The history of the understanding of semiconductors begins with experiments on the electrical properties of materials. The properties of negative temperature coefficient of resistance, rectification, and light-sensitivity were observed starting in the early 19th century.

Thomas Johann Seebeck was the first to notice an effect due to semiconductors, in 1821.[13] In 1833, Michael Faraday reported that the resistance of specimens of silver sulfidedecreases when they are heated. This is contrary to the behavior of metallic substances such as copper. In 1839, A. E. Becquerel reported observation of a voltage between a solid and a liquid electrolyte when struck by light, the photovoltaic effect. In 1873 Willoughby Smith observed that selenium resistors exhibit decreasing resistance when light falls on them. In 1874 Karl Ferdinand Braun observed conduction and rectification in metallic sulphides, although this effect had been discovered much earlier by M.A. Rosenschold writing for the Annalen der Physik und Chemie in 1835,[14] and Arthur Schuster found that a copper oxide layer on wires has rectification properties that ceases when the wires are cleaned. Adams and Day observed the photovoltaic effect in selenium in 1876.[15]

A unified explanation of these phenomena required a theory of solid-state physics which developed greatly in the first half of the 20th Century. In 1878 Edwin Herbert Halldemonstrated the deflection of flowing charge carriers by an applied magnetic field, the Hall effect. The discovery of the electron by J.J. Thomson in 1897 prompted theories of electron-based conduction in solids. Karl Baedeker, by observing a Hall effect with the reverse sign to that in metals, theorized that copper iodide had positive charge carriers.Johan Koenigsberger classified solid materials as metals, insulators and "variable conductors" in 1914 although his student Josef Weiss already introduced the term *Halbleiter*(semiconductor in modern meaning) in PhD thesis in 1910.[16][17] Felix Bloch published a theory of the movement of electrons through atomic lattices in 1928. In 1930, B. Gudden stated that conductivity in semiconductors was due to minor concentrations of impurities. By 1931, the band theory of conduction had been established by Alan Herries Wilsonand the concept of band gaps had been developed. Walter H. Schottky and Nevill Francis Mott developed models of the potential barrier and of the characteristics of a metal-semiconductor junction. By 1938, Boris Davydov had developed a theory of the copper-oxide rectifier, identifying the effect of the p–n junction and the importance of minority carriers and surface states.[18]

Agreement between theoretical predictions (based on developing quantum mechanics) and experimental results was sometimes poor. This was later explained by John Bardeenas due to the extreme "structure sensitive" behavior of semiconductors, whose properties change dramatically based on tiny amounts of impurities.[18] Commercially pure materials of the 1920s containing varying proportions of trace contaminants produced differing experimental results. This spurred the development of improved material refining techniques, culminating in modern semiconductor refineries producing materials with parts-per-trillion purity.

Devices using semiconductors were at first constructed based on empirical knowledge, before semiconductor theory provided a guide to construction of more capable and reliable devices.

Alexander Graham Bell used the light-sensitive property of selenium to transmit sound over a beam of light in 1880. A working solar cell, of low efficiency, was constructed byCharles Fritts in 1883 using a metal plate coated with selenium and a thin layer of gold; the device became commercially useful in phot