May 20, 1941. W. HARTMANN ET AL 2,242,395

ELECTRON EMISSIVE CATHODE

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FIG. 1

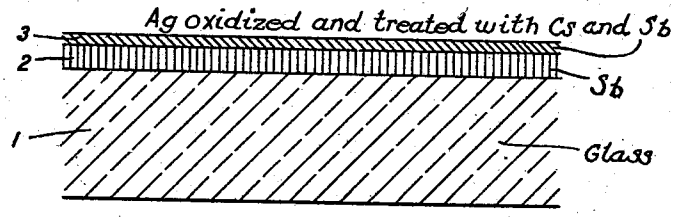
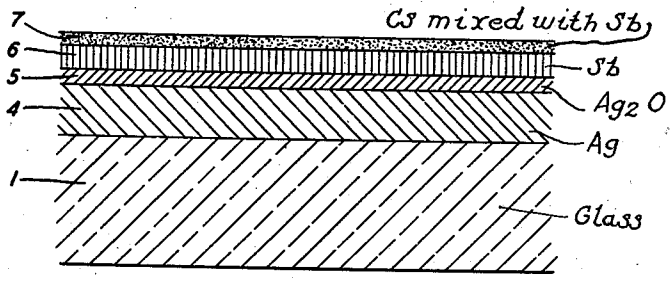


FIG. 2



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UNITED STATES PATENT OFFICE

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ELECTRON EMISSIVE CATHODE

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9 Claims. (Cl. 250—27.5)

This invention relates to electron emissive cathodes, particularly to photocathodes such as are used in the photoelectric tubes, picture analyzers with a continuous photoelectric layer or a mosaic, especially for television purposes, and to secondary emitting layers such as are used in electron multipliers.

It is known to form surfaces preferably of silver and caesium, and to evaporate upon the finished surface a metal such as antimony or bismuth which favorably influences the photosensitivity. A greater sensitivity is then obtained, particularly in the blue-green range. In operation of such cells it has been found that their spectral sensitivity becomes displaced after a certain time and changes in absolute values. This phenomenon is traced back to the fact that the antimony atoms diffuse from the surface into the interior of the layer. It has been observed that the diffusion velocity of antimony atoms at 200 degrees C. is unexpectedly great. Even if the diffusion velocity decreases exponentially with temperature, it still is of considerable magnitude even for the operating temperature of the cell, which is at least room temperature. Inasmuch as the emission of photoelectrons is a surface effect penetrating only slightly below the surface, a displacement in the order of several atoms is sufficient to considerably change the properties of the layer.

According to the invention, this displacement is avoided by decreasing the magnitude of the concentration gradient of the subsequently evaporated metal, for instance, antimony. Hereby it is accomplished that less antimony atoms diffuse at lower speed from the surface of the photosensitive layer into the layer.

In some cases it suffices to provide a blocking layer of a material with a finer crystalline structure, such as copper, to prevent the diffusion of antimony atoms.

The invention will now be described more in detail having reference to the accompanying drawing:

Fig. 1 illustrates one form of photoelectric cathode according to this invention;

Fig. 2 illustrates a modified form of cathode,

The invention may be explained with the aid of two embodiments. In Fig. 1, numeral 1 indicates the cathode carrier, for instance a portion of the glass wall of the photoelectric tube. An antimony layer 2 is evaporated upon this glass wall. A comparatively thin layer 3 of silver is then evaporated upon the antimony layer 2. The silver is then oxidized in the known manner and treated with caesium and antimony. During the forming process antimony atoms will diffuse from the foundation into the silver layer and thus decrease the concentration gradient for the antimony atoms evaporated upon the silver—silver-oxide—caesium layer.

Fig. 2 shows the series of layers for another embodiment of the invention. In this case a silver layer 4 is deposited upon the cathode carrier 1, and the silver layer is oxidized in the usual manner. A thin layer 6 of antimony is then evaporated upon the silver-oxide layer 5. The caesium atoms of a layer of caesium deposited upon the layer 6 of antimony will more or less mix with the antimony atoms so that antimony atoms are present on the surface of the photosensitive layer forming layer 7. In this case a reduction in concentration gradient is also accomplished. It may even be possible to completely compensate the concentration gradient.

Photocathodes produced by the method according to the invention possess at least the same sensitivity and spectral distribution as known photocathodes sensitized with antimony and possess a considerably longer lifetime. Of course, this method is not limited to cathodes which are sensitized with antimony, but is applicable in the same manner also to such cathodes in which sensitization takes place, for instance, with bismuth.

What is claimed is:

1. An electron emissive cathode comprising a supporting surface, a layer of antimony on said surface, a thin layer of silver on said layer of antimony, and a matrix on said silver layer comprising caesium, caesium oxide, and antimony.

2. An electron emissive cathode comprising a supporting surface, a layer of bismuth on said surface, a thin layer of silver on said layer of bismuth, and a matrix on said silver layer comprising caesium, caesium oxide, and bismuth.

3. An electron emissive cathode comprising a supporting surface, a layer of a metal of the group containing antimony and bismuth, a thin layer of silver on said first layer, and a surface matrix on said silver layer comprising an alkali metal and a metal of said group containing antimony and bismuth.

4. A method of forming an electron emissive cathode which comprises evaporating and condensing antimony to form a layer on a cathode carrier, evaporating and condensing a small amount of silver to form a thin layer of silver on said layer of antimony, and forming on said

silver layer a matrix comprising an intimate mixture of alkali metal and antimony.

5. A method of forming an electron emissive cathode which comprises evaporating and condensing antimony to form a layer on a cathode carrier, evaporating and condensing a small amount of silver to form a thin layer of silver on said layer of antimony, oxidizing the surface of said silver layer, and forming on said oxidized silver a matrix comprising an intimate mixture of caesium and antimony.

6. A method of forming an electron emissive cathode which comprises forming a layer of a metal of the group containing antimony and bismuth, forming on said layer a thin layer of a metal of the first group of the periodic table of the elements exclusive of the alkali metals, and forming on said second layer a matrix comprising an intimate mixture of an alkali metal and a metal of said group containing antimony and bismuth.

7. A method of forming an electron emissive cathode which comprises evaporating and condensing bismuth to form a layer on a cathode carrier, evaporating and condensing a small amount of silver to form a thin layer of silver on said layer of bismuth, and forming on said silver layer a matrix comprising an intimate mixture of alkali metal and bismuth.

8. A method of forming an electron emissive cathode which comprises evaporating and condensing bismuth to form a layer on a cathode carrier, evaporating and condensing a small amount of silver to form a thin layer of silver on said layer of bismuth, oxidizing the surface of said silver layer, and forming on said oxidized silver a matrix comprising an intimate mixture of caesium and bismuth.

9. An electron emissive cathode comprising a layer of an electron emissive metal sensitized with a metal of the group containing antimony and bismuth and an underlying layer of a metal of the group containing antimony and bismuth to minimize the concentration gradient of said sensitizing metal.

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