1 of 1

LBL-33967
UC-404

**Lithium Drifted Silicon Detector Fabrication
on Gettered Floating Zone Silicon**

J.T. Walton, Y.K. Wong and N. Derhacobian
Engineering Division, Lawrence Berkeley Laboratory
University of California, Berkeley CA 94720

and

E.E. Haller
Department of Material Science and Mineral Engineering, and
Materials Sciences Division, Lawrence Berkeley Laboratory
University of California, Berkeley CA 94720

November 1993

This work was supported by the Director, Office of Energy Research,
Office of Biological and Environmental Research, Analytical Technology Division,
of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

MASTER *ck*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Lithium Drifted Silicon Detector Fabrication on Gettered Floating-Zone Silicon

J.T. Walton, Y.K. Wong, and N. Derhacopian
Engineering Division,¹

Lawrence Berkeley Laboratory, University of California, Berkeley CA 94720
and

E.E. Haller

Department of Material Science and Mineral Engineering, and Engineering Division,¹
Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

Abstract

A gettering procedure using phosphorus doped glass is shown to remove lithium-ion precipitation sites from p-type Floating-Zone (FZ) silicon. A model involving interaction between grown-in vacancies and oxidation-injected silicon interstitials is proposed to explain the gettering procedure. Examples of silicon lithium-drifted detectors fabricated on ungettered and gettered FZ silicon are presented.

I. INTRODUCTION

The properties of the interstitial donor lithium in germanium and silicon were a very early experimental and theoretical interest in semiconductor physics [1]. These studies indicated that the pairing between lithium ions and various impurities in the semiconductor was a sensitive probe to the nature of these impurities (oxygen, boron) and of their distribution in a crystal [2,3]. It was also found that lithium could be used to determine defect (vacancy) concentrations [4]. With the subsequent realization that thick semiconductor regions could be made nearly intrinsic by the pairing (or compensation) characteristic of lithium ions, fabrication of lithium-ion compensated silicon detectors, Si(Li), as they are now known, was initiated at various laboratories [5]. While the fabrication of these Si(Li) radiation detectors is now the principal application for this lithium-ion compensation technique, there exists a residual interest in the diagnostic capabilities of this process.

In part this interest is fueled by the various defect structures that occur in single crystal silicon and that are still not fully understood, although the technology for growing silicon crystals is highly developed. Silicon crystals are normally grown by either the Czochralski (CZ) or Floating-Zone (FZ) techniques [6,7]. While the FZ process is technically more

challenging, the FZ crystals can have substantially lower impurity concentrations.

The FZ crystals are usually the material of choice for Si(Li) detector fabrication, and we normally use 1–2 k Ω FZ crystals in our Si(Li) detector process. However, even high quality FZ crystals can have impurities and defects that can severely impede the movement of lithium ions and, consequently, Si(Li) detector fabrication. In the following, we first show two results demonstrating the effect of vacancy-like defects on the Si(Li) fabrication process, and then discuss a gettering procedure for removing one defect type from FZ silicon crystals. In this paper, we use the lithium-ion compensation process as a diagnostic tool to assess the effectiveness of our gettering process and, in effect, return to the early studies of lithium in silicon.

II. LITHIUM COMPENSATION NON-UNIFORMITIES

While we have described our Si(Li) detector fabrication process in detail elsewhere [8], for the subsequent discussion we need to recall a few aspects of this process. Briefly, we fabricate Si(Li) detectors by first diffusing lithium into a p-type silicon substrate to form a pn junction. We then apply a reverse bias to this junction. The resulting electric field then moves lithium ions from the n⁺ lithium region into the p substrate. The rate of growth of the lithium compensated region, after an incubation period, is given by [9]:

$$\frac{dW}{dt} = \frac{\mu V}{W} \quad (1)$$

where W is the compensated region, μ the lithium ion mobility, and V the applied reverse voltage across the pn junction. The intrinsic region width, with constant applied voltage, after a time, t , is then:

$$W = (2\mu Vt)^{1/2} \quad (2)$$

¹ We gratefully acknowledge the encouragement and support that J.M. Jaklevic gave to this investigation. We are also appreciative of D. Lewak's efforts in installing SUPREM-IV on UX-5. This work was supported by the Director, Office of Energy Research, Office of Biological and Environmental Research, Analytical Technology Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

This simple equation often fails to predict correctly the intrinsic region growth. Variations in the apparent lithium-ion mobility, extending axially or radially in the crystal, can result in shallower compensated regions than would be expected from Eq. 2. In less severe cases, we have used Eq. 2 with a reduced "effective" lithium ion mobility to predict the Si(Li)

region growth. However, in our model of the compensation process, lithium ions drift through the crystal with a fixed mobility. A fraction of these ions is lost to crystal imperfections [precipitation sites] leading to a lower "effective" lithium ion mobility. This loss of lithium ions via precipitation sites can be accounted for by adding a "loss term" to Eq. 1 as follows [10]:

$$\frac{dW}{dt} = \frac{\mu V}{W} - \frac{W}{T} \quad (3)$$

where T is the lithium-ion lifetime. If the reverse voltage, the lithium ion mobility and lifetime remain constant, the compensated region width after a time, t , is then:

$$W = W_{\max}(1 - e^{-2\mu V t / W_{\max}^2})^{1/2} \quad (4)$$

where $W_{\max} = (\mu V T)^{1/2}$. Equation 4 predicts that the maximum compensated depth cannot grow beyond $W_{\max}$ when the lithium-ion lifetime is short. And we have observed experimentally this limit on W in many FZ crystals. Figures 1 and 2 show the effects of a short lithium-ion lifetime on the Si(Li) compensation depth. In both examples we subjected the wafers to drifting times twice that predicted by Eq. 2 to produce a fully Si(Li) compensated region. The results of Fig. 1 suggest that processes during the FZ growth produced regions of low lithium-ion lifetime and are characteristic of this particular crystal [11]. The results in Fig. 2 suggest a more systematic problem. We fabricated these Si(Li) detectors on two different FZ crystals from one vendor [12] and we have consistently, over many years and many FZ crystals, observed that the center of this vendor's p-type FZ silicon wafers cannot be lithium-ion compensated. We now attribute this to the presence of a high concentration of lithium-ion precipitation

Fig. 1. The entrance contact side of a Si(Li) detector fabricated on silicon cut along a crystal axis. The lightly shaded areas are copper decorated Si(Li) regions.

Fig. 2. Cross-sections of two 5 mm thick Si(Li) detectors fabricated on two different 50 mm diameter p-type FZ silicon crystals. The shallow Si(Li) compensated region in the center of each is evident.

sites at the center of these crystals. The remainder of our paper focuses on a gettering technique for removal of lithium-ion precipitation sites from these crystals.

III. DESCRIPTION OF GETTERING TECHNIQUE

Before 1975 the two principal observed defects in FZ single crystals (the so called A and B swirl defects) were assumed to be vacancy clusters. Since 1975 there has evolved a general agreement that the A and B defects in silicon crystals are agglomerations of silicon interstitials [13]. Further, the concentrations of the A and B defects are dependent on the silicon crystal growth rate. This dependence of the A and B defect concentrations, as well as the D defect concentration (vacancy clusters) which is only present in FZ silicon, is shown in Fig. 3. Roksnoer and Van den Boom [14], and, more recently, Abe and Kimura [15] have reported that, in FZ silicon, there are specific regions of the crystal where one defect type dominates over the others. Abe and Kimura's observations that the center of FZ crystals can have high concentrations of D defects are strikingly similar to our suggestion above that the presence of lithium-ion precipitation sites is responsible for the shallow Si(Li) compensated region at the center of the wafers in Fig. 2.

If the lithium-ion precipitation sites in the Fig. 2 crystals are due the presence of vacancies or vacancy clusters, thermal annealing or gettering should change their concentration. Recent studies have indicated that both vacancies and silicon interstitials have high diffusivities in silicon crystals [16]. Therefore it should be expected that thermal processing at modest temperatures should alter the vacancy or vacancy cluster concentration in a silicon crystal.

In the past decade the removal of detrimental imperfections in silicon crystals has been the subject of extensive theoretical and experimental research [17]. For silicon, the consensus view is that silicon interstitials play a primary role in a variety of gettering techniques. In particular, Abe and Kimura show that, with a gettering schedule of 20 minutes at 1000°C in wet oxygen, they could reduce the D defect concentration in their FZ crystals. The oxidation produced silicon interstitials that apparently combined with the D defects. However, a high concentration of phosphorus at the silicon surface is reported to be a more efficient source of silicon interstitials than an oxide layer alone [18]. Therefore, phosphorus silica glass formation should more effectively "getter" vacancy defects. If the shallow Si(Li) regions of Fig. 2 are due to the presence of vacancies, then a phosphorus glass gettering process should be effective in improving the lithium-ion lifetime in these regions.

The preceding discussion ignores other possible sources for a short lithium-ion lifetime—oxygen, metal impurities or internal strain. We are reasonably confident, based on our experimental results discussed below, that the short lithium-ion lifetimes in these crystals are due to the presence of vacancy clusters.

To test the above assumptions we used a phosphorus glass process to getter some 10 mm x 10 mm x 3 mm thick samples

from four crystals with known short lithium-ion lifetimes [19]. Our gettering procedure is: Phosphorus glass formation using a POCl_3 source and diffusion for 25 minutes at 950°C ; followed by a 100 minute drive-in diffusion at 950°C . Following this, we first removed the phosphorus glass and then fabricated, on each sample, a Si(Li) detector. In each gettered sample the rate of growth of the Si(Li) compensated region followed Eq. 2. There was no evidence of a reduced lithium-ion lifetime as was present in the original ungettered samples.

XBL 9310-1453

Fig. 3. The concentration of A, B, and D defects as a function of FZ crystal growth rate reported by Roksnoer and van der Boom [14].

We have now extended this gettering technique to the fabrication of larger detectors. Figures 4(a) and 4(b) show the lithium compensated regions, revealed by copper staining, present on two 75 mm diameters, 3 mm thick FZ wafers from the same crystal. The wafer in Fig. 4(a) is ungettered, while that in Fig. 4(b) has been gettered using the process described above. Below the wafer photographs are plots of the charge signals that we obtained by scanning a collimated ^{241}Am alpha source across each detector diameter. The detector in Fig. 4(a) is active only in an annular ring region, while the detector in Fig. 4(b) is active across the full diameter. Further, we "drifted" 4(b) only for a time sufficient, according to Eq. 2, to compensate a 3 mm thick wafer, while 4(a) we "drifted" for twice this time. The fact that 4(b) was compensated completely within the expected "drift time" clearly shows the dramatic change produced by our POCl_3 gettering procedure on the lithium-ion lifetime in this crystal.

IV. DISCUSSION

The possible mechanisms involved in this dramatic change in the lithium-ion lifetime can be simply illustrated with Fig. 5. In defect-free p-type silicon, lithium ions move through the crystal to compensate acceptor impurities (normally boron) present in the crystal (Fig. 5(a)). If there are precipitation sites, the lithium ions move to these sites and the flux of lithium ions flowing through the crystal decreases with increasing depth (Fig. 5(b)). With our gettering process,

the phosphorus rich glass growth at 950° C injects silicon interstitials into the wafer. These interstitials remove the precipitation sites (vacancy clusters) present (Fig. 5(c)). With the removal of the precipitation sites, the lithium ions move through the now "defect-free" crystal unimpeded (Fig. 5(d)).

The actual mechanisms involved here are more complicated than the preceding discussion would suggest. The interaction between vacancies and silicon interstitials has been extensively studied, using the dependence of various impurities (phosphorus, boron) diffusivities on the concentration of

these point defects. Law and Dutton [20] and Hu [21] have proposed that the interaction between these point defects can be described by the following coupled differential equations:

$$\begin{aligned}\frac{\partial C_I}{\partial t} &= D_I \frac{\partial^2 C_I}{\partial x^2} - K_r(C_I C_v - C_I^* C_v^*) \\ \frac{\partial C_v}{\partial t} &= D_v \frac{\partial^2 C_v}{\partial x^2} - K_r(C_I C_v - C_I^* C_v^*)\end{aligned}\quad (5)$$

Fig. 4. An ungettered (a) and gettered (b) 75 mm diameter, 3 mm thick FZ p-type wafer. The lightly shaded area on each is the Si(Li) compensated region. The ^{241}Am alpha scans shown below each wafer confirm that only the Si(Li) regions are active on these devices.

where C is the concentration, D the diffusivity, K_r the bulk recombination constant, superscript $*$ refers to the equilibrium conditions, and the subscripts I and V refer to interstitials and vacancies respectively.

Both analytical and numerical solutions to Eq. 5 have been proposed. A flexible solution routine to this equation is contained in the process modeling program SUPREM IV [22]. We have used SUPREM IV to model our gettering process and a few of our calculated results are shown in Figs. 6(a) and 6(b). In these calculations we used the SUPREM IV calculated default values for the diffusivities and bulk recombination constant.

We earlier compared the effectiveness of a 950° C oxidation gettering process with that of our present phosphorus glass processes. We found that the phosphorus glass was slightly more effective in removing lithium-ion precipitation centers. In our modeling of a 950° C, 240 minute oxidation (Fig. 6(a)), there is only a shallow region in which the vacancies are removed. For an oxidation at 1100° C, 240 minutes (Fig. 6(b)) the vacancies are reduced to a greater extent. This process proceeds at a higher temperature and for a longer time than we use in our gettering procedure. It is interesting that, with this higher temperature oxidation, the high initial vacancy concentration has been replaced by a high final interstitial silicon concentration.

The apparent discrepancy between our experimental results and the SUPREM IV modeling may be due to our get-

tering procedure removing vacancy clusters. In a recent speculative note, Buttery [23] suggested that vacancy clusters may move through crystalline structures with higher diffusivities than individual vacancies. Perhaps we have the first experimental confirmation of this hypothesis. Our experimental results, however, are in partial agreement with those of Abe and Kimura where, as we noted earlier, they reduced the

Fig. 5. A schematic representation of the effect of lithium-ion precipitation due to vacancy clusters and the removal of these clusters with our phosphorus gettering procedure.

Fig. 6. The SUPREM IV calculated normalized vacancy and silicon interstitial concentrations for oxidations at 950° C (a) and 1100° C (b) for 240 minutes.

D defect concentration in their crystals with a modest gettering process. We are planning additional measurements to obtain a quantitative understanding of the mechanisms involved here and how they can be used to fabricate thick (>3 mm), large area (>40 cm²) Si(Li) detectors on these crystals.

V. CONCLUSIONS

We have used the lithium-ion compensation process to demonstrate that we can improve the lithium-ion lifetime in some FZ p-type silicon crystals, using a phosphorus glass gettering process. We argue that this gettering process, via silicon interstitial injection, removes vacancy clusters that act as lithium-ion precipitation sites in these crystals. The removal of these precipitation sites improves the lithium-ion lifetime, thereby greatly increasing our ability to lithium-ion compensate completely these crystals.

However, our experimental results with the phosphorus glass gettering process do not agree with the present models of vacancy-silicon-interstitial interactions. We have therefore proposed that our gettering process is removing vacancy clusters, which we suggest may have a higher diffusivity in silicon than do individual vacancies.

Finally, with reference to Fig. 3, we conclude that the FZ crystal growth speed is most likely producing the lithium-ion precipitation sites. In the event that this conclusion is verified, new FZ crystal growth conditions designed to yield Si(Li) detector specific FZ silicon should be developed, thereby solving a problem that has confounded Si(Li) detector fabrication for more than a decade.

VI. REFERENCES

- [1] H. Reiss, C.S. Fuller and F.J. Morin, "Chemical Interactions Among Defects in Germanium and Silicon," *BSTJ*, Vol. XXXV, No.3, pp. 535-636, May 1956.
- [2] E.M. Pell, "Effect of Li-B Ion Pairing on Li⁺ Ion Drift in Si," *J. Appl. Phys.*, Vol. 31, No.9, pp. 1675-1679, Sept. 1960.
- [3] E.M. Pell, "Study of Li-O Interaction in Silicon by Ion Drift," *J. Appl. Phys.*, Vol. 32, No. 6, pp. 1048-1051, June 1961.
- [4] F.J. Morin and H. Reiss, "Precipitation of Lithium in Germanium," *J. Phys. Chem. Solids*, Vol. 3, pp. 196-209, 1957.
- [5] J.N. Elliot, "Thick Junction Radiation Detector Made by Ion Drift," *Nucl. Inst. and Meth.*, Vol. 12, pp. 249-253, 1961.
- [6] W. Zulehner, "Defects in CZ Silicon," *Semiconductor Silicon*, Berlin-Heidelberg:Springer-Verlag, 1989, pp. 127-152.
- [7] P. Drier, "High Resistivity Silicon for Detector Applications," *Nucl. Inst. and Meth.*, Vol. A288, pp. 272-277, 1990.
- [8] J.T. Walton, H.A. Sommer, D.E. Greiner, and F.S. Bieser, "Thin Window Si(Li) Detectors for the ISEE-C Telescopes," *IEEE Trans. Nucl. Sci.*, Vol. NS-25, No.1, pp. 391-396, 1978.
- [9] E.M. Pell, "Ion Drift in a n-p Junction," *J. Appl. Phys.*, Vol. 31, No. 2, pp. 291-302, FEB. 1960.
- [10] A.H. Sher and J.A. Coleman, "Lithium Driftability in Detector Grade Germanium," *IEEE Trans. Nucl. Sci.*, Vol. NS-17, pp. 125-129, 1970.
- [11] J.T. Walton, H.A. Sommer, A.C. Thompson, E.B. Hughes, and H.D. Zeman, "300-Element Silicon Lithium Position-Sensitive Imaging Detector for Angiography," *IEEE Trans. Nucl. Sci.*, Vol. NS-33, No. 1, pp. 537-542, 1986.
- [12] Wacker Siltronic Corp., Portland, OR.
- [13] H. Föll, U. Gösele, and B.O. Kolbesen, "The Formation of Swirl Defects in Silicon by Agglomeration of Self-Interstitials," *J. Crystal Growth*, Vol. 40, pp. 90-108, 1977.
- [14] P.J. Roksnoer and M.M.B. van den Boom, "Microdefects in a Non-Striated Distribution in Floating-Zone Silicon Crystals," *J. Crystal Growth*, Vol. 53, pp. 563-573, 1981.
- [15] T. Abe and M. Kimura, "Behaviour of Point Defects in FZ Silicon Crystals," *Semiconductor Silicon 1990*, Pennington, NJ:Electrochemical Society, 1990, pp. 105-117.
- [16] T.Y. Tan and U. Gösele, "Point Defects, Diffusion Processes and Swirl Defect Formation in Silicon," *App. Phys. A*, Vol. 37, pp. 1-17, 1985.
- [17] A. Ourmazd, "Gettering of Impurities in Silicon," *Oxygen, Carbon Hydrogen and Nitrogen in Crystalline Silicon*, Pittsburgh, PA:Materials Research Society, 1986, pp. 331-340.
- [18] C.S. Chen and D.K. Schoder, "Kinetics of Gettering in Silicon," *J. Appl. Phys.*, Vol. 71(12), pp. 5858-5864, June 1992.
- [19] J.T. Walton, N. Derhacopian, Y.K. Wong and E.E. Haller, "Lithium-ion Mobility Improvements in Floating-zone Silicon by External Gettering," *Appl. Phys. Lett.*, Vol. 63(3), pp. 343-345, July 1993.
- [20] M.E. Law and R.W. Dutton, "Verification of Analytic Point Defect Models Using SUPREM-IV," *IEEE Trans. on Computer Aided Design*, Vol. 7, No. 2, pp. 181-190, Feb. 1988.
- [21] S.M. Hu, "Interstitial and Vacancy Concentrations in the Presence of Interstitial Injection," *J. Appl. Phys.*, Vol. 57(4), pp. 1069-1075, Aug. 1985.
- [22] SUPREM-IV, Stanford University, Office of Technology Licensing, Stanford CA.
- [23] T. Buttery, *New Scientist*, 17 April 1993, p.49.

**DATE
FILMED**

11 / 13 / 94

END