METHOD OF ZONE REFINING FOR IMPURITIES HAVING SEGREGATION COEFFICIENTS GREATER THAN UNITY
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Fig. 1.

Fig. 2.

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METHOD OF ZONE REFINING FOR IMPURITIES HAVING SEGREGATION COEFFICIENTS GREATER THAN UNITY

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The present invention relates to a method for purifying semiconductor materials and more particularly relates to a zone refining technique especially applicable for processing impurities having segregation coefficients greater than unity.

One of the methods currently used for purifying semiconductor materials is a technique known as zone refining. Such a technique is described, for example, by W. G. Pfann, "Principles of Zone Melting," Journal of Metals, July 1952, pages 747—753, and by the same author, "Segregation of Two Solutes, with Particular Reference to Semiconductors," Journal of Metals, August 1952, pages 861—865. The method relies on the fact that many semiconductor carrier impurities are more soluble in liquid semiconductor material than in solid material, thus enabling purification to result from progressive melting and solidifying of a bar of semiconductor material.

In carrying out a zone melting operation, a bar of semiconductor material is subjected to local heating, which results in the formation of a small molten zone. The zone is moved along the bar either by moving the heating source along the bar while holding the bar stationary or by moving the bar relative to a stationary heater.

In describing zone refining techniques, it is convenient to refer to a segregation coefficient defined as the ratio of the concentration of the impurities in the solid phase to the concentration of impurities in the liquid phase. Thus, impurities which have a segregation coefficient smaller than unity are more soluble in liquid than in solid and tend to remain in the liquid phase. As a molten zone is caused to traverse the length of a semiconductor bar, these impurities are carried along the molten zone, and they tend to segregate to the last portion of the bar to solidify. The end of the bar solidifying first is left relatively free from impurities.

The above-described zone refining technique, however, does not work as well when dealing with substances having segregation coefficients greater than unity. Such substances prefer the solid phase to the liquid phase, and thus a molten zone pass made in a bar of semiconductor material, impurities with segregation coefficients greater than unity move slightly toward the first portion of the bar to solidify. The degree of segregation is slight, however.

A process has been tried in which a bar of semiconductor material is uniformly heated to the molten state, and then is progressively solidified by subjecting one end to cooling means and causing the molten material to solidify unidirectionally from one end of the bar to the other end. Such a process results in some degree of segregation, since the impurities with segregation coefficients greater than unity tend to accumulate in the first portion of the bar to solidify. However, this process has the drawback that there is no appreciable improvement in segregation upon repetition of the process.

Therefore, it is a principal object of the present invention to provide an improved method of zone refining which will enable semiconductor materials with impurities having segregation coefficients greater than unity dispersed therein to be purified to a greater extent than can be accomplished by present methods.

It is a further object of the present invention to provide a zone refining technique for impurities having segregation coefficients greater than unity which may be repeated as many times as is necessary to obtain a desired degree of segregation and which technique gives improvements in segregation when repeated.

Other objects and advantages of the present invention will become readily apparent from the following detailed description of a preferred embodiment of the invention when taken in conjunction with the drawing in which:

FIGURE 1 is a graph showing the impurity concentration profile of a bar of semiconductor material when subjected to the various steps constituting the purifying technique of the present invention; and

FIGURE 2 is a graph showing zone width versus zone position.

Referring to FIGURE 1, the impurity concentration as a function of bar length for an untreated bar is shown by the heavy solid line on the graph to be uniform throughout the length of the bar. For illustrative purposes, the impurity concentration is shown to have a relative magnitude of unity. The impurity chosen for this and following examples had a segregation coefficient of three.

In the zone melting technique of the present invention, the bar of semiconductor material is first subjected to uniform heating until all the material is in the molten state. The bar is then subjected to a solidifying operation. The solidifying is accomplished by applying cooling means to one end (designated as the starting end) of the semiconductor bar and by this means, the molten material is solidified unidirectionally. As is shown by the dashed line on the graph, the melting and progressive cooling technique results in some degree of segregation for impurities having segregation coefficients greater than unity. The impurities tend to concentrate in the starting end, which is the first portion of the bar to solidify. As is shown in the drawing, at the starting end the impurities are present in a concentration of relative magnitude three, while at the final end, the impurity concentration has decreased to zero.

Next, a molten zone is caused to traverse the length of the bar, starting from the same end that the cooling operation was started. The width of the molten zone will be adjusted in accordance with the impurity profile of the bar. After a preliminary melt-in of a narrow zone at the starting end of the bar, the zone is adjusted in width to maintain the maximum concentration of impurity in the molten zone. This insures that a maximum amount of impurity is deposited with the freezing interface. For illustrative purposes an example will be given using an impurity whose segregation coefficient is three. If the bar is frozen in one direction as described previously, the relative magnitude of impurity will be three at the first frozen end and will decrease along the bar as indicated by the dashed curve on the graph.

If now a molten zone of variable width with the following program is passed along the bar, the impurity will tend to segregate significantly in the first frozen end. The units in the following table are in fractional length of bar, measured from first-frozen end.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Impurity Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>1.5</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The following equations apply to the above table:

\[ \text{Impurity Concentration} = \frac{1}{\text{Fraction}} \]

The above equations show that the impurity concentration is inversely proportional to the fraction of the bar length.

The process repeats itself on each side of the bar, resulting in a zone refining technique which is very effective for the purification of semiconductor materials.
It is not claimed that this is the ultimate refinement in zone width; rather the technique is constrained by experimental limitations of the present apparatus. Thus, if the melt-in zone is made narrower, the ultimate purification would be better. Further, if finer control on the width of the zone were possible, again purification would be better. The figures quoted represent a reasonable set of values for the present state (or possible refinements) of the zone refining process.

For the conditions as in the above program, the impurity concentration would approach a value of relative magnitude 9 in the first frozen end of the bar and would have a distribution along the bar represented by the dotted curve in the figure.

If a second molten zone pass is now made, still greater segregation results. The width of the second molten zone must be programmed in accordance with the impurity profile of bar, hence a new program must be calculated for each successive pass. In the second pass, the impurity level in the first frozen end should approach 27 for the example; in actual practice, it will be closer to 22 due to practical limitations of the experimental apparatus. The impurity profile after the second pass is represented on the graph by the dotted line.

Still greater segregation can be obtained by employing the following procedure. A bar of semiconductor material is first purified according to the above-mentioned technique. Then a portion of the starting end of the bar is cropped or cut off, after which the entire process is repeated or more desirably only the step of subjecting the bar to a molten zone pass as previously described. In every case the molten zone pass is started from the same end and the width of the molten zone is programmed to maintain a maximum concentration of impurity in the molten zone. The over-all operation of employing the basic zone melting technique of the present invention, cutting off a portion of the starting end of the bar of semiconductor material, and then repeating the molten zone pass technique several times can produce bars having a desirable degree of segregation.

Although the present invention has been shown and described with reference to a particular embodiment, nevertheless various changes and modifications obvious to one skilled in the art are within the spirit, scope and contemplation of the present invention.

What is claimed is:

1. A method of zone refining for impurities having segregation coefficients greater than unity comprising the steps of heating a bar of semiconductor material to the molten state, solidifying said bar progressively from one end to the other, causing a molten zone to traverse the length of said solid bar starting from the said one end, and non-linearly increasing the volume of said molten zone until the freezing face is positioned at about 25% of the bar length and thereafter decreasing the volume of the molten zone to maintain a maximum concentration of impurities in said molten zone.

2. A method as defined in claim 1 wherein the passage of said molten zone along the length of said bar is repeated as many times as is necessary to obtain a given degree of segregation.

3. A method of zone refining for impurities having segregation coefficients greater than unity comprising the steps of heating a bar of semiconductor material to the molten state, solidifying said bar progressively from one end to the other, causing a molten zone to traverse the length of said solid bar starting from said one end, non-linearly increasing the volume of said molten zone until the freezing face is positioned at about 25% of the bar length and thereafter decreasing the volume of the molten zone to maintain a maximum concentration of impurities in said molten zone, and cutting off a portion of said solid bar at said one end and subjecting the remaining portion of said solid bar to a second pass of a molten zone.

4. A method of zone refining for impurities having segregation coefficients greater than unity comprising the steps of heating a bar of semiconductor material to the molten state, progressively solidifying said bar from one end to the other, causing a molten zone to traverse the length of said bar starting from said one end, non-linearly increasing the volume of said molten zone until the freezing face is positioned about 25% of the bar length and thereafter decreasing the volume of the molten zone to maintain a maximum concentration of impurities in said molten zone, repeating the step of causing the molten zone to traverse the length of said solid bar from said one end and the step of non-linearly increasing the volume of said molten zone until the freezing face is positioned at about 25% of the bar length and thereafter decreasing the volume of the molten zone to maintain a maximum concentration of impurities in said molten zone, cutting off a portion of said bar at said one end and subjecting the remaining portion of said bar to another pass of said molten zone.

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