

Effective Purification of Germanium Obtained from Mineral Raw Materials

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Abstract

By studying the heat treatment of metallic germanium obtained from mineral raw materials, in is experimentally established that germanium heating in a certain narrow temperature range leads to a significant decrease in the concentration of uncontrolled impurities. The use of such a heating as a preliminary germanium purification makes it possible to increase significantly the efficiency of subsequent germanium purification by a zone melting method.

Keywords: Germanium; Purification; Volatile impurities; Zone melting

Introduction

Single-crystalline and poly-crystalline germanium is one of the main materials of semiconductor technique and is used for fabricating the elements of infrared optics (such as lenses, protective screens, etc.), detectors of ionizing radiation and other devices. Germanium is contained in the earth's crust in the form of a scattered element and may be found in sulfide and iron ores, some coals, almost in all silicates and in a number of minerals (such as argyrodite, confildite, etc.). By means of the use of certain complex and time-consuming operations, germanium may be extracted from the listed materials in the form of oxide GeO_2 , which may be then chemically reduced with hydrogen at high temperature. Since for most practical applications the high-purity germanium is used as a source material (which subsequently may be doped with certain impurities), processes of metallic germanium purification are very important. Very often the depth of such purification should be very high. For example, to provide germanium transparency in the infrared optical region, i.e. to prepare so-called optical germanium, it should be doped with a certain donor impurity (Sb, Na, etc.) at a concentration from $5 \cdot 10^{13}$ to $3 \cdot 10^{14} \text{cm}^{-3}$ [1,2]. Therefore, the concentration of uncontrolled impurities in the source germanium before its doping should not exceed at least 10^{12}cm^{-3} . As to detector germanium, it should even be much better refined.

As a main method for germanium purification, zone melting is used. It makes it possible to prepare germanium, which is one of the most chemically pure materials known. However, during zone melting, each germanium ingot must be subjected to repeated purification, i.e. the container with germanium should be many times pulled through a narrow zone of melted germanium. This process is rather long, laborious and energy consuming. Obviously that to increase the efficiency of zone melting, it is desirable to use as much as possible purified source material. In this paper we describe the effect observed by us [3] that makes it easy to lower the content of impurities in the source germanium prior to its purification by zone melting. During a long time we successfully used this effect when preparing the initial material for growing large optical germanium crystals used in modern thermal imaging devices [4].

Method of Preliminary Purification

Germanium powder obtained by reducing germanium oxide in a hydrogen flow at a temperature about 650-675 °C, weighing approximately 2kg, was placed in a graphite crucible and heated in a closed chamber under a pressure of 10^{-3} atm with continuous pumping. After the powder was completely melted, the melt was heated to a temperature of 1050-1150 °C. It was found that in this temperature range a quite narrow region existed, up to 20 °C wide, in which a rather unexpected process was observed that looked like boiling of the melt. This

process lasted for about 5-10min. Temperature, corresponding to this region, was different depending on the nature of purified germanium. We explained this process by decomposition and evaporation of some chemical compounds whose composition we could not determine. It seems naturally to suggest that such compounds were initially contained in the germanium dioxide, from which the metal germanium was obtained. As a result of the described process, the content of electrically active impurities in the obtained crystalline germanium dropped by about 5-10 times compared with the material in which the heating in the described narrow temperature region was not carried out. Note that the concentration of electrically active impurities in the obtained germanium ingots was evaluated, as is often done, from the measured value of the electrical resistivity.

It was found that after the subsequent zone melting of the preliminary purified germanium (at 6 passes of the melted zone) the resistivity of almost the entire germanium ingot was approximately 47 Ohm·cm at room temperature, which corresponded to the intrinsic electrical resistivity of germanium [5] and was indicative of its high purity. At the same time, zone purification of germanium, which was not subjected to the preliminary purification described above, resulted in obtaining ingots with a resistivity about 47 Ohm·cm only in the front half of each ingot even after 12-fold passage of the melted zone. As for the rest portions of the ingots, their resistivity did not achieve this value even after the multifold zone-melting purification.

Conclusion

It is shown that heating of the melted metallic germanium obtained from mineral raw materials, carried out in the experimentally determined narrow (approximately 20 °C wide) temperature region, results in a significant decrease of the concentration of contaminants. This results in a significant increase in the efficiency of the subsequent purification of this material by zone melting. The described technique has been successfully used for preparing germanium ingots used as a source material for growing, on an industrial scale, of optical germanium crystals for thermal imaging systems.

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