Feb. 17, 1970 R. K. WILLARDSON ETAL 3,496,118

IIIB-VB COMPOUNDS

Filed April 19, 1966 2 Sheets-Sheet 1

FIG 1

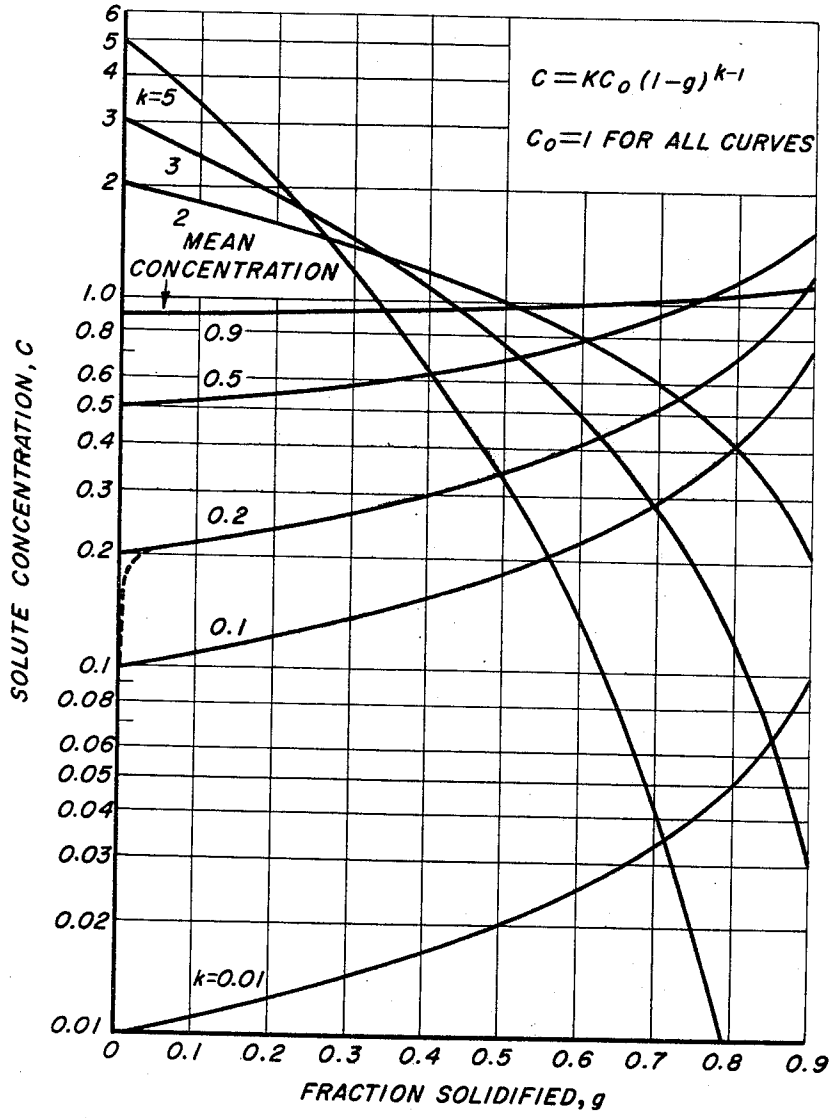

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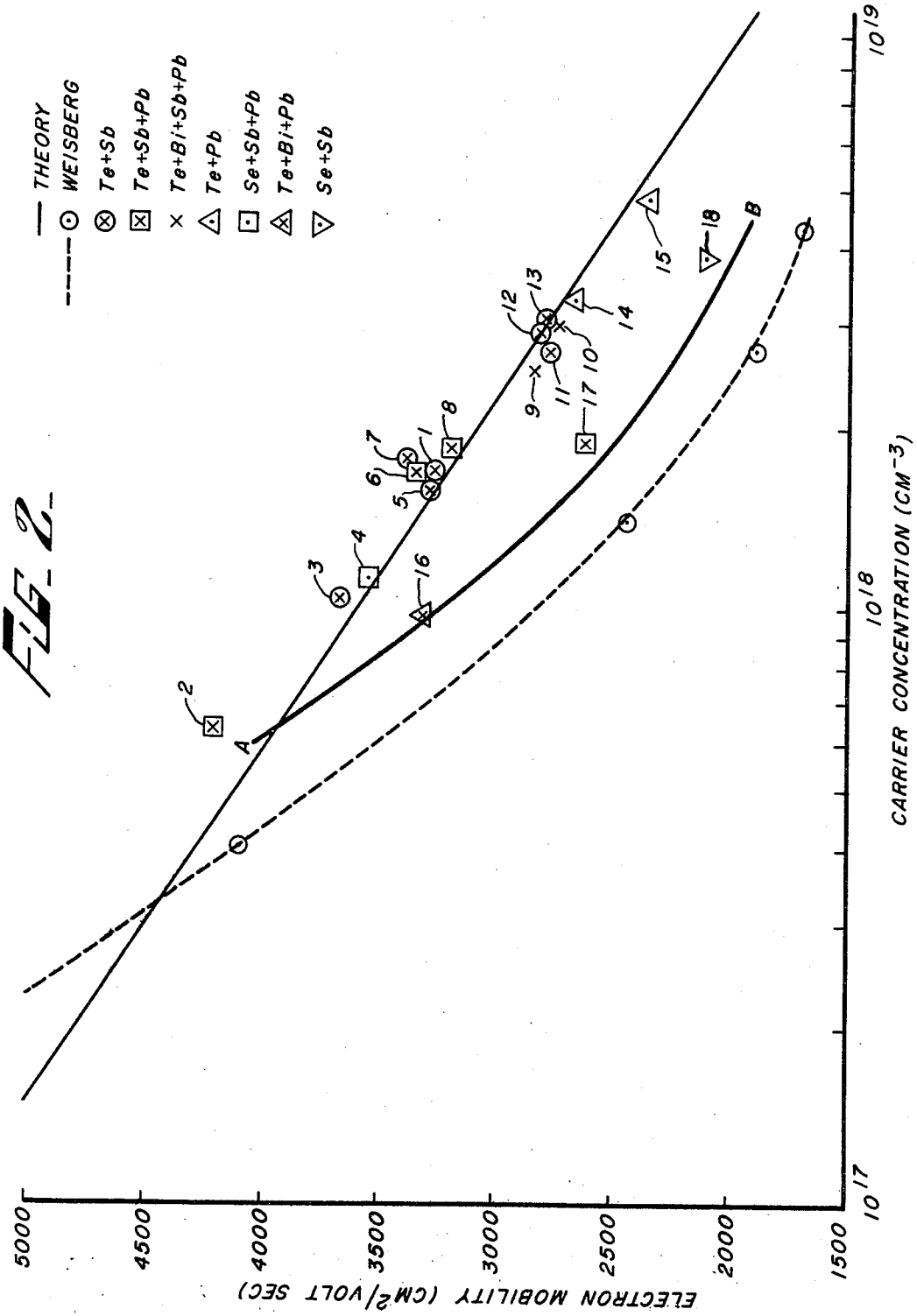
FIG 2


THEORY
WEISBERG
Te+Sb
Te+Sb+Pb
Te+Bi+Sb+Pb
Te+Pb
Se+Sb+Pb
Te+Bi+Pb
Se+Sb
ELECTRON MOBILITY (CM²/VOLT SEC)
CARRIER CONCENTRATION (CM⁻³)
5000
4500
4000
3500
3000
2500
2000
1500
10¹⁹
10¹⁸
10¹⁷
A
B

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3,496,118

IIIB–VB COMPOUNDS

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19 Claims

ABSTRACT OF THE DISCLOSURE

Improved IIIB–VB semiconductor compounds having reduced lattice defect concentration and enhanced electron mobility when containing a carrier dopant. A process for the preparation of such materials is disclosed in which a crystal of the compound is formed from a melt of the compound at a freezing point of the compound lowered by inclusion of an impurity in the melt of the compound. The impurity is different from any constituent element of the compound, has a distribution constant in the compound of less than 1 so as to be substantially occluded from the compound during formation thereof, and is such that unoccluded remnants of such impurity are substantially electrically inactive.

In recent years the IIIB–VB semiconductor compounds have been the subject of intensive investigation. Not only are they structural analogs of the semiconducting elements of the IVB sub-group but even the chemical bonds between the atoms are remarkably similar. With appropriate doping, the electrical properties of these IIIB–VB compounds make them useful for a variety of semiconducting purposes, e.g., in light emitting diodes, high speed switching diodes, transistors and related devices where the electrical properties of the compound play an important role. Deviations from crystal lattice perfection detract from the crystal's electrical properties. Accordingly, it is desirable to obtain IIIB–VB semiconductor compounds having a reduced number of defects or deviations from crystal lattice perfection.

The problem of creating a nearly perfect semiconducting material is similar to that of obtaining a perfect and absolutely pure elemental single crystal with the additional difficulty of determining and maintaining perfect balance among two or more constituents. Initially all crystals have lattice defects in quantities dictated by their thermodynamic properties and the conditions under which they were formed and brought to room temperature. Seeding and growth conditions also determine the density of larger defects. Deviations from crystalline perfection in an otherwise chemically stoichiometric crystal may be caused by dislocations, stacking faults, boundaries, interstitial atoms, vacant lattice sites and/or misplaced atoms, and various combinations of these with each other and with impurity atoms. Departures from precise atomic structure can be determined by measuring the effects of the departure on the physical properties of the crystal, especially those properties involving the movement of atoms or electrons, as well as the electrical, magnetic and optical properties of the imperfections. Methods of making such determinations are known to those skilled in the art.

In one method of preparing single crystals of IIIB–VB compounds, the compound is contained in a crucible, or boat, together with an oriented seed crystal. A zone is melted between the seed and charge and is moved relative to the crucible. Either the crucible is moved past a temperature gradient or a temperature gradient can be arranged to move past the crucible. In another technique, the floating zone method, a semiconductor rod is supported at its two ends and a small zone of the rod is melted and moved along the rod length. The molten section is supported by the surface tension of the liquid and by the solid parts of the rod. In still another method, a pulling, e.g., Czochralski, method, a melt of the compound is contained in a crucible and a seed crystal is dipped in the free surface of the melt. The seed is slowly pulled out of the melt, usually with rotation, a crystal of the compound growing in length at the same rate the seed is withdrawn from the melt. The above and other methods are discussed in "Compound Semiconductors—Volume 1" (1962), edited by R. K. Willardson and H. C. Goering, published by Reinhold Publishing Corp., New York, which is hereby incorporated by reference.

The above techniques attempt to reach stoichiometry, or purify the compound while maintaining stoichiometry, by maintaining a melted section or portion of the compound at its melting point and stoichiometric dissociation pressure of the more volatile constituent. In all of the above methods, deviations occur during the growth of the crystal and substantially detract from its electrical properties. While chemical stoichiometry may be closely approached "physical" stoichiometry has not been closely attained. Thus, chemical analysis of the material may reveal a one-to-one correspondence of the elements involved, but imperfections or deviations from crystal lattice perfection occurring during the use of the above techniques prevent the crystal from being stoichiometric in the physical, i.e., lattice perfection, sense.

It is an object of this invention to provide IIIB–VB semiconductor compounds with substantially reduced concentrations of lattice defects. Another object is to provide carrier containing IIIB–VB semiconductor compounds with enhanced thermal conductivity and electrical properties in substantial agreement with theoretical and yielding significantly improved device characteristics. Still another object is to provide a method for preparing such improved IIIB–VB compounds. A further object is to provide a process whereby small additions of an appropriate foreign element or impurity to a IIIB–VB compound melt results in the growth of a more nearly perfect stoichiometric crystal containing an inconsequential amount of the foreign element or impurity. Other objects will become apparent from the following description taken in conjunction with the accompanying drawing in which:

FIG. 1 is a plot of solute, or impurity, concentration against fraction of melt solidified; and

FIG. 2 is a plot of theoretical and experimental electron mobilities against carrier concentrations for carrier atom-doped gallium arsenide formed by prior methods and by methods of this invention.

Stoichiometric group IIIB–VB compounds having a relatively low melting point, e.g., gallium antimonide and indium antimonide, have been prepared with relatively small deviations from crystal lattice perfection [D. Effer and P. J. Etter, J. Phys. Chem. Solds., 25:451 (1964)]. However, with group IIIB–VB compounds having a melting point above 900° C., crystal lattice perfection has not been significantly approached. Thus, under the conditions in which zone melting techniques have been used, i.e., at the melting point of the crystal under a stoichiometric dissociation pressure of the more volatile constituent, those compounds containing impurities with small distribution coefficients will yield single crystals with uniform composition (e.g., p. 279 of "Compound Semiconductors—Volume 1," supra); but deviations from crystal lattice perfection, at least in compounds with melting points above 900° C., are still relatively high. Anomalies in the measured values of thermal conductivity at low temperatures as compared with theoretical predictions, indicate the presence of about 10^{19}/cm.^{3} lattice defects in such

IIIB–VB compounds supposedly "purified" by the above methods. [Pages 13, 18 and 31 of "Physics of III–V Compounds—Volume II—Semiconductors and Semimetals" (1966), edited by R. K. Willardson and A. C. Beer, published by The Academic Press, New York, which is hereby incorporated by reference.] In the case of electrical conductivity, for carrier concentrations of about $1–2\times10^{18}$/cm.^{3} the experimental electron mobility values of gallium arsenide have been found to be 30 to 40% lower than predicted by theory [H. J. Ehrenreich, J. Appl. Phys., 32, 2155 (1961)]. Anomalous electrical conductivity results, obtained at room temperature, have been labeled "mobility killer phenomena" [L. R. Weisberg, J. Appl. Phys., 33, 1817 (1962)]. Calculations of the effect on mobility of lattice defects, which can behave as so-called neutral impurities, have been made [C. Erginsoy, Phys. Rev., 79, 1013 (1950); N. Sclar, Phys. Rev., 104, 1559 (1956)].

With prior methods, material to be treated is carefully chosen so that it contains a minimum of impurities, which often involves precise chemical analyses of many samples. Our invention involves processes similar to the above-described methods, but rather than using material containing a minimum of impurities, we purposely add impurities of a certain type, impurities that significantly lower the freezing point of the IIIB–VB compound; and the crystal is formed at that lower freezing point. Thus, the above and other objects of this invention are accomplished by providing a process for improving a IIIB–VB compound whiich comprises providing a melt of at least a portion of a batch of IIIB–VB compound, the melt containing an impurity that significantly lowers the freezing point of the compound, and forming a crystal of the compound at a lower freezing point.

By our invention, crystals of IIIB–VB compounds having a melting point above 900° C. can now be obtained with significantly decreased lattice defects and with properties of theoretical magnitude, whereas they have been previously unobtainable; and a more facile method of preparing "purified" crystals of both the higher and lower melting IIIB–VB compounds is provided. Group IIIB–VB compounds having a lattice defect concentration of less than 10^{16}/cm.^{3} are now readily obtainable. Further, such IIIB–VB compounds that additionally contain small amounts of a carrier dopant can now be readily obtained having a carrier-lattice defect concentration ratio of 1:10 and greater. For example, gallium arsenide having a carrier concentration from 10^{18} atoms of tellurium/cm.^{3} can now be obtained with defect concentrations of 10^{18}, 10^{17}, 10^{16}, etc., per cm.^{3}; whereas with prior methods the defect concentrations for such a crystal were at least 10^{16}/cm.^{3}. By means of our invention, the electrical and thermal conductivities of doped IIIB–VB semiconductor compounds can be increased so that the determined values of electron mobilities are significantly enhanced and often correspond substantially with theoretical. For example, electron mobilities for tellurium-doped gallium arsenide obtained by this invention are in agreement with calculations using the Brooks-Herring formula and an effective mass of 0.72 m. Increases in electron mobilities of as much as 40% can now be achieved, e.g., with gallium arsenide, to 3300 cm.^{2}/volt sec. for carrier concentrations of 2×10^{18}/cm.^{3}. Group IIIB–VB crystals with melting points above 900° C., i.e., aluminum phosphide, aluminum arsenide, aluminum antimonide, gallium phosphide, gallium arsenide, indium phosphide, indium arsenide, or mixtures thereof, and having such enhanced characteristics were heretofore unknown; they constitute new compositions of matter.

Our invention can be more fully understood with reference to a prior method of "purifying" gallium arsenide. In prior methods, the gallium arsenide is heated at its melting point of 1238° C. in an evacuated or inert gas-filled closed chamber under 0.9 atmosphere of arsenic pressure. In a particular method of crystal formation, a pulling or

Czochralski method, gallium is placed in a suitable crucible, e.g., of quartz, graphite, alumina, aluminum nitride, or the like, in a closed evacuated chamber containing sufficient arsenic to react with gallium to form gallium arsenide and an additional amount to maintain a stoichiometric dissociation pressure of arsenic, at the melting point of gallium arsenide, in the chamber; e.g., about 115–17 parts by weight of arsenic per 100 parts by weight of gallium. If doping of the material is desired, the dopant (e.g., about 0.05 to about 0.5 part by weight of tellurium per 100 parts of gallium) can be placed on or below the gallium in the crucible. The crucible is heated to melt the gallium, and the dopant if present, and brought up to 1238° C. while the remainder of the chamber is heated so that the coolest point therein is at about 605° C. (so as to ensure an arsenic pressure of 0.9 atmosphere). A melt of gallium arsenide forms in the crucible whereupon a seed crystal of gallium arsenide is lowered into the crucible and after contact with the melt is slowly raised, e.g., at about 0.01 to 2 mm./min. and at a relative rotational rate of about 5 to 50 r.p.m. A chemically stoichiometric crystal of gallium arsenide is formed; however, measurement of its electrical properties discloses the presence of substantially more than 10^{16} lattice defects/cm.^{3} and, in lightly doped crystals, greater than 10 times as many lattice defects as carriers.

In a corresponding process of our invention, a similar procedure is followed except that an impurity, as defined herein, e.g., 0.2 part by weight of antimony per 100 parts of gallium, is placed on or below the gallium in the crucible. The crucible is heated to melt the gallium and the impurity (and the dopant, if present) and brought up to the freezing point of the "impure" gallium arsenide. A melt of gallium arsenide forms in the crucible whereupon a crystal is grown as before, except at the lower freezing point resulting from the impurity. A chemically stoichiometric crystal of gallium arsenide is thereby formed and measurement of its electrical properties discloses the presence of less than 10^{16} lattice defects/cm.^{3} and, in lightly, e.g., 5×10^{15}/cm.^{3}, doped crystals, a carrier: lattice defect concentration ratio of at least about 1:10.

The above describes our process with regard to operation at the dissociation pressure of the more volatile constituent corresponding to the melting point of stoichiometric IIIB–VB compound. Our process can also be used at lower pressures with greater amounts of impurities to yield a greater decrease in freezing point. Similarly, smaller amounts of impurities, but at somewhat higher pressures can be used, yielding correspondingly smaller decreases in the freezing point.

It is also preferred that the method used to form the crystal involve pulling the crystal from its melt, e.g., in the manner of Czochralski, primarily because of easier handling. However, the other techniques are fully applicable provided, of course, that the conditions called for in the method of this invention are maintained.

In a preferred embodiment, the IIIB–VB compound treated by this invention contains a carrier concentration to which has been imparted increased electron or hole mobility properties, which concentration results from doping with appropriate carrier atoms, for example, manganese, tellurium, selenium, sulfur, cadmium, zinc, tin, germanium, silicon, mixtures thereof, and the like. Improvements in electron mobilities are obtained with IIIB–VB compounds containing n-type dopants and treated by this invention, e.g., tellurium, selenium, sulfur, tin, germanium, and silicon. Improvements in hole mobilities are similarly obtained with p-type dopants such as manganese, cadmium and zinc. In general, improved electron mobilities are noted in crystals of our invention when the carrier dopant concentration is at least about 2×10^{17} atoms per cm.^{3}. In a preferred embodiment with gallium arsenide as the IIIB–VB compound and an n-type dopant, a particularly preferred concentration of carrier dopant is about 5×10^{17} up to about 5×10^{18} atoms per cm.^{3}.

The term "impurity" is limited to those elements, or compounds containing an element, different from the constituent elements of the treated IIIB–VB compound. During formation of the crystal from its melt, those impurities useful in our process tend to concentrate in the liquid phase giving rise to a solid/liquid distribution coefficient of less than 1. In some cases it is desired to retain some of the impurities in the crystal, e.g., as dopants to impart particular conductivity or electron mobility properties. In this case, an impurity for the particular IIIB–VB compound melt can be chosen having a distribution coefficient such that the solid IIIB–VB compound will contain the desired amount of impurity. In most cases it is desired to exclude the impurity from the solid, e.g., where a pure IIIB–VB compound is required or where the impurity would interfere with or reduce the effect of a dopant material in the IIIB–VB compound. Here, impurities having distribution coefficients of appreciably less than one, preferably 0.02 or less, should be used. Elements are preferred as impurities but compounds can also be used. The distribution coefficient in IIIB–VB compounds of various elements can be found in the literature or can be determined by methods known to those skilled in the art. Some of the techniques that can be used are discussed on pp. 365–400 of "Compound Semiconductors—Volume 1," supra.

The following table lists some elements having reported distribution coefficients k of less than 1 in various IIIB–VB compounds, along with some reported ionization energies E_i in electron volts and conductivity types t where A and D denote acceptor and donor impurities, respectively.

is somewhat enhanced. The presence of a second impurity can modify the distribution coefficient of a first impurity so that the distribution coefficient of the first impurity increases (e.g., zinc) with the increased concentration of the second impurity (e.g., antimony). Thus, "lattice" in the term "substantial occlusion from the lattice" is meant generally to refer to that portion or portions of the crystal containing the desired impurity concentration.

The distribution coefficient is not the only parameter that should guide the choice of an impurity; other factors must be considered such as the diffusion coefficient of the impurity, whether it is a donor or acceptor type material in the particular IIIB–VB compound, etc., and these parameters and their effects are known to those skilled in the art. Thus, while an element such as copper has a low distribution coefficient in gallium arsenide, the rapid diffusion of these elements might make them unsuitable in preparing stoichiometric gallium arsenide where the effect of diffusion could interfere with a desired property of the semiconductor material. For example, while only a very small amount of copper would remain in gallium arsenide, the electrical properties of even such a small amount may preclude its use in favor of a material having less electrical effects even at a larger concentration. On the other hand, for some specific purpose it may be desired to have the electrical properties of a very small amount of copper in the semiconductor material, in which case copper might well be the impurity of choice.

Compounds can also be used as impurities, e.g., II–VI, II–IV–V, etc., compounds such as CdTe, CdS, CdSe, ZnGeAs, ZnSnAs, CdSnAs, and the like, whose distribution coefficient or geometric properties will result in substantial occlusion of one or more of its elements from the solid.

TABLE I

Element	AlSb			GaAs			GaSb			InAs			InSb		
	k	t	E_i	k	t	E_i	k	t	E_i	k	t	E_i	k	t	E_i
Aluminum				<0.2											
Antimony				<0.016											
Bismuth				0.0005											
Boron	0.01–0.02														
Cadmium		A		0.009	A	0.020	0.02	A		0.13	A		0.26	A	
Calcium		A		<0.02	A			A			A			A	
Carbon	0.6	A		0.8	D			A							
Chromium				0.00057											
Cobalt	0.02			0.00008											
Copper	0.01–0.1	A		<0.002	A	0.14		A			D		0.00007	A	0.023
Germanium	1.2	A		0.02–0.03	D		0.2	A		0.07	A		0.012	A	
Gold					A	0.31							0.000002	A	0.032
Indium				0.1											
Iron	0.01–0.1			0.002–0.003	A	0.037							0.04		
Lead	0.01			<0.0002											
Magnesium	0.1	A		0.05–0.3	A			A		0.70	A			A	
Manganese	0.01			0.02–0.05	A										
Nickel	0.01			<0.02									0.00006		
Phosphorous				3									0.16		
Selenium	0.4	D	0.16	0.3	D		0.4	D		0.93	D		0.17–1.9	D	
Silicon	0.1	A		0.14	D	<0.005	~1	A		0.4	A		0.1	A	
Silver	0.1			0.1	A								0.00005	A	0.022
Sulfur		D		0.3	D			D		1.0	D		0.1	D	
Tellurium	0.3	D	0.068	0.059	D		0.4	D		0.44	D		0.47–~4	D	
Tin	1.0			0.08	D			D		0.09	D		0.06	D	
Zinc		A		0.12	A	0.014	0.3	A		0.77	A		2.3–~3.52	A	

Referring to Table I, it can be seen that many elements not only have distribution coefficients of less than one but also have coefficients of such small magnitude that the element would be substantially occluded from the crystal lattice.

The term "substantial occlusion from the crystal lattice" can be explained with reference to FIG 1, where the change in solute, or impurity, concentration with fraction of melt solidified is shown. With distribution coefficients k of less than one, segregation of the impurity results in an increase in solute concentration as more melt is solidified. Accordingly, even if the distribution coefficient were to remain the same at all solute concentrations, the greater concentration of impurity in later solidified fractions would result in higher impurity concentrations. On the other hand, some impurities do not follow the ideal curve of FIG. 1 but have a distribution coefficient that decreases as its concentration in the melt increases, so that uniformity of the ingot or solid

Mixtures of impurities can also be used. If one of the impurities affects the ability of the IIIB–VB compound to dissolve the other impurity, an adjustment of distribution coefficint, or redetermination for the individual impurities under those conditions, should be made. Thus, if an impurity appreciably raises or lowers the freezing point of the IIIB–VB compound, a second impurity will generally have a somewhat different solubility at the new freezing point. Accordingly, when using mixtures of impurities, appropriate proportions should be determined and used. In an ideal system the distribution coefficient would be substantially temperature-independent, in which case only the amount of impurity added need be adjusted. This generally holds true for even non-ideal conditions where the temperature differences are small.

With larger temperature differences there is generally a curved, rather than straight-line, relation between temperature and distribution coefficient.

In a preferred embodiment of this invention the impurity added is such that it will be substantially occluded from the solidified IIIB–VB compound. In terms of the distribution coefficient it is preferred that the impurity in a particular IIIB–VB compound, at the freezing point of the impurity-containing melt, have a distribution coefficient of about 0.02 or less. The following elements are examples of such impurities: from Group I, copper, silver and gold; from Group II, cadmium and calcium; from Group IV, lead and germanium; from Group VI, chromium; from Group VII, manganese; from Group VII, iron cobalt and nickel; from Groups IIIB and VB, any element having a distribution coefficient of less than 1, since the impurity would be electrically neutral in the Group IIIB–VB compounds.

In a particularly preferred embodiment, the impurity is from Group IIIB or VB and is capable of forming a compound with one of the elements of the treated IIIB–VB compound. Similarly, compounds formed from such a Group IIIB or VB element with an element of the treated compound are particularly preferred impurities and notably effective in our process. These compounds and elements apparently form solid solutions with the treated IIIB–VB compound but are usually substantially occluded from the grown crystal. The Group IVB elements are not particularly preferred, but lead is a notable exception. Although the reasons are not completely understood, lead is particularly more effective than the other elements of Group IVB. Notable examples of paritcularly effective elements are aluminum, bismuth, antimony, arsenic, lead, mixtures thereof in appropriate proportions, and the like. The above preferences are also held for IIIB–VB compounds which contain a dopant such as manganese, tellurium, selenium, sulfur, cadmium, zinc, tin, germanium, silicon, mixtures thereof, and the like.

An impurity concentration is used that significantly lowers the freezing point of the IIIB–VB compound. The term "significantly" refers to a magnitude such that a noticeable decrease in defect concentration is observed in comparison with material otherwise treated the same but without the presence of the impurity. The magnitude of freezing point decrease, and similarly the concentration of impurity to yield such decrease, required for an improvement in stoichiometry varies with compound and impurity, but is readily determined by making side by side determinations at varying levels of impurity concentrations. In general, it is preferred to add at least about 1×10^{18} atoms of impurity per cm.^{3} of compound and, as a practical matter, up to about 4×10^{21} atoms/cm.^{3} to yield a decrease of about 100° C.

The following examples illustrate advantages of our invention.

EXAMPLE 1

Using a Czochralski pulling apparatus similar to that shown in FIGURE 29.5, p. 260 of "Compound Semiconductors—Volume 1," supra, desired amounts of dopant and impurity are placed in a crucible and 100 grams of gallium are placed thereover. The crucible can be of quartz, graphite, alumina, aluminum nitride or the like, and sits in a sealable quartz chamber. A reservoir of 117 grams of arsenic are placed in the chamber which is evacuated and then sealed. A small amount, e.g., about 200 micrograms, of oxygen can be bled into the chamber prior to sealing. (A partial oxygen pressure has been found to somewhat aid the appearance of the crystal, but is not at all critical to the process.)

In one run, 0.24 gram of tellurium as dopant and 1.0 gram of antimony as impurity were used, along with a partial pressure from 200 micrograms of oxygen. The gallium and arsenic were obtained from the Eagle Picker Co. and Consolidated Mining Co., Ltd., respectively. The crucible was heated to melt the gallium, tellurium and antimony. The remainder of the chamber was heated to above 605° C., but while maintaining a point in the chamber at 605° C. A melt of gallium arsenide formed in the crucible whereupon a seed crystal of gallium arsenide, oriented in the <$\bar{1}\ \bar{1}\ \bar{1}$> direction, was lowered into the crucible and, after contact with the melt, was raised at about ¼–¾ inch per hour at a rotational rate of about 12 r.p.m. A crystal of gallium arsenide was thereby formed until the melt was exhausted.

A thin slice of the crystal was cut at about 10 grams from the top. Hall effect measurements revealed a carrier concentration of 1.71×10^{18}/cm.^{3}. Electron mobility of the crystal portion was measured and found to be 3280 cm.^{2}/volt sec.

EXAMPLES 2–18

The procedure of Example 1 was repeated with different dopants and impurities. The following tabulation describes various runs with tellurium or selenium dopants and with antimony, lead or bismuth impurities, or combinations thereof, in varying amounts. Carrier concentrations, obtained from Hall effect measurements, and electron mobilities are given for each run. Examples 6 and 8 are slices from different places in the same crystal. Example 11 is a slice from a different place in the crystal of Example 1 above.

	Dopant, gm.		Impurity, gm.			Partial O_2 pressure, micrograms	Seed orientation	Pull rate, inches/hr.	Rotation rate, r.p.m.	Sliced, gms. from crystal top	Carrier concentration/cm.^{3}	Electron mobility, cm.^{2}/volt sec.
	Te	Se	Sb	Pb	Bi							
Example:												
2	0.1		0.2	0.4		200	<III>	3/4	45	105	6.32×10^{17}	4,220
3	0.1		0.2			200	<III>	3/4	45	113	1.05×10^{18}	3,670
4		0.017	1.0	0.4		200	<III>	1/4	12	28	1.13×10^{18}	3,550
5	0.14		0.5			0	<III>	1/4	12	87	1.58×10^{18}	3,290
6	0.14		0.5	0.4		0	<III>	1/4	12	117	1.7×10^{18}	3,370
7	0.15			0.5		0		1/4	45	99	1.76×10^{18}	3,390
8	0.14		0.5	0.4		200	<III>	1/4	12	149	1.85×10^{18}	3,230
9	0.15		0.5	0.4	2.0	200	<III>	1/4	12	94	2.5×10^{18}	2,850
10	0.22		0.5	0.4	2.0	200	<III>	1/4	12	109	3.0×10^{18}	2,730
11	0.24		1.0			200	<$\bar{1}\bar{1}\bar{1}$>	1/4	12	126	2.7×10^{18}	2,810
12	0.4		0.5			200		1/4	12	17	2.89×10^{18}	2,810
13	0.14		0.5			0	<III>	1/4	12	93	2.96×10^{18}	2,750
14	0.4			2.0		200	<III>	1/4	12	27	3.34×10^{18}	2,690
15	0.4			2.0		200	<III>	1/4	12	82	4.87×10^{18}	2,360
16	0.1			2.0	2.0	0	<III>	1/4	12	40	9.7×10^{17}	3,310
17	0.24		1.0	0.4		200	<III>	1/4	12	10	1.88×10^{18}	2,640
18	0.85		0.5			200	<III>	1/4	12	21	3.85×10^{18}	2,110

Referring to FIG. 2, the electron mobilities of the crystal slices in the above eighteen examples are plotted against carrier concentrations in those slices (the numbers in the drawing referring to the corresponding example number). Also plotted with encircled dots are the data of Weisberg et al., for gallium arsenide [J. Appl. Phys., 29:1514 (1958)], connected with a dashed line. Theoretical values predicted by Ehrenreich, supra, are plotted as a solid line. It can be seen that the data obtained with the above eighteen experiments substantially

corresponds with theoretical values and in some cases are somewhat higher and reveal, indeed, that the slope of the solid line should be somewhat greater.

The term "enhanced" when used with electrical properties, such as electron mobility, refers to a magnitude that is significantly greater than the magnitude of such property for a corresponding crystal but grown by the prior art methods outlined above; i.e., by mere formation of the crystal at the melting point of the compound at a stoichiometric dissociation pressure of the more volatile constituent without use of the impurity addition-occlusion technique of this invention. The term "significant" refers to a magnitude that is greater than can be attributed to experimental error; in the context of the IIIB–VB compounds differences of 15% or higher are significant. In the specific context of gallium arsenide, and referring to FIG. 2, gallium arsenides improved by this invention have, when containing a carrier dopant, electron mobilities relative to carrier concentrations that lie above the solid line AB.

A principal use of doped IIIB–VB crystals, e.g., somewhat heavily doped gallium arsenide, is as the crystalline material used in presently known light emitting diodes, praticularly lasers, in which the enhanced electrical and thermal conductivities, as well as other perfect or nearly perfect crystal properties, permit the fabrication of superior devices. Undoped IIIB–VB crystals of this invention can be used in microwave oscillators, e.g., in Gunn effect type devices, well known in the art. Other uses for the doped and undoped crystals of this invention will be immediately apparent to those skilled in the art.

What is claimed is:

1. A process for increasing the electron mobility properties of a IIIB–VB compound selected from aluminum phosphide, aluminum arsenide, aluminum antimonide, gallium phosphide, gallium arsenide, gallium antimonide, indium phosphide, indium arsenide, indium antimonide, and mixtures thereof, which comprises providing a melt of at least a portion of a batch of said IIIB–VB compound, the melt containing an impurity diffeernt from any constituent element of said compound, having a distribution constant in said compound of less than 1 and selected from aluminum, antimony, bismuth, indium and lead, and forming a crystal of the compound at a freezing point lowered by inclusion in said melt of said impurity.

2. The process of claim **1** wherein said impurity has a distribution constant in said compound of 0.02 or less.

3. The process of claim **1** wherein the melt is subjected to a pressure of the VB component substantially corresponding to stoichiometric.

4. The process of claim **1** wherein a crystal of the compound is grown under stoichiometric pressure of the VB component.

5. The process of claim **1** wherein the compound contains at least about 2×10^{17} carriers per cm.^{3}.

6. The process of claim **5** wherein a substantial portion of the carrier concentration is obtained from dopant atoms selected from manganese, tellurium, selenium, sulfur, cadmium, zinc, tin, germanium, silicon, mixtures thereof, and the like.

7. The process of claim **1** wherein the compound contains carrier concentration from about 5×10^{17} to about 5×10^{18} atoms per cm.^{3}.

8. The process of claim **1** wherein the crystal is formed by pulling a seed of the crystal from the melt.

9. A process for increasing the electron mobility properties of a compound selected from gallium phosphide, gallium arsenide, gallium antimonide, indium phosphide, indium arsenide, indium antimonide, and mixtures thereof, which comprises providing a melt of at least a portion of a batch of said compound, the melt containing at least 1×10^{18} atoms of aluminum per cm.^{3} of said compound, and then forming a crystal of said compound from said melt.

10. A process for increasing the electron mobility properties of a compound selected from aluminum phosphide, aluminum arsenide, gallium phosphide, gallium arsenide, indium phosphide, indium arsenide, and mixtures thereof, which comprises providing a melt of at least a portion of a batch of said compound, the melt containing at least 1×10^{18} atoms of antimony per cm.^{3} of said compound, and then forming a crystal of said compound from said melt.

11. A process for increasing the electron mobility properties of a compound selected from aluminum phosphide, aluminum arsenide, aluminum antimonide, gallium phosphide, gallium arsenide, gallium antimonide, indium phosphide, indium arsenide, indium antimondide, and mixtures thereof, which comprises providing a melt of at least a portion of a batch of said compound, the melt containing at least 1×10^{18} atoms of bismuth per cm.^{3} of said compound, and then forming a crystal of said compound from said melt.

12. A process for increasing the electron mobility properties of a compound selected from aluminum phosphide, aluminum arsenide, aluminum antimonide, gallium phosphide, gallium arsenide, gallium antimonide, and mixtures thereof, which comprises providing a melt of at least a portion of a batch of said compound, the melt containing at least 1×10^{18} atoms of indium per cm.^{3} of said compound, and then forming a crystal of said compound from said melt.

13. A process for increasing the electron mobility properties of a compound selected from aluminum phosphide, aluminum arsenide, aluminum antimonide, gallium phosphide, gallium arsenide, gallium antimonide, indium phosphide, indium arsenide, indium antimonide, and mixtures thereof, which comprises providing a melt of at least a portion of a batch of said compounds, the melt containing at least 1×10^{18} atoms of lead per cm.^{3} of said compound, and then forming a crystal of said compound from said melt.

14. A process for increasing the electron mobility properties of gallium arsenide, which comprises providing a melt of at least a portion of a batch of said gallium arsenide, the melt containing at least 1×10^{18} atoms of aluminum, antimony, bismuth, indium, or lead per cm.^{3} of said gallium arsenide, and then forming a crystal of gallium arsenide from said melt.

15. A process for increasing the electron mobility properties of gallium arsenide, which comprises providing a melt of at least a portion of a batch of said gallium arsenide, the melt containing at least 1×10^{18} atoms of aluminum per cm.^{3} of said gallium arsenide, and forming a crystal of gallium arsenide from said melt.

16. A process for increasing the electron mobility properties of gallium arsenide, which comprises providing a melt of at least a portion of a batch of said gallium arsenide, the melt containing at least 1×10^{18} atoms of antimony per cm.^{3} of said gallium arsenide, and forming a crystal of gallium arsenide from said melt.

17. A process for increasing the electron mobility properties of gallium arsenide, which comprises providing a melt of at least a portion of a batch of said gallium arsenide, the melt containing at least 1×10^{18} atoms of bismuth per cm.^{3} of said gallium arsenide, and forming a crystal of gallium arsenide from said melt.

18. A process for increasing the electron mobility properties of gallium arsenide, which comprises providing a melt of at least a portion of a batch of said gallium arsenide, the melt containing at least 1×10^{18} atoms of indium per cm.^{3} of said gallium arsenide, and forming a crystal of gallium arsenide from said melt.

19. A process for increasing the electron mobility properties of gallium arsenide, which comprises providing a melt of at least a portion of a batch of said gallium arsenide, the melt containing at least 1×10^{18} atoms of lead per cm.^{3} of said gallium arsenide, and forming a crystal of gallium arsenide from said melt.

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