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METHOD OF PRODUCING DIFFERENTIATED DOPING ZONES IN SEMICONDUCTOR CRYSTALS

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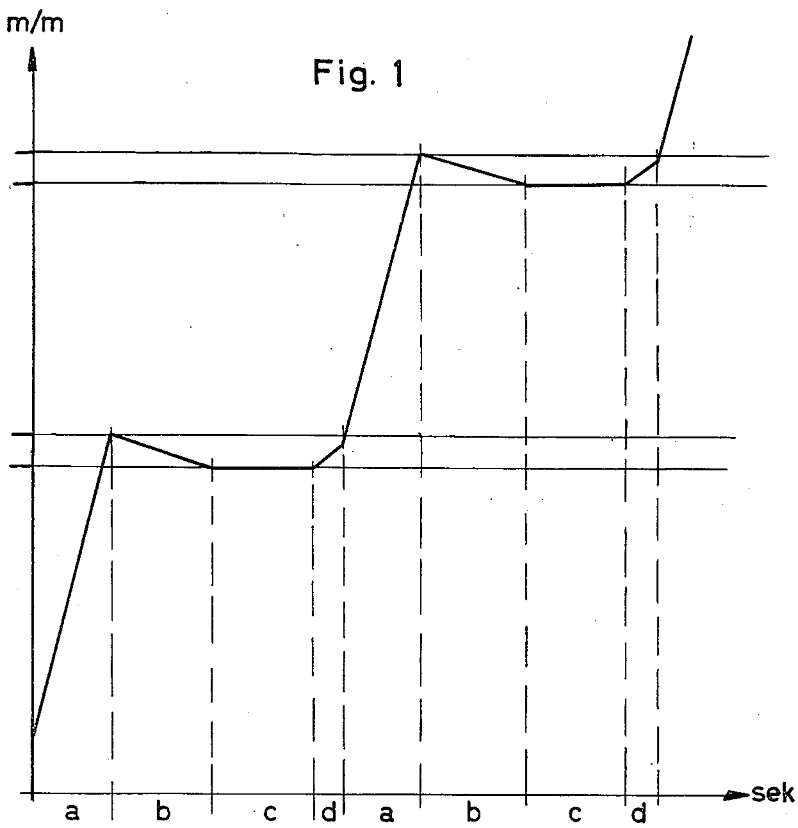
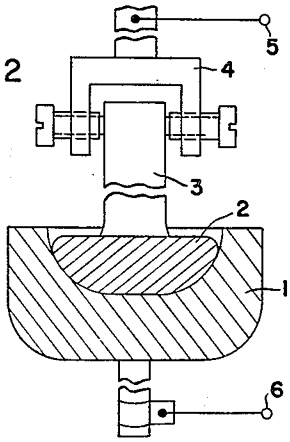


Fig. 1

Fig. 2



Inventors.
Heinz Dorendorf, &,
Heinz Henker.
By. [signature] Atty.

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METHOD OF PRODUCING DIFFERENTIATED DOPING ZONES IN SEMICONDUCTOR CRYSTALS

Heinz Dorendorf and Heinz Henker, Munich, Germany, assignors to Siemens & Halske Aktiengesellschaft, Munich and Berlin, Germany, a corporation of Germany

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This invention is concerned with a method of producing differentiated doping or impurity zones in semiconductor crystals by drawing from a melt.

It is known that zones of different conduction type can be produced in semiconductor crystals by drawing a crystal from a melt with different speed provided that there is in the melt a mixture of acceptor and donator substance (Rate Growth Method, according to papers respectively by Hall and by Slichter and Kolb, Phys. Rev., vol. 88, No. 1, 1952, page 139; and vol. 90, 1953, No. 5, pages 987 to 988). Due to different alterations, of the distribution coefficients of the donator and acceptor, with the drawing speed, one of the doping substances is upon crystallization built into the crystal preferentially at fast drawing speed and the other at slow drawing speed. It is to be observed in the corresponding production of p-n transitions that both doping substances should be present in the melt in a predetermined favorable ratio and that optimal drawing speeds are applied. In the production according to this method, of p-n transitions in germanium, doping mixtures of antimony and gallium on the one hand and antimony and indium on the other hand have been found favorable. The most favorable drawing speeds and mixture ratios are as such known. An alteration of the temperature of the melt is effected with the alteration of the drawing speed so as to keep the crystal cross-section always constant. In the investigations underlying the invention it was found disadvantageous that the solidification front or area, that is, the area between the solid and liquid phase of the semiconductor is spatially shifted, especially upon transition from fast to slow drawing. The result is an indistinctness in the p-n transition produced during this shifting.

This disadvantage is by the invention avoided, and sharply defined p-n or other transitions are produced, that is, transitions, for example, from one to another conduction type within extremely narrow zones, by interposing between changes of drawing speeds, at least upon changing from fast to slow drawing, a brief interval of negative drawing speed (reversal of drawing direction=part of crystal dipped into the melt) and/or of zero drawing speed (drawing interrupted=crystal held stationary) to effect re-melting of part of the solidified crystal at the end thereof which is in contact with the melt. During this interval, the simultaneously changed and, especially the increased temperature incident to change from fast to slow drawing, can spread uniformly in the melt and in the vicinity of the solidification front, whereby the latter is caused to return to its original spatial position, melting off a short piece of the crystal which has already solidified.

In accordance with another feature of the invention, further intervals of other drawing speeds are interposed in the drawing procedure. There is especially a mean drawing speed interposed between slow and fast drawing at which donators and acceptors are in identical manner built in the crystal produced so that an intrinsic range appears between a p- and an n-doped crystal piece. In this manner can be produced for example n-p-i-n or p-n-i-p transitors.

In accordance with a further feature and object of the invention, steady changes are at suitable points of the drawing procedure introduced between the drawing speeds, whereby zones of differentiated doping are produced within the p- and n-regions, respectively. It is in this manner possible to introduce for example at an n-p-n transition in the mean p-region a steady transition of high to low doping, thereby producing an arrangement that has become known under the name of drift transistor.

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During the intervals of mean drawing speed or steadily altered drawing speed there are to be interposed corresponding alterations of the temperature to a mean temperature or a respectively increasing or steadily decreasing temperature. Also, between the interposed intervals in mean or steadily varying drawing speeds, waiting intervals with zero drawing speed or even negative drawing speed may be interposed, so that a new temperature compensation with new crystallization equilibrium can always result.

In accordance with a particular embodiment of the invention, the temperature at the solidification front, that is, at the border-line between the solidified crystal and the liquid phase of the melt is respectively altered or controlled so as to produce by alteration of the current strength and/or the current direction of a current flowing through the crystal and the melt respectively a heating or cooling based upon the Peltier effect. A heating or cooling based on the Peltier effect takes place, as is known, at the border surfaces between different contact materials upon current flow dependent upon the direction of the current and current strength. Investigations underlying the invention have shown that a corresponding cooling and heating also occurs at the border surface between solid and liquid phase of the identical conductive material, specially semiconductor material. Since this heating effect occurs in imediate vicinity of the solid-liquid interphase, it is especially adapted to affect and to regulate the temperature conditions for the growth of the crystal upon drawing from the melt.

The influencing of the temperature by means of the Peltier effect is utilized especially in the sage-drawing during the change from slow to fast drawing speed, and particularly, either by sudden switching in of the current or better yet by reversal of the current flowing previously in opposite direction. The Joule effect does not operate in the last-noted case against the cooling. The influencing of the temperature in accordance with the invention, by utilizing the Peltier effect, may be employed either in place of or additional to the otherwise customary exterior temperature variation of the melt; in the last-noted case, the resulting temperature gradient is actually sharpened.

The above indicated and other objects and features of the invention will appear from the description which is rendered below with reference to the accompanying diagrammatic drawings in which

FIG. 1 shows drawing procedures giving examples for practicing the invention; and

FIG. 2 shows in diagrammatic manner an example of apparatus for practicing the invention.

Referring now to FIG. 1, there is shown a drawing program or procedure according to the invention for carrying out a rate growth method to produce p-n-transitions in a germanium crystal. Upon the ordinate are plotted in mm. the lengths of crystal drawn out from a melt and along the abscissa are plotted the drawing times in seconds. In addition, there are entered upon the abscissa the intervals *a*, *b*, *c*, *d*, during which the drawing is effected with different speeds. The temperatures are varied in corresponding rhythm. Especially, during the interval *a* the drawing is effected quickly at low temperature while the drawing is slow during the interval *d* at high temperature. In accordance with the invention, within the interval b, during the change from fast to slow drawing, the crystal is again slowly somewhat dipped into the melt with negative speed, that is, in reversed direction. The dipping or immersion depth amounts for example to about 1 mm. Thereupon, for an interval c which may amount up to 1 minute (but which may be omitted under some circumstances) the drawing speed may drop to zero, that is, a waiting period may be interposed during which the crystal is held stationary, to allow for compensation or equalization of temperatures in the melt, especially in the vicinity of the solidification front and to obtain a crystallization equilibrium at which the solidification front has again assumed its spatial position which it occupied during the fast drawing in the interval a. There follows slow drawing during the interval d generally up to about 10 seconds, during which the mean zone of a transistor, for example, the p-zone of an n-p-n transistor, grows. From there on there will follow a zone of fast drawing a at lowered temperature. The subsequent zones b, c, d correspond to the previously discussed similarly designated zones.

In FIG. 2, numeral **1** indicates a carbon crucible in which is disposed a germanium melt **2**. At **3** is indicated a crystal which is by means of a device **4** gradually drawn from the melt **2**. Numerals **5** and **6** indicate leads for a current flowing through the crystal and the melt during the drawing operation. The germanium melt contains additions of antimony and gallium in known amounts to operate as donator and acceptor substances. The zones of different doping are produced in accordance with the rate growth drawing, by alteration of the drawing speed of the crystal **3** by means of the drawing device **4**. The current is upon alteration of the drawing speed from slow to fast and fast to slow always reversed, that is to say, in such direction that cooling takes place upon acceleration of the drawing (crucible poled negative) and heating takes place upon slowing up of the drawing speed (crucible poled positive). At a current of about 100 amperes per qcm., there will result temperature variations of about 20° C. In addition, the temperature of the carbon crucible is in known manner altered due to the fact that the regulator device for keeping constant the melt temperature is adjusted to another temperature. Attention may also be called to the fact that it is within the scope of the invention to amplify or to weaken the temperature gradients at temperature inhomogeneities in the crystal drawing apparatus by correspondingly influencing the current by utilization of the Thomson effect. It is furthermore under some circumstances possible, especially when the semiconductor crystals are not very thick, for example, thinner than 3 mm., to separate the various dopings in accordance with the invention with varied drawing speed alone by the temperature effect, that is, without stage drawing.

The invention is not inherently limited to the example described. It is particularly possible, as previously indicated, to change the procedure according to FIG. 1 by interposing between the zones of slow and fast drawing (d and a) at least one zone of a mean drawing speed. Waiting intervals may thereby likewise be interposed always upon changing from slow to fast drawing. At some points, steady drawing speed variations may be carried out to produce steady doping gradients. It is moreover suitable to add to the melt new material stagewise between suitable drawing stages.

The invention is moreover not limited to the use of crystal drawing by drawing from a crucible; the drawing from a melt may also be carried out in accordance with a melting method without crucible, also proposed before, in which a generally vertically disposed rod, held at both ends, is effected by melting at intermediate points, whereby the melt zone is only so thin that the molten material is held together by adhesion forces, the melt zone being gradually moved through the rod. Different drawing speeds may thereby also be used, employing for example, a drawing scheme accoring to FIG. 1 (see also copending applications Ser. Nos. 409,494 and 409,420). The procedure is in accordance with the invention such that the mixture of a donator and an acceptor or more of such or different doping materials are embedded in the rodlike crystal and by different drawing speeds inhomogeneously distributed in the rod in desired manner so as to produce zones of different doping, especially p-n transitions.

The doping mixture may be introduced in the semiconductor body in different ways. For example, it may be homogeneously distributed in the entire rod-shaped semiconductor body in accordance with likewise known zone melting processes. Thereafter is carried out the separation of the donator-acceptor additions by additional drawing through the melting zone with different drawing speeds.

In accordance with a particularly suitable embodiment of the invention, the stagewise melting zone drawing is carried out in an atmosphere containing in suitable admixture the foreign constituents to be built in so that they diffuse into the melting zone from the gaseous phase through the surface. The drawing of the melting zone through the semiconductor rod may if desired be repeatedly effected so as to reinforce the doping on the one hand and to homogenize inside of a cross-section of the melting zone on the other hand. In the last-noted case, it is advisable under some circumstances to work in the last drawing operation or operations in a neutral atmosphere or in a vacuum. It may be mentioned in conclusion that the different doping may apply not only to the conduction type but also to the doping degree and to the building in of other doping means, for example, adhesion points and recombination centers, whereby the diffusion length may be affected under some circumstances. The various different dopings may be produced by the invention either alternatively or in combination. It may also be mentioned that the doping mixture may be introduced into the semiconductor substance, preferably into the melting zone, respectively in solid or liquid or atomic form and that the various doping possibilities may be suitably combined if desired.

Changes may be made within the scope and spirit of the appended claims which define what is believed to be new and desired to have protected by Letters Patent.

We claim:

1. In a process for growing semiconductor crystals in which there is maintained at least one solid-liquid interface which is caused to move with respect to the semiconductor material under treatment in combination therewith the step of passing a controlled direct current through said solid-liquid interface so as to superimpose a component of motion caused by the Peltier effect upon the moving solid-liquid interface.

2. A method according to claim 1, comprising producing the Peltier effect by passing a direct current between the crystal and the melt, polarizing the melt negatively with respect to the crystal to be drawn, to effect cooling thereof, and polarizing the melt positively with respect to the crystal, to effect heating thereof.

3. A method according to claim 2, wherein the melt contains doping substances, comprising drawing the crystal therefrom with varying drawing speed for the different building-in of the doping substances, simultaneously passing direct current through the crystal and the melt, oppositely polarizing said current with each variation of the drawing speed, whereby cooling is effected by the Peltier effect responsive to transition from slow to more rapid drawing speed, while heating is effected by the Peltier effect responsive to transition from slow to more rapid drawing speed.

4. A method according to claim 2, comprising the step of drawing the melt through the semiconductor rod as a molten zone and with varying speed.

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