with different orientations of crystals which are etched also differently. The etching uniformity strongly depends on the composition and the temperature of an etchant.

In the etching solutions with a high HF content, the oxidation rate imposes a restriction. In this case, the etching process is less uniform (anisotropic), because the oxidation is very sensitive to the doping level, crystal orientation, and presence of defects. The oxidation process occurs selectively, in particular, at the places of their output. On the other hand, the etching process runs more uniformly in solutions with a high HNO_3 concentration, with the reaction rate being governed by the dissolution stage. For etchants with a high HNO_3 content and within the temperature interval $30\text{--}50\ ^\circ\text{C}$, the dissolution kinetics is confined by the diffusion of reaction products through the boundary layer to the wafer surface. The diffusion-induced confinement suggests that the reaction rate is much lower than the reagent exchange. Therefore, the etching runs more uniformly.

In our researches, a porous silicon layer was obtained with the use of a stairing etching solution $\text{HF}:\text{HNO}_3:\text{H}_2\text{O} = 1:3:5$, with the HF and HNO_3 concentrations being 48 and 98% , respectively. A characteristic feature of the etching process was the incubation period ranging from $5\ \text{min}$ to several hours. To reduce it, the additional preliminary etching in a more concentrated acid etchant, $\text{HF}:\text{HNO}_3:\text{H}_2\text{O} = 1:3:2$, was used until the reaction started (from 10 to $15\ \text{s}$). A gas, which was emanated at that, interfered the normal supply of reagents to the wafer surface. Therefore, bubbles had to be constantly removed from the surface, e.g., by stirring, an ultrasonic treatment, and so forth. Visually, a good specimen of porous silicon had a black-brown coloring.

The thickness of porous silicon was determined according to the empirical equation

$$d = r(t - t_0), \quad (3)$$

where d is the thickness of porous silicon (\AA), t the etching time (s), t_0 the incubation period, $rt_0 = 80\ \text{\AA}$, $r = aX$, $a = 10^3\ \text{\AA}/(\text{s}\cdot(\text{mol}/\text{l}))$, and X is the concentration of HNO_3 in the etching solution (mol/l).

In Fig. 1, the results obtained while searching for optimum regimes of the formation of a porous layer under the used etching conditions are depicted. The following features draw attention: (i) the thickness of porous silicon is a function of the etching time (one can observe the incubation period $t \approx 2\ \text{min}$, when the porous layer

does not grow), (ii) there exists a maximum in the dependence $d(t)$, and (iii) the porous silicon layer becomes narrower after its treating for $t \approx 8 \div 10$ min owing to the etching of the porous layer by reaction products.

2.2. Peculiarities of the gettering of a polycrystalline silicon wafer with the use of a combined getter

The gettering of recombination-active impurities was carried out according to the following subsequent stages: (i) formation of a porous silicon layer 3–4 μm in thickness on the wafer backside, (ii) sputtering of an aluminum layer 0.5–1.2 μm in thickness onto the porous silicon, and (iii) thermal annealing of the specimen in the temperature range 700–900 $^{\circ}\text{C}$. Such a routine, as was showed by previous researches dealing with single-crystalline solar silicon [11–13], is characterized by a high efficiency for both poly- and single-crystalline silicon. It stimulates the growth of nonuniformities in the course of the following high-temperature annealing, which is used in the semiconductor technology.

The experiment showed that a layer of porous silicon 3–4 μm in thickness can be fabricated with the chemical etching; this method being characterized by a high degree of reproducibility (Fig. 1). However, longer etching times give rise to the dissolution of silicon, so that a thickness of 8–10 μm is maximal for porous silicon.

The deposition of an aluminum film 0.5–1.2 μm in thickness can be executed taking advantage of the thermal, electron-beam, or magnetron sputtering. The annealing temperature was within the interval 700–900 $^{\circ}\text{C}$. The annealing time was varied from 10 to 120 min, which was necessary for aluminum to penetrate into pores in the porous silicon layer and to form Al-Si alloy, thus freeing recombination-active impurities into the gettering region. The annealing time was determined by the thickness of the aluminum film and the time needed for impurities to reach the gettering region. For a typical silicon wafer 250–350 μm in thickness, the optimum annealing time was about 30 min.

Aluminum diffuses along the wafer surface, forms traps for recombination-active impurities, and dissolves them. As a result, the gettering makes the diffusion length for minority charge carriers substantially longer in both single- and polycrystalline silicon ($L_D = 150 \div 200$ μm and even more). The advantages of the method proposed include a capability of implementing the gettering procedure into the technology of solar silicon manufacture and the technology aimed at manufacturing microelectronic devices. In addition, we have a substantial

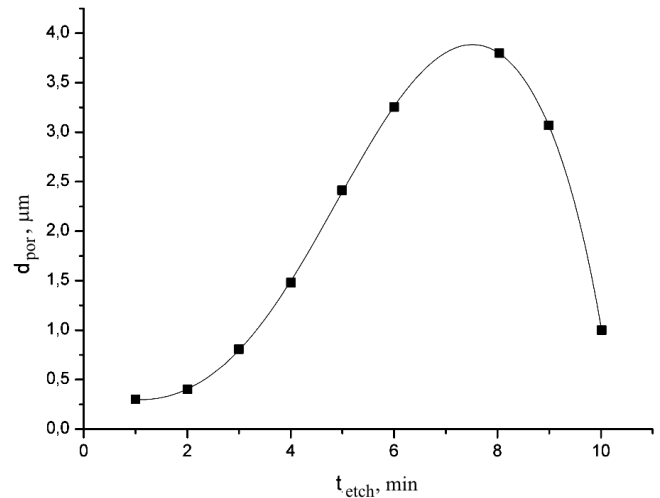


Fig. 1. Dependence of the porous silicon thickness on the chemical etching time

reduction of the thermal annealing temperature in comparison with those applied in other gettering techniques.

2.3. Measurement of recombination parameters. Experimental results

The optimum regime for the creation of a getter and technological procedures was found from the experimental data on the diffusion length L_D (or the lifetime τ_{eff} of minority charge carriers), which were measured with the use of the spectral dependences of the surface photovoltage, $V_F(E_\lambda)$. The corresponding data are depicted in Fig. 2. It is evident that the thickness of the porous silicon layer, where an increase of the maximum diffusion length, L_D , is observed, equals about 3–4 μm (in Fig. 2, squares mark the growing section of curve 1, and circles the descending one) for the aluminum layer 0.5–1.2 μm in thickness (Fig. 3). The gettering time was approximately equal to 30–60 min (Fig. 4), and the annealing temperature to 700–850 $^{\circ}\text{C}$ (Fig. 5). Under those conditions, an improvement in the uniformity of the diffusion length distribution was observed.

3. Results and Their Discussion

Experimental data on a reduction in the amount of recombination-active impurities were obtained by measuring the diffusion length of nonequilibrium electron-hole pairs, L_D , which is connected with their lifetime, $\tau = L_D^2/D$. The probability of the recombination, $w \sim 1/\tau$, is proportional to the concentration of

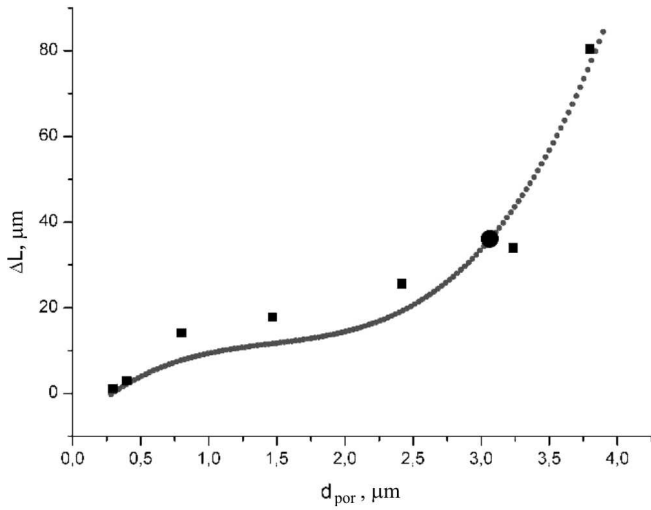


Fig. 2. Dependence of the diffusion length variation on the thickness of a porous silicon layer

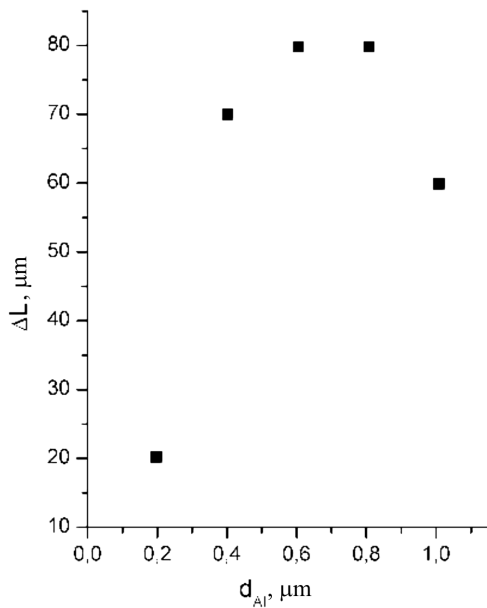


Fig. 3. Dependence of the diffusion length variation for minority charge carriers on the thickness of an aluminum layer

recombination-active centers,

$$N_r = (vC_n\tau)^{-1}, \quad \frac{1}{\tau} = \frac{D}{L_D^2}, \quad (4)$$

In Fig. 5, the data obtained for the temperature dependences of the relative N_r are plotted for two getter types—an Al layer and a combined getter “porous Si/Al layer”. The obtained experimental data can be described in the framework of a model which includes two diffusion coefficients of iron atoms, normal and enhanced ones.

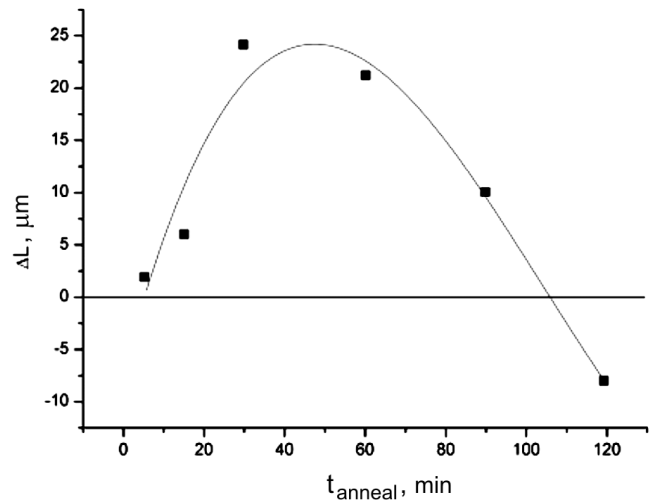


Fig. 4. Dependence of the diffusion length variation for minority charge carriers on the annealing time

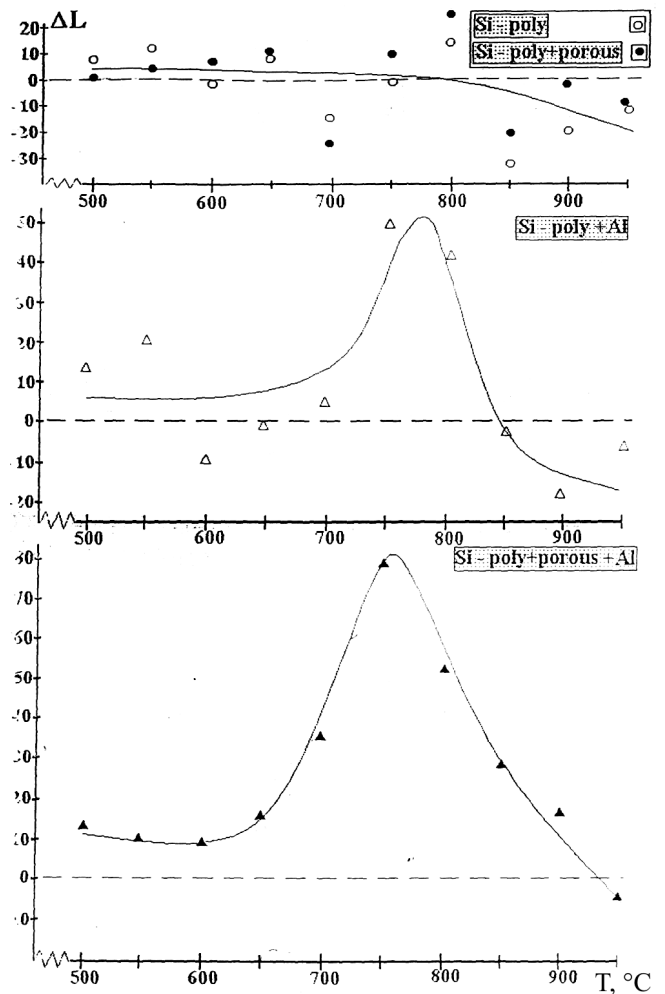


Fig. 5. Dependence of the diffusion length variation ΔL on the annealing time for various layered systems. ($t = 40$ min)

These two channels of diffusion in polycrystalline silicon may correspond to the diffusion in the bulk of a silicon wafer (normal diffusion) and along its surface with a following drain at grain boundaries (enhanced diffusion).

Let us consider the obtained data in detail. As is seen from Fig. 5, in the absence of a getter, a 30-min annealing in the whole temperature range almost did not change recombination parameters. The solid curve in the upper panel reveals a small decrease of L_D at $T \geq 850$ °C for both the initial specimen and the specimen covered with a porous layer which, hence, functions weakly as a getter. On the other hand, the deposition of an Al layer even on the initial surface demonstrates the getter action in the temperature range 730–830 °C (a maximum takes place at 750–800 °C with the almost double increase, Fig. 5). An even larger growth of L_D was observed in the case of a combined getter “porous layer + Al layer” (see the lower panel in Fig. 5). Here, the increased L_D -values are observed in a wider temperature range of 670–900 °C. The quantity concerned attains a value of about 100 μm and more in its maximum, by exceeding the initial value by a factor of 5 to 10.

It is important to mark two more features in the growth of L_D . In the range of low annealing temperatures, at about 500–700 °C, the corresponding growth of the diffusion length (by 25–30%) was almost identical for simple (Al) and combined getters. This low-temperature effect cannot be associated with the mechanism of annealing of thermally induced donors, because it is absent in the case without the Al getter layer (the upper panel in the figure). We connect it with the presence of a near-surface layer which is characterized by an elevated mobility of recombination impurities. The layer thickness was estimated as $d \sim (tD)^{1/2}$, where t is the annealing time amounting to about 0.1–0.2 times the specimen thickness d_p , and D is the diffusion coefficient for getterated impurities [16].

Hence, the obtained experimental data testify to the two-channel gettering on polycrystalline silicon. Note that, for a single-crystalline material where drains (crys-

tallite boundaries) from the external surface are absent, this mechanism is also absent.

Another feature in the dependences of the diffusion length at the annealing is a high-temperature quenching of the photoconductivity, i.e. a reduction of L_D not only to the reference value (at $T \approx 850 \div 900$ °C), but to much smaller values, $L_D \ll L_D^0$. The mechanism of this effect can be partially connected with the activation of internal getters, e.g., precipitated SiO_2 , and with the formation of complexes FeSi_2 , FeB , and others, which are more recombination-active owing to mobile interstitial Fe atoms [3–5]. The elimination of this effect will comprise an important following stage in the researches of processes aimed at the stabilization of the photosensitivity of solar silicon. In the case of the two-channel transport mechanism, the total concentration of centers contributing to the recombination is given by the relation (for independent channels)

$$W_\Sigma = \Sigma \frac{1}{\tau} \approx N_V + N_S. \quad (5)$$

The low- and intermediate-temperature sections of plots in Fig. 5 enable the ratio between the amounts of iron that are generated on the surface and through the bulk of polycrystalline silicon wafers to be evaluated (0.3 and 0.7, respectively).

Let us compare the data concerning the contents of widespread recombination-active impurities in the studied polycrystalline p -silicon material, which were determined using the method of plasma-discharge mass-spectroscopy (see Table), with the estimates of the concentration N_r made for the same elements on the basis of measurements of the initial lifetime of charge carriers and using the known literature data on the transverse cross-section for the electron capture, C_n [2],

$$N_r = D/vC_n l_D^2, \quad (6)$$

where v is the thermal velocity of electrons. Those data are presented in the table.

The table also contains estimates for the effective diffusion coefficient D for various recombination impurities at 900 °C, which were obtained in the approximation of the dominating role of the gettering process in the formation of temperature dependences and assuming the dominating role of the mechanism of diffusion drain of impurities onto an external getter (the Al film). One can see that the coincidence is the best for the Fe impurity with respect to all comparisons (Table), which may indicate that Fe is possibly the main impurity that considerably worsens the photosensitivity of studied silicon wafers.

| Element (impurity) | Ce, cm^2 | N_r , cm^{-3} | D , cm^2/c (900 K) | N_{exp} | |
|-----------------------|-----------------------|-----------------------------|---|----------------------|-------------------------|
| | | | | ppm | cm^{-3} |
| Au | 5×10^{-16} | $\sim 10^{16}$ | 2×10^{-6} | 10^{-3} | $\sim 10^{13}$ |
| Mg | 10^{-15} | 3×10^{15} | 5×10^{-7} | 1.3×10^{-2} | $\sim 5 \times 10^{14}$ |
| Fe | 1.5×10^{-15} | 2×10^{15} | 5×10^{-7} | 2.5×10^{-1} | $(1-5)10^{15}$ |
| C2 | $< 10^{-15}$ | $> 3 \times 10^{15}$ | 10^{-7} | 6×10^{-3} | $\sim 10^{14}$ |
| V | – | – | 10^{-10} | 3×10^{-4} | $< 10^{12}$ |
| Ti | $> 10^{-14}$ | $\leq 3 \times 10^{14}$ | 10^{-12} | 10 | $\leq 10^{12}$ |

4. Conclusions

In this work, the peculiarities in the gettering of recombination-active impurities in polycrystalline silicon have been considered using a technique that includes the consecutive formation of a porous silicon layer 0.5–2 μm in thickness on the backside of a silicon wafer, the deposition of an aluminum layer 0.5–1 μm in thickness, and the thermal annealing at a temperature of 700–950 $^{\circ}\text{C}$ for 30–60 min. A model of the gettering in polycrystalline silicon wafers within this method has been proposed. The model implies the diffusion of iron atoms through two, most probable, independent channels: in the wafer bulk and along grain boundaries. By comparing the results of the model with experimental data, we determined that 30% of gettered impurity atoms diffuse more intensively along grain boundaries, and 70% of them in the grain bulk.

Three stages have been distinguished in a variation of the lifetime τ of photo-induced charge carriers at the annealing:

- 1) relatively low-temperature: at 300–550 $^{\circ}\text{C}$,
- 2) intermediate-temperature: at 600–900 $^{\circ}\text{C}$,
- 3) high-temperature: at 900–1100 $^{\circ}\text{C}$.

In case 1), the lifetime τ grows by about 20–30% and saturates already at $T \approx 500$ $^{\circ}\text{C}$.

The character of τ -variations, as the temperature of the annealing with a getter changes, substantially differs from that for “getter-free” specimens (without an external getter), where those variations are mainly governed by the behavior of “oxygen recombination centers”, in which the dominating role is played by the oxygen binding at defects of various types. Typical of getter-free oxygen-containing Si (of both n - and p -types) is a reduction of τ at the annealing at temperatures below 900 $^{\circ}\text{C}$ and its growth, if the annealing temperature falls within the interval from 900 to 1200 $^{\circ}\text{C}$. It occurs owing to the formation of oxygen recombination centers and their decay, respectively (these phenomena have been analyzed in detail in review [2]), whereas the presence of an external getter gives rise to substantial changes in the behavior of recombination (and, hence, photosensitive) characteristics.

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ДВОКАНАЛЬНЕ ГЕТЕРУВАННЯ РЕКОМБІНАЦІЙНО-АКТИВНОЇ ДОМІШКИ В СОНЯЧНОМУ ПОЛІКРИСТАЛІЧНОМУ КРЕМНІЇ

В.Г. Литовченко, В.М. Насека, А.А. Євтух

Резюме

У даній роботі розглянуто особливості гетерування рекомбінаційно-активних домішок у полікристалічному кремнії методом, що включає послідовне формування шару пористого кремнію товщиною 0,5–2 мкм на зворотному боці кремнієвої пластини, осадження шару алюмінію товщиною 0,5–1 мкм та термічний відпал при 700–950 $^{\circ}\text{C}$ протягом від 30 до 60 хв. Запропоновано модель гетерування даним методом, яка вклю-

чає дифузію атомів заліза по двох найбільш ймовірних незалежних каналах – в об'ємі пластини та по границях зерен. Із зіставлення результатів моделі з експериментальними

даними встановлено, що 30% атомів відгетерованої домішки дифундують прискорено по границях зерен, а 70% – в об'ємі зерен.