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ZONE MELTING OF SEMICONDUCTIVE MATERIAL

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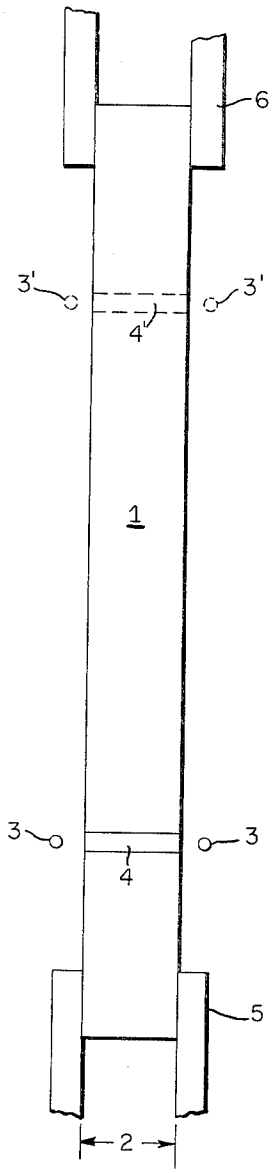

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ZONE MELTING OF SEMICONDUCTIVE MATERIAL

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This invention relates to the refining and crystallization of materials by an improved floating zone process. More particularly, it relates to an improved floating zone process for refining larger quantities of materials and producing single crystals of improved quality.

The process of crystallizing silicon or other material from a floating liquid zone has been described by Keck and Golay in Physical Review 89, 1297, (1953), and by Keck, et al. in the Review of Scientific Instruments 25, 331, (1954), and elsewhere. A heating source consisting of a ring-like element is mounted concentrically around a thin rod of silicon being crystallized. Heat applied from the surrounding ring source causes a short section of the small diameter rod to melt through forming a molten zone which is held stable between the solid parts of the rod by surface tension while the solid parts of the rod are cooled by radiation to room temperature. The molten zone is then caused to travel slowly along the rod by upward or downward movement of the rod or heating source. Refining takes place due to the segregation in the molten zone of impurities rejected during crystallization of the silicon into a single crystal as the molten zone traverses the rod.

The maximum stable length of the molten zone for an ingot of a given diameter undergoing floating zone refining has been determined theoretically by H. Heywang and G. Ziegler, Z. F. Naturforschung, 9*a*, 561–562 (1954). Their results show that for small diameter ingots the maximum stable length is approximately proportional to the diameter, while at larger diameters it becomes independent of the diameter. This limits the size of the ingots one can handle in the conventional manner, because with larger diameter ingots it is impossible to maintain a stable, relatively short molten zone without retaining an unmelted core connecting the solid portions of the ingot.

The rate of traversal on the molten zone is determined by the impurities present and the degree of segregation desired, but in most cases only very slow traversal rates (on the order of a fraction of an inch per minute) can be utilized. This, together with the limitation on the size of the ingot, is extremely restrictive when commercial rates of production of pure metals and semiconductor materials are required. Furthermore, to date, float zone refining of rods having a diameter of more than about ⅞" in diameter has not been accomplished with silicon. Thus, the cost of this operation for a large volume production is extremely high.

The formation of an unmelted core is indicative of the degree of inward curvature of the interfaces between the molten zone and the solid portions of the bar being refined resulting from heat losses by conduction and radiation from the solid portions. These heat losses cause uneven distribution of heat in the crystallizing bar, as the outside is considerably different in temperature from the inside. This in turn causes uneven contraction, creating stresses which relieve themselves by slipping of crystal planes during cooling. The slipping is evidenced by dislocation counts (refer to F. L. Vogel, J. Appl. Physics 27, 1413, (1956), and Physical Review 94, 1791, (1954), for description of a visual method of obtaining dislocation counts). High dislocation counts are indicative of imperfections in the single crystals produced by float zone refining. In the case of semiconductor materials such as silicon and germanium, this is an important quality-determining factor of the material to be used for electronic devices such as transistors, rectifiers, and the like. Float zone refining of silicon by prior art methods produces silicon having dislocation counts of a high order of magnitude. Silicon with lower dislocation counts is more satisfactory, showing less decrease in lifetime on heat treatment, and is produced only by pulling crystals from a melt contained in a crucible where contamination from the crucible material itself becomes an important adverse quality factor.

It is among the objects of this invention to overcome the foregoing and other disadvantages characterizing prior methods of float zone refining and crystalizing. A further object is an improved method of float zone refining refractory metals, insulator and semiconductor materials. A still further object is an improved method of float zone refining silicon in the form of large diameter rods, in particular rods having a diameter greater than about an inch. A still further object is a process to produce semiconductor materials in single crystal form, and with improved quality.

The objectives of this invention are accomplished by the improved process of floating zone refining which comprises establishing a narrow molten zone in a bar of material being refined by application of focussed heating thereto while the entire bar is heated to a temperature close to the melting point of said material by electrical resistance heating. While continuing to maintain the temperature of the solid portions of bar at the temperature close to its melting point, the molten zone is caused to traverse a portion of the bar to cause segregation of segregatable impurities within the molten zone. After cooling, the refined bar is recovered by cropping or other means. The effects of maintaining the solid portions of the bar at an even temperature near the melting point during the floating zone refining are first to reduce thermal flow along the bar away from the molten zone, which tends to flatten the liquid-solid interfaces and thus avoids solid bridging across the molten zone and makes possible the refining of larger bars than previously possible; and second the effect is to reduce the cooling stresses of the solidifying side of the bar, which reduces crystal imperfections. In the case of semiconductors, where impurity and crystal perfection are important for product quality, this is particularly advantageous.

More specifically the objectives of this invention are accomplished by the improved process of floating zone refining, comprising establishing and traversing a narrow molten zone lengthwise through a vertically disposed bar of material to be refined while maintaining the liquid-solid interfaces between said zone and solid portions of the bar substantially flat by passing a resistance heating current through said bar and said molten zone to maintain the temperature of the solid portions both above and below said molten zone below the melting point of said material being refined but not less than eight-tenths the melting point temperature on an absolute scale, discontinuing the application of melting heat before discontinuing resistance heating, and recovering the refined product.

With reference to the accompanying drawing, the objects of the invention are accomplished by the improved process of float zone refining where a cylindrical bar or rod **1** of silicon or other material being refined having a diameter **2** is placed between electrical connections **5** and **6**, which hold the bar in a vertical position and are enclosed within a glass or silica container (not shown), which enables the atmosphere around the bar to be controlled if desired. The connections **5** and **6** are attached to a mechanism not shown for lowering or raising the bar

at a controlled rate. Using an electrical circuit with suitable ballast to prevent a surge of current when the resistance of the rod drops due to the increased temperature, the bar is heated by passing current through the electrodes 5 and 6 to obtain a temperature close to the melting point of the material but not less than 9/10 of the melting point on an absolute scale (Rankine or Kelvin). Additional heat to form a narrow molten zone 4 is produced by a surrounding source 3 which is conveniently a high frequency heat coil.

The rod is lowered slowly at a constant rate to traverse the molten zone through the bar to a position 4' near the upper end of the bar. The segregatable impurities having a segregation constant less than one tend to be held in the molten zone and move to the last molten zone location. High frequency heating around the molten zone is then discontinued. The refined product is recovered by discontinuing the resistance heating, removing the bar, and cropping the portions of the bar containing undesired impurities and the portions which were not traversed by the molten zone.

To illustrate more completely the methods of this invention the following example is given which is not to be construed as in limitation of the underlying principles and scope of the invention:

Example I

A bar shaped ingot of silicon 1½ inches in diameter is placed in a floating zone refining apparatus of the type illustrated in the accompanying drawing. Electrical terminal connections at both ends are provided to heat the bar by resistance heating using an electrical circuit having suitable ballast. The bar is heated to and maintained at approximately 1200° C. A high frequency heating coil having two turns and forming a coil 1⅞ inches in diameter is provided. With the coil near the lower end of the bar, a molten zone ⅜ inch long is established and the bar is lowered at a rate of 3 inches per hour through the coil, causing the molten zone to traverse the bar to a point near the upper end. The molten zone is allowed to freeze by turning off the high frequency coil, and then the resistance heating is discontinued. The product silicon is a single crystal, having a low dislocation count, and high resistivity and lifetime characteristics.

The additional heating energy for establishing and maintaining the molten zone may be supplied by radiant heating, induction heating, electron bombardment, reduction of heat losses by a radiation shield, or other means, as convenient. As the invention is applicable to any material that can be effectively heated by resistance heating, such materials as metals, semiconductors and insulators, and refractory materials can be refined by the process of this invention. It is particularly advantageous for the refining and single crystal production of high melting materials such as silicon, germanium, boron, and the like, for semiconductor uses wherein extremely high purity levels are required. Other materials can be refined by the process of the invention with advantageous results. Multiple passes of the molten zone through the bar can be made by returning the bar to the initial position, and repeating the operation, preferably not allowing the bar to cool between passes below the temperature established by the resistance heating. An advantage of the invention is that it provides a method of floating zone refining suitable for use with bars of large diameter. This is particularly true of silicon and similar types of materials. More particularly it provides a means of float zone refining silicon in bars having a diameter of an inch or larger. Another important advantage is that due to the additional heating of the crystallizing bar, much less evidence of crystal imperfections due to slipping of crystal planes is found. For use in semiconductor applications such silicon is much more effective as the lifetime characteristics are more permanent, particularly with respect to reheating.

We claim as our invention:

1. An improved process for floating zone refining a high-melting material selected from the group consisting of silicon, germanium and boron wherein a molten zone is caused to traverse a bar of said material, which comprises heating a vertically disposed bar of said material by electrical resistance means to establish and maintain throughout said bar an even temperature close to the melting point of said material but not less than 9/10 of its melting point temperature on an absolute scale, applying focused heat to a portion of the bar to create a narrow molten zone completely across said bar, traversing said molten zone along the bar while maintaining the solid portions of said bar at said even temperature by continued resistance heating, during said refining maintaining the liquid-solid interfaces between said molten zone and solid portions substantially flat and said bar and molten zone substantially uniform in cross section, and recovering the refined product.

2. An improved process for floating zone refining a high-melting material selected from the group consisting of silicon, germanium and boron wherein a molten zone is caused to traverse a bar of said material, which comprises heating a vertically disposed bar of said material by electrical resistance means to establish and maintain an even temperature throughout said bar which is close to melting point of said material but is not less than 9/10 of said melting point on an absolute scale, applying focused heat to a portion of the bar to create a narrow molten zone completely across said bar, traversing said molten zone along the bar while the solid portions of said bar are maintained at said even temperature by continued resistance heating, during said refining maintaining the liquid-solid interfaces between said molten zone and solid portions substantially flat to eliminate solid bridging across said zone and the bar and molten zone uniform in cross section, on completion of the refining discontinuing said focused and resistance heating, and recovering the refined bar.

3. An improved process for floating zone refining silicon wherein a molten zone is caused to traverse a bar of said silicon which comprises heating a vertically disposed bar of said silicon by electrical resistance means to establish and maintain throughout said bar an even temperature close to the melting point of the silicon but not less than 9/10 of said melting point temperature on an absolute scale, applying focused heat to a portion of said bar to create a narrow molten zone completely across said bar, traversing said molten zone along said silicon bar while maintaining the solid portions of said bar at said even temperature by continued resistance heating, during said refining maintaining the liquid-solid interfaces between said molten zone and solid bar portions substantially flat and said bar and molten zone substantially uniform in cross section, and recovering the refined silicon product.

4. An improved process for floating zone refining silicon wherein a molten zone is caused to traverse a bar of said silicon which comprises heating by electrical resistance means a vertically disposed bar of silicon having a diameter greater than an inch to establish and maintain throughout said bar an even temperature close to the melting point of the silicon but not less than 9/10 of said melting point on an absolute scale, applying focused heat to a portion of said bar to create a narrow molten zone completely across said bar, traversing said molten zone along the silicon bar while maintaining the solid portions of said bar at said even temperature by continued resistance heating, during said refining maintaining the liquid-solid interfaces between said molten zone and solid bar portions substantially flat and said bar and molten zone substantially uniform in cross section and eliminating solid bridging across said zone, on completion of the refining discontinuing said focused heating and said

resistance heating, and recovering the refined silicon product.

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