

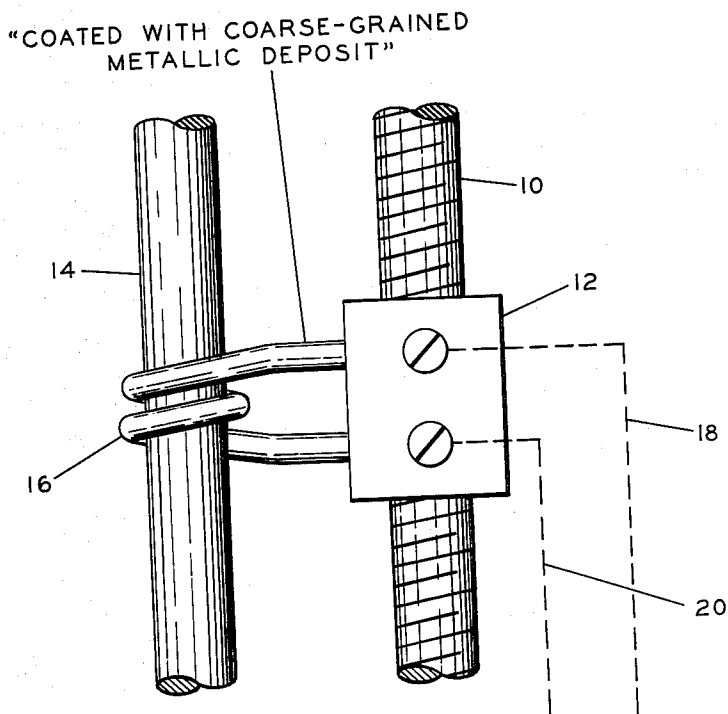
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COATED INDUCTION HEATING COIL FOR ZONE REFINING APPARATUS

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COATED INDUCTION HEATING COIL FOR ZONE REFINING APPARATUS

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This invention relates to apparatus for processing semiconductor materials and more particularly relates to an improved inductive heating element for zone refining apparatus.

Zone refining apparatus is employed in the semiconductor industry to purify or convert to a single crystal a rod or the like of semiconductor material such as silicon. To effect heating of the material being zone refined, the apparatus normally embodies an inductive heating element comprising a coil which is designed to surround a body of semiconductor material and to heat a small segment of the material by induced currents resulting from a flow of radio frequency (RF) current through the coil. Since most if not all semiconductor materials have a substantial vapor pressure at their melting points, some of a semiconductor material being zone refined normally vaporizes and, unless isolated therefrom, condenses upon the inductive heating element. This would not be detrimental except that the condensed semiconductor material tends to flake from the heating element and to be retained largely in the vicinity of the melted segment of the body of the semiconductor material by the magnetic force field created by the RF coil. Frequently the flakes originating from the heating element re-enter the body of semiconductor material being zone refined near the liquid-solid interface and provide nuclei for crystallization. Thus, when one is endeavoring to transform the body of semiconductor material into a single crystal, the crystallization nuclei provided by the flakes of material re-entering the body of semiconductor material from the heating element prevent the obtaining of the desired result and the body of semiconductor material remains a polycrystalline mass.

It has now been found in accordance with this invention that a coil with a reduced tendency to release particles or flakes of semiconductor material is provided by forming a coil of an electrically conductive base material, and thereafter disposing upon an area of the coil upon which condensation of semiconductor material normally occurs a firmly adherent coarse-grained deposit of an electrically conductive material. In accordance with a preferred embodiment of the invention, adherence of the coarse-grained deposit to the base material is strengthened by superimposing upon the coarse-grained deposit a fine-grained deposit of an electrically conductive material so that the area of contact of the grains of the first deposit with the base material is effectively increased without destroying the coarse-grained nature of the surface of the heating element.

A heating element in accordance with this invention can be employed with any conventional type of zone refining apparatus, but the new design of heating element is most advantageously employed in vacuum float zone refining apparatus. This is because it is in this type of apparatus that deposits of semiconductor material upon the heating element cause the greatest difficulty. Difficulty is particularly prevalent with this type of apparatus when it is employed for zone refining silicon of the "n" conductivity type since with this material it is necessary, in order to minimize evaporation of the dopant, that single crystal material be produced in a minimum number of zone passes.

With reference to the attached drawing there is illustrated a portion of a zone refining apparatus utilizing an improved coil in accordance with this invention. The

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reference numeral 10 indicates a rotating, threaded support rod upon which is mounted, in threaded engagement therewith, a coil holder block 12. The block 12 is prevented by any suitable means, not illustrated, from rotating with the support rod 10 so that upon rotation of the rod 10 the holder 12 moves upwardly or downwardly depending upon the direction of rotation of the support rod.

Spaced from support rod 10 and extending generally parallel thereto is a rod of semiconductor material 14 which is to be zone refined. The rod is held at one or both ends by conventional support means, not illustrated, with provision normally being made for rotation of at least one of the end support means so that at least a portion of the rod of semiconductor material 14 is rotated about its longitudinal axis during zone refining.

Carried by support member 12 and extending around the rod of semiconductor material 14 is a heating element comprising a coil 16. The coil 16, which is electrically insulated from the support 12, is connected to a suitable source of RF current through leads 18 and 20 and is designed to melt a thin section of the rod 14 intermediate the two ends of the rod. As shown in the drawing, the surfaces of the coil 16 are at least partially covered with granular metallic material so that flakes of condensed semiconductor material are only infrequently released from the surfaces of the coil.

In operation a polycrystalline rod of semiconductor material is mounted in the apparatus and coil 16 is positioned near the lower extremity of the rod of semiconductor material. The coil 16 is then activated by the passage of RF current therethrough and support rod 10 is slowly rotated so that a molten zone first generated at or near the lower end of the semiconductor material gradually transverses substantially its length. At the start of the first or subsequent zone passage, it is customary to fuse the rod of semiconductor material at the lower extremity to a seed crystal so that the upward movement of the zone results in the rod of polycrystalline semiconductor material being transformed into a single crystal. The rod of single crystal semiconductor material is then sliced and employed in the fabrication of electronic devices.

A coil base used in the manufacture of a heating element for a zone refiner in accordance with this invention can correspond in configuration and construction to a conventional coil for any particular type of zone refining apparatus with which it is to be employed. In most instances, the base coil can suitably comprise a tubular element containing from one to ten turns in the form of a spiral or helix designed to closely surround a rod of semiconductor material. At least the outer surface of the coil should be formed of a material capable of readily conducting an RF current with silver being the preferred material. In most instances, the base coil will be chemically uniform in cross section but if desired the base coil can have an exterior surface of a metal such as silver supported upon a different metal or material since in the conduction of RF currents the chemical nature of the surface layers of the conductor largely determines the conductivity characteristic of the conductor. In place of silver one can employ any material which is a satisfactory RF conductor and which does not result in undesirable contamination of the semiconductor material being zone refined, and examples of other suitable coil base materials include copper, gold, and iron in some instances.

The coarse-grained deposit which is placed upon the base coil in accordance with this invention can be of the same or different material as that of the base, but preferably comprises a metal which is capable of readily conducting RF currents since accepted theory is that RF currents are conducted largely in the surface layers of a

conductor. Further, the deposit is preferably one that will not result in the vaporization of impurities which objectionably contaminate the semiconductor material being zone refined. Because of these considerations, the preferred material for forming the coarse-grained deposit in most instances is elemental silver, with examples of other suitable metals being gold and copper. The coarse-grained deposit can be made by any suitable technique with the two preferred techniques comprising electroplating and flame spraying. For small scale production, electroplating is usually most convenient. One can suitably employ any conventional electroplating procedure known to result in a coarse-grained deposit and, for example, for obtaining a coarse deposit of silver can plate from silver nitrate solution, or for producing a coarse deposit of copper one can suitably employ a copper sulfate solution. It will be understood, however, that in so far as the present invention is concerned, it is the nature of the deposit that is of primary importance and not the procedure employed for producing the same.

The mean grain size of the coarse-grained deposit can vary within wide limits, but is preferably such that the deposit has an obvious grainy nature when viewed through even a low power magnifying device. In other words, for most applications the coarse-grained deposit preferably has a mean grain size of from about 10 to 50 microns and should in almost all instances have a mean grain size ranging from about 5 to 200 microns. The range of grain sizes in the coarse-grained deposit is of little importance and, in fact, can in some instances be advantageously quite large since the smaller grains aid in anchoring the larger grains to the metallic substrate upon which the deposit is made. Satisfactory results can be obtained when the range of grain sizes extends from 200 microns to submicroscopic as long as the deposit has a mean grain size within the range specified above.

The coarse-grained deposit placed upon the metallic coil substrate in accordance with this invention can be of any desired thickness, but for most applications has a maximum thickness not appreciably greater than the maximum grain size of the deposit so that base metal is visible through the deposit. This makes it possible to more readily anchor the deposit to the substrate. This, however, is merely a matter of convenience and satisfactory results can be obtained with an extremely thick deposit if sufficient care is exercised in anchoring it to the substrate, and if the deposit is not so thick that it necessitates undesirably wide spacing between turns of the coil to prevent shorting. In most applications, however, it is seldom advantageous for the coarse-grained deposit to have a maximum thickness greater than about 200 microns.

Substantially all procedures for forming coarse-grained deposits upon a metallic substrate result in a deposit which is so loosely adherent that it can be readily at least partially brushed off by a soft toothbrush or the like, and for best results in accordance with this invention the coarse-grained deposit should be so firmly adherent that it is not appreciably removed by one or two strokes with such a brush. In other words, it is normally necessary subsequent to formation of the coarse-grained deposit to further process the coil to secure better adhesion of the coarse-grained deposit. A preferred procedure for effecting this result is to superimpose a fine-grained metallic deposit which effectively increases the area of contact of the larger grains in the first deposit with the metal substrate. Except for its grain size, the second deposit can be generally similar in nature to the first and, similarly, can be formed of any suitable material which is readily capable of conducting an RF current. Silver is preferred with examples of other suitable materials including gold and copper. The fine-grained deposit can be applied by a vaporization technique or any other suitable means, but is preferably applied by electroplating. Procedures for electroplating fine-grained de-

posits upon metal substrates are well known in the art and any such well known procedure is suitable. When the fine-grained deposit is to be formed of silver, a preferred procedure for electroplating comprises the use of an aqueous solution of silver cyanide. The fine-grained deposit can suitably be of almost any desired thickness provided, however, that it should not be so thick that it obscures the coarse-grained nature of the deposit upon which it is superimposed, and provided it is of sufficient thickness to accomplish the desired result of firmly anchoring the coarse-grained deposit to the underlying substrate. In most instances, the fine-grained deposit is preferably from about 2 to 15 microns in thickness and has a mean grain size not in excess of about 5 to 10 microns and preferably not in excess of about 3 microns.

The invention will now be more specifically illustrated by the following examples:

Example 1

In a suitable container there is placed 10 parts by weight of silver nitrate which is then dissolved in about 400 parts by volume of doubly distilled water. A clean, sand blasted, zone refiner coil formed from a tube of pure silver is then positioned in the bath and is connected to the negative terminal of a source of direct current. An anode, preferably formed from pure silver rod stock, is then inserted into the solution and is preferably disposed such that it extends axially through the center of the coil. The silver anode is then connected through an ammeter to the positive terminal of the source of D.C. Current is then passed through the solution at the rate of 30 to 140 milliamperes for a total of 3 to 4 minutes. The coil is then rinsed in doubly distilled water with care being exercised not to dislodge the coarse-grained deposit resulting from electroplating in the silver nitrate solution.

A zone refiner coil having a preliminary coarse-grained silver deposit applied as above is immersed in a container containing 10 parts by weight of silver cyanide, 10 parts by weight of sodium cyanide and 10 parts by weight of potassium perchlorate and water to make to 400 parts by volume and is connected to the positive terminal of a source of D.C. current as above. A silver anode is introduced axially of the coil and current is passed through the solution for about 3 minutes at the level of 20 to 50 milliamperes. The coil is then thoroughly rinsed in doubly distilled water and dried with acetone. This second plating operation results in the coarse-grained deposit having superimposed thereupon a very fine-grained deposit so that the coarse-grained deposit becomes firmly anchored to the silver coil to the extent that it cannot readily be removed by 1 or 2 strokes of a soft brush.

The coil containing the superimposed fine-grained deposit of elemental silver as prepared above is placed in the coil holder of a Siemens vacuum zone refiner and is employed in an otherwise conventional manner for zone refining silicon. It is found that the number of rods of semiconductor material transformed into single crystal silicon by less than 4 zone passes is normally increased by over 300% as compared to the use of a silver coil having a conventional mirror smooth surface finish.

Example 2

A coarse-grained deposit of elemental silver is applied to a base silver zone refiner coil from silver nitrate solution as in Example 1. The coil is then washed in doubly distilled water, dried with acetone and the dried coil is then heated to a dull red heat for 2 to 10 minutes to effect anchoring of the coarse-grains of silver to the base metal. Subsequent to this sintering operation, it is found that the coarse-grained crystals are so firmly adherent that they cannot be readily removed by 1 or 2 strokes of a soft brush.

The sintered coil is mounted in a zone refiner apparatus as in Example 1 and is found to produce similarly desirable results.

The procedure for metals other than silver can be generally similar to either of the procedures specifically illustrated above except that an appropriate change is made in the chemical nature of the anode and in the salt or salts used in formulating the electroplating solution or solutions.

Having thus described my invention and several specific embodiments thereof, what I desire to claim and secure by Letters Patent is:

1. An inductive heating element for zone refining apparatus comprising a rigid coil for encircling a rod of semiconductor material in a zone refining operation, said coil being formed of a base material having disposed upon at least a portion of its external surface a firmly adherent, coarse-grained deposit of a metal which is a conductor for RF current, said coarse grained deposit having a mean grain size of from 5 to 200 microns.

2. An inductive heating element according to claim 1 wherein both said base material and said deposit comprise elemental silver.

3. An inductive heating element for zone refining apparatus comprising a rigid coil for encircling a rod of semiconductor material in a zone refining operation, said coil being formed of an electrically conductive metallic base material having deposited over at least a portion of its area a coarse-grained deposit of a metal which is a conductor for RF current, said coarse grained deposit having a mean grain size of from about 5 to 200 microns, and a superimposed fine-grained deposit of a metal which is a conductor for RF current, said fine grained deposit having a mean grain size of less than 5 microns.

4. A heating element as in claim 3 wherein the mean grain size of said coarse-grained metallic deposit is from about 10 to 50 microns and the mean grain size of said fine-grained deposit is less than about 3 microns.

5. A heating element according to claim 4 wherein said coarse-grained deposit comprises crystals of metallic silver.

6. A heating element according to claim 5 wherein said base material is selected from the group consisting of copper and silver and said coarse and fine-grained deposits are in each instance metallic silver.

7. An inductive heating coil for zone refining apparatus comprising a rigid coil for encircling a rod of

semiconductor material in a zone refining operation, said coil being formed of a tube of metallic silver upon which is deposited a coarse-grained deposit of silver crystals and a superimposed fine-grained silver deposit, said coarse grained deposit having a mean grain size of from 5 to 200 microns and said fine grained silver deposit having a mean grain size not in excess of about 3 microns.

8. A heating coil as in claim 7 wherein said fine-grained silver deposit has a mean thickness of from about 2 to 15 microns.

9. An inductive heating element for zone refining apparatus comprising a rigid coil for encircling a rod of semiconductor material in a zone refining operation, said coil being formed of an electrically conductive metallic base material having deposited thereon a coarse grained firmly adhering deposit of a metal which is a conductor for RF current, said coarse grained deposit having a mean grain size of from 5 to 200 microns and said deposit having a maximum thickness not greater than about 200 microns.

10. A heating element as in claim 9 wherein said coarse grained deposit is of a metallic silver and has a mean grain size of from 10 to 50 microns.

11. An inductive heating element as in claim 10 wherein said base material is metallic silver.

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