Within the present limits of error the wave-lengths calculated from the observed Raman lines coincide with the wave-lengths at which the liquid air bands were observed in the present study.

In order to check the tentative assignment of the observed bands to N_2 and O_2 further measurements were made on liquid nitrogen and liquid oxygen. In the spectrum of liquid nitrogen, the 4.3μ-band was strong but no band was observed near 6.4μ. In the spectrum of liquid oxygen, the 6.4μ-band was extremely intense and the 4.3μ-band was weak; the weak 4.3μ-band could be attributed to nitrogen, which was present in a concentration of 10–15 percent as an impurity. These results are in agreement with the assumption that the 4.3μ-band is due to the fundamental vibration of N_2 and the 6.4μ-band to the fundamental vibration of O_2.

Concerning the processes involved in absorption by N_2 and O_2, we might mention several possibilities. First, there are quadrupole-radiation processes which are possible for homonuclear molecules. Quadrupole radiation would account for weak absorption by N_2 and O_2 in both gaseous and liquid states; there is no *a priori* reason for expecting a marked increase in absorption when liquefaction takes place. Second, there is the possibility of "enforced dipole radiation," which results from dipole moments induced during collisions between molecules; absorption by this process would be much greater in the liquid than in the gas. In the case of O_2, there is the possibility of magnetic dipole radiation, since O_2 has a large magnetic dipole moment. Finally, there is the possibility that the molecules in the liquid are actually associated as definite polymers which could absorb by dipole-radiation processes. From the work done thus far, it is impossible to ascertain the relative importance of these possible radiative processes in the observed absorption. The work on liquids is being continued, and it is possible that further studies of other absorption bands observed at shorter wave-lengths will yield valuable information.

It might be pointed out that the fact that the close proximity of the N_2 and O_2 bands to the strong atmospheric absorption bands of CO_2 and H_2O may have masked weak absorption bands which may be produced by N_2 and O_2 in the gaseous state. Studies of the infra-red absorption of dry oxygen and CO_2-free nitrogen gas are planned for the near future.

We wish to thank Professor H. H. Nielsen for his interest and encouragement and Professors R. A. Oetjen and E. E. Bell for making the infra-red equipment available to us.

* The infra-red positions calculated from band-head measurements are 4.238μ for N_2 and 6.327μ for O_2.

Dependence of Resistivity of Germanium on Electric Field*

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May 16, 1949

WE have previously reported experiments[1,2] which were originally designed to explain the anomalously low spreading resistance of high back voltage germanium rectifiers. These experiments showed that the resistance of high resistivity ($\rho \gtrsim 1$ ohm-cm) germanium samples is reduced when high field strength pulses are applied. Most of the experiments were carried out with constant current pulses (five microseconds long, with a repetition rate of 60/sec.) applied through soldered contacts to rectangular blocks of germanium, one to five millimeters long. The pulses were observed and measured on an oscilloscope. The experimental arrangement is illustrated in Fig. 1. At fields of the order of 100 volts/cm and even less, appreciable decreases in resistance were obtained. The changes in resistance lagged behind the voltage, producing a delay of one or more microseconds before equilibrium could be obtained.

Subsequent experiments at the Bell Telephone Laboratories[3] indicated that holes are injected into the *N*-type material from the positive metal contact, and that the holes are drawn into the material by the electric field, thereby increasing the carrier concentration and decreasing the resistance. The lag in the resistance changes may be explained by the transit time of the injected holes, which move with a mobility estimated by Haynes and Shockley[4] to be 1200 cm^2/volt sec.

This interpretation is also consistent with Hall effect and resistance-temperature dependence measurements made at high field.

Hall effect measurements were made, utilizing the high field pulse technique. Because of the large current densities, measurable Hall e.m.f. pulses of the order of one volt were obtained across soldered Hall probes in a transverse magnetic field, $H = 4600$ gauss. The Hall constant was found to decrease rapidly with electric field strength, thus corroborating the idea of an increase in concentration of carriers by the high electric field.

The temperature dependence of the conductivity σ was studied at various electric fields across the sample. In Fig. 2 are shown curves of this dependence. From these curves, the temperature dependence of the changes in conductivity at a given field, $\Delta\sigma$, can be calculated. $\Delta\sigma$ is found to increase with rising temperature in the impurity conduction range, but decrease with temperature in the transition to intrinsic conduction. To interpret the temperature measurements both the injection and transmission of the carriers have to be considered. Low voltage Hall and resistivity curves on the same samples showed that in the impurity range the mobility varied as $T^{-\frac{1}{2}}$ and the concentration of carriers was nearly constant down to about 140° absolute. We would expect that as the temperature rises and mobility decreases, the transmission of the injected carriers at a given field would decrease, and consequently $\Delta\sigma$ would become smaller. Since $\Delta\sigma$ actually increases in the impurity range, it appears that the injection rate increases with T, and that this increase more than compensates for the decrease in mobility. The decrease of $\Delta\sigma$ with rising temperature in the transition range may be due to a decrease in the lifetime of the injected carriers as the concentration of the holes and electrons becomes high, or a decrease in injection rate if the barrier height for hole injection has increased.

Very similar effects are obtained in *P*-type germanium[2] with high field strength pulses. Specifically, a decrease in resistance which lags behind the voltage, a decrease in Hall constant with electric field, and qualitatively similar temperature dependence of $\Delta\sigma$, (see Fig. 2) were all found. Further experiments showed that

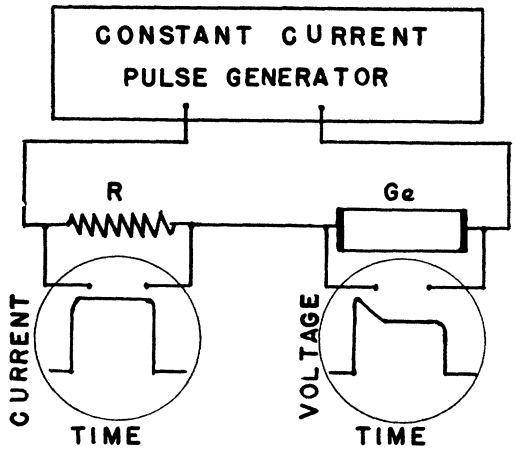

FIG. 1. Schematic illustration of experimental arrangement and of current and voltage pulses for a block of germanium.

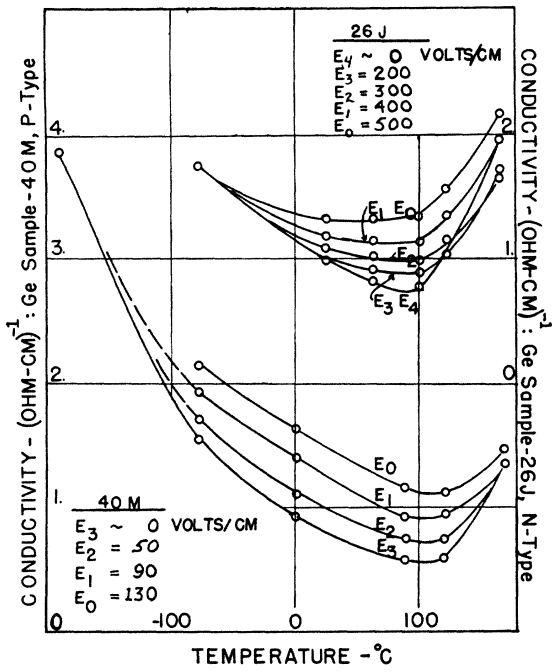

FIG. 2. Dependence of the conductivity of an N- and a P-type germanium sample on the temperature, at various electric fields across the sample. The samples are impurity semiconductors for temperatures below about 100°C; above that temperature, there is a transition to intrinsic conduction. The N-type sample (26J) is 0.21 cm long with a cross-sectional area of 0.011 cm². The corresponding dimensions on the P-type sample (40M) are 0.45 cm and 0.028 cm².

the *injection of electrons from the negative metal contact* accounts for the effects in *P-type germanium*. The latter results will be presented in a subsequent communication.

* Work supported by the Signal Corps.

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[2] Ralph Bray, Phys. Rev. **74**, 1218 (1948).
[3] J. Bardeen and W. H. Brattain, Phys. Rev. **74**, 230 (1948); E. J. Ryder and W. Shockley, Phys. Rev. **75**, 310 (1949).
[4] J. R. Haynes and W. Shockley, Phys. Rev. **75**, 691 (1949).
[5] The median value of hole mobility due to lattice scattering, determined on some 15 P-type germanium samples by d.c. methods by K. Lark-Horovitz and collaborators, is about 550, with values of over 1000 for some high purity samples.

Cathode Sputtering in the Abnormal Glow Discharge

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TO continue the study[1] of intensities of spectral lines from a He low voltage arc, an intense He glow discharge (Geissler tube) was constructed. Some properties of this glow discharge are discussed.

Intensities as a function of pressure (see Fig. 1) agreed qualitatively with results found[1] for the low voltage arc. Since the pressure for maximum intensity was well within the abnormal glow discharge region (<15-mm Hg), cathode sputtering was expected to be high.[2]

To decrease sputtering Al electrodes are useful.[3-6] Our comparison of Al alloy electrodes (4 percent Cu, 0.5 percent Mg, 0.5 percent Mn) with pure Al (99.99 percent Al, 0.003 percent Fe, trace Ca, Cu, Mg, Si) showed markedly reduced sputtering for the latter. If the relatively higher sputtering rate of alloy Al were due to the higher sputtering rate of most of the alloy materials (in pure form),[7] the deposit should be richer in alloy materials. Spectrographic analysis of deposits from pure and alloy electrodes failed to show this enriching effect except for two or three doubtful cases.

The sputtered material appeared to be deposited in two forms. The localized form was characterized by fairly well-defined bands on the glass coaxial with the cylindrical tube and cylindrical hollow electrodes. With the tube axis vertical, the top of the upper band, for example, was in the same plane as the bottom of the upper electrode. Considerations of electrode and tube diameters, and band width and position, imply, for rectilinear motion, that the sputtered material reaching the tube wall came from the inside lower $\frac{1}{4}$ of the electrodes within a certain maximum angle with the normal (*ca.* 45°). The general form was deposited evenly throughout the bulbs and to a lesser extent within the capillary. The rate of deposit of the general form relative to that of the localized form increased with decreasing pressure. These two forms, also observed by Hulbert,[6] may represent different methods of deposition, the localized due to ion bombardment and ejection of solid particles, the general due to high temperatures and subsequent evaporation.

Measurements, with pure Al electrodes, showed that sputtering rate increases with decreasing gas pressure, agreeing with previous results.[7] In our case the region of maximum line intensity (*ca.* 2-mm Hg) was also a region where the sputtering rate changed markedly, increasingly by a factor of 20 as the pressure decreased from 2.70-mm Hg to 1.30-mm Hg. This large difference in sputtering rate results in a correspondingly large difference in the useful life of tubes sealed off at different pressures. Moreover, small changes in gas pressure have a marked effect on spectral intensities in this region. These two effects make it desirable that the sealing-off pressure for high intensity long-life tubes be determined with some certainty.

Investigation showed a region of large current change for small change in pressure (Fig. 2). The curves must have a steep slope at about 1.7-mm Hg since in no case is there an experimental point on neither the upper nor lower curves. The curves, representing data from the same tube, were taken at different times after starting the discharge (causing shift along current axis) and at different gauge temperatures (causing shift along pressure axis).

As gas pressure was decreased across this critical region (near 1.7-mm Hg) the discharge became suddenly and considerably

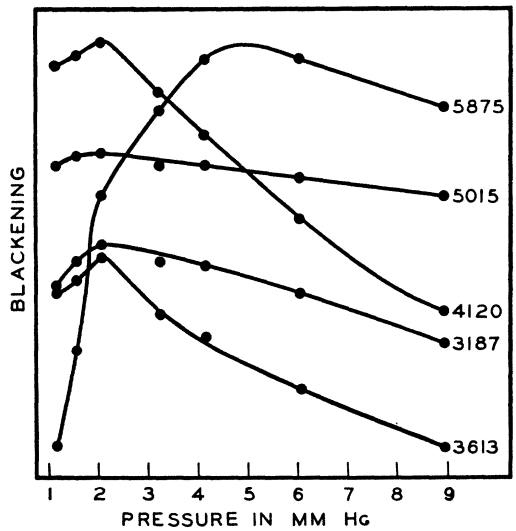

FIG. 1. Photographic blackening as a function of gas pressure. On the blackening axis the origin for each curve is different; the units are arbitrary, but the same for all curves. Four curves (5015, 4120, 3187, and 3613A) are typical. Of 17 lines measured, 16 are similar, showing a maximum intensity at 2.2-mm Hg; line 5875A, however, is anomalous.