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Incorporation of As Into Vapor-Grown Ge

Abstract: The incorporation of arsenic into single-crystal germanium grown by the disproportionation of GeI_2 was studied using As^{76} as a radioactive tracer, and using measurements of the Hall effect. The deposition was carried out in a sealed tube using as source material a single crystal of Ge doped to 2.5×10^{19} atoms/cm^3 with As. It was found that all the As incorporated into the vapor-grown Ge was electrically active, at least for material grown on a (211) Ge seed. The concentration of As in the deposited Ge was lower than that in the source, and appeared to depend on the crystallographic orientation of the growing face.

Introduction

The vapor-growth process for preparing single-crystal germanium has been described in other papers in this issue.[1,2] Volatile iodides are used to transport Ge from a source to a seed, where an epitaxial deposit is grown. Either a closed-cycle or a continuous-gas-flow system can be used. The vapor-growth process promises to provide a novel method of fabricating semiconductor devices, but a very important problem is how to introduce desired doping impurities in a controlled manner. Several doping techniques have been tried.[2] The one adopted for the present study is closed-tube deposition using as the source a single crystal of Ge uniformly doped with the element desired. We report here the results of a preliminary radiochemical investigation of the incorporation of arsenic, chosen as a typical conventional doping impurity, into vapor-grown Ge (VGG). The isotope As^{76} was used as radioactive tracer in this study.

We wished to observe (i) *Whether the concentration of As determined by electrical measurements would be equal to the value determined radiochemically.* Measurements using radiotracers have shown[3] that in melt-grown Ge (MGG) there is a one-to-one correspondence between these two quantities for many of the common impurities used for doping. For VGG this need not be true; some of the impurity might be incorporated at nonsubstitutional sites in the lattice, or as impurity iodide. At first it appeared likely that As did not go to substitutional sites, since for this doping method the electrically measured doping level in the VGG is considerably lower than that in the source Ge, although the transport is carried out in a closed system. This difference in doping level is much more pronounced with As than with P or Sb. (ii) *What governs the incorporation process,* i.e., whether or not an equilibrium is maintained; or, if equilibrium is not maintained, what is the rate-limiting step. (iii) *The homogeneity of doping* when this method is used.

Experimental

• *Radiochemistry and counting techniques*

The 26-hour half-life β- and γ-emitting As^{76} was chosen as tracer since it can be produced by direct neutron irradiation of As^{75}, the only stable isotope of As. O'Rourke, Marinace, Anderson and White,[2] have shown that when this method of doping is used, the best control is achieved by having the impurity dissolved uniformly in single-crystal Ge, which is then used as the source material. We thus wished to obtain single-crystal Ge doped with $As^{75}+As^{76}$ to about 10^{19} atoms/cm^3. Growing such a crystal using neutron-irradiated As offers considerable difficulty because of the short half-life and high volatility of As. Instead we irradiated, with neutrons, a crystal previously grown and doped to this level with nonradioactive As. This has the advantage of convenience but the disadvantage that a number of radioactive species is produced by nuclear reactions of the Ge solvent.[4] These include Ge^{71}, Ge^{75}, and Ge^{77}, which decays into radioactive As^{77}. However, it is possible to determine the As^{76} in this radioactive mixture because there is a high concentration of As, and because a single-channel γ-spectrometer is used to count the activity. This registers only those γ-rays in a desired energy range characteristic of As^{76}.

To confirm that the activity counted could be ascribed to As^{76}, the rate of decay was checked. For each sample the half-life was followed for 9 days; it was found that

the half-life was initially that of As^{76} but that the rate of decay became slower after a period of time, indicating interference from longer lived radioisotopes. This period was about 8 days (7 half-lives) for a sample of pure As irradiated under the same conditions and about 5 days for a sample containing irradiated Ge as well as As. As a further confirmation, one sample of irradiated Ge and As was counted in this way over a period of time, after which a known ratio of the As was separated chemically. When this was counted, the count rate agreed with that expected within $\pm 10\%$. The separation was carried out by the addition of a suitable quantity of carrier, reduction of the As to elemental form with hypophosphorous acid (which will not reduce Ge), dissolution in standard cerium (IV) sulphate and determination of the excess.

A Ge single crystal doped with $\sim 3 \times 10^{19}$ atoms of As/cm^3 and cut into slices 500μ thick, was irradiated at Brookhaven National Laboratory in a flux of 8×10^{12} n/cm^2/sec for 70 hr, together with some samples of 99.999% As to serve as standards. The geometry was such that variations of specific activity due to self-absorption of neutrons[5] would be negligible.

The specific activity of the As was determined by counting weighed aliquots of a solution containing a known weight of irradiated As. This was prepared without evaporation losses by dissolving the As sample in a little bromine under water in a volumetric flask. The As reacts violently with the Br and the whole was brought into solution by shaking.

Samples were counted with a single-channel γ-spectrometer, set to accept the 0.56 Mev γ-rays of As^{76}. Self-absorption and positioning effects were shown to be negligible. All count rates were corrected for radioactive decay and coincidence losses in the usual manner. Because of the difficulties mentioned, and the short times available for counting, the precision estimated is only $\pm 10\%$.

• *Deposition*

The deposition run was carried out by the closed-tube method.[1] The source material and pure Ge were weighed and placed in appropriate positions in a clean, fused silica tube, together with 120 mg of doubly-sublimed I. The tube was sealed at a pressure of $\approx 3 \times 10^{-5}$ mm, and allowed to react for 44 hr, with the seed zone at 410°C and the source zone at 580°C. The exposed surface area of each of the four seeds had a different crystallographic orientation, determined by back-reflection Laue patterns to better than $\pm 1/2°$. The seeds were arranged as shown in Fig. 1. The single-crystal VGG grew on the seeds and polycrystalline material on the walls of the tube in the seed zone ("extraneous" VGG).

At the conclusion of the run the tube was removed from the oven and rapidly cooled with liquid nitrogen. To recover the volatile iodides that had been present in the gas phase, the tube was then opened under acetone, in which GeI_2 and GeI_4 are sufficiently soluble. Ultrasonic agitation completed the dissolution. The fused silica tube was then rinsed with an etch (HF and HNO_3). Both the acetone solution and the etch were kept for examination. The seeds and the source Ge were re-weighed and the extraneous Ge collected and weighed. The total amount of doped Ge transported was 3.05 gm.

Figure 1 **Arrangement of doped source material and pure Ge seeds in tube for deposition.**

Results

• *Radioactivity*

Portions of the deposits on the four seeds, of the source material and of the extraneous VGG were examined for As content by counting their radioactivity as described above.

(i) *Distribution of As.* The procedure was similar to that described in Ref. 7. The deposits on the seeds were sectioned by hand lapping on a glass plate with abrasive powder and water. The slurry was collected and counted to give the As content. The amount of Ge was determined by the loss of weight after lapping. Subsidiary experiments showed that better than 98% of the radioactive material was collected.

Figure 2 shows a plot of As content against weight of Ge removed. The points fall very near a straight line, the slope of which represents the concentration of As. The As thus appears to be distributed homogeneously through the depth of the deposit. An exception to this was found when the sectioning cut through the original interface between seed and deposit. A higher As concentration was found in this region. This can be seen in Fig. 2, where the points marked INTERFACE are those where the sectioning cut through the interface.

(ii) *The concentration of As.* This can be determined as above or by determining the total weight and counting rate where a piece of VGG could be completely removed from its seed. The results obtained are shown in column 4 of Table 1 for the deposits on the four seed orientations, for three samples of the source material, and for four samples of the extraneous VGG.

The table also shows the concentration of As in the Ge in the vapor phase when the reaction was stopped. This figure was obtained by a chemical and a radiochemical analysis of the acetone solution obtained as described above. The chemical analysis gave 104 mg of I and 15 mg of Ge. The amount of I is reasonable since some is lost on evacuating the tube. The ratio corresponds to GeI_4, which indicates that any GeI_2 present disproportionated during cooling. During the deposition run there is thus between 15 and 30 mg of Ge in the vapor. Counting the radioactivity of aliquots of the acetone solution gave the concentration of As shown in the table, which is referred to the 15 mg of Ge.

The etch used to rinse the tube after deposition was examined for radioactivity. The amount found was negligible compared to that in the acetone solution, indicating that the latter had removed substantially all the As originally in the vapor phase.

• *Electrical measurements*

Measurements of low-field Hall effect and of room temperature resistivity were made by the van der Pauw method[6] on several samples of the VGG and of the source Ge. The values obtained for net donor concentration are shown in column 5 of Table 1, and are taken to give the As concentration. The absolute accuracy is considered correct to within $\pm 10\%$ in the samples marked (*). In these samples the surface area was $\sim 5 \times 5$ mm. The rest are reliable only to within a factor of two, since those samples were very small ($\sim 2 \times 2$ mm) and the contacts occupied a considerable area of the surface. The mobility was found to be indistinguishable from MGG with the same As concentration.

Two samples of the VGG were annealed in a hydrogen atmosphere for 10 minutes at 875°C. Subsequent measurement of the Hall effect showed no change, indicating that no precipitation or solution of As had occurred.

Tunnel diodes were made by alloying In-1% Ga to the VGG removed from the (211) seed. In current density and *I-V* characteristic these diodes were indistinguishable from those made from MGG with an As concentration of 5×10^{18} atoms/cm^3.

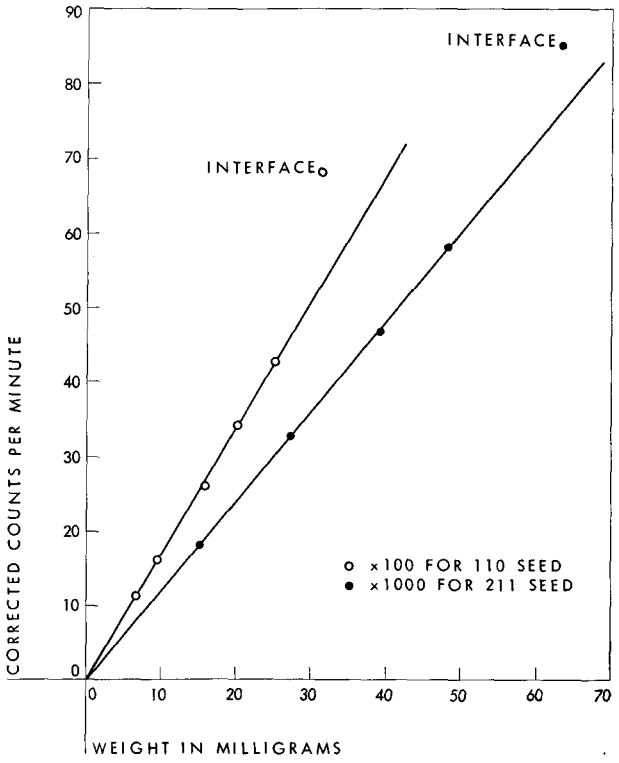

Figure 2 **Graphs showing total As content against total weight of Ge removed for deposits on (211) and (110) seeds.**

Discussion

• *Nature of the incorporated As*

For As incorporated into Ge to be electrically active it must be located at substitutional lattice sites.

If the As concentration determined radiochemically is equal to that found by electrical measurements all the As incorporated must be dissolved in this way. Table 1 shows that the agreement between these two methods is excellent for the melt-grown source material. It is also excellent for the VGG grown on the (211) seed. The apparent disagreement for the deposits grown on the (110) and (111) seeds is within the error of the Hall effect measurements.

Thus at least for the VGG on the (211) seed, and at these concentrations, all the As incorporated into VGG is dissolved substitutionally, as is the case in MGG. This may be compared with the incorporation of gold into VGG where only one in every forty Au atoms incorporated was found to be electrically active.[12] Some indirect information about Ga and P incorporation into VGG can be obtained from measurements of I incorporation into Ge.[7] Doping estimated at $\sim 5 \times 10^{17}$ (electrically active) atoms of Ga/cm^3 or $\sim 2 \times 10^{19}$ atoms of P/cm^3 did not raise the concentration of I incorporated into the VGG ($\sim 10^{16}$ atoms/cm^3). No iodides of these elements were thus incorporated. However, it is possible that a portion of these elements might be incorporated in interstitial positions or as precipitates. This possibility is seen to be excluded for As in VGG.

• *Homogeneity of doping*

Figure 2 shows that the concentration of As in the VGG remains remarkably constant as the deposit grows in thickness. The only departure from this is found when the sectioning cuts the interface between seed and deposit. In this region the concentration of As is higher, but our method of sectioning was too crude to follow the variation of concentration in detail. A similar increase was found for the concentration of I incorporated in this interface region[7] which shows many characteristics of being disturbed and full of imperfections.[8] The higher concentration of As could arise from these imperfections, or from a higher concentration of As in the vapor in the initial stages of deposition. Capacitance measurements on diodes made in this way show that the variation of doping with distance is complex.[9]

• *Mechanism of incorporation*

While the concentration of As appears to be uniform through the deposit on any one seed, and also to be the same in different regions on any one seed, there is a considerable variation from seed to seed and between the VGG as a whole and the source Ge.

Table 1 shows that the concentration of As in the VGG varies from 8×10^{17} atoms/cm^3 of Ge for the deposit

grown on a (110) seed to 6×18^{18} on a (211) seed. This marked difference appears to indicate a dependence of As concentration on growth conditions. It is not due to a variation of temperature since the whole of the furnace zone in which the seeds were held was at a constant temperature, and in addition, the values do not correlate with the position of the seeds in the tube. It would appear probable that this effect is associated with the crystallographic orientation of the growing surface. The incorporation of As thus appears to be a rate process; the rate-limiting step is not diffusion across a boundary layer in the vapor, but is one connected with the growth process itself. A similar dependence of concentration on orientation was found for the incorporation of I into VGG,[7] and for the segregation coefficient of Te in indium antimonide grown from the melt.[10]

The extraneous VGG is seen to have the highest concentration of As. This may also be an orientation effect or may be due to grain boundaries.

Effects of this kind do not appear to be found[13] in the incorporation of impurities into Si. This is probably due to the considerably higher temperatures used for Si.

• *Distribution of As between VGG and vapor*

The results in Table 1 show that the ratio of the As concentration in the VGG to that in the vapor ranges from $\sim$0.3 for a (211) seed to $\sim$0.03 for a (110) seed. This compares with $\sim10^{-7}$ for iodine,[7] and $\sim10^{-4}$ to 10^{-6} for Au in VGG.[12] Thus doping with As can readily be carried out in the continuous-flow process, while doping with Au cannot.

Table 1 **Arsenic concentration in VGG and in source Ge.**

Material	*Region*	*Radioactive Measurements*** *Method*	*As Concentration (atoms/cm³ of Ge)*	*Hall Effect As Concentration (atoms/cm³ of Ge)*
Source	1	Whole piece	2.5×10^{19}	2.0 to 2.9×10^{19}*†
	2	Whole piece	2.4×10^{19}	
	3	Whole piece	2.5×10^{19}	
Deposition on (111) Seed	1	Whole piece	2.5×10^{18}	1.1×10^{18}
	2	Sectioning	2.1×10^{18}	
on (100) Seed	1	Sectioning	2.9×10^{18}	
on (110) Seed	1	Whole piece	7.1×10^{17}	3.5×10^{17}
	2	Whole piece	7.6×10^{17}	4.7×10^{17}
	3	Sectioning	7.1×10^{17}	
on (211) Seed	1	Whole piece	5.6×10^{18}	5.4×10^{18}*
	2	Whole piece	5.7×10^{18}	5.9×10^{18}*§
	3	Sectioning	5.0×10^{18}	
Extraneous VGG	1	Whole piece	7.8×10^{18}	
	2	Whole piece	6.8×10^{18}	
	3	Whole piece	6.9×10^{18}	
	4	Whole piece	8.3×10^{18}	
Acetone Solution			3.0×10^{19}	
Average concentration in VGG			5.1×10^{18}	

*Hall measurements accurate to within $\pm10\%$.
**Errors in radioactive measurements were estimated at $\pm10\%$.
†Data for five samples other than those measured for radioactivity.
§Three other samples measured ranged from 5.3×10^{18} to 5.6×10^{18}.

• *Difference between concentration in VGG and in source material*

Table 1 shows that the average concentration of As in the VGG is less than that in the source Ge, confirming previous experiments[2] using electrical measurements. This is a puzzling feature, since a process of this kind in a closed system would be expected to come to a steady state where the rate at which As left the source would be equal to that at which it entered the VGG.

The results in Table 1 can be used to exclude some of the possible reasons for this. The As cannot be building up in the vapor at the end of the run, as the vapor concentration would be about 10^2 higher than cited in Table 1. It cannot have settled out on the walls of the reaction tube, as either the acetone wash or the etch would be expected to dissolve it. The As could be concentrated in a region of the extraneous VGG not sampled (although four widely separated pieces were chosen). It could also have been left on the source material as a stable phase or compound. There is some evidence for this, as a nitric acid etch of the source material after the deposition run gave a liquid very rich in As, while no loss of weight of Ge (<0.1 mg) could be detected. The nature of this phase, if it exists, deserves further investigation.

Conclusions

All the As incorporated into VGG under the given conditions appears to be electrically active, at least for the material grown on the (211) seed. Arsenic-doped VGG appears to have equivalent electrical properties to MGG with the same concentration of As.

The As is distributed homogeneously through the VGG, with the exception of the interface region between seed and deposit.

The concentration incorporated depends on growth conditions, and apparently on the crystallographic orientation of the growing face.

The ratio of As concentration in the VGG to that in the vapor is of the order of 0.1.

The deposited Ge contains less As than the source material, probably because (a) some of the As is not released from the latter, or (b) there is competition between the various growing faces, including the polycrystalline extraneous VGG which incorporates most of the As.

Acknowledgments

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