# METHODS OF HEATING AND LEVITATING MOLTEN MATERIAL

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FIG. 1

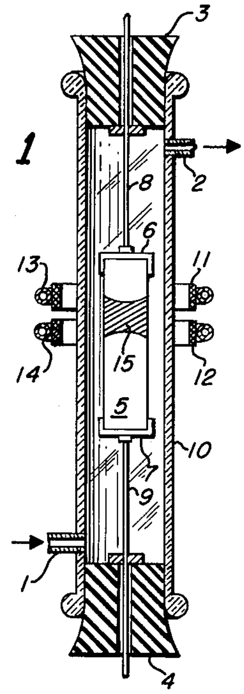



FIG. 2

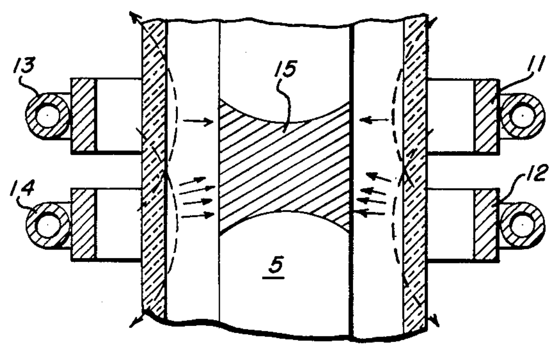



FIG. 3

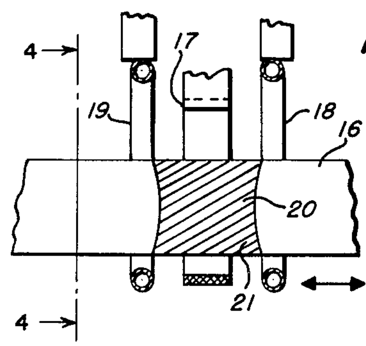
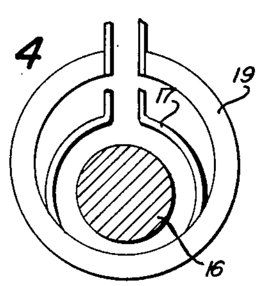



FIG. 4



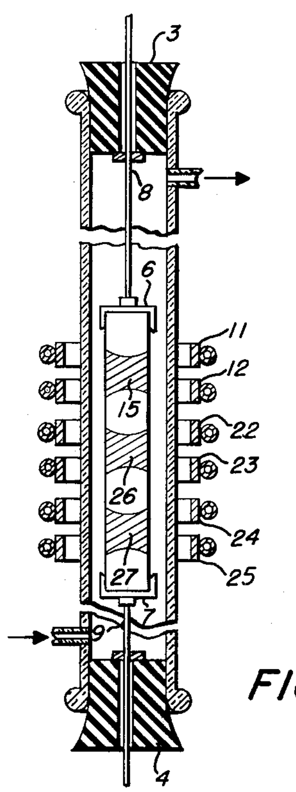




FIG. 5

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METHODS OF HEATING AND LEVITATING MOLTEN MATERIAL

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This invention relates generally to a process for redistributing the ingredients of fusible solvent-solute systems for the purpose of producing material of a desired composition, and more particularly to the preparation and purification of material for use in the manufacture and fabrication of semiconductive devices.

The electrical characteristics of semiconductive material, such as, for example, silicon and germanium, are largely determined by small traces of impurities or slight mechanical defects which are present on the surface or within the bodies of the materials. A pure crystal of silicon or germanium is made up of a cubic lattice in which each atom has four valence electrons, all of which are bound in the lattice. The presence of what is termed "significant" impurities disrupts the lattice structure. These impurities are of two different types; those designated "donor" impurities, which, upon replacing an atom in a crystal lattice, supply more than the four needed electrons, and those designated "acceptor" impurities, which supply less than the needed four electrons. The former type supplies unbonded electrons, which serve as negative mobile charge carriers, and the latter, electron deficiencies or "holes," which serve as positive mobile charge carriers. A semiconducting material in which conduction by "holes" normally occurs is identified as P-type whereas the type in which the principal conduction occurs by electrons is identified as N-type.

At the present time, semiconductive material which is utilized in the production of semiconductive devices undergoes a purifying or refining process, which is designed to remove unwanted impurity materials from the semiconductive material before any attempt is made to introduce the desired "significant" impurities, which yield the aforementioned electrical characteristics. Various methods are now known which look toward the accomplishment of this end, among which the most commonly used may be described as a "zone refining" or "zone melting" process. In the foregoing methods, a bar or rod of semiconductor material is placed into a suitable container, and portions or zones of liquid material are established within the solid bar of semiconductor material, and then subsequently caused to move along the length of the bar to redistribute the impurity materials contained therein. However, these prior art procedures require that the bar of semiconductor material be contained in some form of crucible or container which exposes the bar to the danger of absorbing or picking up undesired impurities from the container itself during the refining process. In other words, contamination introduced by the container in which the semiconductor material is held works against and tends to often defeat the purpose of the purifying procedure.

In accordance with the present invention, a unique method of purifying a body of semiconductive material to remove undesired impurity ingredients is provided in which the bar to be purified makes no physical contact whatsoever with the crucible or container in which the process is being performed. Local regions of melted material are established in the body by utilizing coils which inductively heat the body to establish the molten zone, and further prevent the molten zone from spilling out over the edges of the solid portion. The coils provided for heating and levitating the semiconductive body are energized at two different frequencies; one of which

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is considerably greater in magnitude than the other. The higher frequency essentially does most of the melting, while the lower frequency provides magnetic forces which restrain the molten zone from collapsing over the edges of the bar. Thus, the molten zone may be established in the solid semiconductor body and restrained therein without any physical contact with a crucible or container. Relative movement between the body and the coils provides for moving the molten region along the length of the semiconductor bar in order to redistribute the impurities therein in accordance with established theory.

As is well known, this redistribution of impurities results in a net transfer of impurity material toward the end of the body in the direction of travel of the molten zone. Since the impurity content in the body has a greater affinity for the molten phase than for the solid phase, impurity materials are picked up in the molten region and thus transferred to one end of the body, leaving purified material along the length of the refrozen body which has been traversed by the molten zone or zones. This relationship is usually expressed in terms of the distribution coefficient $k$, defined as the ratio of the solute concentration in the solid freezing-out of the molten zone to that in the liquid in the zone. In one form, this relationship may be expressed by the formula

$$k=\frac{C_S}{C_L}$$

where

$k$ is the distribution coefficient,
$C_S$ is the concentration of impurity in the solid, and
$C_L$ is the concentration of impurity in the liquid.

The present invention will be better understood as the following description proceeds taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a sectional view of apparatus which may be utilized in carrying out the principles of the present invention;

FIG. 2 is a sectional view showing an enlargement of the molten zone established in the body of fusible material;

FIG. 3 is a cross-sectional view of a further embodiment of the invention in which the molten zone traverses the body horizontally rather than vertically;

FIG. 4 is a view taken along the line 4—4 of FIG. 3; and

FIG. 5 is a view similar to that of FIG. 1, but in which a plurality of molten zones are utilized.

Referring now to the drawing, and more particularly to FIG. 1 thereof, there is shown at **10** a tube or container, which may be quartz, for example, and which is provided through inlet and outlet pipes **1** and **2** with a suitable inert atmosphere, such as argon, and is further tightly sealed at both ends by the stoppers **3** and **4**. A rod or bar **5** of semiconductive material to be purified, which may be germanium or silicon or any other semiconductor material suitable for use in a semiconductive device, is held at both ends by clamps **6** and **7** having support rods **8** and **9**, respectively, extending through the ends of the container **10** in air-tight fashion. The bar **5** is adapted to be moved vertically in the container **10** by movement of the supports **8** and **9**, which may be connected to any suitable actuating mechanism (not shown) for obtaining this motion. A plurality of single-turn coils **11** and **12** surround the container **10**, and are in relatively close proximity to each other. The coils **11** and **12** are energized at different frequencies from any suitable source (not shown) in order to control the action of the molten zone to be established in the semiconductive body **5**, and may be provided with cooling tubes **13** and **14** through which an appropriate coolant circulates. In the embodiment shown in FIG. 1, coil 11 may be supplied with the high frequency current, while the lower coil 12 may be supplied with the lower frequency current. Thus, electrical energy at two separate frequencies is employed in substantially the same region of the bar 5; one of which provides for most of the localized melting of the bar to create the molten region 15, while the other provides most of the electromagnetic force which acts to restrain and restrict the molten region in the bar 5 to prevent it from dripping down the sides of the bar or collapsing completely, in which case the operation would be interrupted. Preferably, each source of power supplying the coils has a separate control. In this way, adjustment may be made of the heating to a desired value, while the molten region can be held from spilling by independent variation of the low frequency source of power.

As a specific example of the process of the present invention, the localized melting of region 15 may be established by feeding the coil 11 at a frequency on the order of four megacycles per second, while the lower coil 12 may be fed at a frequency on the order of four kilocycles per second.

Both these frequency currents flowing in the coils 11 and 12 also develop an electromagnetic force acting to push the molten region 15 radially inward. However, the force produced by the four megacycle frequency is relatively weak even though the power supplied to coil 11 is sufficient to melt the localized region 15 in the bar 5. This frequency alone would not restrain the molten region in the bar. On the other hand, the lower frequency of four kilocycles has been found to produce a relatively larger electromagnetic force which tends to push the molten region 15 radially inward with considerably greater force than that due to the four megacycle frequency, even when the power input to the coil 12 is too low to produce any substantial melting. The low frequency induction thus gives rise to relatively more mechanical pushing force than the high frequency induction. In FIG. 2, the small arrows perpendicular to the magnetic fields surrounding the coils are used to illustrate that most of the restraining force is being provided by the lower frequency coil. Thus, the two different frequencies acting in the same region of the bar 5 produce the molten region 15 and restrict it within the outside edges of the original solid bar; the higher frequency provides most of the melting and little of the restraining force, while the lower frequency provides most of the restraining force, and does less of the melting. The reason that the low frequency induction gives rise to relatively more mechanical restraining force is that the magnetic field just outside the bar 5 is large even when the induced current in the bar 5 at this frequency is relatively low. The force per square centimeter is $H^2/8\pi$ dynes, where H is the strength of the field outside the bar 5. The field at a small distance inside the bar 5, say, approximately one millimeter, is practically nonexistent. The so-called skin effect is a necessary factor in this operation. At the high frequency, the same skin effect confines the current induced in the bar 5 to a thinner active layer. Hence, the effective resistance is greater for the high frequency and a smaller current can be employed to obtain a given amount of heating action.

In practice, the above-described effects are obtained by subjecting the bar 5 to frequencies having widely different values. The only limiting factors are that the lower frequency used must have a value high enough ot engender a real skin effect in the bar 5, while the higher frequency must have a value low enough to be amenable to practical operation in an inductive heating system, that is, the higher frequency should not have a value which carries it into the microwave region of the electromagnetic spectrum. By utilizing the four kilocycle and four megacycle frequency described in the above example, it was found that for a given amount of heating, the restraining force produced by the four kilocycle current was theoretically about thirty times the force at the four megacycle current. The magnetic field H created by the low frequency current was about 5.6 times that of the four megacycle current. The magnetic fields were found to have strengths of approximately sixty gauss at the high frequency and approximately three hundred gauss at the lower frequency.

After the molten zone 15 has been established, it may be caused to move along the length of the bar 5 by causing relative motion between the bar and the coils. This may be accomplished either by moving the bar vertically in the tube 10 by actuating the support rods 8 and 9, or by having the coils 11 and 12 actuated upwardly and downwardly along the length of the bar 5. As the molten region 15 thus moves, it picks up impurities in the bar 5 in accordance with previously-explained theory to purify the bar 5. In order to prevent the energy from either coil from feeding into the other coil, the electrical circuit feeding the coils may be arranged in various ways; for example, the coils 11 and 12 could be connected in parallel with a higher resistance in the four megacycle circuit than in the four kilocycle circuit. There is more inductance in the four kilocycle than in the four megacycle circuit, thus minimizing the feeding of energy of one frequency over into the circuit of the other frequency. As an alternative, appropriate filter circuits could be included in the primary of the transformers feeding the high and low frequency coils in order to substantially eliminate the undesired frequency from the particular coil. In any event, it has been found that mutual coupling effects which may occur are not effective to prevent the accomplishment of the freezing process.

Referring now to FIGS. 3 and 4, there is shown another embodiment of the present invention in which the semiconductor body 16 proceeds through an apparatus similar to that shown in FIG. 1, but does so in a horizontal direction rather than the vertical motion shown in FIG. 1. Although only a portion of the bar 16 and the coils are shown in FIG. 3, it should be understood that this embodiment is carried out in a container similar to container 10 in FIG. 1. In this embodiment, a single-turn coil 17 is used to carry the high frequency current, while a plurality of single-turn coils 18 and 19 carry the low frequency current. The molten zone 20 is thereby established in the bar 16 substantially by the coil 17 in a manner similar to that previously described, while the restraining force is substantially provided by the coils 18 and 19, also as previously set forth. The coil 17 is very thin radially and has cooling water flowing in the region between the two thin conducting rings comprising the coil. This type of geometry is preferred in order to present an edge-view to the magnetic fields of the levitating coils 18 and 19. The coils 18 and 19 are preferably provided with equal parallel currents, and are positioned so that the portions of the coils passing below the bar 16 are closer to the bar than the portions above the bar. They may also be spaced from each other along the length of the bar 16 at a distance approximately four times their spacing from the bottom of the bar. The magnetic fields produced by the coils 18 and 19 add together and result in a substantially uniform lifting force being applied to the lower edge 21 of the molten region 20, which force effectively counteracts the gravitational pull being exerted on the molten region. In the instance where the bar 16 is silicon, it may be mentioned that molten silicon is a better conductor than the solid silicon by a factor of approximately 21, thus making it feasible to act upon the molten region with currents along a very definite line of separation between the solid and liquid portions of the bar 16. In the embodiment shown in FIG 3, typical frequency values which have been found useful are five megacycle current for the coil 17 and one hundred kilocycle current for each of the coils 18 and 19. As in the vertical embodiment, the low frequency coils do most of the levitating, since stronger currents and magnetic fields are associated therewith, while the substantial portion of the melting is due to the currents induced by the coil **17**. The strong current in the bar **16**, due to the low frequency coils, encounters less resistance, since the skin depth is large; the penetration of the low frequency current beneath the surface of the bar **16** being substantially $\sqrt{50}$ times that of the high frequency current. As with the embodiment of FIG. 1, the bar **16** may be caused to move relative to the coils in order to progressively melt the solid bar at the line of demarcation between the solid and molten portions, while the trailing edge of the molten region progressively refreezes thereby resulting in the molten region passing along the length of the bar **16**. With the bar **16** in the horizontal position, a strong levitating force directly opposes the gravitational force, a desirable situation not possible when the bar is vertical.

In FIG. 5, there is shown an illustration of the instance wherein a plurality of molten zones may be established in the body of semiconductive material rather than the single zone, thus far described. FIG. 5 is identical with FIG. 1 except for the fact that additional heating and levitating coils **22**, **23**, **24** and **25** have been provided in order to establish three molten zones **15**, **26** and **27**, rather than the single molten zone **15** shown in FIG. 1. In this way, it is possible to purify the bar **5** at a rate three times the rate of the apparatus of FIG. 1, since use of three molten zones accomplishes substantially the same purification in one complete pass of the bar **5** through the coils, as would be accomplished by three complete passes of bar **5** through a single set of coils.

There has thus been provided a method of purifying a bar of semiconductive material in which a molten zone is established in the body and caused to pass along the length of the body in a single direction while the body makes no contact with any contaminating substance. Due to the use of levitating forces, it is also now possible to purify larger volumes of material in a given time, since the molten region may be established in rods or bars having greater cross-sectional dimensions, that is, on the order of an inch or more without spilling the molten region out of the bar. In this way, the applicant has been able to produce semiconductive material for subsequent use in semiconductive devices, which material has substantially higher purity than heretofore attainable, and is produced in more economical fashion.

Although certain exemplary frequencies have been described, it should be understood that other values could equally as well be utilized to accomplish the same object. To this end, it has been found that the difference ratios may vary from on the order of 10 to 1 all the way up to the order of 1,000 to 1, depending upon the particular material to be purified.

Although there have been described what are considered to be preferred embodiments of the present invention, various adaptations and modifications thereof may be made without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. The method of redistributing the ingredients in a body of fusible material, said method comprising subjecting said body to electrical energy of at least two different frequencies to establish a molten region therein and to substantially restrict said molten region therein, and progressively moving said molten region along said body.

2. The method of redistributing the ingredients in a body of fusible material, said method comprising inductively applying electrical energy of at least two different frequencies to said body to establish a molten region therein and to cause said molten region to substantially remain within the original contour of said body, and progressively moving said molten region along said body.

3. The method of redistributing the ingredients in a body of fusible material, said method comprising subjecting said body to electrical energy of a first frequency to substantially establish a molten region therein, subjecting said body to electrical energy of a second frequency to restrain said molten region, said frequencies having a difference ratio effective to provide most of the melting by one of said frequencies and most of the restraining by the other of said frequencies, and progressively moving said molten region along said body.

4. The method of redistributing the ingredients in a body of fusible material, said method comprising subjecting said body to electrical energy of at least two different frequencies to establish a molten region therein, levitating said molten region with respect to said body, and progressively melting and refreezing portions of said body contiguous with the boundaries of said levitated molten region thereby causing said region to traverse said body.

5. The method of redistributing the ingredients in a body of fusible material, said method comprising subjecting said body to electrical energy of at least two different frequencies, one of said frequencies being on the order of 4,000 cycles per second, and the other of said frequencies being on the order of 4,000,000 cycles per second whereby a molten region is established in said body and levitated therein, and progressively moving said molten region along said body.

6. The method of treating a body of semiconductive material, said method comprising subjecting a body of semiconductive material having impurity ingredients therein to electrical energy of at least two different frequencies to establish a molten region therein and to confine said molten region in said body, and progressively moving said molten region along the length of said body.

7. The method of treating a body of semiconductive material, said method comprising subjecting a limited region of said body to electrical energy of at least two different frequencies to cause said region to become molten and to substantially restrict said molten region, and progressively moving said molten region along said body.

8. The method of redistributing the ingredients in a body of fusible material, said method comprising subjecting said body to electrical energy of at least two different frequencies to establish a molten region therein and to substantially restrict said molten region therein, one of said frequencies being relatively high and the other of said frequencies being relatively low when compared to each other, and progressively moving said molten region along said body.

9. The method of treating a body of semiconductive material, said method comprising subjecting a body of semiconductive material having impurity ingredients therein to electrical energy of at least two different frequencies to establish a molten region therein and to confine said molten region in said body, and progressively melting and refreezing portions of said body contiguous with the boundaries of said molten region thereby causing said region to traverse said body.

10. The method of redistributing the ingredients in the body of fusible material, said method comprising subjecting said body to electrical energy of at least two different frequencies, said frequencies having ratio differences ranging from the order of 10 to 1 to the order of 1,000 to 1, whereby a molten region is established in said body and levitated in said body, and progressively moving said molten region along said body.

11. The method of treating a body of semiconductive material, said method comprising subjecting a body of semiconductive material having impurity ingredients therein to electrical energy of at least two different frequencies, said frequencies having ratio differences rang-

ing from the order of 10 to 1 to the order of 1,000 to 1, whereby a molten region is established in said body and levitated in said body, and progressively moving said molten region along said body.

12. The method of continuously treating a body of fusible material, said method comprising subjecting a body of fusible material to electrical energy of at least two different frequencies to establish a molten region therein and to confine said molten region in said body, and progressive melting and refreezing portions of said body contiguous with the boundaries of said molten region thereby causing said region to traverse said body.

13. The method of continuously treating a body of fusible material, said method comprising subjecting a body of fusible material to electrical energy of at least two different frequencies, said frequencies having ratio differences ranging from the order to 10 to 1 to the order of 1,000 to 1 whereby a molten region is established in said body and levitated in said body, and progressively moving said molten region along said body.

14. The method of continuously treating a rod of metal, said method comprising subjecting said rod to electrical energy of a first frequency to substantially establish a molten region in a portion of said rod, subjecting said rod to electrical energy of a second lower frequency to restrain said molten region, said frequencies having a difference ratio effective to provide most of the melting by the first of said frequencies and most of the restraining by the second of said frequencies, and progressively moving said molten region along said body.

15. The method of heating and containing without physical contact an electrically conductive material, comprising subjecting said material to a first frequency to heat said material and subjecting said material to a second lower frequency to contain said material, said frequencies having a difference ratio effective to provide most of the heating by the first of said frequencies and most of the containing by the second of said frequencies.

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