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Germanium: From its discovery to SiGe devices

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Abstract

Germanium, element #32, was discovered in 1886 by Clemens Winkler. Its first broad application was in the form of point contact Schottky diodes for radar reception during WWII. The addition of a closely spaced second contact led to the first all-solid-state electronic amplifier device, the transistor. The relatively low bandgap, the lack of a stable oxide and large surface state densities relegated germanium to the number 2 position behind silicon. The discovery of the lithium drift process, which made possible the formation of p-i-n diodes with fully depletable i-regions several centimeters thick, led germanium to new prominence as the premier gamma-ray detector. The development of ultra-pure germanium yielded highly stable detectors which have remained unsurpassed in their performance. New acceptors and donors were discovered and the electrically active role of hydrogen was clearly established several years before similar findings in silicon. Lightly doped germanium has found applications as far infrared detectors and heavily neutron transmutation doped (NTD) germanium is used in thermistor devices operating at a few milliKelvin. Recently germanium has been rediscovered by the silicon device community because of its superior electron and hole mobility and its ability to induce strains when alloyed with silicon. Germanium is again a mainstream electronic material.

Keywords: Germanium; Semiconductors; Isotopes; Hydrogen; Spectroscopy; Diffusion; Detectors

1. Introduction

The history of the science and technology of the chemical element germanium is at the same time the story of the transition from the "Physics of Dirt" to the birth of modern semiconductor physics and the story of the beginning of solid state electronics. The demonstration of the germanium point contact transistor on Christmas Eve 1947 by J. Bardeen and W. Brattain followed shortly by the invention of the germanium junction transistor by W. Shockley represents the beginning of the "Semiconductor Age," the successor to the Stone-, Bronze- and Iron Ages. In this brief review the major stages of the evolution of germanium from an element predicted by D.I. Mendeleev and named ekasilicium to today's use in high speed silicon devices will be visited. Limited space here does not allow for a detailed account of all the fascinating developments associated with this unusual element but key references will be used to guide the reader to major sources of information. This review is by no means comprehensive but it is an account based on personal choices and on numerous discussions with senior colleagues who played a role in some of these developments. It is with great pleasure that I recount the past 120 years of germanium history.

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2. Discovery of Germanium and early history

In 1871 D.I. Mendeleev predicted the existence of an element in the IVa column of his table of elements between the known elements silicon and tin. He called the unknown element eka-silicon. Fifteen years later, in 1886, Clemens Alexander Winkler found the missing element in the silver-rich mineral argyrodite and called it germanium (Fig. 1). Winkler was a renowned inorganic chemist at the Bergakademie (School of Mines) in Freiberg, Germany [1]. It took him only a few months to determine the major physical and chemical properties of the new element and he published his findings in a detailed 52-page article on August 14, 1886 [2]. Mendeleev had predicted different properties for his eka-silicon and tried to convince Winkler that he may have found something new but definitely not his eka-silicon. Winkler prevailed!

The year 1886 was rich in discoveries and novelties. In addition to the discovery of germanium, the first four-wheel motor car was built by Daimler-Benz, Coca Cola was formulated in Atlanta, Walter Schottky who developed the theory of the metal-semiconductor junction was born and patents for the mass production of aluminum were filed in the USA and Great Britain.

The years following the discovery of germanium did not lead to any major scientific findings or technological applications for this rare, expensive, brittle and metal-like element. In 1923 F.W. Aston found the three most abundant of the five stable isotopes, namely ^{70}Ge, ^{72}Ge and ^{74}Ge [3]. Up to the late 1930s germanium was believed to be a poorly conducting metal. This misunderstanding has persisted in some quarters to the present day: the boxes in which polycrystalline bars of germanium are shipped from the factory are still labeled in large bold letters, ''Germanium Metal''.

3. Reproducible results in the 1940s

The study and understanding of the physics of semiconductors progressed slowly in the 19th and early 20th centuries. Karl Lark-Horovitz wrote a condensed account of early experiments with semiconductors in his article, ''The New Electronics'' [4]. Impurities and defects simply could not be controlled to the degree necessary to obtain reproducible results. This led influential physicists, including W. Pauli and I. Rabi, to comment derogatorily on the ''Physics of Dirt'' [5,6]. The interest in semiconductors was kept alive, however, by the widespread use of crystal radios which used a

Fig. 1. D.I. Mendeleev and C.A. Winkler at the meeting of the 100th anniversary of the Prussian Academy of Science, Berlin, March 19, 1900.