
Introductory Chapter: Advanced Material and Device Applications with Germanium

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1. Introduction

The search for new semiconductor materials began with new technology requirements in the early nineteenth century [1]. One of the pivotal discoveries was silicon (Si) and germanium (Ge), by Clemens Winkler in 1886. The current semiconductor technology is mostly based on Si material to fabricate integrated circuits (ICs) in the era of high-speed Internet-of-Things (IoT). Since Si transistors of ICs have faced physical limitations due to their fundamental properties, a number of researchers are actively searching for alternatives, which reignite the active study of Ge to break through the technology roadblock. The scope of this introduction is to describe the historical background of Ge materials from ores and their application to advanced devices such as photodetectors, solar cells, spintronics, IC, etc., which are essentially semiconductor applications in all areas of our current technologies [2]. Furthermore, this chapter will discuss the opportunities and challenges of Ge materials and advanced device applications for the next technology generation. The last part of this section will outline the topic of each chapter with some practical suggestions on how to efficiently utilize this book for readers.

2. Elemental semiconductor material

Nowadays, almost 95% of all the semiconductors are fabricated on Si material. Si semiconductors began to be used in the mid-1960s. The silicon devices demonstrate better and stable properties at room temperature. Furthermore, generating high-purity silicon wafer can be relatively easily achieved by the so-called Czochralski process. This is a method of crystal growth used to obtain single crystals of semiconductors, where high-quality silicon dioxide can be grown at room temperature [3–8]. From the economic perspective, high-purity Si for

device applications is much cheaper due to the fact that Si consists of 25% of the Earth's crust in the form of silica and silicates, which makes Si the second-abundant material after oxygen. As of now, Si technology is the leading technology surpassing all other material applications combined. However, a preferred choice of material for advanced ICs during the beginning of the semiconductor era in 1960 was interestingly Ge over Si after the invention of the first transistor with Ge in 1947. In the twenty-first century, the return of advanced Ge devices preparing post-Si device era invites us to look into advantages of Ge advanced devices, which makes it only possible with current state-of-art advanced technologies for at least next 50 years.

In 1947, two scientists at the Bell Telephone Laboratories, John Bardeen and Walter Brattain, made a triangular insulating wedge where two thin gold contacts with approximately 50-um-wide gap were glued on. They pressed this wedge into a slab of Ge and made a third contact on the bottom of the slab. They applied forward bias between one gold contact and the bottom of the Ge slab while applying reverse bias between the other gold contact and the bottom. This turned a small signal into a larger signal with the flow of current through this configuration, which had changed forever the history of semiconductors by inventing the first transistor—the amplifier and switch, arguably the most important invention of the twentieth century (see **Figure 1**).

At the critical juncture of the post-Si era, serious efforts searching for a new semiconductor material to replace long-standing Si devices began. In the past 10 years, most of leading semiconductor companies have begun to consider a certain change in components of their IC design such as the current-carrying channel, which is the very heart of a transistor. The idea is to replace the Si with a material that can move current at significantly greater rates. Compared to Si channels, alternative transistors with such channels could allow design engineers to design faster, denser, and low-power circuits, meaning better and cheaper smartphones, computers, and numerous IoT gadgets and applications in the market.

The existence and properties of such a material were first predicted by Dmitri Mendeleev in 1869, by filling a gap in the carbon family, in his periodic table of elements, located between



Figure 1. A stylized replica of the first transistor [2].

silicon and tin; therefore, it was called eka-silicon (Es), with estimated atomic weight of 72.0, which is not far off from 72.630, the standard atomic weight in modern chemistry [2, 9]. Although Ge is 50th in the relative abundance of elements in the Earth's crust, Ge came to be known relatively late in the history of chemistry due to the fact that it is rarely discovered in high concentration [2]. In 1886, a German chemist, Clemens Winkler was able to isolate it, and found it similar to antimony, named in honor of his home country.

Until the late 1930s, Ge was considered to be a poorly conducting metal [10], rather than a semiconductor, which made Ge economically insignificant. However, this had changed after World War II when Ge's semiconducting properties of diodes were found. In other words, the switching property of Ge diodes initiated the initial development of Ge devices [11, 12]. The first application was for the use in radar units as a frequency mixer element in microwave radar receivers by producing pure Ge crystal mixer diodes with the point-contact Schottky diode structure during the war period. During the post-war period, the development and manufacturing of solid-state Ge devices became a major stream in the semiconductor industry. From 1950 to the early 1970s, the Ge-related market increased for applications in transistors, diodes, and rectifiers [13]. For example, in the US, a few hundred pounds of production in 1946 greatly grew to more than 45 metric tons until 1960 in order to meet the market demand. However, soon after, high-purity silicon began replacing germanium in transistors, diodes, and rectifiers [13]. For example, the company that became Fairchild Semiconductor was founded in 1957 with the express purpose of producing silicon transistors. Silicon has superior electrical properties, but it requires much greater purity and that could not be commercially achieved in the early years of semiconductor electronics. Meanwhile, demand for germanium in fiber optics communication networks, infrared night vision systems, and polymerization catalysts increased dramatically. These end users represented 85% of worldwide germanium consumption in 2000 [12, 13].

Under the standard temperature (273.15 K) and pressure (105 Pa), Ge is a brittle, silvery-white, semi-metallic element [12]. As pure Ge is not mined as a primary material, Ge can be produced as a by-product of base metal refining [14]. Ge can be mostly found in the form of sphalerite zinc ores where it is concentrated in amounts as great as 0.3%, argyrodite (a sulfide of germanium and silver), and germanite (containing 8% of the element) [14, 15]. With sphalerite zinc ores, Ge concentrates are first purified using a chlorination and distillation process that produces germanium tetrachloride (GeCl_4) [15]. Germanium tetrachloride is hydrolyzed and dried, producing germanium dioxide (GeO_2), which is reduced with hydrogen to form Ge metal powder. Ge powder is cast into bars at high temperatures over 1720.85 F, which are treated by the zone-refining process to isolate and remove impurities. After this process, high-purity Ge metal bars are finally produced. Commercial Ge metal is often more than 99.999% pure. Zone-refined Ge can further be grown into crystals, which are sliced into thin pieces for use in semiconductors and optical lenses [15].

3. Applications and opportunities of germanium

In general, the United States Geological Survey (USGS) classified Ge applications into five groups such as IR optics (30%); fiber optics (20%); polyethylene terephthalate—PET (20%); electronic and solar (15%); and phosphors, metallurgy, and organic applications (5%) (see **Figure 2**).

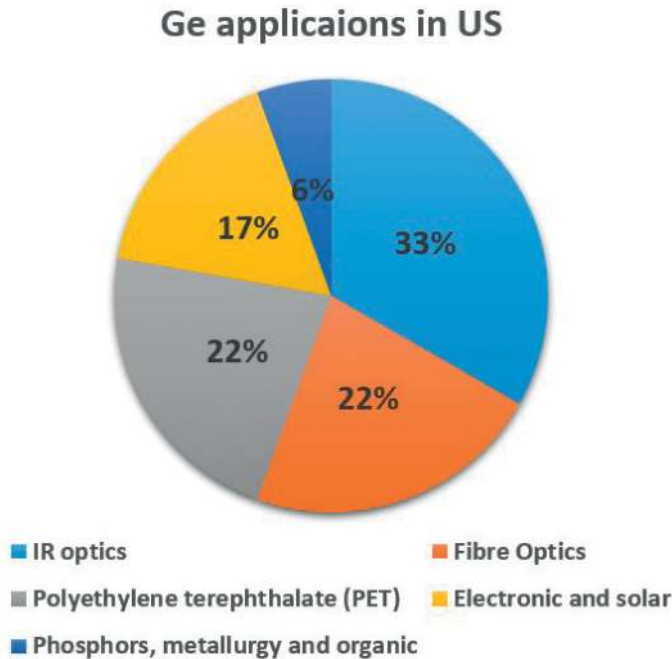


Figure 2. US Ge applications [12].

As mentioned earlier, zone-refined Ge crystals are grown and sliced to form lenses and window for IR and/or thermal imaging optical systems [15]. A major developer and customer is the military, for the application of advanced weapon systems such as small hand-held and weapon-mounted devices.

In fiber optics, telecommunication is possible by confining the light signal to their core, with Ge fibers acting as a waveguide for the electromagnetic light wave. Hence, the higher refractive index of the center of the fibers can improve the confinement of the light signal. Doping fused silica with Ge dopants can improve the refractive index in the silica glass of fiber optic lines by reducing signal loss (see **Figure 3**).

Regarding the production of PET plastics, roughly 17 metric tons of germanium dioxide is consumed each year as a polymerization catalyst. PET plastic is primarily used in beverage, liquid containers, and food.

In recent years, Ge has seen increasing use in precious metal alloys [12, 16]. In sterling silver alloys, for instance, it reduces firescale, increases tarnish resistance, and improves precipitation hardening. A tarnish-proof silver alloy trademarked Argentium contains 1.2% germanium [12, 16].

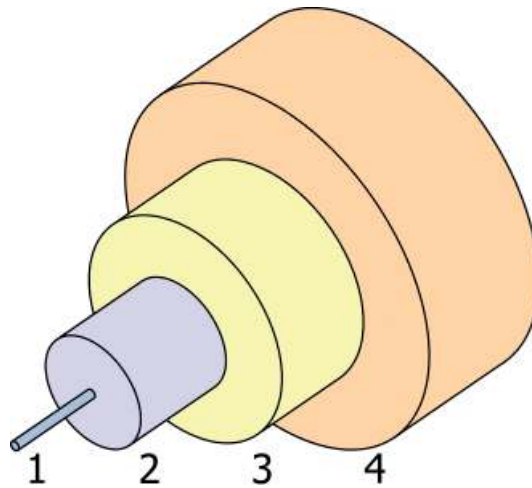


Figure 3. A typical single optical fiber, demonstrating core silica (1) with germanium oxide dopants, (2) cladding, (3) buffer, and (4) jacket [16].

As for spintronics, Ge is an emerging material for spin-based quantum computing applications. After finding the Ge property of spin transport at room temperature in 2010 [17], scientists recently showed very long coherence times of donor electron spins in Ge [16–18].

Soon after the birth of Ge transistors, Si transistors' replacement of Ge transistor happened in the early 1970s due to the reasons mentioned earlier. Today, however, scientists' efforts to achieve lower-power and higher-speed transistors have brought Ge back to the main interest of the semiconductor industry. By implementing Ge as current-carrying channel (channel) of the transistor, transistors are improved based on a fundamental property, which is the mobility of electrons and holes. Electrons move nearly three times as readily in Ge as they do in Si near room temperature. Furthermore, holes move about four times as readily in Ge. This is ultimately related to the difference in band structure between Ge and Si. Consequently, the faster these electrons and holes can move, the faster the resulting circuits can be. Since less voltage can be applied to draw those charge carriers along, circuits can also consume considerably less energy [19].

Since Ge band gap is small, 0.67 eV, Ge is transparent in the infrared wavelengths, which makes it possible to employ them in infrared spectrometers and other extremely sensitive optical equipment such as infrared detectors. There are a number of infrared optical applications for Ge which can be readily cut and polished into windows and lenses [16, 20–22]. In particular, military applications rely on Ge optical properties. For instance, Ge is used in the front optic of thermal imaging cameras working in the 8–14- μm range for passive thermal imaging and for hot-spot detection in the military, mobile night vision, and firefighting applications (see **Figure 4**) [16, 20, 23, 24].

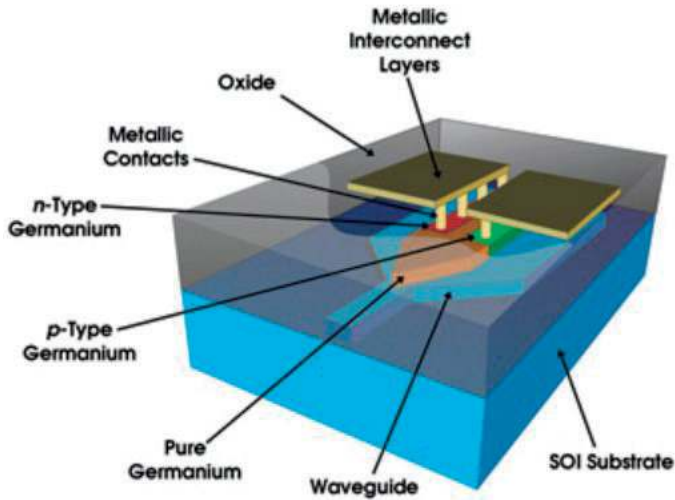


Figure 4. Germanium photodetector comprised of various layers of germanium [21].

4. Summary

We attempt to review germanium elemental materials and summarize the highlights of the history of germanium. Although the complete story of germanium would be lengthy, we have tried to highlight the material and device aspects of germanium. From the Ge application perspective, there are a number of examples; but the main applications could be categorized into five areas such as IR optics; fiber optics; polyethylene terephthalate—PET; electronic and solar; and phosphors, metallurgy, and organic applications. After the first invention of a transistor in 1947, which is arguably perceived as the most important invention in the twentieth century, and silicon replacement, germanium in electronics remarkably returns. The steady-fast increase of germanium application in IR and fiber optics is interesting as well. Furthermore, it is expected that more studies of germanium nanocrystals could contribute to the increased attention to research and development of new germanium applications in near future.

5. Outline of this book

As indicated in the title of this book, it will cover the detailed aspects of germanium. In particular, it is categorized into four sections, which describe critical aspects of germanium application in each field, including this first brief introduction of germanium. In the second part, this book will describe germanium material property and production from economical and engineering perspectives. In the third part, it will discuss germanium optics applications and diffusion characteristics during the process. In the final section with two chapters, this book will describe germanium microelectronic characteristics, in particular, interface characteristics

impacted by the process. The contributing authors are experts in their field with great in-depth knowledge, which is contained in this book. The authors strongly feel that this contribution might be of interest to readers and help to expand the scope of their knowledge.

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