History of Semiconductor Research*

G. L. PEARSON† AND W. H. BRATTAIN†

Summary—**This paper presents a running story of semiconductor research from its earliest beginnings up to the present day, with special emphasis on the inception of new ideas and the resolution of older discrepancies. At several points in the story, short interludes are taken to fill in the status as of that time. Semiconductor research began quite inconspicuously about 120 years ago with some observations on the electrical properties of silver suphide. Progress was very slow for the next 50 years and then, about 1885, a mild interest developed with the discovery of point contact rectifiers. These devices were used as detectors until displaced by the vacuum tube around 1915. Development of selenium and cuprous oxide rectifiers about 1930 revived interest and the publication of a good theory of semiconductors in 1931 added still more momentum. The next period of active interest came around World War II when the catwhisker diode was revived and developed into an excellent radar detector. The announcement of the transistor in 1948 gave this field of research such a boost that it has become a real giant in the last few years and semiconductor electronics now rates as a major field of endeavor.**

Introduction

THE HISTORY of semiconductor research is a very interesting story, in fact it is so interesting that the present authors doubt that they are really doing it justice. One quickly realizes that a thorough job requires a prohibitive amount of time and energy. Two good review articles, one by K. Lark-Horowitz [1] and one by E. W. Herold [2], have recently been published. Each author takes a somewhat different viewpoint and the first mentioned article includes a comprehensive list of references up to 1951. There is, of course, no point in reproducing such a bibliography or in simply rewriting the material in these publications.

We have chosen to emphasize in the present article the interplay of ideas in the development of semiconductor research which has impressed us during our long connection with semiconductors starting in the early 1930's, and have chosen to write from this viewpoint. We are likewise impressed with the length of time required for certain key ideas to become accepted as well as how long some misconceptions lasted. There should be an object lesson in this for future workers. We realize, however, that our perspective becomes clouded as the story approaches the present time. This not only makes the writing more difficult, but likewise makes it almost impossible to distinguish between the current key ideas and misconceptions of today. The lesson is, therefore, of no particular value except possibly to the rare individual who can see the present in its true perspective.

If any of our friends feel slighted because no mention is made of their work, let them remember that the material to be covered is actually too large for one short article and that merely listing all the published papers during the last five years would fill a good sized book [3]. For the sake of brevity, our bibliography often lists one comprehensive article rather than the numerous original contributions. Finally, we freely admit that the latter part of the story draws heavily on the work carried out by our colleagues at the Bell Telephone Laboratories.

Early History of Semiconductors

Probably the first significant observation in the semiconductor field was made by Michael Faraday [4] in 1833 when he found that silver sulfide had a negative temperature coefficient of resistance. This characteristic set it apart from other conductors (metals) whose resistance increased with increase in temperature. The observation that a photovoltage could be produced by shining light on the surface of one electrode in an electrolyte by Becquerel [5] in 1839 was another early contribution. The next significant step was W. Smith's discovery [6] in 1873 that resistance of selenium could be reduced by shining light on it (photo-conductivity).

In 1874 came the discovery that contacts between certain materials would rectify, or more precisely, that the resistance did not obey Ohm's law but depended on the magnitude and sign of the applied voltage. F. Braun [7] observed this for contacts between metals and various sulfides such as galena and pyrites, and A. Schuster [8] for contacts between untarnished and tarnished (probably copper oxide) copper wires. Some workers thought that this phenomenon was a thermal effect, and this idea persisted up to about 1906. The first photoelement of the modern barrier layer type was made of selenium by W. G. Adams and R. E. Day [9] in 1876. While continuing this work on selenium, C. E. Fritts [10] in 1883 produced the first large area dry rectifier. Thus by 1885 four of the fundamental properties of semiconductors—(1) negative temperature coefficient of resistance, (2) rectification, (3) photoconductivity, and (4) photoelectromotive force—had been observed, although not all on the same material.

The demonstration of the existence of radio waves by H. Hertz in 1888 created a potential demand for a suitable detector, but it was not realized until 1904 that semiconductor rectifiers were well suited for this purpose. J. C. Bose [11], H. H. C. Dunwoody [12], L. W. Austin [13], and G. W. Pierce [14] found that point contacts (cat whiskers) on galena, silicon carbide, tellurium, silicon, etc. were good detectors of radio waves. Silicon detectors were found by experience to be most stable, while galena detectors had the best sensitivity. It was G. W. Pierce, by the way, who went to a great deal of

* Original manuscript received by the IRE, August 25, 1955.
† Bell Telephone Labs., Inc., Murray Hill, N. J.

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

effort at this time to show that these devices did not operate on a thermal basis. With the advent of the vacuum tube at about this time, interest in the point contact detector lagged and little of scientific interest was contributed on such detectors for a number of years.

The next period, beginning in the 1920's, saw the development of barrier layer rectifiers and photocells as commercial devices. Some good science and a large amount of art was involved. As we shall see later, the real understanding had to await the help of quantum mechanics and its application to the understanding of solids. The major contributions in this period were the development of the copper oxide rectifier and photocell by L. O. Grondahl and P. H. Geiger [15] and the almost parallel developments using selenium, described by B. Lange [16]. Commercial use of these devices as rectifiers, battery chargers, photographic exposure meters, and in the case of copper oxide as modulators and nonlinear circuit elements, created demand for better scientific understanding of underlying phenomena.

Though not generally accepted until the 1930's, it now appeared that rectification and photovoltage were surface properties occurring at the interface between the semiconductor and metal contacts or between two semiconductors. On the other hand, the mechanism of electrical conductivity which gave rise to the negative temperature coefficient of resistivity and the change of resistance under the influence of light (photoconductivity) appeared to be a body property within the homogeneous semiconductor. Various workers now proposed that electrical conduction within the body obeyed Ohm's law and that photoconductivity was due to an increase in the number of carriers by light excitation. The contributions of B. Gudden and R. W. Pohl [17] (beginning in 1921) on photoconductivity in the alkali halides should be mentioned in this connection. While these materials were more nearly insulators than semiconductors, they were nevertheless much less complicated than copper oxide or selenium. Also they could be fabricated into large *single crystals*, thus giving a more ideal solid for study. Most important of all, however, was the division of the problem into two parts, one of surface phenomena and the other of body properties. In what follows we will consider developments first in one category and then the other, switching back and forth as the story unfolds.

Developments in the Understanding of Body Properties up to 1942

It was natural that semiconductor research should borrow from the experimental progress and understanding of electrical conduction in metals. The discovery by E. H. Hall [18] in 1879 that electrons flowing in a metal could be deflected by a magnetic field perpendicular to the direction of current flow was, of course, a landmark.[1]

[1] The electron itself was not clearly identified until eighteen years later when J. J. Thomson measured the ratio of charge to mass of the cathode rays.

The interpretation of this effect to give the density of charge carriers was a very important tool for investigating conduction processes. Likewise the interpretation of the ratio of Hall field to electric field to give the mobility of the charge carriers was of great importance.

Workers in this field were pleased that the Hall effect in metals had the right sign (i.e., negative) which indicated that the carriers were negative charges and undoubtedly electrons. They were greatly disturbed, however, when it was found that some borderline metals gave positive Hall coefficients thus indicating positive charge carriers. Furthermore, the measured mobilities at room temperature were such as to rule out positive ions. This indicated, if you will, that there were apparently positive electrons long before anyone suspected the existence of positrons or holes.

When Hall effect measurements were performed on semiconductors several conclusions were at once apparent [19, 20, 21]. The number of charge carriers were much smaller than in most metals and the mobilities were somewhat larger. Some semiconductors, for example copper oxide, have a positive Hall coefficient, while others like zinc oxide had a negative coefficient. Disregarding for the moment the primary difficulty of positive carriers with mobilities of the same order of magnitude as electrons, these measurements were a great step forward. They enabled the researchers of this time to separate, conceptually at least, the conductivity σ into its two component parts: (1) the density n of carriers and (2) their mobility μ. The familiar relation $\sigma = en\mu$ had been shown to hold for electronic semiconductors.

It was found that the mobility was a property of the solid or crystal lattice and that for a given lattice it decreased with increase in temperature. On the other hand, the density of carriers increased *very rapidly* with temperature for any given semiconducting specimen, such as copper oxide. In addition it was found that n varied over *wide limits* at a given temperature from specimen to specimen of the same semiconducting material. In other words, n was both temperature and structure sensitive.

The difference between metals and semiconductors had now been pinned down. In metals the mobility was only slightly structure sensitive and it decreased with increase in temperature, whereas the number of carriers was almost constant and of the order of one per atom of solid. The resistivity of metals had a postitive temperature coefficient because of the change of mobility with temperature. In semiconductors the mobility varied with temperature as in metals, but the carrier density was orders of magnitude less and increased rapidly with temperature. The exact value of n at any given temperature was very structure sensitive; at room temperature it varied in the range of one charge carrier per thousand atoms of the solid to one per hundred million. The electrical resistivity of semiconductors was therefore a structure sensitive or *extrinsic* property. The negative

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

temperature coefficient was primarily due to changes in n, the variation in number usually swamping out the dependence of mobility on temperature.

At high temperatures it was observed that the density of charge carriers was no longer structure sensitive but equal for all samples of a given semiconductor. In this region the density of carriers increased even more rapidly with temperature and in general obeyed a simple law. The logarithm of the density was a linear function of the reciprocal of the absolute temperature. It was of course natural to interpret this behavior in terms of an activation energy proportional to the slope of this straight line. This activation energy turned out to be the same for any given semiconductor, such as copper oxide, and therefore was an *intrinsic* property of the solid. Attempts were also made to interpret the low temperature characteristics in terms of a second and smaller activation energy. With material available at the time, however, the results were questionable since this activation energy was found to be structure sensitive and, in general, a function of temperature.

Other important contributions were made in this period by chemically-minded workers such as Carl Wagner [22, 23]. It was found that in compound semiconductors the sign of the Hall coefficient could be correlated with small deviations from the stoichiometric composition. If, for example, in copper oxide there is a deficiency of copper in the solid, say a few parts per million below that necessary to satisfy exactly the chemical formula Cu_2O, then the sign of the Hall coefficient at low temperatures is positive, and this was called a *defect* semiconductor. If the compound is *over-oxidized*, it has a *positive* Hall coefficient. If on the other hand there is usually excess metal, as in zinc oxide (ZnO), then the Hall effect is negative, and this was called an *excess* semiconductor. The compound is slightly *reduced.* Finally at high temperatures in the intrinsic region all semiconductors were found to have negative Hall coefficients.

In the meantime, quantum mechanics was making great strides in interpreting the behavior of electrons in atoms and molecules. The experiments of C. J. Davisson and L. H. Germer and those of G. P. Thomson demonstrated the wave nature of electrons. The concepts of energy levels with one electron per level, electron spin, Pauli exclusion principle, and Fermi-Dirac statistics all led to a clarification of metallic conduction by A. Sommerfeld [24] and his co-workers. The concept of electrons as Bloch waves in a crystal contributed greatly to understanding the behavior of electrons in all types of solids.

In 1931, A. H. Wilson [25] presented a quantum mechanical model of a solid semiconductor which has since become fundamental for understanding the behavior of semiconductors. In retrospect it turns out that the Wilson model can be described from a number of different viewpoints. One of these is the picture of the electrons as waves throughout the solid or *crystal lattice.* At certain frequencies there is interference between these waves and the regularity of the crystal lattice, just as had been found for X-rays. Electron waves of such frequency cannot exist in the lattice. From the relation between frequency and energy, certain energies were thus excluded. This led to the concept of *energy bands* in the solid.

At low temperatures the electrons in the lattice fill the lowest energy bands, one electron of each spin per level, until there is just enough charge to make the entire lattice neutral. When the band structure is such that the last or *valence* electrons completely fill their band, there is a gap in energy E_g from the last filled level to the next possible energy site. Now the process of conduction involves accelerating the electrons by means of an electric field, thus adding to their energy. In order for this to happen there must be, in the quantum mechanical sense, empty energy levels available to receive the electrons. If there are none available (energy gap) then the electron waves cannot be made to drift in the direction of the field. Under these conditions, for every wave traveling in one direction through the lattice there is another in the opposite direction, and this situation cannot be altered except by a discrete jump in electron energy equal to the energy gap.

At any finite temperature there is of course a certain amount of thermal excitation, maintaining some electrons above the gap and thus leaving an equal number of vacant energy levels below the gap. This picture was ideal for explaining the *intrinsic* conductivity in semiconductors at the higher temperatures. The thermally excited electrons would be free to conduct and their density would depend on temperature as found experimentally, the energy of excitation being equal to the gap energy.

The above description is of course over-simplified. Quantum mechanics predicted that vacant sites, or *holes*, should also be free to conduct with possibly as great a mobility as the excited electrons. For each electron excited there would therefore be two carriers available and the product of the carrier densities would increase with temperature according to an activation energy equal to the energy gap. The apparent activation energy derived from the experimental data as described above is thus actually equal to one-half the energy gap. With this refinement it is seen that the Hall effect should be zero for equal mobilities of holes and electrons. The fact that a negative Hall sign was always obtained in the intrinsic range meant that the electrons are more mobile than the holes. The Hall effect measured, in a sense, the difference in mobilities whereas the conductivity measured, in a like sense, the average mobility.

The low-temperature, structure-sensitive part of the conductivity data was explained by the model as follows. In cases where the semiconducting lattice is not exactly perfect, such as a small Cu atom deficiency in copper oxide, the vacant copper site is an irregularity in the lattice resulting in one too few electrons to fill the

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

energy band. This missing electron (hole) is usually bound, at very low temperatures, to the vacant copper position but can be thermally excited so that it becomes a charge carrier. The energy necessary to excite the holes is much less than the energy gap. The hole, when freed, is equivalent to an electron at the defect and so the defect is called the *acceptor state.* Such a state is, of course, localized at the defect and is in this sense a higher energy level to which an electron in the filled band can be excited, leaving a free-to-move hole in the valence band. When thus activated the acceptor site has a localized negative charge.

The explanation of excess conductivity is quite similar. The excess Zn atom in zinc oxide has an extra electron. The energy band is full, but the extra electron can be excited to the higher band where it is free to conduct, leaving a localized positive charge in a *donor state.*

The same general picture of conduction in the body of a semiconducting material can be obtained from another viewpoint (tight binding approximation). Chemical binding in solids is electronic in nature and is now quite well understood quantum mechanically. Such binding can be more or less arbitrarily divided into the following three classes: (1) *ionic* as in NaCl, (2) *covalent* as in H_2 where energy is gained by sharing electrons and pairing spins, and (3) *metallic* where, in a sense, positive ions float in a cloud of electrons. Semiconductors generally range from almost complete covalent binding to various admixtures of covalent and ionic. In any event, the valency is complete and there are just sufficient electrons in the perfect lattice to satisfy all the bonds. It takes considerable energy E_g to free an electron from a given bond. Such excitation leaves a hole as well as producing a free electron. Defects consist of imperfections in the structure where there is either one too many or one too few electrons to satisfy the bonding. Small energies are necessary to *free* the electron or hole from the site of the defect. The filled band mentioned in our first picture is the *valence* band, the next band of possible energy levels in the lattice is the *conduction* band and is more or less empty.

Both pictures represent different quantum mechanical approximations to the actual state of affairs. If the calculations could be carried out with sufficient accuracy in each case, the final results would agree. Since this cannot be done in practice, one gets a better mental picture by thinking in terms of both pictures instead of using one to the exclusion of the other.

In the above description of Wilson's theory of semiconductors we have considered only the thermal mechanism for activating free electrons and free holes. Light quanta are equally effective for this purpose, and the phenomena of photoconductivity are easily described from either the energy band or the chemical valence viewpoint. The energy of a light quantum increases with decrease in wavelength. Light of sufficiently short wavelength has large enough energy quanta to produce hole-electron pairs in intrinsic semiconductors. Longer wavelengths can excite holes or electrons only in the impurity range, and of course there will be some free carrier absorption all the way out to infinite wave length (dc) but this can be very small when the number of free carriers is small.

It should be pointed out that all that has been said here about the above model was not immediately apparent to the workers in the field after reading Wilson's paper. In fact it took about fifteen years for the full light to dawn. One of the blind spots[2] arose from the fact that it was much simpler to consider a semiconductor with one type of defect or the other, rather than both donors and acceptors at the same time. This was a case of plain lazy thinking on the part of many investigators. It is now perfectly obvious that, when one is concerned with defects of the order of one part per million, it would be surprising to find, in nature, defects of only one kind. The statistics of this more general case were discussed by J. H. deBoer and Van Geel [26]. Also it was thought at first that the electron wave viewpoint and the valence bond picture were not consistent with each other.

H. Dember [27] in 1931 found a potential difference between illuminated and unilluminated portions of a cuprous oxide wafer. J. Frenkel [28] explained this effect on the basis that the light created hole-electron pairs, pointing out that this potential difference arises from the unequal diffusion coefficients of the holes and the electrons. Frenkel also explained the photomagnetoelectric effect first discovered by I. K. Kikoin and M. M. Naskov [29] in 1934 by a similar analysis. The explanation of these effects involved both the majority and the minority carriers. The fact that minority carriers might play an important role in the understanding of semiconductor phenomena was more or less overlooked by other investigators. As we shall see later, this was another blind spot.

Developments in the Understanding of Surface Properties Up to 1942

As late as 1935 some investigators thought they had evidence that rectification was a body property. The concept of rectification at a surface may seem obvious now, but it was a controversial subject at that time.

Due to their commercial uses, the best known rectifiers at that time were Cu_2O grown on copper and selenium melted and spread on a metal washer. In each case a second contact was added to complete the electrical circuit. For the cuprous oxide unit this was graphite or aquadag plus a lead washer held under pressure. In the case of selenium the second contact was a low melting-point alloy sprayed on the selenium surface with a great amount of "art" involved in the process.

Another commercial product was the silicon carbide

[2] There were obviously many blind spots in the working concepts about semiconductors in the nineteen thirties. Since the authors were part of the group that was so blind, they offer no apology for being so blunt in this matter.

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

voltage regulator or lightning protector [30]. This was a symmetrical device in that it did not rectify, it was nonohmic in that it had a very high resistance at low voltages but would pass very large currents at higher voltages. It was made by compressing SiC granules in a ceramic flux and heat treating at elevated temperatures. Sprayed or evaporated metal contacts were applied on either side of the fired discs.

In the case of the large area rectifiers there was no geometrical asymmetry between the two electrodes as in the case of the point contact rectifier or catwhisker radio detector. Assuming rectification at contacts between different materials, why did these configurations not leave one with two opposing rectifiers having a symmetrical current voltage characteristic? Gradually it was realized that any contact between a metal and a semiconductor would rectify; some more and some less, depending on the method of fabrication. Potentiometric probe measurements indicated that the material comprising the body of the semiconductor obeyed Ohm's law. Silicon carbide was an especially difficult material to study since it was nearly impossible to make a low resistance potential probe contact. Single pieces of SiC, while generally found to be ohmic, had internal boundaries across which large nonohmic potential drops were observed.

While the above mentioned puzzles were being untangled, it became clear that rectification and nonohmic properties must be surface effects. Although rectifier production was an art and not a science, most contacts to semiconductors were found to rectify to some degree. The art consisted in making one contact as good a rectifier as possible and the other as poor (*i.e.*, as ohmic) as possible. Two such combinations in parallel opposed was an obvious model for the SiC device, the current flowing either way in the easy direction through one unit or the other.

The big question in the minds of all active workers in the field at this time was: What is the scientific explanation of rectification at the surface? Very few were concerned with the fact that explaining the ohmic contact might be equally difficult. In copper oxide the rectifying surface was obviously at the interface between the copper base and the oxide surface layer. In selenium, after much travail, it was shown to be at the sprayed interface. The direction of easy flow in each case was that of positive charges moving from the semiconductor across the rectifying contact. Both copper oxide and selenium had positive Hall coefficients, and it was found that other semiconductors with negative Hall coefficients tended to rectify in the opposite direction.

It was noted that rectifying contacts, when illuminated by a bright light, produced a photovoltage and that in general good photo emf cells were good rectifiers, although some experts disagreed on this correlation as late as 1932. Where it could be shown that the photovoltage was definitely at one surface and not at the other (this was often very difficult to determine), it was found that defect semiconductors became positively charged, while excess semiconductors became negatively charged. Another effect under active investigation at this time was that of thermoelectric emf. The thermal voltages in semiconductors are some orders of magnitude larger than those in metals, so that to a good approximation almost any metal may be taken as the zero of reference. It was found that semiconductors having a given sign of the Hall effect all had a like sign of the thermal voltage with reference to metals and that those of opposite Hall sign had the opposite sign of the thermal voltage. Although it was not understood why there should be mobile carriers with a positive sign (holes) in addition to the well-established negative carriers (electrons), nevertheless the signs of the Hall coefficient, rectification, photovoltage, and thermal voltage were all consistent with the concept that some semiconductors had negative carriers while others had positive ones.

One quantum effect considered theoretically in this period was the ability of electron waves to penetrate potential barriers. This phenomenon was seized upon in an attempt to explain rectification. A number of calculations were carried out for various shaped barriers but the predicted sign of rectification did not agree with experiment. It was well known at this time that surfaces of metals must possess charge double layers. Because of the large density of free electrons these double layers could not be more than about one Angstrom (10^{-8} cm) in thickness. When different metals were put in contact these double layers interacted to give just the proper potential difference across the contact so that there was no net flow of electrons in either direction across the boundary, providing that the metals were at the same temperature (*thermal equilibrium*). These double layers of the order 10^{-8} cm in thickness offered no barrier since the electron waves could easily penetrate them.

W. Schottky [31], N. F. Mott [32] and B. Davydov [33] suggested in 1939 that, due to the low density of carriers in a semiconductor, any such double layer must penetrate to depths of the order of 10^{-4} cm. Simple electrostatic reasoning (Poisson's equation) showed that in such an arrangement, most of the potential difference would be spread out on the semiconductor side of the barrier. It is now easy to see that this situation can explain rectification since penetration of such a broad potential barrier by electrons must be insignificant. Consider a metal contact to an excess (electron) semiconductor and assume that the contact potential difference is such that the charge on the semiconductor is positive and that on the metal negative. The result is a potential hill for electrons between metal and semiconductor.

This situation is almost exactly analogous to two hot cathodes in a vacuum providing both are at the same temperature. In equilibrium (no applied voltage), the contact potential is such as to prevent any net flow in either direction. If a voltage is now applied with such a polarity as to make it more difficult for electrons to go

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

from the lower work function cathode (1) to the higher work function cathode (2), that is (1) is made more positive than (2), the net current will be electrons from (2) to (1) since the counter flow from (1) to (2) has been reduced. As the voltage is increased the current saturates at the total emission value of cathode (2). When the polarity is reversed, the current will at first increase exponentially with voltage since the total emission from cathode (1), with its lower work function, can be orders of magnitude larger than for (2). This is the direction of *easy flow*. This analog has the proper sign to explain the experimental results for excess semiconductors.

For the case of a defect semiconductor where the charge carriers are holes, the picture is analogous with a reversal of the sign of rectification. The transfer of charge in this case is due to the flow of electrons into or out of the valence band and is entirely equivalent to turning the whole picture upside down and considering the vacant places in the electron distribution of the metal as holes. On basis of above considerations, degree of rectification depends on contact potential difference and if contact potential difference is of wrong sign, no rectification will occur. That is, low work function metals in contact with excess semiconductors should not rectify and vice versa for defect semiconductors.

One might be inclined to think that the theory was now in good order. However, while in some cases on cuprous oxide and selenium the low work function metals made better rectifiers than the higher work function metals with the various metals falling in the more or less proper order, the amount of variation and degree of rectification obtained experimentally was far less than predicted by theory [45]. As we shall see later there was a naive assumption hidden here, another blind spot. It should be emphasized that this was a tremendous advance in the theory and was an important building block for future progress.

B. Davydov [34] suggested that rectification might occur at the boundary between an excess and a defect semiconductor. He thought this might be the explanation in copper oxide and suggested that in a thin layer of the oxide near the copper the conductivity was of excess type instead of defect as in the remainder of the oxide layer. In this picture the contacts to both sides of the oxide layer were ohmic and the rectification occurred at the interface between excess and defect layers of the semiconductor. In working out the theory of this effect he recognized the importance of the minority carriers, *i.e.*, holes in the excess layer and electrons in the defect layer. In a companion paper [35] on the photoelectromotive force in semiconductors Davydov points out that it is also necessary in this case to consider the role of the minority carrier. With the emphasis on the success of the space charge theory of rectification these two theoretical papers attracted little attention from other investigators and this blind spot regarding the role of the minority carrier continued to persist.

After having exploited the longer radio wavelengths, research workers began in the nineteen thirties to restudy the short wavelengths which Hertz used in his original experiments and to proceed to even shorter wavelengths. They quickly found that ordinary vacuum tubes were of little use in this region. Some new type of detector was necessary for this purpose. It was only natural for those who had started with crystal detectors to return for a second look. This thought apparently occurred to a number of workers at the time. G. C. Southworth, for one, remembers visiting the Cortlandt Street (New York City) radio market where he ferreted out some old silicon detectors, then almost obsolete, for this purpose.

The next step, initiated by R. S. Ohl about 1935, was a very significant one. In attempting to improve these old detectors he turned to the chemists and metallurgists to obtain purer silicon. First R. O. Grisdale prepared some melts from the purest silicon obtainable and later J. H. Scaff, H. C. Theuerer and E. E. Schumacher [36] conducted a thorough investigation into the whole silicon materials problem. Improvements came rapidly. Not only did silicon detectors become practical devices (far removed from the old catwhisker type), thus making radar feasible in World War II, but important scientific discoveries were made. To start with, the metallurgists learned how to make silicon of either excess or defect type.

Since the easy flow direction for a point contact on excess silicon occurred when the silicon was made negative, it was termed *n*-type and the oppositely poled defect material was termed *p*-type. One dreads to think what would have happened if these investigators had taken the polarity of the metal point instead. These designations have now become universal terms, *n* for electrons and *p* for holes [37]. One of the melts made by Scaff and Theuerer was *n*-type at one end of the melt and *p*-type at the other, with a rather sharp boundary where the two met. A section cut from this melt perpendicular to and including the interface boundary was found by Ohl [38] to be an excellent rectifier and to exhibit a phenomenal photoelectromotive force. This was the *p-n* junction which has developed into a most important circuit element in our present-day semiconductor electronics.

Another development of great significance arose from the conviction of Scaff, Theuerer and Schumacher [36] that segregation of impurities was taking place in the silicon ingots and that both the *n*-type and *p*-type impurities tended to remain in the molten silicon as the ingot solidified from one end. They further deduced that this tendency was greater for one type than for the other. Thus if both were present in about equal amounts in the original molten silicon and the melt were allowed to freeze progressively from one end to the other, the resulting solid would be *p*-type on one end and *n*-type on the other. These workers went on to isolate these impurities and showed that those from the third column of the periodic table are acceptors and that those from

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

the fifth column are donors. They recognized that impurities from the third column could compensate those from the fifth column, in other words, that electron or hole concentrations were determined by the net difference in impurity concentration as suggested by Wilson's theory.

E. Merritt [39] in 1925 found rectification between a metal point contact and germanium, the next element below silicon in the fourth column of the periodic table, and the Siemens and Halske Works were developing germanium diodes as early as 1941.[3]

It is appropriate at this point to discuss the high-frequency limitations of rectifiers and in particular to indicate why the point contact rectifiers should have much higher cutoff frequencies than the larger area barrier devices such as copper oxide or selenium. It was generally recognized that these differences were a matter of geometry rather than some fundamental property of the devices themselves. The equivalent circuit of such a rectifying device consists of the rectifier in parallel with a capacity and this combination in series with an ohmic resistance. When that frequency is reached at which the capacitive impedance is equal to or less than the series ohmic resistance, the rectifier is shunted out. Very little is gained by making a copper oxide barrier rectifier smaller in area since the series resistance and capacitive impedance are both inversely proportional to the area. In a point contact device, however, the series resistance in the forward direction is reduced by its spreading character and is inversely proportional to the radius of the point contact, while the capacity is proportional to the square of this radius. It is thus seen that making the point contact smaller improves the frequency response. This advantage was pushed to the limit in the design of radar detectors.

Active Semiconductor Devices Up to 1942

The analogy between the vacuum tube diode and the semiconductor diode was fairly obvious to any worker in this field in the nineteen thirties. A vacuum tube diode can be operated as a negative resistance and as such is an active circuit element. Some semiconductor diodes also exhibited negative resistance at frequencies as high as several megacycles although they were usually rather unstable and difficult to reproduce. The fundamental physics of these phenomena were not understood, but the most widely accepted explanation was based on thermal effects arising from the large negative temperature coefficient of resistance. Modern counterparts of these early negative resistance diodes are now known as negative or positive gap diodes.

The analogy with the vacuum tube diode also suggested to many workers of those days that what one really should do was put a grid in the semiconductor diode and, eureka, the result would be an active triode with amplifying possibilities. The insurmountable block to this experiment was, of course, the technique of placing this grid at the proper spacing in a region only 10^{-4} cm thick. R. Hilsch and R. W. Pohl [40], working with alkali halide crystals in which the space-charge layer could be made of the order of one centimeter in thickness, did put in a grid and made in principle an active solid-state triode circuit element. The frequency cutoff of this experimental device was of the order of one cycle per second or less.

The Situation After the War

With the advent of World War II many things happened to upset research work in general and semiconductor research work in particular. Scientists in one field were recruited into another and vice versa. It was human nature for those of us who went into new fields to rediscover what experts in that field had already known. This situation was further aggravated when secrecy closed down. Things done in the late 1930's which would normally have been published were placed under secrecy. For example, there were parallel developments on silicon point contact diodes in England [41] and probably in France and Germany, although the literature on this subject is quite sparse. The war work was of course device-minded, however much was done to fill in the scientific picture.

In the United States most of this war work was done at Massachusetts Institute of Technology, Purdue University, University of Pennsylvania, General Electric Company, and Bell Telephone Laboratories. H. C. Torrey and C. A. Whitmer [111] prepared a book entitled *Crystal Rectifiers*, published in 1948 as a part of the Radiation Laboratory Series,[4] which gives an excellent account of this war effort.

After the war these well-equipped semiconductor laboratories continued along their previous lines, excepting that there was generally a swing from device development toward more fundamental semiconductor research. As a starting point it was natural to ask the question why there had not been more success in understanding semiconductor phenomena considering all the work that had been done. This question may seem foolish in context because this story is being written with the perspective of 1955, but it was not foolish then. The answer was, of course, that semiconductor phenomena were very complicated and structure-sensitive. There was a ray of hope, however, in that two relatively simple semiconductors, silicon and germanium, had been extensively investigated during the war.

Silicon and germanium are elements, they have high melting points, and the binding forces which hold the solid together are almost purely of the simple covalent type. This type of bond, thanks to quantum mechanics, was well understood. Substitutional solid solutions of fifth column impurities acted as donors and likewise the third column impurities acted as acceptors. Com-

[3] Private communication from Karl Siebertz.

[4] McGraw-Hill Book Co., Inc., New York, N. Y.

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

pared with silicon and germanium, cuprous oxide was a mess and selenium, though an element, had a very low melting point and solidified into complicated interlocking chains. It thus appeared that the best course of action was to concentrate on these two simple semiconductor elements and try to understand them first. This was where the semiconductor group, organized at Bell Telephone Laboratories after the war, took off, This group was fortunate in two respects. While predominantly made up of physicists, it had the close cooperation of both chemists and metallurgists. R. B. Gibney,[5] a physical chemist, was a member of the group and contributed essentially to its progress. J. H. Scaff and H. C. Theuerer made available their metallurgical experience with silicon and germanium. In many cases it was possible to ask for, and receive quickly, samples of either silicon or germanium having specified concentrations of given impurity elements. It can be said in retrospect that progress from this point on was everywhere largely dependent on close cooperation between physicists, chemists, and metallurgists.

Surface Properties After 1942

As the dust began to settle after the war, it became more and more obvious that the theory of rectification did not fit all of the pertinent experimental facts. In the first place, theory predicted that the rectification between a metal and a semiconductor should depend on the contact potential difference between the metal and the semiconductor. While a qualitative agreement had been found for large area metal contacts on cuprous oxide and on selenium, the quantitative variation of rectification was too small by several orders of magnitude. For metal point contacts on silicon or germanium, the work function of the metal made little or no difference.

Theory also predicted a contact potential difference between n- and p-type silicon, but the experiments of W. E. Meyerhof [42] failed to verify this point. Although theory indicated that contacts between similar n-type or between similar p-type semiconductors should be ohmic, the experiments of S. Benzer [43] with medium doped n-type germanium wedges showed that such contacts acted like two opposing rectifiers. He found that a heavily doped germanium wedge produced good rectification with either of the above wedges. He also showed that the two reverse-current voltage characteristics obtained in the former experiment were in the one direction determined by one wedge, and in the other direction determined by the other wedge.

W. Shockley reasoned that if the contact potential field at the surface could produce a space charge layer in the semiconductor surface, then one should be able to produce such a space charge layer at will with an externally applied electric field. Furthermore, if the semiconductor was very thin, so that this space charge was an appreciable part of the thickness, then the applied field could be used to modulate the conductivity of the semiconductor sample and amplification would be possible (field effect). This experiment [44], although tried in many ways, always produced an effect less than predicted. It appeared to those working in this field that all of the above-described phenomena were related and that an explanation of one would clarify this entire branch of semiconductor research.

The break came when J. Bardeen [45] saw that if he assumed special energy states at the surface (*surface states*) then he could explain this group of puzzling experiments. I. Tamm [46] and W. Shockley [47] had previously suggested the possibility of such states at the free surface of a solid, but the importance of such states at a semiconductor surface had not been realized. In other words, it was naive to assume that the free surface of a semiconductor, not in contact with another conductor, had no charge double layer. The more reasonable assumption was that the space charge layer at the surface was a property of the semiconductor and its surface, so that no matter how complicated the surface (adsorbed atoms, etc.), the surface must be in equilibrium with its interior. As a result, a surface with no space charge layer would be very unlikely indeed. It was also deduced that a very low density of surface states, many times less than one per surface atom, would be sufficient to shield the interior from any reasonable surface field. The rectifying barrier was actually there at the surface before the contact was made. Only in special cases where the surface state density was not too large could the contact potential field modify the space charge layer a little one way or the other. This new understanding of rectifying contacts made the ohmic contact more difficult to understand, and we will discuss this point in more detail a little later.

Having postulated a space charge layer at the free surface of a semiconductor, the question now arose as to the best experiment for verifying its existence. W. Shockley pointed out that, according to this picture, the contact potential between n- and p-type samples should increase with doping. This experiment was successfully performed [48] and out of it came an estimate of the surface state density under fixed experimental conditions. It was likewise realized that if a space charge layer resided at the free surface, then one should be able to change the surface potential by shining a light on it, and this effect should be adaptable to experimental verification. Suitable experimental arrangements were set up; the effect was not only measurable, but the change in contact potential was of the right sign [49]. Further experiments along these lines led to the use of an electrolyte to bias the surface, and it was during the course of this work by J. Bardeen and W. H. Brattain [50] that the point contact transistor was born.

In the course of these experiments it became evident that the minority carrier, even in small concentrations, played a very important role. A large part of the re-

[5] Now at the Los Alamos Scientific Laboratory.

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

verse current in point contacts to n-type germanium consisted of holes flowing to the metal and in the forward direction the resistance was modulated by injection of holes [51]. It is of course not surprising that this blind spot persisted for so long. The minority carriers were, after all, present in too small concentrations in most semiconductors to matter very much. In cuprous oxide (hole conductor), for example, the electrons have a density of about one charge carrier per cubic centimeter! In silicon and germanium the density was greater but still very small until really high purity ingots were obtained.

The point contact transistor was a three-dimensional device. No good physicist likes to work with such a complicated case if it can be reduced to one dimension. This simplification led to the fundamental studies of W. Shockley, *et al.* [52] on carrier injection in germanium rods. This, along with the better understanding of point contacts [53], laid the groundwork for semiconductor electronics.

Another contribution of major importance was that of W. Shockley [54] in working out the theory of p-n junctions and junction transistors. This led to the construction and evaluation of p-n-p and n-p-n junction transistors [55, 56] using the grown crystal method and, shortly thereafter, using metal alloy-diffusion techniques [57, 58]. This latter method of preparing p-n junctions was likewise adapted to both germanium [59] and silicon rectifiers [60] for both low and high power uses. Another method for preparing p-n junctions is that of gaseous diffusion [61, 62] of the desired impurity atoms into the surfaces of semiconductors. This technique has produced high power silicon rectifiers [63] and highly efficient photovoltaic solar energy converters [64].

It is really too early to assess the impact of these developments on the physics of the solid state. Nevertheless, several generalities should be pointed out at this time. The p-n junction in silicon and germanium is probably the simplest surface or phase boundary known, and our understanding of its properties is complete in great detail [65]. Devices such as rectifiers, solar batteries, and transistors made from one of the most abundant elements, namely silicon, will undoubtedly have an important impact on technology. One now sees that a general definition might be proposed for an active circuit element as follows: Two phase boundaries close enough together (within a diffusion length) so that deviations from equilibrium occurring at either will influence the other and with electrical connections to each of the *three* regions bounded by the two phase boundaries. Note that this definition covers the vacuum tube triode as well as the transistor, and also the active diode where the connection to the middle region is missing.

Finally we should explain ohmic contacts, at least in principle. Either holes or electrons can flow easily across the surface of a semiconductor. Most of the nonohmic phenomena occur as a result of deviations from equilibrium densities. If holes and electrons could recombine fast enough or be generated fast enough at the surface to maintain equilibrium for all current densities, then regardless of the dipole layer, the contact would be ohmic. This explains why mechanical damage of the surface is useful in making ohmic contact. Another possibility is to start with a given type of semiconductor and dope it more and more. Then as one approaches the surface the contact becomes essentially that between two metals since the dipole layer is so thin that it is penetrable. Doping in general lowers the lifetime so that this technique works both ways. It should be pointed out that an *abrupt* n-$n+$ or p-$p+$ boundary has interesting properties of its own and is not ohmic.

Body Properties After 1942

In the case of silicon and gemanium it soon became apparent that there was a real hope of obtaining an exact relationship between impurity concentration and conductivity. Data were accumulating from measurements of conductivity and Hall effect on more and more samples of both silicon and germanium and under a wide variety of conditions. These samples were polycrystalline and, as it turned out later, far from perfect. Nevertheless, the analysis of these data to give mobilities and concentrations of electrons and holes began to show definite consistencies. This started with work done at the University of Pennsylvania and at Purdue University. K. Lark-Horovitz and V. A. Johnson [66, 67] did an analysis of the germanium data and G. L. Pearson and J. Bardeen [68] did an even more complete job on silicon. Some of the highlights of these studies are given below.

X-ray studies by E. S. Greiner [68] on the lattice constant as a function of impurity concentration definitely established that phosphorus and boron impurity atoms in silicon occupy normal silicon sites in the lattice: they go in substitutionally rather than interstitially. The inference was very strong that this is also the case for all group III and group V impurities in both silicon and germanium.

It was found that the statistics of electron and hole concentrations obeyed the Wilson model quite well. In particular the various interactions between electrons, holes, donors, acceptors, and energy levels of the solid could be represented by the appropriate mass action laws, and the energy differences between the various levels could be determined. The simplest relation to come out of all this was that, regardless of impurity content, the product of the electron and hole densities was always given by a universal function of temperature, namely

$$np = K \exp\left[-E_g/kT\right],$$

where the chief difference between different semiconductors is in the value of E_g, since K changes very little.

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

For an intrinsic semiconductor, n is always equal to p. Equal concentrations of donors and acceptors leave this equality unchanged but unequal concentrations, at low enough temperatures, make $n>p$ or $p>n$ without changing the product. An apparently simple relation covering this latter situation is

$$n/p = \exp\left[2(E_f - E_i)/kT\right],$$

where E_f measures the Fermi level, or electrochemical potential, and E_i is its value for the intrinsic case where $n=p$. This is actually a complicated relationship since E_f is an involved function of the difference in donor and acceptor concentrations as well as of the absolute temperature T.

Another result of these analyses was a better understanding of the factors that control the mobility. The scattering of holes and of electrons could be separated into two parts. In the case of such covalent nonionic lattices as those of silicon and germanium, one part consists of the interaction or scattering of the charge carriers by the elastic thermal vibrations of the lattice (*phonons*). This effect increased with temperature; *i.e.*, the lattice part of the mobility decreases with increase in temperature. It was found in general that electron mobility is greater than hole mobility at any given temperature. For relatively pure samples at high enough temperatures, this was the whole story. The mobilities are an intrinsic property of the lattice alone and are not structure sensitive. At low temperatures and high impurity concentrations, on the other hand, the second part, impurity scattering, is important. That this part is due chiefly to scattering of holes and electrons by ionized impurity atoms was shown by E. Conwell and V. F. Weisskopf [69]. The temperature coefficient of this effect is opposite in sign to lattice scattering and is therefore limiting only at low temperatures and high concentrations of donors or acceptors.

Finally it was found, at first only qualitatively, that the added concentrations of either electrons or holes (whichever the case) is equal to the difference between donor and acceptor impurity concentrations. It was later shown, using radioactive antimony, that this relation is quantitative [70].

The following simple picture of an elementary semiconductor thus emerged as a result of the work described above. A group V impurity atom will enter into the crystal lattice and replace a group IV atom. Four of the impurity atom's valence electrons are used in covalent electron bonds with each of four tetrahedrally placed nearest neighbors. The fifth electron is loosely bound to the impurity atom by a force that is just about that between an electron and a singly charged ion in a dielectric medium. When excited, thermally or otherwise, this electron is free to conduct. The same reasoning applies to group III impurities which leave an extra hole in the valence band. Simultaneous addition of equal amounts of group V and group III impurity atoms exactly cancel their charge carriers. The extra electron fills the hole in the impurity band, thus leaving all covalent bonds satisfied. However, the donor atom is left positively charged and the acceptor atom negatively charged.

During this time various improvements were being made in semiconductor materials. A big step forward was taken when G. K. Teal and J. B. Little [71] succeeded in growing single crystals of germanium. Sometime later single crystals of silicon were also obtained by G. K. Teal and E. Buehler [72]. In all of this work steps were continually being taken to produce even more perfect crystals both as to lattice perfection and degree of chemical purity. A major breakthrough in this regard came with the ingenious development of zone refining by W. G. Pfann [73]. The impurities in germanium, and in many other chemical elements and compounds, tend to segregate into the molten portion of a solidifying ingot. By passing successive molten zones through a long ingot of germanium, Pfann was able to sweep these inherent impurities into one end of the ingot where they could be removed by cropping. Following a thorough study of the segregation coefficients associated with the various impurities [74], it was possible to prepare germanium ingots in which the harmful impurity content was less than 10^{12} atoms per cc. This amounts to less than one impurity atom for each ten billion germanium atoms and is probably the highest purity attained in any commercially available chemical element or compound. Although silicon is more difficult to zone refine than germanium, it has recently been purified to about the same level by a combination of zone refining and chemical purification. The progress achieved in semiconductor research during the past few years is closely associated with these advances in the preparation of materials.

The ability to produce large silicon and germanium single crystals having a high degree of lattice perfection did not essentially change the over-all picture although it did result in many refinements. There was a period of several years when the mobilities of both electrons and holes in germanium showed a linear increase with the date at which the experiment was performed, finally saturating at the presently accepted values about 1953.

Another very significant advance came with the discovery of transistor action. It then became possible to attain nonequilibrium concentrations of holes and electrons and the importance of the minority carrier concentration was finally realized. The classical experiments of J. R. Haynes and W. Shockley [75] made it possible to measure the drift mobility of holes and electrons directly. Small but significant differences were found between Hall and drift mobilities. Still another parameter was added by the determination of lifetimes of nonequilibrium concentrations of electrons and holes.

The work of M. Becker and H. Y. Fan [76] and the contemporary but independent work of H. B. Briggs [77] on the optical properties in germanium and silicon contributed essentially to the over-all picture as did the

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

quantum efficiency work of F. S. Goucher [78] which showed that one hole-electron pair was produced for each light quantum absorbed.

The work of P. P. Debye [79] and F. J. Morin [80, 81] in carrying out very careful measurements on really good single crystal samples of germanium and silicon over wide ranges of tempertaure and impurity concentrations was another significant contribution. Table I lists the presently accepted physical constants of these two well understood semiconductors.

TABLE I
PROPERTIES OF GERMANIUM AND SILICON

	Ge	Si
Melting point	936°C	1420°C
Density 25°C	5.323 gm/cm^3	2.330 gm/cm^3
Thermal expansion coeff. (25°C)	6.1×10^{-6}/°C	4.2×10^{-6}/°C
Thermal conductivity (25°C)	0.14 cal/sec cm°C	0.20 cal/sec cm°C
Specific heat (0–100°C)	0.074 cal/gm°C	0.181 cal/gm°C
Atomic weight	72.60	28.08
Lattice constant 25°C	5.657×10^{-8} cm	5.429×10^{-8} cm
Atoms/cc	4.42×10^{22}	4.96×10^{22}
Volume compressibility	1.3×10^{-12} cm^2/dyne	0.98 cm^2/dyne
Dielectric constant	16	12
Covalent bond ionization energy 0°K	1.2 electron volts	1.2 electron volts
Impurity atom ionization energy	~0.01 electron volts	~0.04 electron volts
Intrinsic resistivity at 300°K	47 ohm cm	230,000 ohm cm
Electron mobility at 300°K	3800 cm^2/volt sec	1300 cm^2/volt sec
Hole mobility at 300°K	1800 cm^2/volt sec	500 cm^2/volt sec

One could accordingly characterize a given sample of germanium at a given temperature by stating its electron and hole concentrations, the respective mobilities and the lifetime. It now became possible to formulate the mathematical problem of semiconductor electronics. This was accomplished in complete generality, at least for germanium at room temperature, by W. van Roosbroeck [82]. Significant contributions in this field were also made by J. Bardeen [83], W. Shockley [113], C. Herring [84], R. C. Prim [85] and H. Brooks [86]. Theory of recombination by traps was developed by R. N. Hall [87] and by W. Shockley and W. T. Read [88].

We are now getting so close to the forefront that the perspective is insufficient to give a good general picture. It can certainly be said, however, that the availability of such pure and perfect single crystals as we have in present-day silicon and germanium amounts to a major revolution in the physics of solids. New phenomena are turning up all around us. On the one hand the results from experiments on magneto-resistance [89, 90], piezoresistance [91] and cyclotron resonance [92, 93] have shown that the energy band structure in silicon and germanium cannot be characterized by a single isotropic effective mass for the charge carriers. It turns out that the situation is quite complicated [94, 95]. In some cases there are groups of carriers each with anisotropic effective masses. In other cases the effective mass is velocity dependent. The electron spin resonance results [96] in silicon and their analysis [97] lead to a better understanding of impurity energy levels. The new thermal emf results [98] contribute to the knowledge of interaction between phonons and charge carriers. The experiments on radiation damage [99, 100] and dislocations [101–104] lead to an improved understanding of solid structure in general.

The thorough understanding of germanium and silicon is contributing essentially to the understanding of other semiconductors such as lead sulfide [105] and cadmium sulfide [106]. An entirely new series of semiconductors, the group III–group V compounds, first investigated by H. Welker [107], is currently attracting a great deal of attention and some of these may very well rival silicon and germanium in the not too distant future. Table II lists the currently available constants of this series of semiconducting materials. Space as well as perspective just does not permit a complete story of the latest developments. We suggest that the reader consult the current literature.

TABLE II
PROPERTIES OF GROUP III–GROUP V INTERMETALLIC COMPOUNDS

	Melting Point °C	E_g (Optical) eV 300°K	n or p cm^{-3}	μ_n (Hall) cm^2/v sec 300°K	μ_p (Hall) cm^2/v sec 300°K
InSb	523 (a)	.18 (b)	10^{15} (b)	77,000 (b)	~1,250 (b)
InAs	936 (a)	.35 (b)	5×10^{16} (b)	>15,000 (b)	
GaSb	720 (a)	.77 (b)	10^{17} (b)	2,500 (b)	700 (b)
InP	1070 (a)	1.25 (a)		3,400 (a)	650 (a)
GaAs	1240 (a)	1.35 (c)	2.7×10^{17} (c)	4,040 (c)	
AlSb	1080 (a)	1.7 (b)	10^{17} (b)	~100 (b)	

(a) H. Welker, "Semiconducting Intermetallic Compounds," *Physica*, vol. 20, p. 893; (November) 1954.
(b) H. J. Hrostowski and M. Tannenbaum, "Recent Work on Group III Antimonides and Arsenides," *Physica*, vol. 20, p. 1065; (November) 1954.
(c) R. Barrie, F. A. Cunnell, J. T. Edmond, and I. M. Ross, "Some Properties of Gallium Arsenide," *Physica*, vol. 20, p. 1087; (November) 1954.

BIBLIOGRAPHY

[1] Lark-Horovitz, K., "The New Electronics." See [117], p. 57.
[2] Herold, E. W., "Semiconductors and Transistors." *Journal of the Franklin Institute*, Vol. 259 (February, 1955), pp. 87–106.
[3] For a recent bibliography on transistors see: Krull, A. R., "Transistors and Their Applications. A Bibliography 1948–1953." *Transactions of the Institute of Radio Engineers*, Vol. ED-1 (September, 1954), p. 40.
[4] Faraday, M., *Experimental Researches in Electricity*, Bernard Quaritch, London (1839). Vol. I, pp. 122–124.
[5] Becquerel, A. E., "On Electric Effects under the Influence of Solar Radiation." *Comptes Rendus de l'Academie des Sciences*, Vol. 9 (November 21, 1839), pp. 711–714.
[6] Smith, W., "The Action of Light on Selenium." *Jour. of the Soc. Telegraph Engineers*, Vol. 2, No. 1 (1873), pp. 31–33.
[7] Braun, F., "Ueber die Stromleitung durch Schwefelmetalle." *Annalen der Physik und Chemie*, Vol. 153, No. 4 (1874), pp. 556–563.
[8] Schuster, A., "On Unilateral Conductivity." *Philosophical Magazine*, Vol. 48 (October, 1874), pp. 251–257.
[9] Adams, W. G., and Day, R. E., "The Action of Light on Selenium." *Proceedings of the Royal Society of London*, Vol. 25 (June, 1876), pp. 113–117.

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

[10] Fritts, C. E., "A New Form of Selenium Cell." *American Journal of Science*, Vol. 26 (December, 1883), pp. 465–472.
[11] Bose, J. C., U. S. Patent 755840, 1904.
[12] Dunwoody, H. H. C., U. S. Patent 837616, 1906.
[13] Austin, L. W., "A High Resistance Thermo-Electric Detector for Electrical Waves," *Physical Review*, Vol. 24 (June, 1907), pp. 508–510.
[14] Pierce, G. W., "Crystal Rectifiers for Electric Currents and Electrical Oscillators." *Physical Review*, Vol. 25 (July, 1907), pp. 31–60, Vol. 28 (March, 1909), pp. 153–187, Vol. 29, (November, 1909), pp. 478–484.
[15] Grondahl, L. O., and Geiger, P. H., "A New Electronic Rectifier." *Transactions of the American Institute of Electrical Engineers*, Vol. 46 (February, 1927), pp. 357–366.
[16] Lange, B., *Die Photoelemente und Ihre Anwendung.* Leipzig, Johann Ambrosius Barth, 1936.
[17] Pohl, R. W., "Electron Conductivity and Photochemical Processes in Alkali Halide Crystals." *Proceedings of the Physical Society*, Vol. 49 (extra part (1937)), pp. 3–31.
[18] Hall, E. H., "On a New Action of the Magnet on Electric Currents." *American Journal of Mathematics* Vol. 2 (November, 1879), pp. 287–291.
[19] Vogt, W., "Elektrisches und Optisches Verhalten von Halbleitern III." *Annalen der Physik*, Vol. 7 (October 31, 1930), pp. 183–204.
[20] Englehard, E., "Elektrisches und Optisches Verhalten von Halbleitern IX." *Annalen der Physik*, Vol. 17 (July 8, 1933), pp. 501–542.
[21] Schottky, W., and Waibel, F., "Die Elektronenleitung des Kupperoxyduls." *Physikalische Zeitschrift*, Vol. 34 (December 1, 1933), pp. 858–864.
[22] Wagner, C., and Schottky, W., "Theorie der Geordneten Mischphases." *Zeitschrift für Physikalische Chemie*, Vol. B11 (December, 1930), pp. 163–210.
[23] Wagner, C., "Theorie der Geordneten Mischphasen." *Zeitschrift für Physikalische Chemie*, Vol. B22 (July, 1933), pp. 181–194.
[24] Sommerfeld, A., "Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik." *Zeitschrift für Physik*, Vol. 47 (February, 1928), pp. 1–32, Vol. 47 (February, 1928), pp. 43–60.
[25] Wilson, A. H., "The Theory of Electronic Semiconductors." *Proceedings of the Royal Society of London*, Vol. A133 (October, 1931), pp. 458–491, Vol. A134 (November, 1931), pp. 277–287.
[26] DeBoer, J. H., and Van Geel, W. C., "Rotgrenze des Inneren Photoeffektes und Ablosungsarbeit bei Halbleitern." *Physica*, Vol. 2 (January, 1935), pp. 286–298.
[27] Dember, H., "Über eine Photoelektromotorische Kraft in Kuperoxydul-Kristallen." *Physikalische Zeitschrift*, Vol. 32 (July, 1931), pp. 554–556, Vol. 32 (November, 1931), pp. 856–858.
[28] Frenkel, J., "Theory of Some Photoelectric and Photomagnetoelectric Phenomena in Semiconductors." *Physikalische Zeitschrift der Sowjetunion*, Vol. 8, No. 2 (1935), pp. 185–203.
[29] Kikoin, I. K., and Naskov, M. M., "A New Photoelectric Effect in Cuprous Oxide." *Physikalische Zeitschrift der Sowjetunion*, Vol. 5, No. 4, (1934), pp. 586–596.
[30] McEachron, K. B., "Thyrite, A New Material for Lightning Arresters." *General Electric Review*, Vol. 33 (February, 1930), pp. 92–99.
[31] Schottky, W., "Zur Halbleitertheorie der Sperrschichtrichter und Spitzengleichrichter," *Zeitschrift für Physik*, Vol. 113 (July 21, 1939), pp. 367–414.
[32] Mott, N. F., "The Theory of Crystal Rectifiers." *Proceedings of the Royal Society of London*, Vol. 171 (May 1, 1939), pp. 27–38.
[33] Davydov, B., "On the Contact Resistance of Semiconductors." *Journal of Physics* (USSR), Vol. 1, No. 2 (1939), pp. 167–174.
[34] Davydov, B., "The Rectifying Action of Semiconductors." *Technical Physics of the USSR*, Vol. 5, No. 2 (1938), pp. 87–95.
[35] Davydov, B., "On the Photo-electromotive Force in Semiconductors." *Technical Physics of the USSR*, Vol. 5, No. 2 (1938), pp. 79–86.
[36] Scaff, J. H., Theurer, H. C., and Schumacher, E. E., "*p*-type and *n*-type Silicon and the Formation of the Photovoltaic Barrier in Silicon Ingots." *Transactions of the American Institute of Mining and Metallurgical Engineers*, Vol. 185 (June, 1949), pp. 383–388. Although a major portion of the work reported in this reference was done before the war, publication was held up for security reasons.
[37] Scaff, J. H., U. S. Patent 2,402,582. Filed April 4, 1941.
[38] Ohl, R. S., U. S. Patent 2,402,662. Filed May 27, 1941.
[39] Merritt, E., "On Contact Rectification by Metallic Germanium." *Proceedings of the National Academy of Sciences*, Vol. 11 (December, 1925), pp. 743–748.
[40] Hilsch, R., and Pohl, R. W., "Steuerung von Elektronenströmen mit einem Dreielektrodenkristall und ein Modell einen Sperrschicht." *Zeitschrift für Physik*, Vol. 11 (December 8, 1938), pp. 399–408.
[41] Bleaney, B., Ryde, J. W., and Kinman, T. H., "Crystal Valves." *Journal of the Institution of Electrical Engineers*, Part IIIA, Vol. 93 (May, 1946), pp. 847–854.
[42] Meyerhof, W. E., "Contact Potential Difference in Silicon Crystal Rectifiers." *Physical Review*, Vol. 71 (May 15, 1947), pp. 727–735.
[43] Benzer, S., "Ge-Ge Contacts," *Physical Review*, Vol. 71 (January 15, 1947), p. 141.
[44] Shockley, W., and Pearson, G. L., "Modulation of Conductance of Thin Films of Semiconductors by Surface Charges." *Physical Review*, Vol. 74 (July 15, 1948), pp. 232–233.
[45] Bardeen, J., "Surface States and Rectification at a Metal to Semiconductor Contact." *Physical Review*, Vol. 71 (May 15, 1947), pp. 717–727.
[46] Tamm, I., "Über Eine Mögliche Art der Elektronenbindung an Kristalloberflächen," *Physikalische Zeitschrift der Sowjetunion*, Vol. 1, No. 6 (1932), pp. 733–746.
[47] Shockley, W., "On the Surface States Associated with a Periodic Potential." *Physical Review*, Vol. 56 (August 15, 1939), pp. 317–323.
[48] Brattain, W. H., and Shockley, W., "Density of Surface States Deduced from Contact Potential Measurements." *Physical Review*, Vol. 72 (August 15, 1948), p. 345.
[49] Brattain, W. H., "Evidence for Surface States from Change in Contact Potential on Illumination." *Physical Review*, Vol. 72 (August 15, 1948), p. 345.
[50] Bardeen, J., and Brattain, W. H., "The Transistor, a Semiconductor Triode." *Physical Review*, Vol. 74 (July 15, 1948), pp. 230–231; "Physical Principles Involved in Transistor Action." *Physical Review*, Vol. 75 (July 15, 1949), pp. 203–231.
[51] Brattain, W. H., and Bardeen, J., "Nature of the Forward Current in Germanium Point Contacts." *Physical Review*, Vol. 74 (July 15, 1948), pp. 231–232.
[52] Shockley, W., Pearson, G. L., and Haynes, J. R., "Hole Injection in Germanium-Quantitative Studies and Filamentary Transistors." *Bell System Technical Journal*, Vol. 28 (July, 1949), pp. 344–366.
[53] Bardeen, J., "Theory of Relation Between Hole Concentrations and Characteristics of Germanium Point Contacts." *Bell System Technical Journal*, Vol. 29 (October, 1950), pp. 469–495.
[54] Shockley, W., "The Theory of *p-n* Junctions in Semiconductors and *p-n* Junction Transistors." *Bell System Technical Journal*, Vol. 28 (July, 1949), pp. 435–489.
[55] Shockley, W., Sparks, M., and Teal, G. K., "*p-n* Junction Transistors." *Physical Review*, Vol. 83 (July 1, 1951), pp. 151–162.
[56] Wallace, R. L., Jr., and Pietenpol, W. J., "Some Circuit Properties and Applications of *n-p-n* Transistors." *Bell System Technical Journal*, Vol. 30 (July, 1951), pp. 530–563.
[57] Hall, R. N., and Dunlap, W. C., Jr., "*p-n* Junctions Prepared by Impurity Diffusion." *Physical Review*, Vol. 80 (November 1, 1950), pp. 867–868.
[58] Saby, J. E., "Fused Impurity *p-n-p* Transistors." PROCEEDINGS OF THE IRE, Vol. 40 (November, 1952), pp. 1358–1360.
[59] Hall, R. N., "Power Rectifiers and Transistors." PROCEEDINGS OF THE IRE, Vol. 40 (November, 1952), pp. 1512–1518.
[60] Pearson, G. L., and Sawyer, B., "Silicon *p-n* Junction Alloy Diodes." PROCEEDINGS OF THE IRE, Vol. 40 (November, 1952), pp. 1348–1351.
[61] Scaff, J. H., and Theuerer, H. C., U. S. Patent 2,567,970, September 18, 1951.
[62] Fuller, C. S., and Ditzenberger, J. A., "The Diffusion of Boron and Phosphorus into Silicon." *Journal of Applied Physics*, Vol. 25 (November, 1954), pp. 1439–1440.
[63] Pearson, G. L., and Fuller, C. S., "Silicon *p-n* Junction Power Rectifiers and Lightning Protectors." PROCEEDINGS OF THE IRE, Vol. 42 (April, 1954), p. 760.
[64] Chapin, D. M., Fuller, C. S., and Pearson, G. L., "A New Silicon *p-n* Junction Photocell for Converting Solar Radiation into Electrical Power." *Journal of Applied Physics*, Vol. 25 (May, 1954), pp. 676–677.
[65] Brattain, W. H., and Garrett, C. G. B., "Surface Properties of Semiconductors." *Physica*, Vol. 20 (November, 1954), pp. 885–892.
[66] Lark-Horovitz, K., Middleton, A. E., Miller, E. P., and Walerstein, I., "Electrical Properties of Germanium Alloys." *Physical Review*, Vol. 69 (March, 1946), p. 258.
[67] Lark-Horovitz, K., and Johnson, V. A., "Theory of Resistivity in Germanium Alloys." *Physical Review*, Vol. 69 (March, 1946), p. 258.
[68] Pearson, G. L., and Bardeen, J., "Electrical Properties of Pure

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.

Silicon and Silicon Alloys Containing Boron and Phosphorus." *Physical Review*, Vol. 75 (March 1, 1949), pp. 865–883.
[69] Conwell, E., and Weisskopf, V. F., "Theory of Impurity Scattering in Semiconductors." *Physical Review*, Vol. 77 (February 1, 1950), pp. 388–390.
[70] Pearson, G. L., Struthers, J. D., and Theuerer, H. C., "Correlation of Geiger Counter and Hall Effect Measurements in Alloys Containing Germanium and Radioactive Antimony 124." *Physical Review*, Vol. 77 (March 15, 1950), pp. 809–813.
[71] Teal, G. K., and Little, J. B., "Growth of Germanium Single Crystals." *Physical Review*, Vol. 78 (June 1, 1950), p. 647.
[72] Teal, G. K., and Buehler, E., "Growth of Silicon Single Crystals and of Single Crystal Silicon *p-n* Junctions." *Physical Review*, Vol. 87 (July 1, 1952), p. 190.
[73] Pfann, W. G., "Principles of Zone Refining." *Transactions of the American Institute of Mining and Metallurgical Engineers*, Vol. 194 (July, 1952), pp. 747–753.
[74] Burton, J. A., "Impurity Centers in Ge and Si," *Physica*, Vol. 20 (November, 1954), pp. 845–853.
[75] Haynes, J. R., and Shockley, W., "The Mobility and Life of Injected Holes and Electrons in Germanium." *Physical Review*, Vol. 81 (March 1, 1951), pp. 835–843.
[76] Becker, M., and Fan, H. Y., "Optical Properties of Semiconductors, II, Infra-Red Transmission of Germanium." *Physical Review*, Vol. 76 (November 15, 1949), pp. 1530–1531, "III, Infra-Red Transmission of Silicon." *Physical Review*, Vol. 76 (November 15, 1949).
[77] Briggs, H. B., "Optical Effects in Bulk Silicon and Germanium." *Physical Review*, Vol. 77 (January 15, 1950), p. 287.
[78] Goucher, F. S., "The Photon Yield of Electron-Hole Pairs in Germanium." *Physical Review*, Vol. 78 (June 15, 1950), p. 816.
[79] Debye, P. P., and Conwell, E. M., "Electrical Properties of *N*-type Germanium." *Physical Review*, Vol. 93 (February 15, 1954), pp. 693–706.
[80] Morin, F. J., and Maita, J. P., "Conductivity and Hall Effect in the Intrinsic Range of Germanium." *Physical Review*, Vol. 94 (June 15, 1954), pp. 1525–1529.
[81] Morin, F. J., and Maita, J. P., "Electrical Properties of Silicon Containing Arsenic and Boron." *Physical Review*, Vol. 96 (October 1, 1954), pp. 28–35.
[82] van Roosbroeck, W., "The Transport of Added Current Carriers in a Homogeneous Semiconductor." *Physical Review*, Vol. 91 (July 15, 1953), pp. 282–289.
[83] Bardeen, J., "Flow of Electrons and Holes in Semiconductors." See [117] page 128.
[84] Herring, C., "Theory of Transient Phenomena in the Transport of Holes in an Excess Semiconductor." *Bell System Technical Journal*, Vol. 28 (July, 1949), pp. 401–427.
[85] Prim, R. C., III, "Some Results Concerning the Partial Differential Equations Describing the Flow of Holes and Electrons in Semiconductors." *Bell System Technical Journal*, Vol. 30, (October, 1951), pp. 1174–1213.
[86] Brooks, H., "Theory of Diffusion of Injected Carriers in a Semiconductor of Mixed Conductivity Type." *Physical Review*, Vol. 90 (April 15, 1953), p. 336.
[87] Hall, R. N., "Electron-Hole Recombination in Germanium." *Physical Review*, Vol. 87 (July 15, 1952), p. 387.
[88] Shockley, W., and Read, W. T., Jr., "Statistics of the Recombination of Holes and Electrons." *Physical Review*, Vol. 87 (September 1, 1952), pp. 835–842.
[89] Pearson, G. L., and Suhl, H., "The Magneto-Resistance Effect in Oriented Single Crystals of Germanium." *Physical Review*, Vol. 83 (August 15, 1951), pp. 768–776.
[90] Pearson, G. L., and Herring, C., "Magneto-Resistance Effect and the Band Structure of Single Crystal Silicon." *Physica*, Vol. 20 (November, 1954), pp. 975–978.
[91] Smith, C. S., "Piezoresistance Effect in Germanium and Silicon." *Physical Review*, Vol. 94 (April 1, 1954), pp. 42–49.
[92] Dresselhaus, G., Kip, A. F., and Kittel, C., "Cyclotron Resonance of Electrons and Holes in Silicon and Germanium Crystals." *Physical Review*, Vol. 98 (April 15, 1955), pp. 368–384.
[93] Lax, B., Zeiger, H. J., and Dexter, R. N., "Anistropy of Cyclotron Resonance in Germanium." *Physica*, Vol. 20 (November, 1954), pp. 818–828.
[94] Herman, F., "Calculation of the Energy Band Structures of the Diamond and Germanium Crystals by the Method of Orthogonalized Plane Waves." *Physical Review*, Vol. 93 (March 15, 1954), pp. 1214–1225.
[95] Herring, C., "Transport Properties of a Many-Valley Semiconductor." *Bell System Technical Journal*, Vol. 34 (March, 1955), pp. 237–290.
[96] Fletcher, R. C., Yager, W. A., Pearson, G. L., and Merritt, F. R., "Hyperfine Splitting in Spin Resonance of Group V Donors in Silicon." *Physical Review*, Vol. 95 (August 1, 1955), pp. 844–845.
[97] Kohn, W., and Luttinger, J. M., "Hyperfine Splitting of Donor States in Silicon." *Physical Review*, Vol. 97 (February 15, 1955), pp. 883–888.
[98] Herring, C., "Theory of the Thermoelectric Power of Semiconductors." *Physical Review*, Vol. 96 (December 1, 1954), pp. 1163–1187.
[99] Lark-Horovitz, K., "Nucleon-Irradiated Semiconductors." See [114], page 47.
[100] Brown, W. L., Fletcher, R. C., and Wright, K. A., "Annealing of Bombardment Damage in Germanium." *Physical Review*, Vol. 92 (November 1, 1953), pp. 591–596.
[101] Gallagher, C. J., "Plastic Deformation of Germanium and Silicon." *Physical Review*, Vol. 88 (November 15, 1952), pp. 721–722.
[102] Vogel, F. L., Pfann, W. G., Corey, H. E., and Thomas, E. E., "Observations of Dislocations in Lineage Boundaries in Germanium." *Physical Review*, Vol. 90 (May 1, 1953), p. 489.
[103] Pearson, G. L., Read, W. T., Jr., and Morin, F. J., "Dislocations in Plastically Deformed Germanium." *Physical Review*, Vol. 93 (February, 1954), pp. 666–667.
[104] Read, W. T., Jr., "Theory of Dislocations in Germanium." *Philosophical Magazine*, Vol. 45 (August, 1954), pp. 775–796; Vol. 45 (November, 1954), pp. 1119–1128; Vol. 46 (February, 1955), pp. 111–131.
[105] Smith, R. A., "The Electronic and Optical Properties of the Lead Sulfide Group of Semiconductors." *Physica*, Vol. 20 (November, 1954), pp. 910–929.
[106] Smith, R. W., and Rose, A., "Space-Charge-Limited Currents in Single Crystals of Cadmium Sulfide." *Physical Review*, Vol. 97 (March 15, 1955), pp. 1531–1537.
[107] Welker, H., "Über Neue Halbleitende Verbendungen." *Zeitschrift für Naturforschung*, Vol. 7A (November, 1952), pp. 744–749; Vol. 8A (April, 1953), pp. 248–251.

BOOKS

[108] Wilson, A. H., *Semiconductors and Metals*. London, Cambridge University Press, 1939.
[109] Mott, N. F., and Gurney, R. W., *Electronic Processes in Ionic Crystals*. Oxford, Clarendon Press, 1940.
[110] Seitz, F., *The Modern Theory of Solids*. New York, McGraw-Hill Book Company, 1940.
[111] Torrey, H. C., and Whitmer, C. A., *Crystal Rectifiers*. New York, McGraw-Hill Book Company, 1948.
[112] Wright, D. A., *Semiconductors*. New York, John Wiley & Sons, Inc., 1950.
[113] Shockley, W., *Electrons and Holes in Semiconductors*. New York, D. Van Nostrand Company, 1950.
[114] Henisch, H. K., ed., *Semiconducting Materials*. London, Thornton Butterworth, Ltd., 1951.
[115] Moss, T. S., *Photoconductivity in the Elements*. London, Thornton Butterworth, Ltd., 1952.
[116] Kittel, C., *Introduction to Solid State Physics*. New York, John Wiley & Sons, Inc., 1953.
[117] Brackett, F. S., ed., *The Present State of Physics*. Washington, D. C., American Association for the Advancement of Science, 1954.
[118] Spenke, E., *Elektronische Halbleiter*. Berlin, Springer, 1955

Authorized licensed use limited to: Technische Universitaet Muenchen. Downloaded on May 08,2023 at 16:40:17 UTC from IEEE Xplore. Restrictions apply.