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Incorporation of Au into Vapor-Grown Ge

One of the central problems of the iodide vapor-growth process[1] for growing germanium suitable for device fabrication is that of the incorporation of impurities. These fall into two classes in germanium[2]: the *hydrogenic,* such as arsenic, characterized by a high solubility, low diffusivity and low ionization energy, and the *nonhydrogenic,* characterized by a low and usually markedly retrograde solubility, higher diffusivity and higher ionization energy. Work on the incorporation of arsenic into vapor-grown germanium (VGG) has been reported elsewhere.[3] We report here a study of the incorporation of gold, chosen as a representative nonhydrogenic impurity.

Three methods for doping have been proposed;[4] in these the doping element is (i) dissolved in the source Ge, (ii) added to the reaction tube as the iodide, or (iii) as the element. The third of these methods was used; this has the disadvantage that the incorporation of the doping impurity into the VGG may not be homogeneous. On the other hand, higher concentrations may be reached.

Experimental procedure

Au^{198}, used as a radioactive tracer, has a 2.7 day half-life and is a β- and γ-emitter. It is readily prepared by direct neutron irradition of natural Au.

The Au used was of 99.999% purity and was in the form of 0.0015″ wire. This configuration was chosen both to give a large surface area for attack by iodine, and to minimize self-absorption of neutrons during irradiation. The latter effect can lead to serious variations in specific activity,[5] but no effects of this kind were observed. Fifteen mg of this Au wire was irradiated at Brookhaven National Laboratory for 115 hr at a flux of $1.6 \times 10^{13} n/\text{cm}^2/\text{sec}$.

Radioactive samples were counted with a single-channel scintillation spectrometer, set to accept only the γ-rays of 0.41 Mev energy, characteristic of Au^{198}. Effects of self-absorption and sample positioning were shown to be negligible. No interference was found from Au^{199} or any other radioactive isotope. The specific activity of the Au was determined by dissolving weighed portions of the irradiated Au wire in aqua regia, together with carrier Au, and diluting to give activities that would not overload the counter. Agreement among various samples was better than 2%. Highly active samples were checked for several half-lives to make sure that they were not overloading the counter. Suitable corrections for radioactive decay and coincidence losses were applied to all measurements.

The deposition run was of the type described[1] as "closed tube." High-purity Ge was used as source material and the two seeds were a (111) *n*-type wafer and a (211) *p*-type wafer; 140 mg of I was used, and the tube, which had a volume of 110 cm^3, was sealed off after evacuation to a pressure of 1×10^{-5} mm. The deposition run lasted for 5 days, during which time the temperature of the seed zone was 405°C and that of the source zone 555°C. The Au wire to be used as doping agent weighed 10 mg and was placed in the source zone. At the end of the deposition run the tube was opened under water. The seeds with the deposited Ge were removed, together with some of the "extraneous" Ge that had grown on the walls of the quartz tube. No trace was left of the Au wire.

Results

• *Appearance of deposit*

The deposit was of unusual appearance. On both seeds the deposit was thin and appeared to be polycrystalline on the surface. Several regions were etched after various amounts were lapped off; this study showed that the surface was probably polycrystalline and that the rest of the deposit was certainly single-crystal, epitaxial to the substrates. X-ray diffraction patterns showed no departure from single-crystal behavior, indicating that the surface layer, if polycrystalline, was thin. As is usual[1] the thickness of deposit was not uniform, being greatest at the end of each seed nearest the source zone, next greatest at the opposite end and thinnest in the middle.

• *Radioactive measurements*

We wished to study the distribution of radioactive Au in the deposited Ge. This was done by sectioning by hand-lapping on a glass plate with fine abrasive powder and water. The slurry was collected and counted to give the amount of Au. The amount of Ge in the slurry was determined by weighing the seed and deposit before and after lapping. A subsidiary experiment showed that the efficiency of collection is better than 98%. In this way the concentration of Au in the layer lapped off can be obtained. This concentration can be plotted against total weight removed to show how it varies with depth in the deposit. This was carried out on several regions of each seed. Two typical results are shown in Fig. 1. Proceeding towards the left from the interface between seed and deposit, we see that the concentration of Au rises gradually and becomes nearly constant.

The maximum value reached is shown in Table 1 for a number of the samples sectioned in this way.

- *Electrical measurements*

Measurements by the van de Pauw method[6] of low-field Hall effect and resistivity as a function of temperature showed that sample A4 of the Au-doped VGG was *p*-type, with 7×10^{15} acceptors per cm^3. These had the energy levels to be expected from Au (0.16 ev above the valence band) but an unambiguous identification was not possible because of the shape and inhomogeneous doping of the sample.

- *Photoconductive response and infrared transmission*

A weak photoconductive response, which extended to a wavelength greater than 8μ, was observed in samples of the Au-doped VGG. Measurements of infrared transmission proved inconclusive. The samples were very thin and showed a generally high absorption coefficient, which is probably due to surface damage caused by the necessary polishing.

Discussion

- *Distribution of Au*

Figure 1 shows that the Au is not distributed homogeneously in the deposit. This is to be expected when this method of doping is used because the Au may react slowly so that the concentration of Au in the vapor increases with time, giving an increasing concentration of Au in the deposited Ge. A maximum might be reached when no higher concentration of Au could be incorporated or when the concentration of Au in the vapor reached a point at which growth essentially stopped (or became polycrystalline, as appears to have happened.) However, this would lead one to predict that the curves of concentration against depth of deposit should have essentially the same shape irrespective of the total thickness. In particular, they should reach the same maximum value. This is not observed. In fact, the thicker the deposit, the higher the maximum value reached. One explanation could be that whatever mechanism causes higher growth rates at some places in the seed than at others also enables the crystal to grow in these places from a vapor that contains a higher concentration of Au. The apparent cessation of growth should probably be attributed to some poisoning effect caused by the Au. It cannot be due to the removal by Au of all the I from the system, since over four times more Au would be needed.

Table 1 **Maximum concentration of Au.**

Orientation	*Sample*	*Maximum concentration of Au* ($\times 10^{17}$ *atoms/cm*^{3})	*Approximate thickness* (μ)
(211)	A1	6.0	250
	A2	4.5	75
	A3	2.8	40
	A4	3.4	120
	A5	3.3	50
(111)	B1	2.8	100
	B2	2.8	100
Extraneous (polycrystalline)	1	3.3	
	2	3.3	
	3	3.3	

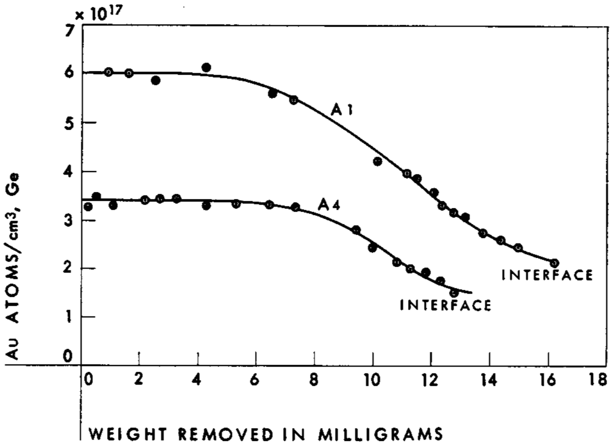

Figure 1 **Concentration of Au in atoms per cm^3 of Ge vs weight of Ge removed for two samples.**
The points marked INTERFACE *are those where the sectioning cut through the interface between deposit and seed.*

- *Amount of Au dissolved*

The results obtained indicate that Au can be incorporated into Ge grown by the vapor-growth process, using the closed-tube method. Previous work by D. C. Cronemeyer[7] had failed to detect any incorporation of Au in VGG prepared by the "open tube" method.

The maximum concentration shown in Table 1 is much higher than that previously reported for Au in Ge grown from the melt. The solubility reported[2] is 5×10^{15} atoms/cm^3 at the melting point of Ge and 2×10^{16} at 920°C. Although the Au-Ge system has a eutectic at 356°C, no work appears to have been published on the solubility of Au in Ge pulled from such low-temperature solutions. However both Cu and Ag show a very markedly retrograde solubility,[8] and by analogy the solubility of Au in Ge at the deposition temperature (405°C), would be expected to be very low ($\sim 10^{14}$ atoms/cm^3). The results of the electrical measurements indicate that not all the Au incorporated was electrically active. Only about one atom in 40 appears to be in substitutional position. However, even the figure of 7×10^{15} atoms/cm^3 is near that reported at the temperature of maximum solubility, and far higher than to be expected in melt-grown germanium (MGG) at 405°C. This demonstrates one of the prospective advantages of the vapor-growth process; since the incorporation of impurity is a rate process, higher than equilibrium amounts of impurity may be built-in during growth and remain frozen-in, since the growth temperature is too low for rapid atom movements to occur.

The electrically inactive Au may be incorporated in nonsubstitutional positions in the lattice or as an iodide with an equivalent quantity of I. It is conceivable that a portion of the Au may be electrically inactive in MGG also, since radiochemical measurements[9,10] of the segregation coefficient appear to give higher values than electrical measurements[2,10] We hope to investigate these possibilities by measuring the I incorporation in Au-doped VGG and the Au concentration in MGG.

It is of interest to estimate the ratio of the Au concentration in the VGG to that in the vapor. To do this we have to make an arbitrary assumption since we do not know at what point during the build-up of Au in the vapor the VGG stopped growing. Let us assume that the maximum concentration of Au in the VGG was reached when half the Au added was in the vapor. This gives a ratio of 10^{-4} for the total Au in the VGG and 10^{-6} for the electrically active Au in the VGG. This explains why Au doping is possible in the closed tube where the concentration of Au in the vapor can build up to very high values, but was not observed by Cronemeyer[7] in the open tube.

Acknowledgments

Thanks are due to W. Reese for infrared and photoconductivity measurements, to J. F. Woods for the measurements of Hall effect and resistivity, to J. F. Reid for assistance with radioactive measurements, and to J. C. Marinace and Miss J. O'Rourke for helpful advice and discussions.

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Received March 11, 1960