

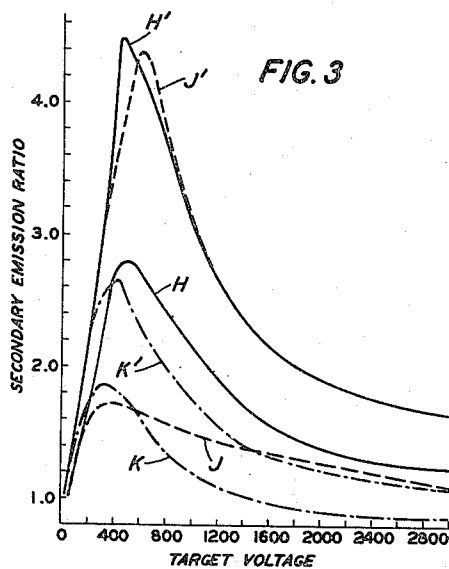
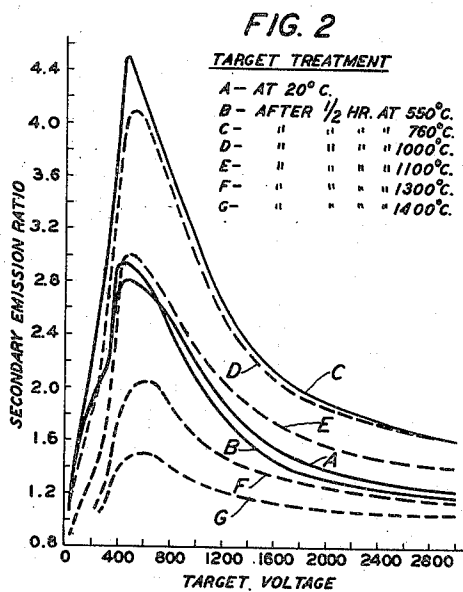
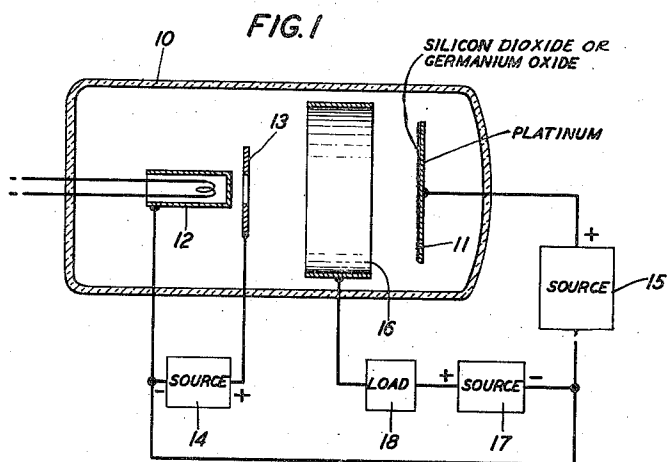
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L. E. CHEESMAN ET AL
SECONDARY ELECTRON EMITTER

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2 Sheets-Sheet 1



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FIG. 4

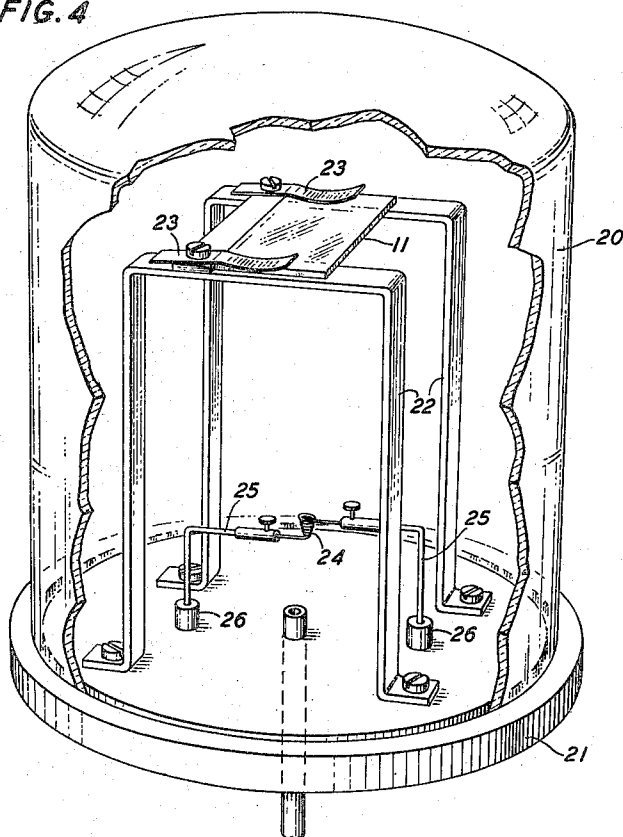


FIG. 5

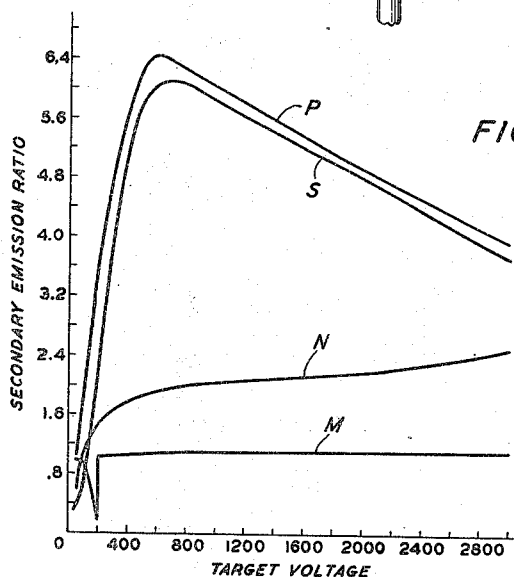
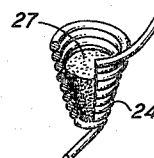


FIG. 6

TARGET TREATMENT

- M - AT ROOM TEMPERATURE
- N - AFTER 700°C. FOR 30 MINUTES (HOT)
- P - AFTER 850°C. FOR 15 MINUTES AND THEN AT 700°C. FOR 30 MINUTES (HOT)
- S - AFTER 850°C. FOR 15 MINUTES AND THEN AT 600°C. FOR 30 MINUTES (COLD)

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UNITED STATES PATENT OFFICE

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SECONDARY ELECTRON EMITTER

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This invention relates to secondary electron emissive electrodes and to methods of making such electrodes.

One general object of this invention is to improve electron discharge devices including one or more secondary electron emissive target electrodes. More specifically, objects of this invention are to obtain large secondary emission ratios for such electrodes, increase the stability and operating life of secondary electron emissive elements and enable attainment of prescribed emissive ratios for such elements.

It has been discovered that oxides of semi-conductive materials, such as silicon and germanium, which oxides normally are highly insulating but very poorly secondary electron emissive, can be treated so that high emission ratios, for example of the order of five, are obtainable therefor. More specifically, it has been discovered that such oxides in the form of layers or thin films upon a base of metal containing small amounts or traces of impurities can be rendered highly secondary electron emissive by proper heat treatment of the oxide-base unit. Further, secondary emission ratios within a range of values can be realized by correlation of the thickness of the oxide film and the time and temperature of the heat treatment.

In one illustrative embodiment of this invention, a target electrode comprises a film of silicon dioxide upon a base of commercially pure platinum. For a film thickness of 100 angstrom units and heat treatment of the oxide-base unit at 760° C. for one-half hour, a secondary emission ratio of substantially 4.6 at a primary electron voltage of about 450 volts is obtained.

In another illustrative embodiment of this invention, a target electrode comprises a layer of germanium oxide upon a commercially pure platinum base. A layer of one milligram per square centimeter corresponding to a thickness of about 10^{-4} centimeters, heat treated at about 700° C. for about one hour, exhibits a secondary electron emission ratio of substantially 6 at a primary electron voltage of about 650 volts.

Comparable emission ratios are obtained for silica and germania films upon chemically pure platinum.

The invention and the various features thereof will be understood more clearly and fully from the following detailed description with reference to the accompanying drawing in which:

Fig. 1 is a diagram of an electron discharge device illustrative of those in which target electrodes constructed in accordance with this invention may be utilized;

Fig. 2 is a graph illustrating the relation between the secondary electron emission ratio of a 100-angstrom silicon dioxide film on a commercially pure platinum base, and the primary volt-

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age, for various heat treatments of the film-base unit;

Fig. 3 is another graph illustrating the secondary emission ratio-primary voltage relation for silicon dioxide films of several thicknesses on commercially pure and chemically pure platinum for different heat treatments;

Fig. 4 is a perspective view of apparatus for producing silicon dioxide films upon a metal base;

Fig. 5 is a perspective view of the crucible included in the apparatus shown in Fig. 4; and

Fig. 6 is a graph showing secondary emission characteristics for germanium oxide upon a platinum base.

Referring now to the drawing, the electron discharge device illustrated in Fig. 1 comprises a highly evacuated enclosing vessel 10 having therein a target electrode 11 and an electron gun which, for purposes of simplicity, is shown as comprising an indirectly heated cathode 12 and an accelerating electrode 13 maintained positive with respect to the cathode by a source 14. It will be understood that the gun may be of well-known construction and projects an electron stream toward the target electrode 11. The target electrode 11 is maintained at a positive potential relative to the electron gun by a direct-current source 15, poled as shown, the potential being variable if desired to control the energy of the primary electrons striking the target electrode. Opposite the target electrode is a collector electrode 16 which may be cylindrical, as shown, and is biased positive relative to the target electrode by a direct-current source 17. A load 18 is connected between the electrodes 11 and 16, the current to the load 18 being determined by the number of secondary electrons emanating from the target and received by the collector electrode 16.

The target electrode 11 comprises, as indicated in Fig. 1, a metallic base, described hereinafter, having on the face thereof toward the electron gun 12, 13, a film of substantially pure silicon dioxide or germanium oxide. Such a film of silicon dioxide may be formed by vapor deposition of the film material, under vacuum, upon the base. Suitable apparatus for such deposition is illustrated in Fig. 4 and comprises a vessel 20 evacuated during the process to of the order of 10^{-5} millimeters of mercury. Mounted within the vessel 20 and upon a base 21 are a pair of brackets 22 upon which the base member of the target is removably held, as by spring clips 23. In juxtaposition to the target base is a basket or crucible 24 of pure refractory material, for example of tungsten wire and conical as shown, which is supported by leading-in conductors 25 extending from terminals 26 affixed to the base 21. The crucible or basket 24 has therein a predetermined quantity of crushed silicon dioxide, indicated at

27 in Fig. 5, the quantity determining the thickness of the film deposited.

In the process, the crucible is heated, by passage of current therethrough, to a temperature sufficient to vaporize the material therein. For example, in the case of silica, the temperature may be about 2000° C. which is sufficiently low to preclude any substantial evaporation of the tungsten, whereby substantially pure silicon dioxide is deposited upon the target base. The time required for evaporation and deposition of a silica film of the order of 50 to 200 angstroms thick is about 15 seconds. As noted heretofore, the thickness of the deposited film is determined by quantity of charge. In one illustrative case, a charge of 2 milligrams of crushed silica produces a layer of a uniform thickness of 100 angstroms over an area of 6 square centimeters upon the target base, the silica being evaporated by heating of the tungsten wire crucible at 2000° C. for 15 seconds, the crucible having an included angle of about 30 degrees.

After deposition of the film upon the base, the target element is heated in an inert atmosphere or vacuum, for example by passage of a current therethrough, or in a furnace. The effects of such treatment of targets comprising films of silica upon a platinum base will be appreciated from a consideration of Figs. 2 and 3. In the former, the relationships between secondary emission ratio and primary electron voltage for a target comprising a 100-angstrom thick film on a base of commercially pure platinum after different heat treatments, are indicated. The measurements represented graphically were made with the target at room temperature.

It will be noted from Fig. 2 that the primary electron voltage at which the maximum secondary emission ratio obtains is substantially the same, about 450 volts, for all the cases represented but that the magnitude of the emission ratio varies markedly with the previous target treatment. Specifically, it will be noted that for the target at room temperature, i. e. without heat treatment (curve A), the maximum emission ratio is slightly below 3, whereas for a target previously heated one-half hour at 760° C. (curve C), the maximum emission ratio is about 4.5, an increase of over 50 per cent. The treatment at a temperature of about 760° C. results in the optimum ratio for, as indicated by the curves B and D to G, treatment at lower or higher temperatures results in a smaller emission ratio. Treatment at the higher temperatures of a target previously heated to about 760° C. results in deactivation of the target.

It appears that the enhanced secondary emission ratio obtained by the heat treatment as described hereinabove is attributable to activation of the silica by donor impurities present in the platinum base. Analyses show that commercial platinum contains a number of impurities in the following approximate ranges:

Tin, palladium—0.01–0.3 per cent
Copper—trace, less than 0.3 per cent
Gold, iron, manganese, nickel, lead—slight trace, less than 0.005 per cent
Barium, manganese, silicon—very slight trace, less than .001 per cent

and that chemically pure platinum, in general, contains the same impurities but in amounts an order of magnitude less than in commercially pure platinum. The ranges are indicated below:

Tin, palladium—trace, less than 0.03 per cent
Copper—slight trace, less than 0.005 per cent
Gold, barium, manganese, silicon—very slight trace, less than .001 per cent

This explanation of the enhanced emission ratios is consistent with results obtained, some of which are illustrated in Fig. 3. In this figure, curve H shows the emission ratio-primary electron voltage relation for a target comprising a 100-angstrom film of silica upon a base of commercially pure platinum, without heat treatment and curve H' shows the relation for the same target after heating at 750° C. for one-half hour. These, it will be noted, correspond to curves A and C of Fig. 2. Curve J indicates the relation mentioned for a target of a 50-angstrom film upon a chemically pure platinum base, without heat treatment; curve J' is for this same target after heat treatment at 750° C. for 20 hours. It will be noted that the treatment results in a maximum emission ratio substantially the same as that for the target represented by curve H'.

Curves K and K' are for a target comprising a 200-angstrom film of silicon dioxide upon a base of commercially pure platinum, the base having been used previously in a target having a silica film thereon heated to 750° C. and then deactivated. Curve K indicates the emission characteristic for the 200-angstrom target without heat treatment; curve K' shows this characteristic for the same target after heating it for 14 hours at about 750° C.

As indicated hereinabove, chemically pure platinum contains lesser amounts of impurities than commercially pure material. It is to be expected, therefore, that the former has available fewer donors which can diffuse into the silica to activate it so that longer heat treatment of the target is necessary to produce emission ratios comparable to that for a base of commercially pure platinum. This is supported by curves J and J' of Fig. 3.

Similarly, in the case of a second use of a base, it is to be expected that the amounts of impurities remaining for diffusion into the silica are less than in the first use so that longer heat treatment is required to enhance the secondary emissive ratio. This is substantiated by curves K and K'.

As has been indicated hereinbefore, germanium oxide also may be utilized, in accordance with this invention. The film or layer may be formed upon a commercially or chemically pure platinum base by vaporization of germanium dioxide in the same manner as described above for silicon dioxide. It may be formed also by spraying germanium dioxide in a suitable binder, for example nitro-cellulose, upon the base and removing the binder by heating the base-film unit.

Fig. 6 illustrates the secondary emission-primary voltage characteristics of a target having thereon a film or layer of 1 milligram per square centimeter of germanium dioxide, applied to a commercially pure platinum base by spraying as noted hereinabove. Curve M illustrates the secondary emission of the target at room temperature, i. e. before heat treatment, the curve N after heating at 700° C. for 30 minutes, before activation is complete. In both cases, it will be noted, the secondary emission ratios are small.

Curve P shows the characteristics of the target, measured at 700° C., after heating at 850° C. for 15 minutes and then at 700° C. for 30 minutes.

The maximum secondary emission ratio of about 6.4 at a primary electron voltage of about 600 volts is to be noted particularly. The secondary emission characteristics for the target at room temperature after heating at 850° C. for 15 minutes and then at 600° C. for 30 minutes are shown by curve S.

It is evident from Fig. 6 that heating of the germanium oxide-platinum target enhances the secondary emission and that very marked increase in this ratio results from heat treatment at the order of 600° C. to 850° C. These increases may be explained, as in the case of silicon dioxide, by activation of the germanium oxide by migration therein of impurity donors from the platinum.

Although specific embodiments of the invention have been shown and described, it will be understood that they are but illustrative and that various modifications may be made therein without departing from the scope and spirit of this invention.

What is claimed is:

1. The method of making a secondary electron emitter which comprises applying to a base of substantially pure metal having only a small fraction of one per cent of impurity therein, a film of an oxide selected from the group consisting of silicon dioxide and germanium oxide, and heating the composite unit to effect diffusion of the impurity from the base into the oxide.

2. The method of enhancing the secondary electron emissive ratio of an oxide selected from the group consisting of silicon dioxide and germanium oxide, which comprises heating the oxide in the presence of an impurity to diffuse the impurity therein.

3. The method of making a secondary electron emitter which comprises applying to a base of platinum having a fraction of one per cent of impurity therein, a coating of an oxide selected from the group consisting of silicon dioxide and germanium dioxide, and heating the composite unit at a temperature of the order of 700° C.

4. The method of making a secondary electron emitter which comprises applying to a platinum base a film of silicon dioxide between 50 and 200 angstroms thick, and heating the composite body at a temperature of substantially 760° C. for between about one-half and about 20 hours.

5. The method of making a secondary electron emitter which comprises forming a film of silicon dioxide on a base of commercially pure platinum, and heating the composite unit to a temperature of the order of 760° C.

6. The method of making a secondary electron emitter which comprises applying a film of silicon dioxide about 100 angstroms thick to a base of commercially pure platinum, and heating the composite unit for approximately one-half hour at a temperature of substantially 760° C.

7. The method of making a secondary electron emitter which comprises applying a film of silicon dioxide to a base of chemically pure platinum, and heating the composite unit at about 760° C.

8. A secondary electron emissive target for

electron discharge devices comprising a substantially pure metal base having therein a fraction of one per cent of impurity, and a film on said base of an oxide selected from the group consisting of silicon dioxide and germanium dioxide.

9. A secondary electron emissive target for electron discharge devices comprising a platinum base, and a coating of silicon dioxide thereon.

10. A secondary electron emissive target for electron discharge devices comprising a platinum base, and a film of silicon dioxide between about 50 and 100 angstroms thick on said base.

11. A secondary electron emissive target for electron discharge devices comprising a base of commercially pure platinum, and a film of silicon dioxide between about 50 and 100 angstroms thick upon said base.

12. A secondary electron emissive target for electron discharge devices comprising a base of chemically pure platinum, and a film of silicon dioxide of the order of 50 angstroms thick upon said base.

13. The method of making a secondary electron emitter which comprises forming a layer of germanium oxide upon a base of metal having an impurity therein, and heating the oxide-base element at a temperature of the order of 600° C. to 850° C.

14. The method of making a secondary electron emitter which comprises forming a layer of germanium oxide upon a base of platinum containing impurity, and heating the composite unit at a temperature of about 850° C. for about 15 minutes.

15. The method of making a secondary electron emitter which comprises forming a film of germanium dioxide upon a base of commercially pure platinum, heating the composite unit at a temperature of the order of 850° C. for about 15 minutes, and then heating said unit at a temperature of the order of 600° C. to 700° C. for about 30 minutes.

16. A secondary electron emissive electrode for electron discharge devices comprising a metal base, and a layer of germanium oxide on said base.

17. A secondary electron emissive electrode for electron discharge devices comprising a base of platinum, and a layer of germanium oxide on said base.

18. A secondary electron emissive electrode for electron discharge devices comprising a base of commercially pure platinum, and a layer of germanium dioxide on said base.

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