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

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ABSTRACT

Thin large-area n+ contacts on high-purity
germanium detectors have been produced by implanta-
tion 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 sur-
face treatment prior to implantation and subsequent
annealing steps have resulted in a dramatic improve-
ment 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.[1] 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[2]
and requires annealing, the lithium diffuses even
further into the Ge hulk, 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.[2] 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) tempera-
tures.

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.[3]
Similar studies have shown that phosphorous ions
implanted in n-type Ge at low energies (~ 15 keV)
become electrically active upon annealing at tem-
peratures between 470 and 670K.[4] 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:[5]
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-inject-
ing 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 sub-
sequently regrown contain 10^7 - 10^8 residual lattice
defects/cm², including a layer of damage extending
500 Å beyond the range of the original implant.[6]

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 10^{15} - 10^{16} 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
10^{15} cm⁻². Subsequent anneals at temperatures
between 570 and 770K resulted in a regrown n-type
surface layer, as determined by thermoelectric prob-
ing. However, all attempts to form 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.[7] 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^{21} 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[7]
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 heat-
ing and samples were implanted 8° 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 pre-
mature regrowth most samples were maintained at liquid
nitrogen temperature (77K) during implantation.[10] A
few implants were made with the samples hot (570K)
and at room temperature (300K). The higher tempera-
ture implants resulted in diodes with excessive leak-
age 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% phos-
phine and 85% hydrogen. Following implantation, most
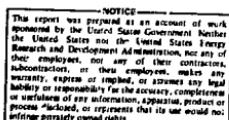
samples were annealed in an argon atmosphere with the
temperature programmed to increase 10°/10 min from
room temperature to 620K. Recently we have also
introduced a 'pre-annealing' stage of 1 - 2 hrs at
420K before continuing to 620K. In samples with high
dose (10^{16} cm^{-2}) it was necessary to anneal 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 ($\approx 10^{-9}$ 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 ^{57}Co gamma radiation and ^{241}Am alpha particles
passed through the n$^+$ contact.

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* 420K is the highest temperature we have ever used
  to remove severe radiation damage incurred in
 nuclear experiments.
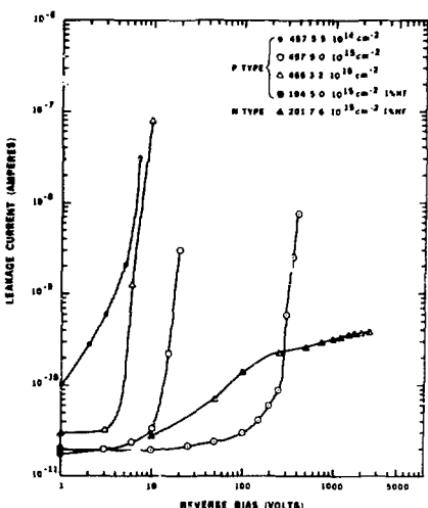
Fig. 1. I/V characteristics of several representative
detectors are shown. Note the dramatic
improvement where the 1% HF treatment was
used prior to implantation. Leakage current
is total leakage for each full size device
(~3 cm dia., 0.5 - 1.0 cm thick). N-type
detector 201-7.6 makes use of a guard ring
on the Schottky barrier face to eliminate
surface effects.

TABLE 1

DETECTOR	(N_A-N_D) (atoms/cm^3)	V_d (Volts)	V_a (Volts)	E_c (Volts/cm)	COMMENTS
457-5.5	3×10^{10}	430	6	200	NONE
457-5.0	5×10^{10}	320	29	570	NONE
466-3.2	4.5×10^{10}	250	7	270	NONE
194-5.0	8×10^9	200	350	1000	1% HF
201-7.6	-1.7×10^{10}	1100	2500	1500	1% HF
473-2.9	4×10^{10}	400	475	2000	1% HF + "Pre-Anneal" after implantation
482-10.0	2×10^{10}	1200	600	1900	

(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^{13} 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^{13} 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^{15} cm^{-2} is equivalent to 10^{20} cm^{-3} in our case, where the implanted layer is 1000 Å thick. This concentration approximates the solubility limit for phosphorous in Ge. It is therefore not surprising that 10^{17} 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^{14} ions 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} cm^{-2} repeatedly produced a contact with the most promising I/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 10% rinse.[8] Application of this method prior to implanting [9] yielded an immediate and reproducible increase in the field sustained by the implant contact. In all cases three to four times greater field could be applied (see Table 1 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[9] 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]

²⁴¹Am 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[12] one can calculate that 57 keV corresponds to a dead layer of ~1 μm, whereas 20 keV represents a layer of only 0.3 - 0.4 μm. 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.
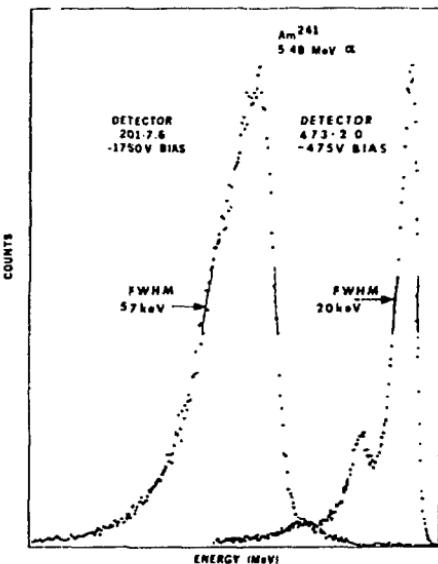

Fig. 2. 5.48 MeV alpha particles are passed through n⁺ contact. Detector 473-2.0 has been given an additional "pre-annealing" stage of 1 ½ hours at 420K. The shift in peak position is due to the difference in dead layer thickness. 20 keV represents a window of 0.3 - 0.4 μm.

The ⁶⁰Co 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, ⁶⁰Co 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 or of damage region. Such an explanation is consistent with the experimental observation that no energy shifts occur in devices made from p-type Ge.
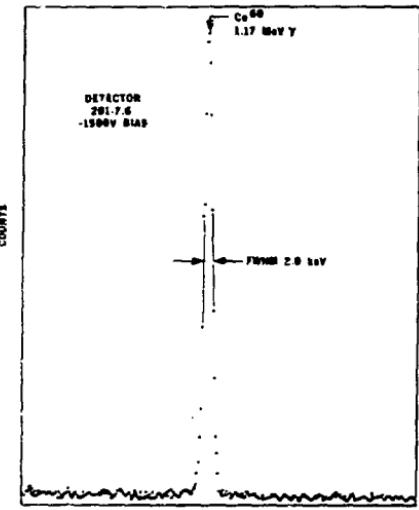
Fig. 3. ^{60}Co gamma-rays through the phosphorous implanted contact show excellent spectrometer performance. This result indicates there was no significant deterioration of the bulk of the crystal from implanting or annealing.

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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