Growth of Germanium Single Crystals Containing *p-n* Junctions

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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.[1] 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 μsec.

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[2] and in their electrical properties as discussed in an accompanying letter.[3]

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.

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[1] G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).
[2] W. Shockley, Bell System Tech. J. **28**, 435 (1949).
[3] Goucher, Pearson, Sparks, Teal, and Shockley, Phys. Rev. **81**, 637 (1951).

Theory and Experiment for a Germanium *p*−*n* Junction

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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 exoerimentally, 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[1] was *p*-type. The unit reported here was 0.65×0.6 cm in cross section.

According to theory[2] the rectification curve for such a junction should be of Wagner[3] form $I=I_s[\exp(eV/kT)-1]$. Figure 1 shows a comparison between theory and experiment, the theoretical value 39 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.

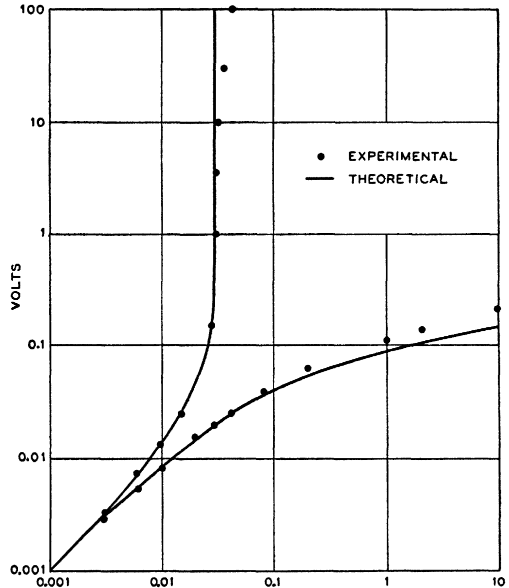

FIG. 1. Rectification characteristics of a *p*−*n* junction.

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 σ_i taken as 0.0165 ohm^{-1} cm^{-1}, the conductivities of the two regions σ_p and σ_n, the lifetimes of injected carriers τ_p for holes and τ_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[4] a distance x to the junction with decay factors of $\exp(-x/L)$, where $L=(D\tau)^{\frac{1}{2}}$ is the diffusion length, a prediction which is in agreement with Fig. 2. Except for the decay due to finite τ, 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.[5] This treatment of light as a voltage-independent current generator is in agreement with the findings of Pietenpol[6] and differs in emphasizing diffusion and photo-current rather than photo-voltage which is usually discussed.[7]

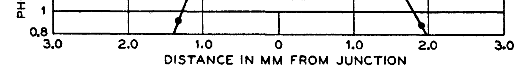

FIG. 2. Photo-response *vs* distance from junction.

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 ohm^{-1} cm^{-2}.

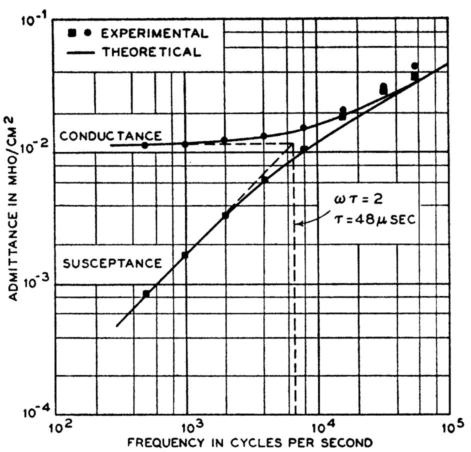

FIG. 3. Admittance of $p-n$ junction *vs* frequency.

A further check of the lifetime results was obtained from the impedance characteristic at zero bias, Fig. 3, which is in good agreement with the theoretical form based on diffusion theory.[2]

For reverse biases, the diffusion term is suppressed and a capacity corresponding to a concentration gradient in the transition region was found. From Eq. (2.46) of reference 2 a value of 10^{18} cm^{-4} was obtained.

The dependence of admittance on bias for intermediate biases has also been found to be in agreement with theory as has the effect of temperature. The dependence of the photo-response on wavelength has been used for the study of surface recombination, which is more important at the short wavelengths which do not penetrate deeply.

We are indebted to W. L. Bond and H. R. Moore for aid with the experimental techniques, and to J. A. Morton for encouragement in connection with the germanium single-crystal program.

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[1] G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).
[2] W. Shockley, Bell System Tech. J. **28**, 435–489 (1949). W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, New York, 1950).
[3] C. Wagner, Physik. Z. **32**, 641 (1931).
[4] F. S. Goucher, Phys. Rev. **81**, 475 (1951).
[5] F. S. Goucher, Phys. Rev. **78**, 816 (1950).
[6] Personal communication.
[7] H. Y. Fan, Phys. Rev. **75**, 1631 (1949) and reference 3 for additional publications.

On the Isomerism of Kr^{83} and Xe^{133}

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IN previous communications[1,2] we have reported β-spectrometer investigations on electromagnetically separated Kr^{83m} and Xe^{133m} obtained in fission. By improvements in the experimental technique used we have obtained some new results which will be reported here.

Kr^{83m}.—Previously we had found[1] that only one γ-ray of energy 32.7 kev is associated with the isomeric transition in Kr^{83}. By the use of a thinner G-M window in the β-spectrometer (cutoff $\sim$5.0 kev) four additional electron lines of energies 7.3, 9.0, 10.5, and 12.1 kev were found (Fig. 1). All six electron lines have the same half-life $\sim$114 min. The first two lines are interpreted as the L and M lines of a γ-ray of energy 9.3 kev. The 10.5- and 12.2-kev lines have energies in agreement with the Auger lines K–$2L$ and K–L–M of Kr.

The $K2$ and $L2+M2$ lines of energies 17.7 and 30.5 kev are hardly absorbed in the G-M window. After making the window absorption correction, we obtain the following intensity relations:

$$N_{L1}/N_{M1}\sim 3, \quad (1)$$

$$N_{K2}/(N_{L2}+N_{M2})=0.35, \quad (2)$$

$$(N_{L1}+N_{M1})/(N_{K2}+N_{L2}+N_{M2})\sim 0.8. \quad (3)$$

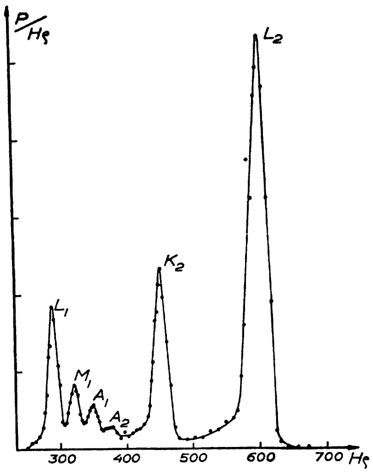

FIG. 1. β-spectrum of electromagnetically separated Kr^{83m} obtained in fission. Resolving power of the β-spectrometer $\sim$5 percent.

From Eqs. (1) and (2) it must be concluded that the 32.2-kev (new energy value) γ-ray is responsible for the isomeric transition. Siegbahn and Thulin[3] have found a γ-ray of energy 27 kev in a separated Kr^{88} sample for which N$_K/(N_L+N_M)\sim 8$. This γ-ray, however, is not associated with an isomeric transition.

Because of the low energy both γ-rays should be almost completely converted. The intensity relation[3] is then in accordance with the assumption that the two soft γ-rays in Kr^{83m} are emitted in cascade.

The half-life 114±2 min (measured with the $L2+M2$ lines in the β-spectrometer) and the energy are consistent with the multipole order 4. The spin of the ground state of Kr^{83} is 9/2. It seems hard to explain the experiments without associating the lowest excited level in Kr^{83} with the spin 7/2 and the isomeric state with the spin $\frac{1}{2}$. Both the multipole order $l=4$ and the spin 7/2 are, however, in contradiction to the spin-orbit coupling nuclear theory. Because of the soft γ-energy 9.3 kev, the first excited state in Kr^{83} is most probably delayed. Delayed coincidence measurements

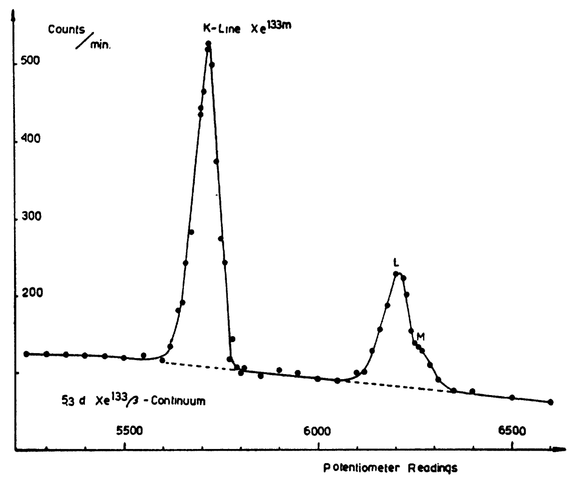

FIG. 2. Conversion lines of Xe^{133m} produced by neutron irradiation. Resolving power of the β-spectrometer $\sim$1 percent.