

## Growth of Germanium Single Crystals Containing $p$ - $n$ Junctions

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December 21, 1950

THE growth in the number of ideas of possible conduction mechanisms of practical value that might be realized in germanium has emphasized the importance of developing specific methods of producing germanium single crystals in which the relevant properties of the material are controlled. Germanium single crystals of a variety of shapes, sizes, and electrical properties have been produced by means of a pulling technique distinguished from that of Czochralski and others in improvements necessary to produce controlled semiconducting properties.<sup>1</sup> Solidifying germanium is very sensitive to a variety of environmental factors such as physical strain (which give rise to twinning), thermal treatment, and minute impurities. Pulling the germanium single crystal progressively from the melt at such a rate as to have the interface between the solid and liquid substantially at the liquid surface is very well suited to this material, since it avoids the constraints inherent in solidifying the expanding germanium within inflexible walls and provides an approximately planar thermal gradient in the neighborhood of the interface, thereby minimizing thermally induced strains. Single crystal rods showing a high degree of crystalline perfection, as long as 8 inches, and as great as  $1\frac{1}{4}$  inches in diameter have been grown. Measurements in these Laboratories have shown the bulk lifetimes of injected carriers in some of these materials to be greater than 600  $\mu$ sec.

One type of such "long lifetime" crystals that is of special interest, which has been produced by the above means, is a single crystal in which the magnitude and type of conductivity in the direction of crystal growth is controlled by addition of a significant impurity such as gallium (acceptor) or antimony (donor) to the melt from which the crystal is being grown. Thus,  $p$ - $n$  junctions have been formed in germanium single crystals which are exceptional in their agreement with theory<sup>2</sup> and in their electrical properties as discussed in an accompanying letter.<sup>3</sup>

We wish to acknowledge our indebtedness to many of our associates at Bell Telephone Laboratories for assistance and advice and especially to J. B. Little, who collaborated in the initial single-crystal program.

<sup>1</sup> G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).

<sup>2</sup> W. Shockley, Bell System Tech. J. **28**, 435 (1949).

<sup>3</sup> Goucher, Pearson, Sparks, Teal, and Shockley, Phys. Rev. **81**, 637 (1951).

## Theory and Experiment for a Germanium $p$ - $n$ Junction

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December 21, 1950

RECTIFYING  $p$ - $n$  junctions in germanium have been produced in which the approach to the idealized conditions is so close that most of the expected theoretical features can be quantitatively verified experimentally, thus putting these junctions in a unique position in the field of solid rectifiers. The junctions discussed in this letter were produced in high back voltage  $n$ -type germanium by the addition of gallium so that one portion of the single crystal<sup>1</sup> was  $p$ -type. The unit reported here was  $0.65 \times 0.6$  cm in cross section.

According to theory<sup>2</sup> the rectification curve for such a junction should be of Wagner<sup>3</sup> form  $I = I_s[\exp(eV/kT) - 1]$ . Figure 1 shows a comparison between theory and experiment, the theoretical value  $39 \text{ volt}^{-1}$  being used for  $e/kT$ . The voltage values were measured between zero current probes near to the junction on each side and employed to eliminate ohmic series resistance.

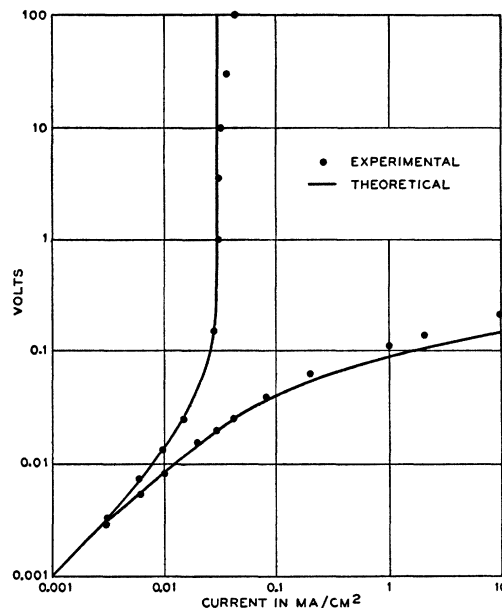


FIG. 1. Rectification characteristics of a  $p$ - $n$  junction.

The conductance of the junction at low voltages,  $eI_s/kT$ , is due to hole flow in the  $n$ -region in parallel with electron flow in the  $p$ -region. It can be calculated in terms of the intrinsic conductivity  $\sigma_i$  taken as  $0.0165 \text{ ohm}^{-1} \text{ cm}^{-1}$ , the conductivities of the two regions  $\sigma_p$  and  $\sigma_n$ , the lifetimes of injected carriers  $\tau_p$  for holes and  $\tau_n$  for electrons, and the diffusion constants  $D_p$  and  $D_n$ , and their ratio  $b = D_p/D_n$ . The lifetimes were measured by scanning with a slit of light of wavelength 1.85 microns, which penetrated deeply into the specimen. The abnormal carriers so produced should diffuse a distance  $x$  to the junction with decay factors of  $\exp(-x/L)$ , where  $L = (D\tau)^{1/2}$  is the diffusion length, a prediction which is in agreement with Fig. 2. Except for the decay due to

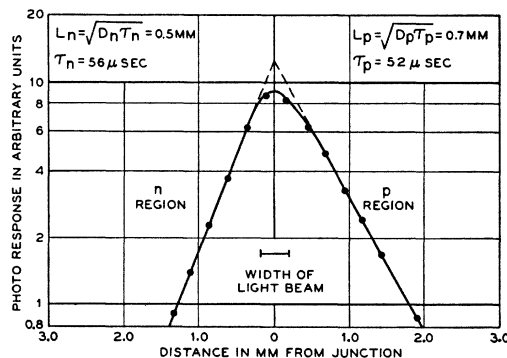


FIG. 2. Photo-response vs distance from junction.

finite  $\tau$ , it was determined that each photon absorbed resulted in a transfer of one electron across the junction, in agreement with the previous finding of unit quantum efficiency.<sup>5</sup> This treatment of light as a voltage-independent current generator is in agreement with the findings of Pietenpol<sup>6</sup> and differs in emphasizing diffusion and photo-current rather than photo-voltage which is usually discussed.<sup>7</sup>

From the lifetimes of Fig. 2 and values of  $\sigma_p = 2.5$  and  $\sigma_n = 0.188$  determined by probe measurements, a value of 0.007 for  $eI_s/kT$  was found, compared with a dc low voltage value of  $0.011 \text{ ohm}^{-1} \text{ cm}^{-2}$ .