generally been reported in the literature. Since these authors discussed this point in detail, there is no need to do so here.

Finally, calculating D_0 from Zener's theory[3] and using the value of the vibration frequency, ν, obtained from the Debye temperature for zinc, one obtains 0.537 cm^2/sec. Similarly, using Nowick's method[4] for calculating Q from the highest-temperature data, one obtains 41 690 cal/mole. These values are in obviously fortuitous agreement with the experimental data.

[3] C. Zener, J. Appl. Phys. 22, 372 (1951).

[4] A. Nowick, J. Appl. Phys. 22, 1182 (1951).

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Amphoteric Impurity Action in Germanium*

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A new type of impurity action in germanium is described. This is "amphoteric" impurity action, to be contrasted with "donor" and "acceptor" action of the usual impurities in germanium. An amphoteric impurity, of which gold is shown to be an example, is an element that may either donate or accept electrons in the semiconductor, depending upon the nature and amount of other impurities present, that is, upon the position of the Fermi level as determined by these impurities. Previously the acceptor action of gold in germanium had been described, and it was shown there were two acceptor levels, 0.15 and 0.55 ev above the valence band. Morton, Hahn, and Schultz have found evidence of a third state which they interpret as the first acceptor level. In the present investigation, the existence of a third state is confirmed, and it is shown, with rather high degree of certainty, to be a donor level 0.05 ev above the valence band. This appears to be the first nonhydrogenic donor state yet observed in germanium. When gold is added to germanium containing third column elements in amounts less than the gold content, the carrier density remains constant, but the carriers acquire an ionization energy of 0.05 ev. Good agreement was obtained with several sources of gold. This behavior, it appears, can be explained most simply by assuming that neutral gold atoms may give up electrons to low-lying empty states to form Au^+. The upper gold states when filled are still interpreted as Au^- and Au^{--}.

INTRODUCTION

THE acceptor action of gold in germanium has been described in several papers.[1] In this work it was shown that gold was capable of taking up electrons at two energy levels, situated about 0.15 and 0.55 ev above the valence band. It was suggested that these levels were probably due to the formation of, first Au^- and then Au^{--}. These states were shown to be highly different in ionization energy from the states due to ordinary donor and acceptor impurities in germanium. Because of the great depth of these levels, a wide variety of new applications were opened up, including studies of trapping and secondary photoconductivity, and studies utilizing the high resistivity available at 77°K.

Morton, Hahn, and Schultz[2] have recently investigated the action of gold in germanium, and, in addition to confirming the existence of the above acceptor levels, have found evidence for a third state. They interpret their results as indicating an acceptor level 0.05 ev above the valence band, which takes up electrons to form Au^-. The upper two levels when filled with electrons would then be Au^{--} and Au^{---}.

There are several difficulties in accepting this interpretation of these results. In the first place, the original investigations[1] had indicated, with an accuracy somewhat better than 25%, that there were only two acceptors per gold atom, these levels being present in approximately equal numbers. Secondly, there is an intrinsic difficulty in assuming an Au^{---} center only 0.5 ev above the valence band. The electrostatic repulsion of the two electrons toward a third electron should be rather large.

Because of these difficulties, an investigation was made of the third gold level. This work confirmed the existence of such a level, but indicated that it was a donor level 0.05 ev above the valence band. With this change of interpretation, all the results were found to be consistent with previous studies on gold-doped germanium. Besides fitting in well with the finding of two acceptor states per gold atom, the new hypothesis agreed with previous results that when gold was added to pure germanium, the product was always p-type. This follows from the great depth of the donor level, and its inability to contribute directly to the number of conducting electrons. The state shows up only in p-type material, where it furnishes a supply of electrons for trapping holes, and for furnishing acceptor levels associated with re-excitation of holes back to the valence band.

* Work performed at General Electric Research Laboratory, Schenectady, New York.

[1] W. C. Dunlap, Jr., Phys. Rev. 91, 1282 (1953); 97, 614 (1955).

[2] Morton, Hahn, and Schultz, Atlantic City Photoconductivity Conference, November, 1954 (John Wiley and Sons, Inc., New York, 1956).

TABLE I. Segregation coefficients for gold and ordinary donor elements, showing concentrations of each donor required exactly to balance out possible acceptor levels of the gold. PPM refers to the required content of each element in the gold used for doping, in parts per million, that will give an electron concentration in the solid crystal, just equal to the gold content.

	Approximate segregation coefficient	PPM by wt to balance gold content in Ge
Gold	1.5×10^{-5}	···
Phosphorus	0.1	2.4
Arsenic	0.01	56
Antimony	0.001	860

In the previous studies of Morton, Hahn, and Schultz, the apparent presence of electrons was ascribed by them to accidental donor impurities in the added gold. In the present work, this hypothesis is ruled out by careful counting of states, and by the demonstration that different sources of high-purity gold lead to almost identically the same results. The effects observed in the present work could be accounted for by assuming the existence in the added gold of a donor impurity capable of furnishing in the germanium an electron density exactly equal (within a few percent) to the gold content. The probability of this occurring is so small that it can be ruled out.

EXPERIMENTAL METHODS

The methods used in the investigation were similar to those used in previous studies on gold. Single crystals were grown containing various quantities of gold and other impurities, and wafers for Hall and resistivity measurements were cut from selected portions of these ingots. Since the donor levels show up only in *p*-type material, the added impurity was usually gallium, added in various quantities up to and equal to the gold content in the crystal. An important assumption is made that the gallium content did not vary rapidly over a distance of about one-fourth inch, the distance required to obtain two wafers of, respectively, zero gold content, and known gold content.

The gold used came from two sources. The first, Johnson-Matthey spectrographically assayed gold, was the same as that used by Morton and his collaborators in their studies.[3] This gold was assayed as 99.999% pure, the analysis showing mostly traces of silver and copper. The second type of gold came from Sigmund Cohn, and was the gold mainly used by the author in his previous studies on gold-doped germanium. This material was assayed in the General Electric Research Laboratory and found to be comparable in purity with the Johnson-Matthey gold-again, silver and copper were found to be the important impurities. Because of the low sensitivity of the spectrograph for detection of phosphorus, arsenic, and antimony, no independent evaluation of the gold with respect to these impurities could be made. To give an electron density in the crystal just equal to the gold content, a donor element must be present in the gold exactly in the amount indicated in Table I.

[3] The author is indebted to Dr. G. A. Morton for a sample of this gold.

RESULTS

Figure 1 shows the properties of a sample of *p*-type gold-doped germanium grown as shown in the inset. After initial doping with gallium, the crystal was grown about one-half inch, when 100 mg Johnson-Matthey gold was added. Two Hall wafers were cut close to the point of doping, one before and the other after. The Hall curve of the wafer taken prior to the gold-doping shows little of interest below 77°K—there is a slow rise of Hall coefficient corresponding to the well-known ionization energy for gallium, 0.01 ev. The Hall curve for the gold-doped specimen, on the other hand, shows several interesting features:

(1) At the lowest temperatures, in the range of 30°K, the resistivity and Hall coefficient are very high, and drop with temperature at a rate indicating an ionization energy of about 0.05 ev.

(2) At saturation, (77°K) the Hall curve drops to almost exactly the level it had before the gold doping.

(3) Above 77°K, the Hall curve drops by an amount to be expected from previous results, as a result of the action of the lower acceptor level.

From (1) we confirm the existence of a third state of gold, as suggested by Morton, Hahn, and Schulz. It remains to be determined whether or not these apparent acceptor levels are due to an acceptor state of the gold, or are due to re-excitation of electrons (to the empty donor gold levels) that were trapped out by the gallium present. Item (2) is particularly pertinent in this res-

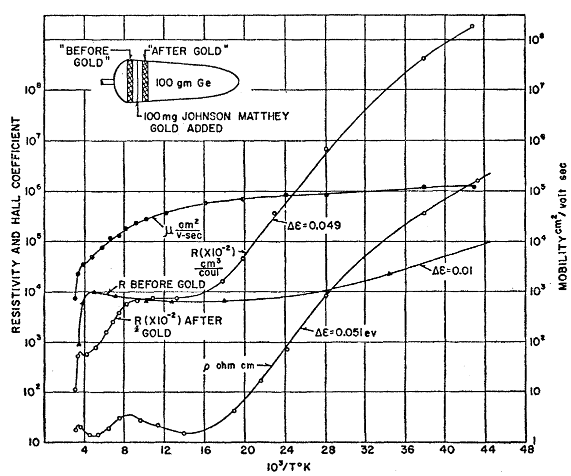

FIG. 1. Hall coefficient, resistivity, and Hall mobility of a sample of germanium doped with gallium and gold during growth of the single crystal. The large slope at lower temperatures indicates the presence of a state of energy about 0.05 ev. Also, the coincidence of the two Hall curves at 77°K is evidence for the donor level hypothesis, barring the occurrence of an extremely unlikely coincidence in which the gold would carry just exactly the required impurity donor content to balance out each and every gold center.

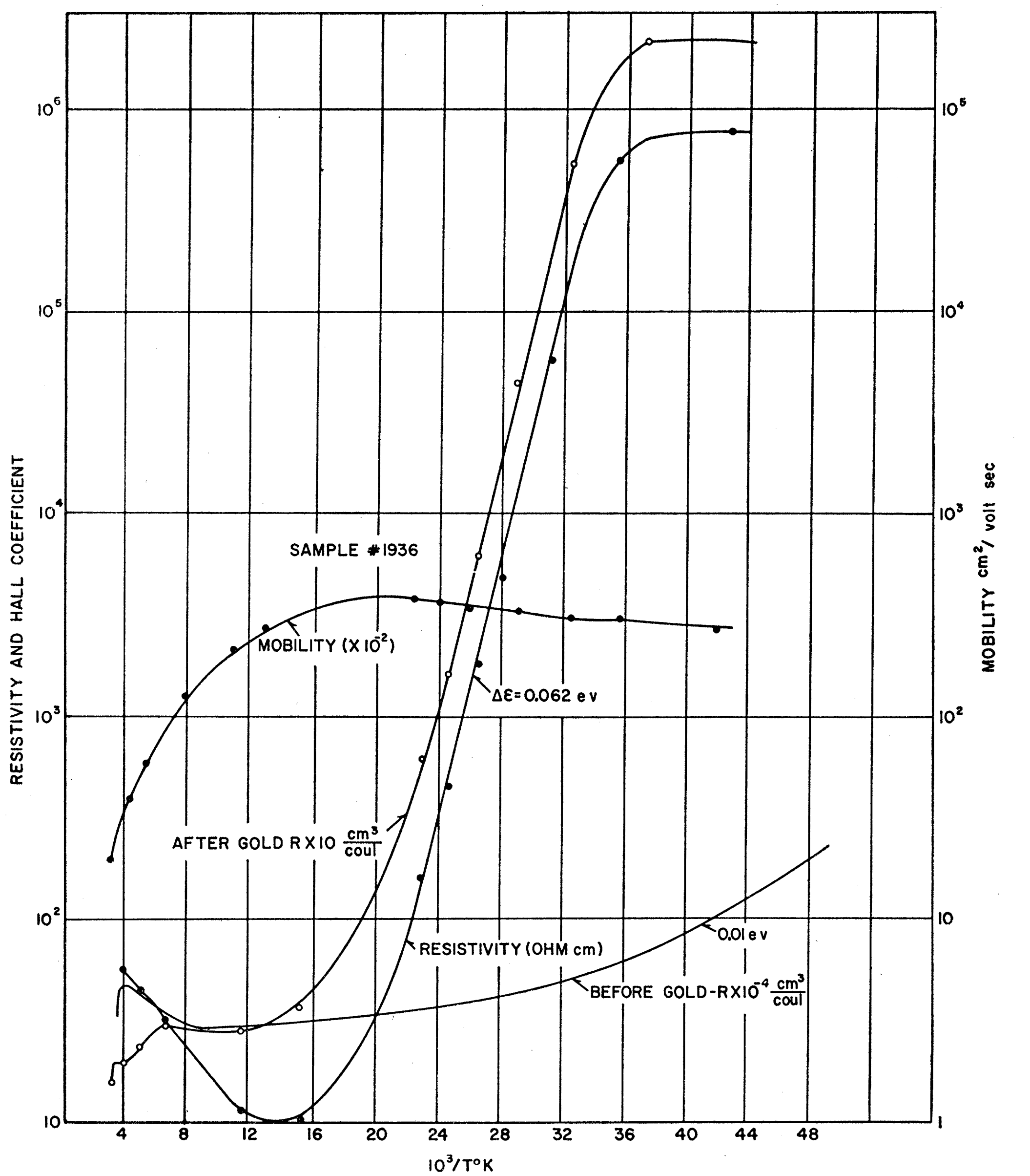

FIG. 2. Similar results to those of Fig. 1, on another sample, and with another source of gold. The conclusions to be drawn are the same as those of Fig. 1. The good agreement is added evidence against the occurrence of accidental donors in the gold.

pect. It shows that if each gold atom were contributing an acceptor level at 0.05 ev, there must be present exactly as many impurity electrons as gold atoms, in order to maintain the carrier content at 77°K equal to the original carrier content due to gallium.

Figure 2 shows results on a similar sample, made with another source of gold. The conclusions obtained from the study of this sample agree with those from Fig. 1. Because of the unlikelihood of the impurity content in gold from two independent sources being accidentally in the very narrow range required to produce the observed effects on the "gold-acceptor+impurity-electron" picture, the necessity of assuming that the gold states are donor levels becomes even more strongly apparent.

The samples of Figs. 1 and 2 show characteristics similar to those of copper- and zinc-doped germanium specimens. The mobility, for example, rises as the temperature is lowered, until a maximum is reached at about 50°K. Below this temperature, because of increased scattering by impurities and lattice imperfections, the Hall mobility tends to fall off slightly, or remain nearly constant. Another effect noticed in these as in other high-resistivity samples, is the leveling off

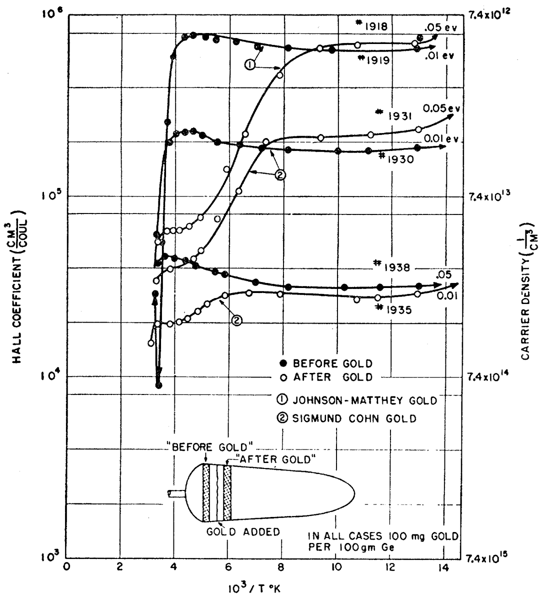

FIG. 3. Plot of Hall coefficient for a number of samples of germanium doped with gold and various amounts of gallium. The high-temperature region is shown, to emphasize the degree of constancy of the carrier density upon addition of gold, at 77°K. In several cases, the change of carrier density is only a few percent of the gold content added.

the Hall and resistivity curve at low temperature. This effect has not been definitely explained, but may be due to (1) surface effects, (2) direct conduction between the impurity levels themselves (impurity banding), (3) conduction through inhomogeneity paths in the germanium along which the ordinary acceptor levels may be dominant.

Figure 3 shows additional results obtained with samples containing fixed gold content, and with increasing gallium content. According to the gold donor level scheme, when gallium is added in concentrations exceeding the gold content, the high ionization energy should be replaced by that of the ordinary (gallium) states. At all intermediate levels of gallium, the gold levels should be effective, and the 0.05-ev level should be seen.

Figure 3 shows the high-temperature portion of the Hall curves of Figs. 1 and 2, with one additional curve for high gallium content. Because of the increased scale sensitivity, the changes in carrier density accompanying the addition of gold can be seen more easily than in the other figures. In the case of curves (1), the addition of gold changed the carrier density by only 3% of the gold content while in the other two cases the differences were less than 10%. In view of the uncertainties in doping experiments of this kind, and the possibilities of accidental addition of donors, the agreement with the donor model is good, as previously indicated.

The gold acceptor level density is determined from the high-temperature portions of these curves—between 77°K and room temperature. There the Hall curves drop from values given by the gallium density to a new value determined by the gold density. From these values the gold-acceptor densities in all three samples could be determined. They were found to be equal within the experimental accuracy. The values were about 2×10^{14} gold atoms/cm^3. When gallium was added to a concentration slightly greater than 2×10^{14}, the resistivity no longer reached high values on cooling to 20°K. This confirms the rough equality in the number of lower states (0.05 ev) with the number of gold acceptor levels (0.15 ev), and indicates further that the donor levels are characteristic of the gold atoms in their normal configuration, not atoms that might have different properties as a result of some abnormal location in the lattice.

Thus the picture of the gold levels in germanium is that indicated in Fig. 4. The half-circles indicate unfilled levels, the filled circles filled levels. The diagrams indicate the emptying of the gold levels into low-lying acceptor states at low temperature, and the refilling of the various levels at each stage of rising temperature.

DISCUSSION

The results obtained in this study have a number of new features. The gold level under discussion is, apparently, the first donor level not of the hydrogenic type to be found in germanium. It is also the first case of donor action due to elements outside the fifth column of the periodic table, with the exception of lithium. Since lithium has an ionization energy of 0.01

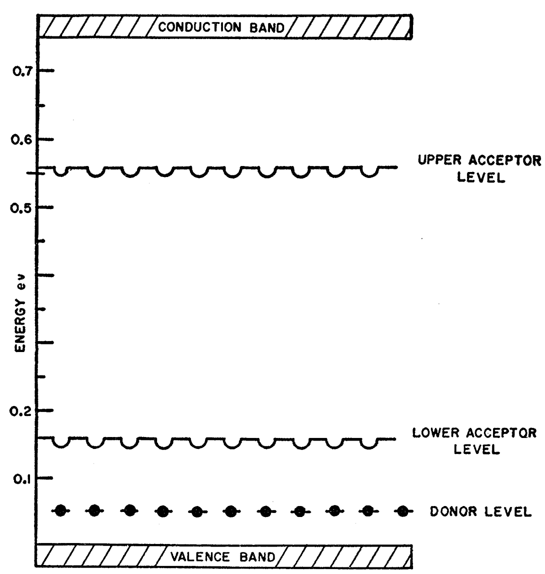

FIG. 4. Model of the gold center in germanium. These levels represent the energy of an electron added to a state containing -1, 0, and 1 electron, respectively, starting at the bottom. Thus the gold ion has the charge 0, -1, and -2, when the respective states are filled with electrons. When the lowest state is empty, the gold ion has the charge $+1$, so that the gold occurs in four ionic states in germanium.

ev, this case falls under the label "hydrogenic." The donor action of the gold may, as in the case of lithium, be ascribed to the single valence electron, in this case a 6*s* electron. It appears probable that gold can give up this electron to low-lying empty levels and thereby become Au^+.

Because of the low level of the donor state, it is not possible to see donor action directly due to gold in germanium, and the effects are seen only through the trapping action upon *p*-type germanium. When gold is added to pure germanium, the product is always *p*-type.

A second significant feature of the present result is that gold appears to be the first element in germanium that is capable of both donor and acceptor action in the same sample. Because gold has both an electropositive and electronegative character in Ge, the term "amphoteric" impurity element appears to describe it accurately.

When the sample, of say, Fig. 1 is heated from 0°K to room temperature, the gold levels initially possess the charge Au^+. As the temperature reaches 77°K, practically all the electrons that had been trapped by the gallium states are re-excited to the gold levels, and these become Au^0. On going to still higher temperatures, the electrons in the valence band have enough energy to be excited directly to the lower acceptor level and the gold becomes Au^-. An interesting feature of the model is that these electrons cannot come from the gold donor level, since the states have to be filled before the lower acceptor level exists, that is before the gold atoms are in a position to take up electrons at this energy. The sequence of events on adding gold, heating from 0°K to 77°K, and from 77°K to 298°K is shown in Fig. 5. Once again we see that at higher temperature the donor levels add no free carriers, and their primary effect is that of a trapping state.

The upper acceptor level, 0.2 ev below the conduction band, does not enter into any of the present data. Because of the onset of intrinsic conduction, it is not possible for an appreciable number of electrons to be excited into these levels—intrinsic conduction, in other words, restrains the Fermi level to the middle of the forbidden region.

The question remains as to the importance of the donor level in the statistical analysis of the *p*-type gold-doped specimens. It appears that no major extension of the work described in the previous paper is needed to account for the presence of this level. Nor is the closeness of the donor level to the valence band and to the lower acceptor level a problem, since for concentrations usually used in experiments of the present type, the excitation in the various regions is confined to separate temperature ranges—the ordinary donors are excited from 1°–20°K, the 0.05 level between 20° and 77°K and, the lower acceptor level between 77°K and 298°K. All that needs to be kept in mind is the availability of a supply of electrons at an energy level 0.05 ev above the valence band, and equal to the number of gold atoms.

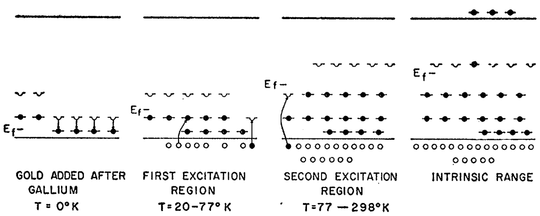

FIG. 5. Diagram showing the sequence of events in the various stages of the experiments shown in Fig. 1. Note that at any particular stage, only the level above that highest one containing an electron exists. As each level in turn is filled the next highest appears. This diagram is not to scale, in terms of energy.

We have seen that in germanium gold may take on, even at low temperatures, four different ionization states, and that there are three energies corresponding to the addition of electrons to the single positive, neutral, and single negative charged states. Besides the different ionization energies, these states are characterized by highly different capture cross sections for electrons and holes—the empty donor level being more selective in capturing electrons, the filled acceptor levels more selective in capturing holes, because of their Coulomb forces. Further studies on the properties of the various states are now in progress.

The results obtained on germanium now appear consistent with those on silicon, in which Taft and Horn[4] found a donor level 0.35 ev above the valence band. This level is probably similar in nature to the donor level in gold-doped germanium. The present work on germanium also makes it appear likely that a search will reveal acceptor levels in gold-doped silicon analogous to those found for germanium.

There also remains the interesting question as to whether there are such donor states of elements other than gold in germanium. Low-lying donors are rather difficult to show up, since they produce no direct effects as donors, but only as trapping centers for holes. It appears quite possible that a search among the transition elements, which have been shown to produce acceptor levels like gold in germanium, may also show up one or more donor levels for these elements.

Also of interest are the other elements of the gold group, particularly copper, platinum, and the other noble metals, such as rhodium and iridium. Previous work on platinum indicated the presence of an acceptor level at 0.04 ev above the valence band, and 0.2 ev below the conduction band. There seems some question as to whether or not the lower of these states might be, in actuality, a donor level as in the case of gold.

ACKNOWLEDGMENTS

The author wishes to acknowledge with thanks the help of Dr. W. W. Tyler in obtaining the low-temperature data.

[4] E. A. Taft and F. H. Horn, Phys. Rev. **93**, 64 (1954).