

[54] **LIQUID PHASE CRYSTAL GROWTH APPARATUS**

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 [51] Int. Cl. B05c 3/02
 [58] Field of Search. 118/416, 500, 503, 425, 423,
 118/52-56; 117/1; 134/1; 269/296; 214/38 CB, 89;
 294/92

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[57] **ABSTRACT**

A liquid phase crystal growth apparatus designed to permit simultaneous growth upon a plurality of substrates is described. The apparatus includes a dipping head having at least one slotted channel, on at least one side, tapered to hold at least one substrate. Affixed to the dipping head by means of a rod is a dipping means which dips the head and thus the substrate into a saturated growth solution. The dipping action forces the growth solution up and over the substrate and growth is initiated thereon by lowering the temperature of the saturated growth solution.

4 Claims, 6 Drawing Figures

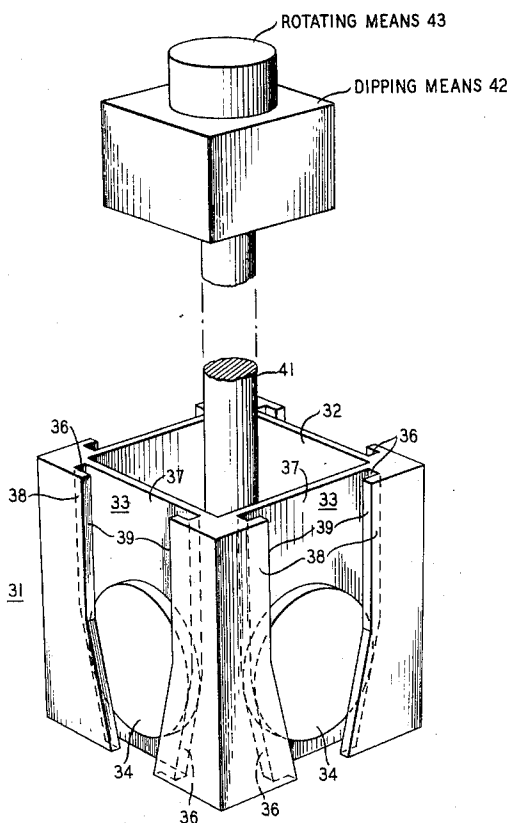
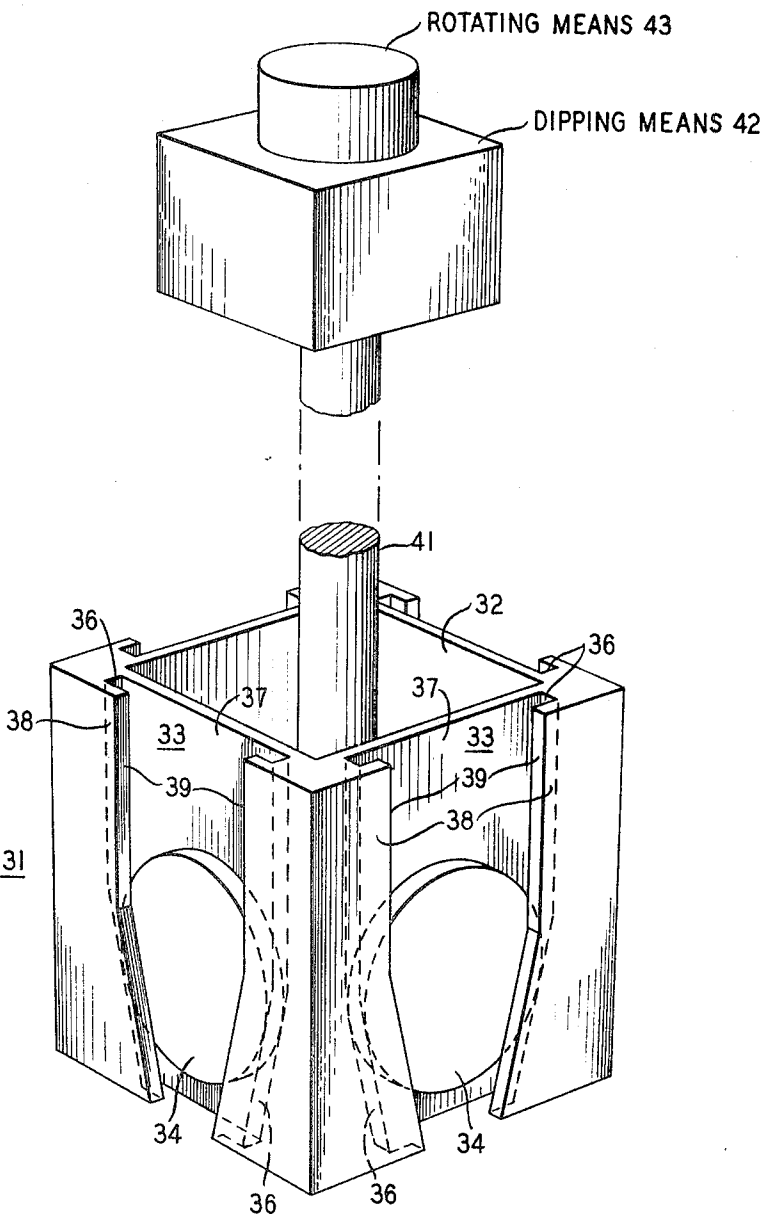


FIG. 1



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FIG. 2A

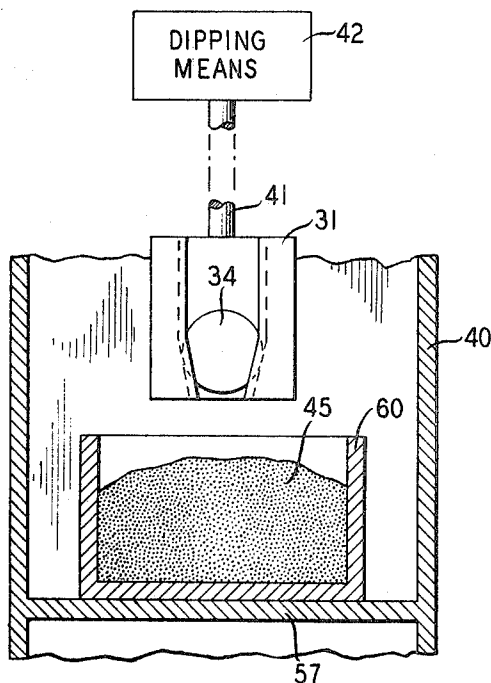


FIG. 2B

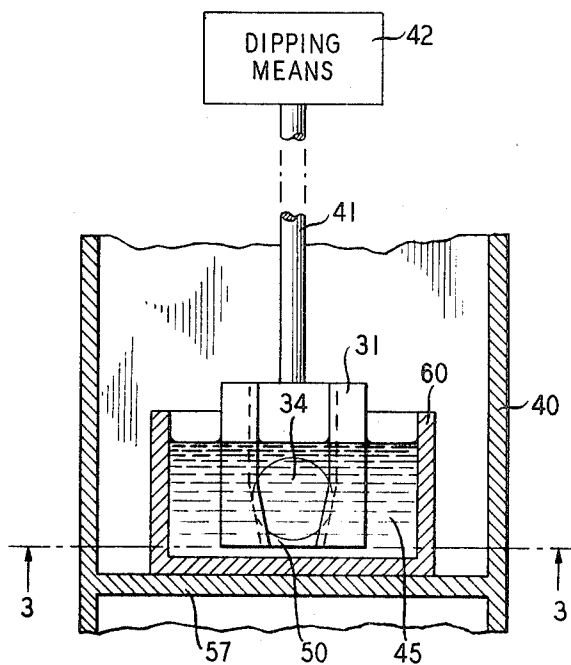


FIG. 3

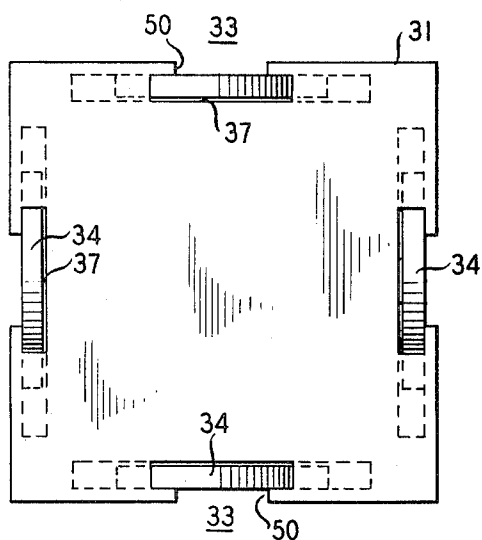


FIG. 5

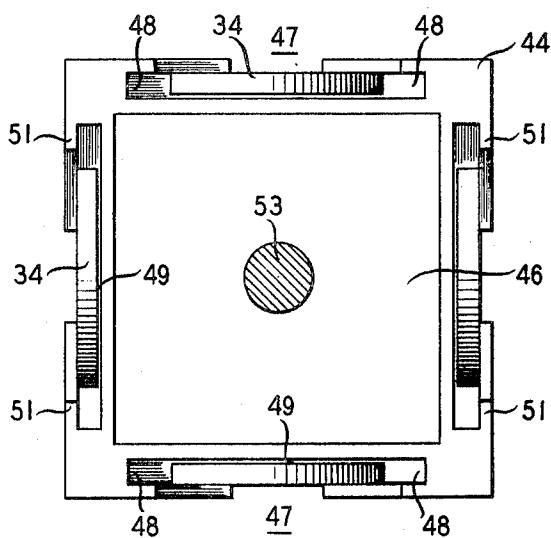
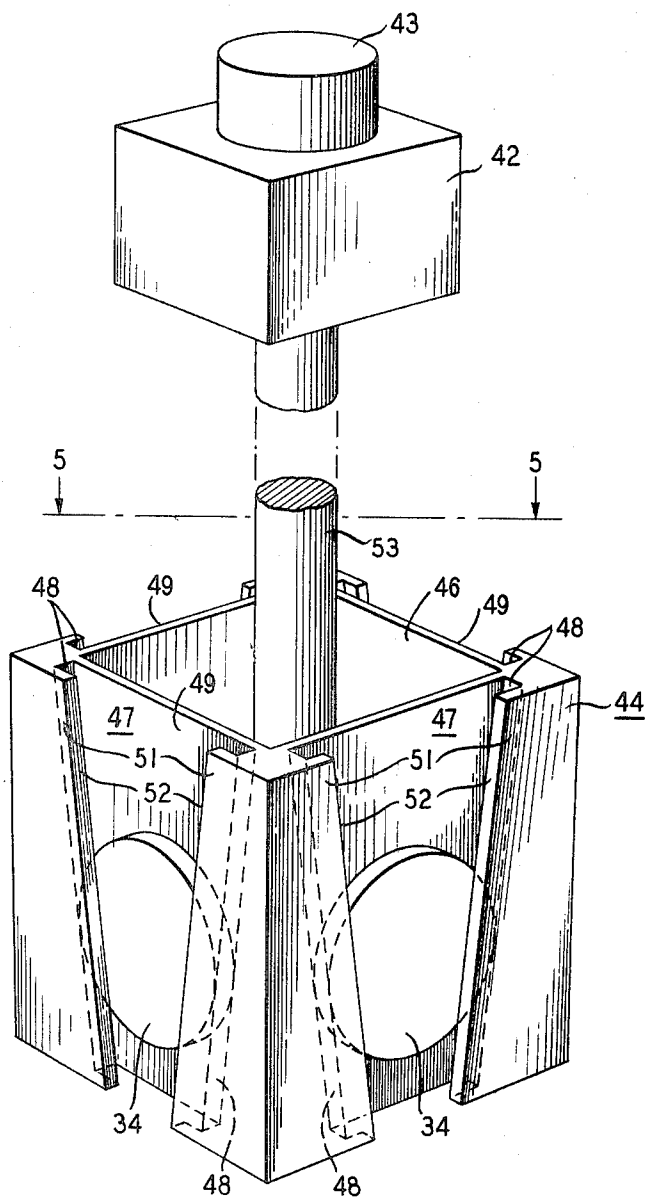


FIG. 4



LIQUID PHASE CRYSTAL GROWTH APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a liquid phase crystal growth apparatus, and more particularly to a vertical dipping apparatus for simultaneous crystal growth from the liquid phase upon a plurality of substrates.

2. Description of the Prior Art

Heretofore, crystal growth from the liquid phase has been accomplished with a multiplicity of vertical liquid phase apparatus. However, the quality of the regrown layers, especially in epitaxial growth has been adversely affected by the quality of the substrate material. Surface degradation of the substrate often occurs from the transfer of foreign particles to the substrate surface from the melt.

Since most impurities have a lower density than the usual melts employed in liquid phase crystal growth, small particles of contamination usually float atop the melt. Apparatus has been developed heretofore in which the melt is "skimmed" prior to contacting the substrate, however the clean surface required entails extreme care. It would be much easier and safer to construct an apparatus which prevents the substrate from contacting the liquid gas interface during growth thereby preventing the transfer of impurities to the substrate surface from the melt. A dipping apparatus would prevent such a transfer.

SUMMARY OF THE INVENTION

The present invention is directed to a vertical liquid phase crystal growth dipping apparatus which optimizes the growth through a dipping or plunging action whereby fresh liquid is forced to cover the substrate and floating particulates are forced above the level of the substrate.

The apparatus consists of a dipping head or holder having at least one slotted channel on at least one side of the head. The slotted channel is dovetailed at some point along its length or tapered along its entire length to hold at least one substrate. Affixed to the dipping head, by means of a rod, is a dipping means which additionally may have incorporated therein a rotating means for rotating the head and thus the substrate.

In operation, at least one suitable substrate is placed in at least one slotted channel. A bath of a suitable saturated growth solution or melt is prepared and at the desired temperature the dipping head is dipped into the growth solution. The melt or growth solution is forced up and over the substrate and growth is initiated by lowering the temperature of the saturated growth solution.

DESCRIPTION OF THE DRAWING

The present invention will be more readily understood by reference to the following drawing taken in conjunction with the detailed description, wherein:

FIG. 1 is a perspective view of the liquid phase crystal growth dipping apparatus of the invention;

FIG. 2A is a cross-sectional view of the apparatus prior to crystal growth;

FIG. 2B is a cross-sectional view of the apparatus during crystal growth;

FIG. 3 is a plan view of the apparatus taken along line 3—3 of FIG. 2B;

FIG. 4 is a perspective view of the liquid phase crystal growth dipping apparatus of the invention adapted to accommodate substrates with variable diameters; and

FIG. 5 is a plan view of the apparatus along line 5—5 of FIG. 4.

DETAILED DESCRIPTION

The present invention has been described only in terms of the epitaxial growth of GaP on substrates of GaP. However, it will be understood that such description is for purposes of exposition and not for purposes of limitation. It will be readily

appreciated that the inventive concept described is equally applicable to nonepitaxial as well as epitaxial growth and to crystal growth of nonsemiconductor materials as well as semiconductor materials. Also the inventive concept described is applicable to many combinations of substrate and melt whereby both homojunctions and heterojunctions are formed. Regarding the epitaxial growth of semiconductor materials, the materials may be selected from among group III(a)—V() compounds, group II(b)—VI(a) compounds or group IV elements of the Periodic Table of the Elements as set forth in the Mendelyev Periodic Table appearing on page B2 in the 45th edition of the *Handbook of Chemistry and Physics*, published by the Chemical Rubber Company.

With reference now to FIG. 1, there is shown the vertical crystal growth dipping apparatus of the present invention. Shown in FIG. 1 is a dipping head 31 which can be fabricated from any inert material including such materials as high purity graphite, alumina, quartz, boron nitride or any inert ceramic material. It is to be understood that although the dipping head 31 has been shown to be rectangular in shape, the inventive concept need not be restricted thereby and the head 31 may be parallelepiped or even cylindrical in shape. The head 31 has a central compartment 32 which prevents head 31 from becoming too great a heat sink as would be the case if the head 31 were solid. In the alternative, the head 31 may be entirely hollow.

Traversing the sides of head 31 are slotted channels 33 which are destined to contain at least one substrate, as for example, 34. The sides 36—36 of channel 33 are parallel to one another at the upper portion of channel 33, but taper or dovetail towards one another at the lower portion of channel 33 to define the bed 37 of channel 33. However, it is to be noted that the sides 36—36 need not necessarily be parallel to one another at the upper portion of channel 33 and the invention is not to be restricted thereby. The sides 36—36 terminate or merge into retaining walls 38—38 which both border and overlap the channel 33 to partially cover the channel 33. As shown in FIG. 1, the edges 39—39 of the retaining walls 38—38 are parallel to the sides 36—36 to which they are contiguous; however, they need not be so, and in this regard it is to be noted that the retaining walls may consist of a plurality of walls on both sides of channel 33 which may border and cover the channel only along intermittent intervals. In the alternative, there may be only one retaining wall on only one side of channel 33.

The retaining walls 38—38 are separated from the bed 37 of channel 33 by a distance sufficient to permit the free insertion of the substrate 34 into channel 33. The diameter of channel 33 and its bed 37 at the upper portion of head 31 is sufficient to permit the unrestricted passage of the substrate 34 therethrough. However, due to the dovetailing or tapering of sides 36—36 and thus bed 37, at the bottom portion of head 31, passage entirely through the channel 33 is prevented.

As illustrated in FIG. 1, there is one channel 33 extending along the vertical axis of the head 31 and containing one substrate 34. However, this is for illustrative purposes only and the invention is not to be restricted thereby. There may be a plurality of channels 33 on one, several, or all sides, which may extend in a plane parallel to the vertical axis of the head 31 or which may extend in a plane outside of the vertical axis of the head 31. Also, each channel 33 may contain one or a plurality of substrates 34.

Affixed to the dipping head 31 is a rod 41 made of the above-mentioned inert materials. It is to be understood that although the rod 41 has been shown to be affixed within compartment 32, the invention is not to be restricted thereby and the rod 41 may be affixed to the head 31 in any suitable manner. The rod 41 is in turn affixed to any standard dipping means 42 which may have incorporated therein a standard means 43 for rotating the rod 41 and thus the head 31.

In operation, a suitable substrate 34 is inserted into channel 33 and is slid along the bed 37 until the substrate 34 reaches a point in the channel 33 where the diameter of the channel 33

is smaller than the diameter of the substrate 34. At this point, the substrate 34 is loosely held between retaining walls 38—38 and bed 37.

Referring to FIG. 2A, a container 60 made of the above-mentioned inert materials is loaded with a suitable melt mixture 45. The container 60 is then placed in a standard vertical furnace 40 and positioned therein on a pedestal 57. The dipping head 31 containing substrate 34 is placed within the furnace 40 above the container 60 whereupon the container 60 is heated to the desired growth temperature to form a melt 45. As shown in FIG. 2B, at the desired temperature, the dipping means 42 lowers rod 41 to immerse the dipping head 31 into the melt 45. As illustrated in FIGS. 2B and 3, when the head 31 is immersed in the melt 45, the melt 45 passes through the lower end 50 of the channel 33 and passes over the substrate 34 and forces the substrate 34 firmly against the bed 37 of channel 33, thereby preventing crystal growth on the surface of the substrate 34 contacting the bed 37. The temperature of the melt 45 is lowered at a controlled rate to initiate crystal growth.

FIG. 4 illustrates an alternative embodiment of the present invention which embodiment can be used with substrates having varying diameters. In FIG. 4 there is shown a dipping head 44 which can be fabricated from the above-mentioned inert materials. The head 44 has a central compartment 46 in order to prevent the head 44 from being too great a heat sink. Traversing the sides of head 42 are slotted channels 47 destined to contain at least one substrate 34.

As illustrated in FIGS. 4 and 5 the sides 48—48 of channel 47 taper toward one another along their entire length to define the bed 49 of channel 47. Again, the sides 48—48 terminate or merge into retaining walls 51—51 which both border and overlap the channel 47 to partially cover the channel 47. Again it should be pointed out that although the edges 52—52 of the retaining walls 51—51 have been shown to be parallel to the sides 48—48 to which they are contiguous, the inventive embodiment need not be so restricted. Also, as pointed out previously, the retaining walls may consist of a plurality of walls which do not border and cover the channel 47 along its entire length and in the alternative there may be only one retaining wall on only one side of channel 47.

The retaining walls 51—51 are separated from bed 49 by a distance sufficient to permit the free insertion of the substrate 34 into channel 47. Channel 47 has a maximum diameter at the top of head 44 and a minimum diameter at the bottom of head 44 thereby preventing the passage of the substrate 34 through the channel 47. However, due to the tapered sides 48—48 of channel 47, substrates 34 having varying diameters may be inserted into channel 47.

Again it should be noted that the embodiment illustrated in FIG. 4 is for illustrative purposes only and that there may be a plurality of channels on one, several or all sides, which may extend in a plane parallel to the vertical axis of the head 44 or in a plane outside the vertical axis of head 44. Also each channel 47 may contain one or a plurality of substrates 34 which may be of the same or varying diameters.

Affixed to head 44 is a rod 53 made of the above-mentioned inert materials. Again the rod 53 may be affixed to head 44 in any suitable position. Rod 53 is affixed to a standard dipping means 42 which may have incorporated therein a standard rotating means 56 for rotating rod 53 and thus head 44.

Referring now to an exemplary technique, a suitable N-type GaP substrate material grown by standard liquid encapsulated pulling techniques was cut to size, lapped and cleaned in accordance with conventional techniques. A predetermined number of lapped and cleaned GaP substrates 34 were inserted into the channels 33 of a quartz dipping head 31 similar to that shown in FIG. 1.

A gallium-GaP-Ga₂Te₃ melt mixture was prepared by first weighing out 68 mole percent of high purity gallium, 2.6 mole percent of high purity polycrystalline gallium phosphide, and 0.004 mole percent Ga₂Te₃ obtained from commercial sources. Utilizing apparatus similar to that shown in FIG. 2, the melt mixture 45 was added to a quartz container 60. The amount of GaP employed was such as to form a saturated gallium solution at the desired growth temperature of 1,030° C.

The container 60 was placed upon a pedestal 57 in the constant temperature zone of a standard vertical furnace 40. The dipping head 31 was inserted in the furnace 40 in direct overhead alignment with container 60 and melt mixture 45. The furnace 40 was then flushed with nitrogen admitted to the system and removed therefrom through suitable inlet and outlet means (not shown). After flushing with nitrogen, hydrogen was allowed to flow into the furnace 40 and the temperature of the furnace 40 was maintained at 800° C. for a sufficient period of time to adequately purge the system.

Referring to FIG. 2B, the container 60 was heated to a temperature of 1,030° C., thereby resulting in the formation of the saturated gallium growth melt 45. The dipping head 31 was lowered by a standard dipping means 42, affixed to head 31 by quartz rod 41, to a point just above the container 60 in the constant temperature zone of the furnace 40. After thermal equilibrium was established between the container 60, the melt 45 and the head 31 containing substrates 34, the dipping means 42 lowered head 31 and thus substrates 34 into melt 45. The flow of the melt 45 up channel 33 covered the substrates 34 and forced the substrates 34 flush against the bed 37 of the channel 33.

After the substrates 34 were completely covered by the saturated growth melt 45, the furnace was cooled at a constant cooling rate of approximately 2° per minute, by means of a controlled cooling program. During this cooling cycle, precipitation of N-type GaP from the melt 45 occurred. The head 31 was immersed in the melt 45, during the cooling cycle, for 30 minutes, whereupon the dipping means 42 raised the head 31 and the substrates 34 out of melt 45 to terminate the growth. A 3μ layer of N-type GaP was deposited on substrate 34.

What is claimed is:

1. A liquid phase crystal growth apparatus which comprises:
 - a. a dipping head having at least one channel traversing at least one side of the head, said channel having sides, which taper towards one another beginning at some point along the length of the channel and terminating at some point along the length of the channel, to define the bed of said channel, said channel being bordered by and partially covered by at least one retaining wall, for loosely holding at least one substrate between the retaining wall and the bed of said channel;
 - b. dipping means affixed to said head to sequentially (1) lower and immerse said head into a saturated growth melt, (2) force the substrate firmly against said bed and (3) raise the head out of said saturated melt; and
 - c. a tank containing said saturated growth melt and disposed in operative relationship to said dipping head.
2. The apparatus as defined in claim 1 wherein the sides of said channel are parallel to one another at the upper portion of said channel and taper toward one another at the bottom portion of said channel.
3. The apparatus as defined in claim 1 wherein the sides of said channel taper towards one another along their entire length.
4. The apparatus as defined in claim 1 which further comprises a rotating means for rotating said head in said saturated melt.

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