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Kurtin

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[54] **INFRARED PHOTOCATHODE**

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[52] **U.S. Cl.** **357/30,** 317/52, 357/15, 357/50

[51] **Int. Cl.** **H01l 19/00**

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

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[57] **ABSTRACT**

An infrared photoemitter and process for fabricating same wherein a thin metal layer is sandwiched in a composite structure between a suitable photoabsorptive semiconductive layer and a low work function insulating layer. The semiconductive layer serves as a photon absorber and photoelection source for the device. The insulating layer is chosen for its low work function. The metal interlayer eliminates the heterojunction which in its absence would exist between the semiconductive and insulating layers and thereby eliminates the restriction that such heterojunctions impose on the efficiency and wavelength response of prior art composition photoemitters.

7 Claims, 5 Drawing Figures

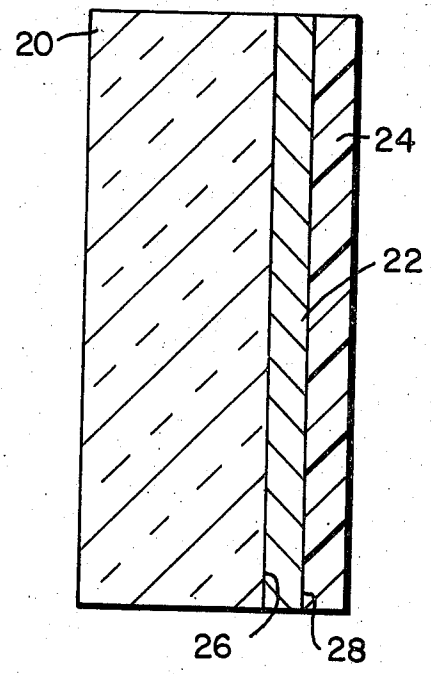


Fig. 1.
(PRIOR ART)

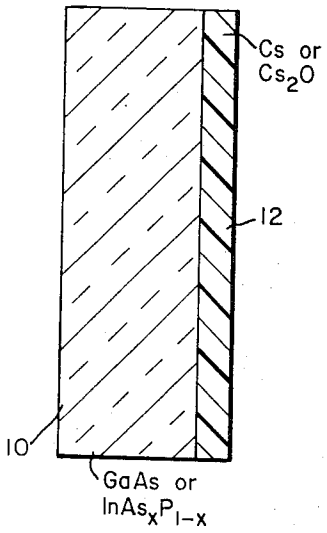


Fig. 2.

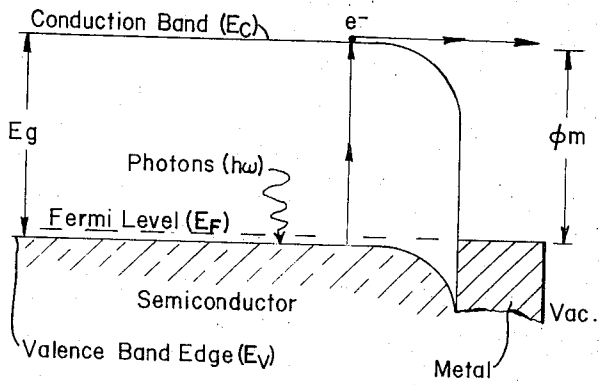


Fig. 3.

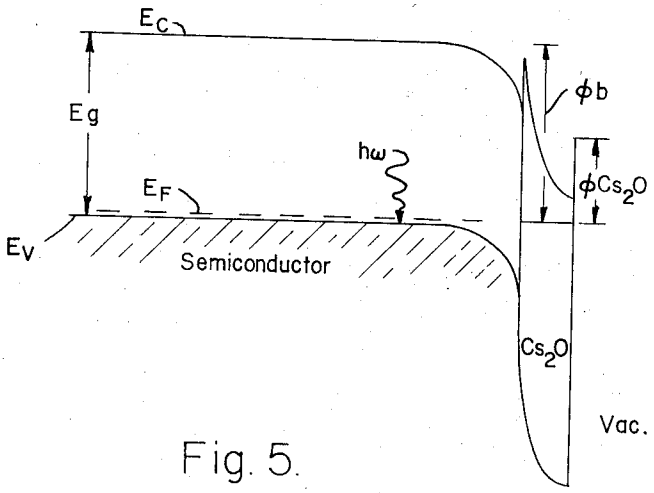


Fig. 4.

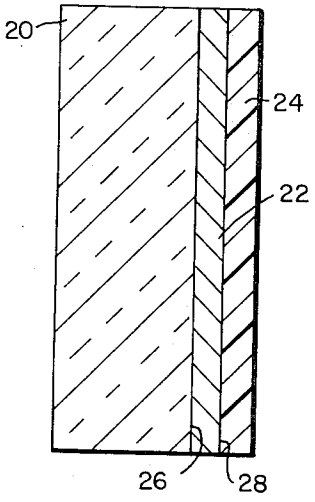
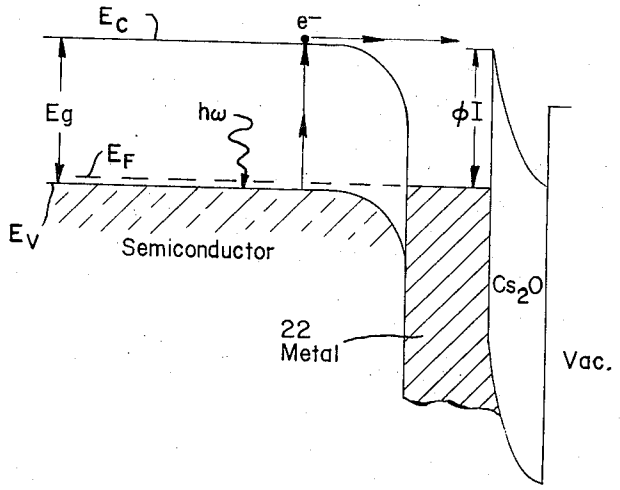


Fig. 5.



INFRARED PHOTOCATHODE

FIELD OF THE INVENTION

This invention relates generally to photoelectric emission from semiconductive structures and more particularly to a novel infrared responsive photocathode with improved quantum efficiency and wavelength response extended into the infrared region of the electromagnetic spectrum.

BACKGROUND

In recent years, there has been great interest in extending the response of photoemissive surfaces into the infrared region of the electromagnetic spectrum. This interest has been heightened by the advent of strong laser sources of infrared radiation, particularly at 1.06 microns wavelength. Thus, the importance of extending photocathode (and hence image converter) performance into the long wavelength portion of the near infrared region of the electromagnetic spectrum is manifest, particularly for surveillance, communications and tracking applications.

PRIOR ART

The best extant technology for providing infrared responsive photocathodes has been reported recently by James et. al.: *Varian Central Research Memorandum CRM*-248, Aug. 13, 1970. This memorandum describes a cesium oxide (Cs_2O)-activated indium arsenide phosphide ($InAs_xP_{1-x}$) photocathode which has a quantum efficiency of 1.5 percent at 1.06 microns wavelength. The performance of this photocathode, which is explainable in terms of the concept of negative electron affinity, considerably surpasses that of any other previously known photocathodes. The concept of negative electron affinity was first demonstrated by Scheer and Van Laar and reported in the *Solid State Communications*, Vol. 3, pp 189, 1965. Negative electron affinity is a term used to identify an unusual spatial distribution of energy states in a solid (presently obtainable only in complex, carefully fabricated, multi-material thin film structures) such that an electron resident at or near the bottom of the conduction band within a solid has an energy greater than that required to escape from the proximate surface of that solid. Scheer and Van Laar first fabricated a structure with negative electron affinity by evaporating a thin film of cesium on a clean, vacuum cleaned surface of a heavily doped p-type gallium arsenide crystal. This structure proved to have a photothreshold at 1.4eV, the minimum band gap energy of GaAs, consistent with the negative electron affinity concept. The work function of the extremely thin (a few monolayers) film of Cs on GaAs was independently measured, in the same series of experiments, and found to be approximately 1.4eV, strongly indicating that negative electron affinity was a viable explanation of the observed 1.4eV photothreshold.

Soon after Scheer and Van Laar reported their work as noted above, it was discovered that performance of the Cs-GaAs photocathode could be improved if some oxygen was admixed with the cesium in the surface activation process to form a Cs_2O, rather than an elemental Cs, surface layer on the GaAs. The work function of Cs_2O layers was thereupon measured and found to be approximately 0.6eV, giving rise to the hope of efficient photoemission out to wavelengths of two microns

($\lambda \approx 2\mu$). Of course, to obtain a structure consistent with the negative electron affinity concept in which significant photoemission could be observed out to such long wavelengths, it would be necessary to deposit a Cs_2O layer on a heavily p-type semiconductor substrate having an energy gap $\gtrsim$ 0.2eV. However, contrary to expectations, when such structures were fabricated, it was discovered that yet another energy barrier apparently contolled the photoemissive threshold energy of the structure. This barrier was identified to be the heterojunction barrier energy at the semiconductor-Cs_2O interface. Unfortunately, the heterojunction barrier energy of semiconductor-Cs_2O structures has been found to be function of the energy gap of the semiconductor material, and this characteristic imposes a serious limitation on the utility of such structures as photocathodes responsive to near infrared wavelengths.

An example of this limitation has been seen in the fabrication of the $InAs_xP_{1-x}$-Cs_2O photocathode which was reported in the above-mentioned Varian work. In this structure, one might expect that an increase in the arsenic concentration would extend the photothreshold into the infrared since the bang gap of $InAs_xP_{1-x}$ decreases with increasing arsenic concentration. However it has been found, as mentioned generally above, that such an increase in arsenic concentration also has the reverse and compensating effect of increasing the height of the heterojunction barrier energy which must be exceeded by the band gap, E_g, of the semiconductor in order for the device to exhibit negative electron affinity. Consequently, optimum long wavelength photo response is obtained only for a small range of composition, in this case such that $1.17 < E_g < 1.34$eV. Thus, the inherent heterojunction energy barrier within the above Varian photocathode seriously limits its efficiency and wavelength threshold.

THE INVENTION

The general purpose of the present invention is to provide an infrared photocathode whose vavelength response has been extended beyond that of the above-identified prior art photocathodes. To attain this purpose, a composite photocathode structure is provided wherein a semiconductive layer and a low work function Cs_2O insulating film are separated by, and are in intimate contact with, a thin layer of metal to form a novel semiconductor-metal-insulator (SMI) photocathode. There is no heterojunction barrier in this structure; instead there are two back-to-back Schottky barriers, one of which is between semiconductor and metal and the other of which is between metal and Cs_2O insulating film. In this novel photocathode structure, the primary threshold-determining energy barrier is the metal-insulator interface barrier, which barrier can be made much lower than the heterojunction barrier of prior semiconductor-Cs_2O photocathodes. The semiconductive layer of this photocathode structure serves as the photon absorber and photoelectron source of the device. Electrons which are promoted to the conduction band of the semiconductor in response to incident photon energy must pass through the metal interlayer. And they must do so without losing sufficient energy to be unable to surmount the metal-Cs_2O barrier if they are to pass through the low work function Cs_2O layer and escape from the structure. As will be deomonstrated below, this condition can be met. Since the metal-Cs_2O energy barrier can also be made considerably

less than the heterojunction energy barrier of prior art photocathode structures, the efficiency and wavelength response of the present photocathode structure is an improvement over the prior art.

An object of this invention is to provide a novel photocathode structure of the type described exhibiting improved photo-electrical performance.

Another object of this invention is to provide a photocathode of the type described having an increased quantum efficiency and a wavelength response improved relative to prior state-of-the-art IR photocathodes.

Another object is to provide a photocathode of the type described whose wavelength response is not limited by a heterojunction energy barrier.

A still further object is to provide a photocathode whose photoemissive yield in response to incident radiation of 1.06 microns wavelength exceeds that of previously known photocathodes.

DRAWING

FIG. 1 is a diagrammatic cross-section of the composite structure of a prior art photocathode;

FIG. 2 is an energy band diagram of a semiconductor-metal photocathode structure of the prior art;

FIG. 3 is an energy band diagram of a semiconductor-insulator photocathode structure of the prior art;

FIG. 4 is a diagrammatic cross-section view of the composite photocathode structure fabricated according to the present invention; and

FIG. 5 is an energy band diagram corresponding to the operation of the photocathode in FIG. 4.

Referring now to FIG. 1, there is shown a prior art semiconductor-metal photocathode structure of the type disclosed in the above-mentioned Scheer and Van Laar publication. This structure includes a suitable photon absorptive semiconductive material **10**, such as gallium arsenide or indium arsenide phosphide, upon which is deposited a low work function metal or metal oxide layer **12**. In the above Scheer and Van Laar publication, the activating layer **12** is cesium, C_s and the semiconductive substrate **10** is a heavily doped P-type arsenide layer upon which the Cs was deposited by evaporation.

The energy band representation of this photocathode structure is shown in FIG. 2. In FIG. 2, if the energy gap, E_g, of the semiconductor exceeds the work function ϕ_M of the metal, then negative electron affinity is said to exist. That is, a photon whose energy exceeds E_g is capable of promoting an electron resident in the valance band of the semiconductor **10** to the conduction band thereof where it can diffuse to the surface. If this electron loses sufficiently little energy in so diffusing, it will be able to surmount the surface work function ϕ_M, thereby escaping into vacuum. During diffusion, scattering mechanisms will cause this electron to lose energy and hence may prevent it from reaching the surface of the metal **12** with sufficient energy to escape. Such scattering, however, only reduces electron yield, but does not materially affect the photothreshold emission level of the device. Hence, external photoelectron yield will increase with an increasing incident photon energy above threshold Since the semiconductor material **10** serves as a photoelectron generation region, a direct bandgap semiconductive material with $E_g \geq \phi_M$ is desired to assure that strong photon absorption occurs near the surface.

The lowest known metallic work function is that of cesium, C_s, and the work function, ϕ_M, of bulk metallic cesium is approximately equal to 2eV. Gallium arsenide is a direct bandgap semiconductor having an energy gap, E_g, $\approx$ 1.4eV. However, when extremely thin monolayer films of C_s are applied to clean crystalline GaAs, the work function of the resulting surface has been measured to be $\approx$ 1.4eV. The Cs-GaAs photoemissive surface has a photoemission threshold $\approx$ 1.4eV, (which corresponds to a wavelength of 0.9μ); in this case the photocathode illustrated in FIGS. 1 and 2 is the Scheer-Van Laar example of a negative electron affinity photocathode.

As previously mentioned, after the original metal-semiconductor photocathode structure was first successfully operated by Scheer and Van Laar, it was discovered that the performance of this photocathode could be substantially improved is some oxygen was admixed with cesium in the activation process to form a Cs_2O surface layer on the GaAs. The work function of Cs_2O layers has been measured to be approximately 0.6eV. The band energy diagram for the semiconductor-cesium oxide photocathode structure is illustrated in FIG. 3 wherein it will be noted that the heterojunction barrier height ϕ_b of the semiconductor Cs_2O interface, and not the relatively low work function Cs_2O, determines the threshold energy of Cs_2O activated photocathodes. In the above-mentioned $InAs_xP_{1-x}$-Cs_2O photocathode, and of which FIG. 3 is also representative, optimum photothreshold in the near infrared is obtained for only a small range of composition (i.e., x) such that E_g of $InAs_xP_{1-x}$ is greater than 1.17eV and less than 1.34eV. For $E_g \approx$ 1.19eV, a quantum efficienty of 1.5 percent at 1.06 has been observed.

The precise applicability of the energy band model shown schematically in FIG. 3 and representing a Cs_2O activated photocathode is questionable because of the extremely thin layers (v 20 A) of Cs_2O required for optimum performance of this device. Nevertheless, the diagram of FIG. 3 will be useful in the discussion of this prior art semiconductor-Cs_2O photocathode relative to the present invention and in the comparison of this energy band diagram with that of FIG. 5.

Referring now to FIG. 4, the photocathode structure embodying the invention includes a suitable photon absorptive semiconductive material **20**, such as indium arsenide phosphide, upon which is deposited a thin layer **22** of metal. In a preferred embodiment of the invention, the metal **22** is silver which is deposited by a conventional metal evaporation process. In this process, a thin film of silver of approximately 20 Angstroms in thickness is deposited to form a first, Schottky barrier junction **26** at the interface **26** between the semiconductor **20** and the metal **22**.

Next, using a conventional metal evaporation system for depositing Cs and by introducing a controlled amount of oxygen into the evaporation system, a thin layer of cesium oxide **24** is deposited as shown on the exposed surface of the metal layer **22** to form a second Schottky barrier junction **28** at the metal-metal oxide interface.

The essence of the present invention is the decoupling or elimination of the dependence of photocathode performance on the physical relationship between a heterojunction energy barrier (none present herein) and the bandgap energy of the semiconductive photon absorptive material. This is achieved by providing the

structure in FIG. 4 which possesses no heterojunction barriers; instead the structure utilizes two back-to-back Schottky barriers **26** and **28** in the semiconductor-metal-insulator (SMT) structure shown. Thus, in the photoemissive operation of this structure, an electron e— which is promoted to the conduction band of the semiconductor **20** and diffuses toward the surface of the semiconductor **20** encounters scattering losses similar to those experienced by photogenerated electrons e— in FIGS. **1** and **2** above, plug the addition of the transmission loss which arises from the presence of the intermediate metallic layer **22.** However, there are many metals in which the mean free path for hot electrons of 1 eV energy is at least 500 Angstroms. Thus, if the metal layer **22** in FIG. **4** is on the order of 100 Angstroms in thickness, this layer will diminish the electron yield of the device only very slightly. Thus, by properly choosing the metal **22** and the insulator **24,** and by matching these layers to a suitable semicondcutive material **20** with a desired bandgap energy, a photocathode may be tailored to a given photocathode application.

The novel photocathode shown in FIG. **4** can be operated in either the opaque or semitransparent mode. In the opaque mode, the incident radiation passes through the metallic layer **22** before entering the direct bandgap semiconductive substrate **20** in which efficient photoexcitation occurs. Hence, in comparison to the heterojunction structure of FIG. **1,** additional reflection occurs at the metal-Cs_2O interface **28,** and some optical absorption will also occur within the metallic film **22.** Of these two effects, reflection is more significant. This reflection can substantially reduce electron yield per incident photon for metal films in excess of 75 Angstroms thick. Of course yield per absorbed photon remains high. Therefore, in order to optimize its external quantum efficiency, it is preferred that an SMI photocathode according to FIG. **4** be constructed with as thin an interfacial metallic layer **22** as is consistent with the desired electrical properties of the structure, thereby diminishing the reflection loss at the intrface **28.**

For operation in the semitransparent mode, a graded bandgap material **20** may be epitaxially grown upon a single crystal substrate (not shown) whose bandgap energy is larger than the energy of the shortest radiation wavelength of interest. Photons enter the semiconductive layer **20** through the wide bandgap substrate (not shown), are absorbed in the graded bandgap layer **20,** and the resulting photoelectrons diffuse through the metal and metal oxide layers **22** and **24** as in the opaque case above. The thickness of the metallic film **22** in the SMI structure is relatively non-critical for this mode of operation since, as previously discussed, the means free path for the 1 eV electrons exceeds 500 Angstroms in most metals.

Referring now to FIG. **5,** the energy band shown for the SMI structure in FIG. **4** embodying the invention may be readily compared to the energy bands in either FIGS. **2** or **3** above. It is seen in FIG. **5** that an electron e—, upon receiving sufficient incident photon energy ($>E_g$) to be promoted into the conduction band of semiconductor layer **20,** must now overcome both the transmission loss associated with the metal layer **22** and the work function ϕ_1 of the Schottky barrier **28** before passing in vacuum. For heavily doped-type semiconductive material **20,** the Fermi level is essentially at the valance band edge, and this means that the longest threshold which can be produced by the photocathode embodying the present invention occurs where: $E_g \approx \phi_1$.

A specific embodiment of the invention illustrated in FIG. **4** is a $InAs_xP_{1-x}$-Ag-Cs_2O photocathode. Since the Ag-Cs_2O barrier energy has been measured to be approximately 1.0eV in experiments preformed on bulk silver, this embodiment should exhibit a photothreshold at a wavelength not shorter than 1.2 microns; and this structure should yield at least an order of magnitude increase in quantum efficiency over the In_xP_{1-x}-Cs_2O photocathode at 1.06 microns wavelength.

In fabricating this specific $InAs_xP_{1-x}$-Ag-Cs'O photocathode embodiment, the Ag layer may be formed by vapor depositing Ag on an $InAs_xP_{1-x}$ substrate cooled to a temperature of approximately −50°C and using a background vapor pressure of between 5×10^{-9} and 2×10^{-7} Torr. The source purity for Ag should be better than 99.999 percent, and for the above conditions, Ag deposition rates on the order of 2–5 A/sec may be appropriate. For a further discussion of the preparation of thin Ag films, reference may be made to an article entitled, "Slow-Electron Mean Free Paths in Aluminum, Silver, and Gold" by H. Kanter in *Physical Review B*, Vol. 1, No. 2, 15 Jan. 1970.

After the Ag layer has been deposited at a chosen thickness between about 25–500A, the $InAs_xP_{1-x}$-Ag sub-structure is ready for deposition of a CS_2O layer by the controlled oxidation of metallic Cs. That is, cesium may be vacuum deposited on the surface of the Ag layer while simultaneously introducing oxygen into the vacuum deposition system to deposit Cs_2O to a chosen thickness between 5 and 200A. For a further discussion of the deposition of Cs_2O films, reference may be made to an article entitled, "3–5 Compound Photocathodes: A New Family of Photoemitters with Greatly Improved Performance" by Ronald L. Bell and Willian E. Spicer in Proceedings of the *IEEE*, Vol. 58, No. 11, Nov. 1970.

Modifications may be made in the above-described photocathode structure and related process embodying the invention without departing from the true scope thereof. For example, in the foreseeable future, semiconductive, metal and metal oxide materials may become available which will enhance the performance of the SMI structure described herein. Therefore, the substitution of materials not disclosed herein for those specifically described above and claimed herein, is clearly within the broad scope of the present invention.

What is claimed is:

1. A photoemissive structure for emitting electrons in response to incident photon energy, including:

a. a first layer of P-type material of a mixed III–V semiconductive compound suitable for absorbing photons and responding thereto by promoting electrons to its conduction band;

b. a second layer of silver in intimate contact with said first layer of semiconductive material and defining at the metal-semiconductor interface a first Schottky barrier junction; and

c. a third layer of suitable low work function material in intimate contact with said silver layer and forming therewith a second Schottky barrier junction, whereby the threshold determining energy barrier of said structure which must be exceeded by the bandgap energy of the semiconductive material

controlled primarily by the energy barrier established betweeen the second and third layers at said second Schottky barrier junction.

2. The structure defined in claim **1** wherein:

a. said first layer is indium arsenide phosphide;

b. said second layer is silver; and

c. said third layer is cesium oxide, Cs_2O.

3. The structure defined in claim **2** wherein:

a. said silver layer is between about 25 and 500 Angstroms thick; and

b. said third Cs_2O layer is between about 5 and 200 Angstroms thick.

4. A photoemissive structure for emitting electrons in response to incident photon energy, comprising:

a. a first layer of indium arsenide phosphide suitable for absorbing photon radiation and responding thereto to promote electrons to its conduction band;

b. a second layer of silver in intimate contact with said first layer of indium arsenide phosphide and defining a first Schottky barrier junction; and

c. a third layer of cesium oxide in intimate contact with said silver layer and forming therewith a second Schottky barrier junction, whereby the photothreshold determining energy barrier of said structure which must be exceeded by the band gap energy of the indium arsenide phosphide to form a negative electron affinity structure is determined primarily by the energy barrier established between said second and third layers at said second Schottky barrier junction.

5. The structure defined in claim **4** wherein:

a. said silver layer is between about 25 and 500 Angstroms in thickness; and

b. said cesium oxide layer is between about 5 and 200 Angstroms in thickness.

6. The structure of claim **4** wherein said indium arsenide phosphide material has a graded bandgap.

7. The structure of claim **5** wherein said indium arsenide phosphide material has a graded bandgap.

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