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**ION IMPLANTED N-TYPE CONTACT FOR HIGH-PURITY GERMANIUM RADIATION DETECTORS**

G. Scott Hubbard, Eugene E. Haller and William L. Hansen

**ABSTRACT**

Thin large-area n⁺ contacts on high-purity germanium detectors have been produced by implantation of 25 keV phosphorous ions. The contacts show leakage current of < 10⁻⁹ A up to fields of > 2000 V/cm. Unannealed lattice damage may still limit the maximum applied field, but proper surface treatment prior to implantation and subsequent annealing steps have resulted in a dramatic improvement in the applied field. Spectra are presented which demonstrate that the n⁺ window is thin and the spectrometer performance is excellent.

**INTRODUCTION**

It is well known that non-injecting contacts on large-volume high-purity Ge radiation detectors can be reliably produced by using an evaporated metal Schottky barrier and a lithium diffused n⁺ contact. The metal barrier is inherently thin (< 1000 Å), but in practice the lithium diffused contact cannot be made thinner than approximately 25 μm. When such a detector is radiation damaged and requires annealing, the lithium diffuses even further into the Ge bulk, increasing the dead layer thickness.

For most applications, the lithium diffused contact is thin enough that alternatives have not been vigorously pursued, although some investigations have been published. However, high-energy charged particle experiments utilizing Ge detector telescopes require n⁺ contacts which are thin (< 1 μm) and remain so upon annealing at moderate (< 420K) temperatures.

It has been known for some time that boron ions implanted in p-type Ge become electrically active without annealing, producing a rectifying p⁺ contact. Similar studies have shown that phosphorous ions implanted in n-type Ge at low energies (~ 15 keV) become electrically active upon annealing at temperatures between 470 and 470K. In light of this seemingly positive result, it is somewhat puzzling that no subsequent published studies have thoroughly examined the use of implanted phosphorous for a thin n⁺ contact.

A slightly different method for making doped implanted layers has been studied for silicon. First, an amorphous layer of silicon was formed by high energy (200 keV) implantation of Si ions, followed immediately by implantation of a donor such as arsenic. At sufficiently high temperatures the amorphous layer was regrown, incorporating some of the donors into the lattice and thereby creating an n⁺ layer. The difficulty in forming a non-injecting contact in this manner lies in removing the lattice damage created by implantation. Remaining lattice defects can cause minority carrier injection, preventing any substantial electrical field at the contact. Transmission electron microscopy has shown that silicon made amorphous in this manner and subsequently regrown contains 10⁷ - 10⁸ residual lattice defects/cm², including a layer of damage extending 500 Å beyond the range of the original implant.

We have produced such regrown doped contacts in Ge by implanting first Ge ions at energies from 40 keV to 200 keV and doses of 10¹⁵ - 10¹⁶ cm⁻² while holding the sample at 77K. This implant created an amorphous layer approximately 1500 Å thick. Without breaking the vacuum, arsenic ions were then implanted at energies between 40 and 120 keV with a dose of 10¹⁴ cm⁻². Subsequent annealing at temperatures between 570 and 770K resulted in a regrown n⁺-type surface layer, as determined by thermoelectric probing. However, all attempts to use this surface as a blocking contact have met with failure. When the implanted samples were prepared as radiation detectors a reverse bias as low as 10 V invariably resulted in reverse currents of at least 1 μA—much too high for our use. 2 MEV alpha particle channeling measurements showed that a single crystal layer was regrown in our samples at 595K. However, the sensitivity of the channeling measurement is such that lattice disorder of less than 1% cannot be detected. This condition would imply an upper limit of 10⁻² defect centers cm⁻³, quite enough to account for high leakage currents.

As will be seen later, other evidence supports the idea that unannealed damage, particularly beyond the end of the range of the implanted ions, limits device performance.

**EXPERIMENTAL**

Following the lines of the work cited earlier we have implanted phosphorous ions into high-purity Ge (both n and p type) at 25 keV. Beam current was held to approximately 1 μA/cm² to reduce sample heating and samples were implanted off the crystal growth axis (100) to avoid channeling. Implant dose as well as pre and post implant treatment were varied. To minimize the end of range damage and prevent premature regrowth most samples were maintained at liquid nitrogen temperature (77K) during implantation. A few implants were made with the samples hot (570K) and at room temperature (300K). The higher temperature implants resulted in diodes with excessive leakage for our application and were not investigated further.

Prior to implantation the samples were first lapped with 1900 grit lapping compound, then etched for 1 - 2 min with a 7:2:1 mixture of HNO₃:HF:red fuming HNO₃ and finally rinsed with distilled de-ionized water (DDW). Additional etching with 1% HF for 5 - 10 min followed by a DDW rinse was used for the later samples. The samples were always blown dry with boil-off N₂.

The phosphorous bombardment was carried out in a vacuum of 2 x 10⁻⁷ torr or better using an Extrion implanter and an ion source gas mixture of 15% phosphine and 85% hydrogen. Following implantation, most
samples were annealed in an argon atmosphere with the temperature programmed to increase $10^\circ/10$ min from room temperature to 620K. In samples with high dose ($10^{16}$ cm$^{-2}$) it was necessary to anneal to 670K to remove the 'bluish' tinge apparently associated with an amorphous surface layer. After annealing, the samples were allowed to cool slowly (~2°/min) to room temperature. The samples were then prepared and tested as radiation detectors.

Leakage current vs applied reverse bias curves were measured. Knowing the net concentration ([N$_A$-N$_D$]) of the sample, the resultant electric field at the n$^+$ contact could then be computed. Figure 1 shows the I/V curves for similar crystals receiving different implant doses and surface treatments. Table 1 gives the concentration and computed field for each crystal at the maximum usable leakage current for typical detector systems ($\sim 10^{-9}$ A).

In practice it has been found useful to evaporate a 1 - 2 mm lithium ring at the periphery of the implanted contact. This ring makes handling of the detector through various lapping and etching stages less critical and helps to prevent breakdown at the edge of the detector where the thin n$^+$ contact makes an abrupt junction with the high-purity Ge. Annealing to a temperature of 420K would not diffuse such a narrow ring far enough to present any substantial dead layer.*

All finished detectors were tested for resolution and contact window thickness by examining the spectra of $^{60}$Co gamma radiation and $^{241}$Am alpha particles passed through the n$^+$ contact.

* 420K is the highest temperature we have ever used to remove severe radiation damage incurred in nuclear experiments.

![Image]

**Fig. 1.** I/V characteristics of several representative detectors are shown. Note the dramatic improvement where the 1% HF treatment was used prior to implantation. Leakage current is total leakage for each full size device (~3 cm dia., 0.5 - 1.0 cm thick). N-type detector 201-7.6 makes use of a guard ring on the Schottky barrier face to eliminate surface effects.

<table>
<thead>
<tr>
<th>DETECTOR</th>
<th>($N_A$-$N_D$)</th>
<th>$V_d$</th>
<th>$V_a$</th>
<th>$E_c$</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>457-5.5</td>
<td>$3 \times 10^{15}$</td>
<td>430</td>
<td>6</td>
<td>200</td>
<td>NONE</td>
</tr>
<tr>
<td>457-5.0</td>
<td>$3 \times 10^{15}$</td>
<td>320*</td>
<td>20</td>
<td>370</td>
<td>NONE</td>
</tr>
<tr>
<td>466-3.2</td>
<td>$4.5 \times 10^{15}$</td>
<td>250</td>
<td>7</td>
<td>270</td>
<td>NONE</td>
</tr>
<tr>
<td>194-5.0</td>
<td>$8 \times 10^9$</td>
<td>200</td>
<td>350</td>
<td>1000</td>
<td>1% HF</td>
</tr>
<tr>
<td>201-7.6</td>
<td>$-1.7 \times 10^{15}$</td>
<td>1100</td>
<td>2500</td>
<td>1300</td>
<td>1% HF</td>
</tr>
<tr>
<td>475-2.0</td>
<td>$4 \times 10^{15}$</td>
<td>400</td>
<td>475</td>
<td>2000</td>
<td>1% HF +</td>
</tr>
<tr>
<td>482-10.0</td>
<td>$2 \times 10^{15}$</td>
<td>1200</td>
<td>600</td>
<td>1900</td>
<td>&quot;Pre-Anneal&quot; after implantation</td>
</tr>
</tbody>
</table>

($N_A$-$N_D$) : Net shallow impurity concentration

$V_d$ : Depletion voltage

$V_a$ : Maximum operating voltage

$E_c$ : Electric field on n$^+$ contact at $V_a$

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Varying the phosphorous dose by three orders of magnitude produced a significant change in the diode characteristics, as can be seen in Fig. 1. Not shown is a sample implanted under the same conditions with a dose of \(10^{15} \text{cm}^{-2}\). In this case no surface color changes were noted immediately after the implant and annealing produced no n-type surface as measured at room temperature by thermoelectric probing. Devices exposed to higher doses exhibited a 'bluish' color on the surface due to lattice disorder after implanting and were clearly n-type on the surface after annealing. We conclude that \(10^{15} \text{cm}^{-2}\) phosphorous is too low a dose to produce substantial electrical activity at our annealing temperatures so all our subsequent work used higher doses. A dose of \(10^{16} \text{cm}^{-2}\) is equivalent to \(-10^{28} \text{cm}^{-3}\) in our case, where the implanted layer is \(-1000 \AA\) thick. This concentration approximates the solubility limit for phosphorous in Ge. It is therefore not surprising that \(10^{16} \text{cm}^{-2}\) ions, exceeding the solubility limit, should produce a poor diode. Precipitation, formation of alloy phases and extreme lattice deformation could all contribute problems. On the other hand \(10^{17} \text{cm}^{-2}\) generate too few active impurities after annealing to 620K and so the resulting diode did not meet our criteria.

Since a dose of \(10^{15} \text{cm}^{-2}\) repeatedly produced a contact with the most promising \(1/V\) curve and sustaining the greatest field, further experiments varied other parameters while holding the dose constant. Of these other variables, the most important for improving device performance has been surface treatment prior to implantation. Previous work on regrown epitaxial layers has demonstrated that effective substrate cleaning prior to layer deposition could be accomplished by a final etching with 1% HF followed by DDW rinse. Application of this method prior to implanting \(^{31}\text{P}\) yielded an immediate and reproducible increase in the field sustained by the implanted contact. In all cases three to four times greater field could be applied (see Table I and Fig. 1).

The dramatic improvement of our contact achieved by use of this cleaning process strongly suggests that unannealed damage beyond the phosphorous doped region, created by knock-on of the light ions (oxygen, fluorine, nitrogen) composing surface contaminants, is the source of excessive reverse currents. Residual radiation damage inside the heavily doped layer is either removed more completely by donor-vacancy complex formation or is overcompensated by the electrically active donor concentration.

It should be noted in Fig. 1 that device 201-7.6 is n-type, thus the device depletes from the Schottky barrier toward the implanted contact. Therefore, no field is present at the n+ layer until after full depletion. 194-5.0, on the other hand is p-type, so a field is present at any bias at the n+ contact. In both cases the devices were full size (3 - 4 cm diameter, 5 mm - 1 cm thick), although the n-type detector had a grounded guard ring applied at the Schottky barrier face to reduce surface leakage problems.

The maximum field at the n+ contact has been further increased a factor of ~2 by introducing a "pre-annealing" stage,\(^5\) of 1 - 2 hrs at 420K. This improvement suggests that the remaining p-type damage layer caused by knock-on of residual light elements may be substantially removed by such a process. By analogy, a similar low-temperature technique has been shown to be very effective in removing neutron damage from high-purity Ge detectors.\(^2\)

\(^{241}\text{Am} alpha spectra (Fig. 2) show the influence of this "pre-annealing" stage and confirm that the contact is quite thin. Using the FWHM and equations given elsewhere\(^1\) one can calculate that 57 keV corresponds to a dead layer of ~1 \(\mu\)m, whereas 20 keV represents a layer of only 0.3 - 0.4 \(\mu\)m. The latter result is in good agreement with published work on the depth vs concentration profile of phosphorous in Ge,\(^6\) again suggesting that the "pre-annealing" has removed a substantial dead layer of additional damage.

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**Fig. 2.** 5.48 MeV alpha particles are passed through n+ contact. Detector 473-2.0 has been given an additional "pre-annealing" stage of 1½ hours at 420K. The shift in peak position is due to the difference in dead layer thickness. 20 keV represents a window of 0.3 - 0.4 \(\mu\)m.

The \(^6\text{Co}\) spectrum (Fig. 3) shows that the charge collection properties of the device are undisturbed by the implanted contact as long as the bias is sufficiently high. In n-type Ge detectors with an implanted n+ contact, \(^6\text{Co}\) gamma peaks are shifted down about 1% in energy from their expected positions when the applied reverse bias is well below depletion. This effect may be explained in terms of a ballistic deficiency caused by the resistance of the undepleted bulk and the capacitance of the n+ implanted layer — p+ damage region. Such an explanation is consistent with the experimental observation that no energy shifts occur in devices made from p-type Ge.
DETECTOR
201.7
-1500V BIAS

ENERGY (keV)

Fig. 3. $^{60}$Co gamma-rays through the phosphorous implanted contact show excellent spectrometer performance. This result indicates there was no significant deterioration of the bulk of the crystal from implanting or annealing.

CONCLUSION

We have demonstrated that phosphorous implantation is a useable technique for producing a thin, stable n+ contact on high-purity Ge radiation detectors. Present contacts appear to be limited by excess current injection at electric fields above -2000 V/cm but several possibilities for improved detector performance include: 1) lower temperature during implantation, 2) sputter etching before implantation, and 3) varied dose.

ACKNOWLEDGMENTS

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REFERENCE

8. L. Csepregi, private communication.
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