Investigation of factors influencing the zone refining process of very high-purity germanium

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Over 70 years, zone refining (ZR) is the principal techniques used to purify the semiconductor materials [1, 2]. Several factors may influence the impurity level in the material during this process method namely container type & purity, ambient gases, and other operating conditions & parameters [3]. There are multiple stages involved in purifying consistently germanium (Ge) to a very high purity of 13Ns. The main impurities are aluminum (Al), boron (B), gallium (Ga) as acceptors and phosphorous (P) as the donor. In this study, we investigate the factors that influence the impurity segregation, microstructural properties, and the yield of highly pure Ge (HPGe) bars in the ZR purification process, which includes analyses of graphite boat, quartz boat, gas flow (nitrogen (N_2)/argon (Ar)/hydrogen (H_2)) and the zone travel velocity. Further, the results were related to the type and concentration of impurities in the ZR polycrystalline Ge bars. The starting 4N-pure Ge metal used for ZR exhibited impurities such as Al, P, and Fe. As the Ge melt meets the container during the ZR process, impurities in the container can diffuse into the melt and can have a significant impact on the final purity of Ge ingots. The impurities that are found in the refined bars with quartz boat is Al, P, Fe and Ga, whereas with graphite boats, contained an increased concentration of Al, but other impurities are less though they are present. Formation of the compounds of Al due to low segregation make it difficult to be removed by the zone refining whereas phosphorous and other electrically active impurities segregate normally and are therefore relatively be removed easily. It has been found that reducing the zone velocity increases the impurity diffusion from the container into the Ge melt and have an impact on the purity of the final Ge bar. On the other hand, if the zone velocity is increased, the degree of super cooling and the number of nucleation sites increases resulting in the formation of multiple small grains with multiple grain boundaries (GBs). At a lower zone velocity, the polycrystalline Ge ingot shows large grains with few GBs which results in low impurity trapping. So, the proper velocity must be optimized to get compromise between diffusion and the grain size. In the ZR process initially performed in an Ar atmosphere, it has been observed that white layers are formed on the surface of Ge bars due to surface oxidation. But in a N_2 gas atmosphere, the formation of white layers could be reduced. ZR in Ar atmosphere results in the average resistivity around 50 Ω·cm and the yield of 60%, whereas ZR in N_2 shows a better resistivity value (~60 Ω·cm) and a good yield of 80% could be obtained. The final ZR process is conducted in an H_2 gas atmosphere in a quartz smoke coated quartz boat, which has a resistivity of 65 Ω·cm and a yield of 80%. Here the yield represents the ZR bar length with required resistivity value (viz. targeted purity level) to the total bar length. The oxide layers formed in Ar and if any in N_2 atmospheres are eliminated when refined in H_2 atmosphere. The different orientation obtained after solidification of polycrystalline Ge has also an impact on the segregation of the impurities. Therefore, grain boundaries, orientation and dislocations observed in these polycrystalline Ge bars are being analyzed to see their influence on the characteristics, say for e.g., lifetime of charge carriers.

References

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