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Pakswer

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[54] **SECONDARY ELECTRON MULTIPLIERS WITH SINGLE LAYER CERMET COATINGS**

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[52] **U.S. Cl.**..... **313/95**, 117/227, 313/105

[51] **Int. Cl.**..... **H01j 1/32**, H01j 43/04

[58] **Field of Search**..... 313/68 R, 68 A, 103–105, 313/346 R, 355, 95; 117/106 R, 107, 210, 221–223, 227

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[57] **ABSTRACT**

Secondary electron multiplier devices having one or more secondary electron emission multiplier elements each consisting essentially of a single-layer cermet coating on a supporting substrate. The coating may be formed by various techniques including flash evaporation, vacuum sputtering, and chemical vapor deposition. Secondary emission ratios of two, three and more are attained with first cross-over voltages in the range from 20 to 40 volts. In applications where optimum temperature stability is required, gold/metal oxide cermets are employed.

2 Claims, 5 Drawing Figures

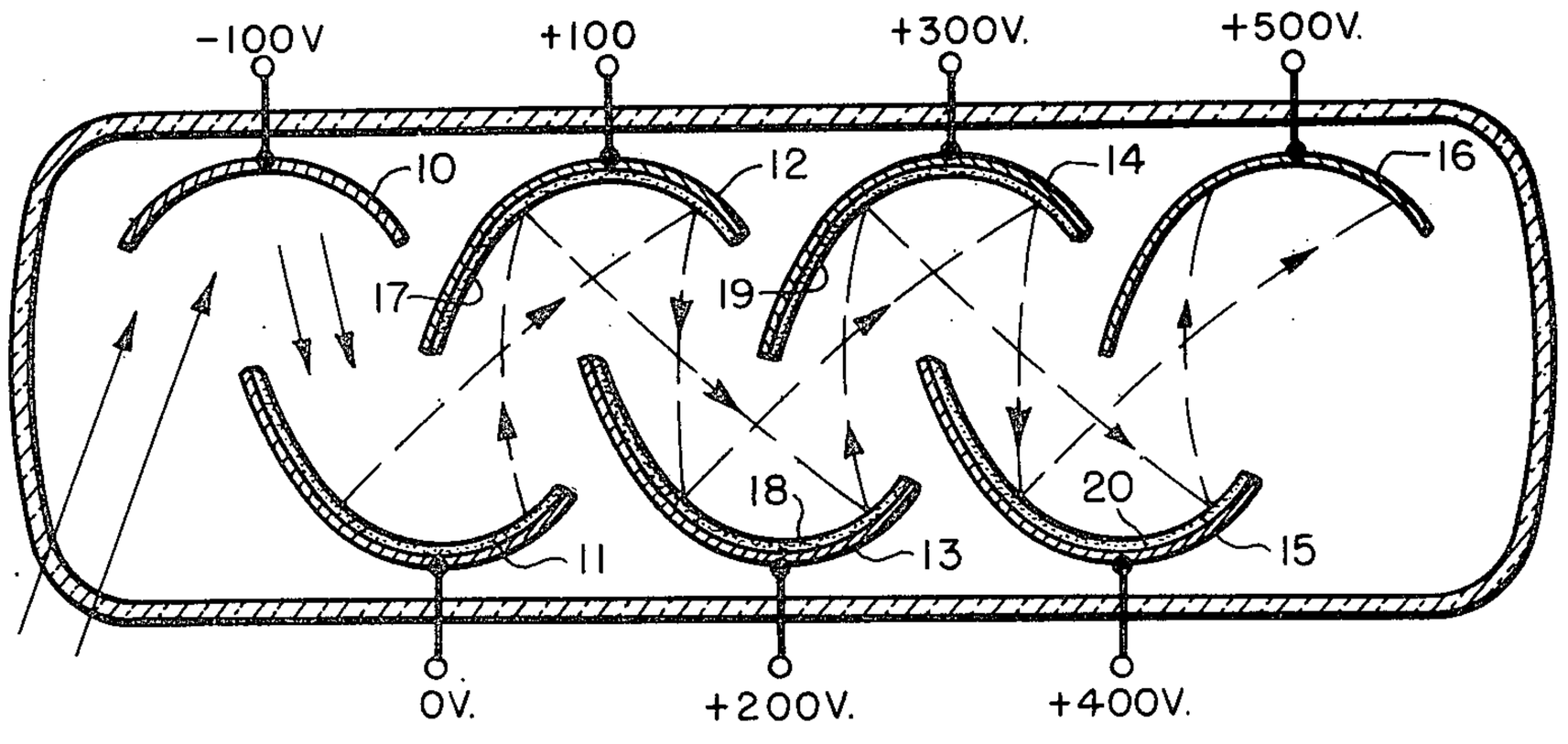


FIG. 1

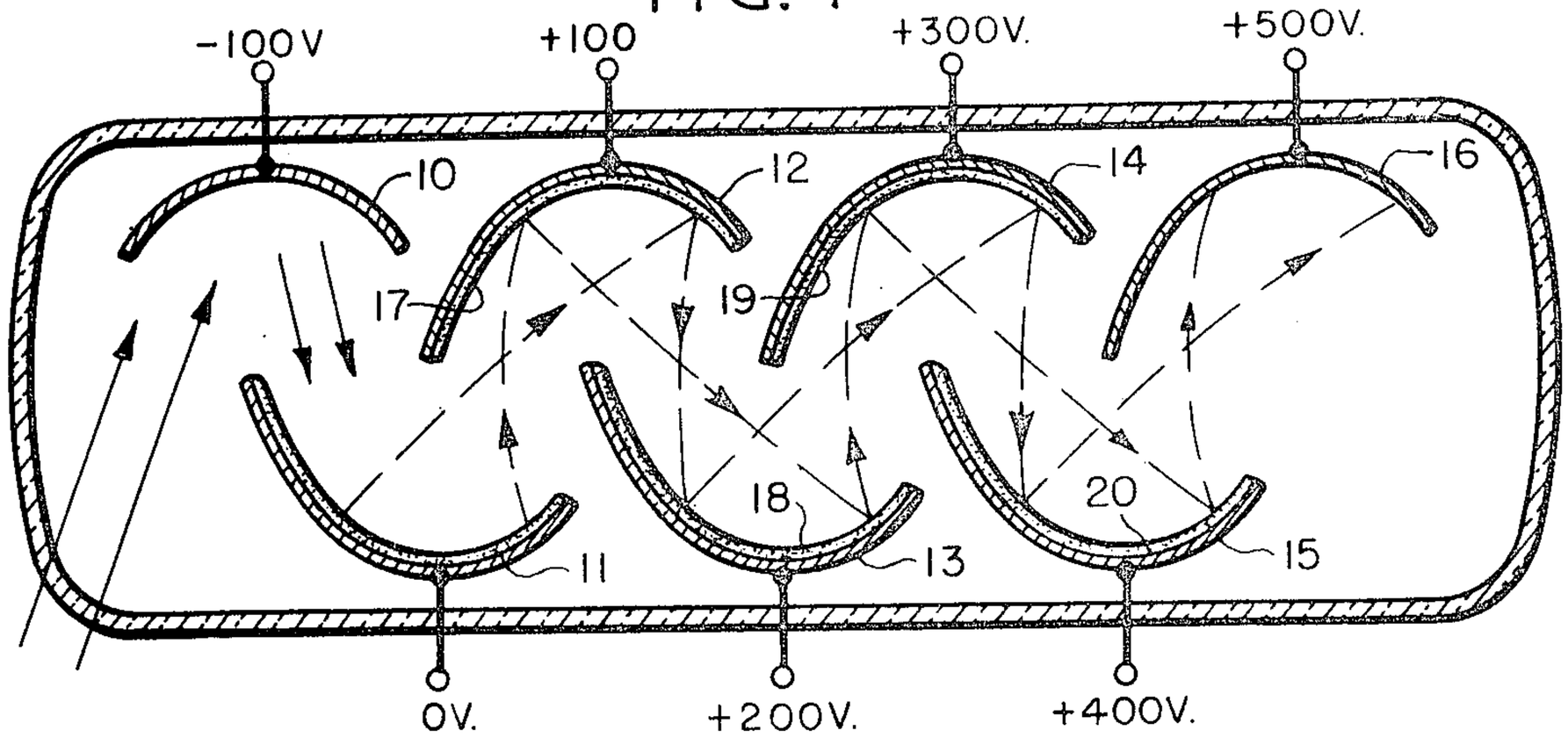


FIG. 2

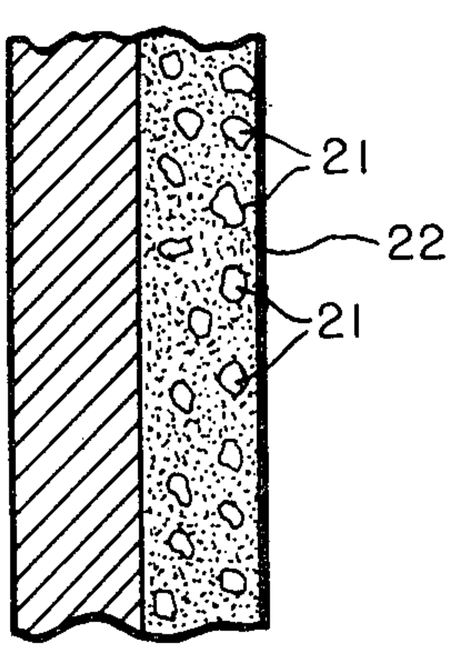


FIG. 3

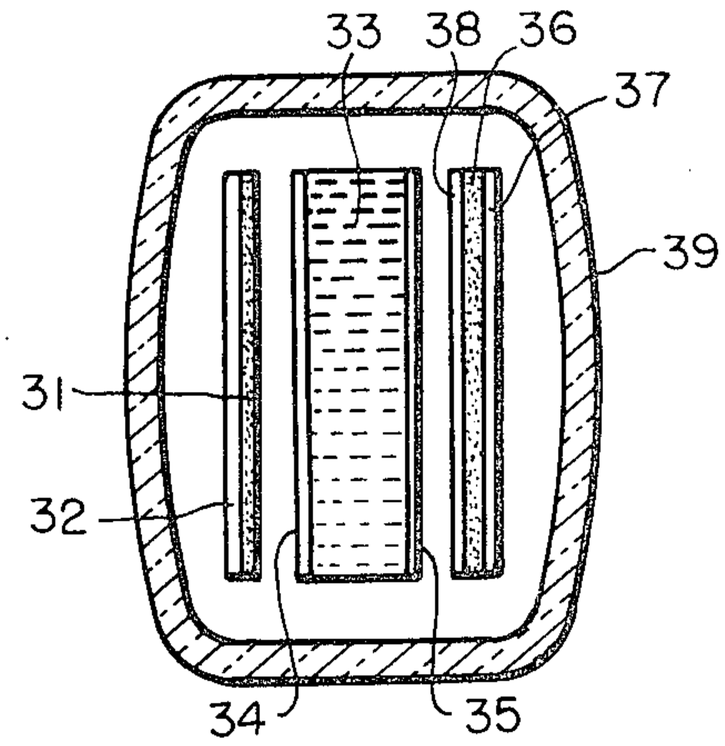


FIG. 4

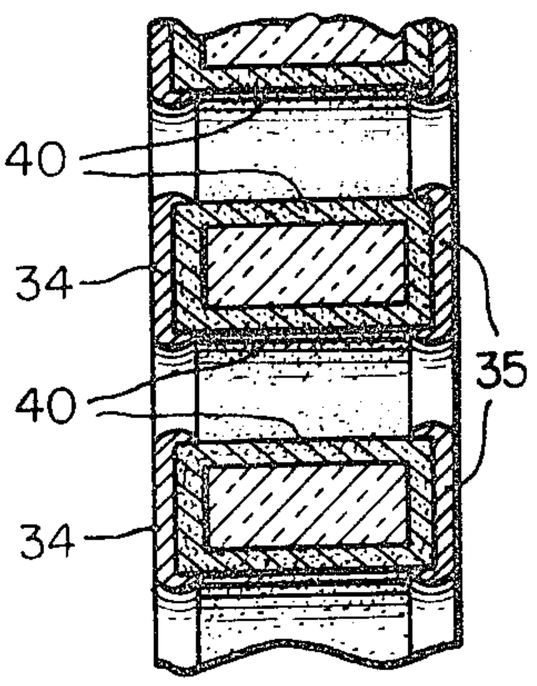
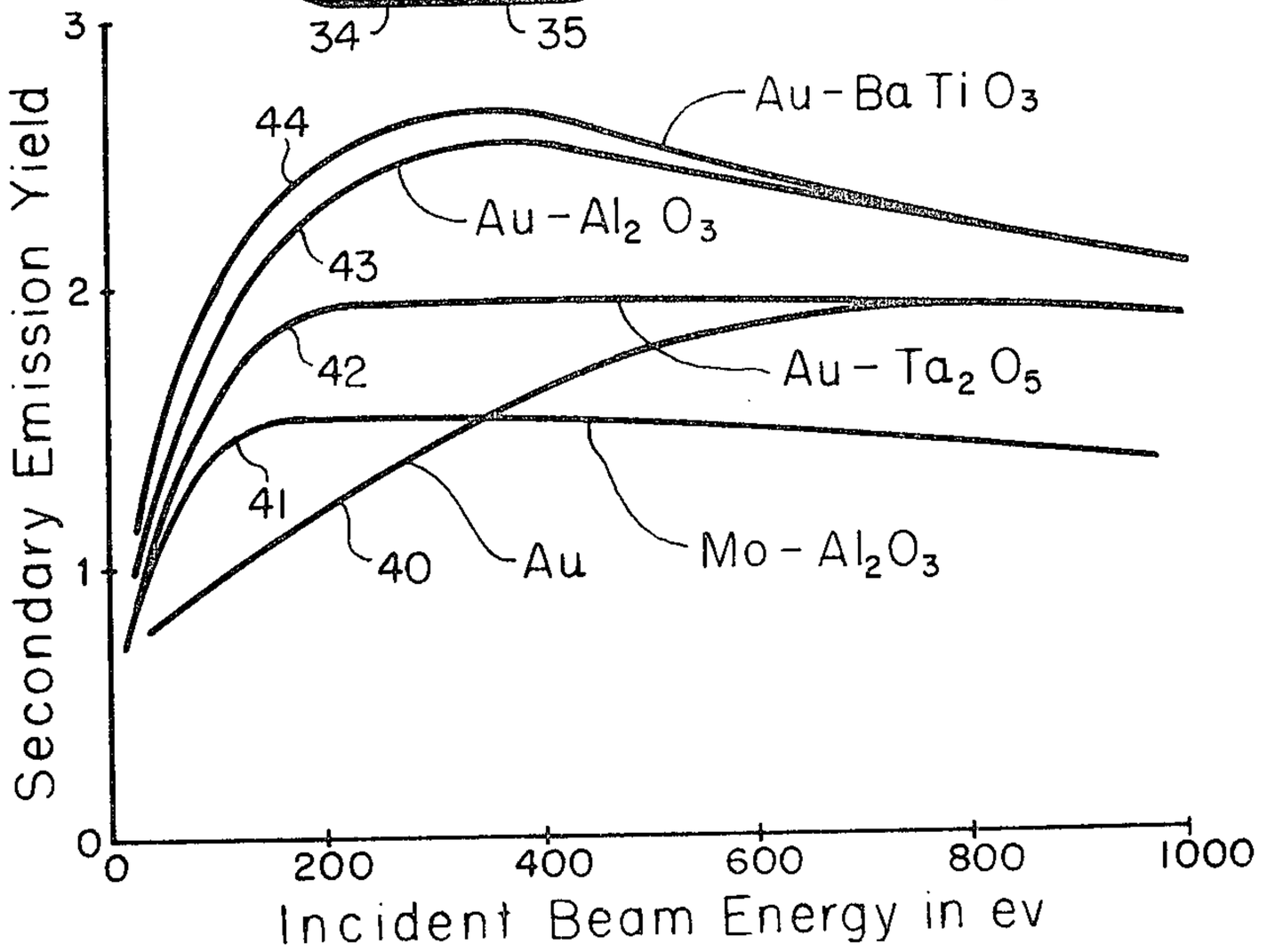


FIG. 5



SECONDARY ELECTRON MULTIPLIERS WITH SINGLE LAYER CERMET COATINGS

This invention relates to secondary electron multiplication devices such as electron multipliers and image devices (e.g., storage devices and display devices) using secondary emission multipliers for enhanced image brightness.

The fabrication of secondary electron emissive surfaces such as those used in the dynodes of secondary electron multipliers is an involved and critical process. In general, the electrodes are formed of special materials which are subjected to surface layer treatment and must be carefully and critically maintained within close tolerances in order to achieve the desired operating parameters. The most critical parameters are the secondary emission ratio δ and the first cross-over voltage, the lowest voltage at which the secondary electron emission ratio is unity. To be useful as a secondary emission multiplier in most applications, the secondary emission ratio should be at least 2 or 3, while the first cross-over voltage should come in the range from 20 to 40 volts. To hold these limits, close control over process parameters is required and in general multi-step processing must be employed.

Secondary electron emissive surfaces of this type are usually formed by appropriate chemical modification of a surface region on a preformed support structure of selected composition, or by the provision of successive metal and insulating layers. In the first type of process, severe limitations are imposed upon the selection of a substrate material, and in both approaches the process parameters must be maintained within critical limits and multiple step processing is required.

It is a primary object of the present invention to provide a new and improved type of secondary electron multiplier device which overcomes one or more of the limitations or deficiencies of prior art devices of this type.

Many of the same considerations are applicable to the provision of secondary emissive internal coatings in channel multipliers such as micro-channel plates used in image-storage or image-display devices. In addition, however, channel multipliers present a special problem in that they are not readily amenable to the use of conventional coating techniques. Because channel multipliers are normally constructed with a large length-to-diameter ratio, it is not feasible to produce uniform coatings by evaporation or sputtering techniques. Accordingly, it has been common practice to construct the multiplier of a special lead glass or other specially selected material and provide the desired secondary emission properties by gas-transport surface reduction. Unfortunately, materials which are subject to such treatment to provide acceptable secondary emission properties are mechanically difficult to work with during the channel forming operations or, stated another way, those materials which are most readily workable to form the channels or micro-channel plates are usually not the most amenable to surface treatment for optimum secondary emission properties.

It is a further object of the present invention to provide a new and improved secondary electron multiplication device whose secondary electron multiplying elements may be produced in any of a wide variety of different processing techniques.

It is a further object of the invention to provide a new and improved method for making a secondary electron

emissive element which has the advantage of optimum flexibility in the selection of substrate materials and the choice of processing techniques.

Still a further object of the invention is to provide a new and improved secondary electron multiplying device which is at least potentially more efficient, as for example by providing higher secondary emission ratios or lower first cross-over voltages, than prior art secondary electron multiplying elements.

In accordance with the invention, a new and improved secondary electron multiplier device comprises a source of primary electrons and one or more secondary emission multiplying elements each consisting essentially of a single-layer cermet coating on a supporting substrate, which coating is responsive to the primary electrons to yield secondary electrons with a secondary emission ratio greater than unity. Means are provided for utilizing the secondary electrons. In general, the primary electron source may be a thermionic cathode, a photo-cathode, or an electron gun, while the secondary electron utilizing means may constitute an output anode in the case of a secondary electron multiplier, a phosphor screen in an image display-device, or an image storage electrode in the case of an image-storage device.

The features of the present invention which are believed to be novel are set forth with particularity in the appended claims. The invention, together with further objects and advantages thereof, may best be understood by reference to the following description taken in connection with the accompanying drawing, in the several Figures of which like reference numerals identify like elements, and in which:

FIG. **1** is a schematic view of a secondary electron multiplier device constructed in accordance with the present invention;

FIG. **2** is an enlarged fragmentary cross-sectional view showing the detailed structure of a secondary emissive element embodying the present invention;

FIG. **3** is a schematic view of an image intensifier embodying a channel multiplier plate constructed in accordance with the present invention;

FIG. **4** is an enlarged fragmentary cross-sectional view illustrating the secondary electron emissive surfaces within the individual channels of the multichannel plate of FIG. **3**; and

FIG. **5** is a graphical representation of illustrative secondary electron emission characteristics of secondary electron multiplier elements embodying the present invention.

FIG. **1** shows a high vacuum electrostatic electron multiplier tube of entirely conventional construction except for the particular construction of the secondary electron emissive dynodes. Incoming light is reflected by a mirror **10** onto the photo-emissive surface of a photo-cathode **11**, and primary electrons originating at photo-cathode **11** are caused to impinge on a series of secondary electron emissive elements or dynodes **12**, **13**, **14** and **15** maintained at progressively higher voltages as indicated by the legends in the drawing. Primary or secondary electrons impinging on a dynode gives rise to the emission of a larger number of secondary electrons, thus causing a progressive increase in the electron current. Means are provided in the form of output anode **16** for collecting the secondary electrons generated by dynodes **12**, **13**, **14** and **15**. The approximate limiting electron paths are illustrated in the draw-

ing, and the configurations of the electrode are such that, in conjunction with the applied voltage differences, practically all the electrons are caused to pass through the multiplier. The total number of electrons increases in geometrical progression from dynode to dynode to provide substantial current multiplication.

In accordance with the present invention, each of the dynodes is formed of an appropriate substrate, which may be metal or metallized glass, and which is provided with a thin-film single-layer cermet coating. Such coatings 17, 18, 19 and 20 are provided on dynodes 12, 13, 14 and 15 respectively. As shown in FIG. 2, the single-layer cermet coating preferably comprises metal islands or globules 21 imbedded or dispersed in a matrix of dielectric material 22. Typically, the metal globules may be from 40 to 500 Angstrom Units in diameter and the overall thickness of the thin film coating in the range from 200 to 2,000 Angstrom Units. The resistivity of the thin film coating is a function of the size and packing density of the metal islands or globules, as well as of the properties of the metal and insulator compositions, while the temperature coefficient of resistance of the cermet layer is a function of the size of the globules 21 for a given film thickness, lower temperature coefficients of resistance being obtained with larger globule sizes. The metal globules are preferably noble metals such as gold or platinum or palladium, although others such as molybdenum, aluminum, tungsten, etc., may be employed. Suitable inorganic dielectric materials to form the insulating matrix are metal-oxygen compounds such as simple or complex metal oxides, metal fluorides and other metal halides. Depending on the application and the required operating characteristics, acceptable results may be achieved with simple oxides such as BeO, MgO, Al_2O_3, or Ta_2O_5, with complex oxides such as tungstates or titanates of calcium, barium, magnesium, or strontium, or with metal halides such as the fluorides of magnesium, barium or calcium.

The single-layer thin film cermet coating may be produced by any of a variety of techniques such as flash evaporation, vacuum sputtering, or the like. In addition, the cermet coatings can be produced by chemical vapor deposition.

Thin film single-layer cermet coatings in accordance with the present invention combine the high secondary emission yield typical of insulators with increased electrical conductivity and hence lack of surface charge typical of metals. The specific properties may be controlled by selection of film thicknesses and globule sizes, by selection of metals and dielectric materials, and by the packing density or concentration of metal globules in the insulating matrix. In general, globule concentrations may be increased without limit and so long as they do not become so tightly packed as to lose their individual globular character they present a negative temperature coefficient of resistance which varies in magnitude directly with the resistivity. The sparser globule concentrations are most useful where high resistivity is desired as in microchannel plate applications where a voltage drop is required. With higher metal concentrations, the construction is more aptly described as comprising dielectric islands in a metal matrix; the temperature coefficient of resistance is then positive, and while useful secondary emission for some applications can be obtained, the resistivity is too low for adaptation to configurations requiring maintenance of a voltage gradient. The lowest temperature coefficients of resistance yet achieved for a specified resistivity have been attained with the gold/metal oxide cermets.

Prior art secondary emissive surfaces for use in secondary emission multiplier devices have in general been composed either of simple insulators or of multiple layers or coatings of metal and dielectric materials. The secondary emitting surfaces in accordance with the present invention are readily differentiated because they comprise both metal and insulating elements in a single-layer coating. In other words, in prior art composite metal/insulator constructions, the metal and insulating components are in discrete transversely displaced layers, whereas with a cermet secondary emitter in accordance with the present invention, there is no transverse displacement — there is rather a lateral displacement — between the metal and dielectric constituents.

The variation of the secondary electron yield at low voltages, especially the low first cross-over potential, indicates that the secondaries are emitted preferentially from the dielectric, rather than from the gold. This is due to the smaller minimum escape energy required in an insulator than a metal. One could hypothesize a model wherein the secondary electron emission of a cermet is entirely due to the dielectric, and the only role the metal component has is to increase the conductivity such that a surface charge cannot develop. In this picture, secondaries are both created in and escape from the dielectric. However, the drastic modifications in yield which occur upon the incorporation of only a small quantity of dielectric in a cermet make this unlikely, but suggest that secondary electrons are also created in the gold globules. These find it easier to cross the gold-dielectric interface than the gold vacuum interface, and, once they are in the dielectric, have the same probability of escaping into the vacuum as the secondaries created there. However, they have a strong advantage over those which do not cross the gold-dielectric interface. Because of the large number of conduction electrons in the gold, most of the secondaries lose energy in collisions with the lattice electrons and hence few of the secondaries reach the surface. Thus, one can consider the dielectric to act as a low-loss bypass from deep inside the cermet to the surface. The net effect is to increase the secondary emission yield of the gold, slightly at high energies and considerably at low energies. The overall result is to make the maximum very broad; for our Au-Ta_2O_5 films the value of δ varies less than 10 percent from 150 volts to 1 kv.

An additional embodiment of the invention, showing the use of cermet secondary emissive coatings in an image intensifier comprising channel multipliers in the form of a micro-channel plate is shown in FIG. 3. In the image intensifier of FIG. 3, primary electrons originating at a photo-cathode 31 disposed on a glass substrate 32 enter a micro-channel plate 33 composed of a multitude of individual channel multipliers. Channel multiplier plate 33 includes conductive end coatings 34 and 35 for applying suitable DC operating voltages as schematically illustrated in the drawing. Output secondary electrons from micro-channel plate 33 are proximity-focused onto a phosphor screen 36 disposed on a glass panel 37 and provided with an aluminum backing layer 38. As is conventional in image display devices or in-

tensifiers of this type all elements are contained within an evacuated envelope 39.

In accordance with the invention, each individual channel in micro-channel plate 33 is internally coated with a single-layer thin film cermet coating 40 as shown in the enlarged fragmentary view of FIG. 4. In an application of this type, where an output DC voltage differential is applied along the length of the channel multiplier, a low conductivity or high resistivity cermet is most desirably employed, requiring a small proportion of metal to dielectric constituents. In any application, the selection of metal/dielectric proportions in the two-phase matrix, as well as the specific metal and insulator compositions are matters of design dependent upon the specific operating parameters desired.

To provide an internal coating of cermet material within the individual channels of micro-channel plate 33, simultaneous chemical vapor deposition of the metal and insulating constituents is preferred. As an example of such a process, $Mo(CO)_6$ or $MoCl_6$ may be transported at atmospheric pressure in an oxidizing atmosphere or a reducing carrier gas together with an alkoxide of the metal forming the dielectric; examples of such alkoxides are aluminum butoxide or a mixture of tantalum 1 methoxy 2 butoxide and tantalum butoxide. In the case of a reducing atmosphere, molybdenum is deposited as a metal at 500° C. for $Mo(CO)_6$ and 600° to 800° C. for $MoCl_6$; in the case of an oxidizing atmosphere it deposits at about 450° C. as an oxide which can be reduced to metal by a subsequent reduction in hydrogen at 500° C.

With reference now to FIG. 5, the secondary emission characteristic of a gold metal film is shown for comparison purposes as curve 40. As noted, the first cross-over voltage is at about 120 volts, which is too high for practical secondary emission applications.

Curve 41 represents the secondary emission characteristic of a molybdenum/aluminum oxide cermet. It can be seen that the first cross-over is now at 25 volts and the peak secondary emission at about 250 volts instead of 800 to 1,000 volts in the case of gold.

Curves 42, 43 and 44 show the secondary emission characteristics of gold/tantalum pentoxide, gold/aluminum oxide, and gold/barium titanate respectively. The sample on which curve 42 is based represents from 19 to 22 percent tantalum pentoxide by weight, whereas curve 44 represents about 6 to 10 percent barium titanate by weight. All of these curves show enhanced secondary emission ratios and lowered first cross-over voltages. Still better results may be obtained with insulators such as beryllium oxide, magnesium oxide, barium fluoride, calcium fluoride or magnesium fluoride.

Gold/metal oxide cermets can be made with any desired sheet resistivity from low values of several hundred ohms per square to values of 1,000 megohms per square and more. With high resistivity cermet films, the temperature coefficient of resistance is negative with values of 300 to several thousand parts per million per degree Centigrade increassing with increasing resistivity. Gold-containing cermets have particularly low negative temperature coefficients of resistance.

Cermets are generally not incompatible with cesium vapor and accordingly cermet secondary emissive layers may be cesiated to increase the secondary emission yield.

Thus the present invention provides a new and improved class of secondary electron multiplier devices in which the secondary emissive elements are thin film single-layer cermet coatings. Such coatings differ from prior secondary emissive structures in permitting single-step processing, full flexibility in the selection of substrate materials and configurations, and in some configurations the possibility of attaining higher secondary emission ratios and lower first cross-over voltages than simple insulator types of secondary emitters or multiple-layer constructions in which the metal and insulating elements are presented in separate layers.

While particular embodiments of the invention have been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects, and, therefore, the aim in the appended claims is to cover all such changes and modifications as may fall within the true spirit and scope of the invention.

I claim:

1. A secondary electron multiplier device comprising, within an evacuated envelope:

a source of primary electrons;

a secondary electron multiplier element consisting of a channel multiplier with a single-layer cermet coating consisting of metal globules disposed in a matrix of inorganic dielectric material inside the channel, said secondary electron multiplier element being responsive to primary electrons from said source to generate secondary electrons; and

means for utilizing said secondary electrons.

2. A secondary electron multiplier device comprising, within an evacuated envelope:

a source of primary electrons;

a secondary electron multiplier element consisting essentially of a single layer cermet coating on a supporting substrate, said single layer cermet coating consisting of metal globules dispersed in a matrix of inorganic dielectric material in which said metal globules are from 40 to 500 Angstrom Units in diameter and said inorganic dielectric material is a thin film having a thickness from 200 to 2,000 Angstrom Units, said secondary electron multiplier element being responsive to primary electrons from said source to generate secondary electrons; and

means for utilizing said secondary electrons.

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