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REVIEW AND EVALUATION OF PAST SOLAR CELL DEVELOPMENT EFFORTS

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ABSTRACT

This report provides a bibliography of scientific papers related to the photovoltaic effect, and also gives a historical review of scientific investigations of this effect during the years 1839-1940. Topics covered include the Becquerel effect, the barrier photovoltaic effect, and the Dember effect. Because of its historical importance, major emphasis has been placed on the barrier photovoltaic effect as seen in copper-cuprous oxide photocells. All experimental investigations as reported in the literature have been covered, and the development of the modern theory of the photovoltaic effect is described.

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SUMMARY

The end product of this contract will be a review of the past research effort in the field of photovoltaic solar energy converter cells, and recommendations to further research and development efforts which would have a good chance of significant future advancements in this field. To arrive at these recommendations, all of the available information on relevant research and development efforts will be assembled. An evaluation and analysis of this material will provide the foundation on which recommendations for future research efforts can be based.

This report covers the period December 1, 1966, through May 31, 1967. During this period, the literature search and abstracting described in Semiannual Report No. 1,* dated December 1966, has been continued. This search has now dealt with all material up to the present in the published literature, and with some of the Government-sponsored research described in contract reports.

The main body of this report is a historical review of the scientific work done on the photovoltaic effect during the more than 100 years since its discovery in 1839. A later volume will deal with the work done from 1940 to the present time, and the present report has been organized with this in mind.

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I. LITERATURE SEARCH

A. Background

During the reporting period, the major effort has been expended on the literature search. This has been completed for the published literature, all papers on the photovoltaic effect or its application having been read, abstracted, and classified using the methods described in Semiannual Report No. 1. Hence, a large amount of material has been added to the indices, and to deal with this the number of categories into which papers are classified has been increased. These subject headings are now:

1. Materials
2. Theory
3. Silicon and germanium cells
4. Compound semiconductor cells
5. Thin-film cells
6. Hetero-junction cells
7. Organic cells
8. High-voltage photoeffects
9. Radiation damage
10. Terrestrial applications
11. Space applications
12. Pre-1940 publications
13. Miscellaneous

In addition to this published material, reports on U.S. Government-sponsored research projects pertaining to the photovoltaic effect have been obtained. Examination of these has shown that a large number are, in fact, not directly related to the present work, as they deal exclusively either with systems research or with production of flight hardware. Of the relevant reports, a proportion has been abstracted and indexed, and the remainder will be similarly dealt with in the immediate future.

Some of the literature covered during the reporting period was published in German, and the authors of this report wish to thank Mrs. S. Winkler of RCA Astro-Electronics Division for her diligence and perseverance in translating a large amount of this material. The authors are also indebted to Dr. R.B. Emmons of Sylvania Electronic Systems for supplying translations of four of Schottky's papers; translations produced under this contract have also been made available to Dr. Emmons.

The remainder of this Section is a bibliography of papers that have been read and abstracted during the reporting period. Together with the similar listing given in Semiannual Report No. 1, this provides what is believed to be a complete bibliography from 1839 to the present day of papers on the photovoltaic effect and its application to power generation, with the exception of some Russian publications for which translations have not yet been completed.

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II. DISCOVERY OF THE PHOTOVOLTAIC EFFECT AND EARLY WORK

A. Introduction

The remainder of this report is the first part of a history of the development of the field of knowledge concerning the photovoltaic effect. The period covered in this part of the history is from earliest work (1839) to 1940. A later report will cover the historical development from 1940 to the present day. The dividing point at 1940 has been chosen because it forms a natural break in the development of the subject. During the earlier period, a large body of phenomenological knowledge was built up on photo-effects seen in a wide variety of semiconductors. Most of this work was unrelated to other work in the field because of poor reproducibility, results from similar experiments sometimes giving apparently contradictory results. However, the development of cuprous oxide rectifiers and photocells brought order to the field, and the subsequent development of a good theory of metal-semiconductor barrier effects was the climax of this early period.

During the second period, attention shifted to p-n semiconductor junctions. With the experimental results from these, theory could be verified to a degree not possible before, and the resulting understanding made possible the development of semiconductor devices and the practical realization of the present generation of solar conversion devices.

This report is based on material assembled during the earlier literature-search phase of this contract, as described in Semiannual Report No. 1, dated December 1966, and Section 1 of this report.

The order of presentation of the material in this history is chronological, but a division has been made into various subject fields, as shown in the index. This has been done to allow a coherent development of each topic. The potential difficulty with this method is that it does not show the interaction between contemporary developments in separate fields. These were, in fact, not strong during most of the early period, but where they did occur, cross-references will be found in the text.

B. The Becquerel Effect

Since the Becquerel effect is of some historic importance, but is judged to be unlikely to yield results of practical significance for power conversion devices, the account which follows does not aim to be an exhaustive study of the subject. Since most of the review papers are mentioned as such in the text, reference to these will provide a more extensive bibliography should this be desired.

The Becquerel effect is seen with two identical electrodes immersed in the same electrolyte solution, when one electrode is illuminated and the other is in darkness. A potential is developed between the electrodes, the voltage value increasing with light intensity. A current can be drawn from the cell, the short-circuit current value also increasing with increase of illumination. It is usual for the illuminated electrode to become electrically positive, but there are exceptions to this rule. In some systems (notably with cuprous oxide electrodes) it is necessary to "activate" the light-sensitive surface by passage of an electric current, before the photosensitivity is developed.

Becquerel's paper (1), published in 1839, marks the beginning of photovoltaic research. The paper is wholly concerned with experimental results, giving data obtained using platinum electrodes in solutions of hydrochloric acid, and brass and silver electrodes, also in acid solutions. It was found that silver halide coatings on the electrodes markedly increased the currents obtained, but that the action was a transient one. Simple spectral response measurements were performed using sunlight passed through a prism, the response peaking in the green for brass electrodes, and the ultraviolet for silver halide electrodes. Care was taken to distinguish the observed effects from any which might arise from thermal action, but no distinction was possible between purely photoelectric and photochemical reactions.

Following Becquerel, reports of further researches were made at various times during the remainder of the nineteenth century, the main contributions being a large increase in the number of electrode-electrolyte systems known to be photosensitive. Kochan (2) published a summary of the work up to 1905. Interest then shifted primarily onto Cu_2O-electrode systems, this being a precursor to the wave of interest in this material in the dry-rectifier photoelement work during the 1920's and early 1030's. Garrison (3) in 1923 reviewed the previous work in this field, and reported the results and conclusions of his own experiments. The principal difficulty lay in separating photochemical from physical photoelectric effects. Garrison's conclusion was that in the systems involving Cu_2O electrodes in neutral electrolytes (e.g., K_2SO_4 and KCl) the primary reaction is chemical, the light producing a displacement of the equilibrium in the reaction:

$$Cu_2O\,(\text{solid}) \rightleftharpoons Cu_2O\,(\text{dissolved}) \rightleftharpoons 2\,Cu^{+} + O^{--}$$

in such a way that Cu_20 was dissolved from the solid. Perhaps the most interesting point brought out in this paper concerns cell output potentials. It was believed that the Becquerel electrode action established a "concentration cell",* and, hence, a logarithmic dependence of cell output potential on illumination intensity is predicted, under reversible thermodynamic conditions, i.e., open-circuit conditions. Experimental verification of this relationship was sought and obtained with fair accuracy. This logarithmic dependence of V_{OC} on illumination intensity was apparently not known for barrier-layer cells until some ten years later.

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* For an exposition on this subject, see any standard text on physical chemistry, e.g., Elements of Physical Chemistry by Samuel Glasstone, St. Martin's Press Inc., New York.

Winther's paper in 1927 (4) reviewed the work up to that date. From this review of the available data and theories it was concluded that incident light caused a primary ionization at the electrode-electrolyte interface (a pure surface effect) with a subsequent change in the adsorption equilibrium. Any photochemical process accompanying this physical process was considered to be a side effect. The lack of correlation between photoconductivity and photovoltage was thought to be due to one being a surface effect, the other a bulk effect, but an intrinsic connection was assumed.

In 1929, Winther (5) presented experimental work on Cu_2O electrodes in dilute KCl solutions. It was found that oxygen was consumed at these electrodes, and it was concluded that in these and other "oxygen-electrodes" a potential difference was maintained across the unilluminated Cu_2O, but on illumination, a drop in electrical resistance occurred which allowed a chemical reaction to take place, producing an emf relative to an unilluminated electrode. This apparent reversal of the author's view of his subject was caused by the great difficulty encountered in separating chemical and physical effects occurring simultaneously. This is probably the main reason why the work done on "dry" systems was to prove so much more effective in elucidating fundamental processes.

A considerable amount of research on photoelectric effects was conducted at Columbia University under C. G. Fink, during the 1930's. Some of the early work done during this period was on Cu_2O Becquerel cells, using Pb $(NO_3)_2$ electrolyte and Pb as a second electrode. (Such a device, of course, generates a dc voltage under no illumination.) Some of this work was published in 1930 (6), but the primary emphasis in this paper was on techniques for fabricating cells, and on discussions of their applications, so that the work is of minimal value to the development of this subject. Later work by Fink and Adler was to prove of greater significance.

In the years 1920-1932, the front-wall barrier Cu_2O cell was developed, and an understanding of its operation was obtained. A major part of this work was done at the laboratories of Siemens in Germany under Schottky, Duhme, Waibel, and others. It is clear that this group understood the relevance of their work to an explanation of the Becquerel effect, as is shown by a comment by Schottky (7), and in a review paper by Duhme (8) both published in 1931. This issue was taken up in detail by Waibel (9) in 1932. The experimental evidence produced by Waibel using Cu_2O electrodes in 5% KCl solution and Cu_2O barrier-layer photocells with a transparent conducting front electrode was as follows:

1. In both cells, photoeffects were seen only when the cuprous oxide surface was activated. This activation could occur by polarization in a liquid solution, or by passing a current through the cell from an external source. After activation, the same electrode showed photosensitivity in both types of cell.

2. The photocurrent in both cells was in the same direction.

3. The spectral sensitivity for both cells was the same.

4. The photogenerated currents were independent of the counterelectrode material in the barrier-layer cells, and the open-circuit voltages were dependent on the oxide resistivity in the same way for the two cells.

From this evidence, it was concluded that the Becquerel effect and the barrier layer photoeffect were fundamentally identical, although, of course, this was true only in the case of cells in which chemical reactions did not dominate the effects.

Independent work leading to the same conclusions was reported by Müller and Spector (10), the experimental evidence presented also being comparative measurements of the behavior of the two types of cell.

Further work was reported by Adler (11) in 1940. The interesting point brought out in this paper is the expressions which were derived for the dependence of the cell open-circuit voltage (V_{oc}) on illumination intensity (J). The analysis is related to that performed by Garrison in 1923, but with a starting point in reaction rate considerations. Again, the logarithmic dependence of V_{oc} on J is deduced for moderate and high light levels, but, in addition, the linear dependence of V_{oc} on J at low light levels is derived.

The general expression which was obtained for electrode potential V_e as a function of illumination intensity J was

$$k_3 J = k_2 [A] \frac{\exp - e\alpha V_e}{kT} \left[\exp \left(\frac{V_e - V_o}{kT} \right) - 1 \right] \tag{1}$$

where k_2, k_3, α are constants,

[A] is the chemical activity of atoms at the electrode surface,

e is the electronic charge, and

V_o is the dark emf of the cell.

It was shown that in the case where $(V_e - V_o) >> kT$,

$$V_e = C + B \ln J \tag{2}$$

where B and C are constants.

When $e(V_e - V_o) \ll kT$, i.e., for low illumination intensities, or for metal electrodes which produce only low voltages under high illumination intensities:

$$V_e = C' + B' J \tag{3}$$

B' and C' are again constants.

The same analysis was presented in another paper by Fink and Adler (12), and further discussion of the points raised is given in a letter published in 1941 (13) in reply to criticism, no new material being presented.

This is as far as we shall pursue this subject at this time. Two main points are to be made concerning the work which has been reviewed.

(1) The Becquerel effect was the earliest photoelectric phenomenon to be studied.

(2) The theoretical interpretations offered by the physical chemists were much in advance of work done by those studying purely physical effects. If these results had been combined with the electrical equivalent-circuit work done at the same time, a quantitative understanding of the barrier-layer cells could have been arrived at much sooner than was actually the case.

C. Barrier Photovoltaic Effect

1. <u>Discovery and Experimental Work.</u> — The earliest work on photovoltaic effects at potential barriers was done with selenium devices, and was reported in 1876, by Adams and Day (14). Both photoconductive and photovoltaic effects in selenium were investigated and used for many years, selenium being the most photosensitive material known until the advent of p-n junction devices in the 1940's. However, the better reproducibility and stability of devices based on Cu_2O, coupled with improved electronic techniques which compensated for their lower sensitivity, partially moved attention away from selenium after about 1930. The work on copper oxide barrier-layer cells proved to be the most important contribution both to the application of photovoltaic effects and to an understanding of the mechanisms of the effects. During this phase of the photovoltaic work, almost all of the concepts used in the manufacture and performance analysis of present-day solar cells were developed.

a. Selenium: Adams and Day (14) studied both photoconductive and photovoltaic effects in bulk selenium specimens in the form of small rods, with platinum contacts scaled onto the ends of the rods by heat. The specimens were annealed before use causing partial crystallization of the selenium, to give low electrical resistivity. The results showed that:

(1) The apparent resistance of the specimen diminished as the applied voltage increased.

(2) The potential first applied to a specimen could cause an asymmetry in the electrical conduction for all later measurements, the direction of initial current having the higher resistance.

(3) Passage of a current increased the electrical resistance of the specimen to further currents in the same direction, and reduced the reverse resistance.

(4) On cutting off an externally applied current through a specimen, a small current in the opposite direction could be generated by the specimen.

These observations are apparently all explicable in terms of barrier effects at the contacts, together with trapping in the bulk.

On examining the effect of light on the specimen, a general increase in conductivity was observed, except in some cases where a drop or even reversal in specimen current was obtained. This suggested that the light was generating a potential in the specimen, a supposition which experiments proved to be correct, the illumination from a single candle being enough to produce an observable current.

Further experiments, using light filtered through water to remove infrared and in finely focussed beams, established the following points:

(1) The effect was not thermal.

(2) The sensitivity was different at different parts of the specimen.

(3) When the platinum contacts were illuminated, current passed from the selenium to the platinum.

The interpretation offered was not that accepted today, but involved photo-activated crystallization of the selenium. Thus, it is seen that these authors observed all of the fundamental phenomena which made selenium such an interesting material for both research and technological purposes in later years.

Commercial application of selenium photoconductor cells to photometry soon followed, and methods for making more sensitive devices were devised. This work greatly improved fabrication methods; all of these points are well exemplified in publications by Fritts in 1883 (15) (16). It seems likely that Fritts saw photovoltaic effects in his work, but because of his concentration on making a practical photoconducting device, his work is of little significance for later photovoltaic developments. It does not even seem to be possible to deduce from his papers the construction methods adopted for his devices.

However, a paper by Uljanin (17) in 1888 gave details of a construction method which was remarkably effective. Here, semi-transparent electrodes of thin metal films were deposited on two sheets of glass, and the selenium was melted and squeezed out into a thin layer between the glass sheets. The cell was illuminated through one of the glass surfaces, and current was drawn from the cell by the two thin-film electrodes. The arrangement, of course, gave a very sensitive device.

A most interesting paper was published in 1917 by Kennard and Dieterich (18). Results were presented from a series of experiments in which surface potential changes were measured. The specimens were both selenium and cuprous oxide. We shall return to discussion of this paper in greater detail in the section on cuprous oxide photovoltaic effects; in the present context, it is sufficient to note that the surface potential was found to increase rapidly with increase of illumination intensity at low light levels, and progressively less rapidly at higher light levels. A later report by Kennard (19) presents experimental results on the changes in surface potential of selenium specimens under illumination by light of various wavelengths. The response was found to be insensitive to wavelength, and the potential change was found to vary approximately as the cube root of the illumination intensity.

The importance of selenium photovoltaic devices of the period is put into perspective by a publication by Lange in 1931 (20), in which comparisons are made among PbS, Cu_2O back-wall, Cu_2O front-wall and selenium cells. The sensitivity of the selenium cells ($0.3\ mV\ lux^{-1}\cdot cm^2$) is shown to be more than an order of magnitude higher than that for even the best Cu_2O cells.

The temperature sensitivity of the photocurrent output for the selenium cells was an order of magnitude less than that for the Cu_2O cells, in the region around room temperature. In spite of the technological importance of the selenium cells, the physics governing their operation was little understood. This is also made clear in Lange's paper, where a photoemission theory is advanced. Basically the same material was presented by Lange in several papers published in 1930 and 1931 (21, 22, 23), the development of front-wall cells of Cu_2O being of great interest during this period. It seems that those working on these Cu_2O front-wall cells realized that the basic idea (of applying a semi-transparent metal film electrode to the illuminated surface of the cell, using the sputtering technique) was applicable to other semiconductors, presumably because of the similarity of the structure to that developed by Uljanin, but the first paper presenting results on such a selenium cell was by Bergmann in 1931 (24). The cell construction described consisted of a thin layer of selenium on an iron substrate, with a semitransparent metal film applied to the exposed selenium surface. Lead, gold, and silver films were tried as electrode materials, gold and silver giving the best results. The spectral response of such a cell is shown in Bergmann's paper, with a peak at 6150 Å . The measured sensitivity was shown to be greater than that of front-wall Cu_2O cells by a factor of 3.5, with even greater sensitivity at low temperatures.

Bergmann also published the results of a series of experiments aimed at testing those theories of the optics of metals which analyze the effect of angle of incidence and angle of polarization on the absorption and reflection of light from metal surfaces. This paper (25) shows the experimental results to agree with those of the theory:

(1) Polarization parallel to the metal surface gives a higher photocurrent than perpendicular polarization (except at 0° and 90° angle of incidence).

(2) The photocurrent for parallel polarization peaks around an angle of incidence of 75°.

(3) The photocurrent for perpendicular polarization falls off monotonically with increasing angle of incidence.

Small departures from the theory were ascribed to cell surfaces not being ideally planar.

A great deal of work on selenium cells into which small amounts (up to 10%) of sulfur were incorporated was done at the National Physical Laboratory, England, by Barnard during the 1930's (26, 27). The sulfur facilitated the preparation of the cells, without apparently altering the performance to any great degree. Various metals were used as sputtered film counterelectrodes, but the high work-function metals such as platinum, silver, and gold were found to give best results, platinum particularly yielding high open-circuit voltage values. In spite of the fact that the primary function of the research was to provide selenium cells for application to lighting-method studies in buildings, it was appreciated that obtaining adequate understanding of the cells' operation, by correlating theory and experiment, would ultimately yield improvements in photometry techniques. Consequently, the major discussion of these papers is to be found in the report section devoted to development of photovoltaic theories.

During the period covered, there were other papers on selenium cells, but these were primarily devoted to theoretical aspects of the subject, and so they also are to be found in the theory sections of this report.

This account of the history of selenium photocells has presented an account of the development of the manufacture of the cells. Their importance as photovoltaic cells is now largely historical, but their very high sensitivity made their use widespread for photometric applications, and they served their purposes well even when their properties were only known empirically. There appears to be an interesting analogy with the present use of selenium in the xerographic process, which is still not fully understood.

b. Copper Oxide: Although Grondahl is usually ascribed the honor of having discovered the photovoltaic effect in cuprous oxide, it is interesting to note that the effect was seen by Kennard and Dieterich (18) in 1917, ten years before Grondahl's discovery. Kennard and Dieterich's paper gives results from experiments in which surface potential changes under illumination were measured by means of the condenser method*, or by an "ion contact capsule"** method. The experimental arrangement used for measurements on cuprous oxide is illustrated in Figure 1. It is a little difficult to understand how the readings were taken, but it appears that two distinct groups of measurements were obtained. In one case, a potential of 20 mV was measured between contacts 1 and 2 even in the dark, and this potential was increased by some 7 mV when the whole top surface was illuminated, but decreased by the same amount if the contact area was shaded. In the other case, contacts 1 or 2, and 3, were connected to the measuring instruments (a potentiometer, with a quadrant electrometer as a null detector), and a surface potential change of +20 to +28 mV under illumination was measured. The first group of measurements indicates that photovoltages were being observed in an experimental arrangement essentially the same as that developed later by Grondahl, but it is also clear that the reported facts leave several questions unanswered, and the authors of the paper also indicate that they could offer no likely suggestion for explaining the observations. Probably because of these uncertainties, the work appears to have aroused little or no interest among those making photosensitive devices.

~~Hence, Grondahl and Geiger's paper (28), published in 1927, is generally taken as~~ the first report in which photovoltaic effects in copper-cuprous oxide junctions are mentioned. (In the years immediately following, there appears to have been some confusion as to who first reported the effect, some authors having ascribed the discovery to Lange. However, Grondahl's letter (29) drew attention to his mention of the effect before Lange's publications.)

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*The method was first described by Lord Kelvin, and can be summarized as follows: The specimen forms one plate of a parallel-plate capacitor, the other plate being a flat metal electrode which can be vibrated at a known frequency and constant amplitude in a direction normal to the specimen surface. The capacitance of the arrangement thus oscillates at the driving frequency of the plate, so that a constant electric charge existing in the capacitor causes an alternating voltage to appear across the capacitor terminals. The charge in the capacitor is determined by the surface potentials of the two plates of which it is composed. Hence, if illumination causes a change in the surface potential of one of the electrodes, a change in amplitude of the ac signal is produced by the apparatus. Absolute surface potentials cannot be measured by the method, which is applicable only to changes in surface potential. The equipment and its use are subject to many precautions; see, for example, Many et al. Semiconductor Surfaces, John Wiley and Sons, Inc., New York.

**Contact to the surface of the specimen was produced by mounting a copper strip coated on one side with polonium in an insulating ring such that when the ring was placed on a flat surface, the uncoated side of the copper was adjacent to the specimen but not touching it, and the polonium-coated side was uppermost. The top of the insulator ring was covered with a metal gauze which was connected to the measuring instruments, and a mica window was sealed over the top of the gauze.

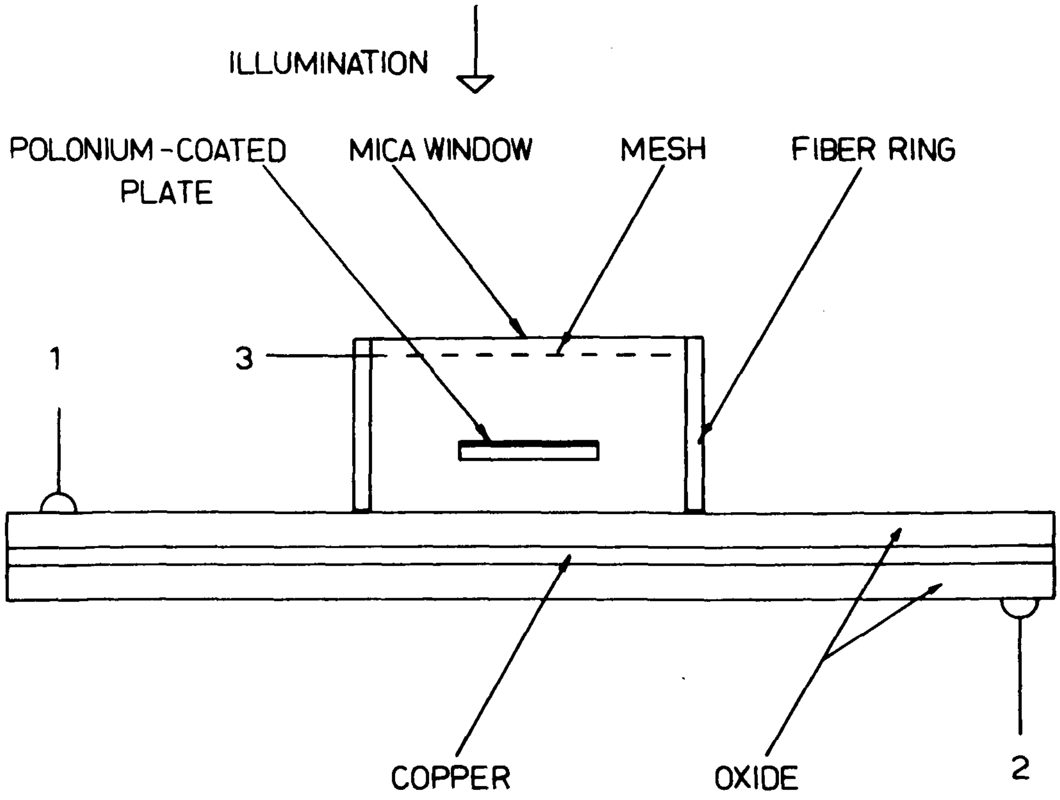

Figure 1. Experimental equipment of Kennard and Dieterich.

Grondahl and Geiger's 1927 article was devoted to an account of the characteristics and applications of the copper-cuprous oxide rectifiers invented by Grondahl in the previous year. The rectifiers were made by oxidizing one surface of a copper disk to produce a cuprous oxide layer 1.5 to 2.0 mils thick. A counterelectrode was applied to this oxide layer by pressing a lead disk tightly against it. The story is recounted by Wilson (30), that the performance of a rectifier assembly was found to alter during outdoor operation, when a shadow fell on the rectifiers. Investigation of this effect was the basis for the remark made by Grondahl and Geiger (p. 363) "For use with very sensitive instruments, the rectifier should be protected against illumination. Illumination not only changes the resistance, but produces a small emf in the rectifier." The method of construction employed in these rectifiers limits the photosensitive area to the edge of the cuprous oxide layer. Hence, it seems remarkable that the sensitivity for this type of cell, quoted by Grondahl in 1933 (31) as 15 to 20 mA for 2000 lux (equivalent to about 5.1 to 6.8 mA under sunlight illumination), should have been observed.

A much more suitable form of construction for photosensitive devices was soon developed, the same general form being arrived at by several workers independently. The earliest change was to replace the opaque lead contact disk with a special lead wire pressed against the oxide with a glass plate. Thus, the cell could now be illuminated normal to the plane of the oxide rather than around the edge only, and a larger sensitive area was obtained. However, this construction gave a rather high series resistance.

Consequently, there were quickly developed alternative methods of applying a collector grid to the cells. These methods all resulted in a metal film grid being produced on the oxide surface. This was done either by sputtering a metal such as copper or gold onto the surface or by chemically reducing a portion of the oxide film at the exposed surface. The desired grid pattern was then produced by etching out regions of this film. The sputtered films gave the better results, so that this method came to predominate.

The photosensitive region of these cells was shown to be localized near the copper-cuprous oxide interface by Schottky (32) in 1930. (It appears that work on Cu_2O photocells had been progressing at Siemens in Germany independently of the work at Westinghouse in the U.S. under Grondahl. Presumably, both companies realized the commercial possibilities of the devices, and for this reason delayed publication of scientific papers until patent rights had been established. Thus, a patent application on the use of Cu_2O grown on a copper base in a photocell was filed by Westinghouse in 1926, before the first reference to the effect in the literature, by Grondahl in 1927.)

To demonstrate that the photocurrent was not being generated at the counter-electrode to oxide interface, Schottky performed an experiment in which a fine light beam was moved away from the edge of a gold electrode sputtered onto the surface of an oxide layer burned on a copper plate. An exponential drop of current with increasing distance was found, with a decay length of 3.8 mm. This correlated with calculations of a decay length of 4.2 mm using the equivalent circuit described in the later section of this report which deals with theory. The experimental results hence confirmed that the current generation was localized in the barrier layer region. This work by Schottky, and the relevance of his analysis to present-day work on photodiodes, has been discussed recently by Emmons (33).

The last section of Schottky's paper describes a most important innovation. Apparently as a result of the experiments described in the previous part of the paper, it was discovered that a barrier-contact could be made to the oxide layer by a semitransparent sputtered metal film; see Figure 2. Schottky distinguished the two different types of cell by the terms "Hinterwandzelle" (back-wall cell) and "Vorderwandzelle" (front-wall cell); this terminology came into general use, sometimes appearing in the abbreviated form of "H-cell" and "V-cell". As is pointed out by Schottky, the thin-film counterelectrode is not advantageous electrically, since it produces a high electrical resistance, but it is very effective optically, since the photoelectron density is higher near the front surface of the Cu_2O than near the back surface. The high electrical resistivity was overcome by the use of grids, to provide a structure closely resembling the barrier-layer solar cells under investigation today.

Another publication on front-wall cells was made by Duhme and Schottky (34). The cells reported were made by deposition of gold and silver counterelectrodes on etched

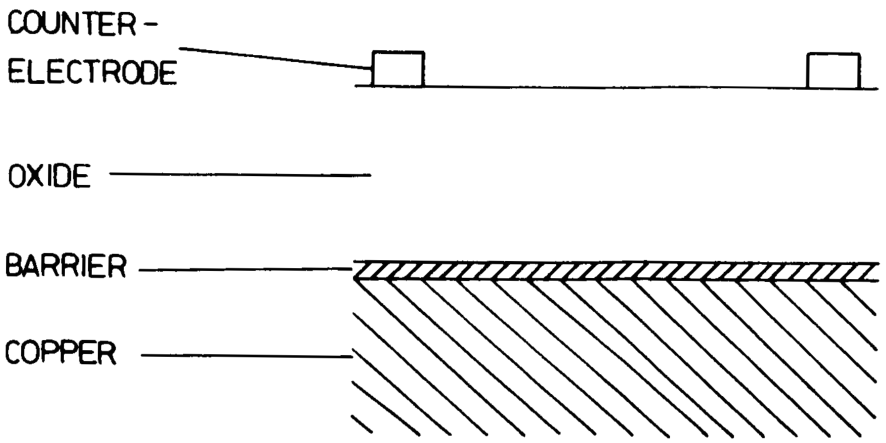

Figure 2(a). Cross section of Cu_2O back-wall cell.

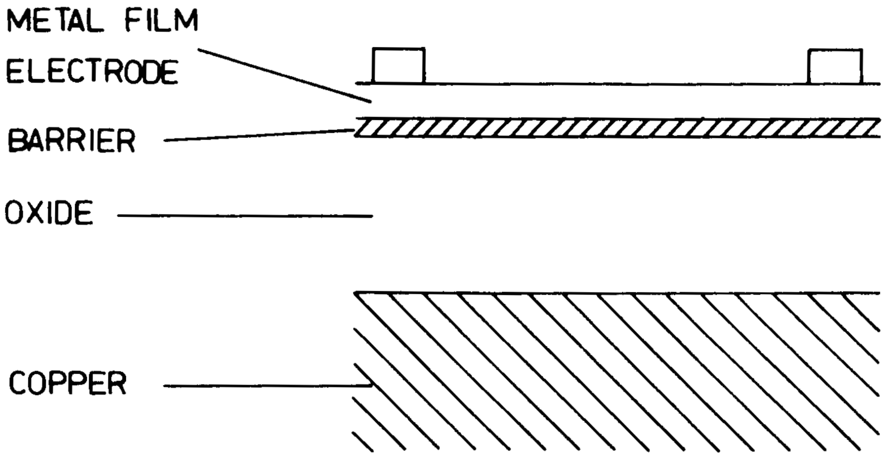

Figure 2(b). Cross section of Cu_2O front-wall cell.

Cu_2O plates. These cells were ten times more sensitive and had a reverse resistance 1000 times higher than previous back-wall cells. Calculation from the reported data indicates that these cells would have a short-circuit current density of about 34 mA cm^{-2} under 100-mW cm^{-2} sunlight. The quoted series resistance figure of 700 ohms-cm^{-2} almost certainly includes the effective resistance of the diode, since the analyses of the day did not provide a diode characteristic, and since it was usual to regard the diode as a photoconductive resistor.

Perhaps the most important contribution of Schottky, however, was in elucidating the mechanism of operation of the cells. Both Schottky and Grondahl independently made measurements on the voltage drop occurring across the oxide layer (in the direction of current flow) during operation of a copper-cuprous oxide rectifier.

These measurements required careful manipulation of a very fine probe across the exposed edge of the oxide layer, but both workers came to the same conclusion, that the major part of the voltage drop occurred in a very narrow region at the oxide-bulk copper interface. This region was so narrow that the probes could not resolve its thickness. Since it had been established that bulk cuprous oxide exhibits only ohmic conduction, this identification of the barrier layer resolved a major unknown in the operation of the cells. This barrier layer was first identified by Schottky, who applied the term "Sperrschicht", which was later used by some English-language authors to identify photocells of the barrier type.

Schottky also correlated his probe measurements with capacitance measurements by Deutschmann on Cu-Cu_2O junctions (35); the capacitance was found to vary with applied bias voltage, but a satisfactory analysis of this effect was not made at the time.

On the technical level, Schottky also found that it was necessary to activate the Cu_2O surface before deposition of the counter-electrode to provide photosensitivity in the front-wall cells. It was probably fortuitous that a glow discharge was found to perform this activation, since this process would also take place during the sputtering operation.

A large amount of work was also done at this time by Lange. This was largely directed toward applications, a major effort being made to provide useful photometric instruments. Lange appears to have been very unfortunate in not being the first to make any of the major discoveries in this field, since it appears that he independently observed many of the effects before reading of the work of others (particularly Grondahl). His subsequent publications mainly review the subject (23, 26) so far as they deal with the photovoltaic effect. On applications, however, several interesting suggestions are made. Quoting verbatim from a translation of reference (23): "Based on our knowledge of the effect, a direct conversion of light into useful electrical energy is possible. However, all the experiments conducted up to now have resulted in little progress toward realization of such a conversion......Using a more appropriate semiconductor for the intermediate layer, it will be possible to select the cell effectiveness for a specific spectral region......Use of a more appropriate unipolar layer is expected to give a further increase in the efficiency of the cell. It is then possible that efficiencies can be reached which allow direct conversion of light into electrical energy."

His remarks concerning matching of the semiconductor to the spectral distribution of the source are highly pertinent to present-day solar cell research, even though the remarks were based on a theory of cell operation now known to be incorrect.

Simple experiments on electrical characteristics of Cu_2O rectifier cells were reported by Graffunder (37). The results eliminated the possibility of the effects seen being thermoelectric. For Graffunder, the main surprise was the direction of current generation. The consistency of the direction was carefully checked experimentally, both for Siemens rectifiers and for American-manufactured devices (presumably Westinghouse units). The generated current was always found to be in the high-resistance direction through the rectifier, a point which had been explained by Schottky, and which will be taken up later in this report. An experimental I-V curve for a rectifier is shown in the publication; the curve shape is good. The effect of bias voltage on the external current of the device under illumination was also investigated, but the results apparently did not show this I-V curve to be correlated with the unilluminated curve, probably because of series resistance and photoconductive effects.

A major contribution to experimental knowledge of back-wall Cu_2O cells was made by von Auwers and Kerschbaum (38). These workers were mainly concerned with arriving at an electrical equivalent circuit for the cells, and at elucidating the physical mechanisms underlying their operation. Their theoretical analysis will be dealt with elsewhere; experimental results were presented graphically showing the relationships between cell voltage, current, apparent resistance, illumination intensity, distance of illuminated region from counter-electrode edge, thickness of oxide layer, and proportion of cell illuminated. Many graphs were plotted on both linear and logarithmic scales, and some of the relationships were measured using filtered illumination to provide light of different wavelengths. It was established conclusively that the short-circuit current was linearly related to light intensity, but this is really the only significant numerical result given. It seems that once again internal resistance and perhaps photoconductivity in the oxide prevented the exponential variation of V_{OC} with illumination intensity from being discovered.

Another conclusion drawn from the experiments was that the open-circuit voltage was not linearly related to illumination intensity. Perucca and Deaglio (39) reported experiments indicating that both V_{OC} and I_{SC} were related linearly to illumination intensity. The other results in their paper show that the specimen resistance was very high, thus leading to an almost linear I-V characteristic. This same point was also noted by von Auwers and Kerschbaum in a reply to Perucca and Deaglio (40); working from present-day concepts of the cell equivalent circuit, the reason for the discrepancy in observations is clear.

Kerschbaum published some results obtained during an attempt to separate the photovoltaic effects from photoconductivity in the specimen (41). The method relied on the two effects having different time constants, the specimen being illuminated by a chopped light beam. A graph is given showing photovoltage as a function of illumination chopper frequency at various values of applied bias voltage. The results were inconclusive, and this measurement approach was apparently not investigated further.

The first of a series of measurements of the dependence of photoelectric properties on temperature between 300° and 170°K were made by Teichmann in 1930 (42), and the temperature range of these measurements was extended to 120°K as described in later publications (43, 44). The specimens used were back-wall cells made from commercially available rectifier plates. The cell resistance and open-circuit voltage were found to increase between about 200° and 170°K. The short-circuit current was also found to increase to a maximum between about 190° and 130°K, but then showed a very sharp drop and a small reverse current at lower temperatures. It seems probable that some of the effects seen were thermoelectric in nature, since the construction of the equipment appears to be such that appreciable temperature gradients could be present in the cell.

Lange, noting Teichmann's work, repeated the measurements on temperature effects, and reported results obtained with both front- and back-wall Cu_2O cells, and selenium barrier-layer cells (19). For the back-wall cell, the same general behavior of the photocurrent as seen by Teichmann was observed. However, the photocurrent was found to peak at a rather higher temperature (about 200°K), and the decrease at lower temperatures was not as sharp and did not reverse. Lange explained the latter difference as arising from the construction of Teichmann's specimens, which would permit some front-wall effect to occur. The photovoltage was found to increase almost exponentially with drop in temperature down to about 150°K.

The cell resistance was also found to increase rapidly with lowering of cell temperature. Lange expected an exponential dependence of free electron concentration on temperature because of a model which would not generally be accepted today, but which assumed Maxwell-Boltzmann statistics. As a consequence, the logarithmic dependence of cell resistance on reciprocal temperature which was obtained experimentally agreed with the theory. However, the results showed two linear regions of dependence, with a breakpoint at about 200°K; this behavior was ascribed to a phase transition in the cuprous oxide, rather than a change of activation energy. (In these back-wall cells, the bulk resistance of the cuprous oxide was high and tended to dominate the effective resistance of the diode.)

For the front-wall cells, the same rapid increase in photo-emf with decreasing temperature was observed. However, the short-circuit current decreased monotonically with drop in temperature, rather than exhibiting a peak, and Lange ascribes the difference between the cells' behavior to the lower bulk resistance of the Cu_2O in the front-wall cells.

This paper by Lange also contains results of spectral response measurements on front- and back-wall cells. Further results were published by the same author (20). For the back-wall cells the response was found to depend on the oxide film thickness which acted as a red filter, giving a peak at 0.63 micron and a cut-off at 1.4 micron. Front-wall cells were found to peak at a shorter wavelength, 0.54 micron, and to be more efficient. This spectral response for the front-wall cells was found to coincide with that for the photoconductive response, with a peak in the region of the highest optical absorption.

For Lange, the main importance of the results was their significance in photometric work, and PbS and Se cells are included as well as Cu_2O cells. Similar results were presented in the same year by other groups, for whom the main interest lay in elucidating the scientific aspects of the cells.

Schottky (45) presents results attributed to Waibel, who measured the spectral response of Cu_2O cells. These results were particularly valuable because they showed absolute quantum yield, i.e., number of electrons crossing the barrier per photon absorbed in the Cu_2O (allowance was made for loss of photons in passing through the metal film counterelectrode). These data were correlated with optical absorption measurements made on Cu_2O, and Schottky deduced from these that the diffusion length for photo-produced electrons could be much larger than the mean free path. He remarks that he felt that the barrier photovoltaic effect may be largely governed by the diffusion process. Auger and Lapicque (46) reported spectral response measurements on Cu_2O front-wall cells, showing results obtained with both silver and gold counterelectrode films produced by sputtering. They also measured the optical transmission of films of these metals sputtered onto glass, and, hence, could calculate the spectral response of the cells relative to the amount of light entering the oxide. The results showed the response to be independent of counterelectrode material.

Dubar (47) took up a point suggested by Auger and Lapicque, and measured the response of a back-wall cell, showing that the response occurred only for illumination wavelengths longer than the absorption edge of the oxide layer. The response peaked very close to the absorption edge around 6000 Å but showed a considerable response even at 12,000 Å.

In 1931, Duhme (48) considered the experimental results obtained with Cu_2O front-wall, back-wall, and Becquerel cells, and showed that all the cells worked in fundamentally the same way; i.e., all exhibited the barrier-layer photoeffect. Also in 1931, Lange (20) reviewed the history of the development of Cu_2O cells, and proposed various photometric arrangements for which the new cells would be suited.

In 1932, Waibel and Schottky published two related papers (49, 50), which report results correlating rectification ratios and photovoltaic output. The ion bombardment method of activation of the Cu_2O surface prior to deposition of the barrier-layer electrode, combined with a chemical etching technique, enabled these workers to make cells with characteristics varying from ohmic conduction to rectification ratios of 20: 1 at 2 volts bias. These specimens showed that the more highly rectifying cells gave much higher photosensitivity. One interesting fact was reported in the latter reference: Some highly rectifying cells, under high bias conditions, showed quantum efficiencies 100 to 1000 times larger than in the usual photovoltaic operation. These quantum efficiencies must have been much higher than unity, and are presumably due to photoconductive gain.

The difference in conductivity between cuprous oxide prepared for rectifiers and that as used in front-wall photocells has already been noted. The reasons for this difference were investigated by Dubar (51). Chemical analysis, transmission micrography, x-ray powder diffraction, examination of electrolytically deposited films on the oxide surface, and electrical resistance measurements on individual crystallites and on compressed powders were all used. From these measurements it was concluded that the two different types of oxide have the same chemical composition and the same crystal structure within the measurement accuracy. It was also observed that the electrolytic deposits followed the crystallite grain boundaries preferentially, indicating that these are electrically conducting regions.

Rupp also investigated the conduction process in the copper oxide of operating photocells (52). The short-circuit currents in the cells under steady illumination were measured as a function of the direction and intensity of an applied magnetic field. Variations were found across the surface of an individual cell, and from one cell to another, but the results showed that the decrease in current and increase in the cell's apparent resistance were generally maximum for a field direction parallel to the plane of the cell, and minimum for a field direction perpendicular to the cell plane. A change in the free path of electrons under the magnetic field influence is noted as an explanation of the effect.

Very similar work to that being done elsewhere was also in progress at the Soviet Union's Central Research Laboratories. Results were presented in the first issue of Physikalische Zeitschrift der Sowjet Union, in 1932, partly as abstracts of conference papers (53, 54) and partly as full papers (55, 56).

Lepeschinskaja (53) described methods used for the manufacture of cells, and there is no indication that these differed in any way from those made elsewhere. Measurements were made on the I-V characteristics, and the dependence of I_{sc} and V_{oc} on illumination intensity. Once again a linear dependence of I_{sc} on illumination intensity was found.

A rather more ambitious series of experiments was reported by Kurtschatow et al. (55, 56). Systematic spectral response measurements of both photocurrent and photovoltage in Cu_2O cells were performed. The influence of the metals (Ni, Cu) used for the top electrode was studied as were the contributions of the front-wall and back-wall effects, and the effect of temperature. A spectral response peak at 0.55 micron is associated with the front-wall effect, and a peak at about 1.0 micron with the back-wall effect. Correlation between photovoltaic and photoconductive response was seen. (The results are closely parallel to the other spectral response measurements described above.) The second paper deals mainly with advancing and testing a hypothesis of cell operation, and will be dealt with in the theory section of this report.

Sinelnikow and Walther (54) described an apparatus for the automatic recording of the spectral distribution of photocell sensitivity, using a monochromator synchronized with a recording galvanometer. Methods for the automatic recording of I-V characteristics were also described.

An extensive historical account and review of Cu_2O rectifiers and photocells was given by Grondahl in 1933 (57), together with an extensive bibliography. Essentially no new experimental results are presented. Indeed, the period of experimental work was now mainly over, the characteristics of the effect having largely been determined.

The published literature which has been reviewed does not give a clear description of the fabrication methods used for the cuprous oxide devices, probably because of commercial competition. However, some of the more academic workers such as Fink (58) discuss fabrication methods, and there is no reason to think that the industry used noticeably different techniques. The copper plates were surface cleaned, and then heated in an electric furnace to a little over 1000° C, to form the oxide layer. The period of heating and the furnace temperature were critical, since cupric oxide is formed below 1040° C, and copper melts at 1083° C. Between these temperatures, cuprous oxide is formed as a glassy layer on the metal. After four minutes in the furnace, the copper plate was lowered quickly into a water bath. Sheets of 6 in. x 10 in. were processed in this way by Fink; Schottky mentions the use of plates 40 cm x 60 cm (~ 16 in. x 24 in.) in Reference (32), but this is probably a misprint, since in Reference (59) the specimen size is given as 40 mm x 60 mm.

Although such large sheets could be produced, the application of cuprous oxide to present-day solar energy conversion does not appear feasible, because of the low efficiencies which can be obtained with this material. This point will be taken up in a future phase of this contract. An essential part of the structure of the cuprous oxide rectifier and photocell is the presence of a region of high-resistivity oxide at the metal-oxide barrier. This material is stoichiometric cuprous oxide, whereas the bulk of the oxide layer contains a very small excess of oxygen, which increases the carrier concentration, and hence the conductivity, by several orders of magnitude. The effect of this particular structure is to produce a "Mott barrier," as discussed in the theory section of this report.

Fink and Fogle published a very lengthy paper in 1934 (58), presenting no fundamentally new data. However, the paper appears to be historic in one respect: It contains the first mention of the use of an antireflection coating. The effect was discovered by accident, when it was found that application of beeswax to a cell, for masking during chemical etching, increased the cell output current. The possibilities of the effect were fully explored, with analyses of the effect of various coatings on various types of cell. (These coatings were not of the modern quarter-wavelength interference type.)

This concludes the history of the experimental work on cuprous oxide cells. Quite aside from the technological importance of the cells, the cells are important historically because it was largely on the experimental data from these cells and the rectifiers from which they were developed that the modern theory of semiconductors was first based. This mainly seems to have been because the effects seen with cuprous oxide could be more readily reproduced than with any of the large number of other materials in which photoelectric effects were seen. It was presumably because of the strong applications-oriented groups working in Germany under Lange and Schottky, and in the U.S. under Grondahl, that empirical knowledge of the effects ran considerably ahead of the theory for some years. It is for this reason that the experimental work has been presented first in this historical review.

c. *Other Materials:* From the time of the earliest work on selenium during the latter part of the 19th century, photoelectric effects were seen in a wide variety of semiconducting materials. However, because of a general lack of reproducibility, these observations did not contribute appreciably to the knowledge of photovoltaic effects which was being built up by the study of selenium, and later of Cu_2O. Since the materials under consideration were compounds, and the specimens were often naturally occurring minerals, the reasons for a lack of reproducibility are not hard to understand. Some of the materials which were studied have received further attention rather recently in pick-up tube research and IR detector development, and even today it is very difficult to obtain reproducible results with these compounds.

Of the various materials studied, Ag_2S gave the most consistent results. Photovoltages at metal contacts to crystals of the naturally occurring mineral argentite (Ag_2S) were measured by Geiger et al. (60, 61) in the early 1920's. The contacts were pressed knife-edges, and the results were found to be independent of the metal used. The generated emf reversed on moving the illumination to the other contact. Experiments showed an increase in photo-emf with intensity of illumination, which was linear at low intensities and reached a saturation value of 0.013 V at higher intensities. Using a monochromator with a thermopile for power measurements, the spectral dependence of the emf was measured and found to peak sharply around 1.0 micron.

The emf was also found to "fatigue" after extended illumination periods, falling to very low output values and sometimes even reversing. This effect may arise partly from trapping, or may be due to field-assisted diffusion of electrically active impurities. Effects such as this are frequently seen during present-day work on the less-well-known compound semiconductors used for sensing devices.

Geiger also found photovoltages to be exhibited by proustite ($Ag_3 AsS_3$), molybdenite (MoS_2), stephanite ($Ag_5 SbS_4$), and acanthite (Ag_2S); all with knife-edge contacts. This list gives some idea of the type and range of compounds which were investigated during this period. Significantly, Geiger also found that some (but not all) cuprite crystals (Cu_2O) exhibited photovoltages, under the same experimental conditions. The difference between this observation, with its uncertainties and nonreproducibility, and the work done later by Geiger and Grondahl, well exemplifies the great advantage which was inherent in the specimen preparation techniques devised by the Cu-Cu_2O rectifier work.

After the development of the work on Cu_2O cells, Lange (20, 23) realized that effects which he had seen at metal point-contacts to PbS crystals were of the same nature as those seen in the barrier-layer cells.

Research on a remarkably large number of minerals and compounds was reported in 1936 by Bergmann et al. (62). The measurements of spectral sensitivity were performed using methods developed by Bergmann (63), in which a chopped light beam was used to generate an ac photovoltage, which was taken from semitransparent metal film electrodes on the crystal to the input of an electronic amplification and measurement system. A full tabulation of the 37 compounds in which photovoltages were measured is unnecessary in this context, but some are worthy of special mention. The spectral response of CdS is shown, with a peak at about 4800 Å and a long tail into the red, rather similar to the response measured in CdS solar cells today. The spectral responses of a series of alloys of varying composition in the BiI_3: PbI_2 system show a graded response through the range 4500 to 6500 Å, the relative responses at the ends of the curve being proportional to the composition of the alloy. This result is the direct precursor to present-day work aimed at producing materials with forbidden-band values which can be adjusted by changing an alloy composition. However, it seems that for some of Bergmann's results, there is the possibility that the specimens were not of the compositions noted, but were of varying stoichiometry and not of a single phase. Another interesting point in this work is Bergmann's mention of photovoltaic activity in organic dyestuffs. Unfortunately, the response obtained was very small, so that spectral measurements could not be made. However, this appears to be the earliest mention of semiconducting effects in organic materials.

This account covers the major points which were established experimentally before 1940. Because these compounds have contributed little to the development of the subject, no attempt has been made to treat the matter exhaustively.

d. Summary of Experimental Results: Before going on to an account of the development of the theory of the photovoltaic effect, it will perhaps be helpful if a summary is given of the major points established experimentally prior to 1934.

(1) Potential differences of up to a few tenths of one volt can be obtained by illumination of a metal-to-semiconductor* boundary.

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*Semiconductors were recognized during early work by their negative temperature coefficient of resistivity.

(2) The effects seen, and particularly the magnitude of the photo-emf, were sensitive functions of the methods used to prepare the specimen.

(3) The effects were usually associated with a nonlinear, and sometimes with a rectifying, type of I-V characteristic.

(4) The short-circuit current was proportional to the light intensity.

(5) At low light intensities, the open-circuit voltage was proportional to light intensity.

(6) At medium light intensities the open-circuit voltage was known to be a logarithmic function of illumination in Becquerel cells, but an unknown and nonlinear function of light intensity in solid barrier layer cells.

(7) At high light intensities, the open-circuit voltage approached a saturation value.

(8) The normalized spectral response of any given cell type was much more consistent than the absolute response of the cell, and was characteristic of the semiconductor of which the cell was made.

(9) The potential drop in the rectifying effect occurred in a region of submicroscopic thickness at the metal-to-semiconductor boundary.

2. Barrier-layer Photoeffect: Development of the Theory

a. *Introduction:* It is useful to divide the theory of operation of photocells into two parts, one part dealing with the fundamental physical processes involved, and the other dealing with the electrical network analysis theory which provides the electrical equivalent circuit for the cell. Most of the work done on photocells before about 1920 was by physicists and so it is natural that theoretical work from this period should be mainly concerned with physical fundamentals. However, without the electrical circuit analysis, theorizing was extremely difficult, and the results from this very early period bear little relationship to our present concepts of cell operation.

The subsequent work on Cu_2O cells was performed mainly by electrical engineers (Grondahl, Schottky, and Lange, among others), and one of the major achievements during this phase was the development of valid equivalent circuits for the cells.

In fact, our present ideas in this area are based almost entirely on circuits developed during the 1920's and 1930's. After the acquisition of these concepts, the physical-fundamentals work was much more likely to be successful, since effects at the cell terminals could be analyzed in terms of changes in the physical operation of the electrical circuit elements.

Unfortunately, the Cu_2O cells, which provided most of the experimental evidence during this period, are metal-semiconductor barrier-layer cells. The physical operation of these barriers is much more difficult to analyze than that of p-n junctions, because of the effects of energy levels near the center of the forbidden band gap which are localized at the metal-semiconductor junction. Even today, the operation of such barriers is not wholly understood, especially where the semiconductor is polycrystalline, as was the case in all of the early photocell work. Consequently, the development of really satisfactory physical concepts had to await the p-n junction work of the 1940's which will be dealt with later in this review. However, toward the end of the 1930's a theoretical foundation had been laid which was adequate to provide equations for the I-V characteristics of the cells. The history of the development of the electrical equivalent circuit, and of the electrical barrier theories of Schottky, Frenkel and Joffe, and Mott, is the major emphasis in the following sections of this report.

b. Equivalent Circuit Development: The first attempt at an electrical engineering analysis of Cu_2O cell operation appears to have been done by workers of the Siemens laboratories in Germany; this first analysis was in all essentials the one accepted today. Schottky (32, 59) showed in 1930 that the major part of the potential drop in both rectifiers and photocells occurred at the junction between the metal and the cuprous oxide. Reasoning from this, it was concluded that only those light-generated electrons which crossed this barrier would contribute to the external current of the cell. In Reference (59) this idea was developed to provide a picture of the motion of electrons in the cell structure [Figure 3(a)] providing also a cell equivalent circuit [Figure 3(b)]. Hence, Schottky says (in translation): "If one works without any bias, none of the photoelectrons can contribute to the photocurrent if they are generated within one of the media and are reabsorbed there; this is attributable to reasons of symmetry. However, for photoelectrons which penetrate the boundary layer between the two media, it [the external current] depends on the number of electrons generated in one or the other media, and whether they cross the boundary layer and whether they go into an area with a large, small or zero resistance. If there is no resistance at the boundary, the smallest counter-voltage across the boundary will be enough to counteract this primary current." The equivalent circuit shown by Schottky is completely valid by present-day theories, the nonlinear resistances being shown as diodes in more recent work. The circuit was of the distributed type, as would be necessary to model the Cu_2O back-wall cells of the day, with their rather high oxide resistance. The active element was a current generator with an output proportional to the illumination intensity, which was one of the first points to be experimentally established about these cells.

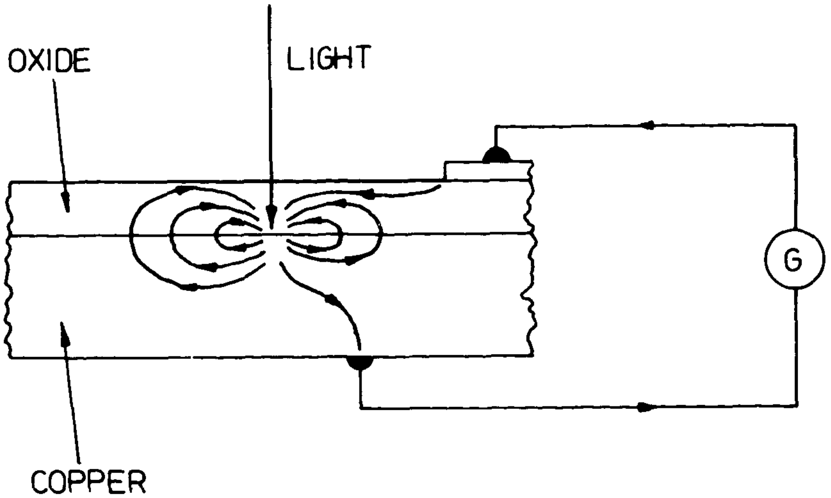

Figure 3(a). Electron flow paths in Cu_2O back-wall cell, after Schottky

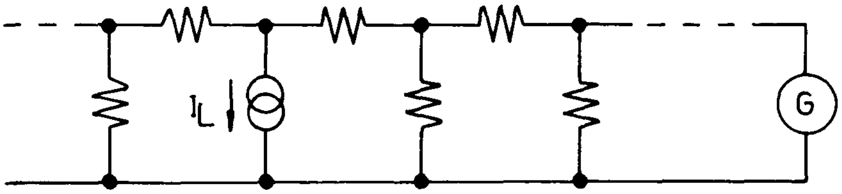

Figure 3(b). Equivalent circuit of Cu_2O cell, after Schottky

Later in the same year (1930), von Auwers and Kerschbaum, also of Siemens, published a particularly complete analysis (38) based on the same ideas as those of Schottky, described above. It was, in particular, shown that the cell was best modelled by a current generator rather than by a voltage generator. The idea that part of the light-generated current which crossed the barrier initially could re-cross it when a bias existed on the barrier due to either external or internal resistances opposing the primary current, was also brought out. The model also provided, at low illumination intensities, an open-circuit voltage proportional to light intensity, as had been established experimentally.

The principal difficulties with the equivalent circuits developed as described above were the values to be assigned to the resistor which is today regarded as a diode, and to that forming the cell series resistance. The diode resistance was certainly known to be nonlinear, but the exact form of the dependence of the resistance on current or voltage was not known. Hence, the form of the dependence of V_{OC} on light intensity at medium and high illumination intensities was not known. The series resistances of the cell were also not known, since in most of the cells made, this resistance arose in the cuprous oxide, which was photoconductive (i.e., exhibited the "inner photoelectric effect" in the terminology of the day).

These difficulties persisted for some years; thus, in 1931 Audubert and Roulleau(64) stated that "in Cu_2O, the photovoltage is proportional to the square root of the illumination intensity...", and Bartlett (65) had to assume a wholly empirical power law for the variation of photovoltage with illumination intensity. An example of the effect of photoconduction in the cell series resistance is well illustrated by the curves of Figure 4, taken from Reference (66). The curves are for a selenium cell; unfortunately, this method of presenting data was not in general use at the time, and similar curves for Cu_2O cells have not been found. However, statements that the photoconductive effect was seen in photovoltaic cells are to be found. The fact that the illuminated and unilluminated I-V characteristics cross can only be explained by a drop in series resistance for the illuminated cell.

The major success of the equivalent circuit developed by the Siemens workers was that it applied perfectly well to the front-wall Cu_2O cell as it did to the back-wall cell, which was a necessity if it were to be accepted as valid. Thus, the photons absorbed in the oxide caused a current to be generated which passed from oxide to parent-copper for the back-wall cells, and from oxide to counter-electrode for the front-wall cells. The rectifying effect and direction of photovoltage were experimentally found to be reversed in the two cells, and this reversal is necessary from the equivalent circuit.

A further analysis based on the same equivalent circuit was performed by Korosy and Selenyi (66). The main objective of this work was the elucidation of physical principles of operation, but to do this they actually constructed a cell equivalent circuit using a vacuum photocell (i.e., a photocathode device) as the current generator, and a selenium barrier rectifier as the diode: the arrangement is shown in Figure 5. The details of this work are discussed below, but it is interesting to note that the characteristics of the equivalent-circuit model matched those of an actual selenium barrier-layer cell qualitatively, though not quantitatively.

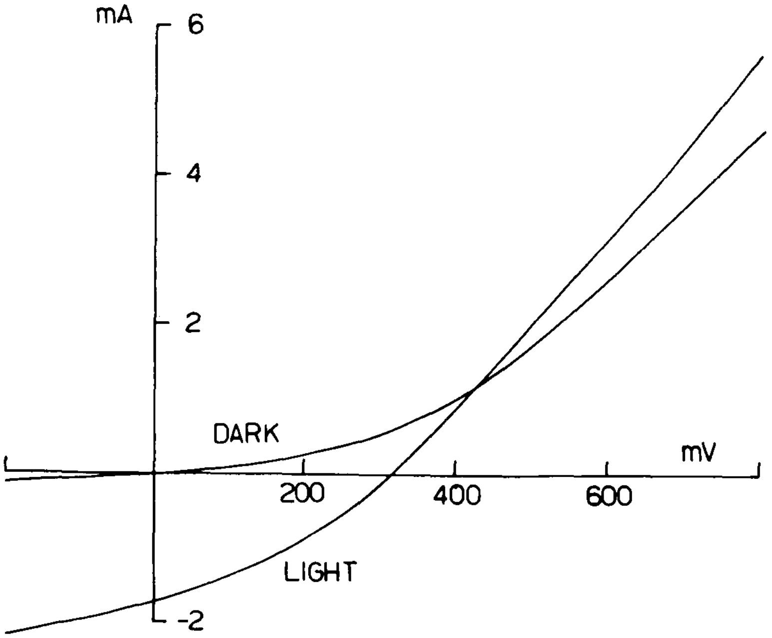

Figure 4. Current-voltage curves of selenium cell, showing the effect of photoconduction, after Korosy and Selenyi

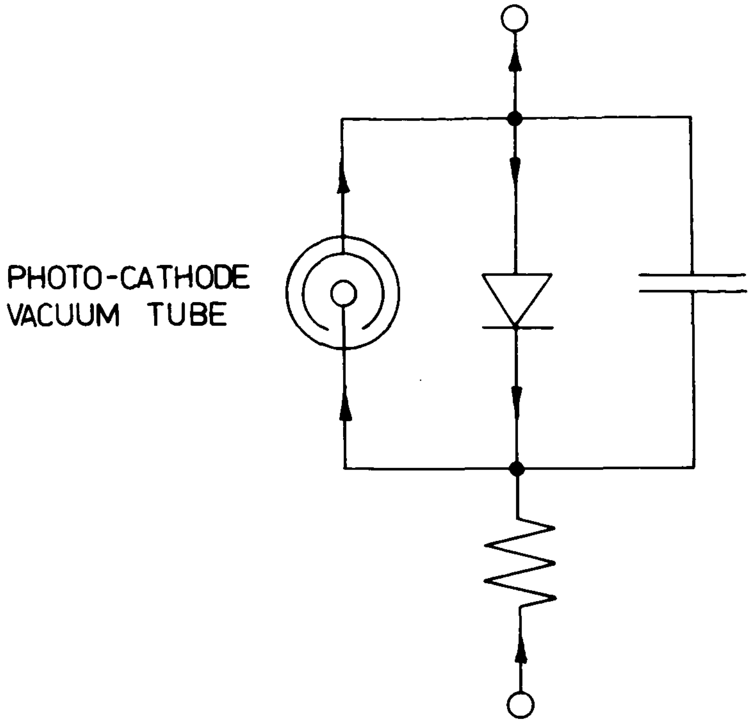

Figure 5. Experimental equivalent circuit of selenium cell, after Korosy and Selenyi

The equivalent circuits produced by this work were applicable to calculations on the matching of the cell to its load, as well as to physical model analysis. Power-transfer calculations were performed by Wilson (30) and by Bartlett (65), but the primary interest of these analyses was in maximizing the change of power transfer under change of illumination, which is the converse of the requirements for solar cell operation. These calculations were also restricted in their validity to the particular devices considered, since the nonlinear resistor (diode) characteristic was of empirical form.

Except for changes in the physical interpretation of the elements in the equivalent circuits evolved by the Siemens group, the same circuits are in use today for solar cell calculations, and this topic need not be pursued further.

c. *Physical Principles of the Fundamental Processes:* By the time theoretical work on the photovoltaic effect had got under way, it was established that conduction of electricity in metals (and, it was thought, semiconductors) was by electron motion. Also, work on photoconductive effects made it clear that the absorption of light in photoconductors produced electrons which were free to contribute to conduction in the solid. The other important point which had been well established was the photoemission effect, and low work-function cathodes had been developed and were in use in photodetectors. The Einstein equation was known to be a valid interpretation, giving maximum energy possessed by an electron on emission from a surface with work-function W by absorption of a quantum of frequency ν:

$$E_{max} = h\nu - W \tag{4}$$

and an emitted current proportional to light intensity. Putting $E_{max} = 0$ gave a threshold for photoemission, photons with energy less than W not causing any current.

A very early theory concerning the photovoltaic effect was that the pressure of photons on the electrons caused the voltage; however, calculation showed that the effect would be much too small to give rise to the voltages observed experimentally.

Following the demonstration by Schottky that a high-resistance barrier existed between the metal and the semiconductor in rectifiers and photocells, many related theories of operation of the photocell were evolved. The similarity between the photoemissive cells and the photovoltaic cells led to a theory of operation in which the photon energy, absorbed by the electron, was used to allow the electron to pass over the barrier between semiconductor and metal [Schottky, 1930, (32)]. This theory of operation covered both front- and back-wall cells, and sucessfully explained the differences in spectral response and sensitivity. In the back-wall cell, the light arriving at the barrier region had passed through the oxide layer, and thus the high-energy photons were absorbed before reaching the barrier, and did not contribute as much to the cell output as lower-energy photons, which were not so highly absorbed. However, for still lower energies of photons, insufficient energy was imparted to an electron by absorption of the quantum, to allow it to pass over the potential barrier. Thus, the spectral response curve should peak at energies near the optical absorption edge of cuprous oxide, as was found experimentally. In the case of the front-wall cells, however, all photons having energies greater than the minimum necessary to allow the electrons to cross the barrier layer should contribute to cell output, and the spectral response should be a maximum in the energy range where the photons are absorbed near the front surface of the cell, i.e., in the high optical absorption region of cuprous oxide. This was verified experimentally by the work of Auger and Lapicque (46) and Dubar (47), whose experimental results taken together showed most elegantly the correctness of Schottky's theory.

This theory also explained an experimental point which caused considerable confusion when the cuprous oxide cells were first examined. Many workers assumed that the electrons would be emitted from the metal into the oxide, thus passing through the barrier layer in the easy direction of current flow. Several workers expressed surprise at the direction of the current, and so firmly held was this belief that Lange assumed that the back-wall cells operated by photoemission of electrons from the counter-electrode into the oxide.

Schottky's account of the processes occurring in the front- and back-wall cells also explained a phenomenon sometimes observed experimentally. This was a reversal of voltage output for the cells on changing the illumination wavelength. Thus, on illuminating a front-wall cell with light of wavelength near the value at which the back-wall cell response peaked, a potential in a direction corresponding to that for the backwall operation would be seen provided the oxide was thin enough to allow this potential to dominate.

It also is clear from this analysis that a continuous gradation in V_{OC} could be observed as the illumination wavelength varied, but that the effect would be also governed by the details of cell construction. This may be the explanation for some effects observed in experiments which were performed by various workers to detect spectral dependence of V_{OC}. Lange (21) and Korosy and Selenyi (67) expected such a variation by reasoning from the photoemissive effect (Hallwach's effect). It was assumed that the cell voltage was caused by the kinetic energy possessed by the electrons in excess of that needed to pass through the barrier layer, i.e., the open-circuit voltage of a cell illuminated by monochromatic light of energy ($h\nu$), with a barrier height of W, would be given by:

$$V_{oc} = \frac{(h\nu - W)}{e} \tag{5}$$

Perucca and Deaglio (68) went one step further, and proposed that the operation of the cells was by a true vacuum emission process, rather than the analogous solid-state process proposed by Lange.

So firmly held was this belief in spectral dependence of V_{OC} that when the experiments were inconclusive or negative, reasons for the discrepancy were carefully sought. It is interesting to note that Schottky appears not to have expected this dependence of V_{OC} on photon energy to occur; there is no reference to such an assumption in his published papers, nor did he perform experiments searching for the effect.

Schottky's theory of cell operation was based on the rectifier characteristic. His discussion of the characteristic involved the contact potential difference between the metal and the semiconductor, and when Waibel and Schottky discovered, in 1932 (49) that the rectifier characteristic was dependent on the temperature at which the metal was deposited on the Cu_2O to form the barrier, the authors concluded that the contact potential theory was insufficient to account for the rectifying characteristic. Although the fact that the surface required special preparation before barrier formation had been appreciated from the start of work on Cu_2O rectifiers, it had been assumed that the problem was one of cleanliness, as with measurements of contact potential differences using the vibrating-condenser method. However, the new results indicated that something more than cleanliness was involved, and this is perhaps the first time that it was realized that surface states, as they are now called, also have an influence on electrical properties.

Kurtschatow et al. (55, 56) discussed the theory of operation of the cells advanced by Schottky. Their spectral response measurements confirmed his basic ideas concerning the front- and back-wall Cu_2O cells, but they proposed a small but important difference from the Schottky theory. Schottky considered that only those carriers generated by absorption of light in the region of the barrier layer would contribute to external current. Kurtschatow et al. proposed that the carrier generation by light occurred in the same way in both photoconductive and photovoltaic effects in Cu_2O. This implied a bulk generation of carriers in the semiconductor, which is closer to our present view of cell operation. However, the Soviet workers proposed that the photons need not onlv energy above a certain threshold value to cause carrier generation, but that in the photovoltaic effect, another increment of energy is necessary to allow the generated carriers to cross the barrier layer. Hence, there should be a difference between the wavelength threshold for photoconduction and that for the photovoltaic effect. To avoid difficulties with front- and back-wall effects in Cu_2O cells, the authors used selenium cells to demonstrate the threshold difference, and they reported finding such an effect. Such an effect would not receive the same explanation today, of course; it may have arisen experimentally because of the particular methods of cell construction that were adopted. The idea of bulk generation of carriers was supported by the experiments of Rupp (52), discussed above, who argued that if the only carrier motion occurred within the barrier region, the effect would have been much smaller than that found because the extremely high fields shown to exist in that region by Schottky would dominate carrier motion and the magnetic field would have had a very small effect.

It appears that Schottky's conception of events taking place in the cell had meanwhile been modified, since in 1932 (69) he remarked on the ability of the generated carriers to penetrate to the barrier from their place of generation within the semiconductor bulk. In other words, it was clearly appreciated that the diffusion length of the carriers could be orders of magnitude larger than their mean free path. His reported measured quantum efficiency of 25 to 50% also supported the concept of one carrier being generated by each photon.

At this stage of development, an acceptable qualitative picture of cell operation had been built up, but because of a lack of a satisfactory analysis of the forward characteristic of the rectifier effect, a valid quantitative concept of cell operation was still lacking. An attempt to overcome this deficiency was made by Frenkel and Joffé. Their series of publications started in 1930 with a rectifier analysis (70), but the first consideration of the photovoltaic effect appeared in 1932 (71, 72). The model analyzed was based on the work of Schottky, with a narrow barrier separating regions of differing electron concentration. The motion of electrons through the barrier was analyzed by means of wave mechanics, the width of the barrier being small enough to permit 'tunneling' of electrons through the potential hill, rather than requiring them to have sufficient energy to pass over the top. For the photoelectric case, a metal-semiconductor contact was considered, with a high density of free electrons in the metal and a comparatively low density of free electrons in the semiconductor. The free electron density (n) in the semiconductor was taken to be:

$$n = N \exp \left(- \frac{\epsilon}{kT} \right) \tag{6}$$

with ϵ about 0.3 eV and N between 6×10^{17} and 2.5×10^{19} cm^{-3}. Initial analyses were valid only for $n << N$, i.e., for values of applied bias small compared with (kT). In Reference (72), a more exact analysis was performed for larger bias values, and the results obtained were

$$J = J_o \left[1 - \exp \left(\frac{eV}{kT} \right) \right] \tag{7}$$

where J = current density,

V = applied bias, and

e = electronic charge.

An expression for J_o was derived from assumptions which are not accepted today, and the analysis relating to J_o was further complicated by an attempt to include the experimental fact that the reverse characteristic of rectifiers did not saturate at J_o, but showed leakage and breakdown effects. In accounting for the nonsaturation in reverse current, an equation was derived of the form:

$$J = J_o \left[1 - \exp \left(\frac{eV}{kT} \right) \right] \exp \left(\beta \left| eV \right| \right) \tag{8}$$

with $\beta \approx 1.5$.

This was based on a voltage-dependence of 'the transparency coefficient' for the junction, whereas Eq. (7) was derived assuming this coefficient to be independent of bias voltage.

However, the expression obtained for J_o did show a rapid variation with temperature, which explained the observed fact that rectification disappears at high temperatures.

However, the main importance of the work lay in the derivation of Eq. (7). Here was the needed forward characteristic of the rectifier, which allowed the open-circuit voltage expression to be derived:

$$J_c = J_o \left[\exp \left(\frac{V_1}{kT} \right) - 1 \right] \tag{9}$$

For the case of low values of V_1 this reduced to

$$V_1 = \frac{kT}{J_o} \times J_c \tag{10}$$

where J_c = light-generated current.

Another topic analyzed by Frenkel and Joffé was the threshold wavelengths for photoconductivity and the photovoltaic effect, but this work is based on premises which are not now regarded as valid, mainly because the experimental effects which the authors attempted to analyze would now not be regarded as fundamental.

The above analysis is based on a fundamentally incorrect model, as was shown later by various workers. However, the exponential dependence of V on illumination intensity, arising from the use of Maxwellian statistics, is a fundamental point which is correct, and which forms a part of later theories.

Also in 1932, Teichmann published a paper (73) in which a novel explanation was offered for the rectifier effect. By analogy with the laws of gas dynamics, a "field funnel" was postulated to act on the electrons passing through the barrier.

The geometry of the concept is illustrated in figure (6). The divergent electric field was thought to arise from the juxtaposition of two crystal lattices (copper and Cu_2O) with different unit cell dimensions. The concept was not widely accepted, and was ultimately shown to be invalid by Fink and Adler in 1940 (12).

Yet another theory concerning the structure of the metal-Cu_2O interface was propounded by Lange in 1933 (74). It was well known that the surface treatment of the Cu_2O was critical for the successful operation of the cells, an "activation" step before deposition of the counter-electrode being necessary for development of good sensitivity in the cells. Lange also found a photovoltaic effect to be present even in some cells in which the rectifying characteristic asymmetry was absent. Hence, it was proposed that the rectifying effect of the metal Cu_2O contact was quite separate and had no bearing on the fundamental mechanism of cell operation. Instead, a chemically activated surface layer on the oxide was proposed, and only those photons absorbed in this layer were thought to contribute to cell output. This theory is partially a reiteration of Schottky's postulate of the existence of a high-resistance layer of stoichiometric Cu_2O at the barrier layer. This region of low acceptor concentration is believed to exist in present-day theories of cuprous oxide rectification, and gives rise to the Mott type of barrier structure, as discussed below. The experiments of Lange were done using chemical reduction processes to activate the oxide surface, and this would certainly produce a low-acceptor density region near the oxide surface.

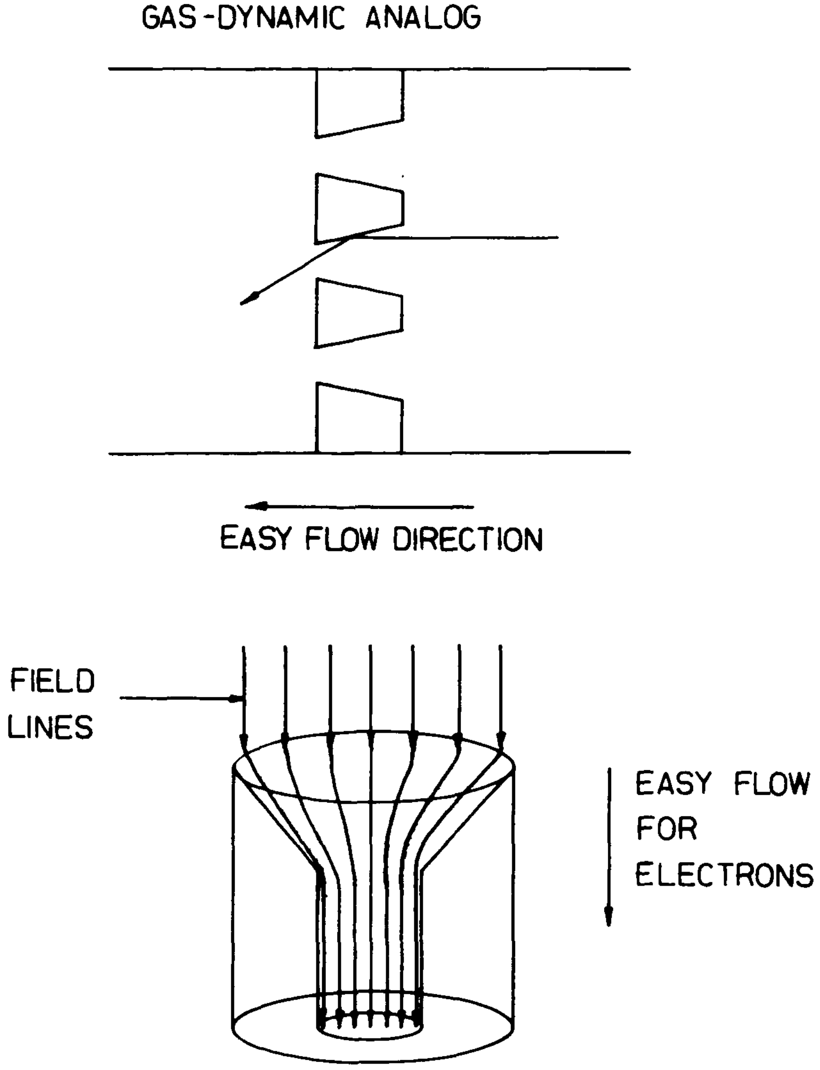

Figure 6. 'Field-funnel' concept of Teichmann, for explanation of the rectifier effect

Lange notes that chemical analysis methods would not be capable of proving or disproving the theory because of the very small quantities of material in the thin surface layer, and the fact that very small departures from stoichiometry could have large effects on the electrical properties of the layers. The attempt to separate the rectification and photovoltaic effects appears to have some validity also. As discussed above, the chemical reduction treatment would probably produce an acceptor concentration gradient in the oxide surface. This would give rise to small displacements of the Fermi level relative to the conduction band in the region of the oxide surface, which would produce correspondingly small photo-emfs. Thus, the results seen by Lange may have been more akin to Dember photovoltages (see the section below on Dember effects).

The equations developed by Frenkel and Joffé were examined for validity with experimental results obtained on selenium barrier-layer cells by Barnard (26). The major point which arose from this work concerned the value of β in Eq. (8). Barnard found a value of about 15 to fit the experimental facts best, but he also found that β was a function of the fraction of the cell area illuminated, reaching the 1.5 value derived by Frenkel and Joffé at vanishingly small illuminated areas. The actual value to be assigned to β was shown to vary widely with the detail of the contact band structure, and the presence of localized levels at the barrier. Theoretical analysis of this point was difficult because assumptions had to be made which did not fit all experimental cases. However, the equations derived by Frenkel and Joffé were partially validated by the work of Barnard, whose analysis of the reasons for deviation from the theory were also significant. The β values observed were ascribed to space-charge limitation of current when the whole cell area was illuminated, an effect which would be absent in the limiting case when the illumination area tended to zero, corresponding to the one-dimensional analysis of Frenkel and Joffé.

The final contribution to the barrier photovoltaic effect theory during this pre-1940 period was made by Mott in 1939 (75, 76). Mott points out that the theories of rectification developed by Frenkel and others assume that the cuprous oxide conducts by containing free electrons. However, Hall effect measurements showed that the current carriers were actually holes, and in this case the theories give incorrectly the direction of rectification. Mott's main contribution was to reconsider the energy band structure at the barrier, and his conclusions coincide with present-day concepts, as shown in Figure 7. The barrier width was taken to be of the order 10^{-4}cm, in agreement with the measured values of Schottky and Deutschmann (35), rather than the 10^{-7}cm which had been assumed by Frenkel. Thus, the electron passage through the junction was by carriers having energy sufficient to surmount the barrier rather than by tunneling as analyzed by Frenkel. By conceptually bringing a metal into contact with a semiconductor, Mott showed that a space-charge region would be established at equilibrium. This would produce a field in the junction region in the correct direction both to explain the rectification direction and the barrier photo-emf direction, and to show that these are of necessity linked in such a way that the light-generated current passes through the junction in the high-resistance direction, the point which had given the experimentalists such difficulty at the start of work on Cu_2O rectifier photocells. For a barrier layer of the thickness considered by Mott, the carrier passage through the junction was partly governed by diffusion processes. The current-voltage relationship derived was

$$J = \frac{V_o - V}{\rho_\infty} \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \qquad (11)$$

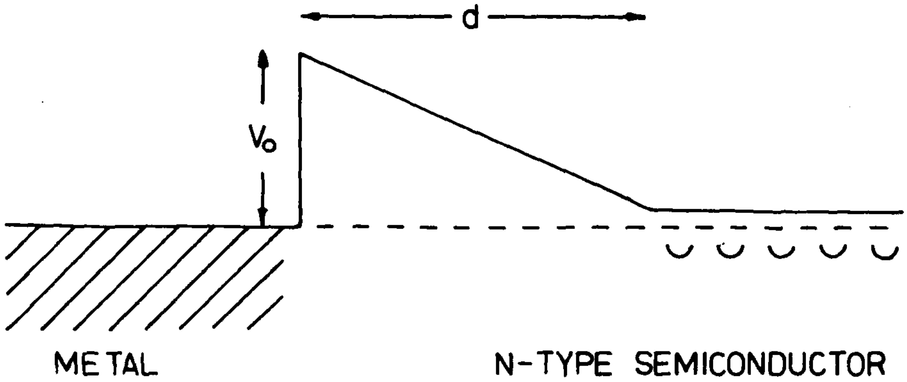

Figure 7(a). Energy band diagram of rectifier, after Mott

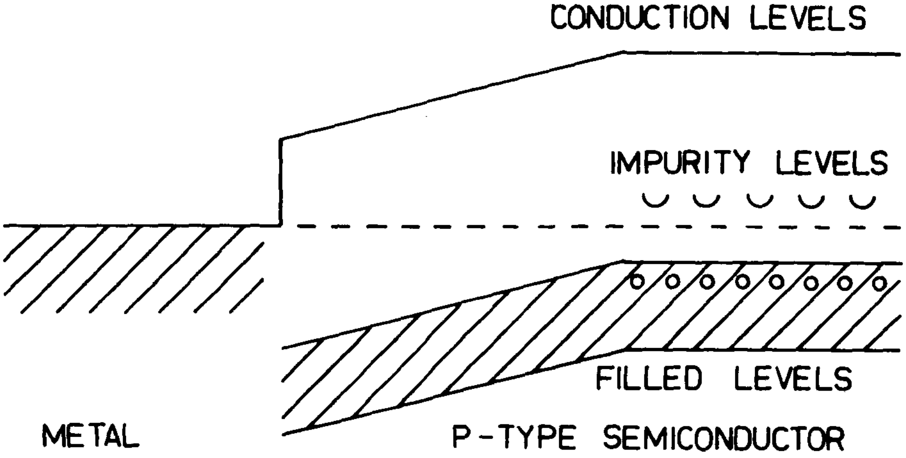

Figure 7(b). Energy band diagram of Cu_2O photocell, after Mott

where V_o = barrier height as shown in Figure 7, and ρ_∞ = limiting reverse resistance. This differs from Eq. (8) of Frenkel, but once again the rectifier operation is governed by the exponential term in $\left(\frac{eV}{kT}\right)$ which arises from the use of a Maxwell distribution function for the occupation of energy levels in the semiconductor.

Equation (11) is valid only for the particular barrier structure visualized by Mott, in which a variation of the impurity distribution near the junction is present such that a thin layer with low impurity density is adjacent to the metal. This thin layer makes an abrupt junction with the semiconductor bulk which has a much higher impurity concentration. If the metal-semiconductor barrier is high (large value of V_o in Figure 7), the junction width (d in Figure 7) is independent of applied bias.

For the copper-oxide rectifier structure, this was a valid model for cells of the type produced by Grondahl, since the impurity concentration was dependent on departures from stoichiometry, and the oxide adjacent to the parent copper was apparently accurately stoichiometric. Hence, Mott's theory explained convincingly the rectifier properties determined experimentally.

Mott's work was the first theory to be produced which is accepted as accurate today. The earlier theories of Frenkel and others, however, although based on physical models which would not now be accepted, contained elements of the later theories. Thus, the exponential dependence of current on applied voltage, arising from the statistical-mechanics treatment is common to these and to today's theories on rectification phenomena in metal-semiconductor and semiconductor p-n junctions.

d. Summary: The development of presently accepted theories of operation of barrier photovoltaic devices can be summarized as follows:

(1) Points established by Schottky in 1930

- A barrier layer exists between metal and semiconductor, and the main potential drop occurs across this during rectifier operation.
- Photocurrent generation is intimately connected with the region in which the barrier layer is situated.
- The cell equivalent circuit contains a current generator whose output is proportional to illuminated intensity.

(2) In 1932, Frenkel and Joffé analyzed the rectifier characteristic, showing an exponential dependence of I on V arising from the Maxwellian distribution of electron energies.

(3) In 1939, Mott proposed an energy band diagram for the rectifier and the photocell, and analysis of this band model provided a correct analysis of the particular barrier structure of the Cu_2O devices. This band model also demonstrated the built-in field in the barrier region.

D. The Dember Effect

1. Introduction. - Whenever a nonuniform distribution of charge carriers of both signs (holes and electrons) exists and the mobilities of the two types of charge carriers are different, diffusion currents occur which cause an equalizing electric field to be set up. Such an effect occurs at an illuminated metal-semiconductor contact at which no potential barrier exists, in the semiconductor bulk under conditions of nonuniform illumination or nonuniform absorption near a semiconductor surface when surface recombination is present, and under any generally nonuniform excitation condition. The effect at a metal-semiconductor interface is called the Dember effect, after its discoverer; similarly, potentials having their origin in the diffusion process are generally called Dember potentials. The discussion given here will be concerned with photostimulated diffusion potentials and not only the specific case of a metal-semiconductor interface.

2. Discovery and Experimental Work. - The discovery of the effect is usually attributed to H. Dember, who published two papers in 1931 (77, 78) describing the results of his studies on cuprite (Cu_2O) and other minerals. Approximately seven years earlier W. W. Coblentz (79) published the results of some studies on Molybdenite (MoS_2) in which he had observed and studied the generation of a photo-emf under conditions of nonuniform illumination. Coblentz had previously studied photoconductivity in molybdenite samples but, at the suggestion of T. W. Case who had observed a photo-emf in his own studies, began to study the "Actinoelectric" properties of the material in 1922.

Coblentz used soldered copper electrodes on his MoS_2 samples and focused the light on areas away from the electrodes. His light source consisted of a ribbon filament tungsten lamp, and a water filter was used to prevent heating of the sample. He found that several localized areas of the crystal produced much stronger responses than the rest of the crystal and that the response reached its peak value "instantaneously" (time short with respect to the response time of the galvanometer). Using a monochromator he investigated the spectral response of the effect and found that the maximum response occurred between 0.2 micron and 0.9 micron with no response beyond 1 micron. It was also noted that the spectral distribution of the photo-emf did not coincide with that of the photoconductivity. Although numerous studies were made, including the effects of intensity and temperature, no explanation for the origin of the observed effect was offered. It was not until Dember's work in 1931 that a reasonable explanation was put forward.

In the first (77) of two papers published in 1931, H. Dember reported the results of his studies on some large uniform crystals of cuprite (Cu_2O). In his first experiment an octahedral crystal was mounted between two brass elecrodes such that it could be rotated and illuminated from various angles. The light source consisted of a 500-watt mercury lamp at a distance of 30 cm from the sample. When the crystal was illuminated in the vicinity of one electrode voltages as high as 0.15 V were observed. When the opposite electrode was illuminated the photo-emf reversed its direction. The author attributed the effect to the direct nonuniform illumination of the boundary between the electrode and the crystal.

A second experiment consisted of contacting a large crystal in such a way that the electrodes were completely shielded from the illumination, and illuminating the specimen from different angles. An emf having one direction occurred when the crystal was illuminated on one face. When the crystal was rotated 110° to illuminate another facet the direction of the photo-emf was reversed. As a result of this and similar experiments it was concluded that the direction of the photo-emf was a function of the direction of illumination.

Other experiments with shielded and ring type electrodes were performed to show that it was not a barrier layer, as in the case of Schottky's photocells, that was determining the direction of the emf. It was finally concluded that the generation of a photo-emf inside a crystal could occur only when the incident light caused the emission of free electrons which could diffuse into the crystal. At the point where the light entered the crystal the electron concentration was greatest, decreasing along the path of the light into the bulk of the crystal. This concentration gradient caused the electrons to diffuse in the direction of the light.

The second paper (78), published in 1931, reported results from similar experiments using different specimens. These included cuprite samples from various countries and a sample of Chinese Proustos (Ag_3AsS_3). The effects of varying the intensity, on the photo-emf and current flux were investigated. A rotating disc was used to vary the intensity. The current was found to vary linearly, while the voltage variation appeared logarithmic in nature. The idea that the photo-emf was caused by a gradient in the concentration of the photogenerated electrons was reiterated. In addition, Dember stated that the light pressure acted on the electrons in the same direction, thus enhancing the effect.

In two papers published in the following year (80, 81), Dember continued his studies on other materials and made further attempts to establish the difference between his "crystal-effect" and Schottky's barrier effect. To this end he illuminated a Cu_2O single crystal plate through platinum nets isolated from the crystal by air or glass plates to prevent the flow of electrons into an external circuit. Under illumination a potential difference between the two sides was detected. Dember then concluded that the photovoltaic barrier explanation did not apply in this case and that the photoelectrons were displaced in the direction of the light by light pressure.

Also in 1932, L. Bergmann published two papers (63, 82) dealing with photo-emfs under intermittent illumination. The intermittent signal was fed to an amplifier and detected by a telephone and in some cases a milliammeter. Signals were detected not only in known photovoltaic structures such as Se-Fe and Cu_2O-Cu rectifiers with metallic contacts but also with iodine, mercury iodide, and CdS powers insulated from the fixture by glass plates. The effect was measured under all possible combinations of illumination, both intermittent and continuous, and on a single side or both sides simultaneously. The effect was cancelled when synchronized illumination was used on both sides but doubled when the sides were illuminated 180° out of phase. Bergmann saw a connection between his observations and the Dember effect and believed that the same mechanism was operative in his specimens.

Four years later, in 1936, Bergmann published the results of an exhaustive study of the photoeffect in some 76 compounds using the above technique (62). In some materials the direction of the photo-emf was dependent on the wavelength of the light source. A satisfactory explanation for the effect was still lacking; however, it was still felt to be related to the Dember effect and was believed to result from several effects connected with light absorption in these materials. Since the samples were naturally occurring minerals with many flaws and impurities these results are not surprising.

3. Development of the Theory. - The first attempts to develop a mathematical theory for the diffusion or Dember potential seem to have been made by J. Frenkel. In a letter published in 1933 (83), discussing the motion of holes and electrons in the presence of trapping, he developed the following expression for the Dember potential

$$\varphi = \frac{kT}{q} \frac{U_{-} - U_{+}}{U_{-} \quad U_{+}} \ln \frac{N_o}{N} \qquad (12)$$

where U_+ and U_- were the mobilities of the holes and electrons, and N_o and N were the carrier concentrations in the illuminated and unilluminated regions. As Frenkel observed, this is the correct expression for the case of high-intensity illumination. It can be seen from the equation that if the two mobilities are equal there will be no potential. The expression for the potential was derived by solving the continuity equation under the conditions that the sample is illuminated along one plane only and that the electric field does not vary with the x coordinate. Frenkel pointed out that it is possible, in principle, to determine the ratio of the hole and electron mobilities from the above equation.

In Frenkel's second paper on the subject (84), published in 1935, a much more detailed mathematical treatment was given. In this paper he attempted to develop an elementary theory of both the Dember effect and the Kikoin-Nisov effect (a photo-magneto-electric effect) in semiconducting solids. Assuming that the velocity distribution of the photogenerated carriers was Maxwellian, fundamental equations for rate of change of hole and electron concentrations with respect to time were developed, by using the particle conservation concept. By combining these equations with Poisson's equations, expressions were obtained for the Dember potential under conditions of weak and strong illumination. The analysis of the high-intensity illumination case was marred by the assumption that an approximation used to obtain a linear relation between illumination and carrier generation for weak illumination was also valid in the high-intensity case, in obvious contradiction of his preceding development. He again obtains substantially correct expressions for the Dember potential in the two extreme cases.

Noting the flaws in the work of Frenkel and others, Landau and Lifschitz in 1936 produced another extensive study (85) which included the effects of contact potentials and the variation of the velocity distribution of the freed carriers from the Maxwellian distribution. It was shown that a photo-emf could exist only if carriers of both types (holes and electrons) were generated and have different mobilities or, in the case where only carriers of one sign are present, if the velocity distribution of the carriers is non-Maxwellian. An accurate calculation of the velocity distribution function indicated that the magnitude of observed Dember potentials is too great to be attributed to the variation of the velocity distribution from that of Maxwell. The analysis of the contact potential change under illumination indicated that this effect may completely compensate the diffusion potential or even change the sign of the observed photo-emf. The following general expression was obtained for the combined Dember effect and contact potential:

$$V = \frac{kT}{e}\left[\frac{1-X}{1+X}\ \ln\left(1+\frac{J_o}{C_1}\right) - \ln\left(1+\frac{J_o}{C_2}\right)\right] \qquad (13)$$

where C_1 and C_2 are proportional to the number of electrons in an unilluminated unit volume, J_o is the photogenerated charge density and X can be related to the ratio of the mobilities of the charge carriers. The first term on the right side of the equation is the voltage due to diffusion; the second term is due to the contact potential changes. This reduces to the Frenkel expression for the case of high-intensity illumination if one ignores, as Frenkel did, the contact potential.

In 1938 B. Davydov published his paper on the Dember effect. (86) With relatively simple calculations he was able to show, as had Landau and Lifschitz previously, that in the case of a single type of charge carrier no photo-emf could be detected unless the velocity distribution of the free carriers were non-Maxwellian and that the potentials caused by this effect would be small compared with those observed experimentally. This indicated, as had the work of Landau and Lifschitz, that the observed effects were due to the existence and diffusion of free charges of both signs.

Davydov's analysis of the Dember potential covered the case of weak illumination only and included the effects of the contact potential. The analysis neglected variations in the charge carrier transmission coefficient with contact potential. The results did not agree with those of Landau and Lifschitz for the low-intensity case. Davydov points out that these workers made several improper approximations and that, consequently, their results were valid only in the case of high contact resistances.

4. Summary. - The concepts finally settled on by the investigators of the 1930's are essentially those held today, and the mathematical expressions developed for the bulk diffusion potential are essentially correct. An analytical discussion of the Dember effect at a metal-semiconductor interface (no barrier) is much more difficult and no such discussion has been found in the period preceding 1940. There is some question whether this effect is understood in general even today.

The Dember effects do not appear to hold much promise in the field of energy conversion. The magnitude of the power produced by this effect is extremely small in comparison with that produced by barrier-type devices for a given light source. The maximum open-circuit voltage under strong illumination is, in principle, the same but the short-circuit current of the barrier photocells is generally much larger. This is because the carriers generated in or near the barrier are accelerated fairly rapidly by the strong field and, thus, are afforded little time for recombination in this region. In the bulk or diffusion photoeffect no such rapid removal occurs and the consequent recombination diminishes the short-circuit current. Computations based on typical values for germanium indicate that the current associated with the diffusion potential will be, at best, approximately one tenth that of a barrier photocell.

There is one situation in which the Dember or diffusion effect can be more efficient than a barrier-type photocell. If the radiation is not strongly absorbed by the cell, as in the case of high energy radiation, it is possible for the diffusion effect to be the more efficient.

Because of the low efficiency there is little current interest in the Dember effect, although it has been proposed as a possible explanation for the high-voltage photovoltaic effect in some materials.

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