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[54] **METHOD OF MANUFACTURING AN ELECTRIC DISCHARGE TUBE HAVING AN ELECTRON EMITTING ELECTRODE COMPRISING A CESIUM-CONTAINING LAYER ON A SUPPORT**

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[58] **Field of Search** 316/3, 4, 5, 6, 7, 8, 9, 316/10, 11, 12, 24; 313/94; 117/219, 107, 224

[56] **References Cited**

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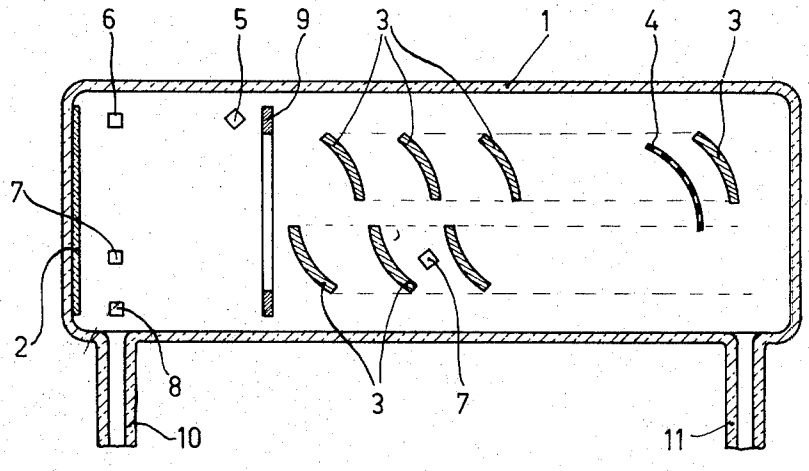
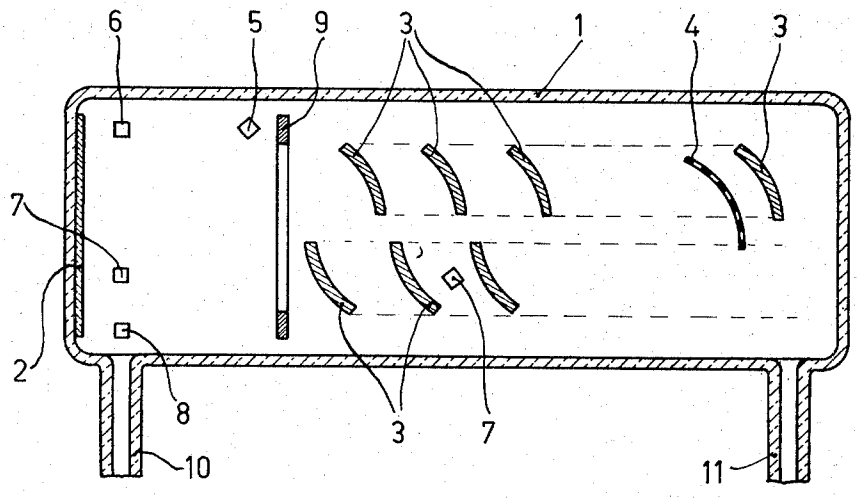
[57] **ABSTRACT**

A method of manufacturing an electric discharge tube having an electron-emitting electrode comprising a support with a cesium-containing layer thereon which is activated by reaction of a gaseous compound of an inactive or inert gas and fluorine until a cesium fluoride layer having a composition (CsF, Cs) is formed. The gaseous compound, at the temperatures prevailing in the tube does not react with the surfaces of other parts.

13 Claims, 1 Drawing Figure

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METHOD OF MANUFACTURING AN ELECTRIC DISCHARGE TUBE HAVING AN ELECTRON EMITTING ELECTRODE COMPRISING A CESIUM-CONTAINING LAYER ON A SUPPORT

The invention relates to a method of manufacturing an electric discharge tube in which an electron-emitting electrode is present which consists of a support on which a cesium-containing layer is provided, which layer is activated by reaction with a gas.

The emitting electrode may be a photo-cathode, an injection photocathode, a *p-n* cathode or a secondary emission electrode.

It is known that, when the support of the cesium-containing layer consists of a *p*-conductive AIII-BV compound, the photo emission is improved by reaction with oxygen in such manner that an oxygen-cesium layer with excess of cesium (Cs_2O, C_s) is formed.

The reaction of cesium with oxygen is not only rapid but in accordance with the metal parts present in the tube and their structure (finely divided as an absorption layer of titanium, or smooth) said metal parts take up non-reproducible quantities of oxygen so that the oxidation of cesium requires great skill. As a result of this it is difficult to obtain the optimum value of the emission. Often, alternately cesium is vapor-deposited and oxygen admitted until the electron emission reaches an optimum value and, if desirable, the last step is the vapor-deposition of a fraction of a monoatomic layer of cesium, as described for photo-cathodes in British Patent Specification 1,200,899.

Oxidation also provides an improved photo and secondary emission on cesium present on cesium antimonide (Cs_3Sb) supports, either by vapor-deposition or as an excess in the compound.

Oxidation does not give any improvement of the photoemission in sodium-potassium antimonide on which cesium is vapor-deposited. The thermal energies of the formation of Na_2O and K_2O, respectively, 100 k.cal/-mol, are so much larger than those of Cs_2O, 76 k.cal/-mol, that the support is more easily oxidized than the cesium layer.

On the other hand, photocathodes are also known in which cesium fluoride and still some free cesium is vapor-deposited on gallium arsenide or on gallium-indium arsenide, until a monoatomic layer is obtained; see S. Garbe, Phys. Stat. Sol. 2, 497 – 501, 1970. An advantage of such a photocathode is the low work function of the (CsF, Cs) layer of 1.0 eV, associated with a high electron transmission. The stability is also slightly better than that of a (Cs_2O, Cs) layer. A difficulty is, however, that the vapor deposition of the cesium fluoride requires a very long evacuation due to the considerable gas supply of the container. Moreover the CsF is very hygroscopic.

It is the object of the invention to provide a method which is more easy to carry out than the known method and furthermore comprises further application possibilities.

In a method of manufacturing an electric discharge tube in which an electron-emitting electrode is present which consists of a support on which a cesium-containing layer is provided which is activated by reaction with a gas, according to the invention, the gas consists of a compound of an inactive or inert gas with fluorine in such a composition that at the temperature occurring in the tube, metal parts and insulators do not noticeably react, the reaction with the cesium being continued at such a temperature and pressure until a cesium fluoride layer has formed with a composition: (CsF, Cs). In general, the fluorination is continued only until an optimum value of the electron emission is achieved. If necessary, some cesium may still be vapor-deposited afterwards.

It is particularly favourable to alternately vapor-deposit cesium on the support and to admit gas as is known for cesium and oxygen. Such a method would not be possible for cesium fluoride vapor-deposited as such with an addition of cesium.

The method according to the invention is preferably carried out with such compounds of fluorine with nitrogen as nitrogen trifluoride NF_3, or with xenon such as xenon difluoride XeF_2, which, at room temperature and already at a pressure of 10^{-7} to 10^{-6} Torr can convert a monoatomic to 5 atoms thick cesium layer into fluoride in a few minutes to a few seconds without appreciably reacting with the metal parts or insulators present in the tube, such as the glass wall. On the contrary, in the known methods, oxygen easily reacts with metal surfaces, in particular when they have a porous structure. Thicker cesium layers also react very quickly with the gaseous fluorides. The vapor of a solid fluoride, such as XeF_2, is of course also to be considered as a gas.

It is also possible to take up the fluoride in a non-reacting carrier gas, such as nitrogen or argon of a higher pressure. This facilitates the manipulation of a flowing system.

The (CsF, Cs) layers obtained with the method according to the invention are not less stable than layers in which the CsF is provided by direct vapor-deposition.

In addition to the advantage of a better stability as compared with (Cs_2O, Cs) layers, the method according to the invention has the advantage, as compared with the vapor-deposited CsF layers, that all the electrodes obtain a uniform coating. This is particularly important in electron multipliers in which the electrodes are arranged very close together and in which a uniform coating is necessary all the same. The introduction of the gases does not involve impurities as can easily be the case when vapor-depositing fluoride.

The method according to the invention may successfully be applied to supports of *p*-conductive $A^{III}B^{V}$ compounds, such as gallium arsenide, which is doped with zinc, silicon or germanium. Also on cesium antimonide (Cs_3Sb) supports, the improvement of the emission as compared with untreated cesium layers and also as compared with oxidized cesium layers is considerable.

The method is particularly favourable on Na_2KSb supports on which cesium is vapor-deposited. Although the increase of the photoemission is not so considerable, it is contrasted with the treatment with oxygen which gives no improvement. Perhaps the improvement is to be ascribed to the fact that the formation energies of NaF, KF and CsF are 136, 135 and 127 k. Cal/Mol, respectively, so that, in contrast with the treatment with oxygen, the conditions for the formation of the compound with cesium which, in contrast with the two other alkali metals, is present in particular at the surface, are not much more unfavourable in this case and are probably more favourable.

The method according to the invention of the fluorination of an activating emission layer by the treatment of cesium with gaseous fluorides also permits the manufacture of activating layers which consist of mixtures of cesium, fluorine and oxygen. It has proved that the electron emission from such electrodes may be higher than when only one activation layer of (CsF, Cs) or an activation layer of (Cs_2O, Cs) alone is present. It is advantageous to perform the method so that first alternatively a few times cesium is vapor-deposited and a fluorination takes place and then a treatment with oxygen takes place which may be alternated once or several times with a fluorination of new cesium layers.

When the support of the activating layer consists of a *p*-conductive $A^{III}B^{V}$ compound, it is very favourable according to the invention when prior to the vapor-deposition of the cesium, the support in the reaction gas is heated at a high temperature, for gallium arsenide, dependent upon the crystal orientation, at approximately 550° to 600° C. Cesium may then immediately be vapour-deposited and fluorination and oxidation, respectively, be carried out, but better results are obtained when heating is first carried out in a high vacuum.

The invention will be described in greater detail the sole FIGURE of which shows an electron multiplier tube and reference to the accompanying drawing with the following examples.

The drawing shows diagrammatically an electron multiplier **1** having a transparent photocathode **2.** The multiplier electrodes are denoted by **3.** Before the last electrode **3** a grid-like output electrode **4** is present. In the vicinity of the photo-cathode **2,** which is present on a transparent conductive layer four evaporation sources **5, 6, 7** and **8** for antimony, sodium, cesium and potassium, respectively, are provided. Between two multiplier electrodes **3** consisting of gallium phosphide supports a further cesium source **7** is present.

After evacuation the tube **1,** the cathode **2** was formed by vapor-depositing antimony, sodium and potassium, which, when slightly heated, (approximately 180° C) formed the alloy Na_2KSb. Cesium was deposited on said alloy simultaneously with the cesium on the gallium phosphide electrodes **3.** An acceleration electrode **9** was present between the photocathode **2** and the electrode **3.**

After evaporation of the cesium, nitrogen trifluoride was admitted through the tubes **10** and **11** in such manner that in the tube **1** a pressure prevailed of 5×10^{-6} Torr at room temperature. In 5 minutes the cesium was converted into (CsF, Cs). The tube **1** was then fully evacuated, pressure smaller than 10^{-8} Torr. If desirable, for example, a mono layer of Cs can be vapor-deposited on all the electrodes. The sensitivity to white light of the cathode **2** was increased by approximately 15 percent due to the treatment with nitrogen fluoride and the work function was reduced by 0.1 eV. The stability was so good that after 8 weeks of storage the emission was substantially unvaried.

For a cathode of Cs_3Sb the improvement of the photo-emission as compared with an oxygen treatment was approximately 100 percent and the reduction of the work function also 0.1 eV.

For a cathode consisting of zinc-doped gallium arsenide, the improvement of the photoemission by fluorination as compared with the photoemission after oxydation was more than 50 percent. Even better results were obtained when the gallium arsenide was heated in nitrogen trifluoride under a pressure of 2 to 4×10^{-6} Torr for 10 minutes at 550° C prior to vapor-depositing the cesium. When the gallium arsenide was then heated for 10 minutes in a high vacuum at the same temperature, sensitivities for white light of approximately 700 μA/lumen were obtained by alternate treatment with cesium and oxygen; by alternate treatment with cesium and fluorine to approximately 1,000 μA/lumen and by alternate treatment with cesium, fluorine and oxygen even more than 1,100 μA/lumen.

In another multiplier tube the multiplier electrodes consisted of *p*-silicon with a doping of 5×10^{19} boron atoms/ccm. The surface of the silicon was purified by a high frequency discharge in argon of 10^{-3} Torr. Cesium was then vapor-deposited and fluorinated in the same manner as described above. With an energy of the primary electros of 800 eV, the secondary emission factor was approximately 70.

What is claimed is:

1. A method of manufacturing an electric discharge tube having an electron-emitting electrode comprising the steps of providing on a support a cesium-containing layer, and activating said cesium-containing layer by reacting the layer with a gaseous compound of an inactive or inert gas with fluorine at a temperature and pressure at which a cesium fluoride layer of a composition: (CsF, Cs) is formed without reaction of the gaseous compound with other parts of the tube.

2. A method as claimed in claim **1,** wherein the reaction gas consists of a compound of fluorine with nitrogen or xenon.

3. A method as claimed in claim **2,** wherein the reaction gas consists of NF_3 or XeF_2.

4. A method as claimed in claim **1,** wherein the reaction is carried our at room temperature at a pressure of between 10^{-7} to a few times 10^{-6} Torr for a few minutes to a few seconds in flowing gas.

5. A method as claimed in claim **1,** wherein the reaction gas is incorporated in a carrier gas of a higher pressure.

6. A method as claimed in claim **1,** wherein the electrode is alternately treated with cesium and the fluorine-containing gas.

7. A method as claimed in claim **1,** wherein the electron-emitting electrode is a photocathode with a Cs_3Sb support, an Na_2KSb support or a *p*-conductive A^{III}-B^{V} support.

8. A method as claimed in claim **1,** wherein the electrode is an injection electrode, a *p-n* cathode or a secondary emission electrode.

9. A method as claimed in claim **8,** wherein the support of the secondary emission electrode is *p*-silicon, cesium is vapor-deposited on the support and is then fluorinated.

10. A method as claimed in claim **6** wherein after one or more treatments with cesium or fluorine, one or more treatments with cesium or oxygen are carried out.

11. A method as claimed in claim **7,** wherein the *p*-conductive A^{III}-B^{V} compound is heated, prior to the treatment with cesium, at a high temperature in the same reaction gas.

12. A method as claimed in claim **11,** wherein between the heating of the support in the reaction gas and the vapor-deposition of the cesium a heating is carried out in a high vacuum.

13. A method as claimed in claim 12, wherein *p*-conductive gallium arsenide is heated at 550° to 600° C in nitrogen trifluoride under a pressure of 2 to 5×10^{-6} for 10 minutes, after which a heating is carried out in a high vacuum and the cesium is finally vapor-deposited and is treated with gaseous fluorides and/or oxygen.

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