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**Lithium-ion Mobility Improvement in Floating-zone Silicon by External Gettering**

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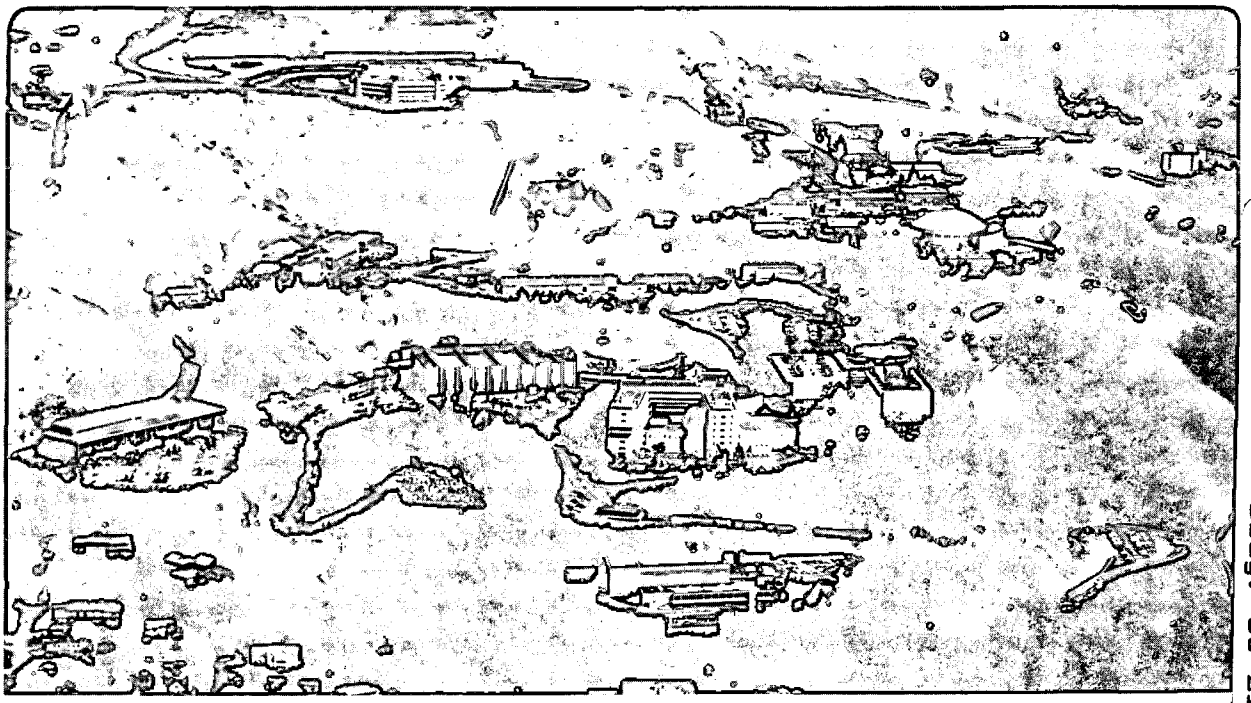

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# Lithium-ion mobility improvement in floating-zone silicon by external gettering

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## ABSTRACT

Phosphorus diffusion for approximately 1 hour at 950° C is shown to be an effective gettering procedure to remove lithium-ion mobility reducing defects in floating-zone (FZ) p-type silicon wafers. The removal of these defects, which can severely impede the movement of lithium ions in silicon wafers during lithium-ion compensation process, is crucial in the fabrication of silicon lithium-drifted radiation detectors.

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Charged particle spectroscopy, elemental x-ray detection, and particle track reconstruction are but a few of the applications in which silicon radiation detectors can be found today.[1] These detectors are based on the principle of collecting the charge produced by radiation passing through or stopping in the depletion region of a reverse-biased p-n junction. A simple reverse-biased silicon p-n junction, however, has a limited detection range due to the narrow depletion region (typically less than 500 μm) that is normally present. This limitation can be overcome by the well-established technique of "lithium-ion compensating" of p-type silicon to produce an extended intrinsic region and a p-i-n diode structure.[2] We have made these silicon lithium-compensated, Si(Li), detectors with depletion regions up to 10 mm wide with this technique, the specific details of which we have reported elsewhere.[3]

In general, Si(Li) detector fabrication consists of first diffusing lithium into the p-type silicon substrate to form a p-n junction and then applying a reverse bias to this junction to transport, with the electric field, lithium ions from the n region into the p substrate. These lithium ions pair with or compensate the boron acceptors present, forming a region that has a net charge density approaching zero (i.e., intrinsic). The electric field "drifting" of the lithium ions through the p-substrate is critically dependent on the substrate crystal perfection. Only a very small fraction of the total p-type silicon crystals produced can be properly lithium-ion compensated. In this paper we report on an effective gettering procedure that makes non-driftable p-type floating-zone (FZ) single crystal silicon driftable.

The effectiveness of any gettering procedure in the fabrication of Si(Li) detectors can be readily examined since, after an initial period, the rate at which the intrinsic region width, W, in a Si(Li) diode increases is given by:

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

where V is the applied voltage across the p-n junction and $\mu$ is the Li ion mobility.[2] The intrinsic region width after a time, t, then is:

$$W = \sqrt{2\mu V t}. \tag{2}$$

Equation (2) indicates that variations in the lithium ion mobility across the substrate will appear directly as variations in the intrinsic region depth in a Si(Li) detector. In an earlier paper we reported on lithium ion mobility variations that we had observed in FZ crystals with different growth conditions.[4] In many years of fabricating Si(Li) detectors, we have regularly encountered crystals with axial and/or radial lithium ion mobility variations. These variations, we believe, are due to the presence of sites in the FZ silicon crystal where the lithium ions are first trapped and in time form precipitates. A typical result is shown in Fig. 1 where the lithium ions have fully drifted through the silicon wafer near the crystal periphery, but have not drifted through in the center. This occurred despite that we "over-drifted" this 5 mm thick wafer for a time long enough to have compensated a region 7 mm thick in a defect free crystal.

For crystals like the one of Figure 1, the growth rate of the intrinsic region, W, is described by expanding Equation (1) to include a second term:

$$\frac{dW}{dt} = \frac{\mu V}{W} - \frac{W}{\tau_L} \tag{3}$$

where $\tau_L$ is defined as "the Li ion lifetime time constant".[5] Assuming the reverse voltage ($V$), the lithium ion mobility ($\mu$), and the "lifetime" ($\tau_L$) remain constant, the compensated region width after a drift time, t, is:

$$W = W_{max}\sqrt{1 - e^{-\frac{2t}{\tau_L}}} \tag{4}$$

where $W_{max}=(\mu V \tau_L)^{1/2}$. Equation (4) shows that the compensated region cannot grow beyond $W_{max}$ when lithium-ion lifetime is short. This limitation on the lifetime results from, as we believe, lithium-ion precipitation sites present in the crystal. This equation well approximates what we observe experimentally on the growth with time of the compensated region.

In the following, we report on a gettering procedure that quantitatively removes lithium-ion precipitation sites which are responsible for the results in Figure 1. In our Si(Li) fabrication process we typically use FZ single crystal [111] p-type silicon wafers with resistivities in the range $10^3 \Omega cm$ to $10^4 \Omega cm$ and lifetimes greater than 1 millisecond. We have restricted our study here to crystals with these nominal specifications.

The removal of detrimental impurities and defects in silicon crystals via various gettering techniques has been the subject of extensive experimental and theoretical research over the past decades.[6,7] These gettering techniques have been classified into two groups, internal gettering and external gettering. There appears to exist a consensus that silicon interstitials play a primary role in both.[8]

In considering either internal or external gettering to reduce or eliminate lithium-ion precipitation sites in silicon wafers, we first had to address the role of oxygen in the silicon lattice. It is known that oxygen at high concentrations in silicon can greatly reduce the lithium ion mobility by forming lithium-oxygen pairs that are somewhat immobile.[9] For example, we have never successfully lithium-ion compensated Czochralski (CZ) grown silicon crystals because, we believe, of their high oxygen content ($10^{18}$ $cm^{-3}$).[9] FZ silicon crystals, conversely, have typical oxygen levels that are much lower ($10^{16}$ $cm^{-3}$) and any difficulties in lithium compensating FZ crystals are more likely due to lithium-ion precipitation sites caused by metallic impurities or crystalline defects.[11] Reported oxygen removal, via internal gettering, requires many hours at high temperatures (>900° C) to effectively "denude" a shallow region (<100 μm) of interstitial oxygen.[12] Clearly, if the problem with the crystal in Fig. 1 were due to oxygen, it would impossible to denude an entire 2–5 mm thick Si wafer of oxygen.

In contrast to internal gettering which, for oxygen, promotes the formation of oxygen precipitates in a crystal, external gettering has been used to remove metallic impurities, specifically the so called fast diffusers (Cu, Ni, Fe, and Au), from silicon crystals.[13] This process, typically based on diffusion from a phosphorus doped glass, can be very fast, with the entire Fe content of a 3 mm thick wafer reportedly gettered in less than 2 hours at 900° C.[8] In addition, external gettering has been demonstrated, with gettering schedules of 20 minutes at 1000° C in wet oxygen, to substantially reduce the concentration of D-

defects (vacancy clusters) in FZ silicon.[14] Therefore, if the nonuniform lithium-ion mobility in the crystals of Fig. 1 is due to the presence of lithium precipitation sites caused by the presence of fast diffusers and/or D- defects, it would be reasonable to expect that lithium driftability of 3–5 mm thick wafers could be improved by an external gettering process with modest processing temperatures and times.

On the basis of the above analysis and published diffusion coefficients for the fast diffusers and silicon interstitials, we decided to getter a few FZ crystals, with known nonuniform lithium ion mobility.[15] The external gettering procedure was as follows: phosphorus glass formation and diffusion using a $POCl_3$ source at 950° C for 100 minutes. The vendor specifications for the p-type FZ crystals employed in our tests are summarized in Table 1.

To test the effectiveness of our gettering process on each crystal listed in Table 1, we fabricated Si(Li) detectors on 10x10 $mm^2$ and 3 mm thick samples that we cut from these crystals. Of five adjacent samples, three were gettered. Two of these and one ungettered sample were run through our Si(Li) fabrication process. We took the other two samples, one gettered and one ungettered, and prepared samples for Deep Level Transient Spectroscopy (DLTS) measurements.[16] We will discuss our Si(Li) results below, while our DLTS measurements we will publish in a subsequent paper.

In fabricating these sample Si(Li) detectors we used computer controlled drift stations.[17] For the 3 mm thick samples we conservatively set the computer program to stop the drift after a calculated compensated drift depth of 4.0 mm was accrued—that is, we purposely over-drifted these samples. Upon termination of the drift, we scanned each sample with a 1.0 mm diameter collimated $^{241}$Am alpha source to find the size of the intrinsic region, if any, present. This is a sensitive test of the intrinsic active volume in a Si(Li) detector since the $^{241}$Am alphas penetrate about 25 μm into the silicon and we detect a full energy signal only when the intrinsic region reaches completely across the Si(Li) detector. In Table 2 we have summarized our gettering experiments and the corresponding results of our $^{241}$Am alpha scans. The voltages listed in the last column are those at which we first obtained a full energy alpha signal across the entire device. Devices specified as "no alpha signal" did not show any alpha signals with 1000 volts reverse bias.

Finally, since a principal use of Si(Li) detectors is the detection of low energy x-rays, we also checked the performance of our gettered Si(Li) samples in detecting Mn X-rays from an $^{55}Fe$ source. The results from one of these measurements are shown in Fig. 2.

While the results summarized in Table 2 clearly show that our phosphorus diffusion gettering procedure is very effective in removing or reducing lithium-ion precipitation sites in these crystals, the gettering does not appear to be due to phosphorus dopant alone. As noted in the table we also attempted to getter using a phosphorus implantation ($5.7 \times 10^{15}$ $cm^{-2}$) and comparable (950° C) annealing schedule without success. In contrast a low temperature (950° C) wet oxidation was successful, but not as effective as the phosphorus diffusion. The oxide gettered devices required a higher voltage (400 V versus 300 V) to deplete than the phosphorus gettered samples.

Thus we conclude that the presence of the phosphorus doped glass resulting from the $POCl_3$ diffusion is the effective gettering agent in removing lithium precipitation sites from these crystals. An unambiguous identification of these sites awaits further experiments. But our gettering results clearly show that we are dealing with a crystalline imperfection that is very rapidly gettered. In the preceding, we suggested that fast diffusers and/or D- defects could be gettered by modest processing temperatures and times. We have not, with our DLTS measurements to date, detected any of the fast diffusing metals in our samples. Therefore, we assume that the phosphorus gettering procedure, by the injection of silicon interstitials, is possibly removing D-defects (vacancy clusters) in these crystals.

In summary, we have shown with several FZ p-type crystals that external gettering using a phosphorus doped glass diffusion for about an hour at 950° C effectively removes lithium-ion mobility reducing imperfections, most likely D-defects, from depths as large as 3 mm and perhaps larger. Our simple gettering procedure overcomes a lithium drifting problem that has been encountered by most Si(Li) manufacturers for more than two decades.

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## References


1. E. E. Haller and F. S. Goulding, in Handbook on Semiconductors vol. 4, edited by C. Hilsum, p. 799 (North-Holland Publishing Company, New York 1981); revised version in press.

2. E. M. Pell, *J. Appl. Phys.* **31**, 291 (1960).

3. J. T. Walton, H. A. Sommer, D. E. Greiner, and F. S. Bieser, *IEEE Trans. Nucl. Sci.* **NS-25 (1)**, 391 (1978).

4. A. Fong, J. T. Walton, E. E. Haller, H. A. Sommer, and J. Goldberg, *Nucl. Instr. and Methods* **199**, 623 (1982).

5. A. H. Sher and J. A. Coleman, *IEEE Trans. Nucl. Sci.* **NS-17 (3)**, 125 (1970).

6. C. S. Chen and D. K. Schroder, *J. Appl. Phys.* **71**, 5858 (1992).

7. F. Shimura and W. Bergholz, in Semiconductor Silicon 1990, edited by H.R. Huff, *et al*, 567 (Electrochemical Society, Pennington, N. J. 1990).

8. A. Ourmazd, in Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon, edited by J. C. Mikkelsen, *et al*, 331 (Materials Research Society, Pittsburgh, PA 1986).

9. E. M. Pell, *J. Appl. Phys.* **32**, 1048 (1961).

10. W. Zulehner, in Semiconductor Silicon 1990, *ibid*, 30.

11. P. Drier, *Nucl. Instr. and Methods* **A288**, 272 (1990).

12. T. Y. Tan, in Defects in Silicon II, edited by W.M. Bullis, *et al*, (Electrochemical Society, Pennington, NJ 1991).

13. A. Seeger, and K. P. Chik, *Phys. Stat. Sol.* **29**, 455 (1968).

14. T. Abe and M. Kimura, in Semiconductor Silicon 1990, *ibid.*, 105.

15. T. Y. Tan and U. Gösele, *Appl. Phys. A* **37**, 1 (1985).

16. D. V. Lang, *J. Appl. Phys.* **45**, 3023 (1974).

17. D. A. Landis, Y. K. Wong, J. T. Walton and F. S. Goulding, *IEEE Trans. Nucl. Sci.* **NS-36 (1)**, 185 (1989).

## TABLE 1

Vendor specifications for the FZ p-type Si crystals employed in our gettering experiments.

| crystal # | diameter (in.) | lifetime (μs) | ρ (Ωcm) |
|---|---|---|---|
| 1 | 5 | >1000 | 1000–2000 |
| 2 | 4 | >3400 | 6600–8200 |
| 3 | 4 | >1000 | 2870–3600 |
| 4 | 3 | >2000 | 900–1200 |

## TABLE 2

Summary of Si(Li) detector performance fabricated on gettered and ungettered FZ p-type Si wafers.

| crystal # | procedure | $^{241}$Am-α scan signal |
|---|---|---|
| 2 | Ungettered | No α signal |
| 2 | Phosphorus diffusion at 950° C for 100 min. | Full area (200V) |
| 2 | Annealed at 950° C for 100 min. | No α signal |
| 2 | Phosphorus implantation and annealed at 950° C for 100 min. | No α signal |
| 2 | Wet oxidation at 950° C for 100 min. | Full area (400V) |
| 1 | Phosphorus diffusion at 1000° C for 100 min. | Full area (400V) |
| 1 | Phosphorus diffusion at 950° C for 100 min. | Full area (300V) |
| 1 | Phosphorus diffusion at 900° C for 100 min. | Full area (200V) |
| 1 | Phosphorus diffusion at 850° C for 100 min. | Full area (200V) |
| 4 | Ungettered | No α signal |
| 4 | Phosphorus diffusion at 950° C for 100 min. | Full area (200V) |
| 3 | Ungettered | No α signal |
| 3 | Phosphorus diffusion at 950° C for 100 min. | Full area (200V) |

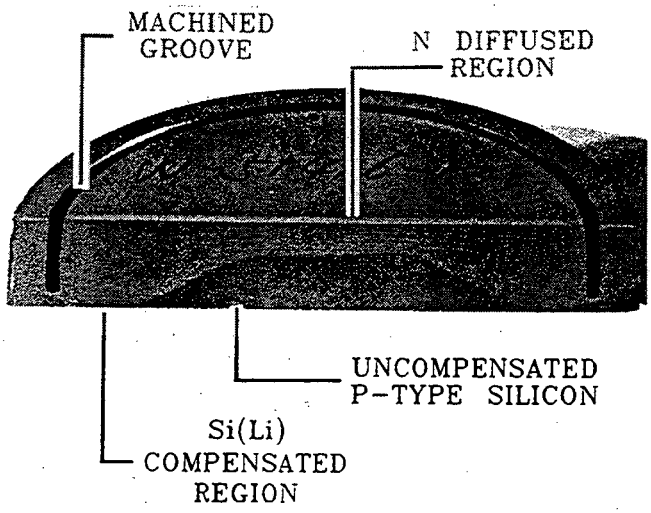


Figure 1 A photograph of a 2 inch diameter, 5 mm thick Si(Li) detector that we cut in half and copper stained to reveal the lithium-ion compensated region. The radially nonuniform compensated region indicates that this silicon crystal has probably a much higher density of lithium-ion precipitation sites at the center than at the edge. The grooves machined into the crystal are part of our Si(Li) detector fabrication process.[3]

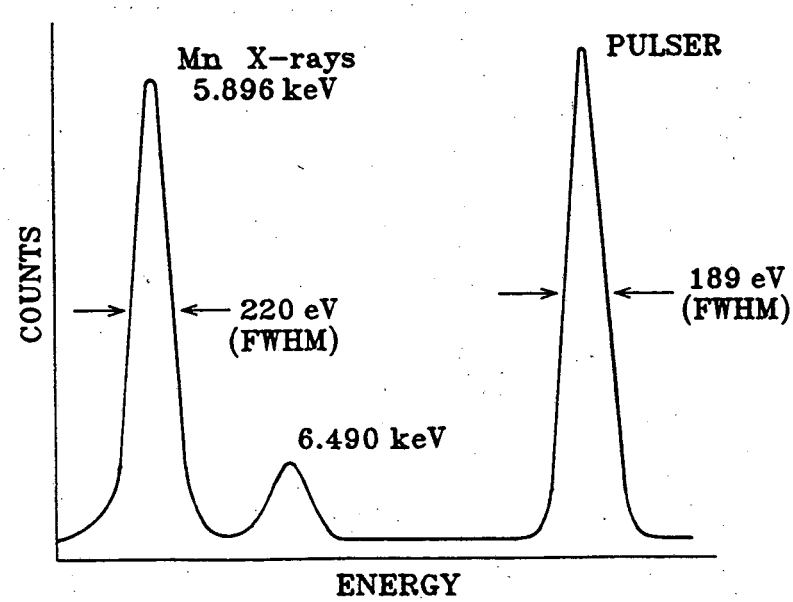


Figure 2 Mn X-rays from an $^{55}Fe$ source observed with one of our gettered 3 mm thick, 8 mm diameter Si (Li) sample detectors. The spectral resolution of 220 eV (FWHM) is what would be expected for the 5.9 keV Mn X-ray and a system resolution of 189 eV (FWHM).

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