Chapter One

Introduction to the History of Semiconductors

1.1 Early History of Semiconductors

According to an article regarding the very early history of semiconductors written by Georg Busch,[1] the first person who mentioned something close to the word "semiconductor" was an Italian scientist Alexandro Volta (1745–1827), who was famous for the invention of the electric battery. Volta was born in Como, Lombardy, Italy. However, during his life span, a unified Italy did not exist; Volta was first under the rule of the Emperor of Austria, then under the rule of Napoleon Bonaparte and then under the rule of the Emperor of Austria again. It is interesting to note that Volta published in the Philosophical Transactions of the Royal Society of London, which is the oldest scientific journal in the English-speaking world, in the United Kingdom since 1665. In 1782, Volta published a paper in Philosophical Transactions of the Royal Society of London.[2] It was unclear if he wrote his paper in Italian or in French; however, at the end of his paper, an English translation appeared. Inside the English translation, a small passage can be found as follows. "The surface of those bodies does not contract any electricity, or if any electricity adheres to them, it vanishes soon, on account of their *semi-conducting* nature; for which reason they cannot answer the office of an electrophorus, and therefore are more fit to be used as condensers of electricity."

Humphry Davy (1778–1829) was a famous UK scientist who served as the President of the Royal Society from 1820–1827. He discovered chlorine and iodine. In 1821, Davy mentioned his observation of the effect of increasing temperature on the electrical conductivity of metals as follows.[3] "The most remarkable general result that I obtained by these researches, and which I shall mention first, as it influences all others, was, that the conducting power of metallic bodies varied with the temperature, and was lower in some inverse ratio as the temperature was higher." Michael Faraday (1791–1867) was an English chemist and physicist. He contributed significantly to the understanding of electromagnetism and electrochemistry. Faraday's experimental work in chemistry led him to the first documented observation of a material which is now known as a semiconductor. In 1833, he found that the electrical conductivity of silver sulfide increased with increasing temperature as follows.[4] "The effect of heat in increasing the conducting power of many substances, especially for electricity of high tension, is well known. I have lately met with an extraordinary case of this kind, for electricity of low tension, or that of the voltaic pile, and which is in direct contrast with the influence of heat upon metallic bodies and decribed by Sir Humphry Davy." In his 1833 paper, Faraday mentioned Davy's 1821 paper. In fact, Michael Faraday once served as Davy's assistant. "The substance presenting this effect is suphuret of silver. It was made by fusing a mixture of precipitated silver and sublimed sulphur, removing the film of silver by a file from the exterior of the fused mass, pulverizing the sulphuret, mingling it with more sulphur, and fusing it again in a green glass tube, so that no air should obtain access during the process. The surface of the sulphuret being again removed by a file or knife, it was considered quite free from uncombined siliver." For a metal, the electrical conductivity decreases with increasing temperature. Sulphuret of silver is now known as silver sulfide (Ag_2S), which is a direct bandgap semiconductor with a bandgap of about 1 eV.[5] Thus this effect usually found in semiconductors, is opposite to the situation usually found for metals.

With the help of modern physics, we can easily see that raising the temperature of most semiconductors increases the density of free carriers (electrons or holes) inside them and hence their conductivity. This effect can be exploited to make thermistors whose resistance is sensitive to a change in temperature. For metals, the density of free carriers (electrons) is not influenced by a higher temperature; however, a higher temperature implies stronger scattering and thus lower electron mobility. For semiconductors, a higher temperature also implies stronger scattering and thus lower electron mobility but the increase in carrier density due to higher temperature can be the stronger and thus the dominant effect. Thus Faraday's 1833 paper can be considered as the first scientific paper loosely related to semiconductor physics.

For semiconductors, the behavior of an extrinsic semiconductor (a semiconductor doped by a shallow donor or acceptor) is similar to that of metals reported by Davy; however, the behavior of an intrinsic semiconductor (for example, an undoped semiconductor) is similar to that of silver sulfide reported by Faraday. Thus a resistor made of an extrinsic semiconductor can show up a positive temperature coefficient of resistance while a resistor made of an intrinsic semiconductor can show up a negative temperature coefficient of resistance.

For modern MOS transistors, the carrier mobility involves 3 scattering mechanisms: Coulombic scattering, phonon scattering and surface roughness scattering. All 3 scattering mechanisms become stronger at higher temperature, resulting in lower mobility at higher temperature.[6] For modern MOS transistors, the on current decreases with increasing temperature just like Davy's report while the off current increases with increasing temperature in a way similar to an intrinsic semiconductor and thus similar to Faraday's observation. An interesting phenomenon is that for MOS transistors there exists a cross-over point where the current is insensitive to temperature variation.[7–11] As shown in Fig. 1.1, the drain current versus gate voltage characteristics of an n-channel MOS transistor show up a TIP at a particular value of gate voltage. TIP stands for "temperature independent point". For gate voltage above TIP, the drain current decreases with temperature. For gate voltage below TIP, the drain current increases with temperature. Similarly, as shown in Fig. 1.2, the drain current versus gate voltage characteristics of a p-channel MOS transistor show up a TIP at a particular value of gate voltage. Thus a resistor made up of the drain and source electrodes of an MOS transistor with a fixed gate-to-source voltage

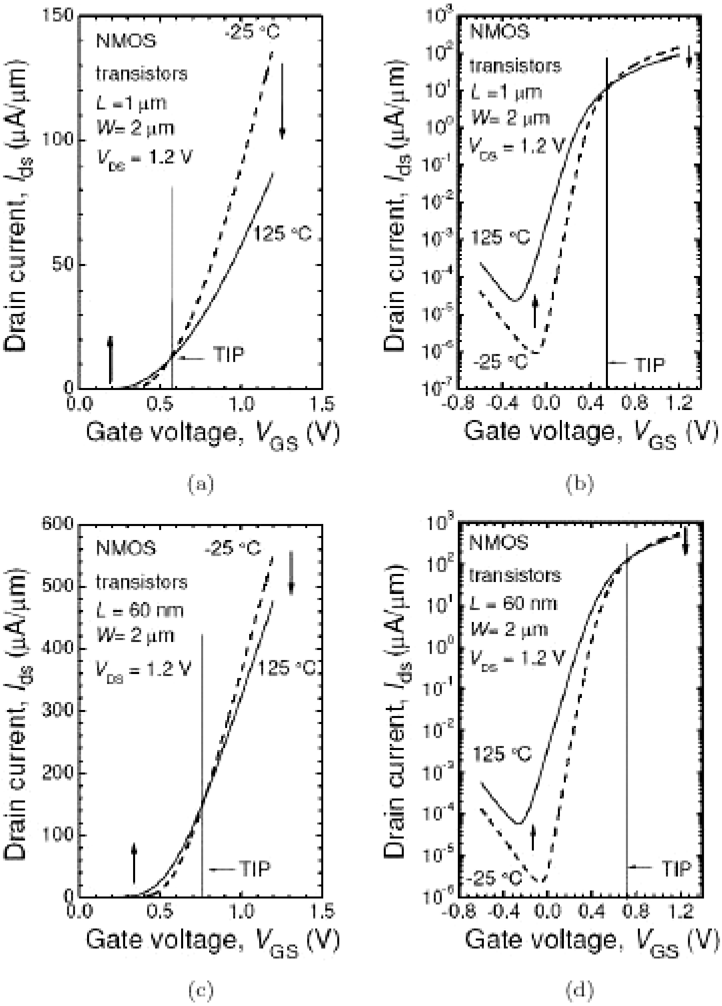

Fig. 1.1 Effects of temperature on the on-state current (/on) and off-state current (/off) of NMOS transistor according to Yang *et al.*[a,11]

can show up a positive temperature coefficient of resistance above TIP and a negative temperature coefficient of resistance below TIP, respectively. Another conclusion can be drawn from Fig. 1.1 and

[a]P. Yang was a PhD student of the author and so this figure is part of the work of the author.

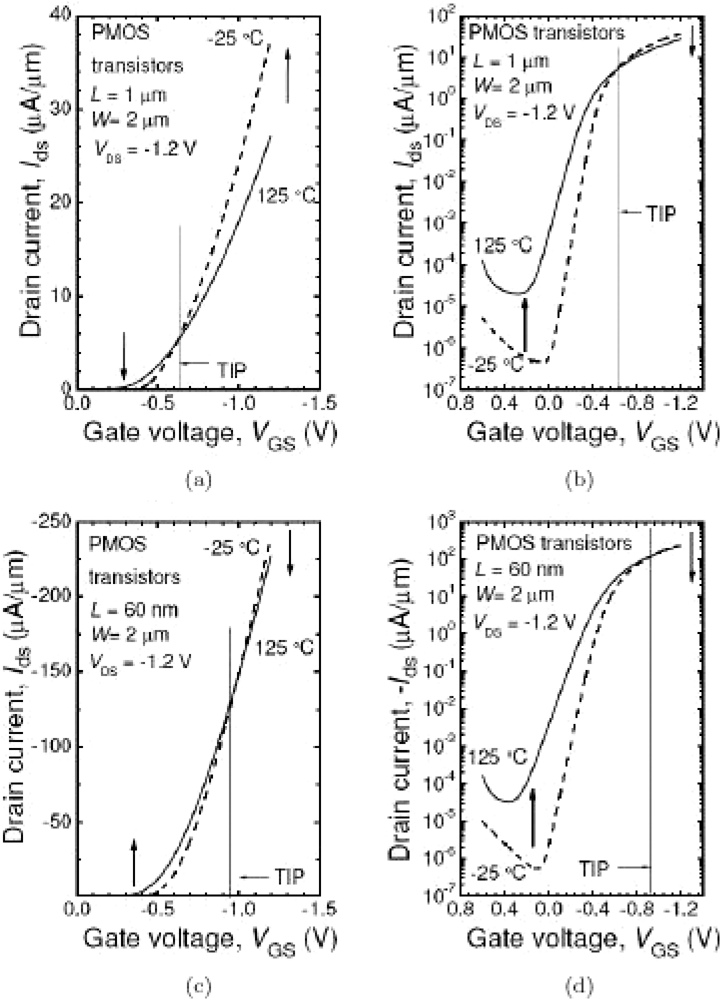

Fig. 1.2 Effects of temperature on the on-state current (/on) and off-state current (/off) of PMOS transistor according to Yang *et al.*[a,11]

Fig. 1.2: operation of MOS transistors at low temperature implies higher on current and lower off current; the implication is that MOS technology usually improves by a decrease in operation temperature. For example, carbon nanotube (CNT) technology has been shown that device operation is possible. However, manufacturability of CNT

devices is doubtful. CNT is known to have high thermal conductivity. Packaging technology using CNT may be useful to lower the actual operation temperature of an MOS integrated circuit housed in a package, resulting in better performance. More discussion can be found in Chapter 3 and Chapter 4.

A French scientist Alexandre-Edmond Becquerel (1820–1891) discovered the photovoltaic effect, which is the physics behind the solar cell, 1839.[12] He published his discovery in Comptes Rendus, which is a French scientific journal published by the French Academy of Sciences since 1835. He was the son of Antoine César Becquerel, who was a French scientist pioneering in the study of electric and luminescent phenomena, and the father of Henri Becquerel who was the more famous French scientist and the winner of the 1903 Nobel Prize in Physics for discovering radioactivity.

The effect observed by Alexandre-Edmond Becquerel in 1839 was via an electrode in a conductive solution exposed to light. The device is now known as a photoelectrochemical solar cell. There can be other names for the same device, for example, a semiconductor liquid junction solar cell. There exist quite some review papers on this subject.[13,14] The key point is that there must be a semiconductor present. There is an electrolyte. It can be in the form of a solution or in the form of a molten solid. The electrolyte is forming a junction with a semiconductor. There are two metal electrodes connecting to the electrolyte and the semiconductor respectively. The semiconductor involved in Becquerel's 1839 report is not clear. Many years later in 1873, Willoughby Smith found that selenium is photoconductive.[15] W.G. Adams (William Grylls Adams, 1836–1915) and R. E. Day (Richard Evans Day, student of Adams) observed the photovoltaic effect in selenium without involving any liquid and reported their observation in 1877.[16] The American Charles Fritts developed a solar cell using selenium with a thin layer of gold in 1883.[17] Thus selenium may be considered the first semiconductor in the solid state discovered by mankind. However at that time both Becquerel and Smith did not know semiconductor physics and thus could not really explain what actually happened.

Photoconductivity is just the formation of free electrons and free holes because light can raise an electron from the valence band to the conduction band leaving behind a hole. It takes many years for the physics of the photovoltaic effect to be understood. Kurt Lehovec (1918–2012) may be the first scientist who can claim that he managed to explain the photovoltaic effect in 1948. Lehovec was born in 1918 in Ledvice, northern Bohemia, Austria-Hungary just a few months before the end of World War I. After the end of World War I in November 1918, Austria-Hungary broke up into several countries. One of these new countries was known as Czechoslovakia with Prague as its capital. According to his own website (www.kurtlehovec.com), after he graduated from high school in 1936, he moved to Prague, where he attended university and received his PhD in Physics in 1941. However, Czechoslovakia was annexed by Nazi Germany in the period of 1938–1939 and Kurt Lehovec became involved in the history of Germany. (Note: Lehovec's website is no longer available after his death in 2012.) At the end of World War II, he spent the next two years in postwar West Germany, continuing with theoretical research and came up with the explanation of the solar cell effect. The US Signal Corps had become aware of his discovery at Prague, and invited him in the summer of 1947 to the USA under the Project Paperclip for outstanding European scientist from the former Nazi-occupied territories. In this way, he ended up in USA. In 1948, he published his theory regarding the photovoltaic effect in the prestigious US journal Physical Review.[18] Besides the photovoltaic effect, he is also known as the inventor of pn junction isolation which is important for integrated circuit technology. He is also known for proposing the theory behind the functioning of light emitting diodes. Many years later, Czechoslovakia broke up into two countries (Czech Republic with Prague as capital and Republic of Slovakia with Bratislava as capital) in 1993. Ledvice, the birth place of Lehovec, is now part of the Czech Republic.

Willoughby Smith (1828–1891) was born in Great Yarmouth, England and was an electrical engineer working on underwater telegraph cable projects. In 1849, he supervised the manufacture and laying of 30 miles of underwater telegraph cable from Dover, which is a town in England facing France across the narrowest part of the English Channel, to Calais, which is a town in France opposite to Dover. He worked closely with Charles Wheatstone (1802–1875) who had designed the machinery for making and laying the cable. (Note: The Wheatstone bridge was named after Charles Wheatstone.) In 1873, Smith developed a method for continually testing an underwater cable as it was being laid. For his test circuit, Smith needed a material with very high resistance but not a complete insulator. He selected selenium rods for this purpose. It turned out that selenium showed some sort of unstable resistance. Joseph May was one of Smith's assistants and he noticed that the resistance of selenium seemed to depend on the amount of light shining on it. The selenium was placed in a box with a sliding cover. With the cover closed, the resistance was highest but it dropped when the cover was open such that light could shine on the selenium. Smith published an article with the title "Effect of light on selenium during the passage of an electric current" in the February 20, 1873 issue of the scientific journal Nature.[15] Nowadays, this phenomenon is commonly known as photoconductivity and selenium is considered a semiconductor. However, at that time, the term "semiconductor" did not exist yet. Selenium was in fact the first elemental semiconductor known to the scientific community. It has a bandgap of about 2 eV. Once upon a time, selenium was commonly used in photocells and rectifiers. Besides photocells and rectifiers, selenium also played a big role in xerography. In the mid 1930's, Chester Floyd Carlson (1906–1968) invented a new method of copying images onto paper. Prior to that time, only a wet process similar to photography was used to make copies. Carlson developed a dry process that transferred powdered ink, called toner, from an optically induced image on a negatively charged transfer device to a piece of positively charged paper. The toner was then heated which melted and fused it onto the paper. In the process of perfecting his new copying technology, Carlson experimented with belts and plates as the transfer device. Neither of these worked very well. Finally, Carlson set upon the idea of using a coated drum as the transfer device. At first, in an attempt to imitate the photographic process, he used silver compounds to coat the drum. On 22nd Oct.

1938, Carlson and his assistant Otto Kornei (1903–1993) had their historic breakthrough using a zinc plate with a sulfur coating.[19] However eventually, Carlson chose selenium as the coating. The process, now known as xerography (from the Greek for "dry writing"), earned Carlson a patent — and now everyone knows about Xerox copiers. Later, when Carlson was asked to identify the most difficult part about inventing xerography, he pointed out that the hardest problem was finding the proper coating. He said, "The primary reason that we settled on selenium is its unique crystal lattice and the way that it retains an electrostatic charge indefinitely. We chose selenium because it truly is the element that never forgets." Now, on the whole, the significance of elemental selenium as a semiconductor has been largely superseded by other semiconductors. Even for xerography, selenium has been challenged by other materials like organic photoconductor (OPC) and amorphous silicon. OPC is cheaper while amorphous silicon is mechanically stronger and so more durable. Besides serving as a photoconductor, selenium can be used for rectifiers. Selenium rectifiers were subsequently more or less replaced by silicon rectifiers. Nowadays (at least up to 2009), some companies can still supply selenium rectifiers. Universal Rectifiers Inc. (Rosenberg, Texas, USA) has a full line of replacement selenium rectifier available. (http://www.universalrectifiers.com/) Cougar Electronics Corp. (New Haven, Connecticut, USA) is another selenium rectifier supplier. (http://www.cougarelectronics.com/)

In 1874, Karl Ferdinand Braun (1850–1918) published a paper in the *Annalen der Physik und Chemie* with the title "Uber die stromleitung durch schwefelmetalle".[20] Annalen der Physik und Chemie was once a very prestigious German journal such that many famous scientists, including Albert Einstein (1879–1955), published their papers in it. An English translation of this paper can be found in the book *Semiconductor Devices: Pioneering Papers*, edited by S. M. Sze. The title, after translated into English, is "On current conduction through metallic sulfides". Braun was a prominent German scientist who shared the 1909 Nobel Prize in Physics with the Italian Guglielmo Marconi (1874–1937) for their contributions to the development of wireless telegraphy. Braun noticed that the current flow can be influenced by the voltage polarity. For materials obeying Ohm's Law, the current-voltage (I-V) characteristics is both linear and symmetric. Thus Braun reported the existence of non-linear asymmetric current-voltage (I-V) characteristics for some metallic sulfides, which are semiconductors according to the modern sense. For example, lead sulfide (PbS) is a semiconductor with a bandgap of about 0.4 eV.[21] Galena is a naturally occurring mineral form of lead sulfide. Once upon a time, a cat's whisker detector based on galena was used in primitive radios. Thus Braun's 1874 paper can be considered the first paper on semiconductors while Faraday's 1833 paper can be considered as the first paper somewhat loosely related to semiconductors.

Braun only reported an interesting phenomenon. Eventually an application was found. Amplitude modulation (AM) is one of the many possible ways to modulate radio waves for wireless communication. In the early days of wireless, a cat whisker detector may be used in very primitive AM radio receivers. It is simply a relatively primitive and unstable metal–semiconductor point-contact junction forming a Schottky barrier diode. One side of the diode is a metal wire. The other side of the diode is a semiconductor. The key point that such a device can be used to demodulate AM radio signal is the asymmetric current-voltage (I-V) characteristics first reported by Braun in 1874. The theory to explain the asymmetric I-V characteristics was subsequently proposed by another German scientist Walter Schottky (1886–1976).[22] There are many possible choices for the semiconductor. As discussed above, galena (PbS, with a bandgap of about 0.4 eV) can be a possible choice. For example, Sir Jagadish Chandra Bose (1858–1937), who was a Bengali scientist born under British rule, got a patent regarding the use of galena and some other materials for radio detector applications.[23] It was Braun who made an important observation but it was Sir J.C. Bose who thought out a practical application. The discovery of the element germanium is usually attributed to a German chemist Clemens Alexander Winkler (1838–1904). A prominent Russian chemist Dmitri Ivanovich Mendeleev (1834–1907) predicted the existence of germanium through the periodic table of elements; however, it was Winkler who discovered germanium in 1886 and named the element after his own country, Germany. Silicon was discovered before germanium. The discovery of the element silicon is usually attributed to a Swedish chemist Jons Jacob Berzelius (1779–1848). In 1824 Berzelius prepared amorphous silicon by heating potassium with silicon tetrafluoride (SiF_4). A German chemist Friedrich Wohler (1800–1882) managed to prepare silicon in a crystalline form. One of the earliest applications of silicon is to add silicon to steel, resulting in a material known as silicon steel which can be used in the iron core of electrical transformers with less eddy current loss. The invention of silicon steel is usually attributed to Sir Robert Abott Hadfield (1858–1940), who was an English metallurgist. In 1906, Greenleaf Whittier Pickard (1877–1956), who was a US radio pioneer, filed a patent for a silicon based radio detector.[24] Nowadays, PbS is no longer used for AM radio detector but PbS or PbSe infrared detectors are still commercially available. For example, Teledyne Judson Technologies (Montgomeryville, Pennsylvania, USA) is still selling PbS infrared detectors for operation in the 1–3.5 μm wavelength region. Hamamatsu is another PbS infrared detector supplier. Primitive Si point contact detector is no longer used for AM radio detector but modern Si point contact detectors are still used at UHF or microwave frequencies. For example, Advanced Semiconductor Inc. (North Hollywood, California, USA) is still selling Si point contact detectors workable up to 16 GHz.

Subsequently, this kind of primitive radio detectors were almost totally replaced by vacuum tube diode detectors. Sir John Ambrose Fleming (1849–1945) was usually considered the scientist who invented vacuum tube diodes; he was a prominent English scientist and he got US Patent 803,684 in 1905 for this invention.[25] The basic principle of the operation of the vacuum tube diode was discovered by Frederick Guthrie (1833–1886), who was a British scientific writer and professor, in 1873. Subsequently, the US inventor Thomas Alva Edison (1847–1931) independently rediscovered it in 1880 and the effect came to be known as "Edison effect". However, it was Sir Fleming who thought out a practical application. Vacuum tube diodes can be used as rectifiers and also as AM radio detectors.

Primitive semiconductor radio detectors had difficulty to compete with vacuum tube diode detectors. Both semiconductor and vacuum tube diode detectors cannot amplify electrical signals. This situation was changed by the invention of vacuum tube triodes, tetrodes and pentodes. Lee de Forest (1873–1961) was an American; he was usually considered the scientist who invented vacuum tube triodes and he got US Patent 879,532 in 1908 for this invention.[26] There is some controversy regarding who really invented the vacuum tube triode; in fact, there is a claim that an Austrian physicist Robert von Lieben (1878–1913) invented something similar. Walter Schottky (1886–1976), who was a prominent German physicist, invented the vacuum tube tetrode; he received German patent 300, 617 in 1916 for this invention. Bernard D. H. Tellegen (1900–1990) was a prominent Dutch scientist and engineer; he was usually considered the scientist who invented vacuum tube pentodes and he got US Patent 1,945,040 in 1934 for this invention.[27]

AM radios based on primitive semiconductor diode detectors simply cannot compete with AM radios based on vacuum tubes. However, the need to develop microwave radar for aircraft detection before and during World War II gave semiconductor diode detectors a new life. This is because vacuum tube diode detectors have difficulty to operate at the microwave frequencies required for radar. The size of the antenna required for radar can be decreased by using higher frequencies. At frequencies of the order of GHz, it was found that the old cat's whisker detector, which is actually a primitive semiconductor diode detector, can perform better than a vacuum tube diode detector, resulting in renewed interest in the old cat's whisker detector. Robert Buderi published a book regarding the invention of radar. He also mentioned that radar technology helped to stimulate the development of semiconductor technology in Chapter 15.[28]

John Orton (Emeritus Professor, School of EEE, University of Nottingham, UK) gave a good explanation regarding this in his book.[29] The depletion region in an old cat's whisker detector is very small and so the transit time is very small compared to a vacuum tube diode. The potential harmful effects of a finite transit time in vacuum tubes were discussed by various authors, for example, Llewellyn

(Bell Laboratories).[30] In addition, the old cat's whisker detector is basically a point contact detector with a very small area and so the capacitance is very small.

1.2 Invention of the p-n Junction

However, the old cat's whisker detector can be very unstable and the reproducibility can be very poor. For example, a "good" spot has to be found. One of the best choices for the semiconductor in a cat's whisker detector was found to be silicon. It was also observed that the detected signal can have two polarities; nowadays, this can be understood because silicon can be p-type or n-type. A lot of effort has been spent on semiconductor research for military applications during World War II. For example, Frederick Seitz (1911–2008) published an article in Physics Today regarding the research done on silicon and germanium during World War II.[31] Russell Shoemaker Ohl (1898–1987) and his co-workers in the Bell Laboratories managed to make p-type silicon, n-type silicon in a reproducible manner. In fact he made the first p-n junction in silicon as follows. In 1947 after World War II, Scaff and Ohl published a report on their effort to develop silicon microwave detectors.[32] Morrison[32] demonstrated the superiority of silicon detectors compared to vacuum tube detectors at microwave frequencies by actual measurement.

Ohl was an American working in the Bell Laboratories. He was quite frequently considered an unsung hero in the semiconductor revolution. Proper credit to Ohl was given by Riordan and Hoddeson in their 1997 article in IEEE Spectrum[33] and their book "Crystal Fire".[34] In 1940, Ohl was working with a silicon crystal sample that had a crack down its middle. He was using an ohmmeter to test the electrical resistance of the sample when he noted that when the sample was exposed to light, the current that flowed between the two sides of the crack made a significant jump. It was known that other semiconductors, such as selenium (Se), generated a small current when exposed to light. However, the cracked silicon sample was quite a curiosity. Ohl showed the sample to his colleagues in the Bell Laboratories and together they deduced that the crack was a fortunate accident: It marked the dividing line that had occurred when the molten silicon froze in the crucible. At that moment, various impurities or contaminants in the silicon had been isolated into different regions, with the crack separating them. As a result, the silicon atoms in the region on one side of the crack had extra electrons around them. The other region was the opposite; its crystallized silicon had a slight shortage of electrons. They named the two regions p and n: p for positive-type and n for negative-type. The barrier between the impurities was called the p-n junction. The junction represented a barrier, preventing the excess electrons in the n-region from traveling over to the p-region which is short of electrons, resulting in zero current. However, when the sample was irradiated by light, there is a current flow, resulting in a simple device which can convert light into electrical energy. Thus Ohl invented the silicon p-n junction solar cell; he got US Patent 2,402,662 in 1946 for this invention.[35] Unlike the earlier selenium solar cells, the silicon solar cells based on the p-n junction converted sunlight much more efficiently. Ohl also got US Patent 2,402,662 in 1946 for his invention of the p-n junction.[36](Note: This phenomenon was subsequently studied in much more detail by scientists. When the silicon melt has impurities, the impurities will be distributed between the silicon solid crystal and the silicon melt during the solidification process. A lot of work has been done on how impurities are incorporated into the silicon crystal during the crystallization process. If the silicon melt has both p-type and n-type impurities present by accident, it is possible that, after solidification, part of the silicon becomes p-type and another part of the silicon becomes n-type, resulting in a p-n junction unintentionally. So far the best explanation came from the book "The story of semiconductors" by John Orton as follows. The silicon melt contained both boron and phosphorus impurities with significantly different segregation coefficients "k". Phosphorus atoms ($k = 0.04$) were swept to the bottom of the freezing silicon ingot, doping it n-type while boron atoms ($k = 0.8$) tended to remain fairly uniformly distributed. At the top of the solidified silicon ingot, the concentration of boron was greater than that of phosphorus, resulting in p-type behavior, while the converse was true at the bottom of the solidified silicon ingot. The readers should note that the segregation coefficients quoted by Orton may not be the same as those numbers published in other books or journal papers. The effective segregation coefficient or distribution coefficient is not a constant but it depends on various parameters like the crystallization speed, rotation speed, etc. Nevertheless, Orton's explanation is the best one found by the author.)

According to Buderi,[28] it was two Bell Laboratories workers: Jack Theuerer and Henry Scaff who theorized that p-type conductivity resulted from trace elements like boron from the third column of the periodic table while n-type conductivity came from trace elements like phosphorus from the fifth column of the periodic table. In fact, Scaff and Theuerer published a paper in 1949 regarding this.[37] However, other scientists might make a similar claim regarding the invention of semiconductor doping. The invention of doping of semiconductors was quite frequently attributed to John Robert Woodyard (1904–1981). He got a patent on the doping of germanium as US Patent 2,530,110, which was filed in 1944 and awarded in 1950.[38]

1.3 Invention of the Transistor

Both the old cat's whisker detector and the p-n junction diode detector cannot amplify electrical signals. After World War II, John Bardeen (1908–1991) and Walter Houser Brattain (1902–1987) invented the point-contact transistor in the Bell Laboratories.[39–41] William Bradford Shockley (Bell Laboratories) invented the junction transistor.[42,43] William Bradford Shockley (1910–1989), John Bardeen (1908–1991) and Walter Houser Brattain (1902–1987) received the 1956 Nobel Prize in physics for their discovery on the transistor effect. It was John Robinson Pierce (1910–2002) who, at the request of Brattain, coined the name "transistor". At that time, Pierce was the supervisor of the Bell Laboratories transistor team. Shockley subsequently left Bell Laboratories to start up his own company with the name of the Shockley Transistor Company, which did not survive long. Currently there is a website (www.shockleytransistor.com) dedicated to the memory of Shockley and his company. 8 important members of Shockley's company, including Jean Amedee Hoerni (1924–1997), Gordon Earle Moore (1929–) and Robert Norton Noyce (1927–1990), quitted to join Fairchild Semiconductor. Jean Hoerni was famous for the development of the planar process. Gordon Moore and Robert Noyce have been famous as two of the three founders of Intel.

Besides US scientists, it is also known that two German physicists Herbert Franz Mataré (1912–2011) and Heinrich Welker (1912–1981), who was working in France after World War II, independently also developed something similar to a transistor in around 1948, roughly at the same time and independently from the Bell Labs engineers.[44,45] Mataré returned to Germany and in 1952 co-founded Intermetall to manufacture diodes and transistors. Welker joined Siemens, eventually becoming its research director. He is also remembered for performing fundamental research on III-V semiconductors. In 1952, he described semiconductors from elements found in column III and V of the periodic table as potentially useful for electronic devices. One of these, gallium arsenide (GaAs) was to feature prominently in the search for an efficient communication laser. Thus Welker failed to be remembered as the inventor of transistor but he is remembered as the scientist who recognized the potential of III-V semiconductors. There exists another claim that a female scientist Nina Aleksandrovna Goryunova (1916–1971) of USSR also recognized the potential of III-V semiconductors. Goryunova described III-V materials as semiconductors for the first time in 1950. In her Ph.D. dissertation, completed in 1951 at Leningrad State University (now known as Saint Petersburg State University), she indicated that III-V compounds with the zinc-blende (cubic zinc sulfide, ZnS) crystalline structure are semiconductors. Her work was not published outside of the USSR until much later due to the Cold War. However, Welker seems to be the more famous person. As we shall see later in this book, some scientists have been investigating the use of III-V semiconductors in mainstream CMOS integrated circuits.

The first transistors made in the Bell Laboratories were based on germanium. Germanium has a small bandgap of about 0.7 eV. When the temperature increases, leakage current increases exponentially.

Silicon has a larger bandgap of about 1.1 eV. It can be easily seen that silicon transistors will have much better thermal stability compared to germanium transistors. The first successful silicon transistors were made in Texas Instruments. Gordon Kidd Teal (1907–2003) was the leader of the TI team responsible for this feat.[46] He worked for the Bell Laboratories before joining TI. The story was that it was late afternoon at a conference organized by the Institute of Radio Engineers (IRE, now known as IEEE) in 1954. People complained the poor performance of Ge transistors at high temperatures and expected that Si transistors would perform better. However, they believed that viable Si transistors would not be available soon. Suddenly, Teal came out to give his talk. He pulled three small objects out of his pocket and announced: "Contrary to what my colleagues have told you about the bleak prospects for silicon transistors, I happen to have a few of them here in my pocket." TI became the first company to produce silicon transistors. After the TI success to make silicon transistors, scientists working in the Bell Laboratories also managed to make silicon transistors. For example, Tanenbaum and Thomas published a paper "Diffused emitter and base silicon transistors" in 1956.[47] Aschner *et al.* published a paper "A double diffused silicon high-frequency switching transistor produced by oxide masking techniques" in 1959.[48] Theuerer *et al.* published a famous paper on "Epitaxial diffused transistors" in 1960.[49] For discrete silicon transistors, the double diffused epitaxial transistor eventually becomes the standard structure.

1.4 Invention of the Integrated Circuit

Jack St. Clair Kilby (1923–2005) is a Nobel Prize laureate in physics in 2000 for his invention of the integrated circuit in 1958 while working at Texas Instruments (TI).[50] He is quite frequently known as Jack Kilby or J.S. Kilby. Many years later, Kilby published about the history of his invention.[51,52] However, Robert Norton Noyce (1927–1990), who was one of the three founders of Intel, also claimed to have invented the integrated circuit.[53] According to Warner,[54] Bell Laboratories missed the chance to be the champion of integrated circuits.

In 2009, Arjun Saxena, an Emeritus Professor of the Rensselaer Polytechnic Institute (USA), published an interesting book on the invention of integrated circuits.[55]

There are more than one transistor in an integrated circuit and thus device isolation is necessary. Kurt Lehovec (1918–2012) pioneered "junction isolation". He obtained US Patent 3,029,366 for this.[56] Later he published a short paper regarding the history of his invention in 1978.[57] While Lehovec pioneered "junction isolation", Jean Amedee Hoerni (1924–1997) pioneered "planar technology". He obtained US Patent 3,025,589[58] and US Patent 3,064,167.[59] He published a few paragraphs in 1961 on his great invention.[60] The process involves the basic procedures of silicon dioxide (SiO_2) oxidation, SiO_2 etching and doping by thermal diffusion. The final steps involve oxidizing the entire wafer such that a SiO_2 insulating film covers the wafer, etching contact holes to the transistors, and depositing a covering metal layer over the oxide, thus connecting the transistors without manually wiring them together. This major milestone was achieved when Hoerni was with Fairchild. Many years later, Riordan wrote a very interesting article in Spectrum regarding this great invention.[61] As Riordan pointed out, the success of the silicon planar technology depends very much on the existence of a good oxide, silicon dioxide, for silicon. (Note: Silicon has two important oxides: silicon monoxide and silicon dioxide. Silicon monoxide can sublime at relatively low temperature and so not suitable for the planar technology. However, silicon monoxide is popularly used as an anti-reflection coating. Silicon dioxide is the oxide which is important both for discrete transistor and integrated circuit technology.) L. Derick and C. J. Frosch (Bell Laboratories) contributed in this aspect by their patent.[62] They also contributed their paper "Surface protection and selective masking during diffusion in silicon" in 1957.[63]

Figure 1.3 shows the cross-sections of 2 double diffused silicon npn transistors according to Aschener *et al.* (Bell Laboratories).[48] The area of the collector-base junction was defined by a mesa etch process. (Note: The mesa transistor structure was probably developed by engineers in Texas Instruments. For example, Texas

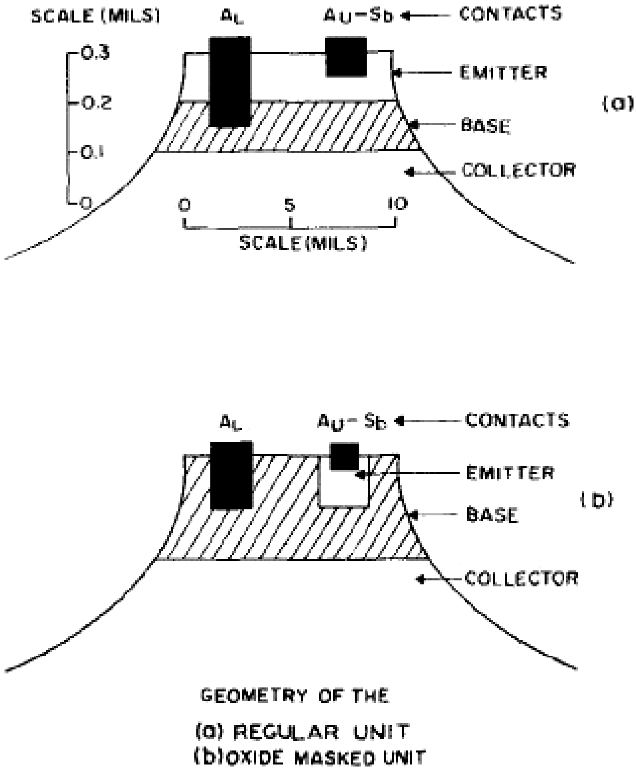

Fig. 1.3 Cross-sections of two double diffused transistor structures: (a) regular unit without oxide masking (b) with oxide masking according to Aschner *et al.* 1959 (Bell Laboratories).[48] (Reprinted with permission from J. F. Aschner, C. A. Bittmann, W. F. J. Hare and J. J. Kleimack, "A double diffused silicon high-frequency switching transistor produced by oxide masking techniques", *Journal of the Electrochemical Society,* vol. 106, no. 5 (May 1959) pp. 415–417. Copyright 1959 Electrochemical Society. Reproduced by permission of The Electrochemical Society.)

Instruments introduced the 2N389 transistor, which was the first silicon power transistor available to industry and used a mesa structure, in 1957.)

In an article by Moore,[64] a figure shows a mesa transistor made by Fairchild in the early days of silicon technology; it is quite similar to the structure of Aschner *et al.* (Bell Laboratories) 1959. In the transistor structure shown in Fig. 1.3, there is no passivation.

Aschner *et al.* did not mention that the masking oxide was removed in their 1959 paper.[48]

Figure 1.4 shows the detailed diffusion and masking process according to Aschener *et al.* in 1959.[48] Gallium was used as the p-type dopant to form the p-type base while phosphorus was used as the n-type dopant to form the n-type emitter. Aschner *et al.* did not mention that the masking oxide was removed. However, Fig. 1.4(e) shows that the masking oxide was subsequently removed.

Bipolar transistors can be fabricated by mesa technology or by planar technology. Planar technology with passivation of the silicon surface by silicon dioxide grown by thermal oxidation was discussed by Riordan;[61] silicon dioxide can also be used as a diffusion mask. Mesa technology once was popular for Si transistors; some sort of mesa technology is still popular for transistors based on III-V materials. Fairchild made the first Si npn mesa transistor 2N697 in 1958 and then later migrated to Si npn planar transistor 2N1613 in 1960. The full fabrication process of 2N696 Si npn mesa transistor can be found in the book "History of Semiconductor Engineering" by Bo Lojek. (Note: According to Moore 1998,[64] 2N697 and 2N696 were similar devices but 2N697 just had higher gain.) Gallium diffusion into n-type Si substrate was performed to form p-type base. (Note: This is similar to Aschner *et al.* 1959.[48]) This was a blanket diffusion into the whole Si substrate and so there was no base mask. (Note: Silicon dioxide cannot be used to mask gallium diffusion into silicon. Nowadays, people seldom used gallium doping in silicon based microelectronics.) Subsequently, phosphorus diffusion into the p-type region was performed to form n-type emitter. This was done through an opening in a silicon dioxide mask and so there was an emitter mask for this step. Further down the process flow, there was a step to do a mesa etch such that most of the p-type region was etched away except for the p-type base. This mesa etch step controls the area of the collector-base junction. For planar technology, boron diffusion into n-type Si substrate was performed to form p-type base. This was done through an opening in a silicon dioxide mask and so there was a base mask for this step. (Note: Silicon dioxide can be used to mask boron diffusion into silicon.) Subsequently, phosphorus diffusion into

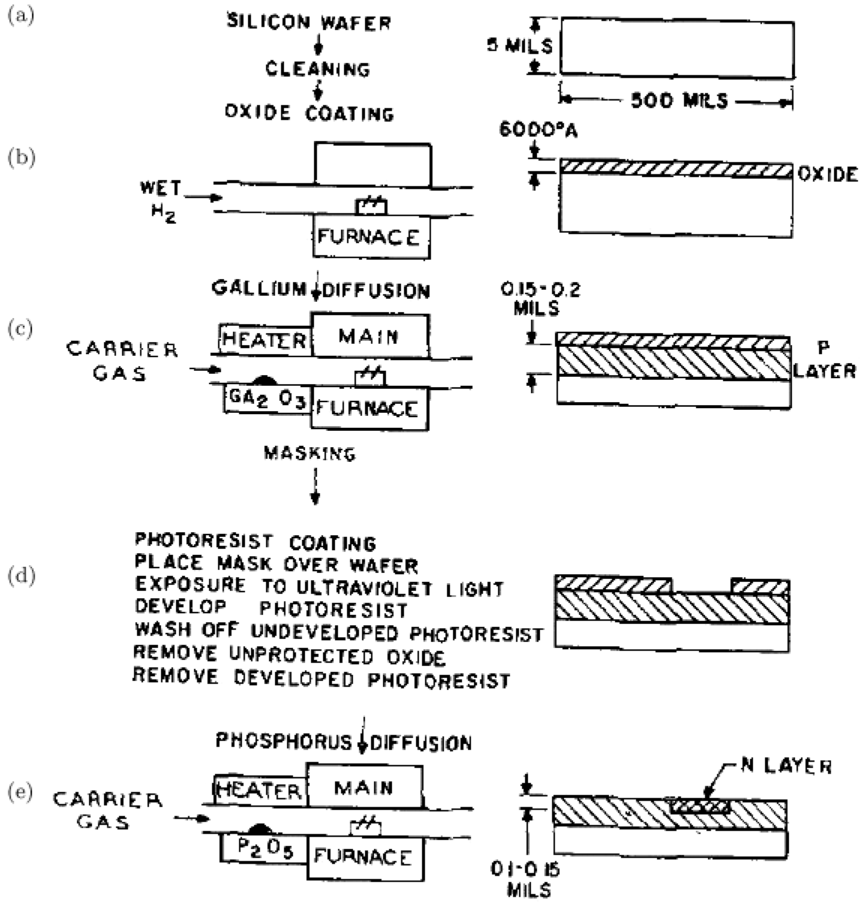

Fig. 1.4 Detailed diffusion and masking process according to Aschner *et al.* 1959.[48] A silicon dioxide film was first grown on n-type silicon and then gallium was diffused through the silicon dioxide film to form a p-type layer for the base of the npn transistor. A window was opened in the silicon dioxide film and then phosphorus was diffusion to form a localized n-type emitter. (Reprinted with permission from J. F. Aschner, C. A. Bittmann, W. F. J. Hare and J. J. Kleimack, "A double diffused silicon high-frequency switching Transistor produced by oxide masking techniques", *Journal of the Electrochemical Society,* vol. 106, no. 5 (May 1959) pp. 415–417. Copyright 1959 Electrochemical Society. Reproduced by permission of The Electrochemical Society.)

the p-type region was performed to form n-type emitter. This was done through an opening in a silicon dioxide mask and so there was an emitter mask for this step. Further down the process flow, there was no more step to do a mesa etch. The top surface of the silicon wafer was always protected by a silicon dioxide film except at the base or emitter contact regions. The readers should note that there is lateral diffusion such that the junctions formed by planar technology will be under the protection of the silicon dioxide film. Riordan pointed out: "Hoerni's idea was to protect the p-n junctions by keeping the oxide layer in place upon the silicon after the diffusion process; the standard practice at the time was to etch that layer away, baring the junctions." However, there is an additional advantage for the planar technology: with an insulating silicon dioxide film covering most of the silicon area, metal lines on top of the insulating silicon dioxide film can be used for interconnection such that planar technology can be used for integrated circuits.

It is interesting to note that in the beginning, Ge pnp transistors could be more easily made than Ge npn transistors. However, for Si, Si npn transistors could be more easily made than Si pnp transistors. The difficulty to make good Si pnp transistors came from the problem that the lightly doped p-type collector region in a Si pnp transistor can be easily inverted. This problem was, for example, observed in Fairchild according to Moore.[64] In fact, Moore mentioned: "While the planar transistor structure solved some of the biggest problems with double-diffused transistors, there were several that persisted. Particularly over the lightly doped collector region of high-voltage p-n-p planar transistors, an inversion layer sometimes developed, effectively extending the base region to the edge of the die. Inversion layers were not a new phenomenon. For example, early grown-junction transistors had problems with such layers developing on the surface of the base's shorting the emitter to the collector. In fact, the reason that Fairchild's first transistor had the base contact completely surrounding the emitter was to eliminate the possibility of such inversion layers." For discrete pnp transistors, this problem was usually solved by etching a mesa or by using a heavily doped p-type guard ring according to Finch and Haenichen.[65] Similar approach can also be found in other references.[66,67] For discrete pnp transistor, usually a heavily doped p-type guard ring is used to prevent possible inversion of the lightly doped p-type collector region; the mesa approach is usually not adopted probably because it is not compatible with "planar technology". However, the silicon bipolar integrated circuit is actually based on silicon npn transistors, maybe with some lateral pnp transistors. Naturally, Si npn transistors perform better than Si pnp transistors because electron mobility is larger than hole mobility, resulting in larger electron diffusion coefficient than hole diffusion coefficient through the Einstein relationship.

At this point, the author would also like to discuss some history about the development of photolithography. Johann Alois Senefelder (1771–1834) was an actor and playwright who became famous because of the invention of the printing technique of lithography in 1796. In 1955, Jules Andrus and Walter L. Bond at Bell Laboratories began the adaptation of existing photolithographic techniques already developed for making patterns on printed circuit boards to produce much finer patterns on silicon wafers to define patterns of a silicon dioxide layer as an impurity diffusion mask. After applying a photosensitive coating or "resist" on the layer and exposing the desired pattern on this coating through an optical mask, precise window areas were defined in the layer and opened by chemical etching where unexposed resist had been washed away. Impurities (n-type or p-type) were diffused through these silicon dioxide openings into the underlying silicon to create regions of n-type and p-type silicon needed in semiconductor devices. For this work, Andrus filed for a patent in 1957 and the patent was formally approved in 1964.[68] An article by Andrus and Bond was also published.[69] In 1957, Jay Lathrop and James Nall of the US Army's Diamond Ordnance Fuse Laboratories in Maryland filed for a patent on photolithography and the patent was formally approved in 1959.[70] A short paragraph about their work was published in 1958.[71] In 1959, Lathrop switched to Texas Instruments and worked for Jack Kilby while Nall switched to Fairchild Semiconductor. Following up on this pioneering work, Jay Last (1929–) and Robert Noyce (1927–1990) built one of the first "step-and-repeat" cameras at Fairchild Semiconductor in 1958 to make many identical transistors on a single silicon wafer using photolithography. In 1961, the David W. Mann division of GCA Corporation was the first firm to make commercial step and repeat mask reduction devices (photo-repeaters). This is now known as a "stepper". Subsequently "scanner" technology was developed. Previously, some scientists suggested that electron beam lithography or X-ray lithography may be necessary but photolithography remains an essential step in semiconductor manufacturing today, with feature sizes below 0.1 μm routinely generated with the help of deep UV technology.

1.5 History of Semiconductor Physics

In the previous paragraphs, the author has neglected those scientists responsible for theoretical development and basic physics. Here the author would like to mention some other prominent scientists directly or indirectly involved in the semiconductor revolution. Georg Simon Ohm (1789–1854) was a German scientist well known because of the Ohm's Law. Ohm's law, which states that the electric current is proportional to the potential difference, was first discovered by a British scientist Henry Cavendish (1731–1810). However, Cavendish did not publish his discovery but Ohm published it such that it subsequently came to bear his name. The law appeared in Ohm's famous book *Die galvanische Kette, mathematisch bearbeitet* (The Galvanic Circuit Investigated Mathematically) published in 1827 in which he gave his complete theory of electricity. Nowadays, Ohm's Law is considered something straightforward but in Ohm's days, his work was actually received with little enthusiasm in the beginning. However, his work was eventually recognized by the Royal Society of London. Ohm received the Copley Medal in 1841. Augustus Matthiessen (1831–1870) was a British physicist and chemist who has been indirectly present in semiconductor books because of the Matthiessen's rule for carrier mobility. The Matthiessen's rule for carrier mobility probably originated from Augustus Matthiessen's study of electrical conduction of metals and alloys.[72–74] In Matthiessen's time, the concept of "mobility" was not established yet. The modern form of

Matthiessen's rule for electron mobility or hole mobility is actually an extension of Matthiessen's work in the 19th century by subsequent scientists. It is sad that Matthiessen was a tragical scientist who committed suicide in 1870 under severe nervous strain. Edwin Herbert Hall (1855–1938) was an American physicist who discovered the Hall Effect.[75] The above discoveries were made before the discovery of the electron. Eventually, a British physicist Sir Joseph John Thomson (1856–1940) discovered the electron in 1897.[76] However, it was an Irish physicist George Johnstone Stoney (1826–1911) who coined the name "electron". Furthermore, it was Paul Drude (1863–1906), a prominent German scientist, who proposed the first theory of electronic conduction,[77] resulting in Drude's model. Busch, a pioneer of semiconductor research, pointed out that, besides Paul Drude, Eduard Riecke was a much less famous scientist who had also worked on electronic conduction.[1] However, like Matthiessen, Paul Drude was another tragical scientist who committed suicide in 1906. Drude's model was later refined by Arnold Sommerfeld (1868–1951) and Hans Bethe (1906–2005).[78] Erwin Schrodinger (1887–1961) was born in Austria. Once he worked in Germany. Eventually he immigrated to Ireland. He is famous for his Schrodinger equations which are important for solving problems in quantum electronics. Felix Bloch (1905–1983) was a Swiss Jew who left Germany and emigrated to the United States when Adolf Hitler came to power in Germany. (Note: There was another Felix Bloch who was born in 1935 and involved in an espionage case.) He was born and educated in Zurich, Switzerland. However, he went to the University of Leipzig, Germany in 1928 for his PhD and Werner Heisenberg (1901–1976), who was a prominent German scientist and famous for the uncertainty principle, was his PhD advisor. At that time, Schrodinger equations were already known. His PhD dissertation provided the theory of electrons in crystal lattices which is the basis for the quantum theory of electrical conduction. According to Bloch,[79] the electrons can move without scattering if the crystal lattice is perfect and there is no lattice vibration. The original Bloch paper was in German. Subsequently, he published an article in English regarding the history of his 1928 work.[80] The significance of Bloch's work for this book is that electrons in silicon can be modeled as Bloch waves. The E-k diagram of silicon shows the energy E, which is a scalar, plotted against the wavevector **k**. E and the 3-D vector **k** are two important parameters for 3-D Bloch waves. The direction of the 3-D vector **k** represents the direction of the movement of a 3-D wave. Sir Alan Herries Wilson (1906–1995) was a British physicist responsible for the modern band theory. In 1930, he recognized the difference between conductors and insulators; conductors have only partially-filled upper energy bands so that electrons in this band can acquire kinetic energy; the upper energy band is filled in an insulator. In a semiconductor, the presence of impurities contribute electrons to the empty upper energy band. Whereas Bloch modeled electrons as waves, Wilson explained the difference between metals, semiconductors and insulators using band theory.[81–83] The valence band and the conduction band of silicon are quite frequently represented by an E-k diagram where the energy E, which is a scalar, is plotted against the wavevector **k**. Cahn published a short article in 2005 to praise Wilson.[84] He pointed out:

Until the end of the 1930s, most physicists looked down their noses at semiconductors and kept clear of them. The man who changed all this was Alan Herries Wilson, a theoretical physicist in Cambridge, who as a young man spent a sabbatical with Heisenberg in Leipzig and applied the brand new field of quantum mechanics to issues of electrical conduction, first in metals and then in semiconductors, as reported in two Royal Society papers in 1930 and 1931. When he returned to Cambridge, Wilson urged that attention be paid to germanium but, as he expressed it long afterward, "the silence was deafening" in response. He was told that devoting attention to semiconductors, those messy entities, was likely to blight his career among physicists. He ignored these warnings and in 1939 brought out his famous book, *Semiconductors and Metals*, which explained semiconductor properties, including the much-doubted phenomenon of intrinsic semiconductivity, in terms of electronic energy bands. His academic career seems indeed to have been blighted, because despite his great intellectual distinction, he was not promoted in Cambridge (he remained an assistant professor year after year). At the end of World War II, he abandoned his university functions and embarked on a notably successful career as a captain of industry, culminating in his post of chief executive of a leading British pharmaceutical company; he kept clear of electronics! In due course he became Sir Alan Wilson.

The British pharmaceutical company mentioned above was GlaxoSmithKline (GSK).[85] In his Nobel lecture delivered in 1956, John Bardeen, who invented the point contact transistor, quoted Wilson's work as his first reference. Thus Wilson's contribution to the basic understanding of semiconductors should not be forgotten.

Methods were developed to compute the E-k diagram for electrons in silicon and germanium, for example, by Herman.[86] Because of periodicity in k space, it is enough to show the E-k diagram in the first Brillouin zone. The concept of Brillouin zone was developed by Leon Nicolas Brillouin (1889–1969), who was a French physicist. Besides the E-k diagram for electrons in silicon, there exists another E-k diagram for phonons in silicon. Because of periodicity in k space, it is enough to show the E-k diagram for phonons in the first Brillouin zone. The quantum of energy in an elastic wave in a crystal was named "phonon" in direct analogy to the photon. According to Walker and Slack, the name probably came from the Soviet scientists Igor Yevgenyevich Tamm (1895–1971) and Yakov Ilich Frenkel (1894–1952).[87] For semiconductor people, Tamm is famous for Tamm surface states. (Note: I. Tamm (1932). *Phys. Z. Soviet Union* **1**: 733.) Frenkel is famous for the Poole-Frenkel effect for modeling the leakage current of insulators. Bertram Neville Brockhouse (1918–2003) was a Canadian physicist who developed the neutron scattering technique used to measure the E-k diagram for phonons in silicon.[88–90] He shared the 1994 Nobel Prize in Physics with another American scientist, Clifford Glenwood Shull (1915–2001), who also worked on neutron scattering. Brockhouse published a review paper in 1995.[91] The optical phonon energy of 63 meV is something semiconductor people have to memorize.

Maxwell-Boltzmann statistics was named after James Clerk Maxwell (1831–1879) and also after Ludwig Boltzmann (1844–1906). Maxwell is famous for Maxwell's equations in electromagnetism. Boltzmann's constant has been frequently used in semiconductor text books. It is a great tragedy that he hanged himself in 1906.[92] Although Boltzmann first linked entropy and probability in 1877, it seems the relation was never expressed with a specific constant until Max Planck (1858–1947) first introduced k, and gave an accurate value for it (1.346×10^{-23} J/K, about 2.5% lower than today's figure), in his derivation of the law of black body radiation in 1900–1901. Before 1900, equations involving Boltzmann factors were not written using the energies per molecule and Boltzmann's constant, but rather using a form of the molar gas constant R divided by the Avogadro's number. Thus the Boltzmann's constant was not created by Boltzmann but was named after him by Max Planck (1858–1947). Fermi-Dirac statistics was developed by Enrico Fermi (1901–1954)[93] and also independently by Paul Adrien Maurice Dirac (1902–1984).[94] Fermi was an Italian physicist who later became a US citizen.[95] Dirac was a UK physicist who contributed significantly to the development of quantum mechanics.[96] In addition, the Einstein's relationship was named after Albert Einstein (1879–1955). Einstein did not work on semiconductors. However, he once worked on Brownian motion.[97–99] The Einstein's relationship for electrons and holes in semiconductors was an extension of Einstein's work on Brownian motion.

1.6 History of Semiconductor Crystal Growth Technology

Besides the device physics and technology, the basic semiconductor material is also important. Thus crystal growth is also an important concern for semiconductor people. Jan Czochralski (1885–1953) was born in Exin, German Empire which existed from 1871 to 1918. He was an ethnic Pole. Previously, Poland suffered from the First Partition of Poland in 1772 by Russia, Prussia and Austria; Poland suffered from the Second Partition of Poland in 1793 by Russia and Prussia; finally Poland suffered from the Third Partition of Poland in 1795 by Russia, Prussia and Austria. In this way, when Jan Czochralski was born in 1885, Poland did not exist as an independent country. Around 1900, he moved to the German capital Berlin, where he worked at a pharmacy. He was educated at

Charlottenburg Polytechnic in Berlin, where he specialized in metal chemistry. Czochralski began working as an engineer for Allgemeine Elektrizitäts Gesellschaft (AEG) in 1907. After War World I, the German Empire became the Weimar Republic and the nation of Poland was resurrected. Anyhow, his birthplace is now known as Kcynia, Poland. In 2004, Kcynia showed a population of only about 4000–5000 and so this is actually a small Polish village. Thus he is now usually considered a Polish scientist. During World War I, he discovered the Czochralski method in 1916, when he accidentally dipped his pen into a crucible of molten tin rather than his inkwell. He immediately pulled his pen out to discover that a thin thread of solidified metal was hanging from the nib of his pen. The nib was replaced by a capillary and Czochralski verified that the crystallized metal was a single crystal. The experiments of Czochralski produced single crystals that were a mm in diameter and up to 150 cm long. Czochralski published a paper on his discovery in 1918 in the Zeitschrift für Physikalische Chemie, a German chemistry journal, with the title "Ein neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle". The German title can be translated into English as "A new method for the measurement of the crystallization rate of metals". In fact, the method was at that time used for measuring the crystallization rate of metals such as tin, zinc and lead.[100]

During his stay in Germany, Czochralski wrote several papers, patents and books and was a member of several scientific societies. With his German friends he founded in 1919 German Society for Metals Science (Deutsche Gesellschaft für Metallkunde) and he was its president in 1925. After World War I, a new independent Republic of Poland was created near the end of 1918 with Warsaw as capital. In 1929, the President of Poland, Ignacy Moscicki (1867–1946, a professor of chemistry who served as the President of Poland from 1926 to 1939) invited him to Poland and he received the position of a professor in the Faculty of Chemistry of the Warsaw University of Technology. At the same time he obtained honorary doctorates. Professor J. Czochralski worked for about 30 years in Germany and from 1928 in Warsaw, Poland. He worked in the Warsaw University of Technology as a professor. Nazi Germany invaded Poland in 1939 and started World War II. After World War II, he was stripped of his professorship due to his involvement with Germany during the war, although he was later cleared of any wrongdoing by a Polish law court. He returned to his native town of Kcynia where he ran a small cosmetics and household chemicals firm until his death in 1953. Some people claimed that Czochralski had been helping the Polish resistance during the German occupation. Some people claimed that he had been a German collaborator. However, nowadays, he is usually considered a hero in Polish science and technology.[101] A website www.janczochralski.com has been dedicated to the memory of Jan Czochralski.

In 1950, Gordon K. Teal and John B. Little, who were Americans working in the Bell Laboratories used this method to grow germanium single crystals.[102,103] Later a similar approach was used to grow silicon single crystals. Subsequently, Teal left the Bell Laboratories to join TI. In TI, Teal developed the first workable silicon transistors as discussed above.

When Czochralski worked on crystal growth by drawing, he was probably a German citizen working in a German company in the German Empire and he published in German in a German journal. In some way, it can be considered a German invention. However, Czochralski can be considered an ethnic Pole. In fact, he later became a professor in Poland. As mentioned above, the method became mature because of two Americans working in the Bell Laboratories. Thus, to be fair to all parties, the invention can be considered a German/Polish/US invention. The Czochralski technique is currently the principal technology to grow large silicon single crystal. Czochralski silicon wafers are usually contaminated by oxygen. However, oxygen contamination is not so bad. It affects the mechanical strength of the silicon. It can also help to getter impurities. The Czochralski silicon single-crystal growth technology is still intensively studied.

As discussed earlier in this chapter, how impurities in dissolved germanium or silicon can end in the frozen germanium or silicon have been studied for many years. Various references for impurity distribution or segregation include.[105–109] Silicon crystals grown by the Czochralski method tends to be contaminated by oxygen. Silicon may be contaminated by various impurities during crystal growth or subsequent processing. "Gettering" of impurities can be important. George Bemski (Bell Laboratories) was one of the pioneers working in this research area. Various references for gettering include.[110–118] In the book, *History of Semiconductor Engineering* by Lojek,[119] there is a discussion on how npn and pnp transistors are fabricated. There is a step of depositing "nickel" on the back side of the silicon wafer, a step of heating the silicon wafer to high temperature with the nickel film present on the back side and a step of removing the nickel film. Lojek did not explain the function of these steps. It was Moore[64] who mentioned that the nickel film was used to getter impurities from the silicon wafer. However, it should be noted nickel can getter metallic impurities but nickel by itself is also a metallic impurity. Thus it is possible to use nickel to getter impurities, resulting in higher minority carrier lifetime and thus higher current, or to use nickel as an impurity to degrade minority carrier lifetime for better switching speed. It just depends on the exact processing conditions.

1.7 Semiconductor Science and Technology in the 21^st^ Century

In conclusion, selenium may be the first elemental semiconductor studied and used but its significance has dropped very significantly. However, research papers on selenium can still be found in the 21st century.[120,121] PbS is still used for infrared applications. By the way, one of the oldest semiconductor with great industrial significance was cuprous oxide (Cu_2O). It is a semiconductor with a bandgap of about 2 eV. Cu/CuO_2 rectifiers once were very commonly used in industry. Lars Olai Grondahl published a review on cuprous oxide in 1931[122] while Brittain, one of the three inventors of transistor, also published a review on cuprous oxide in 1951.[123] Cu/CuO_2 rectifiers are no longer popular. However, research papers on cuprous oxide are still published in the second half of the 20th century[124] and even in the 21st century.[125,126] Germanium was once the main semiconductor used for transistors. Professor Karl Lark-Horovitz, Department of Physics of Purdue University, put in a great effort to study it during

World War II.[127,128] However, it was Bell Laboratories scientists who managed to make the first germanium transistor. It was subsequently replaced by silicon. Silicon grown by the Czochralski technique is currently the dominant semiconductor material studied and used in the semiconductor industry. An alloy of silicon and germanium became important in the semiconductor industry since the 1990's. Recently, there is a chance that germanium may come back as an important semiconductor used in CMOS integrated circuits.[129] In addition, we shall see later in this book that some research groups have been seriously investigating the application of III-V semiconductors to mainstream CMOS integrated circuits. Various references have also been consulted to write this chapter.[130–136] At this point, the author would also like to emphasize the indirect contribution of the physicists to semiconductor physics and technology. For example, Sir Neville Francis Mott (1905–1996) has been famous for his Mott's rule regarding the barrier height of metal-semiconductor junctions[137]: the barrier height is given by the difference between the metal work function and the semiconductor electron affinity. However, Mott's rule has been found to be insufficient to guide the technology of making Ohmic contacts on semiconductors. In 1956, Kroger *et al.* pointed out that a strongly doped surface layer and quantum mechanical tunneling are important for making good Ohmic contacts.[138] Albert Yu followed up on this work in 1970.[139,140] As shown in Fig. 3, Aschener *et al.* used Au-Sb for the n-type emitter contact and Al for the p-type contact. Gordon Moore, one of the three founder of Intel, pointed out that a single metal can be used to contact the p-type base and the n-type emitter.[64] Without the understanding of quantum mechanics, this may not be easily explained. Al is p-type dopant for Si such that Al can form a heavily doped layer in p-type Si after heating, resulting in a good Ohmic contact. As long as the n-type emitter is heavily doped, Al can also form a good Ohmic contact. With this in mind, it is easy to understand that a single silicide can be used to make good Ohmic contact for both n-channel and p-channel MOS transistors as long as the drain/source regions are heavily doped. For example, state-of-the-art CMOS technology uses cobalt silicide or nickel silicide to make contacts to the gate, drain and source for both n-channel and p-channel devices. Recently, the research on Ohmic contacts for Ge-based CMOS is a hot research topic.[141] As we shall see later in this book, quantum mechanical tunnelling is also a source of major current leakage in CMOS, and results in the substantial power drain and heating effects that plague high-speed and mobile technology. Merzbacher gave a history of the early days of the theory of quantum mechanical tunneling.[142] Sir Ralph Howard Fowler (1889–1944) and Lothar Wolfgang Nordheim (1899–1985) were probably the first scientists to apply quantum mechanics to electron tunneling.[143] Thus those scientists who developed the theories of quantum mechanics also indirectly contribute to semiconductor science and technology. At this point, the reader may wonder why the author spent so much time on subjects apparently not related to CMOS technology. As discussed above, Ohmic contacts are important even in state-of-the-art CMOS technology and Ohmic contact physics and technology cannot be understood without the concept of quantum mechanical tunneling. As discussed above, in the early days of semiconductor technology, Ohmic contact to p-type Ge or Si and Ohmic contact to n-type Ge or Si employ different metals. In state-of-art CMOS technology, nickel silicide (NiSi) is used for Ohmic contact to both p-type and n-type Si; as long as the p-type and n-type Si is heavily doped enough, a single type of metal can be used as Ohmic contact according to quantum mechanical tunneling theory. In addition, as pointed out by E. O. Johnson,[144] the MOS transistor is actually a bipolar transistor in disguise; there is an npn parasitic transistor in an n-channel enhancement-mode MOS transistor while there is a pnp parasitic transistor in a p-channel enhancement-mode MOS transistor. The phenomenon of punchthrough is observed in both bipolar transistors[145,146] and MOS transistors.[147,148] Thus the understanding of bipolar transistor physics and technology is also important for the understanding of CMOS physics and technology. By the way, the understanding of MOS physics also has an important impact on bipolar transistor physics and technology; references include.[149–157] As discussed above, the lightly doped p-type collector of discrete pnp transistors may invert; a commonly known solution is to add a p^+ guard ring. Finally, the discussion of the Bloch Theorem, Brillouin zone and band structure of semiconductors can be seen as important later in this book; for example, the author will later point out that rotation by 45° from the conventional ⟨110⟩ direction to the ⟨100⟩ direction can lead to better p-channel transistors and this can be predicted by understanding of the valence band structure of silicon.

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