

[54] **SECONDARY ELECTRON MULTIPLYING
DEVICE USING SEMICONDUCTOR
CERAMIC**

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[52] U.S. Cl. 313/105, 250/207, 250/213

[51] Int. Cl. H01j 43/00

[58] Field of Search 313/103, 104, 105, 346;
250/207, 213

[56] **References Cited
UNITED STATES PATENTS**

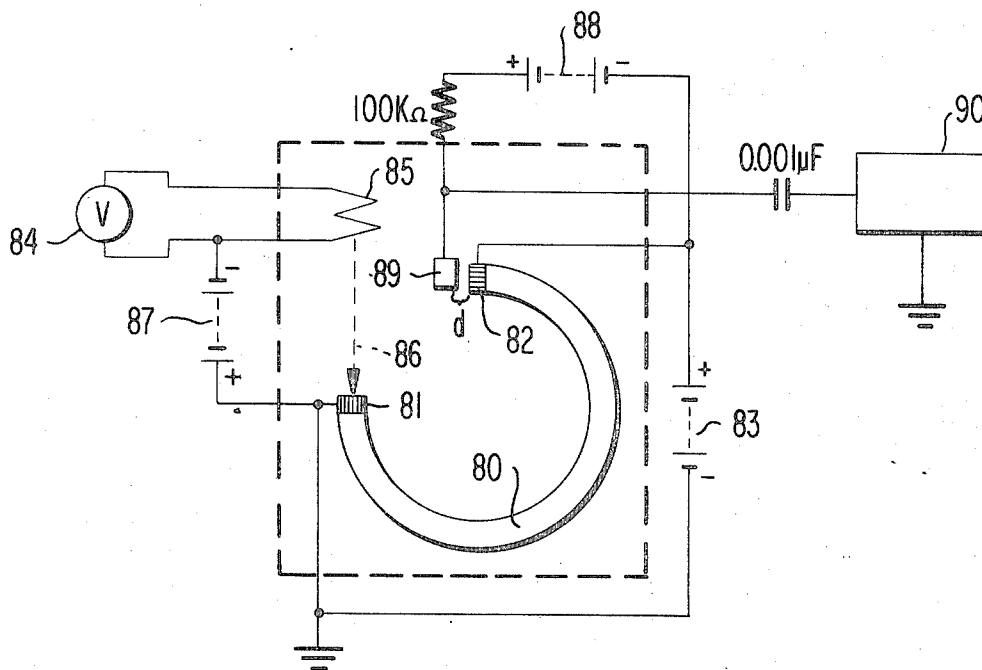
3,612,946 10/1971 Toyoda 313/105

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[57] **ABSTRACT**

A secondary electron multiplying device having high sensitivity for various kinds of electrically charged particles (e.g. electrons, positive ions, negative ions), X-rays, radio active rays, etc., is made of a molded article of a zinc oxide-titanium oxide type semiconductor ceramic, and is provided with at least two electrodes and having at least one hole. The molded article of the device can be produced in form of a single tube or a bundle of a plurality of such tubes. Electrons fed into the tube or tubes impact with the semiconductor ceramic causing secondary electron emission and the number of electrons emitted is greater than the number of electrons fed into the device.

11 Claims, 9 Drawing Figures



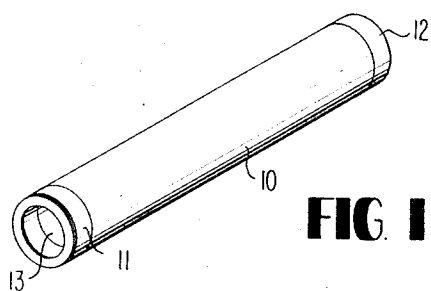


FIG. 1

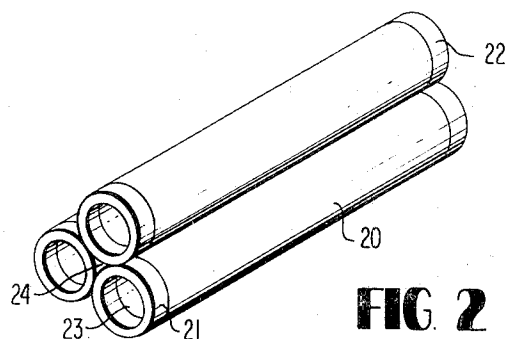


FIG. 2

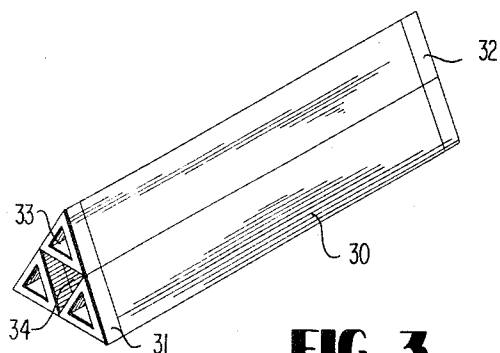


FIG. 3

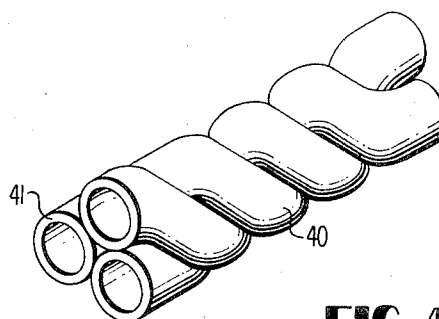


FIG. 4

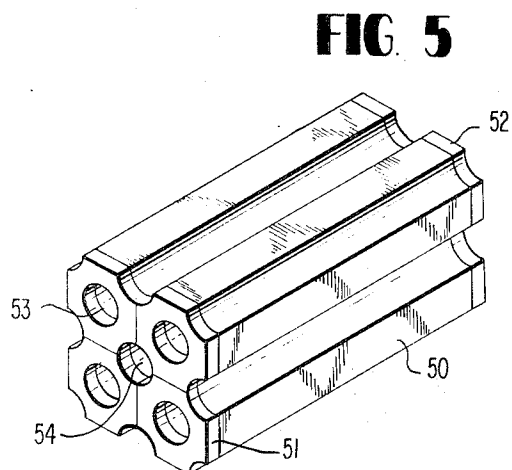


FIG. 5

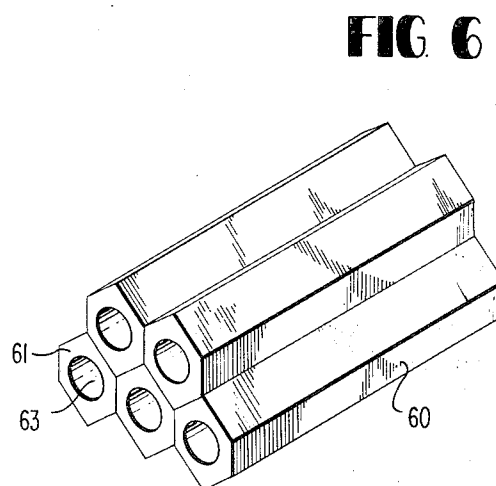


FIG. 6

FIG. 7

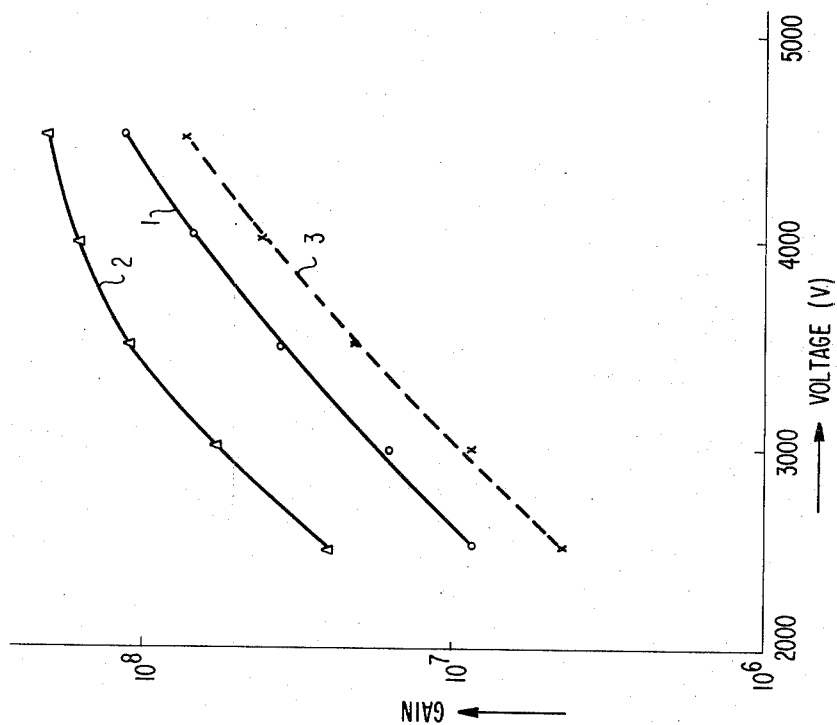
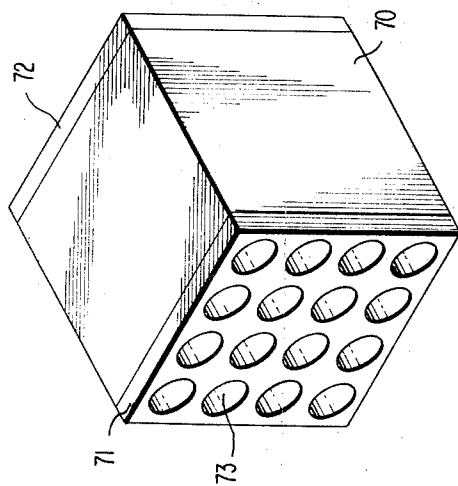
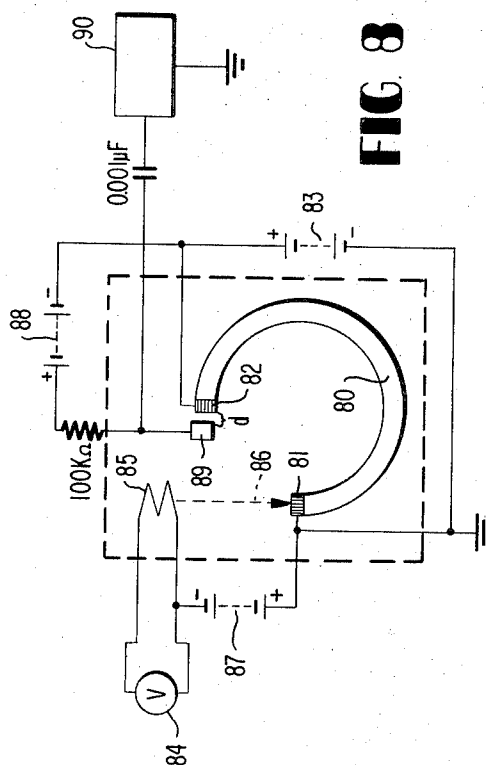


FIG. 9

FIG. 8



SECONDARY ELECTRON MULTIPLYING DEVICE USING SEMICONDUCTOR CERAMIC

The present invention relates to a secondary electron multiplying device.

In the past, various types of the secondary electron multiplying devices have been proposed, and there are a few devices of the solid state type. For example, some solid state type devices are known to have a configuration such that a secondary electron-emitting semiconductor, such as tin oxide, is deposited as a thin film on the inside wall of a tube made of an insulator such as glass. However, the configuration of the secondary electron multiplying devices, as mentioned above has the following disadvantages:

1. Because the layer of the high-resistant substance deposited on the inside wall of the tube is a thin film, it has poor resistance against the impact of electrically charged particles, and it is unstable and has a short life time.

2. When a high voltage is applied to such conventional type secondary electron multipliers, owing to the negative resistance temperature characteristic of the resistant thin film provided therein, the electric current is liable to rise as a result of even a slight degree of self-exothermic action of the high-resistant substance, which can easily lead to thermal runaway, and thus the essential electron emitting operation is prone to become unsteady.

3. As the resistance layer is a very thin film, it is not easy to produce such a film with consistent uniform resistivity distribution and potential distribution.

4. When such film devices operate at temperatures above about 150° C, there is a deterioration of the gain.

The present invention provides a structure of an electron multiplying device made of zinc oxide-titanium oxide type semiconductor ceramic, being sufficiently capable of eliminating the disadvantages that have been unavoidable in the case of conventional types of structures. Also, the present invention offers an electron multiplier which realizes a remarkably high gain of electron multiplication.

It is an object of the present invention to provide a secondary electron multiplying device possessing an extremely high gain of electron multiplication.

Another object of this invention is to provide secondary electron multiplier which is resistant to the impacts of electrically charged particles and has high mechanical and chemical strength, besides being reliably stable in its functional properties and characteristics.

A further object of this invention is to provide a secondary electron multiplying device which prevents deterioration of the gain even when operating at temperatures above about 150° C.

A further object of the invention is to provide a device in which disadvantages such as thermal runaway encountered in the use of conventional devices is entirely eliminated, the device being free from any restriction on the selection of applicable resistance value and can be easily manufactured.

A still further object of the invention is to provide a secondary electron multiplying device which yields a high gain and is highly efficient and can be manufactured easily and economically.

These and other objects will be apparent to those skilled in the art to which the present invention pertains, from the following description.

The secondary electron multiplying device of this invention is constituted of zinc oxide-titanium oxide type semiconductor ceramic. The zinc oxide-titanium oxide type semiconductor ceramic are produced by sintering compositions comprising zinc oxide of about 50 to about 99 mol % and titanium oxide of about 1 to about 50 mol% at a temperature of about 900° to about 1,450° C, and if necessary, one or more elements such as nickel, vanadium, chromium, manganese, iron, cobalt, copper, silver, rhenium, boron, cadmium, magnesium, aluminum, tin, antimony, bismuth, niobium, molybdenum, zirconium, tantalum, tungsten, yttrium, lanthanum or other rare earth elements, calcium, strontium, barium, lead, thorium, or other metallic oxides are incorporated in a total amount less than about 10 mol%. The resultant substance is a ceramic semiconductor having a resistivity of less than about $10^{10} \Omega \text{ cm}$. It has been found that by appropriately selecting the construction or the manufacturing process a semiconductor of any desired shape, optional resistivity or temperature characteristics can be obtained. Further, the resistance temperature characteristic, whether positive or negative, of the resultant substance is remarkably small as compared with that of conventional semiconductor ceramics. It has now been found that zinc oxide-titanium oxide type semiconductor ceramics have a prominent secondary electron emissivity. On the basis of this finding, the present invention provides an improved secondary electron multiplying device which is an improvement on the hitherto known types of secondary electron multipliers with respect to such points as strengthened construction and stable manufacture, as well as higher gain.

The most significant feature of the present invention lies in the use of zinc oxide-titanium oxide type semiconductor ceramics which are employed for the construction of a secondary electron multiplying device. The fundamental construction of the device provides a molded article with at least one hole which is so designed that, as the electrically charged particles or X-rays, etc. are introduced through the hole, the secondary electron multiplying action in the body is guaranteed, the molded article being produced from zinc oxide-titanium oxide type semiconductor ceramics. Further, in order that the molded article may perform secondary electron multiplying action, a direct current voltage must be applied in the same direction as the hole, and for this purpose, at least two electrodes made of a suitable conductive material are provided either at both its ends or suitable spots. When a direct current voltage of suitable magnitude is applied through the electrodes in the same direction as the hole, the charged particles or X-rays, etc. introduced into the said hole from the cathode side impinge against the inside wall of the hole, thereby causing emission of secondary electrons. The secondary electrons having been emitted, in turn, immediately impinge on the inside wall, and thus the secondary electron emitting actions are performed repeatedly; while this sequence of actions proceeds, the number of electrons increases in geometrical progression and the electrons travel to the anode.

Preferred embodiments, which are merely by way of examples, of the present invention will be hereinafter described. It will be appreciated that the shape or construction of molded articles having at least one hole is not limited to the embodiments thereof. An example of

the simplest construction of the molded article is a cylindrical shape. Besides this, various shapes and constructions of the molded article can be devised, like the ones which are shown as the embodiments of the present invention in the subsequent description and the accompanying drawings; other examples of the molded article the ones of with other shapes or constructions, which possess substantially the same action as those stated above, are also conceivable.

The invention will be further apparent from the following description with reference to the embodiments thereof as illustrated in the accompanying drawings.

In the drawings:

FIG. 1 is a perspective view of one embodiment of the present invention, showing a cylindrical tube constituted of a zinc-oxide-titanium oxide type semiconductor ceramic;

FIG. 2 is a perspective view of another embodiment, showing a bundle of a plurality of cylindrical tubes;

FIG. 3 is a perspective view of another embodiment, showing a bundle of a plurality of triangular tubes;

FIG. 4 is a perspective view of another embodiment, showing a plurality of cylindrical tubes twisted together;

FIG. 5 is a perspective view showing an embodiment of a bundle of a plurality of octagonal tubes, alternate sides of which have concave arc-shaped cross sections;

FIG. 6 is a perspective view of another embodiment, showing a bundle of a plurality of a hexagonal tubes;

FIG. 7 is a perspective view of still another embodiment, showing a molded article constituted of a zinc oxide-titanium oxide type semiconductor ceramic, with a plurality of holes bored in the molded article, thereby substantially realizing the unified effects of a group of tubes and thus effectively creating a group of tubes;

FIG. 8 is a schematic diagram illustrating an example of a circuit for operational experiments with respect to the device of the embodiment of the present invention; and

FIG. 9 is a diagram showing the voltage-gain characteristics of the secondary electron multiplying device according to the present invention.

As described above, the fundamental construction of the device according to the present invention is to provide a molded article with at least one hole, the molded article being produced from a zinc oxide-titanium oxide type semiconductor ceramic.

The unit which is illustrated in FIG. 1 is one example of the device of the present invention as set up in the simplest construction. The entire body of the cylindrical tube 10 is constituted of a zinc oxide-titanium oxide type semiconductor ceramic. The inside wall of the hole 13, is, of course, constituted of a zinc oxide-titanium oxide type semiconductor ceramic. Because this material possesses remarkable secondary electron emissivity as has been described in the foregoing, this inside wall of the hole itself functions, as it stands, as the secondary electron emitting and multiplying surface. No restrictions whatever are conceived to be imposed on the construction or shape of this tube. It makes no substantial difference if the tube is in polygonal form or of any other contour. In FIG. 1, there is shown a straight tube, but this may well be varied into recessed arc-shape, or else modified in such a way that it can be bent at one or more portions of the body. The possibility of variation of the tube contour or configuration will be exemplified by a number of embodiments

which follow. Although the exterior periphery of the entire tube may optionally be coated with a material, the whole or at least some parts of the interior walls have to be exposed. In the vicinity of both ends of the cylindrical tube 10, there are provided the electrodes 11 and 12, which are formed by a coating of conductive silver paint. The positions of these electrodes 11 and 12 are not limited to both ends of the tube. They may be mounted at preferred localities other than the extreme ends. As for the quality of the electrode material, it only needs be of a conductive type. Thus, a material such as non-electrically plated nickel layer, baked silver, indium alloy, conductive carbon paint, evaporated tin film or sprayed aluminum film may be employed in place of conductive silver paint. To the electrodes 11 and 12, a direct current voltage of about 100 to 1,000 volts per 1 cm is applied in the longitudinal direction of the tube. When the electrons are introduced from the cathode side to the inside of the hole 13, the electrons will repeat sequentially the actions of impingement, and secondary electron emission and while repeating these actions, the number of electrons is cumulatively multiplied, and at length they travel to the anode. These electrons are collected by means of a suitable collector provided close to the anode.

As one of the additional characteristics of the present invention, the device may be built up by stacking and binding up a plurality of tubes all of equal length; and by doing so, better functional effects are obtainable.

The exemplary embodiments shown in the five figures, FIG. 2 through FIG. 6 clearly indicate some of the configurations of such tubes. The one shown in FIG. 2 represents the primarily fundamental aspect of configuration, in which a plurality of tubes 20 (three in the drawing) are bound together; at both ends of the sheaf of the tubes, the electrodes 21 and 22 are provided. The entire body of each cylindrical tube 20 is constituted of a zinc oxide-titanium oxide type semiconductor ceramic which has a uniform distribution of resistivity, so that both the interior and exterior surfaces of the cylindrical tube 20 have secondary electron emitting properties. Accordingly, not only each of the surfaces inside of the hole 23 of the cylindrical tube 20, but also each clearance space 24 between the respectively adjacent cylindrical tubes 20, can likewise be fully utilized since the tubes have the capability of secondary electron multiplying functions, this resulting in an extremely high electron multiplying sensitivity and resolving power which are obtained in actual operation.

FIG. 3 shows an embodiment of the present invention in which a plurality of tubes 30 of triangular shape (three in the drawing) are stacked and fastened together into a pyramidal configuration, and to both ends of the tubes electrodes 31 and 32 are mounted. With this construction, like the case of FIG. 2 not only the inside surfaces of the hole 33 of the triangular tubes 30 but also the space 34 between the adjacent tubes can produce the secondary electron multiplying function. Further, as illustrated in FIG. 4, it is also feasible to twist together a plurality of tubes 40 (three in the drawing). Comparing this construction with that of linear tubes, it is possible for this construction to repress the positive feedback of positive ions from the collector side; furthermore, the effective length of the duct which actually functions as the electron emitting tube, in contrast with the merely apparent length of the entire body, can be lengthened which, in turn, affords

such advantages as stabilization of functional operation and increased gain of electron multiplication. FIG. 5 also shows an embodiment of the present invention in which a plurality of octagonal tubes 50 (four in the drawing) are bound together in one sheaf. Each individual member tube of the above is of such a contour that every second side is arc-shaped. According to this construction, a clearance space 54 at the center of the four octagonal tubes 50 can be formed into a circular shape in section which is exactly the same in dimensions or area as hole 53 of the octagonal tube 50; hence, as both can be utilized as secondary electron emitting tubes, such a configuration is particularly suitable for use as one element of an image intensifier which requires strict uniformity and regularity of picture elements. Numerals 51 and 52 represent the electrodes.

FIG. 6 shows one embodiment of the invention in which a plurality of tubes 60 (five in the drawing), each tube is hexagonal in shape and each hole 63 is circular in shape, are bound together; this is an example where the space between the respective tubes of the tube group can be successfully eliminated. Further, the exemplary embodiments shown in FIGS. 5 and 6 can, of course, be used with their bodies being twisted or bent when so necessary or so required, as in the configuration shown in FIG. 4. The embodiment shown in FIG. 7 indicates a configuration such that a plurality of holes 73 are bored on the plate 70 which is constituted of a zinc oxide-titanium oxide type semiconductor ceramic, normally to the electrodes 71 and 72, which makes it possible to perform substantially the same function as in the case where a group of plural tubes are stacked or bound up together for an overall mobilized function.

FIG. 8 illustrates an exemplary circuit to be used when operating the device according to the present invention. In this circuit, the power source 83 is connected between the cathode 81 and the anode 82 positioned at both ends of the cylindrical tube 80 which is constituted of a zinc oxide-titanium oxide type semiconductor ceramic and is bent into recessed arc-shape, the electrodes being provided with a coating with conductive silver paint. The power source 83 is intended for applying a direct current voltage on the cylindrical tube 80. The electrons 86 emitted from the filament 85 which is connected to the power source 84, the source exclusively assigned for filament, are accelerated by the electron accelerating power source 87, and then are driven from the cathode 81 to and into the cylindrical tube 80. Upon entering the tube, the electrons are immediately caused to repeat sequentially the functions of impinging and of emitting secondary electrons, inside the tube, thus multiplying the number of electrons; the multiplied electrons are successively driven out of the anode 82. These electrons are collected by the collector 89 which is positioned at the gap d (around 1 mm) which is located just opposite to the anode 82 in a position such as to enable connection with the collector power source 88. After having thus been collected, the number of these electrons is counted by means of the electron counter 90. These units of the device (which are situated in the section encircled by the broken line in FIG. 8; provided that the power source and the electron counter are excluded therefrom) are disposed in a vacuum.

Explanation will now be given with respect to one example of the voltage gain characteristics of the device

according to the present invention, reference being made to FIG. 9.

The compounds zinc oxide, titanium oxide and aluminum oxide are used as the starting materials. These materials are weighed so that the specimens will have the compositional proportions shown in Table 1. These materials are then mixed by the wet process in a pot mill lined with polyethylene using agate pebbles with pure water for about 20 hours. After the mixture is dried, it is milled and is passed through a sieve in order to obtain a particle sizes of 50 to 200 mesh.

TABLE 1

Material Number	Mol ratio of basic composition		
	ZnO	TiO ₂	Al ₂ O ₃
1	72.5	27.5	0.0
2	72.5	27.5	1.25

The powder obtained is added to a suitable amount of binder constituted of paste of wheat flour and paraffin and is formed into a plastic substance. Then the plastic substance is molded into a tubular shape by extrusion molding. The material is placed in an alumina case the bottom of which is covered with a semiconductor ceramic powder having the same properties as the materials and is fired in an electric furnace, which has a SiC heating element, at a temperature of about 1,360° C, for about 1 hour. The semiconductor ceramics are obtained, material No. 1 having volume resistivity at room temperature of $8 \times 10^6 \Omega \text{ cm}$ and material No. 2, $2.8 \times 10^6 \Omega \text{ cm}$. FIG. 9 shows the gain-voltage characteristics of the device according to the present invention.

A cylindrical tube of the device was provided with electrodes formed by coating conductive silver paint on both ends, the tube had an inner diameter of 1.3 mm, an outer diameter of 3 mm, a length of 98 mm and with a radius of curvature of 20 mm. The device was placed in a vacuum of 10^{-5} torr. In the circuit shown in FIG. 8, the voltage of the collector power source 88 was 200 volts, and the voltage of the electron accelerating power source 87 was 200 volts. The solid lines 1 and 2 in FIG. 9 show the voltage gain characteristics of material No. 1 and material No. 2, respectively. The broken line 3 shows the gain-voltage characteristics of a conventional device in which tin oxide-antimony oxide is deposited as thin film on the inside wall of a glass tube.

The present invention permits the provision of an extremely simplified construction of an electron multiplying device, and entirely dispenses with the intricacies of the work of forming the thin layer of high resistant substance on the inside wall of the tube unit, which has hitherto had to be done; further, the device according to the present invention is capable of achieving a secondary electron multiplying gain factor of 10^7 to 10^9 (see FIG. 9).

A still further advantage of the invention is that, as nearly all the parts of the secondary electron multiplying tubes are constituted of semiconductor ceramics of a highly unified ingredient distribution the device as a whole is free of deterioration, exhaustion or detrition, despite the continued impingements or striking by the electrons; further, the device is admirably robust and stabilized, mechanically as well as chemically, thus efficiently secures endurance for long-time use. Also, even in the event when any damage or chipping may have been inflicted upon the part of tube due to some cause of other during usage, mending or reconditioning can

be done very simply by bonding the damaged part with a conductive bonding agent, and this will suffice, because the tube unit is constituted of unadulterated semiconductor ceramics.

In the case of the conventional device, for the material of a thin layer, it has been common practice to use highly resistant substances having negative resistance temperature characteristics. Therefore, when a high voltage was applied to those types of layers, the self-exothermic action was accelerated, thus not infrequently leading to the possibility of the occurrence of self-heating failure. It has been necessary in the conventional devices, to keep the resistance value of the thin layer material in a high range, in an attempt to lower the current flowing inside this layer down to as small a level as practicable. However, if the resistance value is held in an excessively high range, the thin layer is liable to deteriorate, losing the true qualities of a semiconductor, and finally may be reduced to almost a dielectric. When the thin layer is in this state, the electric charge may be detrimentally accumulated and followed by a space charge, thus resulting in a harmful increase in the time constant. These disadvantages inevitably necessitate the allowable range of resistance to be narrowed, thus rendering the manufacturing process and more difficult and intricate. Conversely, in the device according to the present invention, since the fundamental principle is to use a zinc oxide-titanium oxide type semiconductor ceramic having positive or slightly negative resistance temperature characteristic, the device possesses the self-guarding functions which effectively restrict current-flow by repressing self-heating caused by large impressed voltages. There is no fear of thermal runaway with the device of the invention, and thus, the device is able to provide an increased gain of electron multiplication by applying high voltage.

Further, when such conventional devices are used, it is necessary to heat the whole zone in which the device is placed and to eliminate gas (baking operation). Though the conventional type of thin layer is accompanied by rapid deterioration of gain and performance, when the temperature is over 150° C, the device according to the present invention as compared with the conventional device has the advantage that there is no change of the gain and performance even if the temperature is in the range of about 150° C to about 250° C, and it can be seen that the same effects as described above are achieved even though the inventive device is operated at a high temperature, beyond 150° C.

In the cases of the embodiments in which tube units are bound together as illustrated in the five figures, FIG. 2 through FIG. 6, excellent functional effects can be additionally realized in comparison with the conventional type tubes constructed by binding the glass tubes or like together. That is, in the cases embodying the manufacturing methods of the conventional multipliers in which glass or vitreous tube units are stacked or bound up, various difficulties have been encountered, for example, the potential distribution of the individual tube is affected by the resistivity distribution of each tube, so that, in order to obtain the effectively workable image intensifier, it has been mandatory that the resistivity distribution characteristics be made uniform. Contrary thereto, in the present invention, since the whole unit is of semiconductor constitution, when the respective tubes are bound into one sheaf, the individual electron multiplying surfaces are in parallel; there-

fore, there may exist a certain extent of dispersion of resistivity distribution (or, assuming an extreme case, even though there might be chipping or a break on the tube body), the potential distribution may effectively be unified to advantage.

Still a further advantage of the tube unit of the present invention is that when there is a clearance space between the respectively adjacent cylindrical tubes, it also can be utilized just as effectively as the secondary electron multiplier tubes (see FIGS. 2, 3 and 5), thus resulting in extremely high density, high stability, high gain, high sensitivity, high efficiency and high resolving power which are obtained through actual operation.

Another advantage of the tube unit of the present invention is that when the electrodes are to be provided at both ends of the tube group or bank, there is no need of providing them to each individual tube in advance, but instead, it will suffice to mount the electrodes at the end faces at the same time, after the tubes have been bound up together to a complete sheaf as desired. Also, in practice, the electrodes are mounted at the end faces alone as shown in FIGS. 4 and 6; but it is not absolutely necessary to mount them there, and they may be placed at other spots such as the side portions. These advantages of expediency and simplicity are ascribable to the merit that the tube body set up according to the present invention is conductive in its entirety.

In the case of the embodiment shown in FIG. 7, substantially the same effects as above can be obtained. In this connection, it is to be emphasized that one of the features of the present invention is that the tube constitution as stated above is very easy to manufacture, and such ease of working solely comes from the intrinsic nature of the employed material. In order to achieve this with conventional type tubes using glass or other insulating material, it is extremely difficult and it would require prohibitively high costs. According to the present invention, the stated construction of the tube unit can be easily produced at low cost in any desired or preferred shape or construction, because the material is ceramic. From this it follows that the constitution according to the present invention is very well suited for mass production.

The secondary electron multiplying device of this invention is of great use as a general-purpose secondary electron multiplier tube, particularly for various kinds of electrically charged particles (e.g. electrons, positive ions, negative ions), X-rays, radio active rays, etc. or for output designing projects, or further, setting up a suitable photo-electric converter, it is suitable for use as a photo-electron multiplier. Additionally, the embodiments shown in FIG. 2 through FIG. 7 are especially applicable to wide uses. These are suitable for image intensifiers which require high resolving power, high stability and high sensitivity such as X-ray (hard and soft) image intensifying and observing apparatuses. Also, in the device of the present invention, the secondary electron emitting substance is the entire body of the molded article itself, and not mere thin layer, so that it is much more efficacious than the thin layer type, especially when applied to the working or handling of hard X-rays and radio active rays.

While preferred embodiments of the invention have been shown and described in detail to illustrate the application of the principles of this invention, it is to be understood that the invention is not limited to these

embodiments and may have other various embodiments without departing from these principles.

What I claim is:

1. A secondary electron multiplying device comprising a molded article having at least one hole therethrough and at least two electrodes of conductive material on said molded article, said molded article being made of a zinc oxide-titanium oxide type semiconductor ceramic.

2. A secondary electron multiplying device according to claim 1 wherein the molded article is a rectangular block with electrodes on opposite faces thereof and has a plurality of holes therethrough perpendicular to the electrodes.

3. A secondary electron multiplying device according to claim 1, wherein the molded article is a tube.

4. A secondary electron multiplying device according to claim 3, wherein said tube is cylindrically shaped.

5. A secondary electron multiplying device according to claim 3, wherein said tube is polygonally shaped.

6. A secondary electron multiplying device comprising a plurality of hollow tubes each being of a zinc oxide-titanium oxide semiconductor ceramic and each having two electrodes of a conductive material thereon, said tubes being arranged in a bundle.

7. A secondary electron multiplying device according to claim 6, wherein said tubes are cylindrical and straight.

8. A secondary electron multiplying device according to claim 6, wherein said tubes are triangular in cross section and straight and are stacked in the shape of a pyramid and define triangular cross sectional spaces between every set of three stacked tubes.

9. A secondary electron multiplying device according to claim 6, wherein said tubes are polygonal tubes having grooves in some of the sides, and wherein the arrangement of the tubes is such that said grooves lie opposite grooves in adjacent tubes in the bundle to form holes through said bundle.

10. A secondary electron multiplying device according to claim 6, wherein the tubes are mutually twisted around each other.

11. A secondary electron multiplying device according to claim 6, wherein said zinc oxide-titanium oxide type semiconductor ceramic contains zinc oxide in a mol percentage of about 50 to 99 percent mol and titanium oxide in a mol percentage of about 1 to 50 mol %.

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