April 23, 1968 H. J. HANNAM 3,379,566

METHOD OF MAKING A POLYCRYSTALLINE DUAL LAYERED ALUMINUM OXIDE-MAGNESIUM OXIDE STORAGE ELECTRODE

Original Filed May 19, 1960

FIG. 1.

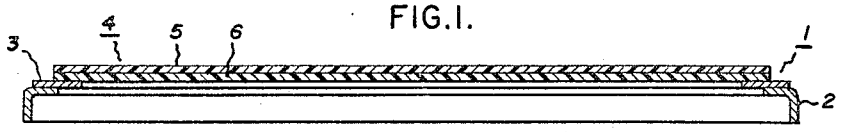


FIG. 3.

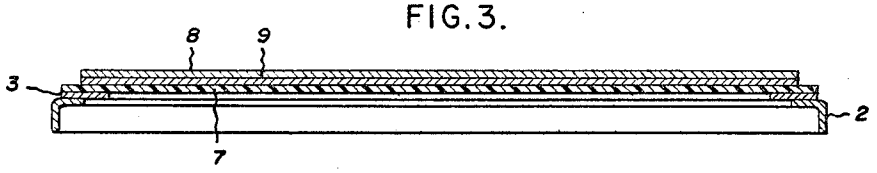


FIG. 4.

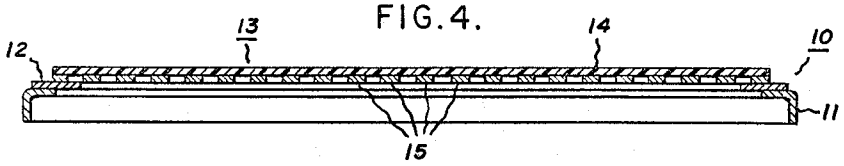


FIG. 2.

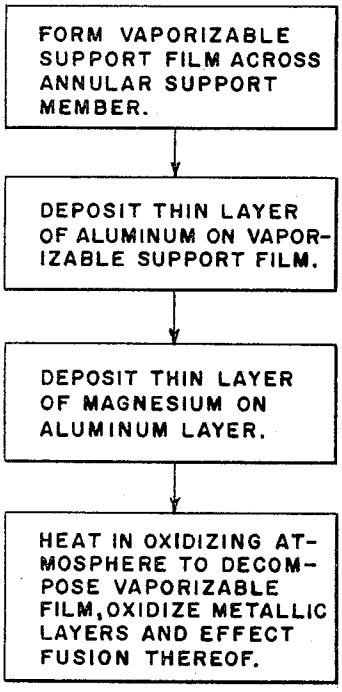
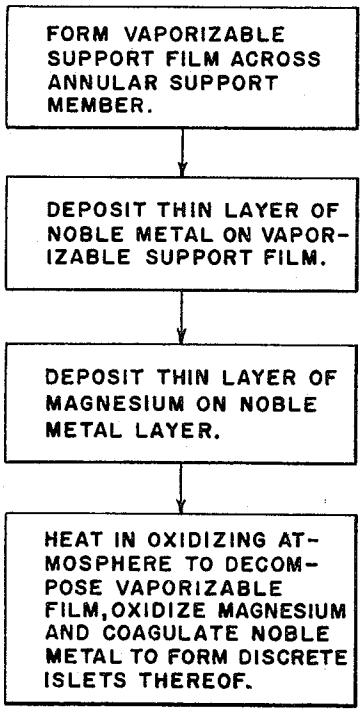


FIG. 5.



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METHOD OF MAKING A POLYCRYSTALLINE DUAL LAYERED ALUMINUM OXIDE-MAGNESIUM OXIDE STORAGE ELECTRODE

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Original application May 19, 1960, Ser. No. 30,153, now Patent No. 3,207,937, dated Sept. 21, 1965. Divided and this application June 4, 1965, Ser. No. 461,239

4 Claims. (Cl. 117—210)

This application is a divisional application of co-pending application Ser. No. 30,153 Hannam, filed May 19, 1960, and now Patent Number 3,207,937, and assigned to the same assignee as the present invention.

My invention relates to improved thin film storage target electrodes of the type for use in producing a point-by-point electric charge pattern corresponding to a visual image or other information to be converted to electrical signals by scanning a target electrode with an electron beam. More particularly, my invention relates to an improved thin-film target electrode and improved methods of manufacturing same.

In my U.S. Patent 2,922,907 issued Jan. 26, 1960, and assigned to the same assignee as the present invention there is disclosed and claimed a thin-film storage target structure comprising an annular support member and an extremely thin taut low mass storage membrane of homogeneous polycrystalline magnesium oxide extending across the annular support member and supported solely at its periphery by said support member. This target is adapted for extremely high sensitivity, improved resolution and high resonant frequencies for avoiding undesirable mechanical vibrations and resultant unwanted electrical signal modulations.

In manufacturing the above-described type of target electrode, it is desirable to increase the tension of the membrane to raise the resonant frequency thereof to desirable high amounts and to reduce the amplitude of vibration to a desirable low amount. Additionally, it is desirable to reduce graininess of the membrane material to avoid detection of the grains in images transmitted with such targets.

The present invention contemplates improved target electrodes and improved methods of manufacturing same which will afford thin film target structures adapted for all of the above-noted desirable properties of my prior device and further adapted for substantially increased membrane tension, reduction in graininess with resultant improved electrical characteristics, and greater ease of manufacture.

Accordingly, a primary object of my invention is to provide new and improved target electrode assemblies including improved target membranes therein.

Another object of my invention is to provide new and improved target structures including new and improved composite thin-film target membranes adapted for improved electrical characteristics.

Another object of my invention is to provide new and improved target structures including new and improved thin-film target electrodes adapted for increased resonant frequencies, reduced amplitude of vibration and reduced membrane graininess.

Another object of my invention is to provide new and improved methods for manufacturing thin-film targets.

Another object of my invention is to provide new and improved storage target electrodes and improved methods of manufacturing same, whereby manufacturing shrinkage is reduced substantially.

Further objects and advantages of my invention will become apparent as the following description proceeds and the features of novelty which characterize my invention will be pointed out with particularity in the claims annexed to and forming part of this specification.

In carrying out the objects of my invention, I provide a target electrode including an annular support member corresponding in diameter or transverse dimension generally to the diameter of a mesh electrode usually used with a target electrode. Extending tautly across the annular electrode support and supported solely thereby is a composite membrane comprising a first layer of a homogeneous polycrystalline magnesium oxide and a second layer of a material selected from the group consisting essentially of the noble metals and a metal from Group III of the Periodic Table of Elements, for example homogeneous polycrystalline aluminum oxide. The target electrode can be manufactured by first forming a vaporizable support film on an annular support member, depositing an aluminum barrier on the support film, then depositing a magnesium coating on the aluminum, and then heating the assembly in an oxidizing atmosphere to decompose the vaporizable support film and to convert the aluminum to homogeneous polycrystalline aluminum oxide and the magnesium to homogeneous polycrystalline magnesium oxide, thereby to leave a taut composite polycrystalline aluminum oxide and magnesium oxide membrane supported solely by the annular support member. Alternatively, the target electrode can be manufactured by first forming a vaporizable support film on an annular support member, depositing noble metal barrier on the support film, then depositing a magnesium coating on the noble metal layer, and then heating the assembly in an oxidizing atmosphere to decompose the vaporizable support film, to convert the magnesium to homogeneous polycrystalline magnesium oxide and to coagulate the noble metal to form a layer of a myriad of discrete islets of noble metal fused to the surface of the magnesium oxide.

For a better understanding of my invention reference may be had to the accompanying drawing in which:

FIG. 1 is an enlarged sectional view of a storage target constructed in accordance with one embodiment of my invention and wherein the thicknesses of the various layers of material are shown exaggeratedly for ease of illustration;

FIG. 2 is a flow chart illustrating the steps in one method of manufacturing a target electrode according to my invention;

FIG. 3 is an enlarged sectional view of a target structure illustrating the structure at a particular point in the method of manufacture;

FIG. 4 is an enlarged sectional view of a storage target electrode constructed in accordance with a modified form of my invention; and

FIG. 5 is a flow chart illustrating the steps involved in another method of manufacturing a target electrode according to my invention.

Referring to the drawings, there is shown in FIG. 1 a storage target structure generally designated **1** and constructed according to one embodiment of my invention. The target **1** includes a first annular support member **2** to the upper surface of which is suitably secured a second annular support member or ring electrode **3**. If desired these members may be integral and constitute a unitary element.

Extending across the ring **3** and supported solely thereby is a composite transparent semi-conductive membrane generally designated **4**. The membrane **4** includes a first layer **5** of a homogeneous polycrystalline oxide which is semi-conductive and adapted for substantially straight through grain boundary electron conduction and a superposed fused second layer **6** of a material which is adapted for maintaining the desired through conductivity

of the oxide layer and for lower secondary electron emissivity than the mentioned oxide layer.

Preferably the membrane 4 is constructed such that the first layer 5 consists of interconnected granules of homogeneous polycrystalline magnesium oxide and the second layer 6 consists of interconnected granules of homogeneous polycrystalline aluminum oxide fused by a reaction product to the granules of the magnesium oxide layer. The magnesium oxide granules are formed of magnesium oxide crystallites of approximately 300 angstroms. The overall thickness of the composite membrane 4 is between approximately 500 and approximately 1000 angstroms and preferably about 750 angstroms. Additionally, the thickness of the second or aluminum oxide layer is between approximately 0.5% and approximately 10% of the overall thickness of the membrane. Preferably the thickness of the second layer is between approximately 1% and approximately 3% of the overall thickness of the membrane.

The target structure 1 is adapted for being incorporated in a target electrode assembly of the type disclosed and claimed in my above-noted patent which includes an election-permeable mesh supported in closely spaced parallel relation with the magnesium oxide layer, and the assembly is adapted for use in a camera tube structure of the type illustrated in my mentioned patent, for example an image orthicon tube. In such a device the magnesium oxide surface is exposed to the photocathode in the head or front end of the tube and the aluminum oxide surface is exposed to the electron beam usually emanating from the opposite end of the tube. In the target electrode illustrated, the membrane 4 is extremely taut and the exposed surface of the magnesium oxide layer 5 is fine grained and substantially free of mottling with the grains being up to approximately only 10 microns. This fine graininess reduces the presence of substantially large grain boundaries in the membrane which are subject to greater secondary emission and thus can undesirably appear on a transmitted image. The aluminum oxide layer 6 is also adapted for through electron conductivity and, thus, does not subtract from the desirable electrical characteristics of the magnesium oxide. Additionally, the aluminum oxide is adapted for less secondary electron emission than magnesium oxide and, thus, is better suited for exposure to impinging electrons from the beam and also serves to minimize the appearance of grain boundaries in a transmitted image.

In accordance with one method of constructing the target electrode of FIG. 1, and as outlined in the chart shown in FIG. 2, a suitable thin vaporizable film which can advantageously be nitrocellulose is formed across the annular support member 3 as illustrated at 7 in FIG. 3. The vaporizable film 7 can be formed by first dropping onto the surface of a pan of water a small quantity of nitrocellulose dissolved in a suitable organic solvent such as amyl acetate. This solution spreads on the surface of the water to a thin film due to surface tension and the solvent evaporates, leaving a plastic film on the surface of the water. Thereafter, the membrane support ring 3 which has been placed in the water either prior to formation of the film or which is immersed in the water at the outer portion of the film, is raised gently to pick up the film on the surface of the ring.

After the film has been dried completely on the ring, the ring is placed in an evaporator and a thin coating of aluminum shown at 8 in FIG. 3 is evaporated on the plastic film to a thickness up to that corresponding to approximately 2% to 35% optical opacity.

Subsequently, a magnesium coating 9 is evaporated on the aluminum coating. The thickness of the magnesium thus evaporated on the aluminum is determined by the desired mechanical and electrical characteristics of the target electrode and is controlled to provide the desired through electron conductivity and proportions of the finished oxide layers described above.

Thereafter, the structure is placed in an oven and heated in an oxidizing atmosphere which can be air, starting at a temperature of approximately 170° centigrade and terminating at temperature of about 430° centigrade with the heating continuing for a period in the order of approximately 5 hours. This baking step serves to decompose and vaporize the nitrocellulose film which disappears completely and is also effective for converting the aluminum to homogeneous polycrystalline aluminum oxide and the magnesium to homogeneous polycrystalline magnesium oxide and for fusing the resultant layers of the interconnected crystalline oxide granules to provide the above-described composite self-sustaining homogeneous polycrystalline oxide membrane adapted for being supported solely at its periphery by the support ring. Additionally, the membrane is of substantially greater tautness and the grain size of the magnesium oxide constituting the layer thereof is uniformly substantially finer than that obtained with the prior method involving depositing the magnesium directly on the vaporizable film during the formation process.

As presently understood, the increased tightness of the membrane and the desirable fineness of the grain structure of the magnesium oxide is due to several aspects of my invention. First, the deposition of the metallic aluminum on the plastic film before deposition of the magnesium is believed to provide a smoother, more planar and a more water-free surface upon which the evaporating magnesium lands during deposition thereof. These conditions of the surface upon which the magnesium is deposited are believed to contribute substantially to the increased tightness of the membrane and the smoother, more fine-grained texture of the magnesium oxide layer obtainable with my method. Additionally, aluminum does not react with nitrocellulose as readily as magnesium. Thus, it is believed that the metallic aluminum layer deposited on the vaporizable film for the evaporization thereon of metallic magnesium serves as a barrier between the magnesium and the vaporizable film material, thereby to avoid reactions between the hot magnesium and water in the thin film or the breakdown of organic compounds in the film. It is believed that such reactions of hot magnesium and water and breakdown of the film material can have the undesirable effect of increased grain size and reduction of the tension of magnesium oxide. It is also believed that these reactions may occur during subsequent processing of the electron structure as when magnesium is oxidized by baking in an oxidizing atmosphere.

The aluminum layer serves as an effective barrier during the evaporation of the magnesium and during subsequent processing to avoid the undesirable reactions with the water-carrying film and decomposition products of the vaporizable film material and thus serves to retard grain growth for improving the grain structure and to afford a tighter membrane. Additionally, the use of aluminum is highly desirable because when converted to an oxide it too is adapted for high lateral resistance and high straight through electron conductivity comparable to that of the magnesium oxide. Thus, the aluminum oxide is ineffective for electrically shunting discrete points of the magnesium oxide layer and thus does not subtract from the desired electrical characteristics of the magnesium oxide layer. Additionally, and as pointed out above, the aluminum oxide layer is characterized by lower secondary emissivity than the magnesium oxide and thus is better adapted for use on the electron-beam-impinged side of the membrane.

Illustrated in FIG. 4 is a modified form of my improved target electrode generally designated 10. This structure is also adapted for the same applications as the structure disclosed and claimed in my above-noted patent. Additionally, the structure also includes first and second annular support members 11 and 12, respectively. Extending across the member 12 is a composite storage membrane generally designated 13 including a semi-conduc-

tive layer **14** and a layer comprising a myriad of discrete islets **15** of non-oxidizing conductive material such as a noble metal, for example gold fused to one surface of the layer **14**. The layer **14** is constituted of interconnected granules of a homogeneous polycrystalline oxide which is self-sustaining in that it is adapted for being supported solely at its periphery. Additionally, it is semi-conducting and adapted for substantially straight through electron conduction. The islets **15**, by being discrete for forming a discontinuous conductive surface are rendered ineffective for electrically shunting the discrete points on the layer **14** and thus do not subtract from the desired through electron conductivity of the oxide layer. Additionally, the islets **15** are formed of a material having a lower secondary emissivity than the oxide layer.

Preferably, the structure in FIG. 4 includes a first layer **14** of homogeneous polycrystalline magnesium oxide and a fused second layer of a noble metal subdivided into a myriad of discrete islets or coagulations. The overall thickness of the composite membrane **13** is between approximately 500 and approximately 1000 angstroms and preferably about 750 angstroms. Additionally, the thickness of the layer of islets **15** is between approximately 1% and 10% and preferably approximately 5% of the overall thickness of the membrane. In this embodiment of my invention also, the membrane **13** is extremely taut and the magnesium oxide layer **14** is substantially free of mottling and is fined-grained in that the grain size is up to approximately only 10 microns. This fine graininess also reduces substantially the presence of large grain boundaries in the membrane which would be subject to greater secondary emission and thus could appear on a transmitted image. Additionally, in this structure the noble metal is a lower secondary emitter than the magnesium oxide and thus is better adapted for impingement by the electron beam. As pointed out above, the fact that the noble metal is broken up into a myriad of discrete mutually spaced and thus electrically isolated islets renders the noble metal ineffective for electrically shunting discrete points on the first layer which would adversely affect the electrical characteristics of the oxide layer.

Outlined in FIG. 5 is one preferred method whereby I construct the target electrode of FIG. 4. This method includes a step of forming a vaporizable film across the annular support member **12** which can be carried out in the same manner as that described above in connection with the construction of the electrode of FIG. 1. After the vaporizable film has been formed and completely dried the support is placed in an evaporator and a layer of from approximately 10 to approximately 100 angstroms of a noble metal such as gold is deposited on the vaporizable film. Thereafter, a magnesium coating is evaporated on the noble metal layer. The thickness of the magnesium thus deposited is determined by the desired through electron conductivity and the mechanical and electrical characteristics of the target electrode and is controlled to provide the desired properties of the finished composite membrane structure described above. At this point of the process of manufacture the unfinished structure has an arrangement of layers of material and an appearance comparable to that shown in FIG. 3.

Subsequently, the assembly is subjected to the same heating step as described above in connection with the structure in FIG. 1. This has the desirable effect of decomposing and vaporizing the plastic support film and converting the magnesium to a homogeneous polycrystalline magnesium oxide which is self-sustaining in that it requires only peripheral support as provided by the annular support member **3**. During the heating process the noble metal serves as a barrier between the magnesium and nitrocellulose in the same manner as the aluminum in the first-described method, thereby to provide a taut membrane having a fine-grained magnesium oxide surface and for providing a low secondary emission surface facing the photocathode in a camera tube.

At the elevated temperature and after the noble meta has served its function as a barrier means, the noble meta coagulates to form a discontinuous film or a layer of a myriad of discrete islets **15** on and fused to the surface of the magnesium oxide. The discontinuous nature of this film, or the electrical isolation of the discrete islets, insures against adverse effects on the through conductivity of the magnesium oxide in the manner described above Additionally, the islets **15** have low secondary emissivity relative to that of the magnesium oxide which is desirable for a surface exposed to beam impingement.

In addition to providing target electrodes of increased membrane tightness and improved surface textures my above-described methods facilitate and reduce the cost of manufacture. Specifically, nitrocellulose films of lower grades than previously required can be used in view of the fact that the evaporating magnesium in the present methods do not "see" or become deposited on the nitrocellulose and, thus, costly adverse effects by the nitrocellulose on the magnesium oxide are reduced substantially. Additionally, the magnesium evaporation rate can be slowed down considerably during the deposition step due to the fact that the interposed metal barrier or layer prevents the evaporating magnesium from liberating gas from the plastic support member.

While I have shown and described specific embodiments of my invention I do not desire my invention to be limited to the particular forms shown and described; and I intend by the appended claims to cover all modifications within the spirit and scope of my invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of manufacturing a storage electrode comprising the steps of forming a vaporizable support film across a support member, depositing on said film a first layer of a noble metal which does not readily react with the ingredients of said support film, depositing a layer of metallic magnesium on said first layer of metal, and heating the assembly in an oxidizing atmosphere to decompose and vaporize said vaporizable film and to convert said magnesium to a taut homogeneous polycrystalline magnesium oxide member supported by said support member, said heating step further results in coagulating said noble metal to provide a discontinuous layer constituted of a myriad of discrete noble metal islets fused to the surface of said magnesium oxide.

2. The method of manufacturing a storage electrode comprising the steps of forming a vaporizable support film across a support member, depositing on said film a first layer of aluminum which does not readily react with the ingredients of said support film, depositing a layer of metallic magnesium on said aluminum layer, and heating the assembly in an oxidizing atmosphere to decompose and vaporize said vaporizable film and to convert said magnesium to a taut homogeneous polycrystalline magnesium oxide member supported by said support members, said heating step further results in converting said aluminum to a layer of homogeneous polycrystalline aluminum oxide fused to said layer of magnesium oxide and constitutes therewith said taut membrane.

3. A method of manufacturing a storage electrode comprising the steps of forming a vaporizable support film across an annular support member, depositing on said film a layer of aluminum from approximately 2% to approximately 35% optical opacity, depositing a layer of metallic magnesium on said aluminum layer, and heating the assembly in an oxidizing atmosphere commencing at approximately 170° C., increasing to approximately 430° C. and continuing for a period of approximately 5 hours, whereby said vaporizable film is decomposed and completely vaporized, said aluminum is converted to homogeneous polycrystalline aluminum oxide and said magnesium is converted to a layer of homogeneous polycrystalline magnesium oxide fused to said aluminum oxide layer and constituting therewith a taut composite storage

membrane wherein said magnesium oxide is granular and has a grain size up to approximately only 10 microns.

4. The method of manufacturing a target electrode comprising the steps of forming a vaporizable support film across an annular support member, depositing on said film a layer of a noble metal of approximately 10 to approximately 100 angstroms, depositing a layer of metallic magnesium on said layer of noble metal, and heating said assembly in an oxidizing atmosphere commencing at approximately 170° C., increasing to approximately 430° C. and continuing for a period of approximately 5 hours, whereby said vaporizable film is decomposed and completely vaporized, said magnesium is converted to a homogeneous polycrystalline magnesium oxide membrane supported solely by said annular support member, and said noble metal is subdivided into a myriad of discrete islets fused to said magnesium oxide layer.

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