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[54] **SEMITRANSPARENT PHOTOCATHODE**

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[51] **Int. Cl.** **H01j 39/16**

[58] **Field of Search** ..... 313/65, 94, 95, 102, 108 D, 313/366, 373, 383; 317/235 N; 357/30, 31

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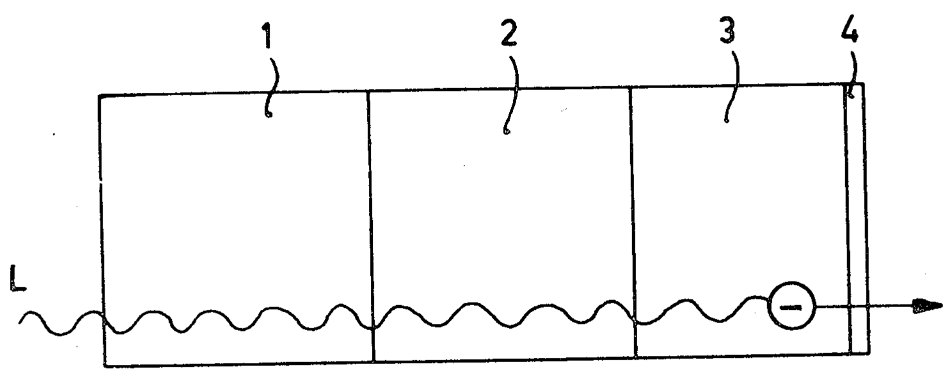
[57] **ABSTRACT**

In order to obtain an optimum freedom in the choice of the material in a semitransparent photocathode which consists of III-V semiconductor compounds and in which the matching of the lattice constant of the active layer to that of the substrate is achieved by an intermediate layer, and thus to arrive at a sensitivity and/or optical wide band condition which is as high as possible, according to the invention the composition of the intermediate layer is independent of the substrate and of the active layer and its lattice constant differs from the lattice constant of the active layer by less than 0.3% and differs from the grid constant of the substrate up to several per cent, for example up to 3%. Such a photocathode may consist in particular of a substrate of GaP, an intermediate layer of $Al_x Ga_{1-x}As$ with $x>0.8$ and an active layer of GaAs.

15 Claims, 4 Drawing Figures



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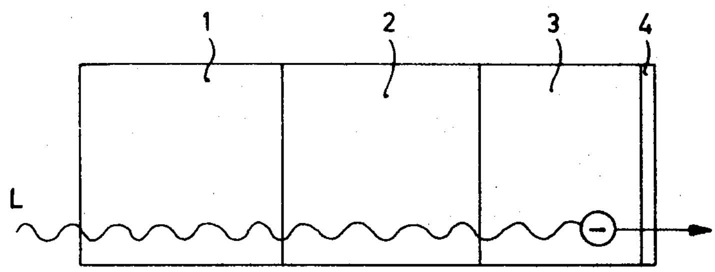

Fig. 1

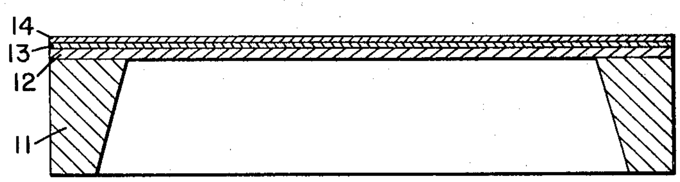

Fig. 1a

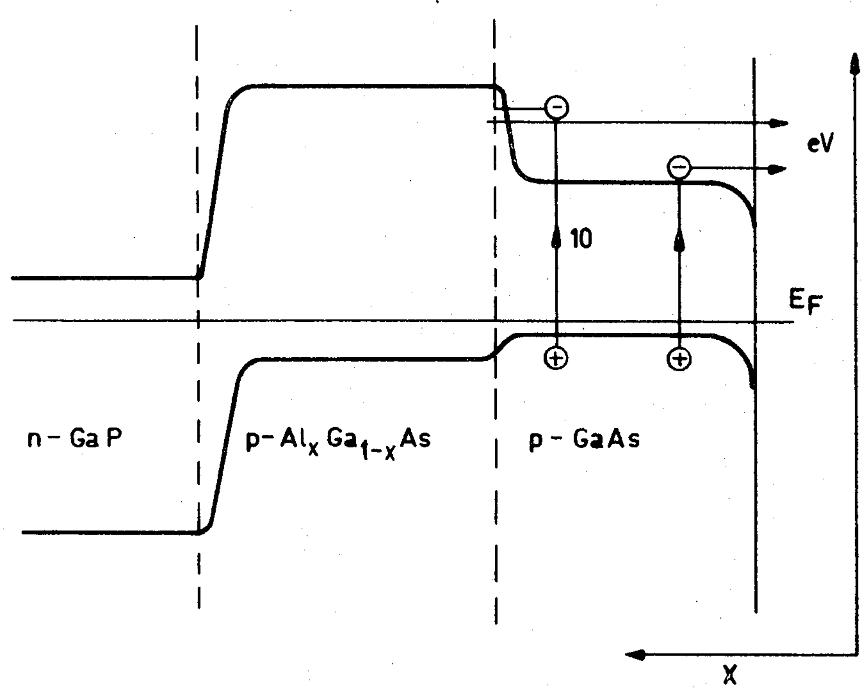

Fig. 2

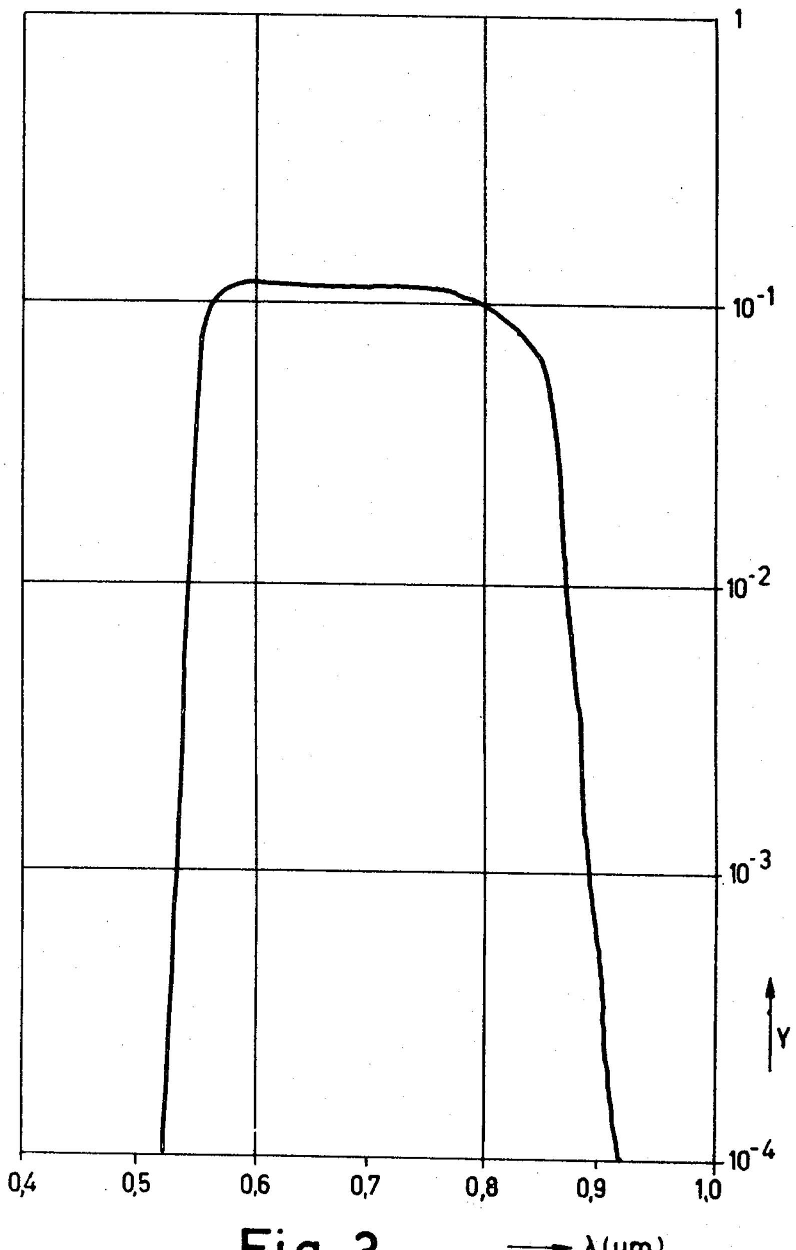

Fig. 3

SEMITRANSPARENT PHOTOCATHODE

The invention relates to a semitransparent photocathode from 3-5 semiconductor compounds having a substrate, an intermediate layer and a p-doped active layer, the energy gap of the p-doped active layer being smaller than that of the p-doped intermediate layer.

A semitransparent or transparent photocathode is to be understood to mean an arrangement in which the light is radiated from one side on a photosensitive layer but the excited electrons are emitted in the vacuum on the other side of the photocathode. Because reproduction problems can easily be solved with transparent photocathodes, they are of particular importance for a number of applications, such as photomultipliers, image converters — in particular such of the "close proximity" type — but also camera tubes of the type of the vidicon with internal amplification.

3–5 semiconductor photocathodes in thick layers in reflection, that is to say when light is radiated on the side of the electron-emitting surface, have higher quantum efficiencies as photocathodes of the multi-alkaliantimonide type hitherto used. The high photoemission in the proximity of the optical band edge of semiconductors with so-called direct energy gap is a result of the negative effective electron affinity at the surface which was achieved first in Cs-covered p^+-conductive GaAs. By coatings in the order of magnitude of monolayers of cesium and oxygen, lower work functions and hence a higher photoemission of p-doped GaAs could be achieved.

Sensitivities of 1,500 to 2,000 μS/lumen have been achieved with such GaAs reflection photocathodes. The wavelength limit of the GaAs photocathode is given by the energy gap of the GaAs of 1.43 eV. By activating coatings with cesium and oxygen or cesium and fluorine, however, p-doped simiconductor compounds having a smaller energy gap up to approximately 1.1 eV. could also be brought in the condition of the effective negative electron affinity as a result of which the wavelength limit of such photocathodes could be shifted above 1 μm in the infrared region. Examples therefore are ternary 3–5 compounds of suitable compositions x such $Ga_xIn_{1-x}As$, $GaAs_xSb_{1-x}$, and also silicon.

The quantum efficiency Y of a 3-5-semiconductor photocathode is determined by surface properties and volume properties, in particular by the diffusion length of the electrons. In the case of a certain material, for example GaAs, the diffusion length L should hence be as large as possible. Besides on material properties and the doping, however, the diffusion length also depends on impurities and in particular on the crystal perfection.

Large diffusion lengths have been achieved only for monocrystalline layers of high perfection and purity. For these reasons, experiments have also failed to use semitransparent layers of GaAs which were polycrystalline and were provided on glass as a photoemitter. GaAs layers which were manufactured by epitaxy from the gaseous phase on sapphire and as a monocrystalline light-permeable substrate did not show the expected high photoemission either.

The photoelectrically active layer should satisfy in particular the two following requirements:

1. The diffusion length of the electrons should be large, preferably larger than the layer thickness of the active layer.

2. The recombination of electrons at the interface of the active layer on the light entrance side results in a decrease of the quantum efficiency and should be avoided.

From these requirements also follow two requirements for a support, on which semitransparent photoemitters of 3–5 compounds of a few μm thickness are to be manufactured:

1. The lattice match of substrate and semiconductor layer should be optimum in order that thin monocrystalline layers with the required electrical properties can be manufactured.

2. The substrate should have a rather large energy gap and be p-conductive in order that at the interface with the layer a reflection of the electrons which diffuse towards the interface on the light entrance side is ensured in the direction of the electron-emitting side of the layer of the photocathode by a barrier in the conductance band.

In order to avoid the said matching difficulties between the active layer and the substrate of a semitransparent photocathode it is already known (German Patent Specification No. 2101941), starting from a 3–5 semiconductor substrate, to achieve the matching to the lattice constant of the active layer in that between the substrate and the active layer an intermediate layer is provided which comprises at least one component of the substrate and the composition of which changes continuously or in steps in the direction of the active layer until it passes into the active layer.

Such a layer is difficult to manufacture and, due to the close relation between substrate, intermediate layer and active layer as regards its composition, does not allow such a selection of the substrate and intermediate layer, respectively, as would be desirable in connection with an optimum sensitivity and/or optical wide band condition of the photocathode.

It is therefore the object of the invention to considerably mitigate the above-described drawbacks of the known photocathodes. According to the invention, this object is achieved by a photocathode of the type described in the preamble which is characterized in that the composition of the intermediate layer is independent of the substrate and the active layer and its lattice constant differs from the lattice constant of the active layer by less than 0.3% and from the grid constant of the substrate up to several per cent. The deviation from the lattice constant of the substrate may be, for example, up to 3 %.

In a photocathode thus designed the lattice mismatch between the substrate and the active layer is compensated for by the sufficiently thick intermediate layer and the manufacture of a monocrystalline active layer of high perfection is thus enabled. By a suitable choice of the lattice parameters of substrate, intermediate layer and active layer, optimum electrical properties can be given to the provided monocrystalline active layer.

In such a photocathode, the intermediate layer may preferably consist of $Al_xGa_{1-x}As$ or $In_xGa_{1-x}P$ and the substrate may consist of GaP, sapphire or spinel, so that a considerable matching to the desired spectral sensitivity can be achieved with high sensitivity.

In particularly suitable photocathodes according to the invention, the substrate consists of GaP, the intermediate layer consists of $Al_xGa_{1-x}As$ with $x \geq 0.8$ and the active layer consists of GaAs.

According to a further embodiment of the invention it is also possible to construct the substrate, after growing the layers, in the form of a ring or frame so that in the active part of the photocathode the intermediate layer and the active layer are self-supporting.

The advantage achievable in particular with the invention is that it is possible to achieve a high quantum efficiency which is substantially independent of wavelength, so a high sensitivity, in a larger wavelength range.

The invention will be described in greater detail hereinafter with reference to the accompanying drawings of a few embodiments.

FIG. 1 shows the construction of a photocathode according to a first embodiment,

FIG. 1*a* shows another embodiment of the invention.

FIG. 2 shows the energy band diagram associated with the photocathode shown in FIG. 1,

FIG. 3 shows the spectral sensitivity (quantum efficiency) Y of the photocathode shown in FIG. 1.

FIG. 1 shows diagrammatically a first embodiment of a semitransparent photocathode according to the invention. An approximately 5–15 μm thick, weakly p-doped $Al_xGa_{1-x}As$ layer 2 is provided on an approximately 150 μm thick GaP substrate 1, wherein $x > 0.8$. A 2–4μm thick p^+ doped GaAs layer 3 is provided thereon according to the method of the multi-layer epitaxy. The lattice constant a_0 of the substrate 1 is 5.45 A, that of the layer 2 is 5.662 A and that of the layer 3 is 5.6535 A. The layer 3 is covered at its surface with a monolayer 4 of cesium and oxygen.

FIG. 1*a*shows another embodiment in which the substrate 11 is in the form of a ring or frame, the central portion of which has been etched away. Substrate 11 supports an intermediate layer 12 approx. 5–15 μm thick and consists of Al_xGa_{1-x} As on a substrate of GaP. Over the intermediate layer a layer 13 of p^+ GaAs is provided on which a monolayer 14 of cesium and oxygen is provided as in the previous embodiment.

The energy band diagram of this photocathode shown in FIG. 2 illustrates that due to the barrier at the (p)-GaAs-(p)-$Al_xGa_{1-x}As$ interface the recombination of electrons can be neglected. The reflection of electrons at said barrier is shown diagrammatically for the electron produced from the excitation process 10. Since according to the invention the lattice constants of the active layer and the intermediate layer deviate from each other by less than 0.3%, the interface between them shows substantially no recombination centres.

The photocathode shown diagrammatically in FIG. 1 can be manufactured according to known methods, for example, by means of the multilayer epitaxy from the liquid phase.

The use of several melts in a boat is of decisive importance for the manufacture of a good $Al_xGa_{1-x}As$-GaAs interface. Starting material is a (111) p-oriented (deviation < 6'), chemically polished GaP substrate (6 × 14mm). Other orientations, for example (100), are also possible.

The composition of the melt for the $Al_xGa_{1-x}As$ epitaxy was: 1.6765 g Ga; 0.06 g GaAs; 0.045 g Al and 0.0169 g Zn. The epitaxy of the $Al_xGa_{1-x}As$ layer of 12μm thickness occurs upon cooling the melt from 934°C to 836°C at a cooling rate of 3.3°C per minute, duration 29 minutes and 20 seconds. A rapid change during the second melt is necessary so as to avoid an oxidation of the $Al_xGa_{1-x}As$-layer (with $x > 0.8$) also during the flow of purified hydrogen. The GaAs epitaxy from the second melt of 2.032 g Ga, 0.1744 g GaAs and 0.0184 g Zn occurred upon cooling from 836°C to 834°C in approximately 2 minutes, during which a 3 μm thick GaAs layer grew. After cooling in the epitaxy tube under hydrogen, the remaining gallium adhering to the edges of the layer was removed with a dimethylformamide-$HgCl_2$ solution and the resulting calomel was wiped off with plugs of wadding soaked in acetone. The structure was then cleaned in trichloroethylene and etched in cold 3 H_2SO_4 : 2 H_2O_2 : 2 H_2O for 20 seconds, the thickness of the GaAs layer being reduced to approximately 2 μm. After incorporation in a vacuum apparatus and heating same, the photocathode was cleaned in the usual manner (20 minutes at 580°C) from surface oxides by heating and was activated with Cs and oxygen.

FIG. 3 shows the quantum efficiency Y (electron-/impinging photon) measured in transmission of a photocathode manufactured in this manner.

A sensitivity to white light (tungsten radiation of the colour temperature 2,800°K) of 600μA/lumen was found. The comparison of the measured quantum efficiency with calculated curves shows that a diffusion length L in the GaAs layer of $\geqslant 1.5$ μm is achieved and that the interface recombination rate is negligible.

An SiO_2 layer on the GaP substrate to reduce the reflection on the light entrance side can additionally produce an amplification of the light excitation in the GaAs photoemission layer at least for a limited wavelength range.

In order to make a photocathode according to the invention independent of the optical properties of the substrate, according to a further embodiment the intermediate layer and the active layer may be provided, preferably also by epitaxy from the liquid phase, on a GaAs substrate, for example, in the following succession of layers: 150μm GaAs – 4 μm (p) $Al_xGa_{1-x}As$ – 4μm (p) GaAs. After covering the (p) GaAs layer with apiezon lacquer, the GaAs layer could be detached, up to an edge which is to remain, by selective etching with 5 H_2O_2, 1 NH_4OH, by means of an etchant which does not attack $Al_xGa_{1-x}As$ ($x > 0.5$). After removing the coating layer and providing an SiO_2 layer on the $Al_xGa_{1-x}As$, a self-supporting layer in the sequence SiO_2, $Al_xGa_{1-x}As$ and GaAs remains in the inner part, the GaAs layer having the properties required for a high photoemission in transmission.

Transparent photocathodes according to the invention may furthermore be realized in that substrates of sapphire or spinel are used as the starting material on which the intermediate layer and the active layer are depostied by epitaxy from the liquid phase or gaseous phase.

For example, starting material may be a sapphire substrate on which a monocrystalline 5–20μm thick p-doped AlAs layer is produced as an intermediate layer by epitaxy from the gaseous phase with trimethylaluminum and arsenic hydrogen. The subsequent provision of the active GaAs layer may succeed immediately by switching to trimethylgallium.

When the starting material is a substrate from a spinel which is transparent throughout the sensitivity range, preferably a Mg-Ga spinel, the intermediate layer from $Al_xGa_{1-x}As$ adapted to the above layer of

GaAs, with $x > 0.8$ as described above, may be provided by epitaxy from the liquid phase.

For photoemitters with a ternary compound, such as (Ga, In) As or In (As, P) as an active layer, are to be considered, in addition to GaP, also mixed spinel systems such as $Mg(In_xGa_{1-x})_2O_4$ as a substrate on which a photocathode having a wide optical window can be manufactured with an intermediate layer matched to the grid constant.

As intermediate layers are to be used ternary semiconductor compounds having the same grid parameters as the active layer but with a larger energy gap in the interest of a wide optical transparency. Examples are: for $Ga_{0.85}In_{0.15}As$ with an energy gap of 1.18 Ev the matching of the grid constant can be achieved by an intermediate layer of $Ga_{0.6}In_{0.4}P$ with an energy gap of 1.9 eV, or by an intermediate layer of $Al_{0.85}In_{0.15}As$ with an energy gap of 2.1 eV or also by an intermediate layer of $Al_{0.5}Ga_{0.1}In_{0.4}P$ with an energy gap of 2.5 eV.

What is claimed is:

1. A semitransparent photocathode of III-V semiconductor compounds having a substrate, an intermediate layer and an active layer, the energy gap of the active layer being smaller than that of the intermediate layer and the active and the intermediate layer being p-doped, the intermediate layer having a composition having elements which differ from those of the substrate and the active layer and a lattice constant differing from the lattice constant of the active layer by less than 0.3% and from the lattice constant of the substrate up to several per cent.

2. A photocathode as claimed in claim **1,** wherein the intermediate layer consists of $Al_xGa_{1-x}As$.

3. A photocathode as claimed in claim **1,** wherein the intermediate layer consists of $In_xGa_{1-x}P$.

4. A photocathode as claimed in claim **1,** wherein the intermediate layer consists of $Al_xIn_{1-x}As$.

5. A photocathode as claimed in claim **1,** wherein the intermediate layer consists of $Al_xGa_yIn_{1-x-y}P$.

6. a photocathode as claimed in claim **1,** wherein the substrate consists of GaP.

7. A photocathode as claimed in claim **1,** wherein the substrate consists of sapphire.

8. A photocathode as claimed in claim **1,** wherein the substrate consists of spinel.

9. A photocathode as claimed in claim **8,** wherein the substrate consists of Mg-Ga spinel.

10. A photocathode as claimed in claim **9,** wherein the substrate consists of a mixed spinel system such as $Mg(In_xGa_{1-x})_2O_4$.

11. A photocathode as claimed in claim **1,** wherein the active layer consists of a material selected from the group consisting of GaAs, (Ga, In) As and In (As, P).

12. A photocathode as claimed in claim **1,** wherein the substrate consists of GaP, the intermediate layer consists of $Al_xGa_{1-x}As$ with $x > 0.8$ and the active layer consists of GaAs.

13. A photocathode as claimed in claim **1,** wherein the substrate is a frame, consists of the same material as the active layer, and the intermediate layer and the active layer in the operative part of the photocathode are self-supporting.

14. A photocathode as claimed in claim **1,** wherein the substrate consists of sapphire, the intermediate layer consists of AlAs, and the active layer consists of GaAs.

15. A photocathode as claimed in claim **1,** wherein the substrate consists of a spinel, the intermediate layer consists of $Al_xGa_{1-x}As$ with $x > 0.8$, and the active layer consists of GaAs.

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