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THE COPPER OXIDE RECTIFIER

By

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“Luck sometimes visits a fool, but never sits down with him.”

- German Proverb

To put the copper oxide rectifier in the proper context, a little history is essential. The point contact diode, while well suited to the detection of radio signals, was not able to handle high voltages or high currents. Hard vacuum tube rectifiers (thermionic diodes), while superbly able to handle high voltages, could not easily work at high currents [and low voltages] due to their very high internal resistance.¹ In addition, vacuum tubes suffered from excess baggage due to the necessity of having to have a filament power supply. The so-called wet type rectifiers could handle high currents [at low voltages] but not high voltages; they were also restricted to rectifying low frequencies, although, it appears that this caveat was only true where large currents were concerned. Because wet type rectifiers are no longer part of the modern technologist's repertoire, a brief description of their construction and mode of operation is in order.

At its simplest, a wet type rectifier consisted of, for example an electrolytic cell composed of an aluminum plate and a lead plate dipped into a solution of water and borax. If an alternating voltage was applied across these two electrodes, the lead electrode was indifferent to its polarity, but not so for the aluminum electrode. When the aluminum electrode was positive (anode), oxygen was evolved at its surface producing a thickening of the alumina (Al_2O_3) passivation layer, which due to its insulating nature would prevent any current from flowing; the passivation layer rapidly dissolved when the aluminum electrode was negative (cathode), thus allowing the current to pass unimpeded through the cell. It was this growth and dissolution of the insulating alumina layer which gave rise to rectification in the wet type rectifiers. Though wet type rectifiers are long gone, their direct descendants are still with us: aluminum electrolytic capacitors, which depend for their proper functioning on the

¹ Mercury-vapor rectifiers and ignitrons did not have the high internal resistance of hard vacuum tubes and so could provide high currents. In fact, the voltage drop across these devices was almost independent of the current. Early automobile battery chargers used an offshoot of the mercury-vapor rectifier called the Tungar® rectifier (circa 1915), which substituted high pressure argon in place of mercury. The advantage of argon over mercury was that the filament and plate voltages could be applied simultaneously since the argon was already in the gaseous state. In the mercury-vapor rectifier, the filament had to be turned on first and allowed to warm up the globule of mercury, and so increase the pressure of the mercury vapor, before applying the plate voltage. Turning on both the filament and plate voltage together would result in a large voltage drop across the tube, specifically in the cathode fall of the gas discharge, resulting in the cathode being bombarded by very high energy positive mercury ions accelerated through the abnormally large cathode fall, with the result being the eventual destruction of the cathode. The potential drop along the length of a gas discharge was not uniform, almost all of the drop occurred close to the cathode, hence, the term 'cathode fall'.

electrolytically 'formed' insulating layer of alumina on their plates. These capacitors are, of course, polarity sensitive, if put in the circuit backwards the alumina film will dissolve resulting in the shorting out and possible destruction of the capacitor, due to overheating as a direct result of increased current flow.² Tantalum capacitors also work because of the presence of an electrolytically 'formed' insulating film, but they have a higher capacitive density (microfarads/volume) due to the sintered nature of their electrodes with their concomitantly larger surface areas.

Electrolytic detectors for wireless telegraphy were also in vogue in the time period 1900-1910 (see APPENDIX B of the 1993 Thesis titled "Coherers, a review" by Thomas Mark Cuff, which is available on ResearchGate).

Wet type rectifiers initially served in battery chargers working off of the normal 60 Hz 110 VAC found in most households, but they were prone to leaking their electrolyte to name just one of their problems. In short, a new rectifier was needed, preferably of the dry type. One promising candidate was the copper oxide rectifier or varistor as it was sometimes called³; another up and coming contender was the selenium rectifier.⁴ Coincidentally, the rectifying properties of

² C.I. Zimmerman; The Aluminum Electrolytic Condenser; Transactions of the American Electrochemical Society; Vol. 5; 1904; pp. 147-170.

Harold P. Manly, L.O. Gorder; Drake's Cyclopedia of Radio and Electronics; Frederick J. Drake & Co.; 1951; see RECTIFIER, ELECTROLYTIC. [Most electrolytic rectifiers used lead for the inactive electrode; the active electrode was usually made of tantalum (in sulfuric acid), aluminum (in a saturated solution of ammonium sulfate or ammonium phosphate) or magnesium (in a solution of sodium fluoride).]

³ The inventor of the copper oxide rectifier appears to have been a Mr. Lars Olai Grondahl who was working at the time for the Union Switch and Signal Co. see,

L.O. Grondahl; A new type of contact rectifier; Physical Review; Vol. 27 (2nd Series); January-June 1926; p. 813.

Idem; Theories of a New Solid Junction Rectifier; Science; Vol. 64; No. 1656; 1926; pp. 306-308.

Lars O. Grondahl also claimed that he and a coworker (Paul H. Geiger) were the first ones to observe the photoelectric effect at a copper-cuprous oxide interface. It is important to note, as Grondahl does, that what he and Geiger observed was an external photoelectric effect; A.H. Pfund had already observed the internal photoelectric effect in cuprous oxide, which gave rise to the photoconductive effect. The photoconductive effect was a passive effect in that it would only be observed by applying an external source of EMF (ElectroMotive Force) across the oxide, while the external photoelectric effect caused the copper oxide rectifier to become a source of EMF, itself, i.e., it could act as a solar cell.

L.O. Grondahl; Note on the Discovery of the Photoelectric Effect in a Copper-Oxide Rectifier; Physical Review; Vol. 40 (2nd Series); April-June 1932; pp. 635-636.

For more information on the internal photoelectric effect in cuprous oxide see,

A.H. Pfund; The Light Sensitiveness of Copper Oxide; Physical Review; Vol. 7 (2nd Series); No. 3; 1916; pp. 289-301.

⁴ The copper oxide rectifier was replaced eventually by the selenium rectifier, which had been invented around 1925 by E. Presser. However, copper oxide rectifiers still had a large market share even as late as 1948. The following are references to the discovery of rectification in selenium,

E. Presser; Selen als Gleichrichtermaterial [Selenium as a Rectifier Material]; Funkbastler [Radio Amateur]; Vol. 44; January 1925; pp. 558-559. [**Warning**, there is an error in Fig. 1. The

the copper oxide and selenium rectifiers were discovered in the same way. Both cuprous oxide and selenium had been known to exhibit photoconductivity and so they were configured as photoconductive cells for use in light meters; in addition, both cuprous oxide and selenium exhibited photovoltaic effects and were, in fact, the earliest solar cells.⁵ Grondahl and Presser discovered the asymmetrical I-V characteristics of copper oxide and selenium cells, respectively, by examining their own versions of these photoconductive cells. This led to the construction of copper oxide structures solely for the purpose of rectification.

right hand 'e', which is pointing at the metal foil layer, should be a 'c' to be in accordance with the text, and not cause confusion with the left hand 'e' which is pointing at the layer of selenium under the foil.]

Idem; Der Selengleichrichter [Selenium Rectifier]; Elektrotechnische Zeitschrift [Electrical Engineering Journal]; Vol. 53; April 7, 1932; pp. 339-341.

⁵ The first photovoltaic cell was constructed around 1839 by Edmond Becquerel, E. Becquerel; Mémoire sur les effets produits sous l'influence des rayons solaires [Memoirs on the effects produced by the influence of sunlight]; Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences (Paris); Vol. 9; 1839; pp. 561-567. Among the many photovoltaic cells he constructed, one of the first was an electrolytic cell composed of a shiny brass electrode and an oxidized brass electrode (cuprous oxide) dipped in a dilute nitric acid solution.

During their researches in 1876 on the electrical effects of light on selenium, W.G. Adams and R.E. Day noticed that the increase in the conductivity of selenium (internal photoelectric effect) upon exposure to light depended on the polarity on the Wheatstone bridge used to measure its resistance, i.e., the conductivity was a function of the direction of the DC current through the selenium sample. They wondered if this asymmetrical behavior was due to an electrical current created in the selenium by the light. If such was the case, then they reasoned that it might be possible that this current could be made to flow in a closed circuit. To test this hypothesis, they connected a sample of selenium up to a galvanometer and observed a deflection only in the presence of light, confirming their hypothesis. Adams and Day showed great physical intuition in their researches. They correctly surmised that the photovoltaic effect was not a thermal effect because its time constant was so short, i.e., the light induced current started immediately upon the application of the light and ceased without delay after the light was removed. And they appreciated that different samples of selenium from the same lot, while possessing the same qualitative behavior, had vastly different quantitative behavior - a problem that was to plague semiconductor researchers until the 1920s & 30s when Robert Pohl showed that it was due to heterogeneous distributions of impurities. For more information see,

W.G. Adams, R.E. Day; The Action of Light on Selenium; Proceedings of the Royal Society (London); Vol. 25; 1876-77; pp. 113-117.

Further improvements in the construction of the selenium photocell followed the ground breaking work of Adams and Day. See, for example,

C.E. Fritts; On a New Form of Selenium Cell, and some Electrical Discoveries made by its use; American Journal of Science; Vol. 26 (3rd Series); Nos. 151-156; July-December 1883; pp. 465-472.

To realize a copper oxide rectifier, one took a copper disk; heated it up in an air or an oxygen oven until the resulting reddish cuprous oxide layer achieved the desired thickness; after cooling down, the oxide layer was removed from one side of the disk; the oxide layer on the opposite face was treated to remove the overlayer of black cupric oxide (CuO);⁶ finally, a counterelectrode was deposited on this cuprous oxide layer.⁷ The counterelectrode could be either a metal film sputtered or evaporated over top of the oxide, or it could be that colloidal graphite, a.k.a. Aquadag®,⁸ was painted on the oxide and then a flat piece of tinned lead was firmly pressed against the Aquadag®-oxide-copper combination. The electrically conducting Aquadag® filled any spaces between the free surface of the cuprous oxide and the lead counterelectrode, while the tin coating on the lead prevented a chemical reaction from occurring between the lead and the cuprous oxide at those points where these substances came into direct contact. Unlike the semiconductor rectifiers, which would later replace it, the copper oxide rectifier's active layer - the cuprous oxide - was polycrystalline. The polycrystalline nature of the cuprous oxide layer of the copper oxide rectifier was what made analysis of its behavior by standard solid state physics techniques difficult. The sensitivity of this rectifier to variations in the stoichiometry of the cuprous oxide layer, in particular, to excess oxygen, which seemed to increase its conductivity, was suggestive of doping to produce an extrinsic semiconductor.⁹ It should also be noted that the electrical properties of these rectifiers were a

⁶ Initially this layer was removed mechanically via abrasion with an emery wheel, nitric acid was also tried, but in the end the production units had their cupric oxide layers removed chemically using a solution of sodium cyanide. See,

L.O. Grondahl; *The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell*; *Reviews of Modern Physics*; Vol. 5; April 1933; pp. 141-168.

⁷ The trick to making these devices was in the intimate nature of the junction achieved by growing the cuprous oxide directly out of the copper electrode and insuring that the oxide was formed with excess oxygen. Joseph A. Slepian - a very well known electrical engineer/designer at the Westinghouse Electric & Manufacturing Co. - admitted as to how he had failed in his attempts to build a copper oxide rectifier due to not growing the oxide properly; the tricks were not obvious even to someone as clever as Slepian. See,

L.O. Grondahl, P.H. Geiger; *A New Electronic Rectifier*; *Transactions of the American Institute of Electrical Engineers*; Vol. 46; February 1927; pp. 357-366.

⁸ According to the H. Bennett; *Concise Chemical and Technical Dictionary*; Chemical Publishing Co.; 1986; p. 123; Aquadag® is a "...colloidal solution of deflocculated Acheson graphite in water...". Aquadag® was invented by Edward Goodrich Acheson who was also the discoverer of the industrial process for making Carborundum® (SiC); silicon carbide had been, like aluminum, a laboratory curiosity for many years. He also invented the process for making artificial graphite. Natural graphite was mined in Ceylon (now called Sri Lanka) and Canada for many years, but its lack of purity would prevent it from being used in such critical applications as moderator material in nuclear reactors. Aquadag® is still used by the electronics industry as an opaque, electrically conductive layer inside TV picture tubes and oscilloscope tubes, it forms the anode in these types of vacuum tubes.

⁹ Eberhard Spenke; *Electronic Semiconductors*; McGraw-Hill; 1958; pp. 39-40, 56-57. [According to Spenke, when cuprous oxide with excess oxygen was examined via the Hall effect, the result indicated the presence of positive charge carriers. And since ionic conduction could be ruled out for various reasons, this result implied that holes were the culprits. Thus, cuprous oxide with excess oxygen was an acceptor or P-type semiconductor created by defects, i.e., the absence of Cu atoms; acceptor or P-type semiconductors could also be created by adding

strong function of heat treatment history of the cuprous oxide layer: slow cooling of the cuprous oxide-copper combination in air yielded rectifiers with high reverse breakdown voltages, while rapid cooling - water quenching - produced rectifiers with low forward and reverse resistances, which were not able to support as large a reverse voltage as the slow cooled, high resistance, rectifiers, but could tolerate higher currents.¹⁰ One thing that was not explicitly mentioned about the processing of the rectifier was whether or not the copper, on which eventually was grown the oxide, was pretreated in some way, e.g., polished. My feeling is that for all of Mr. Grondahl's candor in his description of how these devices were made, there were probably some proprietary steps in the manufacture of these rectifiers which he was not willing to divulge.

In addition, while a pure cuprous oxide layer will work, it was not optimal. The presence of impurities could produce higher rectification ratios and smaller reverse leakage currents. In particular, the impurities inherent in Chilean copper had been found to yield the best rectifiers.¹¹ The exact nature of these impurities and the history of how Chilean copper was discovered to make the best rectifiers does not seem to have made it into the open electrical engineering literature.¹²

acceptor substitutional impurities, i.e., substituting aluminum for silicon atoms.

Note, the absence (defect) of a Cu atom left the attendant oxygen atoms unfulfilled as far as their outer orbitals were concerned. If the temperature was high enough, an electron from the filled valance band could hop into the unsatisfied oxygen orbital associated with the defect position, leaving a positive electron or hole free to migrate (conduct) in the valence band; the defect position, upon picking up the extra electron, became negatively charged and was spoken of as being ionized.]

¹⁰ L.O. Grondahl; The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell; Reviews of Modern Physics; Vol. 5; April 1933; pp. 141-168.

¹¹ W.H. Brattain; The Copper Oxide Varistor; Bell Laboratories Record; Vol. 19; September 1940 - August 1941; pp. 153-159. See also,

Idem; Specific Resistance of Cuprous Oxide; Physical Review; Vol. 45 (2nd Series); January-June 1934; p. 745.

¹² A good source of information on the subject of copper oxide rectifiers is: The Archives Coordinator; AT&T Bell Labs; Rm. 1D-423; 101 JFK Parkway; Short Hills, NJ 07078. The Archives Coordinator provided me with an exhaustive bibliography on this subject at no charge - I wish to thank Edward Eckert of AT&T Archives for responding to my request for information in such an efficacious manner.

With regards to the term 'Chilean copper', the only other place I have seen it mentioned - besides the two articles by Brattain - was in an article on the history of the point contact transistor,

L. Hoddeson; The discovery of the point-contact transistor.; Historical Studies in the Physical Sciences; Vol. 12; Part 1; 1981; pp. 41-76.

According to Hoddeson, when Joseph Becker and Walter Brattain began investigating the properties of copper oxide rectifiers, one of the many questions they had to answer was the following. "And why do certain samples of Chilean copper not work in rectifiers?" This quote, which came from p. 46 of Hoddeson's article, was annotated with a footnote referring to some "Case reports (BLC) [Bell Telephone Laboratories, Private Collection]". In an effort to learn more about the use of Chilean copper by Bell Labs, I wrote, again, to the AT&T Archives Coordinator asking if he or she could find these case reports? Edward Eckert wrote back to inform me that he could find no such case reports based on the information I had provided. I then decided to ask Hoddeson if she either had copies of these reports or knew where they were located? Her address is: University of Illinois at Urbana-Champaign, Department of Physics 1110 West Green

In fact, in an earlier review article L. O. Grondahl stated almost unequivocally that of all the impurities, that he had occasion to try, none improved the performance of the rectifiers. He did admit, when questioned, that he knew of something - he called it a "...condition..." - that appeared to improve the characteristics of the rectifiers, but then he added, rather cryptically, that "...I am not prepared to talk about that." ¹³

The properties of Chilean copper - whatever they were - should have been well known given the fact that Sir Charles Tilston Bright's 1898 tome on the subject of submarine telegraph cables made mention of the desirable qualities of copper ore from, among other places, Chile. Specifically, he cited four geographical regions which yielded, at that time, the world's supply of copper for electrical signaling use: U.S./Canada (Lake Superior), Australia (Burra-Burra), Chile and Japan. While most of the copper was found in the form of ores, e.g., copper pyrites, the lone exception was the Lake Superior source where copper was found naturally in the uncombined state, and so was very inexpensive to process because fewer smelting and refining steps were required. Bright indicated that of those sources of copper ore, Chile provided one of the best ores in the sense of being free from objectionable impurities; an example of an objectionable impurity was arsenic, small quantities of which can reduce the electrical conductivity tremendously and removing it completely was very difficult. ¹⁴ This last statement appears to indicate that it was the relative freedom from impurities which made Chilean copper desirable. I do not know whether I will ever be able to figure out the mystery behind Chilean copper - if, in fact, there ever was one.

It should be mentioned that commercial production of copper from Chile can in fact be traced as far back as 1800, ¹⁵ while copper production for internal use, i.e., as religious, political and cultural artifacts, by the indigenous people of this region has been recently verified by archeologists and shown to date back as far as 500 A.D. ¹⁶

Just before putting the final touches on this thesis, I stumbled - as I have done so often and so fruitfully in the past - upon an article devoted to the subject of Chilean copper. ¹⁷ This article was doubly unusual: first, because it confined

St., Urbana, Illinois 61801-3080. I have yet to receive a response.

¹³ L.O. Grondahl; Copper Oxide Rectifiers; Transactions of the Electrochemical Society; Vol. 72; 1937; pp. 225-245.

¹⁴ Charles Bright; Submarine Telegraphs, Their History, Construction and Working; C. Lockwood; 1898; Part II, Chapter 1, The Conductor [Reprinted in 1974 by Arno].

¹⁵ Joseph Newton, Curtis L. Wilson; Metallurgy of Copper; John Wiley & Sons; 1942; pp. 450-452.

¹⁶ I. Shimada, J.F. Merkel; Copper-Alloy Metallurgy in Ancient Peru; Scientific American; Vol. 265; No. 1; July 1991; pp. 80-86.

¹⁷ C.C. Hein, W.M. Hickam; Carbon, Oxygen, and Sulphur Content of Chilean Coppers as related to Cuprous-Oxide Rectifiers; Journal of Applied Physics; Vol. 22; September 1951; pp. 1192-1195. [I found this article while perusing the subject indexes of the various abstracting services concerned exclusively with metals such as the ASM Review of Metal Literature, Review

itself to the subject of Chilean copper and its use in copper oxide rectifiers, and second, because it used the term 'Chilean copper' in its title. Before delving into the gist of this paper, I am going to review the contents of the first article referenced by Hein and Hickam, a relatively unknown article by Lars O. Grondahl.¹⁸ This particular article by Grondahl, which appeared almost 25 years after the paper in which he first announced the discovery of the copper oxide rectifier, gave a firsthand account what really happened as far as the history of the copper oxide rectifier was concerned including information on the use of "... Chile copper...".

Grondahl revealed important details about the history of the copper oxide rectifiers which appeared in print nowhere else. For example, the first paragraph of his paper disclosed that the copper oxide rectifier was invented in November 1920 and that by 1924 these devices were in commercial service - specifically, as he discussed later, in train control equipment on the Delaware, Lackawanna and Western railroads. So that by the time of his announcement in the 1926 edition of the *Physical Review*, it was already a *fait accompli*. I assume that Grondahl's employer, Union Switch and Signal Company, Swissvale, Pennsylvania, prevented any earlier revelations due to concerns about patent rights. That the company's caution was well founded was adequately demonstrated by Grondahl's detailing how Westinghouse Electric Corporation began manufacturing the rectifiers in the fall of 1926 - probably by a licensing agreement with Union Switch and Signal, although Grondahl was noncommittal on this point - to be used in an 'A battery' charger;¹⁹ according to Grondahl, in the "...latter part of 1926 this production rose to 6,000 'A battery' chargers a day [Emphasis added]." Clearly there was an enormous amount of money to be made in exploiting the copper oxide rectifier. The main reason was that the competing rectifiers had a rectifying efficiency of no better 20% and, to add insult to injury, a very short lifespan. Towards the end of the article, Grondahl finally acknowledged that a "...Chile copper prepared for rectification production by special rolling processes was used universally because it produced the most consistently satisfactory results." Why was Chilean copper better than say OFHC (Oxygen Free High Conductivity) copper? Grondahl could only point to

of Metal Literature, and Metal Abstracts. Specifically, the Hein and Hickam piece was found abstracted in the Review of Metal Literature; Vol. 8; 1951; p. 59, abs. no. 118-C.

The ASM Review of Metal Literature was published by: American Society for Metals, Cleveland 3, Ohio.

The Review of Metal Literature was published by: American Society for Metals, Cleveland 3, Ohio.

The Metal Abstracts is published by: The American Society for Metals and The Metals Society.]

¹⁸ L.O. Grondahl; Twenty-Five Years of Copper-Copper Oxide Rectifiers; Transactions of the American Institute of Electrical Engineers (AIEE); Vol. 67 (Part I); 1948; pp. 403-410.

¹⁹ The terminology 'A battery', 'B battery' and 'C battery' were associated with vacuum tubes. The 'A battery' was the low voltage, high current battery used the heat the filament, while the 'B battery' and 'C battery' were the high voltage, low current batteries used for the plate and control grid, respectively, of the vacuum tube. See,

Stuart Ballantine; Radio Telephony for Amateurs; David McKay Company; 1922; pp. 46-48.

the fact that the best rectifiers were produced from copper which contained approximately 0.03% oxygen, which Chilean coppers did. According to a 1941 article by Williams and Thompson, the 0.03% oxygen was necessary to assure good adhesion between the mother copper and its thermally grown oxide layer; OFHC had been tried, but the copper-copper oxide interface was found not to have satisfactory adhesion.²⁰ Grondahl apparently did not know if there were any other beneficial impurities present in Chilean coppers; the purity of this copper was 99.95% Cu, ~0.035% O₂ [N.B., I am not assuming that the oxygen existed in the copper existed in its diatomic form. I used the symbol O₂ simply out of convention.], and the remaining 0.02% composed of other elements. The confusion about what 'really' constituted a good copper, out of which to construct copper oxide rectifiers, can be illustrated by the following quote from the discussion following the paper by Williams and Thompson (1941),

Dr. R. E. Blakey: ...

... My experiments indicate that it is possible for the copper to be too pure, and as a result of prolonged experiment I find that for our own process a figure of 99.96% is the most suitable. This does not imply that any copper of such purity will perforce produce satisfactory rectifiers. Indeed, this is far from being the case.²¹

Carl C. Hein and W. M. Hickam, were employees of the Westinghouse Research Laboratories, which was a part of the Westinghouse Electric and Manufacturing Company. Their paper focused on examining the carbon, oxygen and sulfur content of lots of Chilean copper that had been employed in the manufacture of commercial rectifiers over a period of ten years (~1940 to 1950). They also attempted to correlate the amounts of these impurities with the electrical performance of the rectifiers (specifically, the reverse leakage currents) in a bid to determine which of these impurities gave Chilean copper its advantage. The results indicated that only oxygen and sulfur correlated with the rectifier electrical characteristics, and that these substances worked best only in small amounts on the order of 220 and 5 ppm (parts per million),²² respectively.

That the use of Chilean copper in the manufacture of copper oxide rectifiers was a closely guarded secret can be supported by two pieces of evidence. First, in all the articles and patents he wrote or coauthored, Grondahl never mentioned anything about Chilean copper. Only in his last paper on the

²⁰ A.L. Williams, L.E. Thompson; Metal Rectifiers; Journal of the Institution of Electrical Engineers; Vol. 88 (Part I); No. 10; October 1941; pp. 353-383. [See, in particular, p. 358.]

²¹ Ibid.; p. 372.

²² To calculate the ppms of O₂ in a sample of Cu, the following formula is used,

$$\text{ppm O}_2 = (\text{weight O}_2 \text{ in the Cu sample} / \text{total weight of Cu sample}) 10^6.$$

Note, % O₂ = pph O₂, i.e., the percentage of O₂ (by weight) in a Cu sample is equivalent to parts per hundred of O₂ in the same sample. According to Hein and Hickam, an oxygen content of ~220 ppm yielded copper oxide rectifiers with good electrical characteristics. Since there are 10⁴ ppm in each pph (%): 220 ppm O₂ = 0.0220 pph O₂ = 0.0220 % O₂, which is close to the value of 0.03 % O₂ championed by Grondahl.

subject, in 1948, when the copper oxide rectifier was about to be eclipsed by its old rival the selenium rectifier, and the selenium rectifier was itself about to be usurped by the germanium and then silicon rectifiers, did he finally mention the fact that Chilean copper "...was used universally..." in the production of copper oxide rectifier units. And we know that Chilean copper was used as far back as 1940 from the article by Hein and Hickam. In addition, Grondahl admitted that several years after the start of commercial manufacturing of rectifiers began Chilean copper became the *sine qua non* for the process. Second, Heinz K. Henisch's 1949 book, Metal Rectifiers, which was an exhaustive compendium of all available knowledge on copper oxide, selenium and other metal rectifiers, made no mention of Chilean copper, even though Henisch did spend a considerable amount of time on other esoterica related to the rectifier manufacturing process. Henisch's thorough bibliography, which was organized by year, did not contain a citation to Grondahl's last article in the 1948 section nor did it cite the 1941 *Bell Laboratories Record* article by Walter Brattain which appeared to be the first public mention of the term 'Chilean copper'.

One mystery which still remains has to do with how Walter Brattain knew about the Chilean copper? He wrote about how Chilean copper was the material of choice for the manufacture of copper oxide rectifiers in an article in the 1940/41 volume of the *Bell Laboratories Record*. Since he worked for the Bell Telephone Company and not for either Westinghouse Electric and Manufacturing Company or Union Switch and Signal Company, it was not obvious how he came by this knowledge. As already mentioned, this paper was absent from the bibliography in Henisch's book. Brattain was supervised during his initial work on the copper oxide rectifier by Joseph Adam Becker. It is possible that Becker was the actual source of information regarding Chilean copper, and that Brattain was simply the messenger. The best evidence for this hypothesis comes from the fact that Joseph Adam Becker, before he began to work at Bell Labs in 1924 as a Research Engineer, had previously been employed by the Westinghouse Electric and Manufacturing Company as a Research Assistant from 1919 to 1924.²³ Thus, Becker was present at Westinghouse during the very years when Grondahl first discovered the copper oxide rectifier and when it was initially put into production.

As a postscript to the mystery of Chilean copper, it should be noted that the annals of the history of selenium rectifiers were haunted by a *Doppelgänger* to Chilean copper known as the "...thallium catastrophe...".²⁴ According to

²³ Winfield Scott Downs (Ed.); Who's Who in Engineering, A Biographical Dictionary of the Engineering Profession, 1948; Lewis Historical Publishing Company, Inc.; 1948; p. 129.

²⁴ Ernest Braun; Selected Topics from the History of Semiconductor Physics and Its Applications; in Lillian Hoddeson, Ernest Braun, Jürgen Teichmann, Spencer Weart (Eds.); Out of the Crystal Maze, Chapters from the History of Solid-State Physics; Oxford University Press; 1992; p. 445. [Note, it was odd that this tome made no mention of the Chilean copper episode. This was doubly curious given that one its editors/contributors, Lillian Hoddeson, had explicitly brought up the subject in an earlier article,

Eberhard Spenke, the production of selenium rectifiers for the German war effort came to a standstill in 1942 when the electrical characteristics of these devices suddenly and inexplicably changed. Specifically, the electrical characteristics which degraded were associated with the forward bias region of the current-voltage curve; no degradation was observed in the reverse bias region, in fact, the characteristics in this region actually experienced a dramatic improvement, even as those in the forward region were denigrated. During the ensuing scramble to uncover what had changed in the manufacturing process, someone noticed that one of the things that had changed was that the solder used to attach electrical leads to the devices came from a different manufacturer than the solder used previous to the catastrophe. A chemical analysis of the 'new' solder revealed the presence of thallium in amounts higher than in the 'old' solder. The inference was drawn, and apparently verified by experiment, that the thallium was indeed the culprit. Changing the solder brought the manufacturing process back into line with no one the wiser, especially about why thallium had such a strong influence? The preceding tale came from an unpublished report authored by Spenke and reviewed by Ernest Braun.²⁵

Further corroborative evidence for the disproportionate influence of thallium on the electrical characteristics of selenium rectifiers can be found in the book by Heinz K. Hensch.²⁶ Hensch stated that small amounts of thallium alloyed with the metal used to form the counter electrode improved the reverse voltage characteristics of the rectifier, but that excessive amounts of thallium adversely affected its ageing characteristics (especially the forward bias

L. Hoddeson; The discovery of the point-contact transistor.; Historical Studies in the Physical Sciences; Vol. 12; Part 1; 1981; pp. 41-76.]

²⁵ E. Spenke; Beitrag zur Frühgeschichte der Halbleiter-Elektronik und der Kupferoxydul und selen-Gleichrichterentwicklung vornehmlich im Hause Siemens [Contributions to the early history of semiconductor electronics and of the copper oxide and selenium rectifier development with emphasis on the work at Siemens]; unpublished report. [As part of its commitment to the International Project on the History of Solid State Physics, the AIP (American Institute of Physics) has published an index to source material relating to the history of condensed matter physics,

Joan Warnow-Blewett, Jürgen Teichmann; Guide to Sources in the History of Solid State Physics; American Institute of Physics; 1992; ISBN 156-396-0680.

According to the author index of this guide, Spenke's unpublished report can be found at the Deutsches Museum of Munich, Department of Sciences.

The Guide to Sources... itself can be purchased for \$21.50 (\$19.00 + \$2.50, shipping and handling; make out the check to the American Institute of Physics) from: AIDC (American International Distribution Corporation), 64 Depot Rd., Colchester, Vermont 05446, (800)488-2665.]

²⁶ Heinz K. Hensch; Metal Rectifiers; Oxford University Press; 1949; pp. 11-12. [Hensch indicated that he obtained some of his information about the influence of thallium on the electrical characteristics of selenium rectifiers from the following reference,

A.L. Williams, L.E. Thompson; Metal Rectifiers; Journal of the Institution of Electrical Engineers (JIEE); Vol. 88 (Part I); No. 10; October 1941; pp. 353-383.

Note, Hensch's book contained a very extensive and invaluable bibliography containing many references to both copper oxide and selenium rectifiers. **Warning**, Hensch's bibliography contains a significant number of errors including misspellings of the last name of the author(s), incorrect volume numbers, improper journal titles, etc.]

resistance). The junction between the counter electrode and the selenium was the site of the rectification action.

So while the ability of impurities to enhance its electrical behavior was something copper oxide rectifiers had in common with present day silicon rectifiers, their polycrystalline morphology was something not shared with modern semiconductor devices, with the exception of perhaps the early 1N2X point contact diodes which also initially employed a polycrystalline piece of semiconductor. Nevertheless, cuprous oxide rectifiers worked because cuprous oxide was a semiconductor. Note, a competing but erroneous theory of why copper oxide rectifiers work was the thermoelectric theory,²⁷ which also saw service in trying to explain why the galena point contact diodes and other crystal detectors functioned, until George Washington Pierce *et al.* debunked this claim. The thermoelectric scenario attempted to explain the asymmetrical I-V characteristic in the following manner. When current flowed across the copper-cuprous oxide junction, the resulting I^2R heating induced a thermoelectric voltage at the dissimilar materials junction. The sense (direction) of this thermoelectric voltage aided current flow in one direction while opposing its flow in the other and so yielded an asymmetrical I-V curve. Among the many reasons for disavowing this mechanism of action were: the sense of the thermoelectric voltage in the case of copper-cuprous oxide was the opposite of what it should be to account for the observed current asymmetry; and slight amounts of flexing of the copper-cuprous oxide junction irreversibly reduced the rectification ratio, due to its degrading the required intimate association between the base metal and its oxide, but without affecting the corresponding thermoelectric voltage.²⁸ In a similar vein, it was shown recently that two dissimilar metals could form a thermocouple junction even though they were separated by 5-15 Å. Briefly, this thermocouple was simply an STM (Scanning Tunneling Microscope) with the emission tip made of one metal and the flat counterelectrode made of a different metal with the counterelectrode being heated from underneath via a chopped laser beam.²⁹

27 S.P. Chakravarti, S.R. Kantebet; Current Rectification at Metal Contacts; Proceedings of the IRE; Vol. 20; No. 9; September 1932; pp. 1519-1534.

28 L.O. Grondahl; The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell; Reviews of Modern Physics; Vol. 5; April 1933; pp. 141-168, see p. 157. [For Grondahl, the reduction in the rectification ratio brought about by flexing the copper-cuprous oxide interface was an undesirable effect since he was interested in rectification. However, the nonlinear but almost symmetrical I-V curves that resulted from flexing were ideal for modulation. On the other hand, a normal copper oxide rectifier could only modulate in the forward direction, since it passed almost no current in the reverse direction. Joseph A. Becker of Bell Laboratories got the bright idea of using deliberately flexed copper oxide rectifiers as modulators in the phone system.

J.A. Becker, Bell Telephone Laboratories, Inc.; Unidirectional Current Passing Device; U.S. Patent No. 1,980,176; November 13, 1934.

Anon.; Varistors as Modulators; Bell Laboratories Record; Vol. 20; December 1941; p. 105.]

29 J.M.R. Weaver, L.M. Walpita, H.K. Wickramasinghe; Optical absorption microscopy and spectroscopy with nanometre resolution; Nature; Vol. 342; December 14, 1989; pp. 783-785.

Given that the thermoelectric theory had been discredited as the mechanism by which the copper oxide diode worked, what was the mechanism? Before Grondahl and other researchers could even pose this question, they had to first determine the exact location of the rectifier action. They knew that the seat of the action was not the cuprous oxide itself since no materials, then or now, exhibited asymmetrical behavior by itself. Because of the planar nature of the copper oxide diode and the relatively thick layer of oxide which was permissible, researchers were able to directly probe the voltage drop across the various layers making up the device, using a sharpened metal tip. When the diode was reverse biased - what they used to call 'blocking' - it was found that all of the voltage drop was across the copper-cuprous oxide interface. By carefully transversely sectioning this interface and also by peeling thinned copper off the immobilized oxide, the presence of what was called a 'reticulum' was demonstrated. This exceedingly thin honeycombed layer appeared to be the site of the rectifying action. It should be noted that while the reverse bias character of the copper oxide diode was mediated by the copper-cuprous oxide interface, the forward bias behavior was a strong function of the counterelectrode material.³⁰ Having localized the site of the diode action, researchers were eventually able to show that the injection theories of Mott, Schottky and Davydov (see main section entitled THE RESURRECTIONS for references) accounted for a plurality of the observed behavior. This still left much that was not understood about these fascinating devices.

The semiconducting cuprous oxide (Cu_2O) layer was found not to not be homogeneous electrically. As one moved through this oxide from the free surface to closer to the copper base (sometimes called the mother copper), from which the oxide was grown, one observed that the resistivity, ρ , decreased. This effect was shown in 1941 in a paper by Walter H. Brattain.³¹ The experimental procedure utilized to secure this observation was as follows. The oxide was initially grown thicker than normal; the resistivity of this initial thick layer of oxide was determined; a few mils (1 mil = 0.001 inch) of the oxide layer were removed - presumably by chemical etching although Brattain does not say; the resistivity of the new thinner oxide was evaluated; and the etching and measuring process was then repeated. Thanks to a bibliography on copper oxide research at AT&T provided by AT&T's Archives Department, I was able to find two papers by Brattain *et al.* which detailed some of the work they had done on this resistivity problem before and after the Second World War.³² Unfortunately, both these

³⁰ Similar investigations were performed on the selenium rectifiers and yielded slightly more complicated results due to the possibility of forming a compound semiconductor during the manufacturing process, i.e., this type of diode resembled the typical PN junction of a modern silicon diode.

³¹ W.H. Brattain; The Copper Oxide Varistor; Bell Laboratories Record; Vol. 19; September 1940 - August 1941; pp. 153-159.

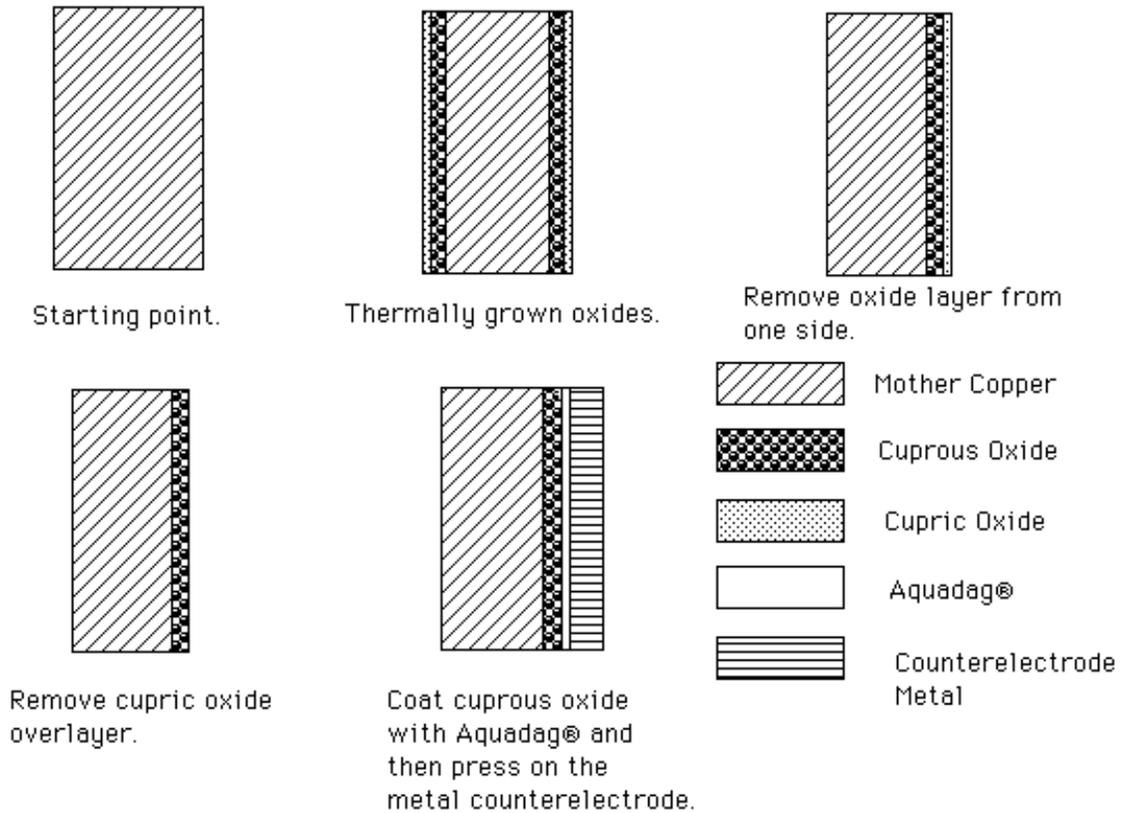
³² J. Bardeen, W.H. Brattain, W. Shockley; Investigation of Oxidation of Copper by Use of Radioactive Cu Tracer; Journal of Chemical Physics; Vol. 14; No. 12; December 1946; pp. 714-721.

W.H. Brattain; The Copper Oxide Rectifier; Reviews of Modern Physics; Vol. 23; No. 3; July 1951; pp. 203-212. [This paper mentioned the term 'Chilean copper' but offered no historical

informative papers are too massive and complicated to be reviewed in this already overburdened thesis.

The manufacturing processes showed quite an amount of ‘artistry’ due to the rather incomplete understanding of the underlying mechanisms controlling these devices. A look at some of the relevant patents of the day revealed that while many facts were known, there was little in the way of an overarching theory to tie them together.

FIGURE G1 - Manufacturing a Copper Oxide Rectifier



U.S. patent #2,205,263 assigned to Carl C. Hein appeared to indicate that Brattain may not have been the first person to have understood that the cuprous oxide was not electrically homogeneous.³³ Mr. Hein’s idea was to increase the maximum permissible reverse voltage of the copper oxide rectifier by growing the oxide layer thicker than necessary and then chemically removing the excess thickness of cuprous oxide, together with the undesired overlayer of cupric oxide, until the proper thickness was achieved. Specifically, if the desired cuprous

insight into its origins or commercial uses. The reader interested in learning ‘more’ about this term was urged by Brattain to consult his 1940 paper in the Bell Laboratories Record. Unfortunately, this advice was not really helpful, since the *Bell Laboratories Record* paper offered only slightly more information regarding the use of Chilean copper.]

³³ Carl C. Hein, Westinghouse Electric & Manufacturing Co.; Copper Oxide Rectifier; U.S. Patent No. 2,205,263; June 18, 1940.

oxide thickness was 3 mils (1 mil = 0.001 inch), then the oxide was grown to a thickness of say 6 mils, and then the excess thickness of oxide was removed by chemical etching using a solution of 2% sulfuric acid + 0.1% hydrochloric acid @ 80°C. Rectifiers built according to this scheme could take an impressed voltage three times (3X) higher than normally constructed copper oxide rectifiers. Hein's explanation for this enhanced capability was that "...the removal of the excess thickness of oxide also removes certain surface containing impurities of the copper, or it may remove some undesirable boundary condition existing between the black cupric oxide and the red cuprous oxide. I do not desire, however, to be limited to the possible explanation just stated." In other words, he didn't know, but the data on the oxide resistivity presented by Brattain does provide a rationale for his procedure without itself elucidating why the resistivity should change as one approached the copper base.

Another puzzling result of a manufacturing process was to be found in U.S. patent #1,901,563 assigned to George F. Martin.³⁴ Mr. Martin's idea was to simplify the process of removing the cupric oxide overlayer and then depositing a counterelectrode. Martin's process consolidated these two steps into one. After the oxide layer was thermally grown on the base copper, this structure was transferred to an annealing oven, and from there it was quenched in a specially prepared mineral oil bath. The quenching operation reduced the cupric oxide overlayer to a low resistance copper contact without affecting the rectifying properties of the copper-cuprous oxide interface. The copper counterelectrode produced by this procedure was, surprisingly, an ohmic junction. A fact which does not make a lot of sense given that the copper base-cuprous oxide junction formed by oxidation was rectifying. The cuprous oxide-counterelectrode interface would seem to be as intimate a junction as that formed at the copper base-cuprous oxide rectifying junction. It should be noted that if after removing the cupric oxide overlayer, one deposited a counterelectrode on the oxide, as opposed to growing one out of the cupric oxide layer, this junction was not rectifying, i.e., it was ohmic, as one would expect. In spite of my carping, a non-rectifying counterelectrode, especially a low resistance one, was desirable because an ohmic counterelectrode would not 'buck' the main rectifying junction and cause a reduction in the overall rectification efficiency. In fact, Bell Telephone Laboratories, Inc. had taken out two patents on a process for depositing low resistance, non-rectifying counterelectrodes.³⁵

³⁴ George F. Martin, Westinghouse Electric & Manufacturing Co.; Copper Oxide Rectifier; U.S. Patent No. 1,901,563; March 14, 1933.

³⁵ Joseph A. Becker, Walter H. Brattain, Bell Telephone Laboratories, Inc.; Electrically Conductive Device and the Manufacture Thereof; U.S. Patent No. 2,239,770; April 29, 1941.

Joseph A. Becker, Walter H. Brattain, Bell Telephone Laboratories, Inc.; Electrically Conductive Device and the Manufacture Thereof; U.S. Patent No. 2,239,771; April 29, 1941. [Examination of the Index of Patents for the time period 1926-1941 revealed that Becker was the sole assignor on all the early copper oxide rectifier patents for Bell Telephone Laboratories, Inc., and only in 1941 did he become a coassignor with Brattain. Becker's key *rôle* in Bell's development of the copper oxide rectifier was corroborated by an article he wrote in their in-house technical journal,

It is my opinion, that someone should revisit the copper oxide rectifier. It may yet surprise and inform us even more than it has already.

J.A. Becker; Varistors: Their Characteristics and Uses; Bell Laboratories Record; Vol. 18; July 1940; pp. 322-327.

Given Becker's prominence in this field, it came as a shock to find that he had written no technical articles in peer reviewed journals on this subject. Perusal of Science Abstracts, Series B (Electrical Engineering) Vol. 29B (1926) - Vol. 44B (1941) showed no papers by Becker, while Science Abstracts, Series A (Physics) Vol. 29A (1926) - Vol. 47A (1944) yielded a large number of papers on thermionic emission, but none on copper oxide rectifiers. Note, Becker's name was mentioned earlier in this thesis with regards to his pioneering investigations into the mechanism of enhancement of electron emission of alkaline oxide coated cathodes.]