Short History of Semiconductors

By DON TAYLOR

Brief resume of some of the early uses of crystals that have led up to the modern transistor and diode.

THE formal study and investigation of semiconductors began in 1874, without fanfare, and without the elaborate tools of modern-day physics. Those were the days when lightning and solar radiation ruled the radio-frequency spectrum. Although this was 73 years before *Bell Labs* invented the first real transistor, men like Dr. Braun learned some amazing things about crystals.

Ferdinand Braun was born June 6, 1850. He received his PhD in 1872 at Berlin University. Later, he taught mathematics and physics at universities in Marburg, Carlsruhe and Strassburg.

Braun's fertile imagination turned to electricity and rocks in 1874. He studied the electrical properties of crystals of galena and other metallic sulphides. He found that these crystals exhibited a unilateral conductivity, that is, they had rectification properties. He looked further. He found that they showed no evidence of electrolytic conduction or of thermoelectric effects which would account for this one-way conductance. But man-made electromagnetic radiation had not yet been devised! So, with no radio-frequency signals to detect, Braun laid his crystals aside.

As early as 1835, Joseph Henry had observed, but could not explain, spark transmission and detection by coherence of a magnetic needle detector. In 1879, a vertical water jet was found to have a reaction (by molecular cohesion) to a charged sealing-wax stick. The water cohered by electrical disturbance, *ergo*, it detected electricity and could detect r.f. signals. Frog-leg nerves were used with some success as sensitive current meters; as such, they could detect the presence of an r.f. signal. But, of all things, a prehistoric tribolite probably utilized the first r.f. detector; it had an organic cavity in its skin which could detect lightning flashes.

An r.f. detector that retained popularity for many years was the coherer—made of substances that would cling together and change their internal conductivity in the presence of an r.f. signal. Metal filings in a glass tube cohered by molecular welding in an r.f. field, which lowered the impedance to a bias current through the coherer, but they had to be tapped to regain their previous high impedance. Marconi used the coherer as late as 1906.

Crystals abounded in nature. Galena could be found at the nearest lead mine; silicon literally lined the ocean beaches, but the hardy pioneers persisted in the use of other devices. Around 1900, responders were made of two metal plates placed very close together, with an intervening electrolyte which formed little bridges for low impedance conduction. These bridges were broken by boiling hydrogen in the electrolyte. The bridges would soon re-form, giving a detectable noise in a telephone receiver. Notice that this device provided a low impedance *until* it was disturbed by an r.f. signal. This was opposite to the cohered devices, and was naturally called an "anti-coherer."

Shortly after the turn of the century, L. W. Austin studied silicon-steel junctions. He found that an e.m.f. of 2.5 volts would pass 25 milliamps from steel to silicon, but would only pass 6 milliamps in the opposite direction. He concluded that silicon, at least with a steel junction, had rectification properties.

After these preliminary studies by Braun and Austin, little was done with crystals until about 1905. At this time, Braun made further studies of crystals, and persuaded the *Telefunken Radio* station to use psilomelane (hydrated barium manganate) as a detector. In this case, the crystal was placed between two metal electrodes under *light* pressure, and was one of the first commercial uses of the crystal detector. Still, few people had faith in crystals, probably because they did not understand them. What is the magical property of these rocks? How do they perform their mysterious task? The thermoelectric theory was popular, but it had many deficiencies.

Consider the crystal galena. It was used as a detector, rather infrequently, until about 1920, when germanium and silicon became predominant. Galena is a lead sulphide crystal, about 86% lead and 13% sulphur, with a trace of silver, or antimony, or gold, or selenium. Nothing really impressive. But today it is seen as an *n*-type crystal, having an excess of electrons in its internal structure.

Pierce, Dunwoody, Pickard, Eccles and other notable "radio engineers" studied crystals in the period from 1905 to 1910. In 1906, General H. H. C. Dunwoody studied carborundum (an artificial silicate of carbon). He found that it had unilateral conductivity, with or without a bias, and used it successfully as an r.f. detector. However, these men considered crystals as *thermal* detectors. A fine metal point was required to contact the crystal, and it was believed that this fine point heated the crystal in a small area and changed the impedance of the contact area. They used such devices as tellurium wire contacting galena, tinfoil-galena, graphite-galena, and other crystal-metal detectors.

The crystals worked fine; but there were complaints about their delicacy and the difficulty of "tickling" them into operation. The crystals were far from pure and homogeneous. It took a steady hand to find a good semiconducting area. Since no one understood the crystal as a concept of pressure contact, it was pure coincidence that they got the right pressure and the right area.

Some later observations proved that pressure had some effect. A successful detector was made with a plumbago (graphite) point in *light* contact with a piece of galena. Amateurs used carborundum crystals in special jigs, and regulated the pressure by a thumbscrew until the signals in the telephone receivers were the loudest. Other crystals used in this period were galena, silicon, germanium, zirconium, chalcopyrites (copper iron sulphide), and many more. The best performers were those containing iron or sulphur.

In 1915, J. A. Fleming observed that rectification depended in some cases on a surface action and in others upon the internal structure of one of the materials. He suggested that a distinction be made between "surface" and "body" rectification. Another conclusion of this period was that oxygen and oxides were necessary at the contact area to produce rectification. This is seen today as a matter of providing an environment necessary to give the required pressure by the conducting wire. The pressure at the surface of the crystal changes the internal structure of the crystal in a small area.

And so it went. The crystal was good; it was bad; it was thoroughly understood; it was a complete mystery. As the 1920's roared and went, the "cat whisker" crystal detector bowed to the superior vacuum-tube diode.

About 1947, after much success in WW II as a radar wave detector, the marvelous crystal was taken into *Bell Labs* for study and experimentation. After much discussion, the following theory was expounded. The crystal, when refined, had certain impurities in it. Germanium, for example, had some impurities in it that gave it a slight excess of electrons when it was in a relaxed state. When pressure was applied with a metallic contact, the material suddenly developed a *deficiency* of electrons in the small area under pressure. This created a junction within the crystal between the region under pressure and the unstressed region. A second electrode (a metallic contact also providing slight pressure) was found to have the ability to control the action of the other junction. This effected amplification; a small input current controlled a large output current.

The point-contact transistor came into being. This electron-excess and electron-deficient condition was later reproduced *without* pressure in a crystal, and the junction transistor was born. The junction transistor is rugged, dependable, and reasonably inexpensive.

Much has been learned about the crystal since that first formal study, but even greater secrets remain locked in the rocks. ▲