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Short Communication

Physical Features of Double Sided Diffusion of Lithium into Silicon for Large Size Detectors

R.A. Muminov[1], A.K. Saymbetov[2,*], N.M. Japashov[2,†], Yo.K. Toshmurodov[1], S.A. Radzhapov[1],
N.B. Kuttybay[2], M.K. Nurgaliyev[2]

[1] *Physico-Technical Institute of the Academy of Sciences of Uzbekistan, Tashkent 100084, Uzbekistan*
[2] *Al-Farabi Kazakh National University, Almaty 050000, Kazakhstan*

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In this paper, we propose a new method for double sided diffusion of lithium ions into a monocrystalline silicon wafer for the further fabrication of Si (Li) *p-i-n* nuclear radiation detectors with a diameter of the sensitive surface of more than 110 mm and a thickness of the sensitive region of more than 4 mm. It was found that the optimal regime for lithium diffusion into large-diameter silicon is at a temperature of $T = (450 \pm 20)$ °C, time $t = 3$ min, thickness $h_{\text{Li}} = (300 \pm 10)$ mm. The theoretical assumptions and experimental characteristics of double sided diffusion are considered. As initial material the dislocation free monocrystalline cylindrical silicon crystal of the *p*-type, obtained by the floating-zone method (with a diameter 110 mm, thickness 8-10 mm, resistivity $\rho = 1000 \div 10000$ Ohm·cm and life time $\tau \geq 500$ μs) and the silicon crystal of the *p*-type (with a diameter of 110 mm, resistivity $\rho = 10 \div 12$ Ohm·cm, lifetime $\tau \geq 50$ μs, grown in an argon atmosphere) obtained by the Czochralski method were used. Correspondingly, the technological processes of mechanical and chemical processing of semiconductor wafers based on silicon of a large area have been improved.

Keywords: Si(Li) detectors, Li diffusion, Double sided diffusion.

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1. INTRODUCTION

In the last half century, different types of semiconductor detectors [1-2] and modern methods of their manufacture [3-5] which are widely used in various fields of electronic engineering have been created. Nowadays, both elementary (silicon, germanium) and complex semiconductor compounds are used to fabricate silicon detectors [6-8]. However, the use of nuclear radiation detectors based on monocrystalline silicon significantly influences the development of nuclear physics [9]. They have the following advantages: speed, linearity of signal in a wide energy range for charged particles of various types [10], high energy resolution, insensitivity to magnetic fields and small dimensions.

One of the long and energy-intensive processes in the technology of manufacturing Si (Li) *p-i-n* nuclear radiation detectors is the formation of the *i*-region by diffusion and drift of lithium ions [11]. So, to create a sensitive area of the detector with a thickness of more than 4 mm, months of painstaking work are required. In addition, providing a large sensitive surface of semiconductor detectors in combination with high energy resolution is still a rather difficult task. This is primarily due to a special requirement for the technology of growing semiconductor materials for semiconductor detectors. The most developed industrial detector silicon materials of large diameters contain significant inhomogeneities in the distribution of electro-physical parameters over the crystal volume [12]. The local and impurity bands present in the sensitive volume of semiconductor detectors significantly impair its radiometric characteristics. Consequently, the requirements of a large sensitive surface and high energy expansion are mutually exclusive.

To shorten the manufacturing time and avoid inhomogeneities in the fabrication of Si (Li) *p-i-n* nuclear radiation detectors, we propose a double sided diffusion method for lithium ions, which precedes a further double sided drift, which is the next stage after double sided diffusion in the development of the detector. The fabrication of the Si (Li) *p-i-n* structure by means of double sided technology helps to shorten the manufacturing time of the detector and optimizes the physical parameters of the detector. The double sided technology of manufacturing *p-i-n* structure has a number of advantages, they are: with the double sided formation of the *p-i-n* structure the manufacturing time is reduced by several times, the structure becomes more homogeneous, etc. Because in penetration of lithium ions in silicon, lithium ions are distributed from the surface of the crystal into the depth; while the deeper the distribution, the greater the non-uniformity appears in the crystal. Accordingly, with the double sided technology, the ion penetration length is halved [13] and this noticeably reduces the manifestations of the non-uniform distribution of lithium ions in monocrystalline silicon.

2. MATERIALS AND METHODS

To obtain the structure, dislocation-free p-type monocrystalline silicon with a diameter of 110 mm, a resistivity of 10-12 Ohm × cm and a lifetime of more than 50 μs, grown in an argon atmosphere by the Czochralski method, was taken as the starting material. Silicon obtained by the floating-zone method with a specific resistance of

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[*] asaymbetov@kaznu.kz
[†] nursultan.dzhapashov@mail.ru

1-5 kOhm × cm and a lifetime of more than 500 μs, was also used for this experiment. Image of the crystal is shown in Fig. 1. To remove the layer disturbed during cutting, double-sided grinding is used on the grinding machine with the use of micropowders M-14, M-5 with a successive reduction in the diameter of the abrasive. At the same time, a layer of at least 50 μm thick is removed from each side.

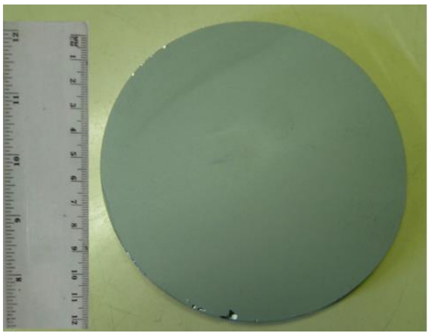

Fig. 1 – Image of monocrystalline silicon

To clean the surface of the plates for this procedure, along with existing surface cleaning methods, we also used new optimized and improved methods. In particular, a) boiling for 15 min in a peroxide-ammonia solution. While treating in this slightly alkaline environment, non-polar organic compounds-contaminants, such as mineral oils, paraffin, etc. are effectively removed. The dipole moment of the molecules of such substances is small, therefore they have high specific surface energy and cause the thermodynamic instability of the surface. b) Boiling for 7 min in concentrated nitric acid and washing in deionized water. In this treatment, ionic chemical contaminations (Na^+, Ka^+, Ca^+, Mg^+, Fe^{++}, etc.) are removed from the surface by transferring them to water-soluble salts, followed by washing in deionized water. c) Re-treatment in peroxide-ammonia solution for 15 min and rinsing in deionized water. In this process, hydrophobic porous oxide films are effectively removed from the surface. Lithium diffusion was carried out in vacuum of $p = 10^{-5}$ mm Hg at a depth of 300 μs, on the entire surface of both sides of the plate for $t = 3$-4 min at a temperature of 380-450 °C.

3. RESULTS AND DISCUSSION

Next we will consider the theory of diffusion. It is known that the diffusion of lithium atoms in silicon serves as an example of diffusion through internodes, since diffusing atoms are small, and the lattice is rather loose. The diffusion coefficients of helium atoms are determined from the penetration rate of lithium atoms in silicon. One of the most important problems in the study of diffusion is the determination of the concentration profile of diffusing particles. To solve such a problem, there are a lot of numerical and analytical methods [14, 15]. Here we consider both numerical and analytical methods for solving the problem of finding the concentration profile of double sided diffusion on a rectangular plate of monocrystalline silicon. These methods include the method of separation of variables, the method of integral transformations, the variation method and the numerical calculation method. To find solutions, an ordinary diffusion equation [16] with the corresponding initial and boundary conditions is used

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}\,. \tag{1}$$

The initial condition consists in setting the concentration values $c(x, t)$ at the initial time t_0; then the function takes the form of $c(x, t_0)$. The boundary conditions describe the behavior of the concentration at the ends of the range of x values: for example, the nature of the change in the concentration or flux of particles

$$c(0,t) = c(L,t) = c_s\,. \tag{2}$$

To solve the equation of double sided diffusion of lithium ions in monocrystalline silicon, it is necessary to determine the boundary conditions, proceeding from the fact that the acceptor concentrations in silicon are $5\cdot10^{15}$ cm^{-3}, the concentration of the traps is of the same order. The temperature of introduction of lithium ions corresponds to a range from 200 °C to 450 °C.

For the fabrication of Si (Li) *p-i-n* structures of large areas with silicon, we often encounter with problems that need to be addressed through an integrated approach. This is often due to the intense complexity of Li-O [17], the generation of thermal donors in the bulk of the crystal, and the formation of dipole structures in the places of accumulation of acceptor impurities. Especially monocrystalline Si grown by the Czochralski method consists of high amount of oxygen. However, the presence of oxygen and associated Li-O complexes largely determine the stability of the *p-i-n* structures.

Based on Rice's theory, it is going to be introduced the effect of oxygen complex on the effective diffusion coefficient of lithium. Suppose, we have constant concentration of oxygen complex (C_{O2}) in the total volume of *p*-type silicon, then the concentration of lithium atoms can be found as $C_{Li}(x) - p(x)$, where $p(x) = P$ is the concentration of Li_O complex. For lithium ion flux it is convenient to write:

$$J = -D_0\frac{\partial(C_{\mathrm{Li}} - p)}{\partial x}\,, \tag{3}$$

where D_0 is the diffusion coefficient without oxygen complexity.

Then the expression for the determination of lithium concentration can be found as

$$D(x) = \frac{D_0}{2}\left[\frac{C_{\mathrm{O2}}C_{\mathrm{Li}} - 2C_{\mathrm{Li}} + P^2}{C_{\mathrm{O2}}C_{\mathrm{Li}} - P^2}\right]. \tag{4}$$

To determine the temperature-time diffusion regimes of the diffusion profiles to be processed, the diffusion equation (1) must be solved taking into account the large concentration of the Li-O complex and boundary conditions (2). The solution of equation (1), when $D = \mathrm{const}$, can be represented as

We note that the diffusion coefficient depends on coordinate, because it is a function of the concentration distribution. To determine the diffusion profile in Si by the proposed method with respect to oxygen complex, the diffusion coefficient can be assumed

$$\frac{C(x,t)}{C_{\text{Li}}}=\frac{\int\limits_0^{L/2}\exp\left(-\frac{x^2}{4Dt}\right)dt+\int\limits_L^{L/2}\exp\left(-\frac{x^2}{4Dt}\right)dt}{\int\limits_0^{\infty}\exp\left(-\frac{x^2}{4Dt}\right)dt}= \quad (5)$$

$$=erfc\left\{\frac{x}{2\sqrt{Dt}}+\frac{L-x}{2\sqrt{Dt}}\right\}$$

$$D\left\{\begin{matrix} D_0/(1+K(T_0)C_{O2}),\text{when } 0<t<t_0 \\ D_0(t)/(1+K(T_0)C_{O2}),\text{when } t>t_0 \end{matrix}\right\} \quad (6)$$

Here $D_0 = A\exp(-B/T_0)$, $K(T) = K[T(t)]$ is the equilibrium constant for a given temperature T at time t. $A = 23 \times 10^{-4}$ cm²/sec and $B = 15200$ calories/deg are, respectively, the pre-exponential factor and the activation energy of the diffusion.

The solution of the diffusion equation (1) can be presented in the form:

$$\frac{c(x,t)}{c_s}=erfc\left\{\frac{x}{\sqrt{\frac{D_0t_0}{1+K(T_0)N_{O_2}}+A\int\limits_{t_0}^{t}\frac{exp(-B/T(t))}{1+K(T_0)N_{O_2}}dt}}+\right. \quad (7)$$

$$\left.+\frac{L-x}{\sqrt{\frac{D_0t_0}{1+K(T_0)N_{O_2}}+A\int\limits_{t_0}^{t}\frac{exp(-B/T(t))}{1+K(T_0)N_{O_2}}dt}}\right\}.$$

Fig. 2 shows the diffusion profiles in silicon samples after the double sided diffusion of Li ions grown by the Czochralski method and the floating zone method.

The diffusion profiles of two samples obtained by different methods differ significantly. This is due to a decrease in the effective diffusion coefficient because of the complex formation of Li-O in oxygen-containing silicon [18]. As seen from Fig. 2, a monocrystalline silicon grown by the Czochralski method has a large complex formations of Li-O. The Li-O complex reduces the concentration of electrically active lithium, but at the same time increases the solubility of lithium in low-ohmic silicon due to the high boron concentration (Rice's theory). As a result, there is a practical full compensation of most of the diffusion crystal by lithium ions, and incomplete compensation in the p-n junction region leads to a positive effect, that is, the boundary turns out to be sharper than in conventional silicon detector.

Fig. 3 shows the theoretical calculation of the diffusion profiles of lithium ions in monocrystalline silicon. The solution of the differential equation (1) was carried out taking into account the boundary conditions (2). The resulting profile in Fig. 3 shows the general solution of the differential equation of double sided diffusion in the form of expression (7). As can be seen from the figures, theoretical calculations are in complete agreement with the experimental data. The obtained graph of the theoretical distribution of lithium ions in silicon indicates a symmetrical concentration distribution with respect to the middle of the crystal. The sequence in expression (7) converges well for large values of DT/L^2.

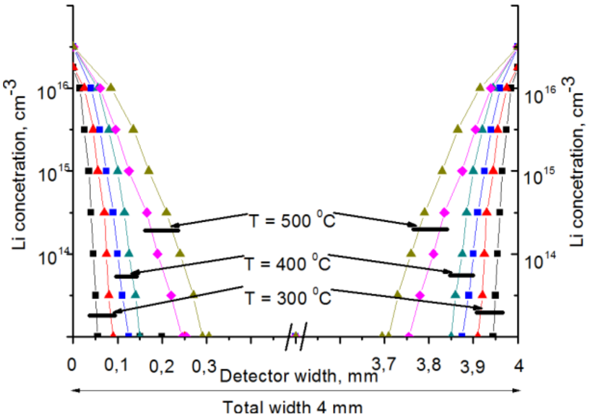

Fig. 2 – Experimental diffusion profiles of lithium ions in monocrystalline silicon for different temperature regimes: ■ – grown by the Czochralski method, Δ – grown by the floating zone method

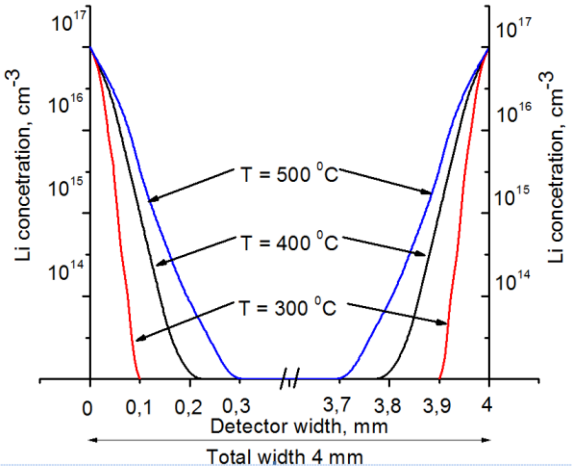

Fig. 3 – Theoretical diffusion profiles of lithium ions in monocrystalline silicon for different temperature regimes

4. CONCLUSIONS

In conclusion, the calculations and experimental data have shown that the optimal regime for lithium diffusion to obtain large-diameter detectors (≥ 110 mm) with a thickness of the sensitive region of more than 4 mm, at a temperature of 430-450 °C, $t = 3$ min, lithium penetration depth $h_{\text{Li}} = 300 \pm 10$ mm. According to the results of the experimental diffusion profile, it can be seen that monocrystalline silicon obtained by the floating zone method is well diffusible. The penetration of lithium ions into monocrystalline silicon obtained by the Czochralski method has a peculiar slowed-down character. This is due to a decrease in the effective diffusion coefficient due to the complex formation of Li-O in oxygen-containing silicon obtained by the Czochralski method.

For semiconductor detectors used for low-background installations, this result is very important because it opens up possibilities for improving their performance – increase in the registration efficiency through the formation of precision diffusion of thin controlled "dead layers" and decrease in the slope of the counting characteristic, especially in the area of low operating voltages. Moreover, the result obtained improves the energy resolution of a semiconductor detector.

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Фізичні особливості двосторонньої дифузії літію в кремній для великогабаритних детекторів

R.A. Muminov[1], A.K. Saymbetov[2], N.M. Japashov[2], Yo.K. Toshmurodov[1], S.A. Radzhapov[1], N.B. Kuttybay[2], M.K. Nurgaliyev[2]

[1] *Physico-Technical Institute of the Academy of Sciences of Uzbekistan, Tashkent 100084, Uzbekistan*
[2] *Al-Farabi Kazakh National University, Almaty 050000, Kazakhstan*

У роботі ми пропонуємо новий метод двосторонньої дифузії іонів літію в монокристалічну кремнієву пластину для подальшого виготовлення детекторів ядерного випромінювання Si (Li) з діаметром чутливої поверхні більше 110 мм і товщиною чутливого шару більше 4 мм. Встановлено, що оптимальний режим для дифузії літію у силікон великого розміру має місце при температурі $T = (450 \pm 20)$ °C, часі $t = 3$ мін та глибині проникнення літію $h_{\mathrm{Li}} = (300 \pm 10)$ мм. Розглянуто теоретичні припущення та експериментальні характеристики двосторонньої дифузії. Як вихідні матеріали, використовували монокристалічний циліндричний кремнієвий кристал p-типу без дислокацій, отриманий методом зонного плавлення (діаметром 110 мм, товщиною 8-10 мм, з питомим опором $\rho = 1000 \div 10000$ Ом·см і часом життя $\tau \geq 500$ мкс), і кремнієвий кристал p-типу, отриманий методом Чохральського (з діаметром 110 мм, питомим опором $\rho = 10 \div 12$ Ом·см, часом життя $\tau \geq 50$ мкс, вирощений в атмосфері аргону). Відповідно, вдосконалено технологічні процеси механічної та хімічної обробки напівпровідникових пластин на основі кремнію великої площі.

Ключові слова: Si (Li) детектори, Дифузія Li, Двостороння дифузія.