

# United States Patent

Kressel et al.

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[45] May 30, 1972

[54] SEMICONDUCTOR ELECTRON  
EMITTER

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[73] Assignee: RCA Corporation

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317/235 AG

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[58] Field of Search.....317/235 N, 235 AC, 235 AG,  
317/235 AQ

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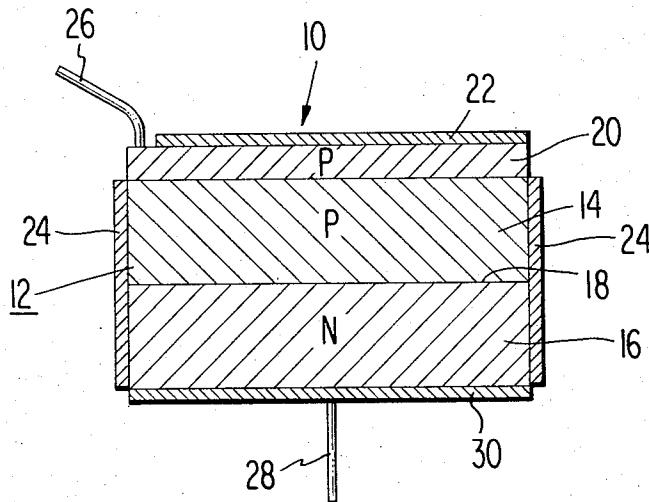
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[57]

## ABSTRACT

An electron emitter comprising a body of a semiconductor material which is adapted to generate light therein when properly biased but which is a poor absorber of the generated light. On a surface of the body is a thin region of a semiconductor material which is a good absorber of the generated light and which has an index of refraction which substantially matches the index of refraction of the material of the body. The thin semiconductor material region is adapted to absorb the light from the body and convert the light into free electrons. On the surface of the semiconductor material layer is a thin film of an electropositive work function reducing material which is adapted to emit the electrons formed in the semiconductor material layer.

5 Claims, 2 Drawing Figures



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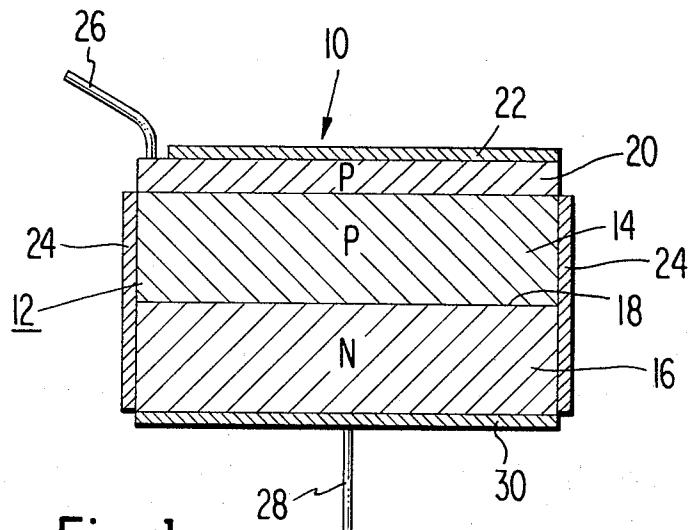


Fig. 1.

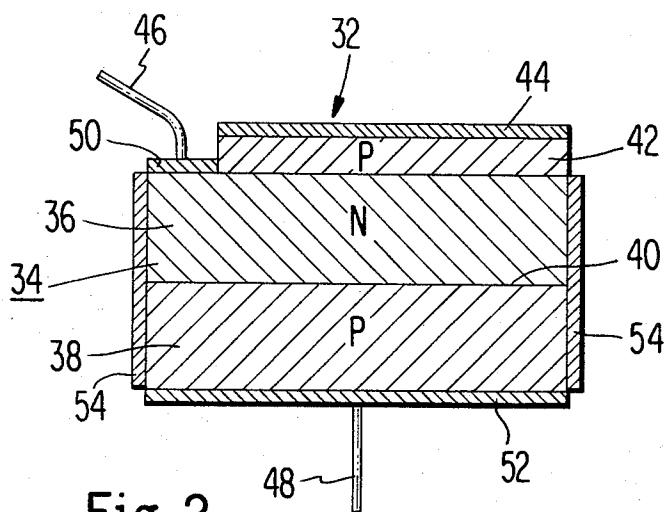


Fig. 2.

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## SEMICONDUCTOR ELECTRON EMITTER

## BACKGROUND OF INVENTION

The present invention relates to semiconductor electron emitters, and more particularly to a semiconductor electron emitter which includes an electroluminescent semiconductor element.

One type of electron emitter or cathode which has been used in electron discharge devices is known as a "cold" cathode in that it does not use heat to generate the electrons. One type of cold cathode uses a semiconductor element as the source of the electrons and a layer of an electropositive work function reducing material, such as an alkali or alkaline earth metal, on the surface of the semiconductor element as the means for emitting the electrons. To obtain a high degree of electron emission from such a cold cathode it is necessary that the semiconductor element produce an abundance of electrons and that the electrons produced be delivered to the emitting surface, usually necessitating that the emitting element be very close to the region where free electrons are available.

Another type of "cold" cathode uses two parts, one an emitter of light, and the other a photoemitter that absorbs at least part of the emitted light. See for example J.M. Lavine et al, "Cold Cathode Electron Emitter," *Solid-State Electronics*, Vol. 6, pp. 674-676, 1963, and T.S. Moss and J.B. Coombes, "An Opto-Electronic Cold Cathode Ray Tubes," *Solid-State Electronics*, Vol. 11, pp. 661-666, 1968. These two parts have been of widely different materials, and although they were optically coupled together, the two parts did not match well with respect to the good absorption of the emitted light and good transfer of the light from the emitter to the absorber. As a result, the overall quantum efficiencies achieved were as small as  $10^{-5}$  to  $10^{-10}$ .

## SUMMARY OF INVENTION

An electron emitting element including a body of semiconductor material having adjacent P type and N type regions with a PN junction therebetween. The semiconductor material of the body being capable of generating light when the PN junction is properly biased and the semiconductor material of at least one of said regions being a poor absorber of the generated light. A region of a semiconductor material which is a good absorber of light is provided on a surface of the region of the body which is a poor absorber of light. A layer of an electropositive work-function-reducing material is on the surface of the good absorbing semiconductor material region.

## BACKGROUND OF INVENTION

FIG. 1 is a sectional view of one form of the electron emitting element of the present invention.

FIG. 2 is a sectional view of another form of the electron emitting element.

## DETAILED DESCRIPTION

Referring to FIG. 1, a preferred form of the electron emitting element of the present invention is generally designated as 10. The electron emitting device 10 comprises a monolithic body 12 of a semiconductor material having opposed flat surfaces. The body 12 has a P type region 14 contiguous to an N type region 16 so as to provide a PN junction 18 therebetween. For reasons which will be explained, the P type region 14 can be relatively thick, at least 5 microns in thickness. The body 12 is of a semiconductor material which is capable of generating light in the vicinity of the PN junction 18 and preferably over a broad area of the P type region 14 when the PN junction is biased so as to inject charge carriers of one type into the P type region which combine with charge carriers of the opposite type in the P type region to generate the light. The preferred semiconductor materials for the body 12 are the III-V compound semiconductors and alloys thereof, such as the nitrides, phosphides, arsenides and an-

timides of boron, aluminum, gallium and indium. Preferably, the body 12 is of the compound semiconductor  $Al_xGa_{1-x}As$ , where  $x$  is less than 0.34, which has a high energy band gap and is capable of efficiently producing light at room temperature. In addition, the semiconductor material of at least the P type region 14 should be a poor absorber of the generated light.

One form of the body 12 is a body of  $Al_xGa_{1-x}As$ , where  $x$  is less than 0.34, with the body containing silicon as a conductivity modifier to form the P type region 14 and the N type region 16. The single conductivity modifier can be used to form the two regions of opposite conductivity type since silicon is amphoteric in the III-V compound semiconductor materials. The silicon is incorporated in different portions of the crystal lattice of the III-V compound semiconductor material depending on the temperature at which it is incorporated. Thus, the silicon will act as a donor if incorporated at one temperature and will act as an acceptor if incorporated at a lower temperature. For details, see for example H. Kressel et al, "Luminescence in Silicon-Doped GaAs Grown by Liquid-Phase Epitaxy," *Journal Applied Physics*, Vol. 39, No. 4, pp. 2006-2011, March 1968. The silicon compensated P type and N type regions 14 and 16 can be formed in the body 12 by liquid-phase epitaxy such as described in the article of H. Kressel et al, "Properties of Efficient Silicon-Compensated  $Al_xGa_{1-x}As$  Electroluminescent Diodes," *Journal Of Applied Physics*, Vol. 40, No. 5, pp. 2248-2253, April 1969. Also, by using silicon as a conductivity modifier to form the P type and N type regions 14 and 16, the P type region 14 will be a poor absorber of the light emitted in the body 12.

Another suitable form of the body 12 is a wafer of an N type III-V compound alloy semiconductor material having a high energy band gap, such as  $Al_xGa_{1-x}As$  containing tellurium as a conductivity modifier, as the N type region 16. On a surface of the wafer is a layer of a P type III-V compound alloy semiconductor material, such as  $Al_xGa_{1-x}As$  containing germanium or silicon as a conductivity modifier, as the P type region 14. The semiconductor material of the P type region 14 should have a band gap energy which is lower at the surface of the N type region 16 than the band gap energy of the N type region 16 and which increases to the surface of the P type region 14. By using  $Al_xGa_{1-x}As$  as the semiconductor material for the P type region 14, the band gap energy can be varied by varying the amount of aluminum in the material. The band gap energy increases with increasing amounts of aluminum. Also, the PN junction between the P type region and the N type region must be a heterojunction.

This body can be formed by epitaxially growing P type  $Al_xGa_{1-x}As$  on the surface substrate of gallium arsenide by liquid-phase epitaxy. The first portion of the  $Al_xGa_{1-x}As$  deposited on the substrate will have a high concentration of aluminum and the concentration of aluminum will gradually decrease as the thickness of the epitaxial layer increases. When the P type epitaxial layer is of a thickness of at least 5 microns, N type  $Al_xGa_{1-x}As$  having a high concentration of aluminum is epitaxially grown on the P type layer by liquid-phase epitaxy. After the N type epitaxial layer of the desired thickness is grown, the gallium arsenide substrate is removed, such as by etching and polishing. This provides a P type region on an N type region with a heterojunction between the two regions and the P type region has the desired graded band gap energy.

This body can also be formed by epitaxially growing the P type region on a substrate of the N type semiconductor material using vapor phase epitaxy. Vapor phase epitaxy comprises forming a mixture of gases containing the elements of the semiconductor material to be deposited and pyrolytically reacting the gaseous mixture in the presence of the substrate to deposit a mixture of the elements on the substrate. For an example of vapor phase epitaxy see J.J. Tietjen et al, "The Preparation and Properties of Vapor-Deposited Epitaxial  $GaAs_{1-x}PB_x$  Using Arsine and Phosphine," *Journal Electrochemical Society*, Vol. 113, pg. 724, 1966. By gradually increasing the amount of the aluminum containing gas in the

mixture as the P type layer is deposited on the substrate, the desired graded band gap energy can be achieved.

A region 20 of a P type semiconductor material is provided on the surface of the P type region 14. The region 20 is of a semiconductor material which is a good absorber of the light generated by the body 12 and which has an index of refraction which at least substantially matches the index of refraction of the semiconductor material of the region 14 of the body 12. Suitable semiconductive materials for the region 20 are the III-V compound semiconductor materials or alloys thereof. The region 20 should be of a thickness of 1 to 5 microns and should provide a heterojunction with P type region 14. The region 20 can be provided on the body 12 by epitaxially depositing a layer on the surface of the region 14. This can be achieved either by liquid-phase epitaxy such as described in the article by H. Nelson, "Epitaxial Growth From the Liquid State and its Application to the Fabrication of Tunnel and Laser Diodes," RCA Review 24, pg. 603, 1963, or by vapor phase epitaxy such as previously described.

A thin layer 22 of an electropositive work function reducing material is provided on the surface of the P type semiconductive material region 20. The electropositive layer 22 comprises an alkali or alkaline earth metal and oxygen, and is monomolecular or has a thickness not exceeding a few atomic diameter of the electropositive material. The alkali or alkaline earth metal of the electropositive layer 22 may be cesium, potassium or barium, with cesium being the preferred metal. The electropositive layer 22 may be applied by evaporation in a vacuum. A thin film 24 of a light reflecting material, such as silicon monoxide covered with gold, may be coated on the peripheral edge surface of the body 12 completely around the body so as to prevent any of the light generated in the body from being emitted from the periphery of the body and to reflect more of the light toward the electropositive layer 22. The reflecting film 24 may be applied to the body by evaporation in a vacuum.

Terminal wires 26 and 28 are electrically connected to the P type region 14 and N type region 16 of the body 12. As shown, the terminal wire 28 is connected to the N type region 16 through a contact layer 30 on the surface of the N type region. The contact layer 30 is a film of a metal, such as tin, which will make good ohmic contact to the semiconductor material of the N type region 16. The tin film may be coated with a film of nickel and a film of gold to provide for greater ease of securing the terminal wire 28 to the contact layer 30. The terminal wire 26 is connected to the P type region 14 through the P type region 20. As shown, the terminal wire 26 is fused directly to the P type region 20. However, the terminal wire 26 can be secured to the P type region through a small contact layer on the surface of the P type region 20. Such a contact layer could be a film of a metal which would make a good ohmic contact to the semiconductor material of the P type region 20, such as nickel, which can be coated with a film of gold.

In the use of electron emitting device 10 the terminals 26 and 28 are connected to a source of voltage with the terminal 28 being connected to the negative side of the voltage source and the terminal 26 to the positive side. The voltage biases the PN junction 18 so as to inject charge carriers of one type from the N type region 16 into the P type region 14 where they combine with charge carriers of the opposite type and generate light in the P type region 14. By having a relatively thick P type region 14 current crowding at the contact between the terminal 26 and the P type region 20 is prevented and the current spreads across substantially the entire bulk of the P type region 14. Thus, substantial generation of light is achieved even though the contact between terminal 26 and the P type region 20 is small.

Since the semiconductor material of the P type region 14 is a poor absorber of light and the semiconductor material of the P type region 20 is a good absorber of light and has an index of refraction which at least substantially matches the index of refraction of the region 14, the light generated in the body 12

is absorbed in the P type region 20. The reflecting layer 24 prevents any light from being emitted from the edge of the body 12. In the P type region 20 the light absorbed is converted into free electrons. Since the P type region 20 is thin, a high concentration of electrons is provided at the surface of the electropositive layer 22. Also, the thickness of the P type region 20 is such that the electrons generated therein have sufficient energy to pass into the electropositive layer 22 and be emitted therefrom in the manner described in the article of R.F. Simon et al, "Electron Emission from a 'Cold Cathode' GaAs P-N Junction," Applied Physics Letters, Apr. 1, 1969, Vol. 14, No. 7, pgs. 214-216. The heterojunction between the P type region 20 and the P type region 14 prevents the electrons generated in the P type region 20 from passing back into the P type region 14. Thus, the electron generating element 10 delivers to the emitting layer 22 a large number of electrons so as to provide a high degree of electron emission.

An electron emitting device of the construction shown in FIG. 1 was made with a body 12 of  $Al_{1-x}As$  containing silicon as a single conductivity modifier to form the P type region 14 and N type region 16 in the manner previously described. The P type region 14 was of a thickness of about 10 microns. The P type region 20 was a layer of gallium arsenide containing zinc as a conductivity modifier at a doping level of about  $10^{19} cm^{-3}$ . The P type region 20 was about 1 micron in thickness. The electropositive layer 22 was of cesium and oxygen and was of an area of approximately  $5 \times 10^{-2} cm^2$ . Contacts were made to the P type region 22 and the N type region 16 by pressure contact only. When a current was passed through emitting electron emitting device light at a wavelength of 8,700 Å, peak value, was generated in the body 12. Electrons were emitted from the device into a vacuum and it was found that the efficiency of emission was  $10^{-3}$ , i.e. it took 35,000 electrons crossing the junction to get one electron into the vacuum. This efficiency is an improvement by a factor of about 1,000 over the reported efficiencies for PN junction semiconductor cold cathode electron emitting devices previously developed.

Referring to FIG. 2, another form of the electron emitting element is generally designated as 32. The electron emitting element 32 comprises a monolithic body 34 of a semiconductor material having an N type region 36 contiguous to a P type region 38 so as to provide a PN junction 40 therebetween. As in the electron emitting device 10 of FIG. 1, the body 34 is of a semiconductor material which is capable of generating light in the vicinity of the PN junction 40 when the junction is properly biased, such as the III-V compound semiconductors and alloys thereof. In the body 34, the N type region 36 should be relatively thick, at least 5 microns in thickness, and at least the N type region 36 should be of a semiconductor material which is a poor absorber of light.

A form of the body 34 is a wafer of a P type III-V compound alloy semiconductor material, such as  $GaAs_{1-x}P_x$ , where  $x$  is greater than 0 and equal to or less than 1, containing a P type conductivity modifier, such as zinc, beryllium or cadmium, as a P type region 38 having on surface thereof a layer of N type III-V compound alloy semiconductor material, such as  $GaAs_{1-x}P_x$  containing tellurium or selenium as a conductivity modifier as an N type region 36. The semiconductor material of the N type region 36 should have a band gap energy which, at the surface of the P type region 38 is larger than or equal to the band gap energy of the P type region 38. By using  $GaAs_{1-x}P_x$  as the semiconductor material for the N type region 36, the band gap energy can be varied by varying the amount of phosphorous in the material with the band gap energy increasing with increasing amounts of phosphorous. This body can be formed by epitaxially growing P type  $GaAs_{1-x}P_x$  on the surface of a substrate of gallium arsenide by vapor phase epitaxy in the manner described in the previously referred to article of J.J. Tietjen et al. Then N type  $GaAs_{1-x}P_x$  is epitaxially grown on the P type region. By gradually increasing the amount of phosphorous containing gas in the mixture as the N type layer is deposited, the desired graded band gap

energy can be achieved. After the N type epitaxial layer of the desired thickness is grown, the gallium arsenide substrate is removed, such as by etching and polishing.

A region 42 of a P type semiconductor material is provided on the surface of the N type region 36. The P type region 42 is the same as the P type region 20 of the electron emitter device 10 of FIG. 1. Thus, the P type region 20 should be of a semiconductor material which is a good absorber of light and which has an index of refraction which substantially matches the index of refraction of the semiconductor material of the body 34. Also, the P type region 42 should be of a thickness of between 1 and 5 microns. A thin layer 44 of an electropositive work function reducing material is provided on the surface of the P type region 42. The electropositive layer 44 is of the same composition as and is formed in the same manner as the electropositive layer 22 of the electron emitter device 10 of FIG. 1.

A pair of terminal wires 46 and 48 are electrically connected to the N type region 36 and P type region 38 of the body 34. As shown, the terminal wire 46 is connected to the N type region 36 through a small contact layer 50 on the surface of the N type region. The contact layer 50 is a film of a metal which will make good ohmic contact to the semiconductor material of the N type region 36, such as tin which may be coated with nickel and gold. A small portion of the P type region 42 is removed, such as by etching, to permit the contact layer 50 to be applied to the surface of the N type region 36. The terminal wire 48 is connected to the P type region 38 by a contact layer 52. The contact layer 52 is a film of a metal which will make good ohmic contact to the semiconductor material of the P type region, such as nickel which may be coated with gold. A thin film 54 of a light reflecting material, such as silicon monoxide coated with gold, may be coated on the peripheral edge surface of the body 34 so as to prevent any of the light generated in the body from being emitted from the periphery of the body.

In the use of the electron emitting device 32 the terminals 46 and 48 are connected to a source of voltage with the terminal 46 being connected to the negative side of the voltage source and the terminal 48 being connected to the positive side. The electron emitting device 32 operates in substantially

the same manner as described with regard to the electron emitting device 10 of FIG. 1 except that the light is generated in the P type region 38 and passes through the N type region 36 to the P type region 42. The light is absorbed in the P type region 42 and converted to free electrons which are emitted from the electron emitting device 32 by the electropositive layer 44.

We claim:

1. An electron emitting element comprising:
  - a. a body of semiconductor material having adjacent P type and N type regions with a PN junction therebetween, the semiconductor material of said body being capable of generating light when the PN junction is properly biased and the semiconductor material of at least the P type region being  $Al_xGa_{1-x}As$
  - b. a region of P type gallium arsenide on a surface of the P type region of the body and forming a heterojunction therebetween, said P type gallium arsenide region being a better absorber of light than the semiconductor material of the P type region of the body,
  - c. a layer of an electropositive work function reducing material on the surface of the P type gallium arsenide, region, and
  - d. a separate terminal connected to each of the P type gallium arsenide region and the N type region of the body.
2. An electron emitting element in accordance with claim 1 in which the P type region of the body is at least 5 microns in thickness.
3. An electron emitting element in accordance with claim 1 in which the P type region of the body contains silicon as the conductivity modifier to lower the light absorption properties of the P type region of the body.
4. An electron emitting element in accordance with claim 1 in which the concentration of the aluminum in the P type region of the body varies from a minimum at the PN junction to a maximum at the heterojunction so that the band gap energy of the P type region of the body increases from the PN junction to the heterojunction.
5. An electron emitting element in accordance with claim 1 in which the P type gallium arsenide region is between 1 and 5 microns in thickness.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3667007 Dated May 30, 1972

Inventor(s) Henry Kressel and Jacques Isaac Pankove

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

Column 2, lines 3, 26 and 55, change " $Al_x Ga_{1-x} As$ " to  
-- $Al_x Ga_{1-x} As$ --.

Column 2, line 71, change " $GaAs_{1-x} PB_x$ " to -- $GaAs_{1-x} P$ --.

Column 4, line 19, change " $Al_x^{1-x} As$ " to -- $Al_x Ga_{1-x} As$ --.

Column 4, line 25, change " $10_{19} cm^{-3}$ " to -- $10^{19} cm^{-3}$ --.

Column 4, line 30, change "emitting" (first occurrence)  
to --the--.

Signed and sealed this 5th day of December 1972.

(SEAL)

Attest:

EDWARD M.FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents