

Nov. 11, 1969

R. E. SIMON ET AL
 PHOTOMULTIPLIER OR IMAGE AMPLIFIER WITH SECONDARY EMISSION
 TRANSMISSION TYPE DYNODES MADE OF SEMICONDUCTIVE
 MATERIAL WITH LOW WORK FUNCTION MATERIAL
 DISPOSED THEREON

3,478,213

Filed Sept. 5, 1967

2 Sheets-Sheet 1

Fig. 1.

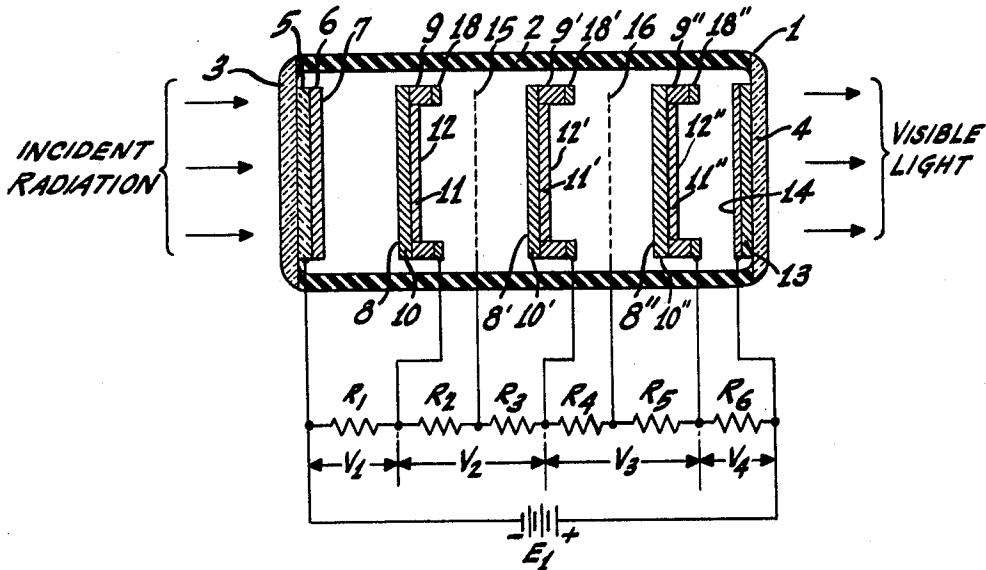
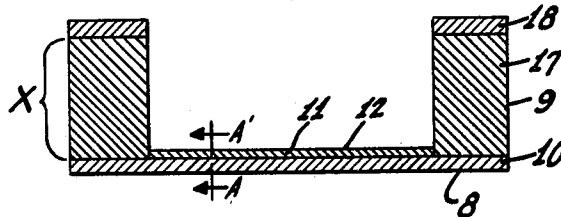


Fig. 2.



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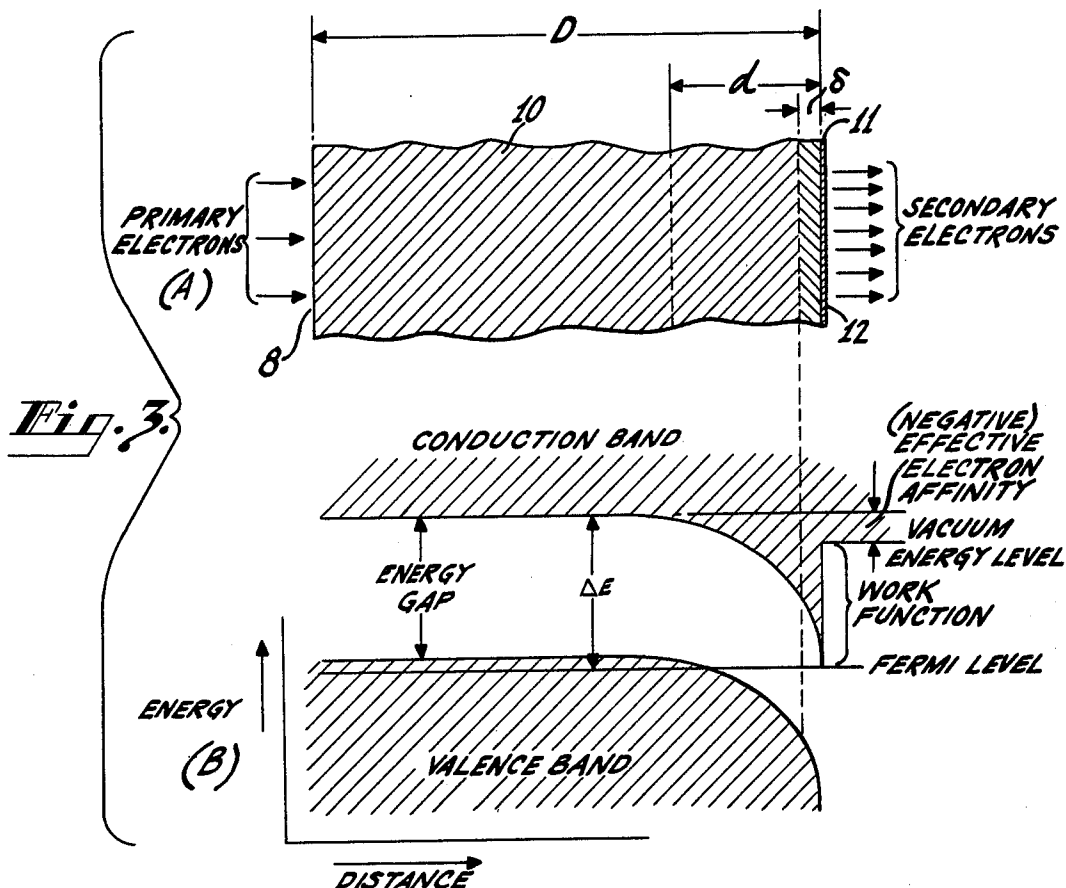
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PHOTOMULTIPLIER OR IMAGE AMPLIFIER WITH SECONDARY EMISSION TRANSMISSION TYPE DYNODES MADE OF SEMI-CONDUCTIVE MATERIAL WITH LOW WORK FUNCTION MATERIAL DISPOSED THEREON

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9 Claims

ABSTRACT OF THE DISCLOSURE

A secondary emission device of the transmission type which may be used as a photomultiplier, light amplifier, or X-ray image intensifier. The device achieves amplification of an electron image by causing the electrons to impinge upon a thin film of semiconductor material at high velocity, thus generating a large number of secondary electrons for each incident (primary) electron. The secondary electrons diffuse through the semiconductive film and are emitted from the opposite surface of the film which is coated with a monomolecular layer of cesium to reduce the work function at the emitting surface.

The secondary emission semiconductive film consists of highly doped P type gallium phosphide. The energy levels in the film structure are such that electrons in the conduction band can reach the emitting surface with a residual energy above that of the vacuum energy level, so that electrons are emitted from the cesium-coated surface without the necessity of supplying additional energy.

Background of the invention

This invention relates to the field of secondary emission transmission type devices, and more particularly to an improved secondary emission device utilizing a dynode which includes semiconductor material.

The secondary emission electron tube devices which are presently in common use are of the "reflecting" type; i.e., they operate in a manner wherein the secondary electrons are emitted from the same surface as that upon which the primary electrons to be "amplified" impinge. The transmission type of secondary emission electron amplifying structure is well known in the art, but has not achieved commercial acceptability due to a number of inherent disadvantages of the transmission structure in devices heretofore known.

Basically, the transmission type of secondary emission device utilizes a dynode element in the form of a very thin (on the order of a few hundred Angstroms in devices heretofore known) composite film, such that when incident primary electrons bombard one major surface of the film, secondary electrons are emitted from the opposite major surface of the film. Such a device is exemplified, e.g., by U.S. Patent No. 2,898,499.

Since the secondary emission materials employed in such prior art devices rapidly attenuate any movement of conduction electrons in the bulk material, it has heretofore been necessary to make the dynode films extremely thin, and consequently mechanically fragile. When the secondary emission layer is made very thin, it does not absorb all of the incident (relatively high energy) primary electrons. As a result, some of the primary electrons pass completely through the dynode film and impinge upon the phosphor screen or other detection means utilized in the device so as to greatly reduce the effective image contrast obtainable.

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Since the very thin dynode structures previously employed do not absorb all incident primary electrons, they necessarily operate at reduced efficiency. The very thin dynode film, being somewhat transparent to visible light, permits feedback from the phosphor screen (when the device is employed as an image intensifier) to the photosensitive structure at the device input; such feedback sometimes causes electrical instabilities to develop.

In addition to the foregoing disadvantages of conventional transmission type secondary emission devices, the materials heretofore available for such devices exhibit relatively low secondary emission yields (less than 10 secondary electrons for each primary electron) so that a great many cascaded stages are required to achieve useful values of electron image amplification.

An object of the present invention is to provide an improved secondary emission transmission type device having a dynode structure of relatively great thickness compared to those heretofore known, and exhibiting a secondary emission yield and signal to noise ratio substantially greater than that of prior art devices of this type.

Summary

According to the invention there is provided a transmission type secondary emission device including (i) a source of primary electrons which are made to impinge upon one major surface of a secondary emission dynode of semiconductive material to produce secondary electrons which are emitted from the opposite major surface of the dynode, and (ii) means for utilizing the emitted secondary electrons, in which the dynode comprises a highly-doped film of P type semiconductive material and a thin layer of an electropositive work function reducing material on the surface of the semiconductor from which the secondary electrons are emitted; the energy gap of the semiconducting material, the work function at the surface of the electropositive layer, and the acceptor impurity concentration in the semiconductor bulk are such that the bottom of the conduction band in the semiconductor bulk lies at an energy level above the vacuum energy level at the exposed surface of the electropositive layer; the thickness of the semiconductive film is chosen sufficiently great so as to absorb the incident primary electrons, but not greater than a value on the order of a few times the diffusion length for electrons in the semiconductor bulk, so that the secondary electrons may diffuse toward and be emitted from the exposed surface of the electropositive layer.

In the drawing

FIGURE 1 shows an electron photomultiplier device employing the invention;

FIGURE 2 shows a cross sectional view of a dynode according to the invention utilized in the device of FIGURE 1; and

FIGURE 3A shows a partial cross sectional view of the dynode of FIGURE 2 taken along the cutting plane A-A' and FIGURE 3B shows an energy level diagram useful in explaining various features of the invention.

Detailed description

FIGURE 1 shows an electron multiplier device 1 constructed according to the invention. The device 1 is in the form of a cylinder having an opaque outer insulating shell 2 which may comprise a suitable ceramic material. At opposite ends of the cylinder are transparent end plates 3 and 4 which may comprise a suitable glass.

The device 1 may be employed as a light image amplifying device, or as a simple photomultiplier. Incident radiation, which may comprise visible, infrared or ultraviolet light or X-rays, passes through the end plate 3 (which must, of course, be designed to transmit the par-

ticular type of incident radiation to be detected) and through the transparent conductive film 5 to impinge upon the photoemissive layer 6.

Where the incident radiation is a visible light image, the conductive layer 5 may comprise a material such as stannic oxide, which is substantially transparent to visible light. The photoemissive layer 6 may then comprise one of the well known materials which emits electrons when subjected to irradiation by visible light, such as cesium antimony. Electrons are emitted from the exposed surface 7 of the photocathode 6 in accordance with the incident radiation, to form an electron image which corresponds to the visible light image to be amplified. The emitted electrons are accelerated by the voltage V_1 across resistor R_1 (which is supplied by a voltage divider network consisting of voltage source E_1 and resistor R_1 through R_6) to impinge upon the surface 8 of the secondary emission dynode 9. These incident primary electrons, which have a relatively high kinetic energy due to the potential difference between the dynode 9 and the transparent conductive layer 5, are absorbed by the semiconductive film 10 of the dynode 9, so that each incident primary electron produces a relatively large number of secondary electrons in the bulk of the semiconductive film 10. A relatively large proportion of these secondary electrons diffuse toward the low work function layer 11 and are emitted from the exposed surface 12 of the layer 11.

The improved "efficiency", i.e. the ratio of the number of secondary electrons emitted from the layer 11 to the total number of secondary electrons created in the bulk of the film 10, of our dynode structure is attributable to the fact that conduction band electrons having thermal energies can travel relatively large distances in the bulk of the film 10 and be emitted from the exposed surface of the layer 11.

Due to the improved efficiency and higher gain of our dynode structure, random fluctuations of the number of emitted secondary electrons (corresponding to an invariant stream of incident primary electrons) are minimized, thus resulting in an improved signal to noise ratio.

The secondary electrons emitted from the surface 12 of the dynode 9 are accelerated by the potential difference V_2 across resistors R_2 and R_3 to impinge upon the surface 8' of the next dynode 9', so that the aforementioned process is again repeated, leading to the emission of additional secondary electrons from the exposed surface 12' of the low work function layer 11'. The process then proceeds in similar fashion, with the electrons emitted from the surface 12' being accelerated by the potential difference V_3 across resistors R_4 and R_5 to impinge upon the surface 8'' of the dynode 9'', so as to cause additional secondary electrons to be emitted from the exposed surface 12'' of the low work function layer 11''.

The resultant amplified electron image, in the form of secondary electrons leaving the surface 12'', is converted into visible light by causing the electrons to impinge upon a phosphor screen 13 which may comprise an electron-sensitive light-emitting material such as zinc sulphide. The electrons emitted from the surface 12'' are accelerated toward the phosphor screen 13 by means of a potential difference V_4 applied between the dynode 9'' and a thin electron-permeable aluminum layer 14 applied to the surface of the phosphor layer 13.

Typically, the source E_1 may have a voltage on the order of 10 kilovolts, while the voltages V_1 , V_2 and V_3 may have values on the order of 2 kilovolts, the phosphor screen accelerating voltage V_4 being on the order of 4 kilovolts. These values will, of course, depend upon the desired parameters of the specific device to be constructed.

In some cases, it may be desirable to modulate or more uniformly control the acceleration of electrons between the various dynodes by means of grids 15 and 16. Where necessary or desirable, the electrons traveling

through the device 1 may be focused by means of a magnetic field directed parallel to the axis of the cylinder formed by the insulating shell 2.

FIGURE 2 shows an enlarged cross sectional view (not to scale) of the dynode 9 of FIGURE 1. The dynode 9 consists of an annular supporting ring 17 of monocrystalline gallium arsenide P type semiconductive material of relatively low resistivity. Disposed on the supporting ring 17 is a monocrystalline epitaxially-grown film 10 of a wide bandgap semiconductor material such as gallium phosphide. The supporting ring 17 may typically have a thickness x on the order of 5 mils, while the thickness of the epitaxial semiconductive film 10 may be on the order of 2000 Angstroms.

Disposed on one surface of the semiconductive layer 10 is a monomolecular layer 11 of an electropositive work function reducing material such as cesium. The layer 11 need not necessarily be monomolecular, but should preferably have a thickness not exceeding a value on the order of a few atomic diameters of the electropositive material.

Disposed on the upper surface of the ring 17 is a conductive layer 18 comprising an acceptor material such as indium, which forms an ohmic contact with the P type semiconductor material 17. The indium layer 18 is preferably alloyed to the adjacent gallium arsenide layer 17.

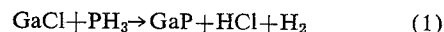
While we have shown the supporting ring 17 as comprising monocrystalline gallium arsenide, this material is employed only for convenience in growing the epitaxial film 10, as it is extremely difficult to grow an epitaxial layer on a non-crystalline substrate.

While we prefer to utilize a semiconductive film 10 of monocrystalline material, the film 10 may alternatively comprise polycrystalline semiconductor material if the grain diameter of the polycrystalline material is on the same order as the thickness of the semiconductive film. Where polycrystalline material is employed, the supporting layer 17 may comprise a suitable metal or other conductive material.

Electrical contact to the dynode 9 may be made by soldering or otherwise bonding a terminal lead to the indium layer 18; the terminal lead may also serve to mechanically support the dynode within the shell 2.

The semiconductive film 10 should comprise P type material which is heavily doped with acceptor impurities to provide a hole concentration on the order of 10^{18} to $10^{20}/\text{cm}^3$. We prefer to employ beryllium as the acceptor material, although other suitable acceptors such as zinc or magnesium could be utilized.

The manufacture of the dynode 9 is initiated by providing a monocrystalline wafer of P type gallium arsenide of relatively low (on the order of .01 to 1.0 ohm centimeters) resistivity. The gallium phosphide monocrystalline film 10 is epitaxially grown on the gallium arsenide wafer by the vapor phase reaction of gallium subchloride and phosphine according to Equation 1. Hydrogen is employed as the carrier gas for the reactants.



A small amount of beryllium chloride (BeCl_2) is mixed with the reactant gases to provide acceptor doping of the epitaxial film 10. The beryllium chloride concentration is chosen so as to provide a net hole concentration in the film 10 on the order of 10^{18} to $10^{19}/\text{cm}^3$.

The epitaxial deposition of the film 10 is continued until a thickness on the order of 2000 Angstroms is reached, at which time the deposition process is terminated.

After cleaning the exposed surfaces of the gallium arsenide-gallium phosphide laminate, a suitable masking material is applied to the exposed surface of the gallium phosphide film 10 and to an annular peripheral portion of the exposed surface of the gallium arsenide wafer,

and the laminate is immersed in the following etching solution:

- 5 parts (by volume) concentrated sulphuric acid
- 1 part (by volume) of a 30% volumetric solution of hydrogen peroxide in water
- 1 part (by volume) water

This solution rapidly etches the exposed central portion of the gallium arsenide wafer. Since the gallium phosphide film 10 is relatively insensitive to this etching solution, the etching process virtually halts when the central portion of the gallium arsenide wafer has been removed.

After removing the masking material and washing the etched laminate, a thin ring 18 of indium is placed upon and alloyed to the exposed surface of the remaining gallium arsenide ring 17.

One surface of the gallium phosphide film 10 is next carefully cleaned and heat treated to remove undesired contaminants, after which a monomolecular layer 11 of cesium is evaporated onto the cleaned and treated surface. The resultant structure is that shown in FIGURE 2.

We have observed that when the gallium phosphide material of the film 10 is bombarded with electrons having energies on the order of 200 electron volts, a secondary emission ratio on the order of 100:1 can be obtained. That is, for each primary electron striking the surface 8 of the film 10, an average of 100 or more secondary electrons are emitted from the low work function opposite surface 12.

Since the film 10 comprises monocrystalline material (or polycrystalline material of proper grain size), electrons in the conduction band of the semiconductor material can travel relatively long distances before recombining with holes in the material. The average distance which an electron will travel in the film 10 before recombining is given by the diffusion length L_n defined as

$$L_n = \sqrt{D_n \tau_n} \quad (2)$$

where

L_n = diffusion length for electrons

D_n = diffusion constant for electrons

τ_n = electron lifetime.

The diffusion constant D_n may be obtained from the Einstein relationship,

$$\mu_n = \frac{e}{kT} D_n \quad (3)$$

where

μ_n = electron mobility

e = electronic charge

k = Boltzmann constant

T = absolute temperature.

Combining Equations 2 and 3, we have

$$L_n = \sqrt{\mu_n \tau_n kT / e} \quad (4)$$

The thickness of the epitaxial secondary emission semiconductor film 10 should be sufficiently great so as to absorb substantially all incident primary electrons, but not so great that the secondary electrons produced cannot diffuse through the semiconductor film to reach and be emitted from the surface of the low work function electropositive layer 11. Thus, the thickness of the film 10 should not exceed a few times (usually not exceeding three times) the above-defined diffusion length L_n . Preferably, the thickness of the film 10 should be on the order of the diffusion length provided this does not conflict with the requirement that the film be sufficiently thick to absorb substantially all incident primary electrons. For the 2000 Angstrom gallium phosphide film of our example, the diffusion length L_n is on the order of 2000 to 3000 Angstroms at room temperature.

The theoretical basis for the electron emitting properties of the dynode 9 will best be understood by reference to FIGURE 3.

FIGURE 3A shows a partial cross sectional view of the dynode 9 taken along the cutting plane A—A' of FIGURE 2. Vertically aligned with FIGURE 3A, FIGURE 3B shows an energy level diagram for the dynode structure. It is seen from the diagram that the semiconductor film 10 has been degeneratively doped with acceptor impurities so that the Fermi level in the semiconductor film lies slightly below the top of the valence band. In practice, practical doping concentrations result in a Fermi level so close to the top of the valence band that the difference between the energy gap (between the top of the valence band and the bottom of the conduction band) and the energy differential ΔE (between the Fermi level and the bottom of the conduction band) is negligible.

The electropositive metallic layer 11 constrains the Fermi level to substantially coincide with the bottom of the conduction band at the emitting surface 12. Assuming the dynode to be in thermal equilibrium, and the effect of any externally-applied electric field across the composite consisting of film 10 and layer 11 (due to the potential differences V_1 through V_4) to be negligible, the Fermi level will be substantially constant throughout the film 10 and layer 12.

Since the energy gap is substantially constant throughout the structure, the energy bands necessarily bend in the immediate vicinity of the emitting surface 12, as is seen in FIGURE 3B. The band bending extends a distance d into the film 10 which is small compared to the total thickness D of the film. The actual value of the distance d depends primarily upon the energy gap and the impurity doping level within the semiconductor film 10.

The energy level diagram indicates that within a very small distance δ inward from the electropositive layer 11, the Fermi level lies closer to the bottom of the conduction band than to the top of the valence band, while in the bulk of the film 10 the opposite is true. It is therefore evident that the bulk of the film exhibits P type conductivity, while the extremely thin ("inversion") region within a distance δ from the electropositive layer 11 behaves as though it were of N type conductivity.

If the electropositive layer 11 on the film 10 has a work function less than the energy differential ΔE (or in our example the substantially equivalent energy gap), the vacuum energy level at the emitting surface 12 (corresponding to the energy at electron must have to escape from the surface) will lie below the bottom of the conduction band in the bulk of the semiconductor film 10.

Due to this height of the conduction band bottom above the vacuum energy level, electrons in the conduction band of the semiconductor film 10 (secondary electrons in the conduction band are produced as a result of collisions with incident primary electrons) may diffuse toward the emitting surface 12 while retaining a residual energy at the emitting surface which is greater than the vacuum energy level. The net result is that electron emission can take place from the surface 12 without the necessity for applying any external force to overcome the surface work function and the dynode behaves as though it had a negative effective electron affinity.

The high doping levels employed in the semiconductor film 10 according to our preferred embodiment insure that the distance d in which band bending occurs is extremely small (on the order of 30 to 100 angstroms), so that energy loss of electrons diffusing toward the emitting surface 12 is minimized.

For the dynode of our preferred embodiment, the gallium phosphide material employed has an energy gap on the order of 2.3 electron volts while the work function exhibited by the cesium-coated emitting surface is on the order of 1.3 electron volts, resulting in a negative effective electron affinity of approximately 1.0 electron volt.

We claim:

1. A secondary emission device, comprising:
 - a source of free electrons;

at least one dynode including a film of semiconductor material having first and second opposed major surfaces,

said material having spaced valence and conduction energy bands with a given energy gap therebetween,

said material having a net excess concentration of acceptor impurities such that the Fermi level in said material lies relatively proximate to the uppermost energy level of the valence band and relatively remote from the lowermost energy level of the conduction band,

said dynode including a thin layer comprising an electropositive work function reducing material on said second surface, said layer having a thickness not exceeding a value on the order of a few atomic diameters of said electropositive material, said electropositive layer reducing the work function of said second surface so that the vacuum energy level at said second surface lies below the lowermost energy level of the conduction band in the bulk of said film;

means for accelerating said free electrons to impinge upon said first surface with a kinetic energy sufficient to produce secondary electrons in the conduction band of said material;

the thickness of said film being sufficiently great so that said impinging electrons are absorbed by the film, said film thickness not exceeding a value on the order of a few times the diffusion length for electrons in said material,

whereby said secondary electrons may diffuse toward and be emitted from said second surface; and

means for utilizing the secondary electrons emitted from said second surface.

2. A secondary emission device according to claim 1, wherein said impurity concentration is sufficient to pro-

vide a hole concentration on the order of 10^{18} to $10^{19}/\text{cm}^3$ in said material.

3. A secondary emission device according to claim 1, wherein said film is monocrystalline.

4. A secondary emission device according to claim 1, wherein said film is polycrystalline with an average grain diameter on the order of the thickness of said film.

5. A secondary emission device according to claim 1, wherein said material comprises gallium phosphide.

6. A secondary emission device according to claim 5, wherein said impurity comprises beryllium.

7. A secondary emission device according to claim 6, wherein said film thickness is on the order of 2000 angstroms.

8. A secondary emission device according to claim 5, further including film supporting means comprising an annular ring of monocrystalline gallium arsenide, said film being epitaxially grown on said supporting means.

9. A secondary emission device according to claim 7, wherein the kinetic energy of said impinging free electrons is on the order of 2000 electron volts.

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RALPH G. NILSON, Primary Examiner

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U.S. Cl. X.R.

250—213; 313—68, 95, 103

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,478,213 Dated November 11, 1969

Inventor(s) Ralph E. Simon, Brown F. Williams & Ralph Wasserman

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

Column 4, line 11 "typicalls" should read -- typically --

Column 5, line 24 "200" should read, -- 2000 --

Column 5, line 38, Equation (2) should read

$$-- L_n = \sqrt{D_n \tau_n} --$$

Column 5, line 49 "μ" should read -- μ_n --

SIGNED AND
SEALED
MAY 26 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents