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[54] **METHOD OF PRODUCING DYNODE STRUCTURES**

[75] Inventors: **Jonathan Ross Howorth,** Maldon; **Erik Werner Ludwig Trawny,** Colchester, both of England

[73] Assignee: **English Electric Valve Company Limited,** Chelmsford, England

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[51] **Int. Cl.²** .. **H01L 7/44;** H01L 21/00; C23F 1/00

[58] **Field of Search** 148/1.5, 187; 156/2

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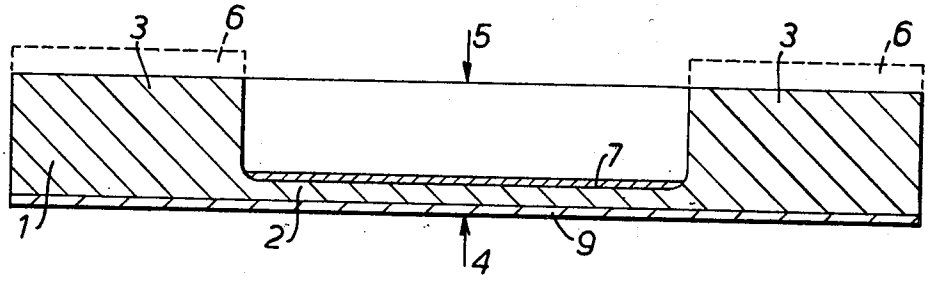
Primary Examiner—Peter D. Rosenberg

Attorney, Agent, or Firm—Baldwin, Wight & Brown

[57] **ABSTRACT**

A dynode structure which emits electrons in response to incident electrons or incident light consists of a thin layer of gallium-arsenide which is formed integrally with a surrounding frame of gallium-arsenide. The structure is robust and straight forward to produce.

15 Claims, 1 Drawing Figure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METHOD OF PRODUCING DYNODE STRUCTURES

This invention relates to dynode structures and to methods of producing them and to electron tubes containing such structures. By the expression "dynode structure" as used herein is meant a structure which emits electrons in response to an incident stimulus, which stimulus would usually be incident electrons or incident light. The term dynode structure is therefore intended to include both photocathodes and electron multipliers.

The invention is concerned specifically with a dynode structure having gallium-arsenide as its active material. The use of gallium-arsenide for this purpose is known and generally is preferred to other materials as it exhibits satisfactory characteristics; for example it exhibits a sufficiently long minority carrier lifetime coupled with a sufficiently low "dark current," the dark current being the rate of electron emission in the absence of any incident stimulus. For satisfactory operation of a dynode structure of this kind it is essential that the active portion of the structure from which electrons are emitted should be very thin and of fairly uniform thickness. In the past it has proved difficult to produce such a dynode structure because the aforesaid portion of the structure is far too thin and delicate to be handled and commonly the production of such a dynode structure has been complicated by the need to mount the structure on some kind of strong support.

The present invention seeks to provide a method for producing a dynode structure which reduces this difficulty.

According to one aspect of this invention a method of producing a dynode structure having a thin active area of gallium-arsenide includes the step of etching a relatively thick body of gallium-arsenide to produce the relatively thin active area surrounded by a relatively thick frame integral with the active area.

According to a second aspect of the invention a dynode structure includes a thin gallium-arsenide active area surrounded by a relatively thick frame integral therewith.

According to a third aspect of the invention an electron tube includes a dynode structure having a thin gallium-arsenide active area surrounded by a relatively thick frame integral therewith. Typically the active area or membrane should be approximately 5 μm thick. Although there is no precise limit that can be put upon the original thickness of the relatively massive body of gallium-arsenide since this is dictated only by considerations such as convenience of handling and the provision of sufficient strength and rigidity in the frame of the completed dynode structure. A thickness of the order of 100 μm has been found experimentally to produce a satisfactory structure with a membrane thickness of 5 μm and a circular area of about 2 cms diameter. It will thus be appreciated that with reference to these figures (which are given by way of example) a thickness of 95 μm of gallium-arsenide is etched away over the said region to leave a membrane of only 5 μm thick. It is fairly important to make a membrane of uniform thickness, and preferably this is achieved by masking those areas of the body of gallium-arsenide which are not to be etched, placing the whole body in a liquid etchant and rotating the body whilst etching takes place.

It has been found that uniformity of etch rate (resulting in a membrane having improved uniformity of thickness) may be obtained by inclining the body of gallium-arsenide during etching and rotating it fairly slowly whilst the area of the body to be etched is totally submerged in the etchant. A convenient speed of rotation has been found in practice to be 30 r.p.m.

The etchant should be chosen to give a slow rate of etch. A fast rate of etch results in a less uniform thickness of the membrane being produced. Typically a slow rate of etch is considered to be one in the region of 1 μm to 2 μm per minute, but significant deviations from this may be acceptable in some cases.

In order to improve the operational characteristics of the dynode structure the surface from which electrons are emitted is usually and preferably coated with a thin layer of a substance which serves to reduce the effective work function of the surface, (i.e. which produces negative electron affinity). The substance preferably is a caesium compound for example caesium oxide.

During operation of the dynode electrons are emitted from one face of the membrane, in response to an incident stimulus, such as incident electrons or light, received by the other face of the membrane. This other face is preferably provided with a thin surface layer which causes the surface to exhibit an increased work-function (i.e. positive electron affinity) as compared with the untreated body of gallium-arsenide. This is conveniently achieved by rendering the surface P+ by suitable doping. The P+ surface layer need be no more than ½ μm to 1 μm thick. Suitable dopants for this purpose are for example, zinc, silicon or germanium.

The invention is further described, by way of example, with reference to the accompanying drawing which illustrates in section a dynode structure in accordance with the present invention.

The FIGURE illustrates a compleded dynode structure composed of a body **1** of gallium-arsenide, the body consisting of a thin membrane or active area portion **2**, surrounded by and integral with a relatively thick annular frame portion **3**.

The dynode structure is produced from a body of gallium-arsenide having originally two opposed parallel faces **4** and **5**, spaced apart by 100 μm. A wax mask **6** indicated by the dotted line is deposited on to face **5** and the whole of face **4** coated with a layer of wax (not shown). The edge of the body may be covered by wax or left unprotected if the side etching which will result is unimportant. The whole body **1** is then immersed in a bath of etchant. The etchant consists 3 parts by volume sulfuric acid, **1** part by volume hydrogen peroxide and **1** part by volume de-mineralised water. This etchant when used at a temperature of 25°C gives an etch rate of approximately 1 μm to 2 μm per minute. The wax used for masking must, of course, be resistant to the etchant. The choice of such a wax presents no difficulty since waxes are widely used in etching processes and their properties are well known.

The body **1** is totally submerged in the bath of etchant and mounted so as to be inclined slightly to the vertical and rotated at a speed of 30 r.p.m. When the membrane **2** is of the required thickness (typically 5 μm) the body **1** is removed from the etchant washed and the wax removed. A thin layer of caesium oxide **7** is then produced on the inner surface of the membrane **4** by any suitable method known *per se*. This layer of caesium oxide should be much thinner than the mem-

brane **4.** The presence of the caesium oxide greatly reduces the work function of the surface and enhances the emission of electrons therefrom.

The surface **4** of the body **1** is provided with a thin P+ layer **9.** This layer is conveniently produced by doping the gallium-arsenide with zinc. Typically whereas the body of gallium-arsenide contains between 10^{16} and 5×10^{18} acceptors per c.c. the P+ layer contains 10^{20} acceptors per c.c. Although the boundary between the body and the P+ layer will in practice be ill-defined, the approximate thickness of the P+ layer is of the order of ½ μm to 1 μm. For clarity the P+ layer is illustrated as being formed externally to the body of gallium-arsenide but it will be appreciated that in fact the doping process merely modifies the existing surface layer of the body of gallium-arsenide.

In the drawing the vertical dimensions have been greatly expanded relative to the horizontal dimensions for ease of illustration.

As an alternative to the above described methods it is possible to dispense with the layer of wax covering the surface **4,** and consequently to uniformly etch the whole of this surface whilst the specified region of the surface **5** is being etched.

In an electron tube the dynode structure will be mounted with at least the caesium oxide surface in a vacuum and the face **4** subjected to an incident stimulus. The incident stimulus consists usually of either electrons or light. In the former of these cases the whole structure, will of course, be in the electron tube. In either case secondary electrons are generated within the body of the gallium-arsenide, and secondary electrons travelling towards the layer of caesium oxide are emitted because of the effect of the reduced work-function of the surface. Conversely secondary electrons travelling towards the P+ layer are inhibited from leaving that surface because of the increased work-function resulting from the presence of this layer.

Instead of the etchant described above an etchant consisting of bromine dissolved in methanol in the ratio of 2 parts by volume to 100 parts by volume respectively could be used.

Also, silicon or germanium could be used as the P+ deposits instead of zinc.

We claim:

1. The method of producing a dynode structure which comprises the steps of:

a. providing a slab of gallium-arsenide having flat, parallel opposite side surfaces and a predetermined large thickness;

b. preferentially etching a restricted region of said slab within the boundaries thereof to reduce the thickness of such region to a substantially uniform value sufficiently thin as to permit emission of secondary electrons at one side surface of said region in response to incident stimulus at the other side surface of said region, while retaining a thickness of said slab surrounding said region which is sufficient to impart and maintain structural integrity of the finished dynode structure.

2. A method as claimed in claim **1** and including the steps of masking those areas of the body of gallium-arsenide which are not to be etched, placing the whole body of a liquid etchant and rotating the body whilst etching takes place.

3. A method as claimed in claim **2** in which during etching said body is inclined and rotated whilst the area of the body to be etched is totally submerged in the etchant.

4. A method as claimed in claim **1** in which after etching the surface from which electrons are to be emitted is coated with a thin layer of a substance which serves to reduce the effective work-function of said surface.

5. A method as claimed in claim **4** wherein said substance is a caesium compound.

6. A method as claimed in claim **1** in which after etching, the face of the thin active area opposite to the surface from which electrons are to be emitted is provided with a thin surface layer which causes the said opposite surface to exhibit an increased work-function as compared with the untreated body of gallium-arsenide.

7. A method as claimed in claim **6** in which said increased work-function is achieved by rendering said opposite surface P+ by doping.

8. The method according to claim **1** wherein step (*b*) includes the provision of a body of etchant, totally immersing said slab in said body of etchant with said opposite side surfaces inclined slightly with respect to vertical and rotating said slab slowly while so immersed.

9. The method according to claim **8** wherein the thickness of said region is in the order of 5 μm and the thickness of that portion surrounding said region is in the order of 100 μm.

10. The method according to claim **9** wherein the rate of etching performed in step (*b*) is in the order of 1--2 μm per minute.

11. A method as claimed in claim **10** in which after etching the surface from which electrons are to be emitted is coated with a thin layer of a substance which serves to reduce the effective work-function of said surface.

12. A method as claim in claim **11** in which after etching, the face of the thin active area opposite to the surface from which electrons are to be emitted is provided with a thin surface layer which causes the said opposite surface to exhibit an increased work-function as compared with the untreated body of gallium-arsenide.

13. A method as claimed in claim **4** in which after etching, the face of the thin active area opposite to the surface from which electrons are to be emitted is provided with a thin surface layer which causes the said opposite surface to exhibit an increased work-function as compared with the untreated body of gallium-arsenide.

14. A dynode structure including an etched-thin gallium-arsenide active area surrounded by a relatively thick frame integral therewith, produced by the method of claim **1.**

15. An electron tube including an etched-thin gallium-arsenide active area surrounded by a relatively thick frame integral therewith, produced by the method of claim **1.**

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