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United States Patent [19]

Schetzina

[11] Patent Number: 5,294,833

[45] Date of Patent: Mar. 15, 1994

[54] INTEGRATED HETEROSTRUCTURE OF GROUP II-VI SEMICONDUCTOR MATERIALS INCLUDING EPITAXIAL OHMIC CONTACT AND METHOD OF FABRICATING SAME

[75] Inventor: **Jan F. Schetzina**, Cary, N.C.

[73] Assignee: **North Carolina State University**, Raleigh, N.C.

[21] Appl. No.: **934,190**

[22] Filed: **Aug. 21, 1992**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 881,599, May 12, 1992.

[51] **Int. Cl.**^{5} **H01L 33/00**; H01L 29/161; H01L 29/205; H01L 29/225

[52] **U.S. Cl.** **257/741**; 257/743; 257/749; 257/78; 257/99; 257/94

[58] **Field of Search** 257/741, 191, 201, 78, 257/99, 743, 94, 749

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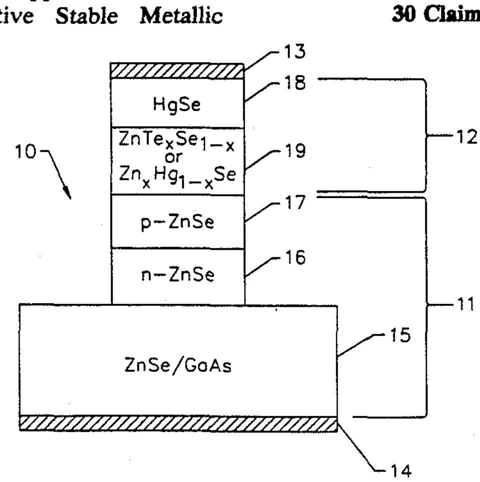
(List continued on next page.)

Primary Examiner—William D. Larkins
Assistant Examiner—Stephen D. Meier
Attorney, Agent, or Firm—Bell, Seltzer, Park & Gibson

[57] **ABSTRACT**

An ohmic contact to a p-type zinc selenide (ZnSe) layer in a Group II-VI semiconductor device, includes a zinc telluride selenide ($ZnTe_xSe_{1-x}$) layer on the zinc selenide layer, a mercury selenide (HgSe) layer on the zinc telluride selenide layer and a conductor (such as metal) layer on the mercury selenide layer. The zinc telluride selenide and mercury selenide layers between the p-type zinc selenide and the conductor layer provide an ohmic contact by eliminating the band offset between the wide bandgap zinc selenide and the conductor. Step graded, linear graded, and parabolic graded layers of zinc telluride selenide may be provided. An integrated heterostructure is formed by epitaxially depositing the ohmic contact on the Group II-VI device. A removable overcoat layer may be formed on the Group II-VI device to allow room temperature atmospheric pressure transfer of the device from a zinc based deposition chamber to a mercury based deposition chamber, for deposition of the ohmic contact. A large area emitter may be formed by limiting the thickness of the mercury selenide layer so that optical radiation passes therethrough. A high efficiency optical emitter may be provided by using zinc telluride selenide or zinc sulfur telluride selenide to form an isoelectronic trap which produces broad and intense light output in the blue/-green region.

30 Claims, 28 Drawing Sheets



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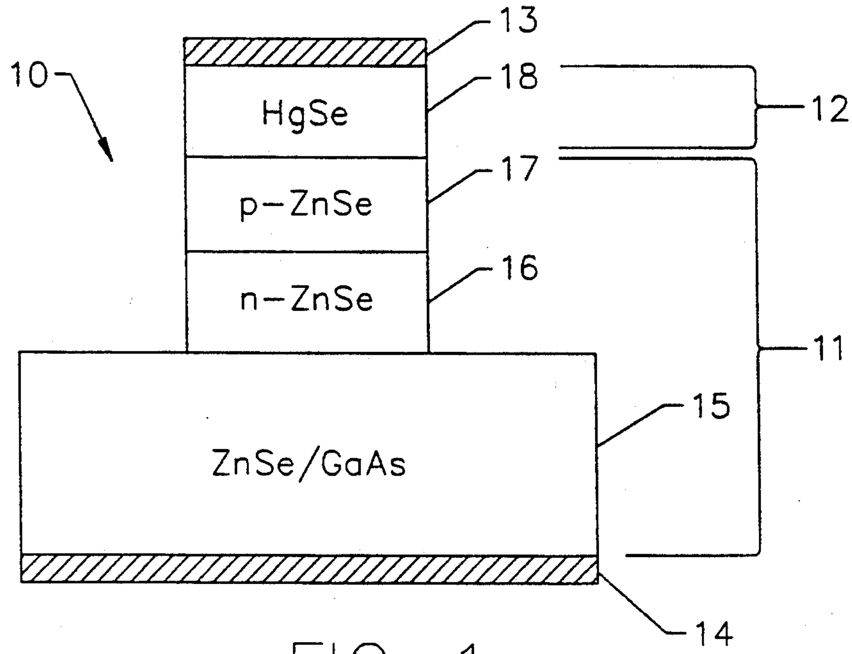

10
13
18
HgSe
12
17
p−ZnSe
16
n−ZnSe
11
15
ZnSe/GaAs
14

FIG. 1.

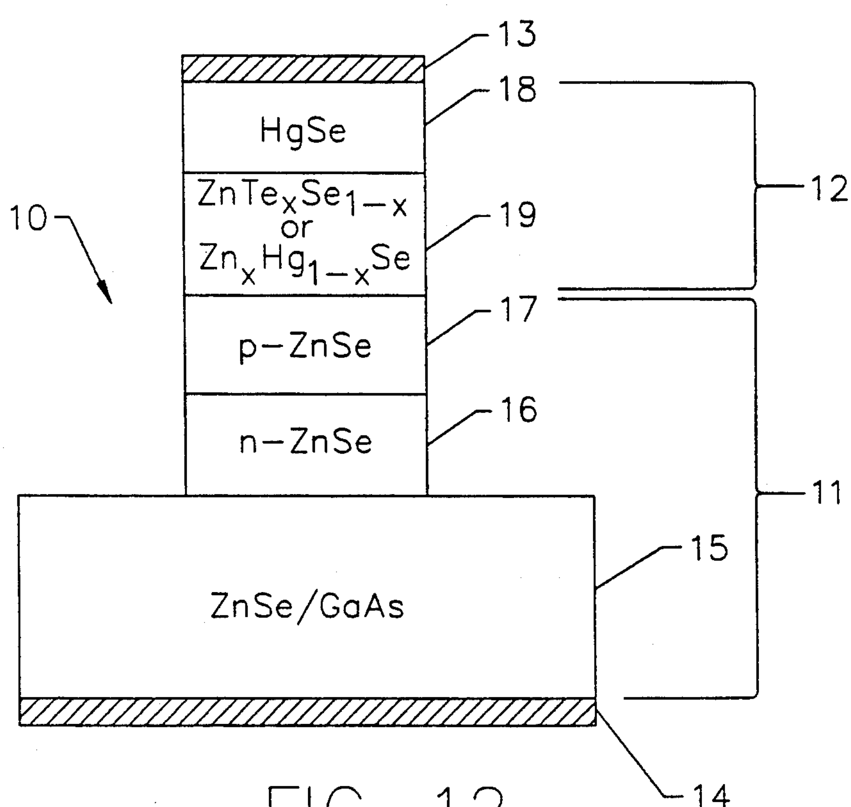

10
13
18
HgSe
12
19
ZnTe$_x$Se$_{1-x}$
or
Zn$_x$Hg$_{1-x}$Se
17
p−ZnSe
16
n−ZnSe
11
15
ZnSe/GaAs
14

FIG. 12.

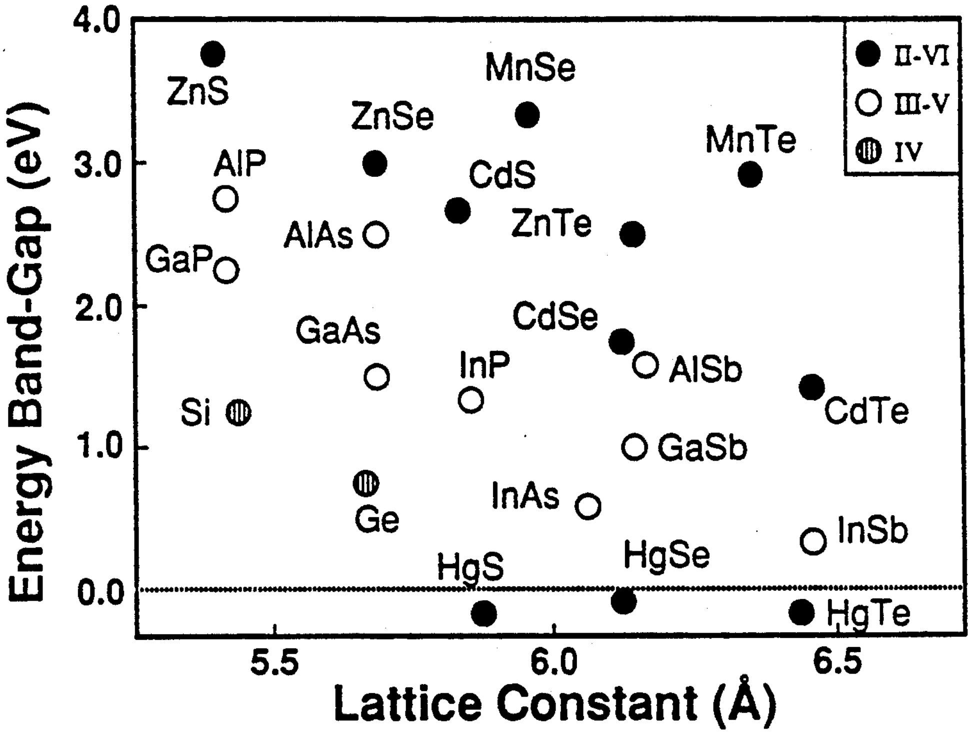

4.0
3.0
2.0
1.0
0.0
Energy Band-Gap (eV)
5.5
6.0
6.5
Lattice Constant (Å)
ZnS
MnSe
ZnSe
MnTe
AlP
CdS
AlAs
ZnTe
GaP
GaAs
CdSe
InP
AlSb
Si
CdTe
GaSb
InAs
Ge
InSb
HgS
HgSe
HgTe
II-VI
III-V
IV

FIG. 2.

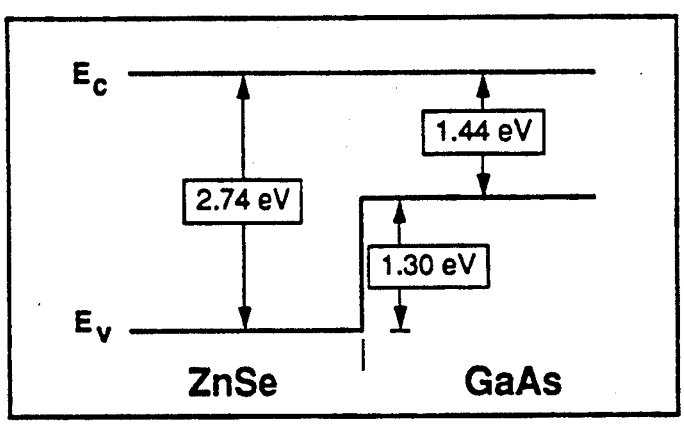

E_c
1.44 eV
2.74 eV
1.30 eV
E_v
ZnSe
GaAs

FIG. 3.

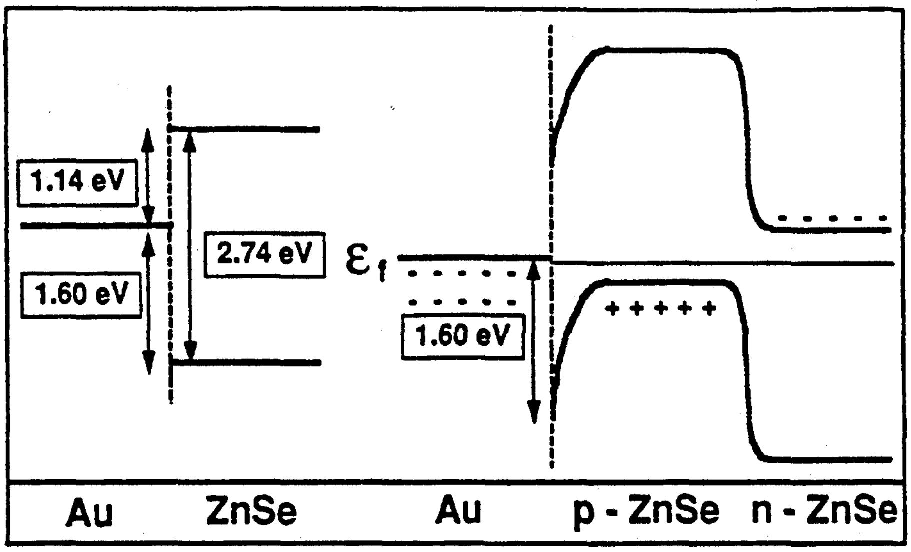

1.14 eV
1.60 eV
2.74 eV
ε_f
1.60 eV
+ + + + +
Au
ZnSe
Au
p - ZnSe
n - ZnSe

FIG. 4.

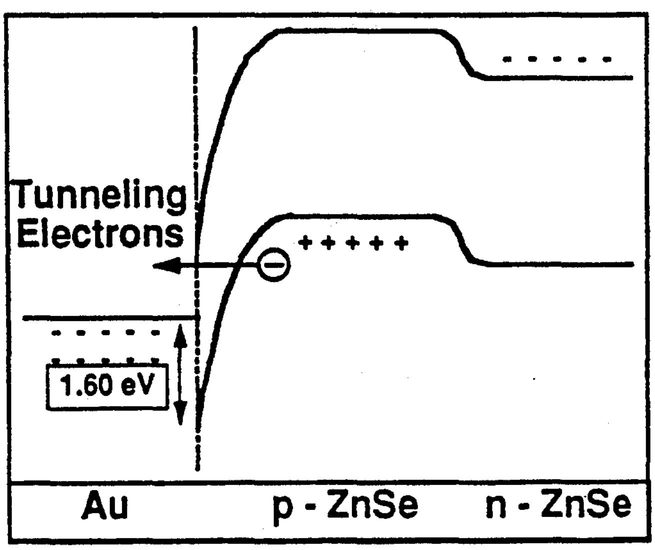

Tunneling
Electrons
+ + + + +
1.60 eV
Au
p - ZnSe
n - ZnSe

FIG. 5.

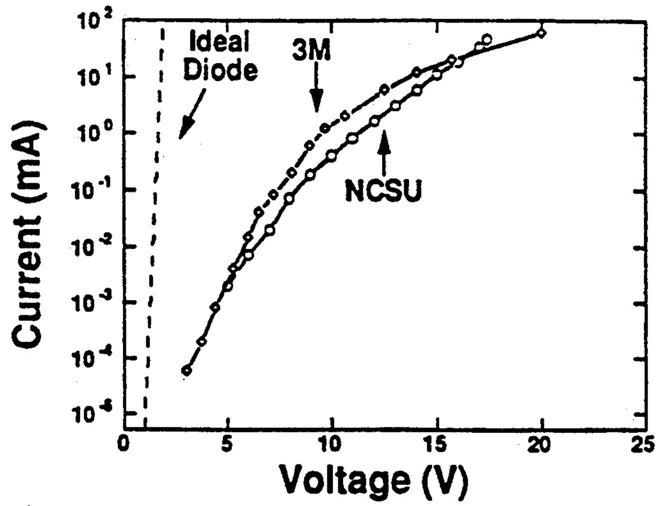


FIG. 6.

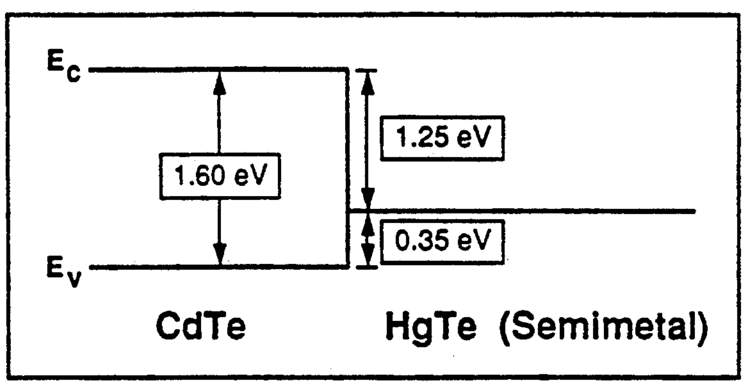


FIG. 7.

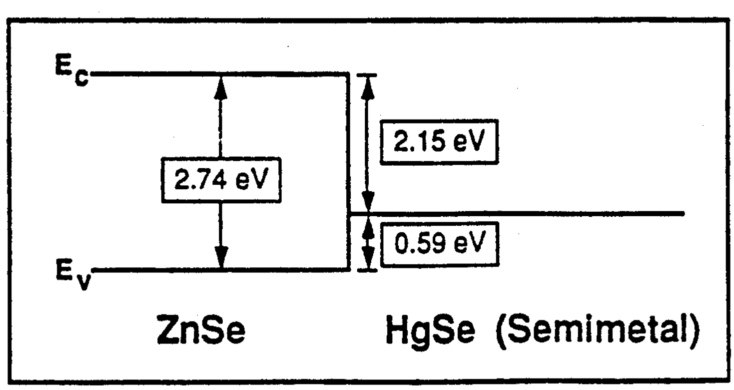


FIG. 8.

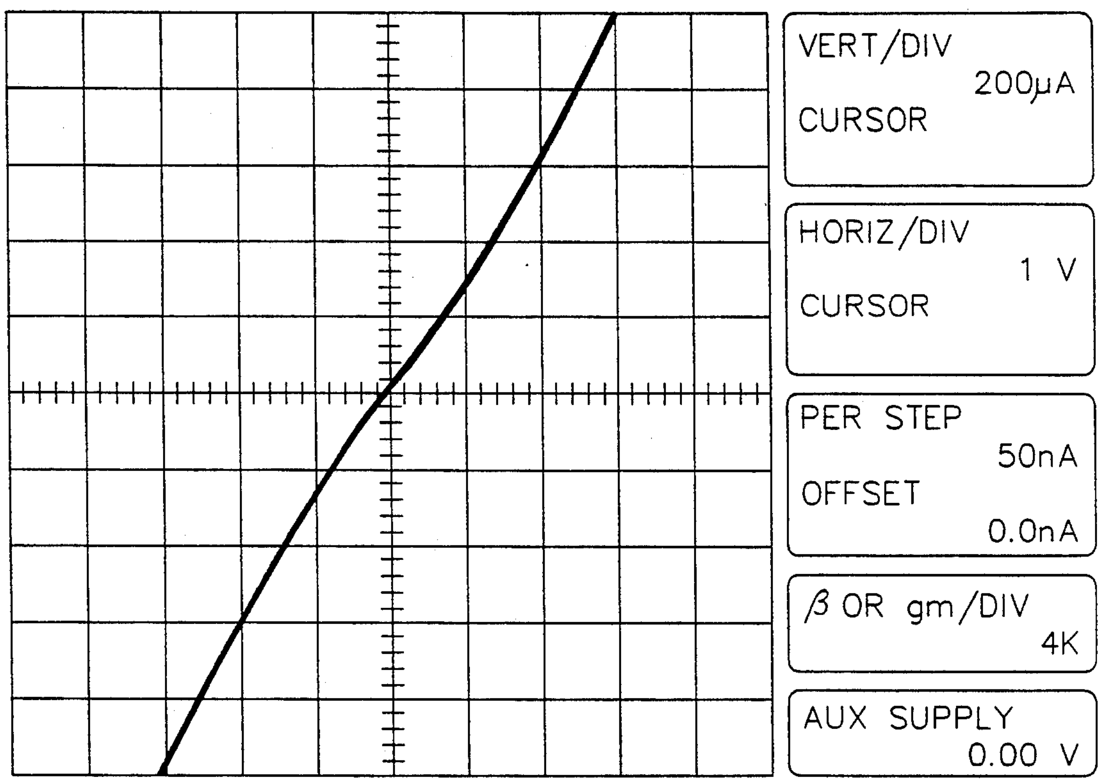

VERT/DIV
200μA
CURSOR
HORIZ/DIV
1 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
4K
AUX SUPPLY
0.00 V

FIG. 9.

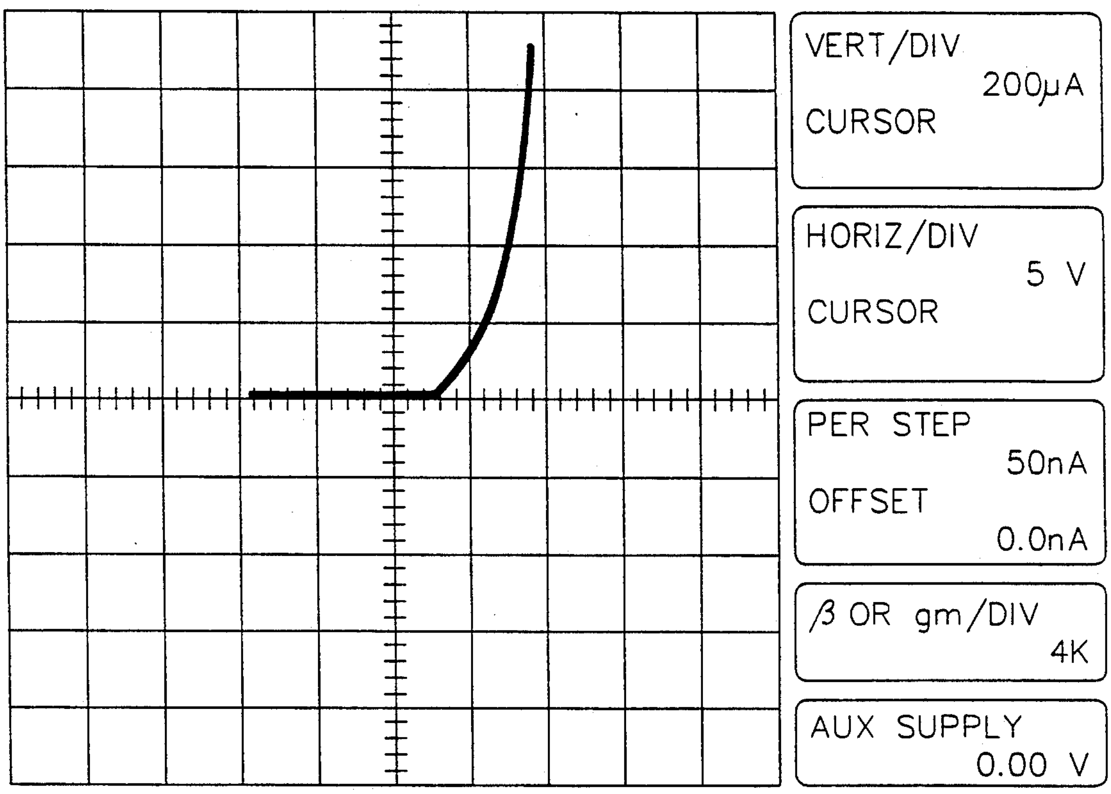

VERT/DIV
200μA
CURSOR
HORIZ/DIV
5 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
4K
AUX SUPPLY
0.00 V

FIG. 10a.

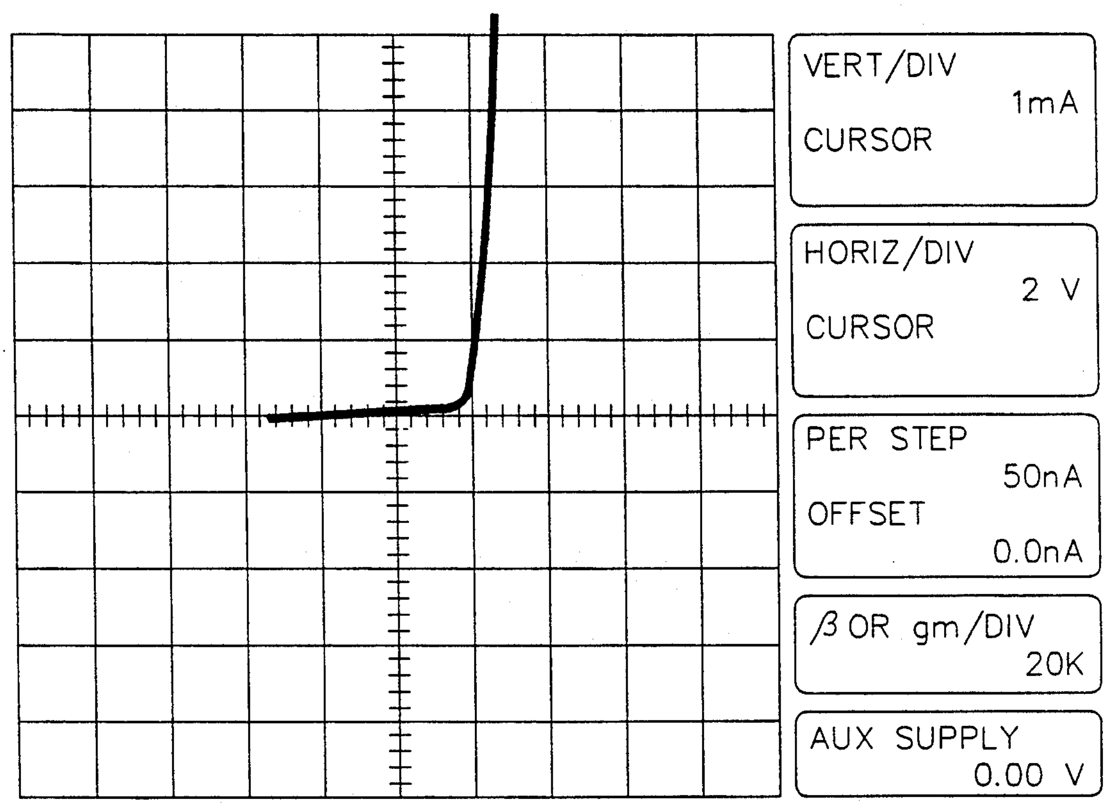

VERT/DIV
1mA
CURSOR
HORIZ/DIV
2 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
20K
AUX SUPPLY
0.00 V

FIG. 10b.

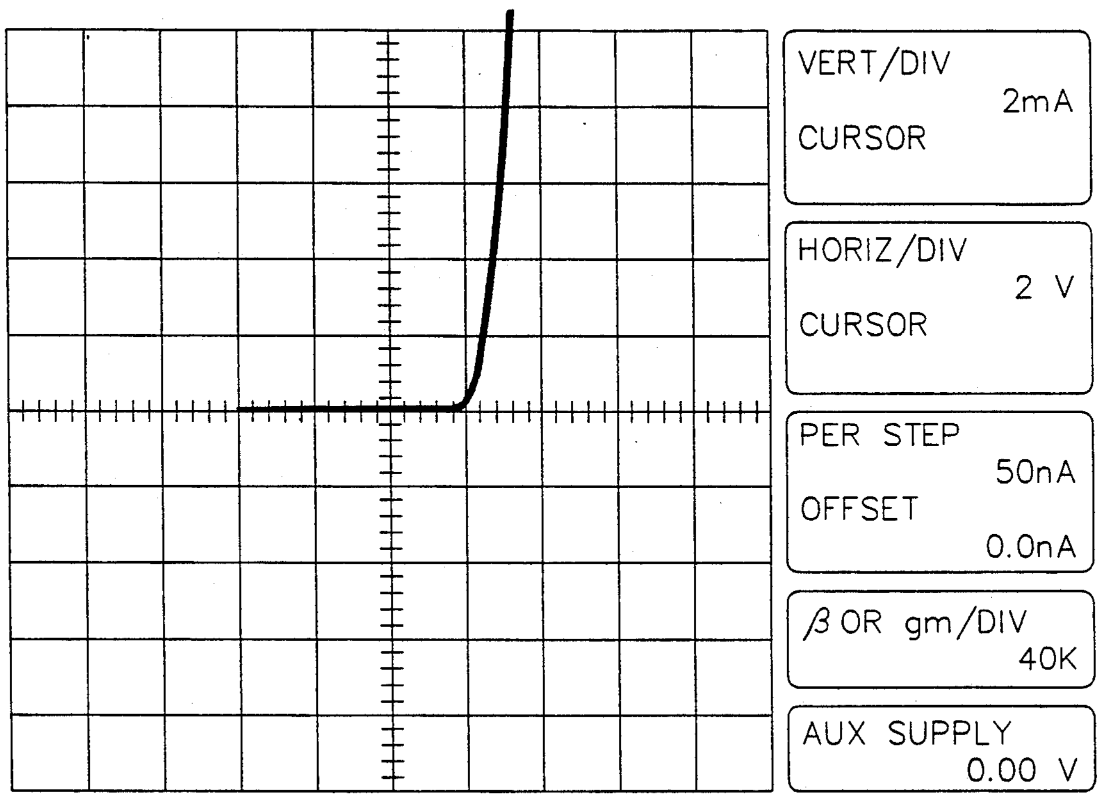

VERT/DIV
2mA
CURSOR
HORIZ/DIV
2 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
40K
AUX SUPPLY
0.00 V

FIG. 10c.

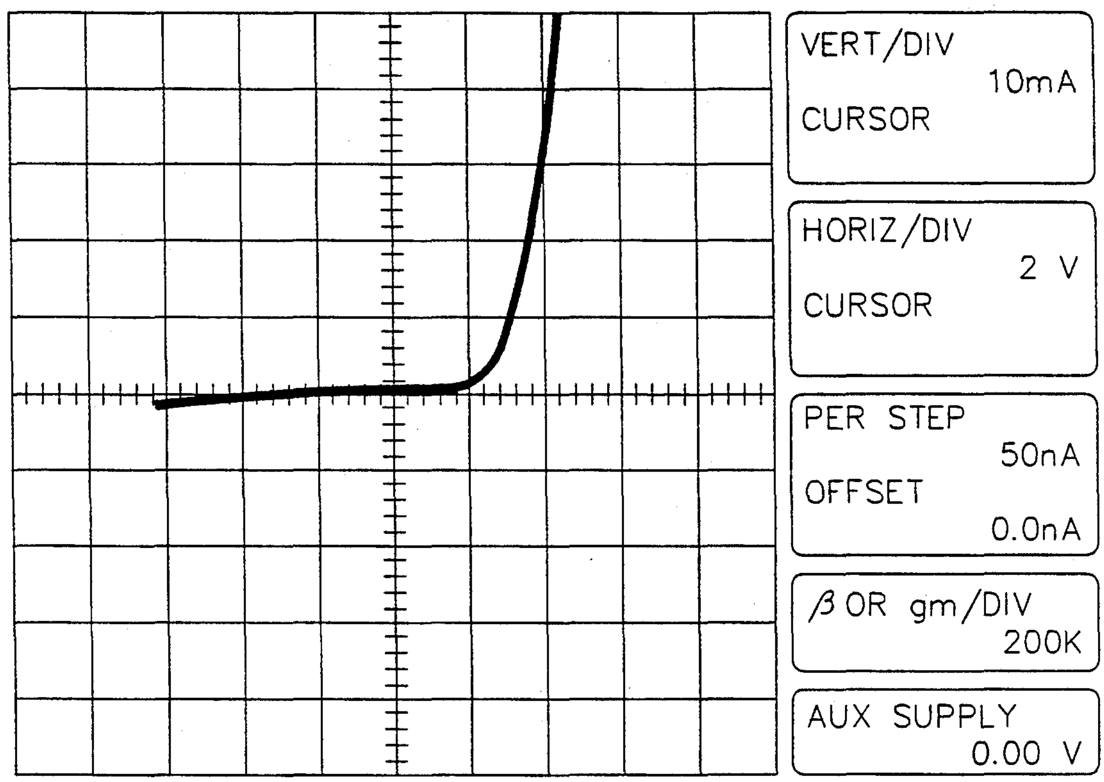

VERT/DIV
10mA
CURSOR
HORIZ/DIV
2 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
200K
AUX SUPPLY
0.00 V

FIG. 10d.

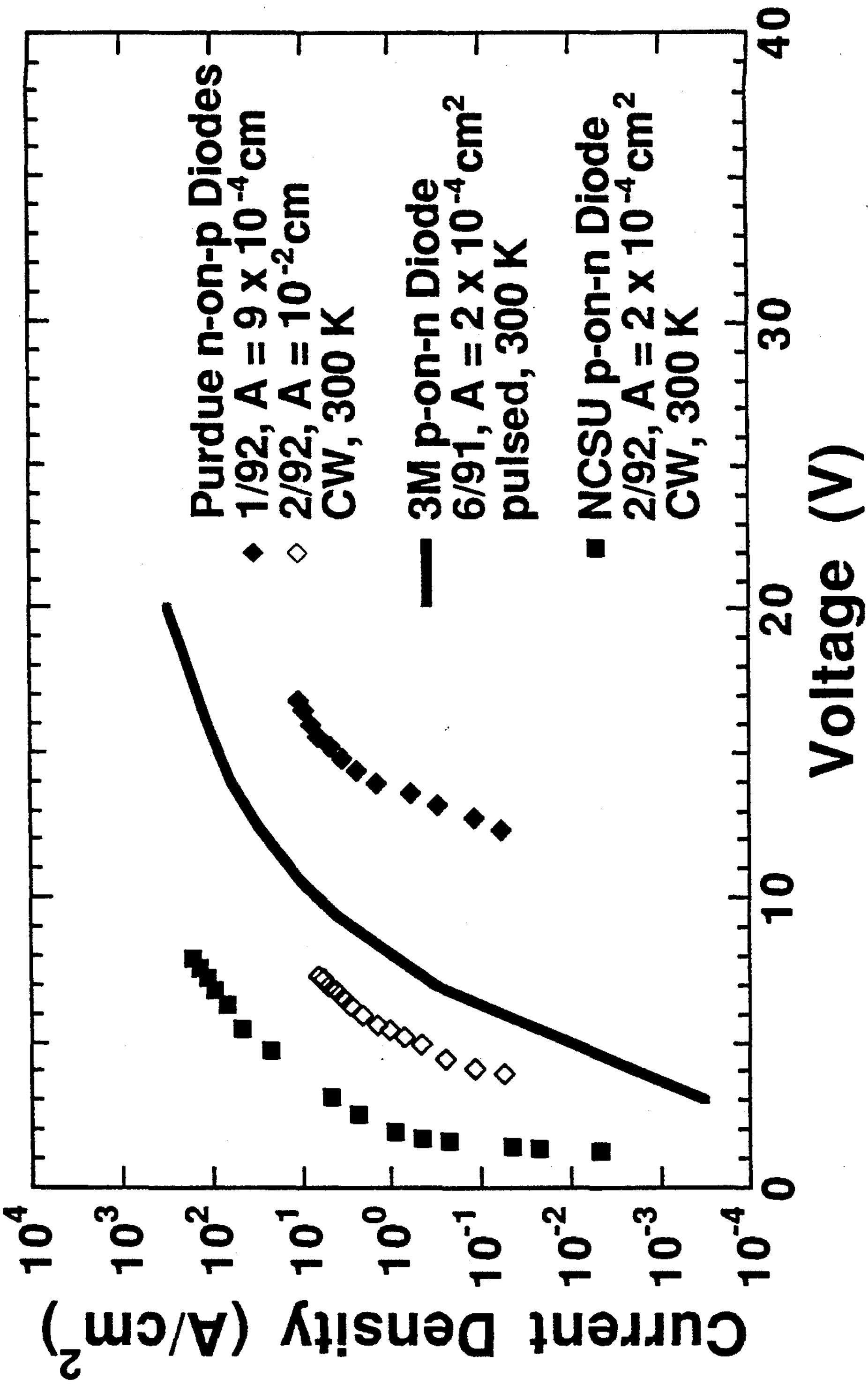

Purdue n-on-p Diodes
1/92, A = 9 x 10^-4 cm
2/92, A = 10^-2 cm
CW, 300 K
3M p-on-n Diode
6/91, A = 2 x 10^-4 cm^2
pulsed, 300 K
NCSU p-on-n Diode
2/92, A = 2 x 10^-4 cm^2
CW, 300 K
Voltage (V)
Current Density (A/cm^2)
0
10
20
30
40
10^-4
10^-3
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4

FIG. 11.

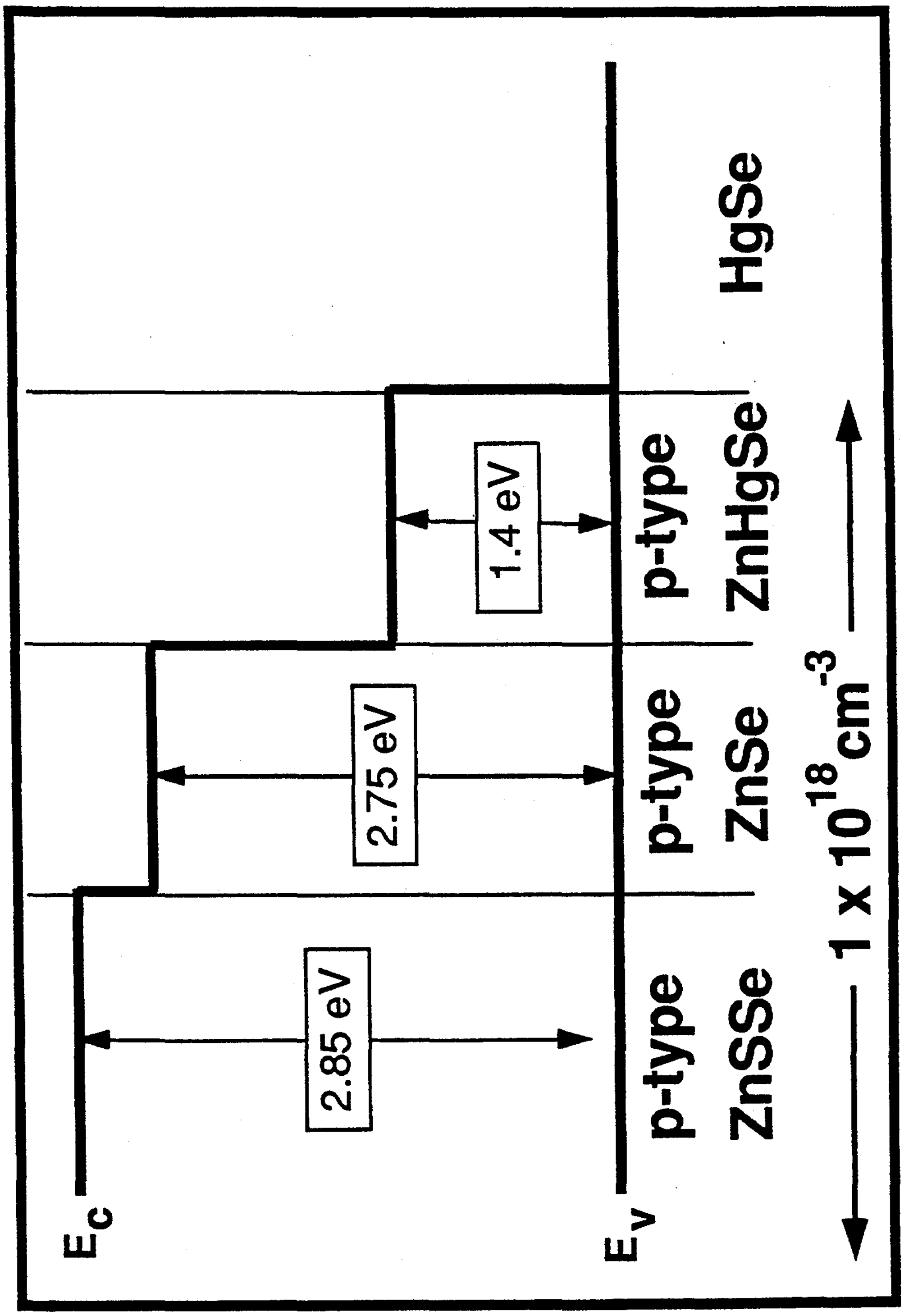
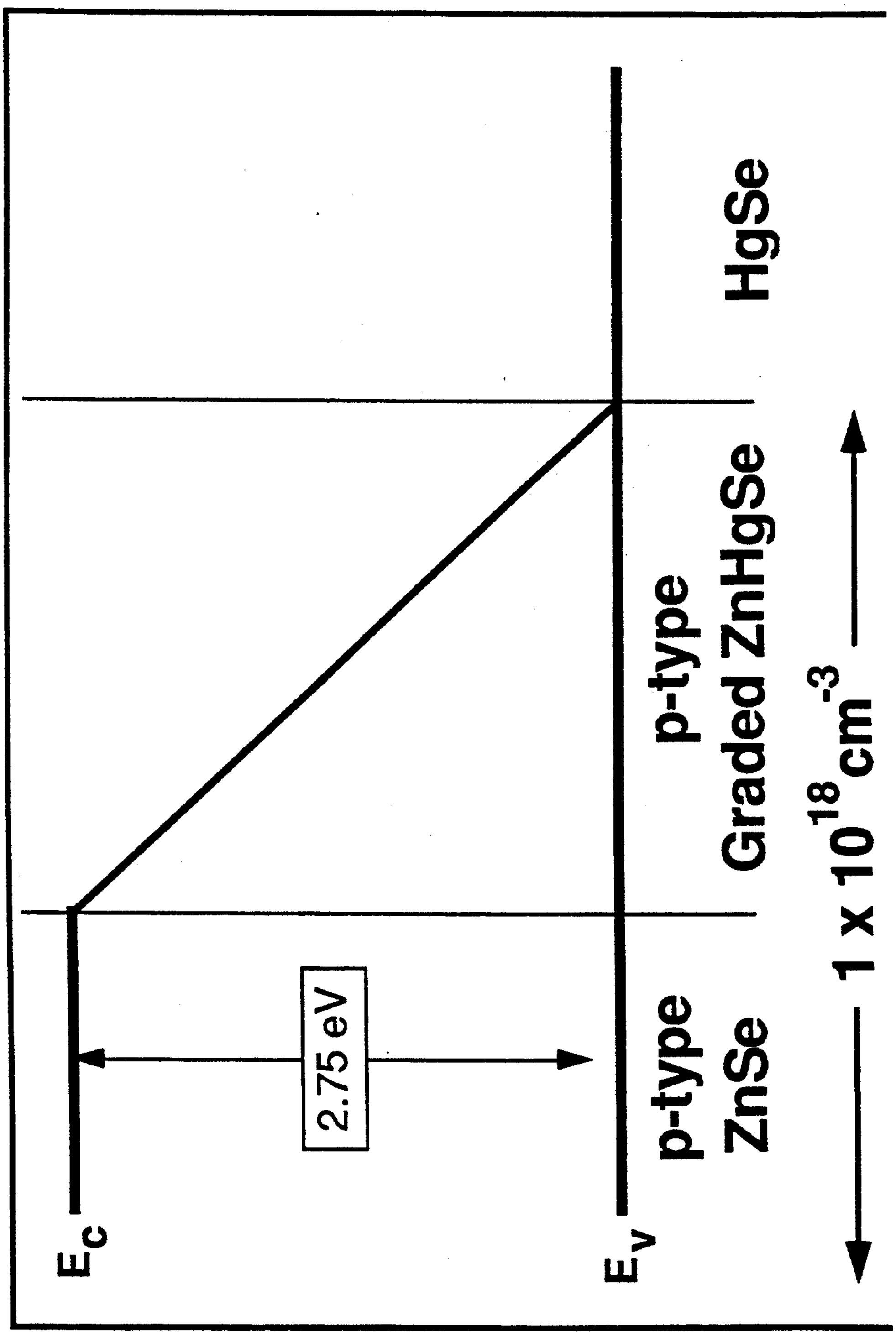
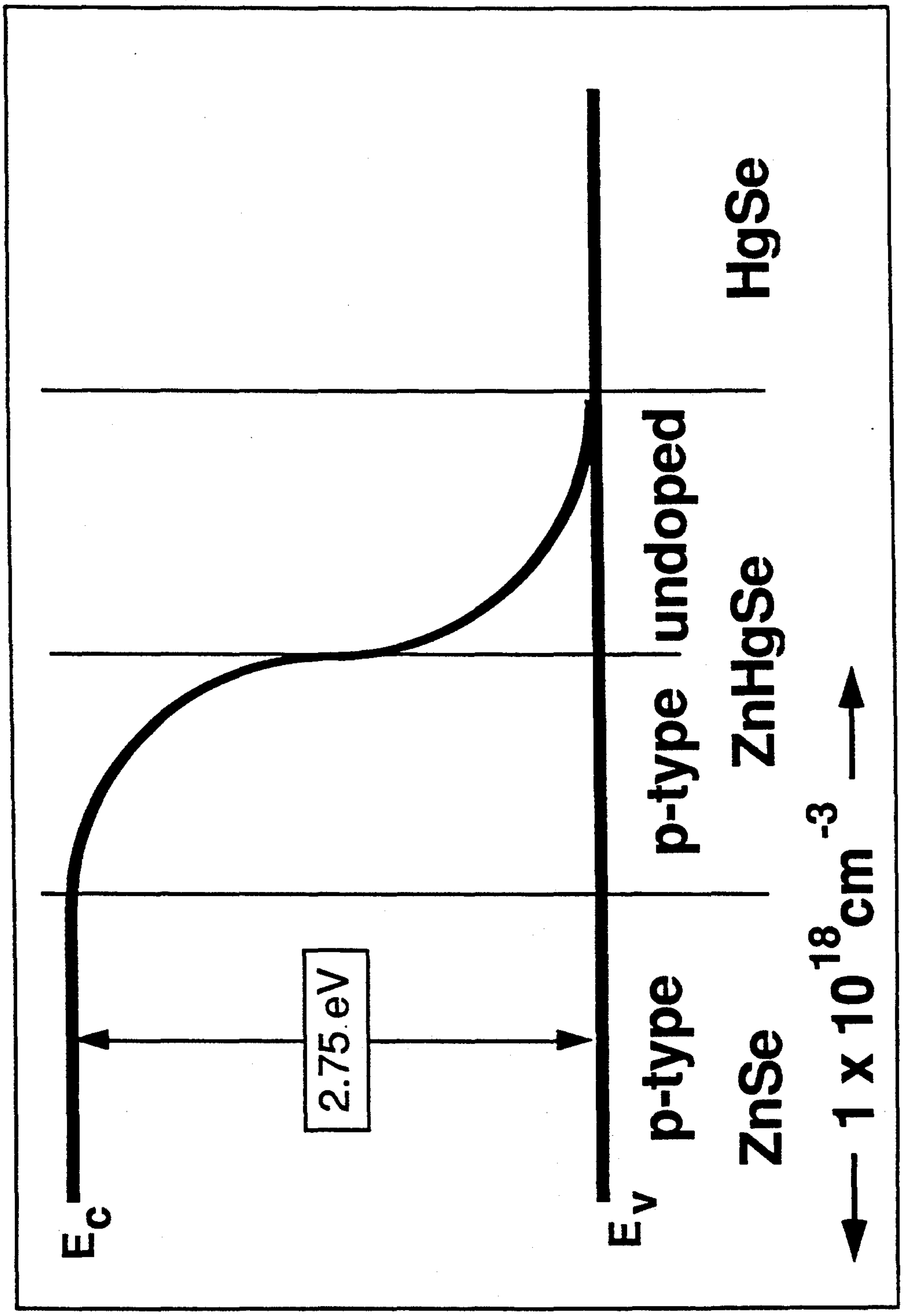

E_C
E_V
2.85 eV
2.75 eV
1.4 eV
p-type ZnSSe
p-type ZnSe
p-type ZnHgSe
HgSe
1 x 10^18 cm^-3

FIG. 13.



E_c
E_V
2.75 eV
p-type ZnSe
p-type Graded ZnHgSe
HgSe
$1 \times 10^{18} cm^{-3}$

FIG. 14.



E_c
E_v
2.75 eV
p-type
ZnSe
p-type
undoped
ZnHgSe
HgSe
$1 \times 10^{18} cm^{-3}$

FIG. 15.

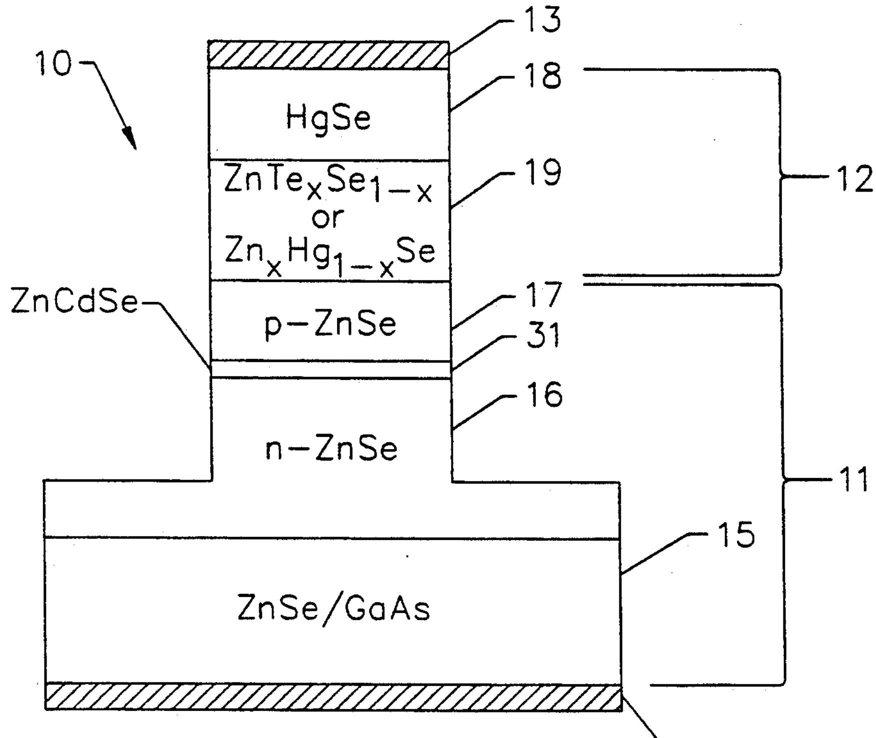


FIG. 16a.

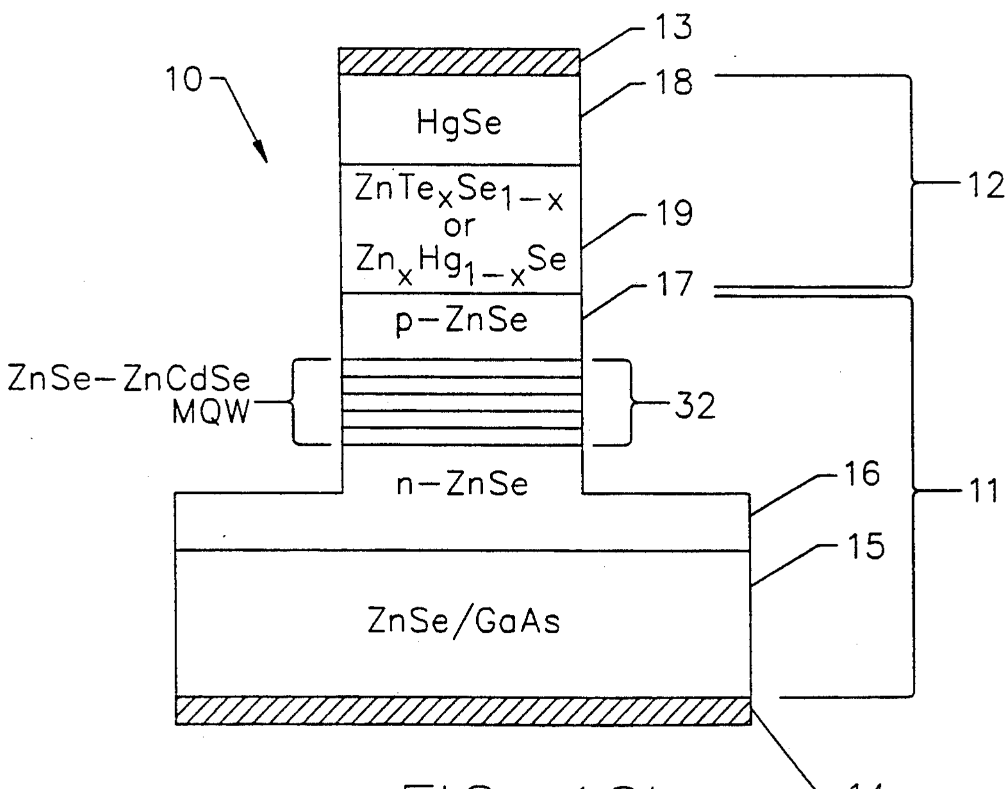


FIG. 16b.

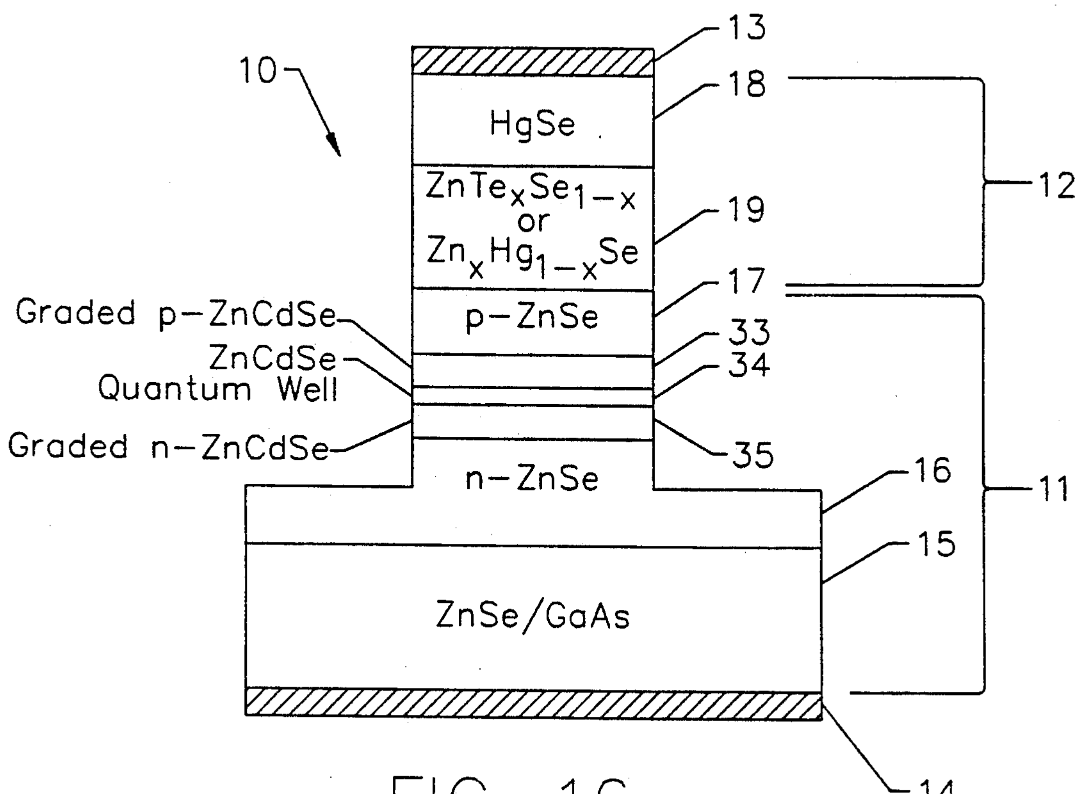


FIG. 16c.

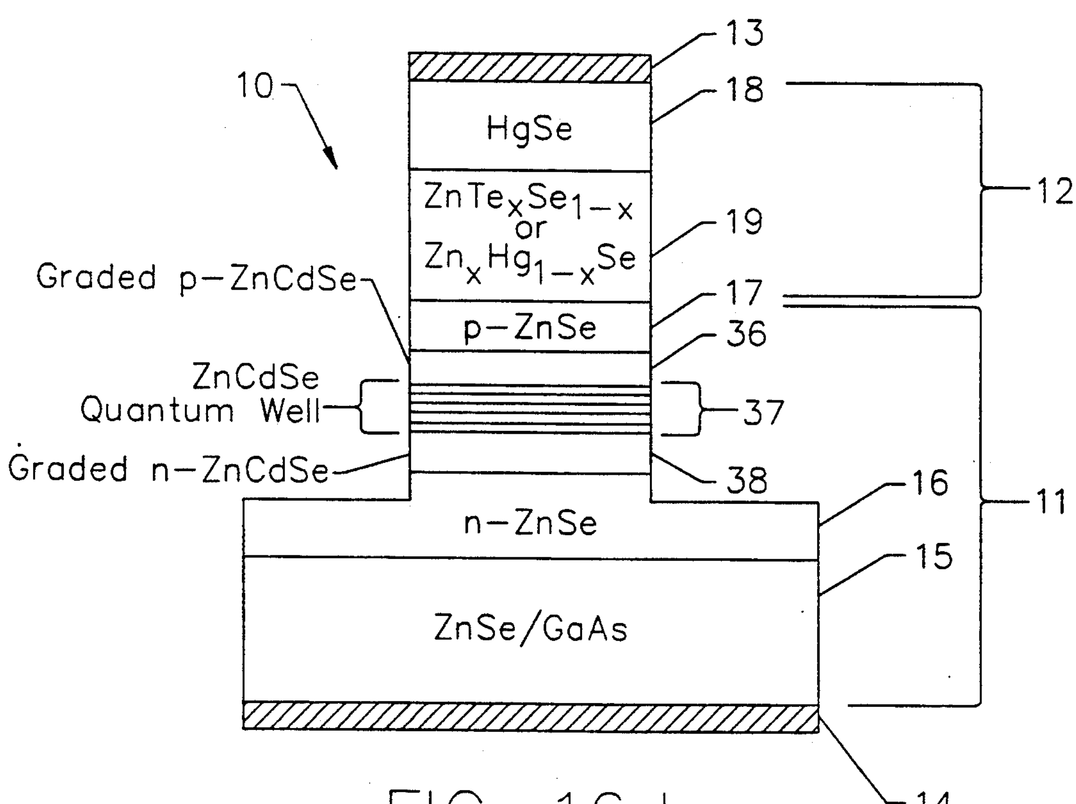


FIG. 16d.

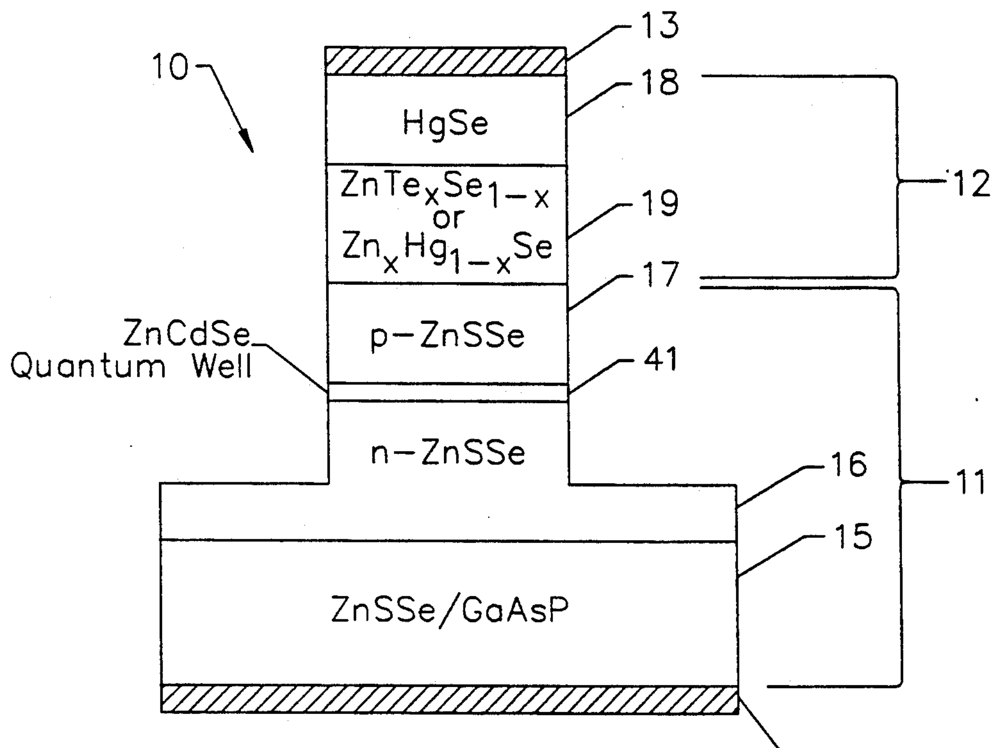


FIG. 16e.

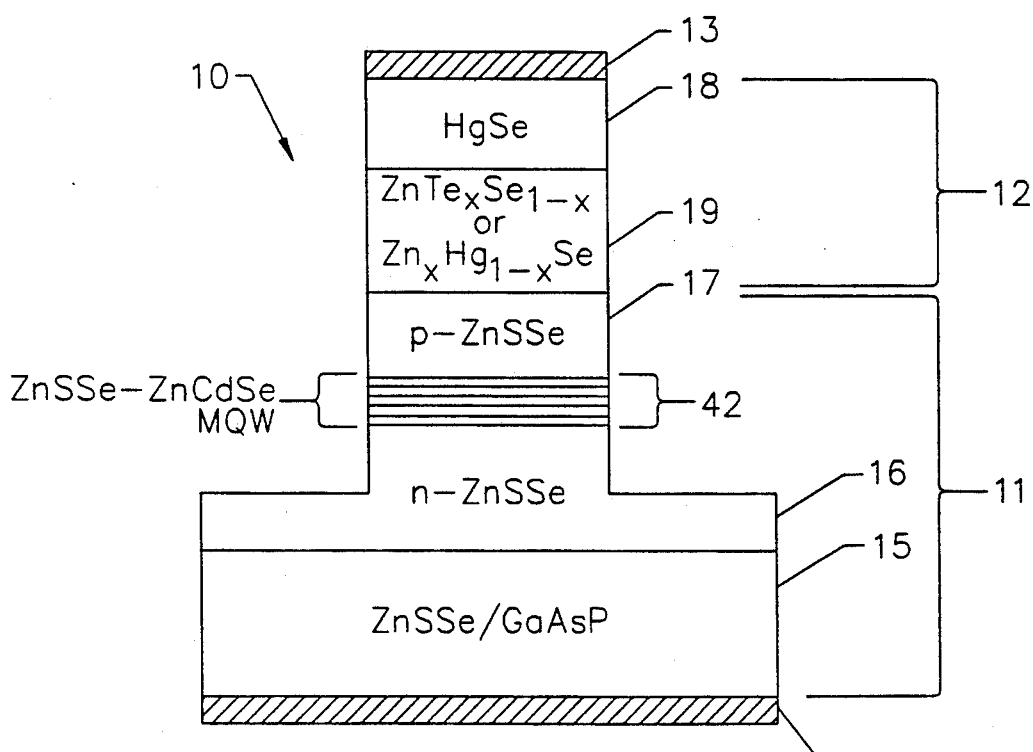


FIG. 16f.

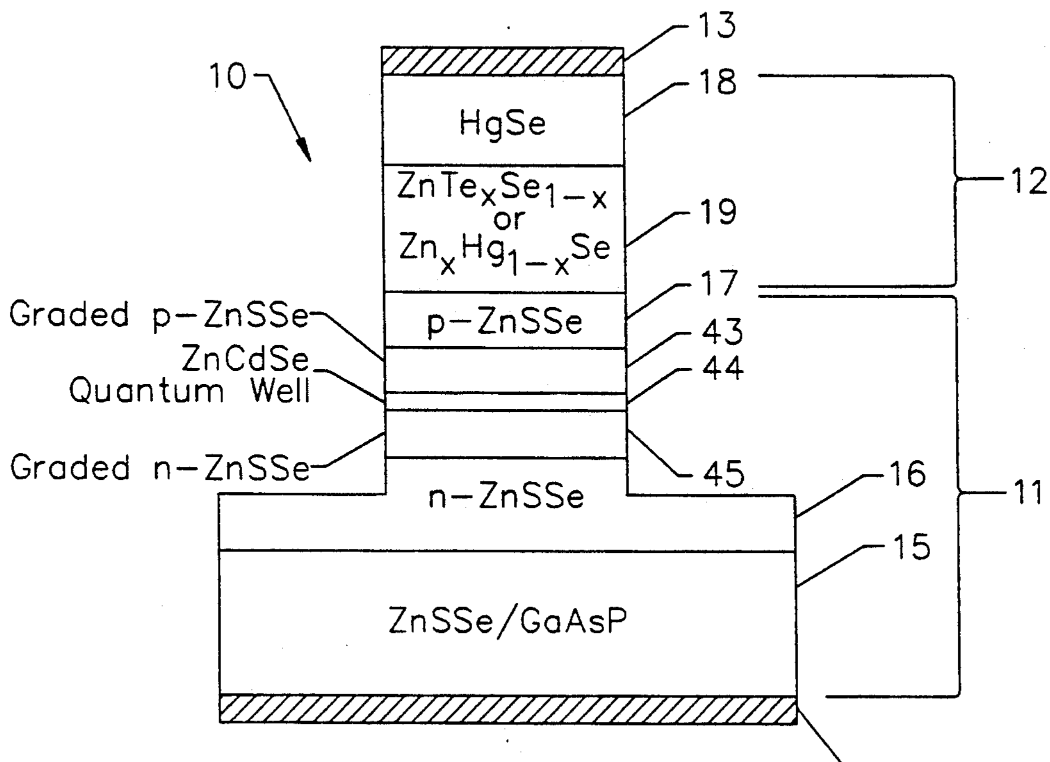


FIG. 16g.

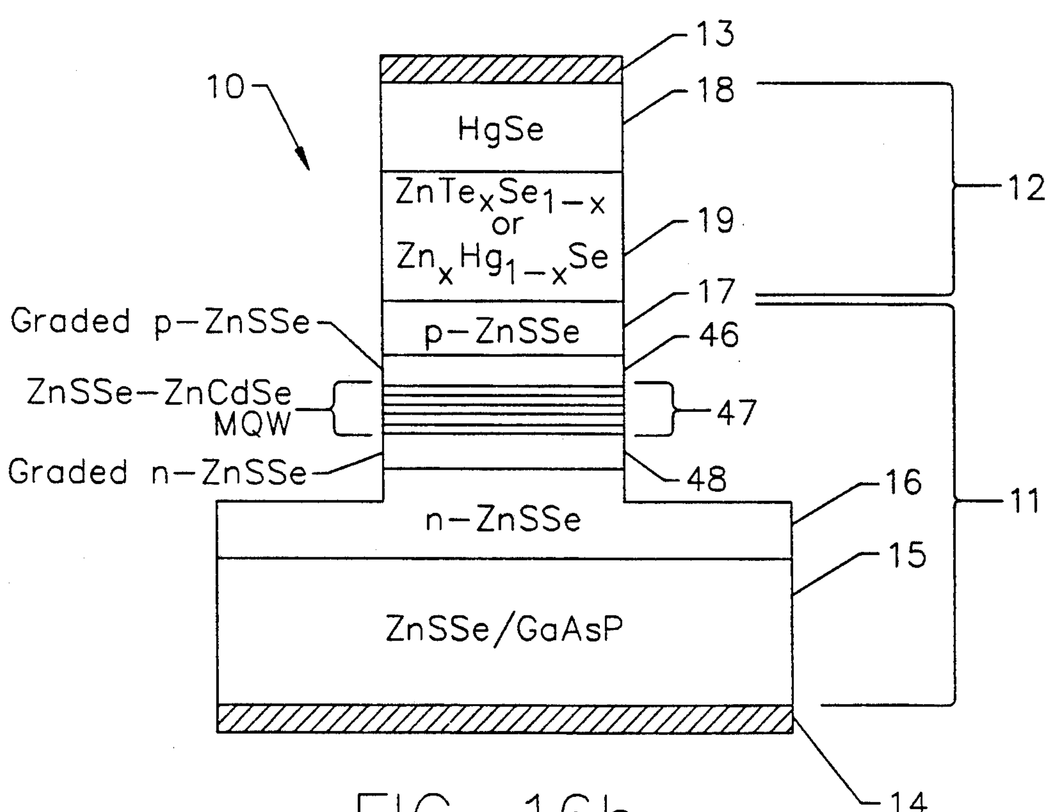


FIG. 16h.

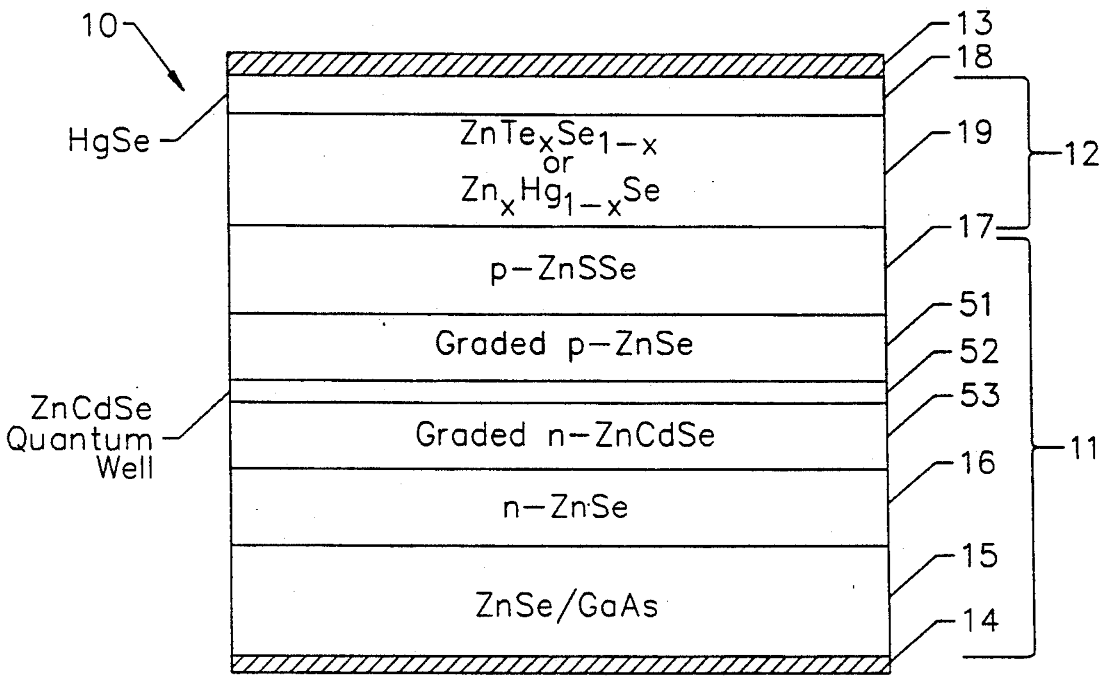


FIG. 16i.

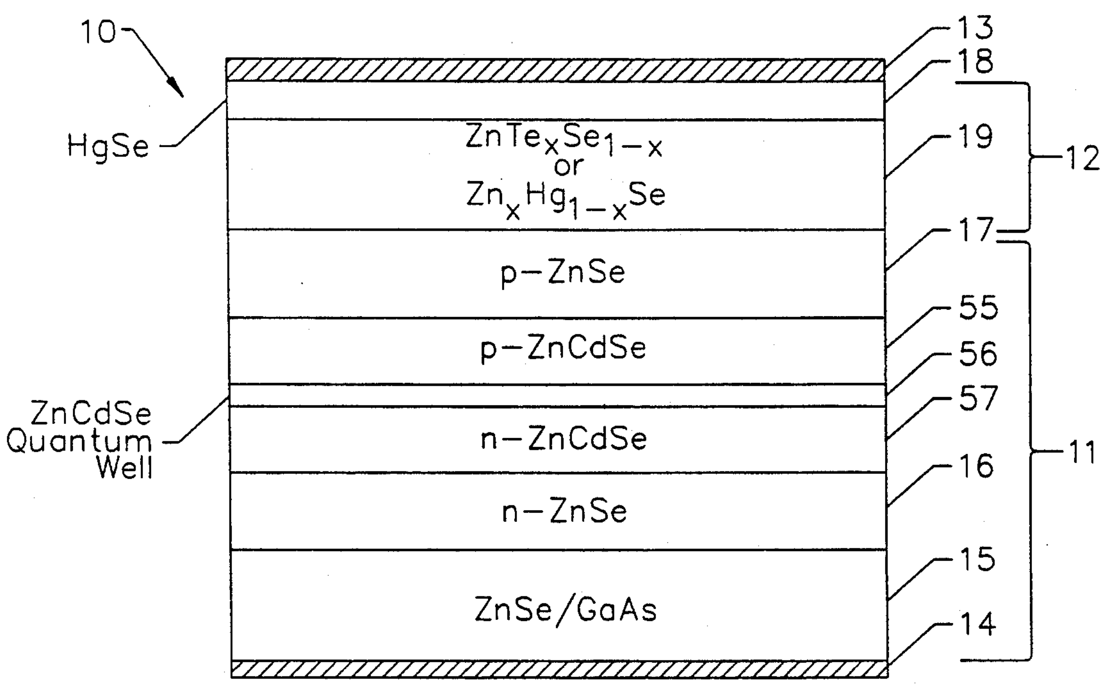


FIG. 16j.

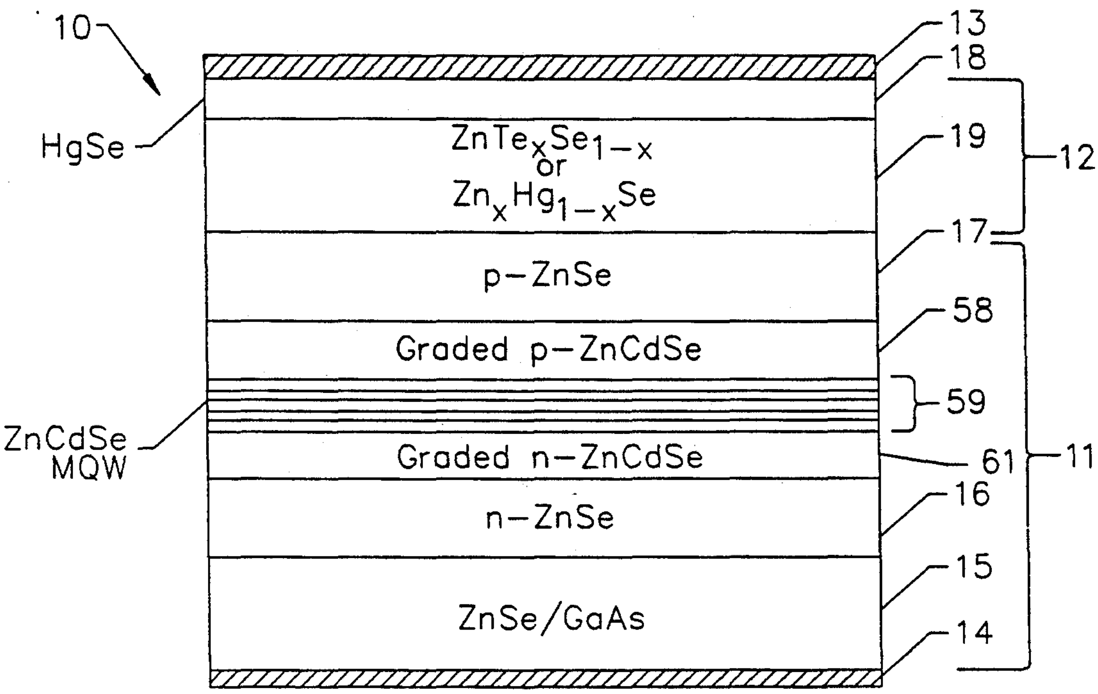


FIG. 16k.

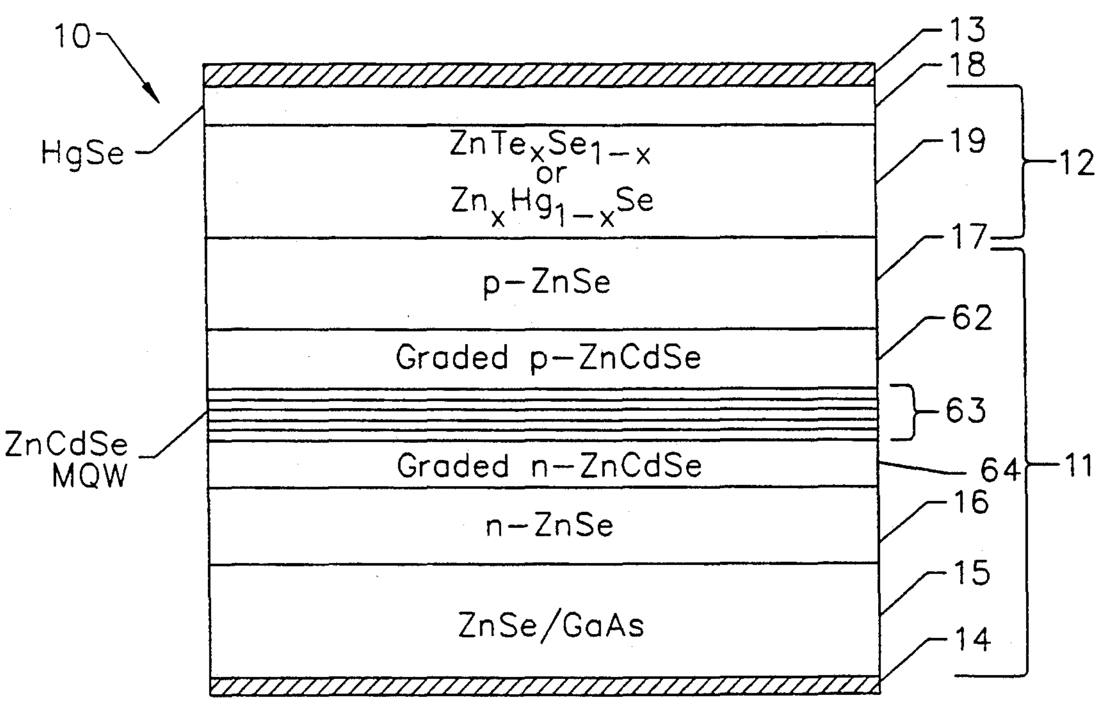


FIG. 16l.

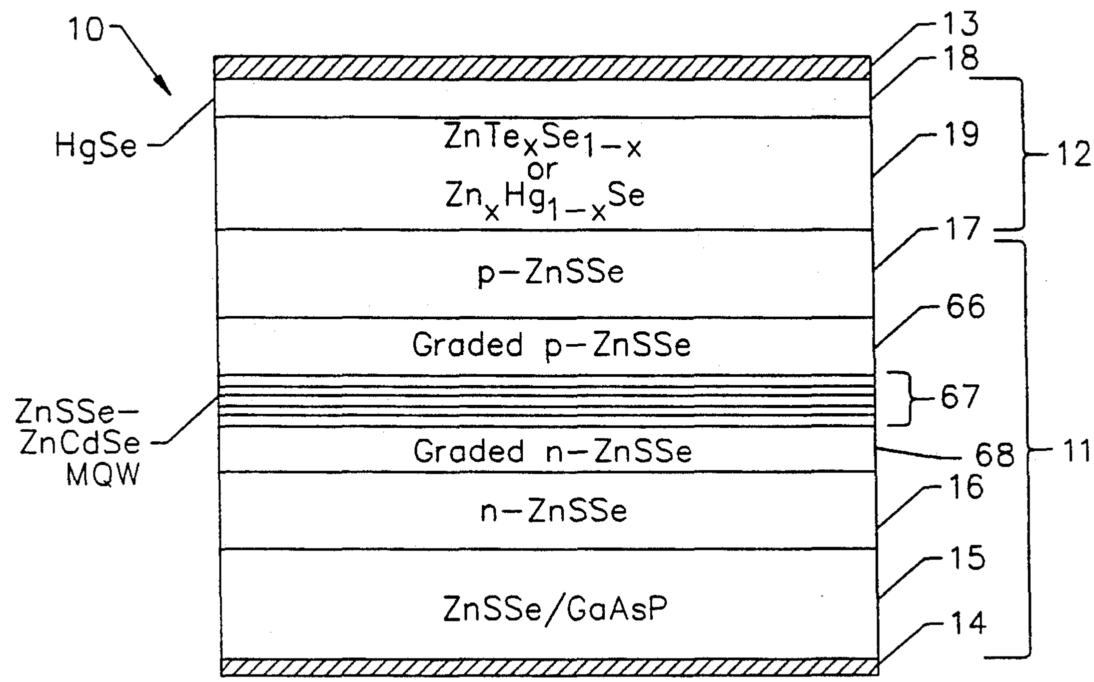


FIG. 16m.

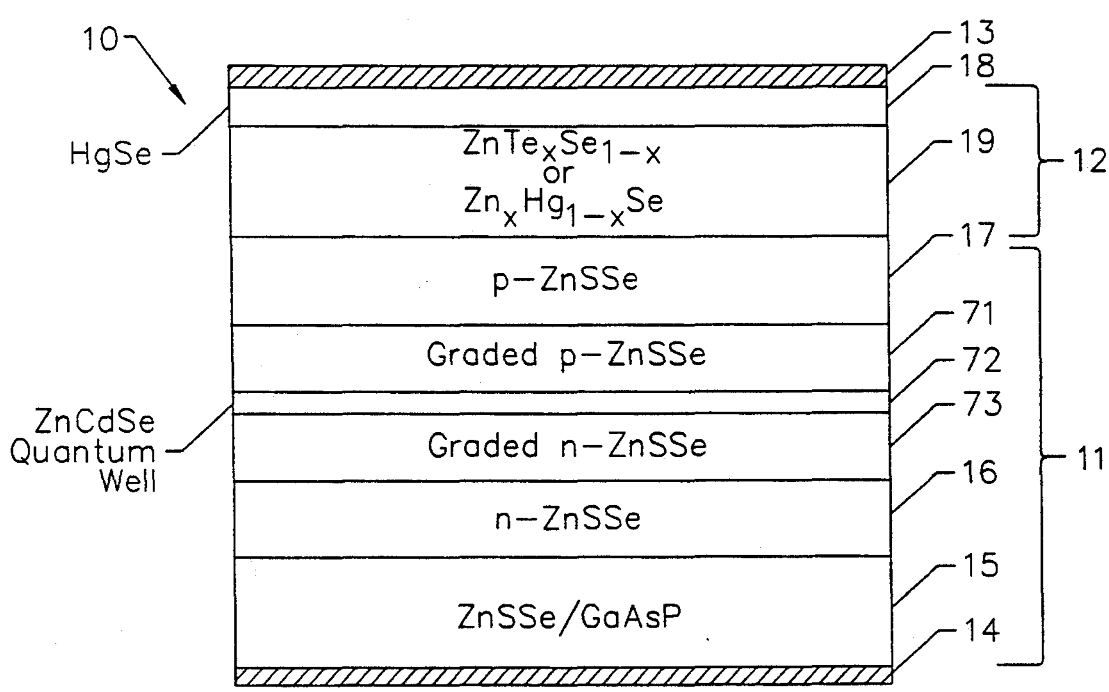


FIG. 16n.

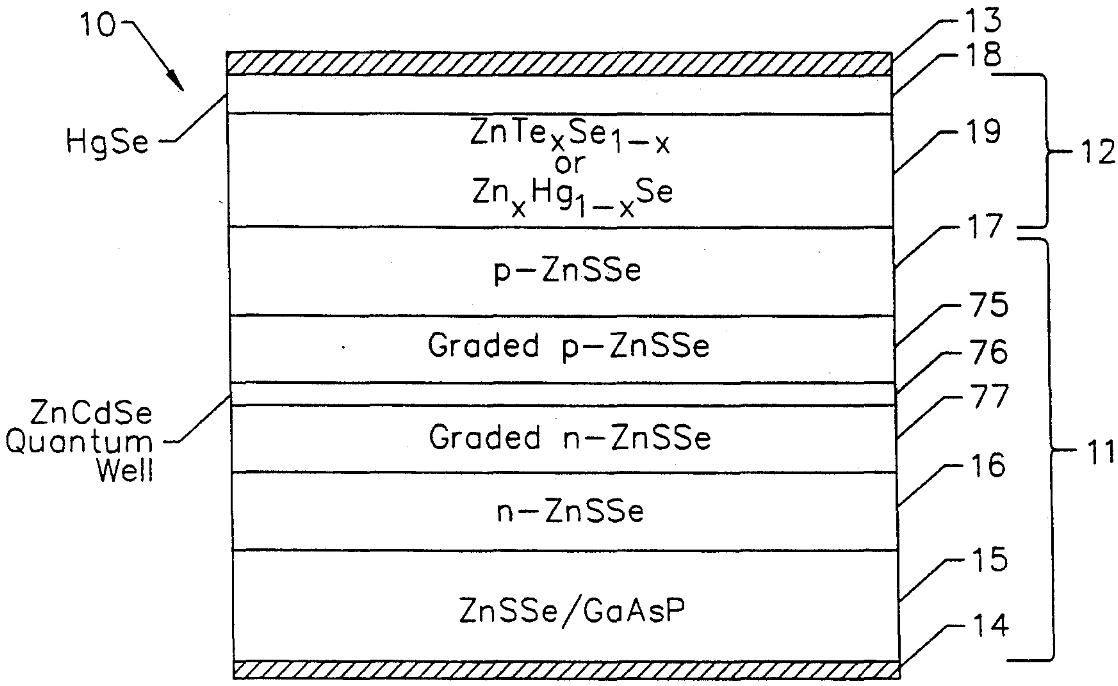


FIG. 16o.

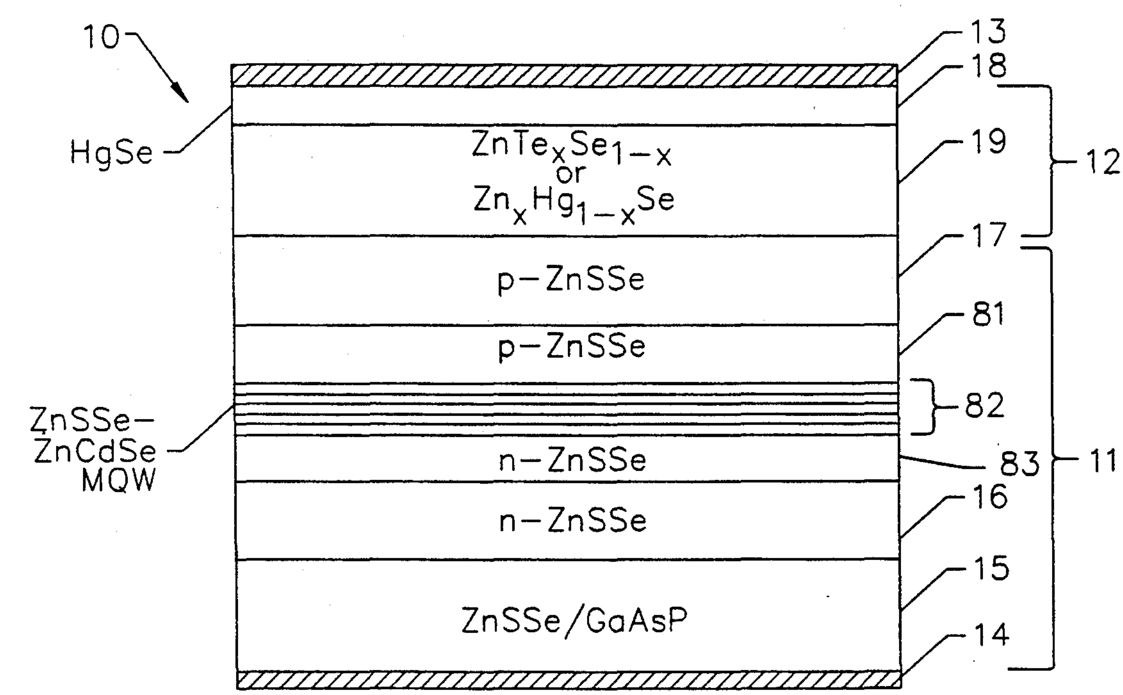


FIG. 16p.

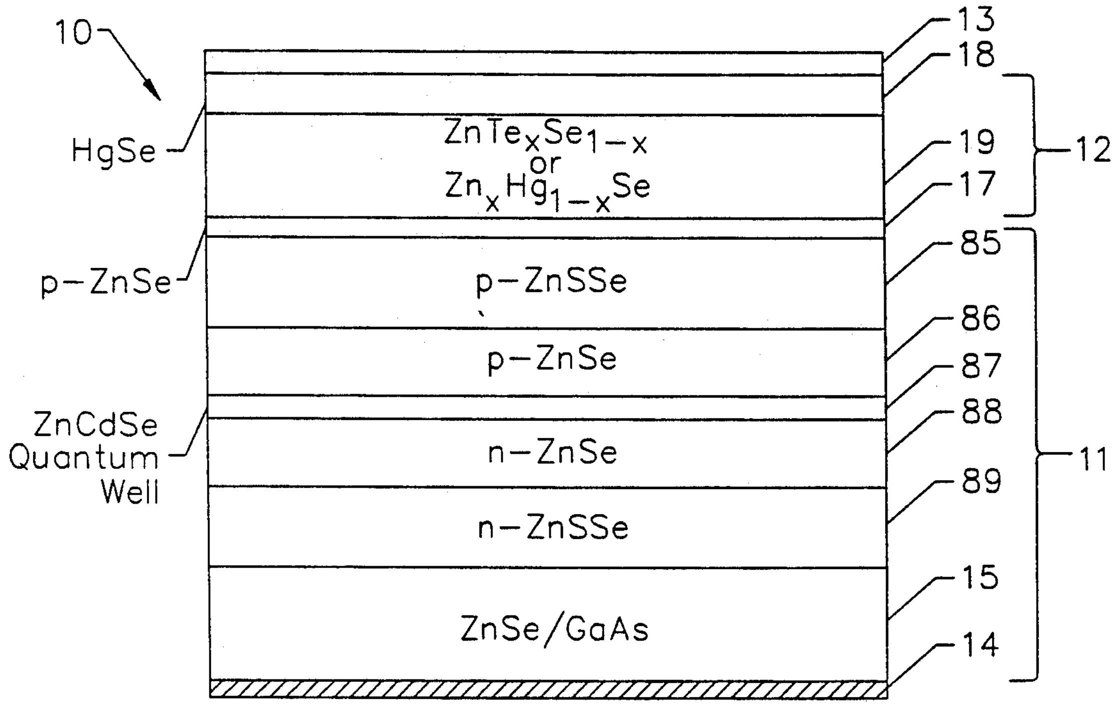

10
13
18
12
HgSe
ZnTe$_x$Se$_{1-x}$
or
Zn$_x$Hg$_{1-x}$Se
19
17
p-ZnSe
85
p-ZnSSe
86
p-ZnSe
87
ZnCdSe
Quantum
Well
88
n-ZnSe
11
89
n-ZnSSe
15
ZnSe/GaAs
14

FIG. 17.

FIG. 18a.

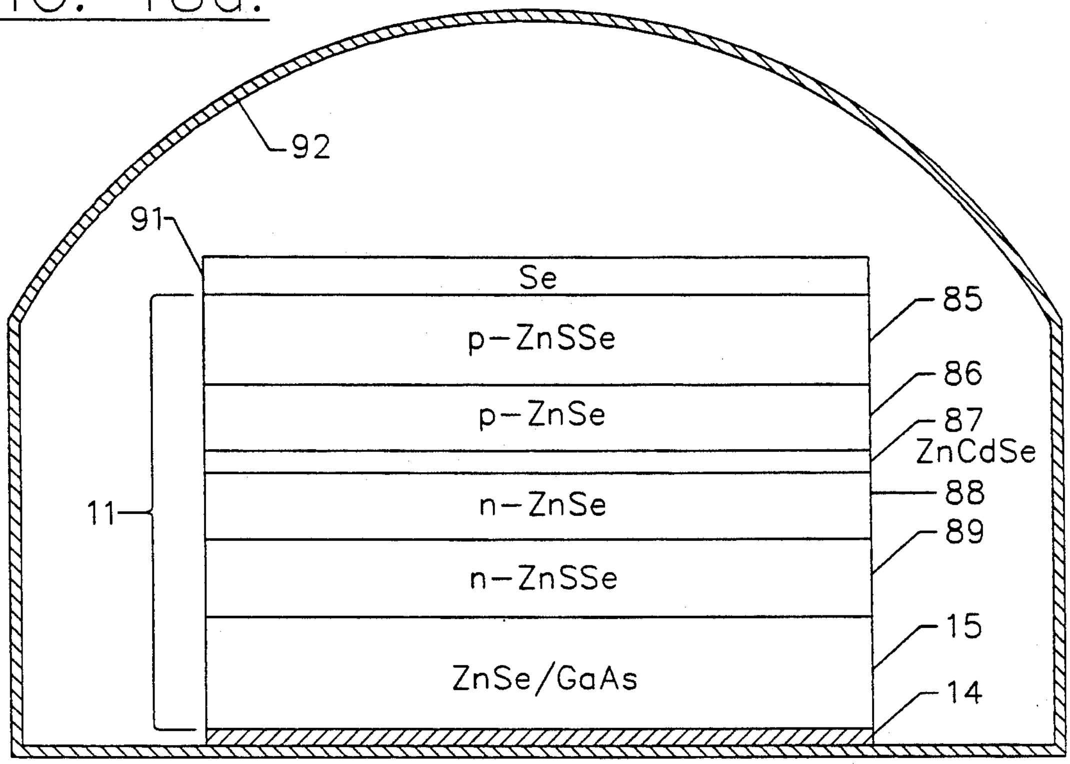


FIG. 18b.

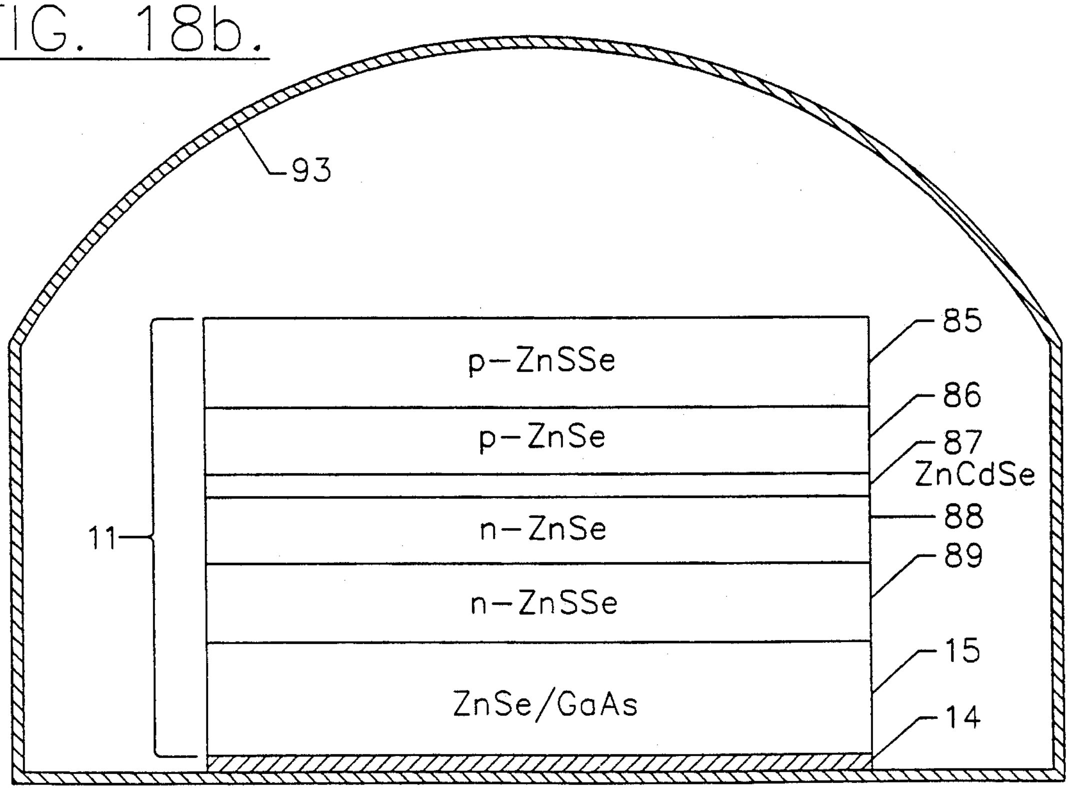


FIG. 19a.

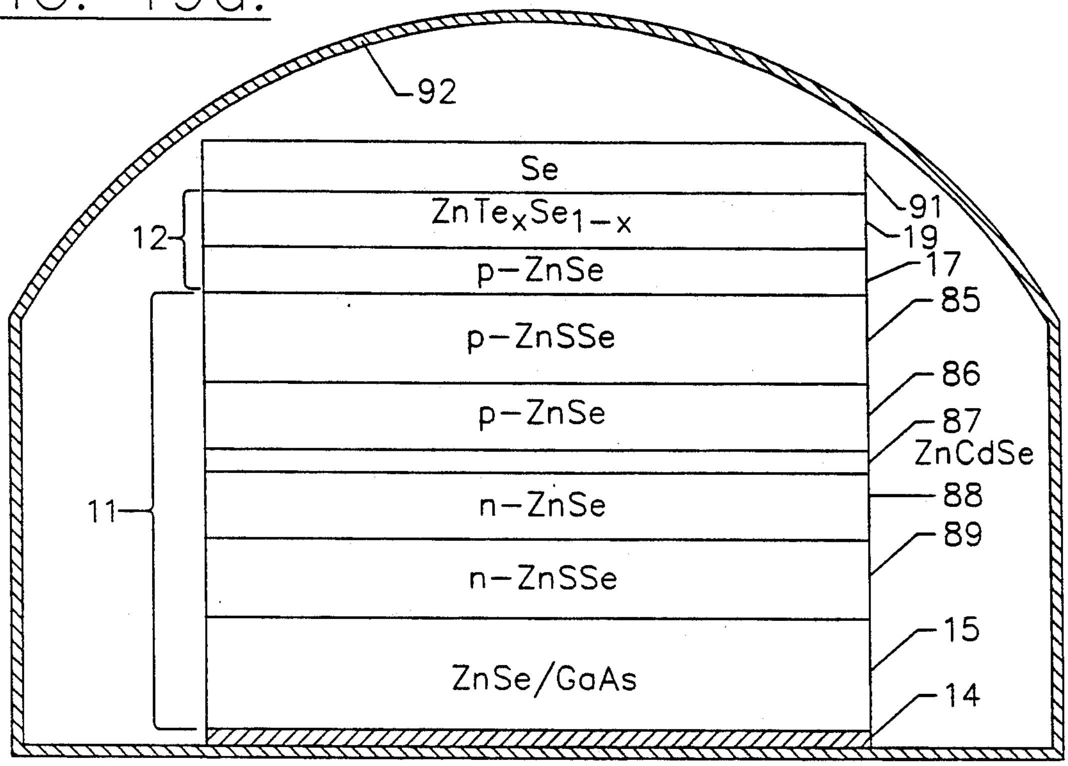
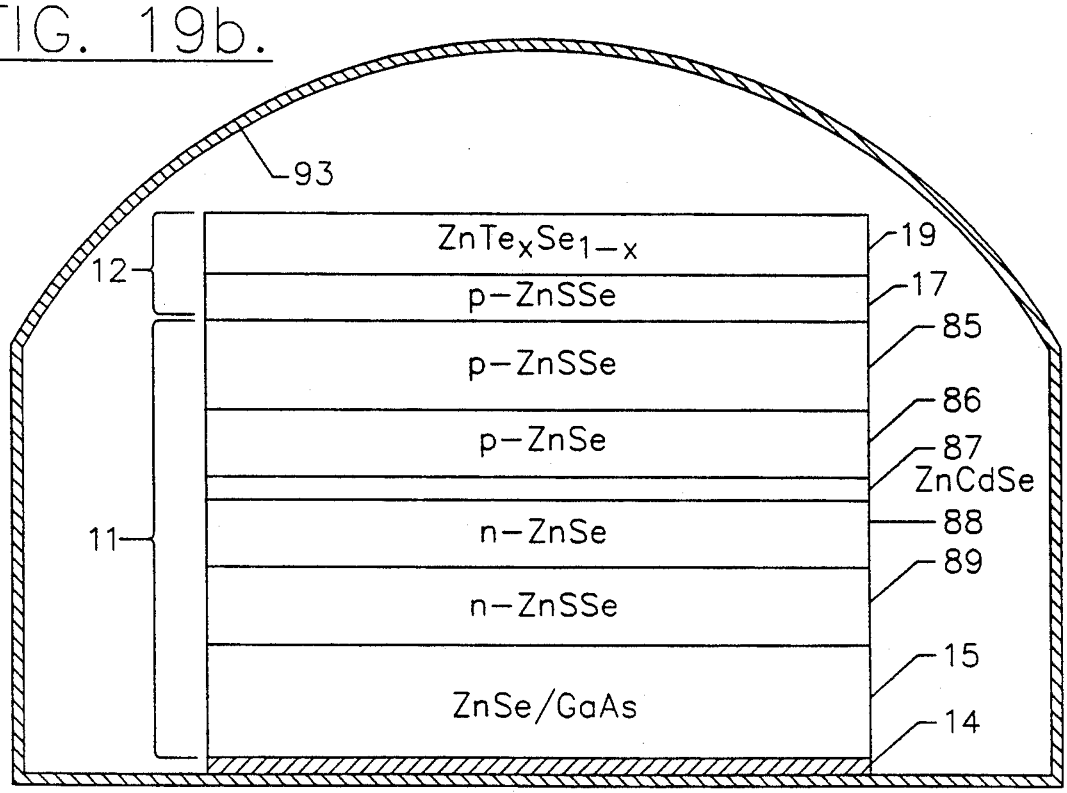


FIG. 19b.



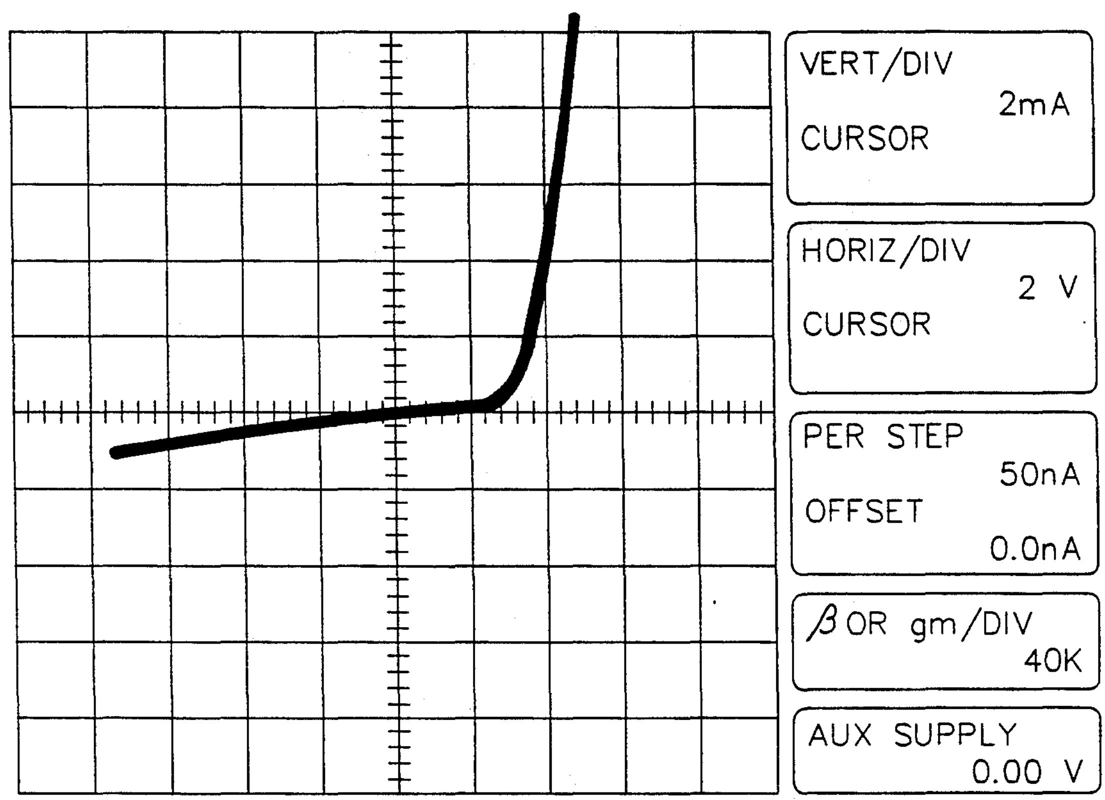

VERT/DIV
2mA
CURSOR
HORIZ/DIV
2 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
40K
AUX SUPPLY
0.00 V

FIG. 20.

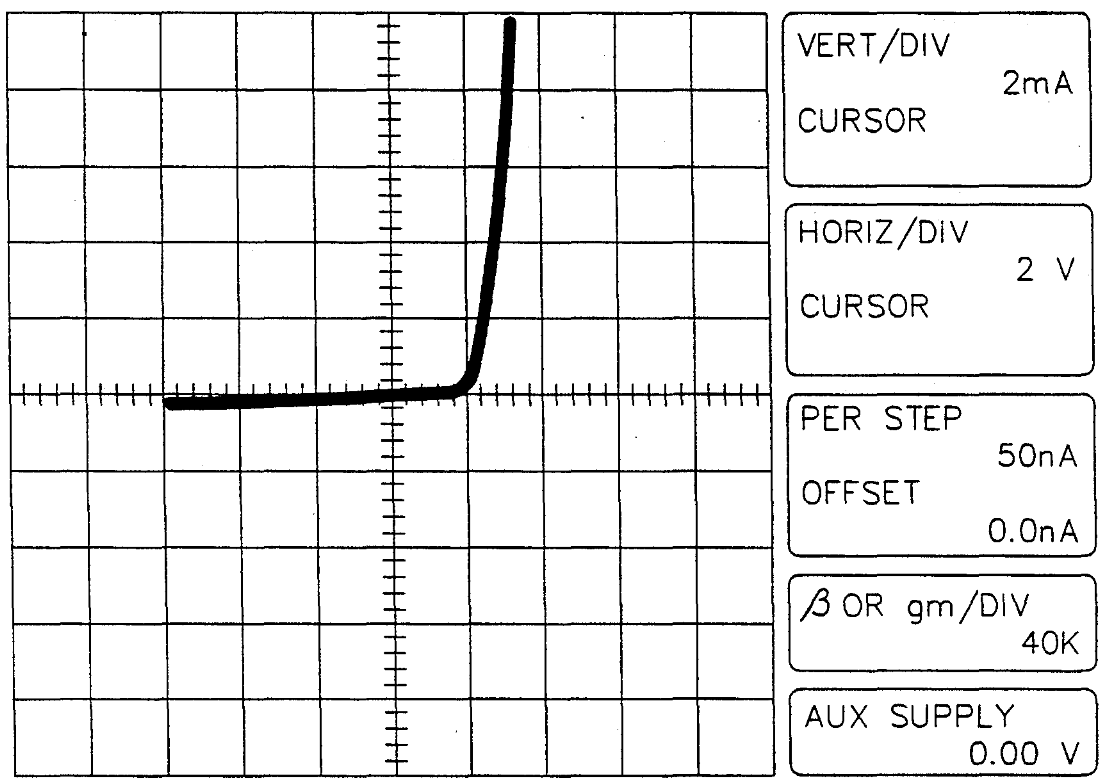

VERT/DIV
2mA
CURSOR
HORIZ/DIV
2 V
CURSOR
PER STEP
50nA
OFFSET
0.0nA
β OR gm/DIV
40K
AUX SUPPLY
0.00 V

FIG. 21.

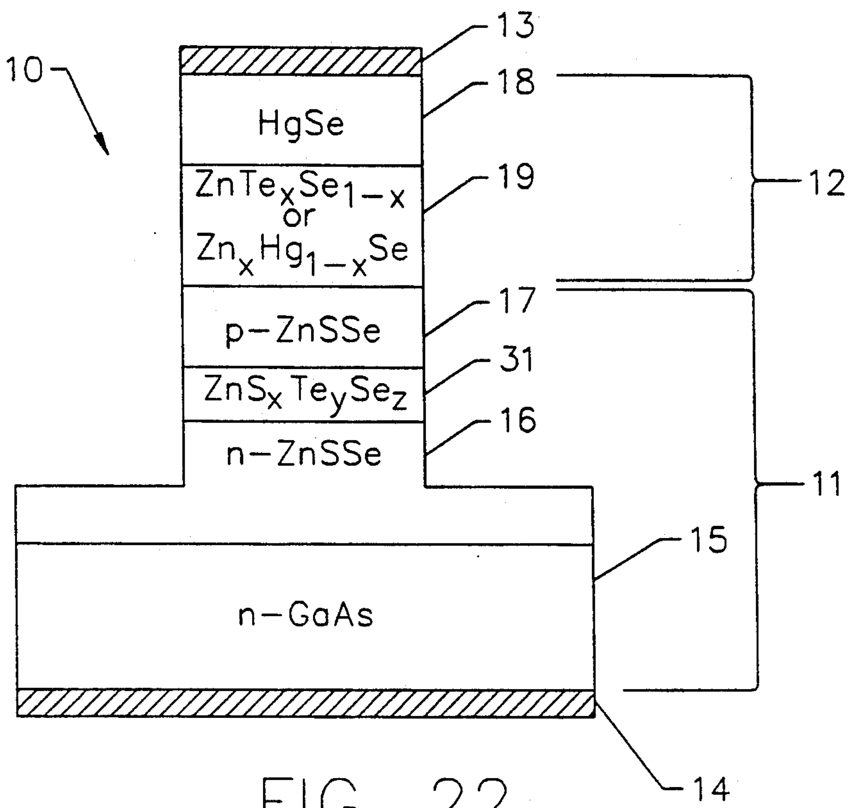

10
13
18
HgSe
19
$ZnTe_xSe_{1-x}$
or
$Zn_xHg_{1-x}Se$
12
17
p−ZnSSe
31
$ZnS_xTe_ySe_z$
16
n−ZnSSe
11
15
n−GaAs
14

FIG. 22.

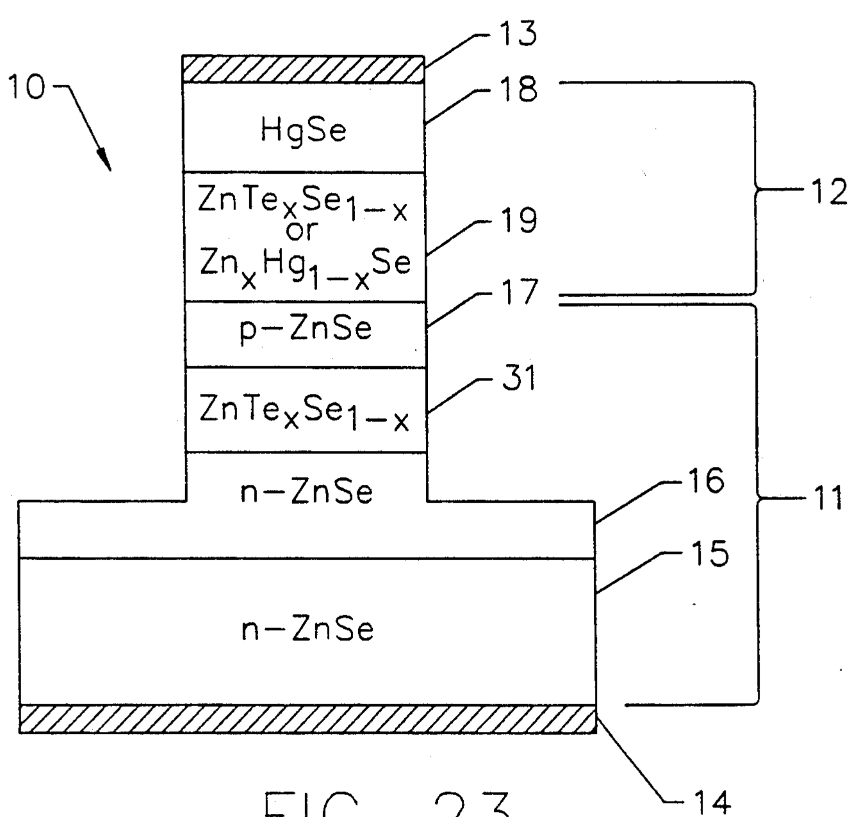

10
13
18
HgSe
12
$ZnTe_xSe_{1-x}$
or
$Zn_xHg_{1-x}Se$
19
17
p−ZnSe
31
$ZnTe_xSe_{1-x}$
n−ZnSe
16
11
15
n−ZnSe
14

FIG. 23.

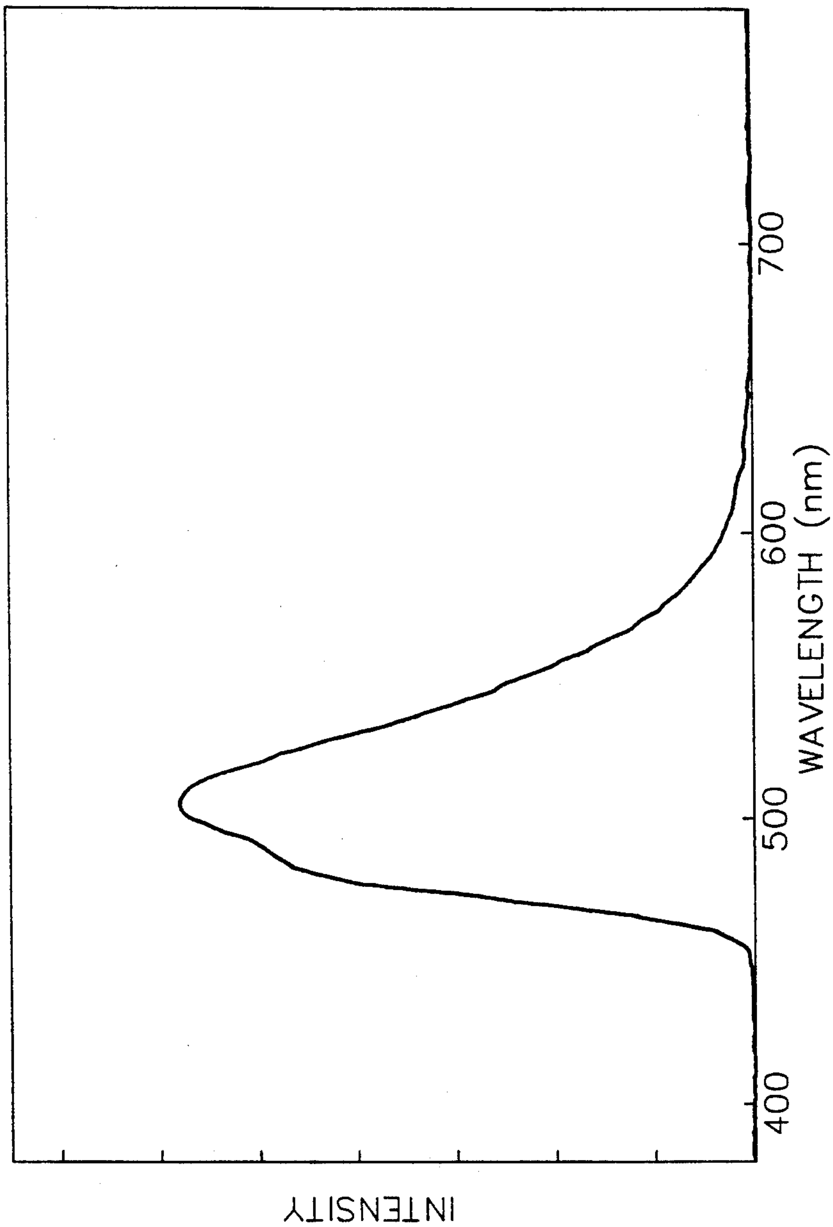


FIG. 24.

INTEGRATED HETEROSTRUCTURE OF GROUP II-VI SEMICONDUCTOR MATERIALS INCLUDING EPITAXIAL OHMIC CONTACT AND METHOD OF FABRICATING SAME

U.S. GOVERNMENT RIGHTS

This invention was made with government support under Grant No. DMR-88-13525 awarded by the National Science Foundation. The U.S. Government has certain rights in the invention.

CROSS REFERENCE TO RELATED APPLICATION

This application is a Continuation-in-Part of application Ser. No. 07/881,599 filed May 12, 1992.

FIELD OF THE INVENTION

This invention relates to semiconductor devices, and more particularly to semiconductor devices formed of Group II-VI compound semiconductor materials.

BACKGROUND OF THE INVENTION

Microelectronic applications of Group II-VI semiconductor materials have been widely investigated. In particular, the wide bandgap Group II-VI semiconductor zinc selenide (ZnSe), and its related alloys such as zinc cadmium selenide (ZnCdSe) and zinc sulfur selenide (ZnSSe), are being widely investigated as optoelectronic devices which are effective from the blue to the green region of the visible spectrum. As is well known to those having skill in the art, the wide bandgap of these Group II-VI devices compared to their equivalent nearly lattice matched Group III-V or elemental semiconductor materials, make these wide bandgap Group II-VI semiconductors potential candidates for blue to green optoelectronic devices. Blue to green optoelectronic sources are currently sought for a number of applications, including full color electroluminescent displays, read-write laser sources for high density information storage on magnetic and optical media, sources for undersea optical communications and other applications.

Molecular beam epitaxy and other fabrication techniques have recently been developed so that both n-type and p-type doped layers of zinc selenide and other related II-VI semiconductor materials may be grown. See for example a publication by Ren et al. entitled *Substitutional Doping of ZnSe Films,* Journal of Crystal Growth, Vol. 111, pp. 772-775, 1991. It has also long been known to make Schottky contacts to n-type zinc selenide using mercury selenide (HgSe). See the publications entitled e, *a Highly Electronegative Stable Metallic Contact for Semiconductor Devices* by Best et al., Applied Physics Letters, Vol. 29, No. 7, pp. 433-434, 1976; *Highly Electronegative Contacts to Compound Semiconductors* by Scranton et al., Journal of Vacuum Science and Technology, Vol. 14, No. 4, pp. 930-934, 1977; and *Lattice-Matched Heterostructures as Schottky Barriers: HgSe/CdSe* by Best et al., Journal of Vacuum Science Technology, Vol. 16, No. 5, pp. 1130-1133, 1979.

As a result of these and other developments, at least four research groups have recently described the fabrication of blue and/or green light emitting diodes and/or laser diodes from Group II-VI semiconductors.

The first group is from North Carolina State University (NCSU) and includes the present inventor. The fabrication of blue and green light emitting diodes based on ZnSe and alloys thereof is described in a publication entitled *ZnSe Light-Emitting Diodes* by Ren et al., Applied Physics Letters, Vol. 57, No. 18, pp. 1901-1903, October, 1990, and *Blue (ZnSe) and Green* ($ZnSe_{0.9}Te_{0.1}$) *Light Emitting Diodes* by Ren et al., Journal of Crystal Growth, Vol. **111**, pp. 829-832, 1991.

A second group of researchers from Brown University and Purdue University have also described zinc selenide based laser diodes and light emitting diodes in publications entitled *Blue-Green Injection Laser Diodes in (Zn,Cd)Se/ZnSe Quantum Wells* by Jeon et al., Applied Physics Letters Vol. 59, No. 27, pp. 3619-3621, December, 1991; *Blue/Green pn Junction Electroluminescence from ZnSe-based Multiple Quantum-Well Structures* by Xie et al., Applied Physics Letters Vol. 60, No. 4, pp. 463-465, January, 1992; *ZnSe Based Multilayer pn Junctions as Efficient Light Emitting Diodes for Display Applications,* Jeon et al., Applied Physics Letters, Vol. 60, No. 7, pp. 892-894, February, 1992; *Blue and Green Diode Lasers in ZnSe-based Quantum Wells,* Jeon et al., Applied Physics Letters, Vol. 60, No. 17, April, 1992; and *Room Temperature Blue Light Emitting P-N Diodes from Zn(S,Se)-Based Multiple Quantum Well Structures,* Xie et al., Applied Physics Letters, Vol. 60, No. 16, April, 1992, pp. 1999-2001.

A third group from 3M Company described a zinc selenide based laser diode in an article entitled *Blue-Green Laser Diodes* by Haase et al., Applied Physics Letters, Vol. 59, No. 11, pp. 1272-1274, September, 1991. A fourth group from the University of Florida and Bellcore described fabrication of LEDs and light emitting diodes using zinc selenide in an article entitled *Noncontact Electrical Characterization of Low-Resistivity p-type ZnSe:N Grown by Molecular Beam Epitaxy* by Park et al., Applied Physics Letters, Vol. 59, No. 15, pp. 1896-1898, 1991.

The above publications indicate that the art has now successfully fabricated blue and green optoelectrical devices from ZnSe-based materials. As Group II-VI fabrication processes are further refined, optical characteristics such as frequency spectrum width and operational lifetime are expected to improve due to reduced dislocation densities in the materials and other improvements.

A major problem with all of these devices, however, has been the ohmic (nonrectifying) contact to zinc selenide, and in particular to p-type zinc selenide. This is a fundamental problem, which is related to the very deep energy of the valence band of zinc selenide. As a consequence, contacts to p-type zinc selenide and related alloys, using conventional metals such as silver or gold, are not ohmic. In effect, the contacts which have been considered by researchers as being ohmic, actually constitute a reverse biased Schottky diode in series with the device, resulting in a large voltage drop across the supposedly ohmic contact. This large voltage drop results in almost all of the input power to the device being lost as heat. High voltages, of 20-50V or more, have been required in order to induce optical emission, and the resultant heat destroys the devices.

The "ohmic contact problem" for zinc selenide optical emitter devices has been widely reported. See for example the above cited 1990 Ren et al. article from the NCSU group, at page 1901: "It was not possible for us to complete Hall effect studies on the ZnSe:Li samples because of problems associated with non-ohmic contacts." See also the above cited 1992 article by Xie et al. from the Brown-Purdue group, at page 463: "Hall measurements on the p-type layers were unreliable due to the difficulty in forming ohmic contacts to the wide-gap semiconductor." See also the Haase et al. article by the 3M group at page 1273: "Heating in these samples is a serious problem as the contact between the Au and the p-ZnSe presents a large barrier." Finally, see the Park et al. article from the University of Florida/Bellcore group which notes that "... serious problems currently exist with regard to providing low-resistance ohmic contact to p-type ZnSe material ... "

The above survey indicates that although significant advances have been made in fabricating Group II-VI devices, and in particular zinc selenide based optoelectronic devices, the ohmic contact to these devices, and in particular to p-type zinc selenide, remains a fundamental concern that has heretofore eluded multiple independent groups of researchers.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved Group II-VI semiconductor device including an ohmic contact therefor.

It is another object of the invention to provide an improved Group II-VI optoelectronic device including an ohmic contact therefor.

It is still another object of the invention to provide an ohmic contact for p-type zinc selenide and alloys thereof.

These and other objects are provided, according to the present invention by an ohmic contact for a semiconductor device formed of Group II-VI semiconductor materials, wherein the contact includes a lattice matched monocrystalline ternary compound Group II-VI semiconductor material on the Group II-VI semiconductor device, a lattice matched monocrystalline Group II-VI semimetal on the Group II-VI semiconductor material and a conductor, such as a metal, on the Group II-VI semimetal. The ternary compound Group II-VI semiconductor material and the semimetal, between the Group II-VI semiconductor material and the conductor layer, eliminate the band offset between the wide bandgap Group II-VI semiconductor material and the conductor layer, to thereby provide an ohmic contact for the Group II-VI semiconductor material.

In particular, according to the invention, an ohmic contact for zinc selenide (ZnSe) or an alloy thereof, and particularly for p-type zinc selenide or an alloy thereof, is provided by a heterostructure including a zinc mercury selenide ($Zn_xHg_{1-x}Se$) layer or a zinc telluride selenide ($ZnTe_xSe_{1-x}$) layer on the layer of zinc selenide or alloy thereof, and a mercury selenide (HgSe) layer on the zinc mercury selenide or zinc telluride selenide layer. A conductor (such as metal) layer is formed on the mercury selenide layer. The zinc mercury selenide or zinc telluride selenide layer, and the mercury selenide layer between the p-type zinc selenide and the conductor layer, provide an ohmic contact by eliminating the band offset between the wide bandgap zinc selenide and the conductor.

Many alternative formulations of the zinc mercury selenide layer and the zinc telluride selenide layer of the present invention may be provided. In particular, the ratio of zinc to mercury, or tellurium to selenium, may be constant across the layer to provide a step graded zinc mercury selenide layer or zinc telluride selenide layer. Alternatively, the amount of mercury or tellurium may increase from the zinc selenide layer to the mercury selenide layer. One form of increase is a linear increase, to provide a linear graded zinc mercury selenide or zinc telluride selenide layer. Alternatively, and preferably, the amount of mercury or tellurium increases nonlinearly from the zinc selenide layer to the mercury selenide layer to provide a nonlinear graded zinc mercury selenide or zinc telluride selenide layer. Preferably, a parabolic graded layer is provided, in which the amount of mercury or tellurium increases parabolically.

According to the invention, at least some of the zinc mercury selenide layer or zinc telluride selenide layer adjacent the p-type zinc selenide layer is doped p-type. Preferably, half the thickness of the zinc mercury selenide layer or zinc telluride selenide layer, adjacent the zinc selenide layer, is doped p-type, and the other half of the zinc mercury selenide layer or zinc telluride selenide layer, adjacent the mercury selenide layer, is of neutral conductivity. Modulation doping may also be used in the parabolically graded zinc mercury selenide layer or zinc telluride selenide layer.

It has also been found, according to the present invention, that a p-type layer of mercury selenide between the p-type zinc selenide layer and the conductor layer, can provide an ohmic contact for p-type zinc selenide which is far superior to conventional gold or silver ohmic contacts. The ohmic contacts of the present invention produce a nearly ideal (linear) voltage-current relation, indicating that the contacts are indeed ohmic. Hall effect measurements may also be taken, which verify that the contacts are ohmic. When a Group II-VI optoelectronic device is integrated with the ohmic contacts of the present invention, an integrated heterostructure device is formed, with one heterostructure providing an optical function such as e.g. light emission, and another heterostructure providing an electrical function such as ohmic contact. These integrated heterostructures can emit radiation in the blue to green frequency range with an input voltage of five volts or less, resulting in high efficiency Group II-VI optoelectronic devices.

According to another aspect of the present invention, in certain applications it is desirable to provide large area optical emitters such as light emitting diodes (LED), in which the light is emitted from the top and sides of the LED. Such large area LEDs can be used to produce numerical display arrays and many other devices. According to the invention, the integrated heterostructures of the present invention may be used to produce large area optical emitters by providing a mercury selenide layer, or a mercury selenide layer on the zinc mercury selenide or zinc telluride selenide layer, which is sufficiently thick to provide an ohmic contact to the p-type zinc selenide layer, and is sufficiently thin to pass optical emissions from the optical emission heterostructure therethrough. Preferably, a mercury selenide layer less than about 100 Å thick, is provided. Although mercury selenide is a semimetal which absorbs radiation through the visible and infrared spectral regions, the thin mercury selenide layer is thin enough to limit the light absorption losses to less than 10%. Moreover, since mercury selenide is of very high conductivity, the mercury selenide layer is sufficiently thick to act as a semitransparent electrode which covers the top of the heterostructure. In order to further reduce the surface contact resistance, a transparent conductor layer such as indium tin oxide may be formed on the thin layer of mercury selenide.

An integrated heterostructure according to the present invention may be formed by epitaxially forming an optical heterostructure and an electrical heterostructure as described above. Typically, the optical heterostructure (such as a laser diode or light emitting diode) is formed in a first chamber, using molecular beam epitaxy (MBE) of zinc selenide and related alloys. The zinc mercury selenide electrical heterostructure (ohmic contact) is typically fabricated in a second deposition chamber because of the special requirements for depositing mercury based materials. Transfer between the first and second chambers typically must take place under ultra high vacuum conditions.

Alternatively, according to the present invention, a mercury based electrical heterostructure may be formed on a zinc selenide based optical heterostructure without the need for ultra high vacuum transfer between MBE chambers, by forming a thin overcoat layer, for example, selenium, on the optical heterostructure. This structure can then be removed from the zinc selenide MBE chamber and inserted into a mercury based MBE chamber at room temperature and under atmospheric conditions. Once the structure is placed in the mercury based chamber, and the chamber is evacuated, the selenium overcoat layer may be evaporated and the mercury based electrical heterostructure may be epitaxially formed on the zinc selenide based optical heterostructure.

Similarly, in order to prepare the integrated heterostructure of the present invention which includes a zinc telluride selenide layer, the optical heterostructure (such as a laser diode or light emitting diode) is formed in a first chamber, using molecular beam epitaxy (MBE) of zinc selenide and related alloys. The zinc telluride selenide layer of the electrical heterostructure (ohmic contact) is also fabricated in the first deposition chamber, for example by continuing molecular beam epitaxy growth at about 250° C. Growth of a graded zinc telluride selenide layer may be accomplished by decreasing the temperature of the selenium MBE source oven, preferably under computer control, while increasing the source temperature of the tellurium MBE source oven. An optional thin layer (about 100 Å) of p-type zinc telluride may be formed on the graded layer of zinc telluride selenide.

Following deposition of the zinc telluride selenide graded layer, a thin overcoat layer, for example selenium, is formed. The structure can then be removed from the first MBE chamber and inserted into a second, mercury based MBE chamber at room temperature and under atmospheric conditions. Once the structure is placed in the mercury based chamber, and the chamber is evacuated, the selenium overcoat layer may be evaporated, and a layer of mercury selenide may be deposited at about 100° C. in the second MBE chamber. Accordingly, the zinc telluride selenide layer can be grown in a first MBE chamber using the same low growth temperature (about 250° C.) as the optical heterostructure of the integrated heterostructure device. The graded layer can be doped p-type using nitrogen from the same remote plasma source that is used to prepare the p-type layers of the optical portion of the integrated heterostructure device. Accordingly, growth of the layer of zinc telluride selenide is simpler than the growth of the zinc mercury selenide layer of application Ser. No. 07/881,599.

According to yet another aspect of the present invention, a high efficiency blue/green optical emitter is formed using a layer of the quaternary alloy zinc sulfur telluride selenide ($ZnS_xTe_ySe_z$, where $x+y+z=1$) between two layers of zinc sulfur selenide (ZnSSe), or a layer of the ternary compound zinc telluride selenide ($ZnTe_xSe_{1-x}$) between layers of zinc selenide (ZnSe). The zinc sulfur telluride selenide or zinc telluride selenide layers form a quantum well, and multiple layers may be used to form multiple quantum wells. In an LED application, a layer about 1000 Å thick will typically be formed while in a laser, a layer about 100–200 Å thick will be formed. Tellurium forms an isoelectronic trap which produces broad and intense light output in the blue/green spectral region.

The cladded zinc sulfur telluride selenide or zinc telluride selenide structure is preferably formed on a substrate such as gallium arsenide or zinc selenide. Zinc sulfur selenide and zinc sulfur telluride selenide ar used with gallium selenide substrates because of their close lattice match thereto. For zinc selenide substrates, zinc selenide and zinc telluride selenide are used. A mercury selenide, zinc mercury selenide or zinc telluride selenide layer is used to form an ohmic contact to the zinc selenide or zinc sulfur selenide. The emitters are relatively easy to fabricate because no adjustments need be made to the zinc, sulfur, tellurium or selenium fluxes. Rather, these fluxes need only be turned on and off at the appropriate time during deposition to form the structure.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional illustration of a first embodiment of an optical emitter having an ohmic contact according to the present invention.

FIG. **2** graphically illustrates energy bandgap versus lattice constant for selected semiconductor materials.

FIG. **3** is an energy band diagram illustrating the band offsets between zinc selenide and gallium arsenide.

FIG. **4** is an energy band diagram showing the energy band lineup between gold and zinc selenide.

FIG. **5** is an energy band diagram illustrating the band lineups of a zinc selenide p-on-n diode under forward bias.

FIG. **6** graphically illustrates the current-voltage characteristics of various zinc selenide based heterostructures.

FIG. **7** is an energy band diagram showing the band lineup between cadmium telluride and mercury telluride.

FIG. **8** is an energy band diagram showing the band lineups between zinc selenide and mercury selenide.

FIG. **9** is a graphical illustration of the voltage current relationship for an ohmic contact according to the present invention.

FIG. **10*a*** illustrates the current-voltage relationship for a known zinc selenide light emitting diode.

FIGS. **10*b*–10*d*** illustrate the current-voltage relationships for light emitting diodes including an ohmic contact according to the present invention.

FIG. **11** is a graphical illustration of the current-voltage relationship among known light emitting diodes and light emitting diodes fabricated according to the present invention.

FIG. **12** is a cross-sectional illustration of a second embodiment of the present invention.

FIG. **13** is an energy band diagram for the device shown in FIG. **12**, including a step graded zinc mercury selenide layer.

FIG. 14 is an energy band diagram for the device shown in FIG. 12, including a linear graded zinc mercury selenide layer.

FIG. 15 is an energy band diagram for the device shown in FIG. 12, including a parabolic graded zinc mercury selenide layer.

FIGS. 16a–16p are cross-sectional illustrations of alternative combinations of integrated heterostructures according to the present invention.

FIG. 17 illustrates another integrated heterostructure according to the present invention.

FIGS. 18a and 18b illustrate steps for forming the integrated heterostructure of FIG. 17 according to the present invention.

FIGS. 19a and 19b illustrate alternative steps for forming the integrated heterostructure of FIG. 17 according to the present invention.

FIG. 20 graphically illustrates the current-voltage relationship for a light emitting diode which does not include an ohmic contact according to the present invention.

FIG. 21 graphically illustrates the current-voltage relationship for a light emitting diode which includes an ohmic contact according to the present invention.

FIGS. 22 and 23 are cross-sectional illustrations of alternative integrated heterostructures according to the present invention.

FIG. 24 graphically illustrates wavelength versus intensity for the structure of FIG. 22.

DESCRIPTION OF A PREFERRED EMBODIMENT

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which a preferred embodiment of the invention is shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiment set forth herein; rather, this embodiment is provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

Referring now to FIG. 1, a first embodiment of an optical emitter having an ohmic contact according to the present invention is illustrated. Optical emitter **10** is an integrated heterostructure including an optical heterostructure **11** and an electrical heterostructure **12**. Optical heterostructure can be a well known blue to green light emitting diode or laser diode structure, or any other Group II-VI device now known or discovered later. As shown in FIG. 1, the optical heterostructure i is a blue light emitting diode (LED). The blue LED is formed on a substrate **15** of zinc selenide, gallium arsenide or any other known material. The LED is a p-n junction between n-type zinc selenide layer **16** and p-type zinc selenide layer **17**. Both zinc selenide layers may be formed on substrate **15** using well known techniques such as molecular beam epitaxy, and both layers may be doped at 10^{18} carrier per cubic centimeter Bottom contact **14** is formed of metal such as gold-germanium for n-type GaAs or indium for n-type ZnSe, or other well known conductors. It will be understood by those having skill in the art, that, as used herein, when a layer is formed "on" another layer, it may be formed directly on the underlying layer, or one or more intervening layers may be present.

Still referring to FIG. 1, the electrical portion **12** of the integrated heterostructure **10** comprises a layer of mercury selenide. As is well known to those having skill in the art, mercury selenide is a semimetal rather than a semiconductor, because it has a bandgap that is zero. It will be understood by those having skill in the art that the integrated optical structure **11** and electrical structure **12** is epitaxially formed as a monolithic structure, with lattice match between adjacent layers so as to produce minimal dislocations at the junctions between the layers. FIG. 2 illustrates the energy bandgap versus lattice constant for various Group IV single element semiconductors, Group III-VI compound semiconductors and Group II-VI compound semiconductors and semimetals.

It has been found, according to the invention, that mercury selenide forms a good ohmic contact to p-type zinc selenide and thereby solves the last fundamental problem in development of high efficiency Group II-VI devices. FIG. 3 illustrates the origin of the ohmic contact problem. As shown in FIG. 3, there is essentially no conduction band (E_c) offset between zinc selenide and gallium arsenide. As a consequence, valence band (E_v) offset is very large: about 1.3 electron volts (eV). The deep valence band of zinc selenide is the source of the ohmic contact problem. Gold, which has the largest work function of all metals, has proven to be an ineffective ohmic contact to zinc selenide. Gold forms a barrier of about 1.1 electron volts on n-type zinc selenide. A gold/zinc selenide interface, as shown in FIG. 4, produces a band offset of about 1.6 electron volts. Accordingly, the use of gold as an ohmic contact to a p-on-n zinc selenide homojunction, produces the band bending shown in FIG. 5.

Under forward bias of the zinc selenide diode, the gold/p-type zinc selenide junction is reverse biased and current flow is limited by carrier tunneling through the heterobarrier. This is illustrated by the current-voltage characteristics shown in FIG. 6 as reported by the 3M Group for their initial laser diode. Data for LED's prepared by the NCSU group is also shown to illustrate that the forward characteristics are similar for samples prepared in different laboratories. This data strongly suggests that the current limiting device is a series diode undergoing reverse breakdown. This diode is associated with reverse breakdown via carrier tunneling of the gold-zinc selenide Schottky diode heterointerface.

In order to develop high efficiency LEDs and lasers from zinc selenide and related materials, the ohmic contact problem must be solved. A solution to the ohmic contact problem has been found by studying the valence band offset between mercury telluride (HgTe) and cadmium telluride (CdTe). As shown in FIG. 7, it has been found that the valence band offset is 0.35 electron volts. Earlier estimates, based on the "common anion rule" implied a band offset of zero. Accordingly, the common anion rule must be rephrased as a "modified common anion rule" for Group II-VI materials containing mercury which is consistent with the mercury telluride/cadmium telluride valence band offset results. As shown in FIG. 7, a modified common anion rule gives:

$$\Delta E_c/\Delta E_v = 1.25/0.350 = 3.6 \quad (1)$$

If Equation (1) holds for the mercury selenide/zinc selenide interface, then

$$\Delta E_c + \Delta E_v = Eq_{(ZnSe)} = 2.70\ eV \quad (2)$$

and a valence band offset ΔE_v of 0.59 electron volts is obtained for the mercury selenide/zinc selenide interface as shown in FIG. **8**. This represents nearly a threefold decrease compared to a gold/zinc selenide interface barrier of about 1.6 electron volts. Thus, a layer of epitaxial mercury selenide on p-type zinc selenide should provide a much better ohmic contact than gold.

FIG. **9** graphically illustrates the voltage-current relationship for an ohmic contact according to the present invention. In order to fabricate this ohmic contact, a layer of mercury selenide was grown, by molecular beam epitaxy, onto p-type (nitrogen doped) zinc selenide samples. Standard photolithographic processing was then used to define four contacts on each of the samples for Hall effect measurements. FIG. **9** shows the current-voltage relationship between adjacent Hall contacts one centimeter apart of a representative sample. Apart from a small (about 0.1 volt) offset, the contacts are very nearly ohmic, thus indicating that electrical contacts, good enough for Hall effect measurement, are now available.

Several diode structures were prepared using molecular beam epitaxy deposition. The p-type layers included zinc sulfur selenide doped with nitrogen followed by a layer of nitrogen doped p-type zinc selenide and a layer of mercury selenide. Diodes were then prepared for testing using standard techniques.

FIG. **10***a* illustrates the current-voltage relationship of an earlier device which used lithium as the p-type dopant and gold as the electrical contact to the p-type zinc selenide layer. As shown, about 10 V is required to obtain 1 mA current under forward bias conditions for a diode having a cross sectional area of 10^{-3} cm^2. FIGS. **10***b*–**10***d* illustrate diodes including zinc selenide and mercury selenide layers, according to the present invention. As shown, these diodes of cross-sectional area 10^{-3} cm^2 turn on at a much lower voltage (2.1 V to obtain 1 mA, 3.2 V to obtain 10 mA and 4.4 V to obtain 50 mA as shown in FIGS. **10***b*–**10***d*, respectively). This dramatic increase in current at a given voltage compared with earlier diodes provides clear evidence that the ohmic contact of the present invention is effective.

FIG. **11** graphically compares the diodes fabricated according to the present invention as described above ("NCSU p-on-n diodes 2/92") with those produced by 3M and Purdue. As shown, the p-on-n diodes of the present invention are substantially improved from those reported by 3M. Indeed, the diodes of the present invention are substantially better than the Purdue results for n-on-p diodes, particularly when diodes of similar cross-sectional areas are compared.

Referring now to FIG. **12**, a second integrated heterostructure **20** is shown which includes a further improved ohmic contact from that of FIG. **1**. As shown in FIG. **12**, the optical heterostructure **11** is identical to that of FIG. **1**. However, the electrical heterostructure comprises a layer of zinc mercury selenide ($Zn_xHg_{1-x}Se$) **19** or Zinc telluride selenide ($ZnTe_xSe_{1-x}$) between the layer of mercury selenide **18** and the p-type zinc selenide layer **17**. The layer of mercury selenide **18** and the layer of zinc mercury selenide or zinc telluride selenide **19** provide an improved ohmic contact between p-type zinc selenide layer **17** and conductor **18**.

According to the invention, alternative embodiments of zinc mercury selenide layer or zinc telluride selenide layer **19** can provide an ohmic contact. In one embodiment, zinc mercury selenide layer or zinc telluride selenide layer **19** is a step graded layer having uniform ratio of zinc to mercury or tellurium to selenium respectively, across the entire thickness thereof. A preferred uniform ratio for this layer is about 1:1. FIG. **13** illustrates the energy band diagram for such a step graded zinc mercury selenide layer. Preferably the step graded layer of zinc mercury selenide or zinc telluride selenide is doped p-type with the same doping concentration (e.g. 10^{18}) as the zinc selenide layer. Nitrogen doping is preferred.

Another alternative is shown in FIG. **14** wherein the amount of mercury or tellurium increases linearly across the zinc mercury selenide or zinc telluride selenide layer respectively, from the zinc selenide layer to the mercury selenide layer, to thereby provide a linear graded zinc mercury selenide or zinc telluride selenide layer. Preferably, the linear graded layer of zinc mercury selenide or zinc telluride selenide is doped p-type with the same doping concentration as the p-type zinc selenide (e.g. 10^{18}).

Referring now to FIG. **15**, the most preferred embodiment presently contemplated by the inventor, is a parabolic graded zinc mercury selenide or zinc telluride selenide layer. As further shown in FIG. **15**, at least part of the zinc mercury selenide layer or zinc telluride selenide layer is doped p-type, and preferably a portion of the zinc mercury selenide layer or zinc telluride selenide adjacent the zinc selenide layer is doped p-type. Most preferred is a configuration wherein half the thickness of the zinc mercury selenide layer or zinc telluride selenide layer adjacent the zinc selenide layer is doped p-type, with the same doping concentration as the zinc selenide, and with half the layer adjacent the mercury selenide being undoped. In one configuration, the zinc mercury selenide layer or zinc telluride selenide layer is 1200 Å thick, with 600 Å adjacent the zinc selenide layer being doped p-type (preferably with nitrogen) at 10^{18} carriers per cubic centimeter to match that of the p-type zinc selenide, and with 600 Å adjacent the mercury selenide being undoped. An optional thin (about 100 Å) layer of p-type zinc telluride (ZnTe) may be formed on the graded zinc telluride selenide layer, to ensure that the interface with the mercury selenide layer is pure ZnTe.

It will be understood by those having skill in the art that in display and other applications it is desirable to provide broad area optical emitters which preferably emit light from the entire top and sides of the emitter. According to the invention, the thickness of mercury selenide layer is limited so that the mercury selenide layer acts as a semitransparent electrode, with a substantial portion of the light emitted from the optical emitter passing through the layer of mercury selenide **18**. Preferably, the layer of mercury selenide is less than about 100 Å thick. In this case, although mercury selenide is a semimetal which absorbs throughout the visible and infrared spectral regions, the mercury selenide layer is thin enough so that the light absorption losses are less than about 10%. In addition, the very high conductivity of the mercury selenide layer allows it to act as a semitransparent electrode which covers the entire top of the optical structure. Blue light emitting diodes which emit light at 476 nm over a large surface area with a room temperature efficiency of greater than 0.02% may be obtained using operational voltages of only 4.5 volts to produce 50 mA through the integrated heterostructure.

In order to further reduce the resistance of the large area emitter, conductor **13** may be formed of indium tin oxide, a well known transparent electrode material. The use of indium tin oxide conductor **13** in combination with a mercury selenide layer **18**, less than 100 Å thick, enhances the current spreading at the top of the emitter so that numerals or other symbols approaching 1 cm by 1 cm in surface area can be fabricated.

It will also be understood by those having skill in the art that any of the ohmic contacts **12** of the present invention may be combined with any Group II-VI devices to form an integrated heterostructure device. FIGS. **16a–16p** illustrate various combinations.

FIGS. **16a–16d** illustrate green LEDs. In particular, FIG. **16a** illustrates a mesa diode green LED including a ZnCdSe quantum well **31**. FIG. **16b** illustrates a multiple quantum well (MQW) mesa diode green LED including an MQW **32** of ZnSe and ZnCdSe. FIG. **16c** illustrates a GRaded Index Separate Confinement Heterostructure ("GRINSCH") mesa diode green LED including a layer of graded p-type ZnCdSe **33**, a ZnCdSe quantum well **34** and graded n-type ZnCdSe **35**. FIG. **16d** illustrates a GRINSCH-MQW mesa diode green LED including a graded layer of p-type ZnCdSe **36** and a layer of ZnCdSe **37**, and a graded layer of n-type ZnCdSe **38**.

FIGS. **16e–16h** illustrate blue LEDs. FIG. **16e** illustrates a mesa diode blue LED including p- and n-type layers of zinc sulfur selenide and a zinc cadmium selenide quantum well **4**. FIG. **16f** illustrates an MQW mesa diode blue LED including an MQW **42** of zinc sulfur selenide and zinc cadmium selenide. FIG. **16g** illustrates a GRINSCH mesa diode blue LED including a layer graded p-type zinc sulfur selenide layer **43**, a zinc cadmium selenide quantum well **44** and a graded n-type zinc sulfur selenide layer **45**. FIG. **16h** illustrates a GRINSCH MQW blue LED including a graded layer of p-type zinc sulfur selenide **46**, an MQW of zinc sulfur selenide and zinc cadmium selenide **47**, and a graded layer of n-type zinc sulfur selenide **48**.

FIGS. **16i–16l** illustrate green lasers. FIG. **15i** illustrates a GRINSCH green laser, including a graded layer of p-type zinc cadmium selenide **51**, a zinc cadmium selenide quantum well **52**, and a graded layer of n-type zinc cadmium selenide **53**. FIG. **16j** illustrates a separate confinement green laser formed by a layer of p-type zinc cadmium selenide **54**, a zinc cadmium selenide quantum well **56** and an n-type zinc cadmium selenide layer **57**. FIG. **16k** illustrates a GRINSCH MQW green laser including a graded layer of p-type zinc cadmium selenide **58**, a zinc cadmium selenide MQW **59** and a graded layer of n-type zinc cadmium selenide **61**. A separate confinement MQW green laser is shown in FIG. **16l** including a p-type layer of zinc cadmium selenide **62**, a zinc cadmium selenide MQW **63** and n-type zinc cadmium selenide layer **64**.

FIGS. **16m–16p** illustrate blue lasers. In particular, FIG. **16m** illustrates a GRINSCH MQW blue laser formed of graded p-type zinc sulfur selenide layer **66**, an MQW **67** of zinc sulfur selenide and zinc cadmium selenide, and a graded layer of n-type zinc sulfur selenide **68**. FIG. **16n** illustrates a GRINSCH blue laser including graded p-type zinc sulfur selenide layer **71**, a zinc cadmium selenide layer quantum well **72** and a graded n-type zinc sulfur selenide layer **73**. FIG. **15o** illustrates a separate confinement blue laser including a p-type layer of zinc sulfur selenide **75**, a zinc cadmium selenide quantum well **76** and an n-type zinc sulfur selenide layer **77**. Finally, FIG. **15p** illustrates a separate confinement MQW blue laser including a p-type layer of zinc sulfur selenide **81**, an MQW of zinc sulfur selenide and zinc cadmium selenide **82**, and an n-type layer of zinc sulfur selenide **83**.

Each of the structures of FIGS. **15a–15p** includes the ohmic contact shown in FIG. **12**, including a layer of mercury selenide **18** and a graded zinc mercury selenide layer or zinc telluride selenide layer **19**. The ohmic contact of FIG. **1**, which includes a mercury selenide layer **18** and is free of a zinc mercury selenide layer **19**, may also be used. It will be understood that other configurations of the optical structure **1** may also be used.

It will also be understood that in any of the heterojunctions previously described, band discontinuities can be reduced or eliminated by modulation doping. Modulation doping is a technique which is well known to those having skill in the art, and is described for Group III-V semiconductors in an article by Shupert et al. entitled *Elimination of Heterojunction Band Discontinuities By Modulation Doping*, Applied Physics Letters, Vol. 16, No. 4, January 1992, pp. 466–468.

Techniques for fabricating the ohmic contacts of the present invention will now be described. At present, molecular beam epitaxy (MBE) is the preferred deposition technique for preparing integrated heterostructure devices of Group II-VI compound semiconductors for blue to green light emitter applications. This is because p-type doping is possible using nitrogen excited in a remote-plasma-enhanced MBE source, such as the model MPD21 marketed by Oxford Applied Research, Oxfordshire, England. Organometallic vapor deposition (OMCVD) is a second potential deposition technique for growing integrated heterostructure devices, if p-type doping is developed. At present, p-type doping of zinc selenide and related alloys by OMCVD has not been demonstrated, to the best of the inventor's knowledge.

The integrated heterostructure devices of the present invention may be fabricated using a two chamber MBE deposition system. In the integrated heterostructure including the zinc mercury selenide layer **19**, a first deposition chamber may be used exclusively for the deposition of wide bandgap Group II-VI semiconductor layers including zinc selenide, zinc cadmium selenide and zinc sulfur selenide, to grow the optical portion **11** of the integrated heterostructure device according to any of the structures described above or any other Group II-VI optical structure. The sample is then transferred to a second chamber where mercury selenide, or zinc mercury selenide and mercury selenide, is heteroepitaxially formed on the p-type zinc selenide. A second chamber is typically required because of the special requirements for depositing mercury based materials which are necessitated by the extremely high vapor pressure of mercury (about 3 mTorr at room temperature). Accordingly, as is well known to those having skill in the art, special MBE sources, cryoshrouding and other special techniques may need to be employed.

A detailed process for forming a separate confinement green laser having an ohmic contact using zinc mercury selenide according to the present invention will now be described. The laser structure is shown in FIG. **17** and includes an optical heterostructure **11** comprising a zinc cadmium selenide quantum well **87** between p- and n-type zinc selenide layers **86** and **88**, respectively, which are placed between p-and-n zinc sulfur selenide layers **85** and **89**, respectively. The optical heterostructure **11** is formed on substrate **15** and includes a top layer **17** of p-type zinc selenide. The ohmic contact heterostructure comprises a layer of graded zinc mercury selenide **19** and a layer of mercury selenide **18** between metal electrode **13** and p-type zinc selenide layer **17**.

Conventional substrate preparation processes are used to form an n+gallium arsenide or zinc selenide substrate **15**. Epitaxial growth of the p-on-n heterostructure is initiated at a substrate temperature of 220°-260° C. Chlorine, in the form of the solid zinc chloride, is presently the preferred n-type dopant for the n-type zinc sulfur selenide layer **89** and the n-type zinc selenide optical confinement layer **88**. Doping levels for layers **88** and **89** should be about $10^{18}cm^{-3}$. The zinc cadmium selenide quantum well **87** is then deposited, followed by the p-type zinc selenide layer **86** and the p-type zinc sulfur selenide layer **85**.

Two techniques may be used to effectively form layers **17**, **18** and **19** on layer **85**. A first technique transfers the already completed structure into a second chamber under ultrahigh vacuum, using commercially available ultrahigh vacuum interlocking systems or a portable ultrahigh vacuum wafer transfer device. Alternatively, a second technique avoids the need to transfer the optical heterostructure to a second deposition chamber under ultrahigh vacuum by forming a thin overcoat layer, for example selenium, on the structure.

FIGS. **18***a* and **18***b* illustrate the use of the selenium overcoat layer. Referring to FIG. **18***a*, a thin (e.g. about 0.1 μm) layer of selenium **91** may be formed in the first chamber **92** after the deposition sequence described above. The selenium layer deposition may take place at room temperature. Then, the sample can be removed from the first chamber **92** and inserted into a second chamber **93** for mercury based heterostructure growth. In the second chamber **93**, the selenium layer **91** may be evaporated by heating the substrate at 300° C. for several minutes just prior to mercury based film growth to obtain the structure of FIG. **18***b*.

Once the sample in chamber **93** is ready for deposition, a thin (approximately 200 Å) p-type layer of zinc selenide **17** is deposited followed by a graded p-type zinc mercury selenide region **19**, and a thin (approximately 200 Å) layer of mercury selenide **18**. The exact thickness of the layers is not critical. Preferably, at least part or all of the graded zinc mercury selenide layer is doped p-type to effectively eliminate band discontinuities. At present, nitrogen from a remote plasma source is the preferred p-type dopant. During deposition of the $Zn_xHg_{1-x}Se$ graded layer, in which the x value is graded from x=1 to x=0, the substrate temperature is preferably reduced from about 220°-260° C. initially to about 100° C. in order to effectively incorporate the mercury into the graded zinc mercury selenide layer **19**. Zinc and selenium fluxes must also be adjusted for proper growth of the zinc mercury selenide layer. If this adjustment is not done, practically all of the mercury reevaporates and grading of the layer does not occur. The final mercury selenide layer **18** is then deposited at about 100° C.

FIGS. **19**A and **19**B illustrate a two chamber process using a selenium overcoat layer to form an integrated heterostructure device including a zinc telluride selenide layer **19**. Referring to FIG. **19**A, the optical heterostructure **11** and p-type zinc selenide layer **17** are fabricated in first chamber **92** as Was already described in FIG. **18**A. Then, zinc telluride selenide layer **19** is grown in first chamber **92** by continuing growth at about 250° C. A graded layer of zinc telluride selenide that is doped p-type with nitrogen from the plasma source is grown by decreasing the temperature of the selenium MBE source oven under computer control while increasing the source temperature of the tellurium MBE source oven. In this way, a p-type graded layer which initially is composed of zinc selenide and finally is composed of zinc telluride is prepared. A preferred thickness of between about 500-1500 Å is grown. The final fluxes may be maintained for an additional short time period to form an optional thin layer (about 100 Å) of p-type zinc telluride. Additional growth of zinc telluride ensures a pure zinc telluride interface with the mercury selenide layer formed thereon.

Following deposition of the zinc tellurium selenide layer **19**, a capping formed as was already described in connection with FIG. **18**A. The selenium capped structure is then transferred to the second MBE chamber **93** as shown in FIG. **19**B. As was already described in connection with FIG. **18**B, in the second chamber **93**, the selenium layer **91** is desorbed and a thin layer of mercury selenide **18** (FIG. **17**) is deposited at about 100° C. in the mercury based MBE chamber.

The zinc telluride selenide layer **19** of the present invention can be grown in the first MBE chamber **92** using the same growth temperature (about 250° C.) as the optical heterostructure **11** of the integrated heterostructure device. Moreover, the graded layer can be doped p-type using nitrogen from the same doping source that is used to prepare the p-type layers of the optical portion **1** of the integrated heterostructure device. Accordingly, the fabrication process for the graded layer of zinc telluride selenide is simpler than the graded zinc mercury selenide layer described in FIGS. **18**A and **18**B.

FIGS. **20** and **21** graphically illustrate the improved performance obtained using the zinc telluride selenide layer **1** according to the present invention. Two identical structures, differing only in the presence of the zinc telluride selenide layer were grown to compare the performance of the integrated heterostructure with and without the zinc telluride selenide layer. In particular, the optical heterostructure **11** of FIG. **16**E was grown in the first MBE system **92** (FIG. **18**A or **19**A) and capped with a thin layer of selenium. The structure was then transferred to the second MBE system **93** (FIG. **18**B or **19**B) where the selenium was desorbed and the thin mercury selenide layer was grown at about 100° C. Then, half of the sample was processed into light emitting diodes, while the other half was reinserted into first chamber **92** (FIG. **18**A or **19**A). The mercury selenide layer was desorbed and a linear graded, all p-type layer of zinc telluride selenide was grown. The sample **18** was again capped with selenium and reinserted into the second MBE chamber **93** (FIG. **19**B) where the selenium layer was desorbed and the thin mercury selenide layer was grown by MBE. Accordingly, a sample with identical optical heterostructures was prepared, with and without the zinc telluride selenide layer **19**.

FIG. **20** illustrates the properties of the LED structure with the zinc tellurium selenide layer **19** absent. As shown, the diode turns on, or begins conducting appreciable current, at about 2.8 volts and generates 10 milliamperes at about 4.4 volts. The forward bias characteristics are "soft", because of the 0.6 electron volt barrier between mercury selenide and zinc selenide.

FIG. 21 graphically illustrates the properties of the identical LED structure including the layer of zinc telluride selenide. As shown, the turn-on voltage is reduced to about 1.9 electron volts and the LED generates 10 milliamperes at about 3.2 electron volts. In addition, the forward bias characteristics of the diode correspond to a series resistance of only about 75 Ω. This is reflected in the much sharper forward bias characteristics compared with FIG. 20.

Hall effect measurements using a mercury selenide ohmic contact yield a room temperature mobility m_p of 19 cm^{-2}/V-s and a room temperature hole concentration of $5\times10^{18}cm^{-3}$. Based on a review of the literature, it is estimated that the valance band of zinc telluride is within 0.2 eV±0.4 eV of that of mercury selenide. See the publications by R. H. Miles et al. entitled *Superattices of II-VI Semiconductors*, Journal of Crystal Growth, Vol. 85, pp. 188–193 (1987), Kobayashi et al. entitled *Growth and Characterization of ZnSe-ZnTe Strane-Layer Superlattices*, Journal of Crystal Growth, Vol. 81, pp. 495–500 (1987), and Y. Rajakarunanayake et al. entitled *Ban Offset of the ZnSe-ZnTe Superlattices: A Fit to Photoluminescence Data by k.p Theory*, Journal of Vacuum Science Technology, Vol. B6, No. 4, July/August 1988, pp. 1354–1359. By optimizing the p-type doping of the zinc telluride selenide layer and its grading, shape and thickness, it should be possible to further reduce the series resistance to less than 10 Ω.

Similar procedures may be used to fabricate a variety of other integrated heterostructures for blue laser, blue LED, green laser and green LED applications, and other applications. The color output of a particular device is determined by the cadmium content of the zinc cadmium selenide layers in the active regions of the structure. The degree of optical confinement is determined by the sulfur content in the zinc sulfur selenide cladding layers. The graded structure of p-type doped zinc mercury selenide or zinc telluride selenide **19** further reduces the valance band offset between mercury selenide and zinc selenide and thus further reduces the series resistance of the ohmic contact. The series resistance and turn-on voltage of the optical device is thereby minimized.

It is also possible to grow p-on-n integrated heterostructure devices on insulating substrates. This might be desirable, for example, because of the limited availability of n-type ZnSe substrates at present. If an insulating substrate is employed, the multilayered growth sequence remains unchanged from that described above. However, the finished wafers are processed differently so that an ohmic contact can be made to the initial n-type epitaxial layer of the structure. This can be done by employing standard photolithography/etching techniques to define mesas and etch down to the n-type layer as shown in FIG. **16**. A 1% bromine in methanol solution is a suitable etchant for the Hg-based layers. A solution of **1** gm potassium dichromate ($K_2Cr_2O_7$), 10 ml sulfuric acid (H_2SO_4) and 20 ml of deionized water is suitable for etching ZnSe and related alloys. Both solutions are compatible with available photoresists. Following this etching step, ohmic contact to the n-type layer can then be achieved by photolithographically defining and opening via regions to the n-type layer and depositing an appropriate metal such as indium, or indium/gold. Standard liftoff techniques can then be used to remove the deposited metal from unwanted areas of the structure.

Referring now to FIG. **22**, a high efficiency blue/-green light emitting diode according to the present invention is illustrated. Diode **10** includes the quaternary alloy Zinc sulfur telluride selenide ($ZnS_xTe_ySe_z$, where x+y+z=1) between layers of zinc sulfur selenide (ZnSSe). In particular, as shown in FIG. **22**, a substrate **15** Of n=type gallium arsenide includes a layer of n-type zinc sulfur selenide thereon. Preferably, layer **16** is $ZnS_{0.07}Se_{0.93}$, which is lattice matched to gallium arsenide. Region **31** of $ZnS_xTe_ySe_z$ is formed on region **16** and p-type zinc sulfur selenide region **17** is formed thereon. An ohmic contact such as a layer of zinc mercury selenide or zinc telluride selenide **1** and a layer of mercury selenide is included. Metal contact layers **13** and **14** are also included as was described above. Cladding layers **16** and **17** are preferably doped at 1×10^{18} dopants cm^{-2} and layer **31** is preferably about 1000 Å thick for an LED and about 100–200 thick for a laser. It will also be understood by those having skill in the art that a multiple quantum well of zinc sulfur telluride selenide and zinc sulfur selenide may be provided between cladding layers **16** and **17**.

FIG. **23** illustrates a similar structure which is optimized for formation on n-type zinc selenide substrate **15**. Since the substrate **15** is zinc selenide, sulfur is not employed in this structure.

Tellurium is known to form an isoelectronic trap in zinc selenide and zinc sulfur selenide which produces a broad and intense light output in the blue/green spectral region as measured by photoluminescence and electroluminescence experiments. The addition of tellurium to the active region **31** of the optical emitter produces an isoelectronic trap similar to that which occurs when tellurium is added to zinc selenide, which results in intense broadband photoluminescent and electroluminescent output in the green to blue/green spectral region at room temperature, depending on the tellurium content of the alloy **31**. FIG. **4** illustrates the spectral output (wavelength versus arbitrary intensity) of an LED fabricated according to FIG. **22**. At a temperature of 300° K. and an input current of 50 milliamps, the green LED exhibits an absolute efficiency η of 6×10^{-4} and an output power of 85 microwatts. The peak wavelength is 504 nanometers and the dominant wavelength is 503 nanometers. The optical purity is 61%. Optimization of the materials growth parameters, layer thicknesses and device packaging may be expected to give rise to even higher LED efficiencies at room temperature.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.

That which is claimed:

1. An ohmic contact for a semiconductor device formed of Group II-VI compound semiconductor materials and including a layer of at least one of p-type zinc selenide (ZnSe) and an alloy thereof, said ohmic contact comprising:

a zinc telluride selenide ($ZnTe_xSe_{1-x}$) layer on said layer of at least one of p-type ZnSe and an alloy thereof, where $0<x<1$;

a mercury selenide (HgSe) layer on said $ZnTe_xSe_{1-x}$ layer; and

a conductor layer on said HgSe layer.

2. The ohmic contact of claim 1 wherein x is constant in said $ZnTe_xSe_{1-x}$ layer to provide a step graded $ZnTe_xSe_{1-x}$ layer.

3. The ohmic contact of claim 1 wherein x decreases across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a graded $ZnTe_xSe_{1-x}$ layer.

4. The ohmic contact of claim 3 wherein x decreases linearly across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a linear graded $ZnTe_xSe_{1-x}$ layer.

5. The ohmic contact of claim 3 wherein x decreases nonlinearly across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a nonlinear graded $ZnTe_xSe_{1-x}$ layer.

6. The ohmic contact of claim 5 wherein x decreases parabolically across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a parabolic graded $ZnTe_xSe_{1-x}$ layer.

7. The ohmic contact of claim 6 wherein a first half of said $ZnTe_xSe_{1-x}$ layer adjacent said ZnSe is p-type, and a second half of said $ZnTe_xSe_{1-x}$ layer adjacent said HgSe layer is of neutral conductivity.

8. The ohmic contact of claim 1 wherein at least a portion of said $ZnTe_xSe_{1-x}$ layer is p-type.

9. The ohmic contact of claim 8 wherein said $ZnTe_xSe_{1-x}$ layer is p-type adjacent said ZnSe layer, and is of neutral conductivity adjacent said HgSe layer.

10. The ohmic contact of claim 1 wherein said zinc telluride selenide layer is p-type modulation doped.

11. The ohmic contact of claim 1 wherein said $ZnTe_xSe_{1-x}$ layer includes a thin layer of ZnTe adjacent said HgSe layer.

12. A semiconductor device formed of Group II-VI compound semiconductor materials comprising:

an optical emission heterostructure formed of Group II-VI compound semiconductor materials, and including a layer of at least one of p-type zinc selenide (ZnSe) and an alloy thereof;

a zinc telluride selenide ($ZnTe_xSe_{1-x}$) layer on said layer of at least one of p-type ZnSe and an alloy thereof, where $0<x<1$;

a mercury selenide (HgSe) layer on said $ZnTe_xSe_{1-x}$ layer; and

a conductor layer on said HgSe layer.

13. The semiconductor device of claim 12 wherein x is constant in said $ZnTe_xSe_{1-x}$ layer to provide a step graded $ZnTe_xSe_{1-x}$ layer.

14. The semiconductor device of claim 12 wherein x decreases across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a graded $ZnTe_xSe_{1-x}$ layer.

15. The semiconductor device of claim 14 wherein x decreases linearly across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a linear graded $ZnTe_xSe_{1-x}$ layer.

16. The semiconductor device of claim 14 wherein x decreases nonlinearly across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a nonlinear graded $ZnTe_xSe_{1-x}$ layer.

17. The semiconductor device of claim 16 wherein x decreases parabolically across said $ZnTe_xSe_{1-x}$ layer, from said ZnSe layer to said HgSe layer, to provide a parabolic graded $ZnTe_xSe_{1-x}$ layer.

18. The semiconductor device of claim 17 wherein a first half of said $ZnTe_xSe_{1-x}$ layer adjacent said ZnSe layer is p-type, and a second half of said $ZnTe_xSe_{1-x}$ layer adjacent said HgSe layer is of neutral conductivity.

19. The semiconductor device of claim 12 wherein at least a portion of said $ZnTe_xSe_{1-x}$ layer is p-type.

20. The semiconductor device of claim 19 wherein said $ZnTe_xSe_{1-x}$ layer is p-type adjacent said ZnSe layer, and is of neutral conductivity adjacent said HgSe layer.

21. The semiconductor device of claim 12 wherein said zinc mercury selenide layer is p-type modulation doped.

22. The semiconductor device of claim 12 wherein said $ZnTe_xSe_{1-x}$ layer includes a thin layer of ZnTe adjacent said HgSe layer.

23. A semiconductor device formed of Group II-VI compound semiconductor materials comprising:

an optical emission heterostructure formed of Group II-VI compound semiconductor materials, and including a layer of at least one of p-type zinc selenide (ZnSe) and an alloy thereof;

at least one of a zinc mercury selenide ($Zn_xHg_{1-x}Se$) layer and a zinc telluride selenide ($ZnTe_xSe_{1-x}$) layer on said layer of at least one of p-type ZnSe and an alloy thereof, where $0<x<1$;

a mercury selenide (HgSe) layer on said at least one of a $Zn_xHg_{1-x}Se$ and a $ZnTe_xSe_{1-x}$ layer, said contact to said at least one of a $Zn_xHg_{1-x}Se$ and a $ZnTe_xSe_{1-x}$ layer, and being sufficiently thin to pass optical emissions from said optical emission heterostructure therethrough; and

a conductor layer on said HgSe layer.

24. The semiconductor device of claim 23 when said HgSe layer is less than about 100 Å thick.

25. The semiconductor device of claim 23 wherein said conductor layer is a transparent conductor layer.

26. The semiconductor device of claim 25 wherein said conductor layer is indium tin oxide.

27. A semiconductor device formed of Group II-VI compound semiconductor materials, comprising:

an optical emission heterostructure formed of Group II-VI compound semiconductor materials, and including a layer of at least one of p-type zinc selenide (ZnSe) and an alloy thereof;

a mercury selenide (HgSe) layer on said layer of at least one of p-type ZnSe and an alloy thereof, said HgSe layer being sufficiently thick to provide an ohmic contact to said layer of at least one of p-type zinc selenide layer and an alloy thereof and being sufficiently thin to pass optical emissions from said optical emission heterostructure therethrough; and

a conductor layer on said HgSe layer.

28. The semiconductor device of claim 27 when said HgSe layer is less than about 100 Å thick.

29. The semiconductor device of claim 27 wherein said conductor layer is a transparent conductor layer.

30. The semiconductor device of claim 29 wherein said conductor layer is indium tin oxide.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,294,833

DATED : March 15, 1994

INVENTOR(S) : Schetzina

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, line 53, "e" should be --HgSe--.

Column 6, line 18, "ar" should be --are--.

Column 7, line 51, "i" should be --11--.

Column 7, line 59, after "centimeter" insert --.--.

Column 10, line 51, after "layer" insert --18--.

Column 11, line 30, "4" should be --41--.

Column 12, line 13, "1" should be --11--.

Column 13, line 68, "Was" should be --was--.

Column 14, line 33, "1" should be --11--.

Column 14, line 40, "1" should be --19--.

Column 14, line 55, after "sample" delete "18".

Column 14, line 59, after "layer" insert --18--.

Column 15, line 20, "*Strane-Layer*" should be --*Strained-Layer*--.

Column 15, line 22, "Ban" should be --Band--.

Column 16, line 7, "Of n=type" should be --of n-type--.--

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,294,833

DATED : March 15, 1994

INVENTOR(S) : Schetzina

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 16, line 8, after "layer" insert --16--.

Column 16, line 13, "1" should be --19--.

Column 16, line 18, "100-200" should be --100-200Å--.

Column 16, line 39, "Fig. 4" should be --Fig. 24--.

Signed and Sealed this

Fourth Day of October, 1994

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks