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2,861,905

PROCESS FOR CONTROLLING EXCESS CARRIER CONCENTRATION IN A SEMICONDUCTOR

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This invention relates to methods for producing bodies of extrinsic semiconductive material manifesting substantially uniform conductivity characteristics within substantial portions of such bodies of a given conductivity type.

In the processing of extrinsic semiconductive materials for use in transducers such as transistors and rectifiers, the need frequently arises for such materials having a constant conductivity level. Since conductivity level in extrinsic semiconductive materials such as silicon, germanium and in binary and ternary compounds having similar characteristics is dependent in turn on the concentration level of significant impurity within such material, this need has been interpreted in terms of the requirement of uniform distribution of such significant impurity.

To meet this need, several processes have been developed. In some of these processes solid crystalline material is solidified from a melt, the volume of which decreases as material is crystallized therefrom. In such processes, the natural distribution coefficient of the significant impurity of concern, in indicating a preference for either the liquid or the solid phase, results in either an increasing or a decreasing concentration of such impurity in the melt. In such processes, it is necessary to compensate for such changing melt concentration. This has been done, for example, by varying the rate of crystal withdrawal in such manner as to, in effect, continuously vary the distribution coefficient in the direction which compensates for the changing melt composition. See for example, United States Patent 2,768,914. Other methods of compensating for such varying concentration within the melt include various mechanisms by which the material with respect to which the melt is depleted is gradually added in such amount as to exactly compensate for the amount removed through crystallization.

A second approach utilizes a melt of constant volume and of constant composition which is maintained by producing a second solid-liquid interface which advances into solid material of substantially uniform concentration at the identical rate of the freezing interface at which the crystalline body is being produced. One method of crystallizing from such a constant volume, constant composition melt, sometimes referred to as "zone leveling," is described in United States Patent 2,739,088.

The degree of success obtained in the production of a crystalline body manifesting uniform resistivity along the growth axis in any one of the above processes and in any other process utilizing a freezing solid-liquid interface is dependent upon the precision with which growth conditions may be controlled. The requirement of such precise control over growth conditions such as rate of advancement of the freezing interface, melt temperature at the interface, and stirring within the melt whether due to natural or forced convection, arises out of the existence of a discrete layer of molten material on the liquid side of the freezing interface within which all circulation of liquid material takes place exclusively by the diffusion mechanism.

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This diffusion layer, of a thickness in the growth direction to which the symbol Δ is here ascribed, is the material from which the crystalline material is actually solidified, so that the concentration of any ingredient in the solidifying material is related through the distribution coefficient not to the average melt concentration but rather to the concentration of the melt adjacent to the interface within the diffusion layer. The thickness of the diffusion layer Δ is in turn dependent upon various factors, all of which are affected by conditions of growth. Such factors include the diffusion rate of the ingredient of concern within the liquid material which varies with temperature, the rate of movement of the freezing interface, and the degree of stirring within the melt whether by natural or artificial means.

As the thickness of the diffusion layer increases in the direction of growth, the concentration of this ingredient within this layer increases in the instance of such an ingredient having a distribution coefficient less than 1, and decreases in the instance of an ingredient having a distribution coefficient greater than 1. Effectively, therefore, as the thickness of the diffusion layer increases, the concentration of such an ingredient in the layer adjacent the interface varies in such a direction as to oppose the non-uniform distribution between phases dictated by the distribution coefficient with reference to the mean melt composition even though the distribution of such an ingredient at such an interface is always that dictated by the distribution coefficient with reference to the concentration of the liquid material adjacent the interface. The virtual impossibility of measuring the concentration of the liquid at the interface and the comparative ease of measuring the concentration in the body of the melt has resulted in a definition of such distribution conditions in terms of body concentration. Since the concentration of the body of the melt varies more or less from the concentration at the interface, depending upon growth conditions, the concentration realized in the crystallizing material is not that dictated by the equilibrium distribution coefficient in terms of body concentration. This has given rise to use of so-called effective distribution coefficients which are empirically determined and which invariably compare with the equilibrium coefficient in that they are numerically closer to 1.

The variations in the value of the effective distribution coefficient relative to growth rate and stirring rate are known and advantage is taken of such variation in processes known to the art. For example, in the process known as "rate growing" an extrinsic semiconductive material containing both p-type and n-type impurity of proper amount is crystallized from a melt while varying the growth rate under conditions such that changes in conductivity type are produced. Changes in the effective coefficient are also utilized in the crystal pulling of constant resistivity sections of semiconductor materials by increasing or decreasing the rate of growth so as to offset the gradual change in composition of the melt.

The methods herein are directed to eliminating overall microscopic non-uniformity of resistivity. Such microscale fluctuations of resistivity are a serious problem, especially in transistors and diodes made by the diffusion technique, for in such cases, very irregular p-n junctions result from microscale resistivity variations in the base material.

Prior art developments directed toward eliminating concentration variations in growing crystals due to random variations in growth conditions have, for the most part, been directed toward elimination of the random variations themselves. Such developments include the use of steeper temperature gradients in the vicinity of the interface, exceedingly slow crystalline growth rates, extremely close control of temperature and cooling con-

ditions, and various special furnace configurations. The processes of this invention represent a new approach in that no special attempt is made to eliminate such random variations. In a species of this invention recognition is made of the fact that for the levels of impurity concentration involved in the usual extrinsic semiconductor system, the conductivity characteristics including the resistivity of the final crystal are dependent not upon the total amount of such impurity contained, but are dependent on the excess of such predominant impurity over any opposite conductivity type inducing material which may be present.

In essence, the processes of this invention attain the objective of uniform resistivity and uniformity of other conductivity characteristics by including in the melt from which material is being crystallized both a first significant impurity imparting the desired conductivity characteristics and a second significant impurity imparting either the same or the opposite conductivity characteristics, the second impurity being of such character and being included in such amount that random variations in growth conditions produce a variation in concentration level of both impurities so that the excess amount of impurities imparting the desired conductivity characteristics remain substantially constant in the crystallizing material. If the specific requirements set forth herein are met, these processes operate in identical fashion whether the second impurity is such as imparts the desired conductivity type or the opposite conductivity type, the excess impurity in the crystallized product in the first instance being equal to the sum concentration of the two impurities and in the second instance being equal to the difference concentration of the first impurity less the second. In this manner, assuming given growth conditions, the uniformity of resistivity of the final product may be improved several orders of magnitude over the same growth conditions as applied to a semiconductive material containing only the one impurity imparting desired conductivity type.

The processes of this invention are referred to herein as "compensation" methods. The usual system discussed herein comprises, as the major ingredient, a fusible semiconductive material such as germanium or silicon, a significant impurity imparting the desired conductivity type referred to herein as the "first significant impurity," or "first solute" and a second significant impurity or "second solute" compensating for concentration variations in the excess significant impurity, referred to herein as the "second significant impurity" or "second solute." Although the invention is described in terms of such simple ternary systems, it is to be recognized that the invention is not so limited and may contain both types of second impurities and/or any number of additional ingredients which may contribute to the desideratum of uniform resistivity or which may serve any other function.

The following discussion is in terms of two solutes, solute 1 and solute 2, one of which is an acceptor and one of which is a donor. Although the derivation differs slightly, the final equations are identical in absolute value for two acceptor or two donor solutes in accordance with this invention. The small changes involved are indicated at the end of this section.

In this section the properties of the solutes are set forth, expressions for critical concentration ratios are developed, and the sensitivity of the effect to growth variations and deviations from the critical ratio are indicated.

In this discussion the subscripts 1 and 2 have reference, respectively, to solutes 1 and 2, C_1 and C_2 designating melt concentrations of these solutes in that order. The symbol k designates the effective distribution coefficient or concentration of solute in the solid phase divided by the concentration of the solute in the bulk liquid. Consider a melt containing solutes 1 and 2 of concentrations C_1 and C_2 at a mean growth rate f . Let k_1 and k_2

be the values of the respective distribution coefficients at growth rate, f , and under given conditions of stirring. Under these conditions, the difference concentration, Z , in the freezing solid is given by the equation

$$Z = k_1 C_1 - k_2 C_2 \quad (1)$$

The electrical conductivity of the semiconductor is proportional to this difference concentration. Let the ratio R be defined as:

$$R = C_2 / C_1 \quad (2)$$

Then, from (1) and (2):

$$Z = C_1 (k_1 - R k_2) \quad (3)$$

Allowing a change, df , in growth rate f to occur, producing changes dk_1 and dk_2 in the effective distribution coefficient, then:

$$\frac{\delta Z}{\delta f} = C_1 (dk_1 - R dk_2) \quad (4)$$

There is no change in Z produced by the change in f , that is, $\delta Z / \delta f$ is zero, if the ratio, R , has the critical value R^* , defined as:

$$R^* = \left(\frac{dk_1 / df}{dk_2 / df} \right) = \frac{dk_1}{dk_2} \quad (5)$$

The ratio R^* is a definite function of growth rate, f , and other variables, and is obtainable from Equation 6, the Burton-Prim-Slichter equation, for the steady state value of the effective distribution coefficient.

$$k = \frac{1}{1 + \frac{1 - k_0}{k_0} e^{-f \Delta / D}} \quad (6)$$

where

k_0 denotes the equilibrium value of k , which holds at very low growth rates

Δ denotes effective thickness of diffusion layer in centimeters, and

D denotes diffusivity of the solute in the liquid in centimeters squared per second.

From Equation 6, R^* can be expressed as:

$$R^* = \frac{dk_1}{dk_2} = \frac{k_1^2 (1 - k_{01}) k_{02} (\Delta / D)_1 \exp [f \Delta / D]_2}{k_2^2 (1 - k_{02}) k_{01} (\Delta / D)_2 \exp [f \Delta / D]_1} \quad (7)$$

It is seen that for a given solute pair and a given value of the dimensionless growth parameter ($f \Delta / D$), R^* is a constant. An assumption is made here that k_0 is independent of concentration. This assumption is justified in the range of concentrations of interest in the preparation of extrinsic semiconductive materials.

While Equation 5 indicates the requisites for eliminating fluctuations in Z , more insight into the requirements for a suitable solute pair is gained by examining the concentration ratio in the solid. From Equations 2 and 5, at the critical ratio:

$$\left(\frac{C_2}{C_1} \right) = \frac{dk_1}{dk_2} \quad (8)$$

Multiplying each side of (8) by k_2 / k_1 , gives:

$$\frac{k_2 C_2}{k_1 C_1} = S^* = \frac{dk_1 k_2}{dk_2 k_1} = \frac{d \ln k_1}{d \ln k_2} \quad (9)$$

in which S^* = the critical ratio in terms of concentrations in the solid rather than the liquid phase.

Since the amount of compensating solute is to be less than the amount of excess solute 1 in the crystallizing solid, $k_2 C_2$ is less than $k_1 C_1$ (Z being considered to be positive), and S^* is numerically less than 1. It is generally preferable in the processes herein to maintain the fraction compensated, S^* , small. This requires that the fractional change of k_2 with f or Δ , be relatively large compared with that of k_1 .

In the processes of this invention it is preferred that the concentrations and characteristics of solutes be

such as to result in the critical ratio, R^* . Although such operating conditions are to be preferred, an advantage, nevertheless, exists even where the amount of compensating solute added is such as to result in a ratio which deviates to a certain extent from R^* . The range of conditions which result in an improvement in uniformity of resistivity in the crystallizing solid is indicated by the following discussion.

It is shown above that:

$$\left| \frac{\delta Z}{\delta f} \right|_{R^*, f^*} = 0 \quad (10)$$

where the subscripts denote that R and f have the values R^* and f^* and that the derivative is evaluated at $R=R^*$, $f=f^*$, where f^* is the growth rate corresponding to R^* . Let ratio R deviate from the critical value and equal

$$(1+\epsilon)R^*$$

Then

$$\left| \frac{\delta Z}{\delta f} \right|_{R, f^*} = C_1 \left(\frac{dk_1}{df} - (1+\epsilon)R^* \frac{dk_2}{df} \right) \quad (11)$$

It is here assumed that the deviation in the value of R from R^* is brought about through a change in C_2 , holding C_1 constant. Therefore,

$$\left| \frac{\delta Z}{\delta f} \right|_{R, f^*} = C_1 \epsilon R^* \frac{dk_2}{df} = -\epsilon C_1 \frac{dk_1}{df} \quad (12)$$

Thus, it is seen that a fractional deviation ϵ , of R from R^* , produces a growth rate coefficient of Z , $|\delta Z/\delta f|$, which is ϵ times the growth rate coefficient of solute 1 alone, which is $C_1(dk_1/df)$. The ratio Q of the growth rate coefficient of Z to that of $k_1 C_1$, the concentration of solute 1 alone, where Z equals $k_1 C_1$ is:

$$Q = \frac{-\epsilon}{1-S} \quad (13)$$

It can be seen from Equation 13, that for any value of R from 0 to $2R^*/(1-S)$, the presence of solute 2 decreases the effect of fluctuations in f or Δ on the resistivity. Thus: at $R=0$, $\epsilon=+1$, and $Q=+1$; at $R=R^*/(1-S)$, $\epsilon=0$, and $Q=0$; at $R=2R^*/(1-S)$, $\epsilon=-1$, and $Q=1$; small S is favored where a low fraction compensated and a low sensitivity to the critical ratio R^* are desired.

The following indicates the effect of deviations from the critical growth rate f^* . The above equations apply strictly for small changes in f . If the change in f from f^* is sufficiently great, since f^* is the rate at which R^* was determined, then dk_1/dk_2 is no longer equal to R^* . The new value of the ratio is designated R' .

An expression for the fraction R'/R^* in terms of f and f^* is developed:

$$R' = \frac{dk_1/df}{dk_2/df} = \frac{(k_1^2) \frac{(1-k_{01})}{(k_{01})} \frac{(\Delta_1)}{(D_1)} e^{-f\Delta_1/D_1}}{(k_2^2) \frac{(1-k_{02})}{(k_{02})} \frac{(\Delta_2)}{(D_2)} e^{-f\Delta_2/D_2}} \quad (14)$$

A corresponding expression can be written for

$$R^* = \left| \frac{dk_1}{dk_2} \right|_{f^*}$$

by substituting f^* in the right side of Equation 14. The ratio R'/R^* is found to be

$$\frac{R'}{R^*} = \left| \frac{dk_1/dk_2}{dk_1/dk_2} \right|_{f^*} = \left[\frac{k_1/k_2}{k_1/k_2} \right]_{f^*}^2 \exp \left[(f^* - f) \left(\frac{\Delta_1}{D_1} - \frac{\Delta_2}{D_2} \right) \right] \quad (15)$$

This expression can be set equal to $(1+\gamma)$, where:

$$R' = (1+\gamma)R^* \quad (16)$$

in a procedure similar to that used in Equation 11. The effect of the deviation, γ , of R' from R^* produced by the change $(f-f^*)$ in growth rate, is evaluated as in Equations 12 and 13.

A useful approximation in the instance of a segregation coefficient k equal to or less than 0.1 is:

$$k = k_0 e^{f\Delta/D}$$

Using this approximation it is found that the right side of Equation 15 is equal to unity. Hence, the quantity $(\delta Z/\delta f)$ is quite insensitive to growth rate where the distribution coefficients of both impurities is equal to or less than 0.1. This approximation applies, for example, to a germanium system containing gallium and antimony as excess and compensating impurities. This approximation has been experimentally substantiated.

That the method is fairly insensitive to growth rate even where the values of the distribution coefficients are greater than 1 is seen from the following example: Assume $(\Delta/D_1) = (\Delta/D_2)$. Then:

$$\frac{R'}{R^*} = \left[\frac{k_1/k_2}{k_1/k_2} \right]_{f^*}^2$$

Let $f(\Delta/D) = 1$, $f^*(\Delta/D) = 0.5$, $k_{01} = 0.7$, $k_{02} = 0.3$. Then

$$\frac{R'}{R^*} = \left[\frac{.86/.54}{.78/.41} \right]^2 = .70 = 1 + \gamma \text{ and } \gamma = -0.30$$

Hence:

$$\left| \frac{\delta Z}{\delta f} \right|_{R, R^*} = -\gamma C_1 \frac{dk_1}{df} = 0.3 C_1 \frac{dk_1}{df}$$

Thus, doubling the growth, so that $f=2f^*$, produces a growth rate coefficient of Z that is only $0.3/(1-S)$ of that for an equal concentration of solute 1 alone. The factor $(1-S)$ has the same significance here as in Equation 13.

The above analysis has been given in terms of changes in f . A similar analysis can be given in terms of film thickness Δ , as the two parameters, f and Δ , are equivalent in their effect on k .

As is noted above, the processes of this invention are used to advantage, either to maintain constant the difference concentration between two significant solutes of opposite type, both having k values either larger than or smaller than unity, or to maintain constant the total concentration of two significant solutes of like type, one having a k value greater than unity and one having a k value less than unity. The class of solute pairs to which these processes are applicable include all significant impurity pairs fulfilling the following conditions: (a) the conductivity type and (b) the sign of the quantity $(1-k)$ must be opposite for the two solutes and the other of the characteristics must be the same for the two solutes.

All of the combinations of suitable characteristics of two solute materials A and B meeting the requirements of this invention are summarized in the table below:

Table

Solute A		Solute B		Quantity maintained constant
Type	Sign of $(1-k)$	Type	Sign of $(1-k)$	
(1) Acceptor.....	+	Acceptor.....	-	Total.
(2) Donor.....	+	Donor.....	-	Do.
(3) Acceptor.....	+	Do.....	+	Difference.
(4) Donor.....	-	Acceptor.....	-	Do.

Equations defining the requirements of solute material are derived above in terms of solutes of opposite conductivity type both having k values either greater than or less than unity. Equations so derived are equally applicable to solute pairs, each member imparting the same conductivity type in which one has a k value greater than unity and the other has a k value less than unity.

Since in reality the difference concentration Z in Equation 1 has reference to the excess majority significant solute which, as is well known in the art, is a measure of the total amount of significant impurity imparting conductivity characteristics to the semiconductive material, Z , may with equal validity be considered to define the total concentration of all significant impurities of a given type where opposite conductivity type imparting solutes are not of concern in the system. Since this condition applies to the processes of this invention in which the compensating solute 2 is of the same type as solute 1, that is, for either of instances 1 or 2 in the above table, Z is now defined as,

$$Z = k_1 C_1 + k_2 C_2 \quad (17)$$

in which Z is the difference concentration and continues to represent the difference between concentrations of opposite type solutes, one of which is not of concern here, and in which the other symbols are as defined above.

With this change in sign of the quantity $k_2 C_2$, Equation 8 may now be rewritten as

$$\left(\frac{C_2}{C_1}\right) = -\frac{dk_1}{dk_2} \quad (18)$$

However, since the concentrations of the solutes 1 and 2 vary in opposite directions with growth rate, in this instance one of the two quantities dk_1 and dk_2 is always negative so that C_2/C_1 is here also equal to a positive value of dk_1/dk_2 .

The remainder of the derivation set forth above is now directly applicable to either of instances 1 and 2 of the table above.

Example 1 below is illustrative of the method of determining the proper amount of compensating solute to offset variations in growth conditions in a typical semiconductive system.

Example 1.—From experimental data of Bridgers (Journal of Applied Physics, volume 27, pages 746–751 (1956)) for the system germanium plus antimony (a donor, or n-type, impurity) plus gallium (an acceptor, or p-type impurity), it is found that the critical ratio R^* has the value 0.14 at a growth rate f of 0.0025 centimeter per second in a pulled crystal rotated at 144 R. P. M. Thus, the ratio of melt concentrations of antimony to gallium, C_2/C_1 , where 2 denotes antimony, is

Let the desired concentration in the solid, $Z = k_1 C_1 - k_2 C_2$, be 0.73×10^{14} atoms per centimeter³

corresponding to a p-type resistivity in the solid of about 10 ohm-centimeters at room temperature. The values of the k 's, at these growth conditions are:

$$k_1 = 0.105 \text{ and } k_2 = 0.0046$$

Using the relationship $C_2 = 7C_1$, the required melt concentration C_1 is given by

$$\begin{aligned} Z &= k_1 C_1 - k_2 C_2 \\ 1.0 \times 10^{14} &= 0.105 C_1 - 0.0046(.14) C_1 \\ C_1 &= 1.0 \times 10^{15} \text{ atoms gallium/centimeters}^3 \\ C_2 &= 7.0 \times 10^{15} \text{ atoms antimony/centimeters}^3 \end{aligned}$$

The fraction compensated, S , is

$$\frac{k_2 C_2}{k_1 C_1} = \frac{.0046}{.105} (.7) = \frac{.032}{.105} = 0.30$$

Examples 2 and 3 below illustrate the leveling effect of the use of a compensating solute in accordance with this invention in two crystallizing processes in which the growth rate is varied.

Example 2.—Consider a germanium system containing gallium as the solute conductivity imparting solute. The mean growth rate of f is 0.0025 centimeter per second at a crystal rotation rate of 30 R. P. M. An increase of 50 percent to the growth rate produces a con-

centration increase of gallium in the growth crystal of 25 percent producing a conductivity deviation of 25 percent.

Consider a germanium system containing gallium as solute 1 and antimony as solute 2 in amount such that the difference between the two at a mean growth rate of 0.0025 centimeter per second and a crystal rotation rate of 30 R. P. M. produces a conductivity level the same as that of the germanium system above. The quantities of gallium and antimony in the melt are those determined by the critical ratio R^* in accordance with the equations. The growth rate of the growing crystal is increased 50 percent. Under these conditions the variation in difference concentration in the growing crystal is less than 1 percent. The percentage deviation in conductivity is also less than 1 percent.

Consider a germanium system containing gallium and antimony, the amounts being such as to result in the same difference concentration of gallium as that of the system of the first paragraph in this example under the identical growth conditions. The quantities of gallium and antimony in the melt are such as to result in a ratio R equal to $R^* \pm 20$ percent. Increase the growth rate 50 percent. Under these conditions, the excess gallium concentration in the crystallizing material deviates 6 percent with the conductivity showing the same percentage deviation.

Example 3.—Consider a germanium system containing gallium as the sole significant impurity with a crystal growth rate of 0.0025 centimeter per second and a crystal rotation rate of 144 R. P. M. Increasing the growth rate 50 percent results in an increase in gallium concentration in the growing crystal of 20 percent.

Consider a germanium system containing both gallium and boron as significant impurities in amounts such that the total concentration of the two impurities in the crystallizing material at a mean growth rate of 0.005 centimeter per second and at a crystal rotation rate of 144 R. P. M. is such as to result in a crystal of the same conductivity level as that of the first paragraph under this example. The amounts of gallium and boron are such that the concentration of boron in the liquid divided by the concentration of gallium in the liquid is equal to R^* (numerically equal to 0.0038). Increasing the growth rate by 50 percent results in a conductivity deviation in the growing crystal of less than 2 percent.

Consider a germanium gallium-boron system in which the amounts of gallium and boron in the melt are such as to result in the conductivity level of the system of the first paragraph of this example under identical growth conditions. The amounts of gallium and boron in the melt are further such that the ratio R equals $R^* \pm 20$ percent. An increase of 50 percent in the growth rate results in a conductivity deviation in the growing crystal of about 5 percent.

As is seen from the above examples taken in conjunction with the discussion herein a deviation in the ratio of the melt concentrations of solutes 1 and 2 from the critical value R^* although it does not result in the ideally compensated product crystallized from a melt in which the ratio R^* applies nevertheless results in a substantial improvement over the use of a single solute alone. For the common two-solute systems of this invention, reasonable operating ranges of ratio R are considered to be $0.8R^*$ to $1.2R^*$. Although this is a preferred operating range, it is seen from the discussion that deviations from this range within the limits set forth above nevertheless result in an improvement in the uniformity of conductivity characteristics of a crystallizing material prepared in accordance with this invention as compared with such a material solidifying from a melt containing no compensating solute.

The requisite characteristics of solutes 1 and 2 in accordance with this invention may be determined from the

discussion and equations. By way of illustration, several suitable combinations are listed below:

Major ingredient	Solute 1	Solute 2
Germanium.....	Gallium.....	Antimony.
Do.....	Indium.....	Arsenic.
Do.....	do.....	Antimony.
Silicon.....	Gallium.....	Do.
Do.....	Arsenic.....	Boron.
Do.....	Phosphorus.....	Do.
Germanium.....	Gallium.....	Do.
Indium antimonide.....	Zinc.....	Cadmium.

In the discussion of instances 1 and 2 of the above table, it is tacitly assumed that the compensating solute or solute 2 is that which has the greatest variation in k with variation in growth condition. It should be noted that unlike the processes of instances 3 and 4 the solute predominating in the liquid or in the crystallizing material may be either solute 1 or solute 2 as desired and may in fact vary from one to the other in the solid under certain conditions. Where both solutes are either acceptors or donors this is of no consequence since the solute concentration of concern in the crystallizing material is the sum concentration.

The processes have been discussed in terms of simple ternary systems containing as solutes either one acceptor and one donor, both having k values greater than or less than 1, or two solutes of the same conductivity imparting type, one having a k value of greater than 1 and one having a k value less than 1. Crystals prepared in accordance with this invention may contain additional solutes. Such solutes may contribute to the compensation of this invention as in the instance of a solvent material containing a first significant impurity and two additional significant impurities, one of which is of opposite conductivity type and one of which is of the same conductivity type as solute 1. Additional ingredients may also be included for any of the reasons known to the art as, for example, for the purpose of controlling lifetimes. These processes are not limited to zone-melting operations but are applied advantageously to normal freezing operations such as by crystal pulling. Where the processes are so used, monitoring the growth rate so as to offset varying concentration in the melt may result in a greater constant conductivity portion than is otherwise attainable. Where the compensating solute is of the same conductivity imparting type and has the other characteristics set forth above the amounts contained in the melt may be so chosen that the increase of the one offsets the decrease of the other in the melt in a constant pull rate crystal pulling process so as to result in a substantial constant conductivity portion.

Although the processes have been discussed in terms of random variations in growth conditions the compensation technique is usefully applied under certain steady state conditions. For example where film thickness Δ is not uniform at a freezing interface due, for example, to variations in stirring velocities from one portion of the interface to the other, use of a compensating solute as described herein effectively secures uniform resistivity over a cross-section corresponding to such interface.

10 What is claimed is:

1. A process of crystallizing semiconductive material evidencing uniform electrical conductivity characteristics from a body of liquid comprising as a major ingredient a fusible extrinsic semiconductive material, and as minor ingredients, two significant solutes, such that one of the characteristics, (a) the conductivity imparting type, and (b) the sign of the quantity $(1-k)$, is opposite for the two solutes, and the other is the same for the two solutes, in which the ratio of the concentration of solute 2 in the liquid to that of solute 1 is from 0.8 to 1.2 times the absolute value of R^* where R^* is the ratio of the growth rate coefficient of the distribution coefficient of solute 1 to that of solute 2 and in which k is the effective distribution coefficient.

2. The process of claim 1 in which the ratio of the two solutes in the liquid is substantially equal to the absolute value of R^* .

3. The process of claim 1 in which the body of liquid is a molten zone of a zone-leveling process.

4. The process of claim 1 in which the body of liquid is the melt of a normal freezing process.

5. The process of claim 4 in which the normal freezing process is a crystal pulling process.

6. The process of claim 1 in which the fusible extrinsic semiconductive material is germanium and solute 2 is antimony.

7. The process of claim 6 in which solute 1 is gallium.

8. The process of claim 1 in which the fusible extrinsic material is silicon and solute 2 is antimony.

9. The process of claim 8 in which solute 1 is gallium.

10. The process of claim 1 in which the fusible extrinsic semiconductive material is silicon and the solutes are boron and phosphorus.

11. The process of claim 1 in which the fusible extrinsic semiconductive material is germanium and the solutes are boron and gallium.

12. The process of claim 1 in which the fusible extrinsic semiconductive material is indium antimonide and the solutes are zinc and cadmium.

No references cited.