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Radiotracer Studies of the Incorporation of Iodine into Vapor-Grown Ge

Abstract: Measurements of the incorporation of iodine into single crystals of Ge grown by the disproportionation of GeI_2 have been made using I^{131} as a radioactive tracer. The results show that I is not likely to be a hindrance to device use of this material since the amount incorporated is moderately low (10^{14} - 10^{15} atoms/cm^3), and does not appear to be correlated with electrical effects. It does not diffuse appreciably ($D_{875^\circ} < 10^{-13}$ cm^2/sec). No excess is found at an all-deposited *p-n* junction. The concentration of I incorporated appears to decrease with increasing temperature, to be independent of growth rate on a (111) orientation of the seed, but to vary by a factor of up to 50 from one orientation to another. It is deduced that the I is incorporated by a mechanism intimately connected with the crystal growth.

Other papers in this issue[1,2] have shown that single-crystal germanium of a quality suitable for semiconductor devices can be grown by the iodide vapor-growth process, i.e., the disproportionation of GeI_2. Since a large amount of iodine is present during the crystal growth, it is possible that a large amount (by semiconductor standards) could be incorporated into vapor-grown germanium (VGG). Nothing is known about the "doping" properties of I or the other halogens in Ge. To gain a greater understanding, a radiochemical investigation seemed appropriate, in which radioactive I was traced by nuclear counting techniques.

Experimental techniques

• *Preparation of radioactive iodine*

No convenient radioactive isotope of I can be made by direct neutron bombardment. The radioactive I used in this experiment was thus prepared by synthesis, using the 8.05-day β- and γ-emitting I^{131}. This was supplied by ORNL in the form of an aqueous solution of carrier-free sodium iodide^{131} stabilized with sodium sulphite. The solution was evaporated to dryness and exchanged with several successive portions of pure, dry I. Most of the radioactivity was then found in the I, which was then sublimed several times. In this way, it was possible to prepare ~100 mg of I labelled with 10-200 mC of I^{131}. An auxiliary experiment showed that there was no detectable contamination from the sodium sulphite.

The "specific activity" of the I used in the experiment, i.e., the number of measured counts per unit weight of I, was determined in the following way. Some of the crystals of germanium iodides left at the end of the deposition run were collected and converted into silver iodide. This was then weighed directly into portions of about 100 μgm and put into tubes for counting. This method has the advantage that the I measured is that actually used in the deposition, and that it has been made thoroughly radiochemically homogeneous by the reaction itself. The agreement between different samples was better than 2%.

• *Counting procedures*

I^{131} has a well defined γ-ray spectrum, and we used a single-channel γ scintillation spectrometer for counting, set on the 0.364 Mev peak. The scintillating crystal was of the well type, which is insensitive to the positioning of the sample. The γ-rays of this energy are only weakly absorbed and self-absorption effects were shown to be negligible.

Since this type of equipment is sensitive to drifts in the amplifier gain or high-voltage power supply and each series of measurements lasted from 2 to 4 weeks, all measurements were made with reference to an I^{131} standard of convenient activity. No interfering effects were found from other radioactive isotopes. Highly active samples were checked for several half-lives to be sure that they were not overloading the counter. Suitable corrections for radioactive decay and coincidence losses were applied to all measurements.

- *Deposition*

All the deposition runs were made in a similar way to that described by Marinace[1] as the "closed tube method." The labelled I is loaded into a clean quartz tube, together with source Ge and seed Ge in appropriate positions. After evacuation to $\sim 1 \times 10^{-5}$ mm of Hg the tube is sealed off and placed in the deposition furnace. The source and seed zone are raised to the temperatures desired.

At the conclusion of the deposition the tube was removed from the furnace and broken under water to prevent evaporation of radioactive iodides. The remaining source material, the seeds with deposited Ge, and any "extraneous" Ge that had grown on the quartz tube, were removed and kept for examination. Some of the germanium iodide was selected for use as standards.

- *Sectioning of deposits*

Samples for counting were generally obtained by sectioning the deposits by hand-lapping on a glass plate with fine abrasive powder and water. The amount of Ge removed was determined by weighing before and after lapping. The slurry was collected into tubes for counting. We found that better than 98% of the radioactivity was collected. A "differential" plot of *concentration* of I against weight removed can then be made. Alternatively a piece of VGG could be successively weighed, counted, and etched or lapped. An "integral" plot of total amount of iodine against total weight can then be made.

Results

- *Seed*

The seed Ge was examined to see if any I had diffused into it during crystal growth. When all deposited material was carefully removed, there was no detectable radioactivity and thus no evidence for diffusion. This is to be expected in view of the very low upper limit established for the diffusion coefficient at much higher temperatures (see the section on the out-diffusion of incorporated I).

- *Deposit*

The concentration of iodine found in the deposited Ge was generally low, in the range 10^{14} - 10^{15} atoms/cm^3. The amount will be discussed in detail as a function of other variables in the sections below.

Under any given set of conditions it appeared to be distributed uniformly through the thickness of the deposit. This can be seen from Fig. 1, which shows an integral plot. The length of the vertical line through each point indicates the statistical counting error, i.e., the limits within which there is a 95% chance of finding the "true" count rate. The points are seen to lie on straight lines passing through the origin. The same result was found whether the deposit was sectioned by hand lapping or by etching with CP4 or with Superoxol. The slope of the line gives the concentration of I.

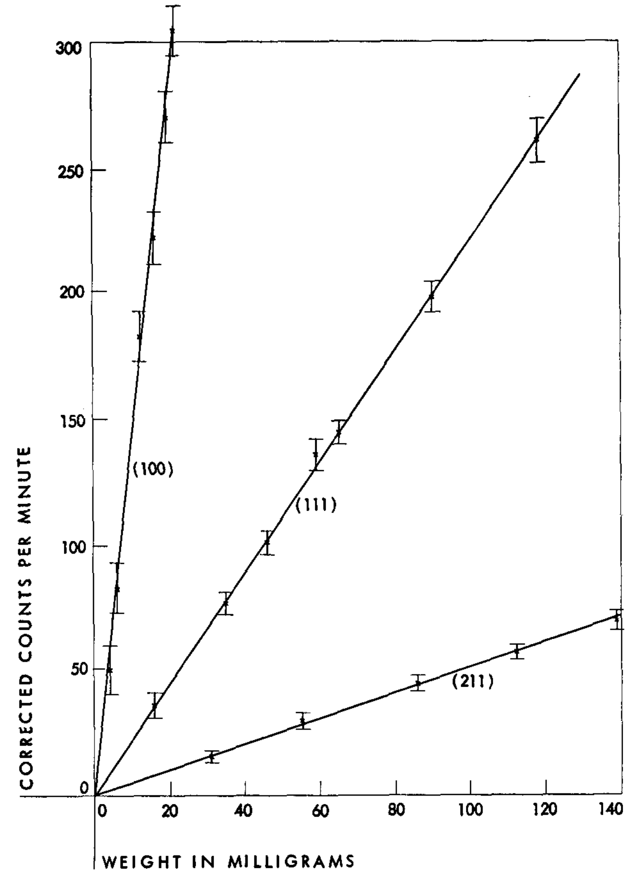

Figure 1 **Corrected counts per minute of I^{131} vs weight for samples of vapor-grown germanium grown on seeds with (100), (111), and (211) orientations.**

A brief study was made of the dependence of I concentration on growth rate on different seeds of the same orientation. A deposition run was carried out using a number of seeds of (111) orientation. Half were *n*-type and half *p*-type. The seed zone temperature was 400 ± 5°C and the source zone temperature 580 ± 5°C. Five of the deposits were examined and the concentration of I found is shown in Table 1.

Table 1 **Iodine concentration in VGG on (111) seeds at different growth rates.**

Seed No. and type	*Method*	*Concentration of I (atoms/cm^3)**	*Approx. growth rate (μ/hr)*
1(*n*)	Graph slope	$1.20 \pm 0.05 \times 10^{15}$	2.8
2(*p*)	Graph slope	$0.93 \pm 0.12 \times 10^{15}$	1.5
3(*p*)	Graph slope	$1.20 \pm 0.05 \times 10^{15}$	1.1
3(*p*)	Graph slope	$1.11 \pm 0.02 \times 10^{15}$	0.75
4(*n*)	Average in whole piece	$1.19 \pm 0.39 \times 10^{15}$	0.19

*Range of error shown is that arising only from counting statistics.

We see that the concentration of iodine is nearly the same from one deposit to another. It is interesting to note that the concentration is independent of growth rate (the differences in growth rate are found because the seeds were at increasing distances from the source). The concentration is also independent of the *n*- or *p*-type nature of the seed Ge.

The deposition run used a number of seeds of various crystallographic orientations, with the source zone at 560°C and the seed zone at 420°C. The deposits were sectioned and in each case we found that the "integral" plot of concentration against weight was a good fit to a straight line. Three examples are shown in Fig. 1. The slope of the straight line gives the concentration of I in the vapor-grown Ge. The results are shown in Table 2. The differences in concentration found cannot be attributed to variation of temperature since they were not correlated with the position of the seed in the tube.

Only qualitative studies were made of temperature dependence. These indicated that iodine concentration decreased with increasing seed temperature.

In order to determine the I dependence on dislocation content of seed, deposits were grown at 420°C on "dislocation free" seeds that showed the Tweet "bath-tub" effect.[3] The I concentration of the deposited Ge was 2.3×10^{15} atoms/cm^3, showing no significant difference from those shown in Table 2.

A study was then made of the relation of I concentration to doping of deposit. A run was made in which *p*-type and *n*-type Ge were deposited in succession on a seed. This was carried out in the way described by Marinace.[1,2] The seeds are placed between two source zones and the changeover is effected by lowering the temperature of one source and raising that of the other. The *p*-type source was doped with Ga at a concentration of $\approx 3 \times 10^{19}$ atoms/cm^3 and the *n*-type source with P at $\approx 2 \times 10^{19}$ atoms/cm^3. The Ga- and the P-doped regions of the deposited Ge were sectioned and their I concentration determined. They will be referred to as *p-type* and *n-type*. At the end of the seeds nearer the *p*-type source, the *n*-type deposit contained a considerably higher concentration of I than the *p*-type deposit, (Fig. 2, Curve A.). However, at the opposite end of the same seed the situation appears to be reversed, although the *p*-type deposit was too thin to be able to obtain an accurate measurement (Fig. 2, Curve B). Values are given in Table 3.

Table 2 **Iodine concentration in VGG on seeds of different crystallographic orientation.**

Seed No.	*Orientation**	*Concentration of I (atoms/cm^3)*
3	100	2.0×10^{16}
4	111	3.0×10^{15}
5	110**	4.3×10^{14}
6	211	6.9×10^{14}
7	110	5.0×10^{15}

*The orientations were obtained from back reflection X-ray Laue patterns and are correct to within 1°.

**Seed had itself been grown by the iodide process.

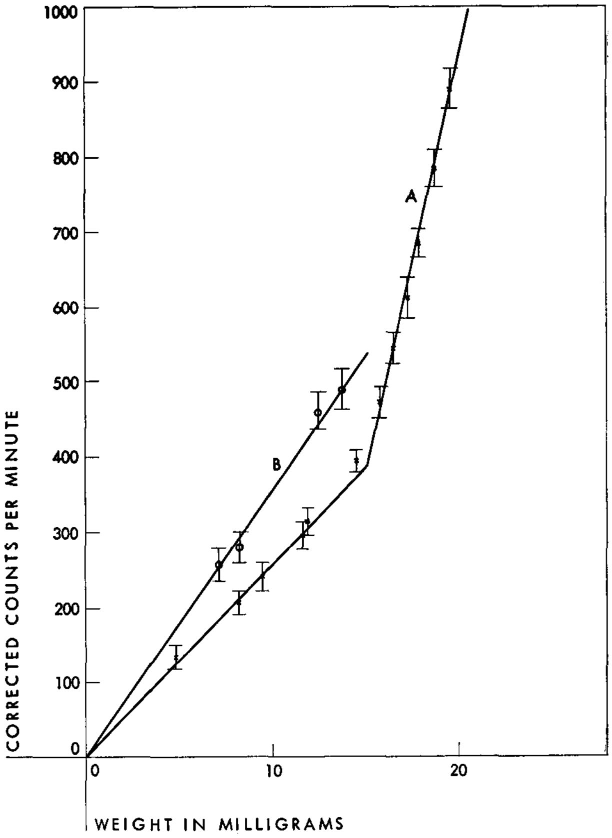

Figure 2 **Corrected counts per minute of I^{131} vs weight for two regions of a sample of *p*-type and *n*-type germanium deposited successively.**
Curve A, top section, n*-type VGG;*
bottom section, p*-type VGG.*
Curve B, n*-type VGG, other end.*

Table 3

Deposit	*Concentration of iodine (atoms/cm^3)* *n-type*	*p-type*
end nearer *p*-type source	1.2×10^{16}	2.5×10^{15}
end nearer *n*-type source	3.5×10^{15}	

It is thus clear that the incorporation of Ga or P in these amounts into the growing Ge crystal is by itself responsible for at most a small effect on the I concentration. The effects observed are best explained by temperature gradients along the seed. The end of the seed nearest the source being used is heated to some extent by the hot vapors, since the source zone is at a higher temperature.

- *Interface and other boundaries*

The interface between seed and deposit has been shown by Marinace[1] and Ingham and McDade[4] to exhibit characteristics that might be attributed to a disturbed region. One of these is that on etching it is attacked more rapidly than either the seed or deposit, so that a line is formed. In each of 25 observations we found a much higher concentration of iodine in this interface than in the deposit. The technique used for sectioning was not capable of removing thin slices parallel to the interface, nor was the interface itself planar. It was thus not possible to study the thickness of the interface, and results were tabulated in concentration of I per *unit area* of interface. In these terms the lowest concentration found was 2×10^{14} atoms of iodine/cm^2, and the highest 5×10^{15}. No significant differences were found in the values for interfaces on seeds that were *n*-type or *p*-type, of the orientations (111), (110), (100) or (211), with dislocation density from 10^4cm^{-2} to zero, and where the seed itself was deposited by the iodide process. All seeds were etched and dried in air before deposition.[5]

An estimate of the concentration of iodine in the interface can be based on the observation that in no case was the region of high concentration found to be more than 25 microns in thickness. Using this value, the concentration is thus 1×10^{17} to 2×10^{18} atoms of iodine/cm^3 of Ge.

Certain other boundaries were examined to see if they contained excess I. A deposit was grown on a twinned seed. No excess I was found at the twin boundary which is propagated into the deposit. Attempts were also made to grow on seeds with grain boundaries of large and small angle. It did not prove possible to isolate regions of grain boundary in the deposit. It is interesting to note that the "extraneous" Ge, i.e., that growing on the walls of the silica tube in the seed region, has a concentration of I higher than that in the deposit by a factor of 10 to 100. This may be so because it is polycrystalline and has grain boundaries.

- *All-deposited junction*

Much of the prospective importance of the iodide process lies in the ability to deposit successive layers of *n*-type and *p*-type Ge, forming an all-deposited *p-n* junction that can be used in a device. We have seen that the interface between substrate and deposit has a high concentration of I. This might have a deleterious effect on the electrical properties, and it is thus important to know whether there is the same high concentration in an all-deposited *p-n* junction. The data in Figs. 2 and 3 give information on this point.

Figure 3 shows a differential curve of concentration against weight removed from the crystal. Marked below the curve is the type of the deposit, as determined by thermoelectric probing. This curve starts at the left at the surface of the deposit which is, at this point, all *n*-type. We see that the I concentration is possibly constant in all the *n*-type material. The concentration then drops continuously until it levels off again in the *p*-type region. After this it rises again to very high levels as the sectioning enters the region of the interface between seed and first deposit. Finally, it falls towards zero in the seed region. The interface appears broad because the plane of sectioning was not strictly parallel to the original surface of the seed.

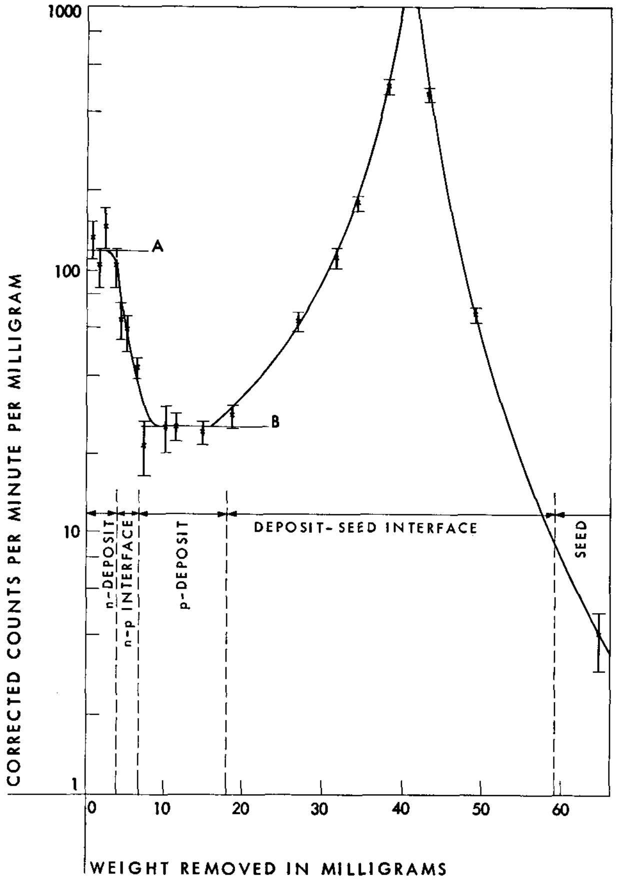

Figure 3 **Concentration of iodine vs weight removed for a sample of *p*-type and *n*-type germanium deposited successively.**

We can see that while there is the usual large excess of I in the interface, there is no evidence for any such excess in the all-deposited junction. This is made even more clear if we examine an integral plot of the I concentration in the deposit in this run. An example is Curve A of Fig. 2. The close fit to two straight lines indicates that the concentration of I is fairly uniform inside each of the regions, and the absence of any step shows that there is no excess I at the all-deposited junction. This last result was confirmed in each of the six regions investigated in this way.

- *Out-diffusion of the incorporated iodine*

We noted above that there was no evidence for the penetration of I into the Ge seed during deposition. Similarly, an examination of the source Ge showed that no I could be detected once the Ge redeposited during the cooling down process had been removed.

Table 4 **Out-diffusion of iodine on baking in vacuum.**

Sample	*Thickness*	*Time, sec*	*Temp., °C*	*Count rate, cpm*	*Count rate expected from radioactive decay only (cpm)*	*Upper limit to diffusion coefficient, cm^2/sec*
1	0.5 mm	2.34×10^5	850	3672 ± 18	3644 ± 13	5.0×10^{-14}
2	0.5 mm	0.612×10^5	901	19.4 ± 1.27	19.6 ± 0.9	2.6×10^{-11}
3	0.5 mm	5×10^5	875	81.0 ± 0.5	79.6 ± 0.8	3.0×10^{-13}

A more sensitive test for diffusion of I in Ge is to see if any I can be removed from the deposited material by baking in a vacuum in an arrangement that permitted counting its radioactivity without removal. In no case was any significant loss of weight observed. The pieces were flat slabs with area large compared to thickness. The results are shown in Table 4.

The limits of error quoted are those arising from counting statistics only and are for 95% confidence limits. Sample 1 probably included some of the interface region. In each case the radioactivity was completely lost when the sample was melted and held above the melting point for a few minutes. This indicates that the I could leave the Ge if it can reach the surface.

The upper limit for the diffusion coefficient shown in the last column is calculated in the following way: It can be shown[6] that for out-diffusion from an infinite plane slab of thickness d cm, the ratio of diffusant lost to total amount present $(\Delta s/s_0)$ is approximately $(2/\pi^{1/2})(Dt)^{1/2}/(d/2)$, where $D(\text{cm}^2/\text{sec})$ is the diffusion coefficient and t the elapsed time in seconds.

Thus $D \approx (1/t)(\Delta s/s_0)^2(\pi/4)(d/2)^2$. Surface barriers[7] are assumed to have a negligible effect. The quantities Δs and s_0 are derived from the count rates and the statistical error.

We may compare these values with that for the self-diffusion of Ge[8] at 875°C, where $D = 7 \times 10^{-13}$ cm²/sec.

Discussion

The foregoing results may be discussed from two points of view: What prognosis do they give for the feasibility of making semiconductor devices by the iodide process, and what light do they shed on the way in which I is incorporated?

- *Device considerations*

The result described does not show that the incorporation of I into VGG is any bar to device use. The amount incorporated is only moderately low (10^{14} to 2×10^{16} atoms/cm³), but no electrical level has been found that can be correlated with these amounts, either before or after heat treatment. Iodine incorporated in this way thus appears to be electrically inert. Chlorine has been reported[9] to be electrically inert in indium arsenide.

The low diffusion rate is favorable in that it shows that the I is fixed in the lattice and thus cannot become electrically harmful by migrating to some sensitive region, such as a junction.

The high concentration of I found in the interface region correlates with the poor electrical properties of a *p-n* junction here and with the enhanced etch rate;[1] it is thus encouraging to note that an all-deposited *p-n* junction shows no such excess I.

- *Interpretation of results*

We would like to understand what form incorporated I takes in VGG and what is the exact mechanism of its incorporation. Both these questions are premature, and full understanding will have to wait until more is known about the details of the crystal growth. However, the following comments can be made.

The nature of the incorporated I. The chemical binding energies involved suggest that the I is incorporated as a germanium iodide, but no direct information on this has been obtained. Little of the I can be incorporated as the iodides of the doping elements, since there was no real difference in I concentration betwen *p*- and *n*-type VGG. Other measurements[2] have shown that with the source materials used, we could expect the doping levels in the VGG to be 5×10^{17} Ga atoms/cm³ and 2×10^{19} P atoms/cm³. This compares with an I concentration of about 5×10^{15} atoms/cm³.

The mechanism of incorporation is still a matter for speculation, but we can immediately rule out the idea that the process is analogous to growth from the melt in that an "equilibrium" solubility of iodine is reached, this value depending only on the temperature and on the concentration of iodine or iodide in the vapor phase. Table 2 shows that the I concentration can vary by a factor of 50 with variation of crystallographic orientation of the seed. This indicates that the incorporation of I is a rate process. The variation found is not likely to be due to a simple variation of growth rate itself, analogous to diffusion-controlled doping[10] (rate-growing) from the melt, since the results in Table 1 show that, at least for a (111) orientation, the I concentration is independent of growth rate over a considerable range. If the incorporation process is intimately connected with the mechanism of crystal growth the variation shown in Table 2 is readily understandable. The detailed mechanism of growth must depend on orientation, as for example the growth rate does.[1] The adsorption energy of the iodide molecule being incorporated would also be expected to vary with crystallographic orientation. The sign of the dependence of I concentration on temperature is that to be expected from the naive view that at higher temperatures a molecule of iodide has more chance of being desorbed before it is incorporated. Effects of a similar nature have been reported[11] for the segregation of tellurium in indium antimonide grown from the melt, which appears to depend on the crystallographic orientation of the growing face.

However, the amount of I does not appear to depend only on the nominal orientation of the seed (compare seeds 5 and 7 in Table 2). We have also examined the possibility that the I might be incorporated very largely on dislocations in the VGG. This seems unlikely. An I concentration of 10^{15} atoms/cm^3 in a crystal of VGG with 10^5 dislocations/cm^2 would imply that each dislocation had a core with a cross-sectional area of about 300 iodine atoms. Further, in all deposits that we examined the density of dislocations revealed by etch pits varied in all directions in a similar way, although to a somewhat smaller extent, to that found in crystals grown from the melt. The linearity and low scatter shown by the count-weight plots (e.g., Fig. 1) thus would not be expected. In addition, an autoradiograph failed to reveal any clustering of the I. However, the interface region, which appears to be disturbed,[4] contains a considerable quantity of excess I. The polycrystalline extraneous VGG also contained considerably more I than any of the single-crystal deposits. This shows that excess I can be incorporated at grain boundaries or other disturbed regions, but does not give any evidence as to the mode of incorporation in single crystals.

It is clear that a fuller understanding of the method of incorporation of I will be closely related with a more detailed knowledge of the mechanism of crystal growth.

Conclusions

We may conclude that

(1) Incorporation of iodine into VGG is not likely to be a bar to device use.

(2) Although detailed speculation is premature, it appears likely that the I is incorporated by a mechanism intimately connected with the crystal-growth process. This leads one to suppose that desirable impurities may be incorporated in the same way and that a detailed analysis of their behavior should be made.

Acknowledgments

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