

May 21, 1963

R. P. WELLINGER

3,090,881

STORAGE TARGET ELECTRODE AND METHOD OF MANUFACTURE

Filed May 19, 1960

FIG.1.

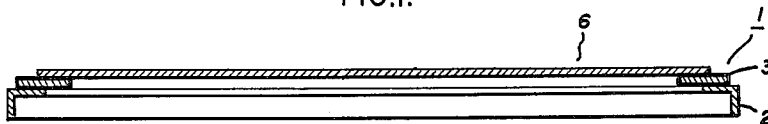
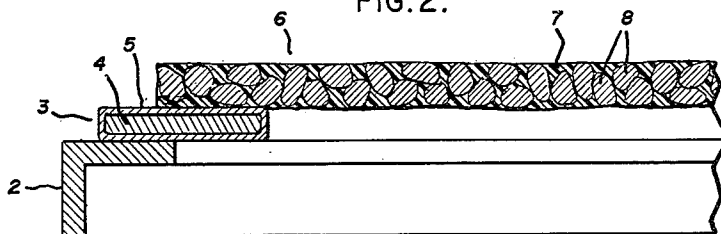


FIG.2.



INVENTOR:
ROGER P. WELLINGER,
BY *Philip Z. Schlam*
HIS ATTORNEY.

1

3,090,881 STORAGE TARGET ELECTRODE AND METHOD OF MANUFACTURE

Roger Paul Wellinger, Scotia, N.Y., assignor to General Electric Company, a corporation of New York
Filed May 19, 1960, Ser. No. 30,152
7 Claims. (Cl. 313-68)

My invention relates to an improved storage target electrode of the type for use in producing a point-by-point charge pattern corresponding to a visual image or other information to be converted to electrical signals by scanning the 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 U.S. Patent 2,922,907 issued January 26, 1960, and copending divisional application Serial Number 838,012 filed August 18, 1959, now U.S. Patent 3,032,859 both of which are in the name of Herbert J. Hannam and are assigned to the same assignee as the present invention, there are disclosed and claimed a thin-film storage target structure and methods of making same. The patent target structure comprises an annular support member and an extremely low-mass thin-film storage membrane of a homogeneous polycrystalline low-mass thin-film storage membrane of a homogeneous polycrystalline oxide extending across the annular support member and supported solely at its periphery by the support member. This type of structure is particularly adapted for extremely high sensitivity and improved resolution. Additionally, it is particularly adapted for high resonant frequencies to avoid undesirable mechanical vibrations and resultant unwanted electric signal modulations. The methods disclosed and claimed in the mentioned Hannam application are effective for forming the described thin-film target.

In manufacturing the above-described type of target electrode, it is desirable to insure sufficient tensioning of the membranes so as to maintain the resonant frequency thereof at a desirable high amount thereby to insure that the amplitude of vibrations will be maintained desirably low. Additionally, it is desirable to reduce the grain size of the oxide grains in the target membrane to avoid detection of grain boundary lines in images transmitted by such targets. Further, it is desirable to avoid adverse effects on the electrical characteristics of targets which can result from materials evolving from the target support means and depositing on the membrane during processing and operation.

In co-pending application Serial Number 30,153 of H. J. Hannam filed May 19, 1960, and assigned to the same assignee as the present invention are disclosed and claimed improved target electrodes and manufacturing methods which are adapted for obtaining some of the above-noted desiderata. The present invention contemplates another improved target electrode and other improved manufacturing methods which are also adapted for obtaining such desiderata. Additionally, the present invention contemplates the provision of an improved target electrode assembly including improved membrane support means adapted for overcoming the above-noted adverse effects on the electrical characteristics of targets resulting from material evolving from the target support.

Accordingly, a primary object of my invention is to provide a new and improved target electrode assembly and a new and improved target membrane therein.

Another object of my invention is to provide a new and improved target structure including a new and improved

2

thin-film target membrane adapted for improved performance.

Another object of my invention is to provide a new and improved thin-film target electrode adapted for increased resonant frequency, reduced amplitudes of vibration and substantially reduced membrane graininess.

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

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 storage target structure 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 across the support member and supported solely thereby is a membrane of approximately 500 to approximately 1000 angstroms thick formed of a layer of interconnected fine-grained homogeneous polycrystalline magnesium oxide held taut by a glassy phase oxide binder filling the interstices between the crystalline oxide grains for enhancing the adhesion of the crystalline oxide grains. The target electrode can be manufactured according to several methods of my invention all of which involve, in one form or another, the introduction into the process of forming the membrane, of an oxide or hydroxide ingredient which is caused to wet the crystalline oxide and provide the glassy phase binder in the finished article.

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

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

FIGURE 2 is an enlarged fragmentary sectional view illustrating in detail the structure of my improved target assembly.

Referring to the drawing, there is shown in FIGURE 1 a storage target assembly generally designated 1 and constructed according to an embodiment of my invention. The target 1 includes a first annular support member 2 to the upper surface of which is secured a second annular support member or ring 3. As better seen in FIGURE 2, the ring 3 includes a core 4 formed preferably of molybdenum and bearing a coating 5 formed of a metal which is highly oxidation resistant and preferably has a low vapor pressure. The particular structure and purpose of the described ring 3 will be brought out in greater detail hereinafter.

Extending across the ring 3 is a transparent semi-conductive membrane generally designated 6. The membrane 6 is formed basically of a layer of interconnected fine-grained homogeneous polycrystalline oxide which is semi-conducting and adapted for substantially straight through electron conduction along the boundaries between the grains. Preferably the grains are homogeneous polycrystalline magnesium oxide having an average grain size up to approximately only 10 microns and the thickness of the membrane 6 is between approximately 500 angstroms and approximately 1000 angstroms and preferably about 750 angstroms. Additionally, the membrane 6 is self-sustaining in that it is adapted for being supported solely at its periphery by the ring 3.

To this point the membrane 6 is substantially identical to that disclosed in the above-noted Hannam patent. My invention differs from the patented Hannam structure, however, in that it provides a binding agent present in the interstices between the granules of the membrane 6 which binding agent insures tautness of the membrane. In some cases the tightening can be up to approximately 10 times greater than where no binder is used.

More specifically, and as illustrated exaggeratedly in FIGURE 2, the binder comprises a viscous phase or glassy phase which is indicated at 7 and both fills the interstices between the individual grains of oxide crystals indicated at 8 and extends over the exposed surfaces of some of the grains 8. Thus, the glassy phase 7 gives the membrane a glassy, smooth appearance. However, the glassy phase is of a material and of such thinness on the exposed surfaces of the oxide granules as not to subtract from the desired substantially straight through grain boundary conduction of electrons through the membrane. In other words, the binder 7 serves to tighten the membrane without detracting from the desired electrical characteristics of the thin homogeneous polycrystalline magnesium oxide of which the membrane is basically formed.

The binder 7 can advantageously comprise the glassy phases of the oxides and hydroxides of boron, silicon, calcium, strontium, barium, sodium, lithium, potassium, germanium and combinations thereof. Hereinafter for ease of reference this group of materials will be referred to as the "preferred group."

The methods of my invention and whereby the membrane structure of FIGURES 1 and 2 can be formed are all directed to membrane-forming processes into which is introduced a compound adapted for providing the described glassy phase binder between the crystalline oxide granules and, in most cases, for reducing the grain size or retarding the grain growth of the polycrystalline oxide during oxidation. In accordance with my invention the compound for forming the glassy phase can be introduced into the process before the granular polycrystalline oxide portion of the membrane is formed. Thus, the glassy phase forming ingredient will be present during the formation of the polycrystalline oxide portion of the membrane to assist in retarding grain growth and thus determining the final grain size of the polycrystalline oxide and to insure satisfactory permeation of the interstices between the oxide grains by the glassy phase binder. Alternatively, the glassy phase forming compound can be introduced into the process of manufacturing the membrane of FIGURES 1 and 2 after the granular polycrystalline oxide portion of the membrane is formed. In this case the compound will still be present for forming the glassy phase binder in the interstices between the polycrystalline oxide grains. Thus, the important feature of my invention involving the reaction between the glassy phase forming compound and the granular polycrystalline oxide, or wetting of the crystalline oxide by the glassy phase, can be accomplished by various methods of introducing the mentioned glassy phase forming oxide so long as it is present and heated in association with the granular polycrystalline oxide which can be either while the polycrystalline oxide is forming into a membrane or after it has been formed as a membrane.

Several specific methods of forming a tightened storage membrane according to my invention are as follows:

Method #1

One method of manufacturing a storage membrane according to my invention involves dissolving a compound of materials selected from the above-noted preferred group in a nitrocellulose solvent. The resultant solution is then used as a thinner for nitrocellulose and the thusly thinned nitrocellulose is used to form a vaporizable support film on an annular support member which thus carries the mentioned compound from the preferred group. Subsequently, a magnesium coating is

provided on the support film and the assembly is heated in an oxidizing atmosphere to decompose the vaporizable film, convert the magnesium to a fine-grain homogeneous polycrystalline magnesium oxide membrane and to convert the compound in the vaporizable film to the glassy phase binding agent between the grains of the crystalline oxide constituting the major portion of the membrane. In the processing, the mentioned compound also serves in causing the grain size to be smaller than would be obtained in the absence of such compound.

By way of a specific example of this method, one can dissolve either boron oxide or boron hydroxide up to complete saturation in a common nitrocellulose solvent such as butyl acetate. Preferably, the concentration is approximately .25 part of the compound to approximately 1000 parts of the solvent by weight.

Subsequently, a quantity of nitrocellulose is thinned with the solvent bearing the mentioned compound in a proportion of approximately 0.1% to 10% by weight. Thereafter, a small quantity of the thusly thinned nitrocellulose is dropped onto the surface of a pan of water. This solution spreads out on the surface of the water and into a thin film due to surface tension and the solvent evaporates, leaving a plastic film bearing the oxide compound 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 under vacuum a thin layer of metallic magnesium is formed on one side of the vaporizable film. The thickness of the magnesium coating thus evaporated on the film is determined by the desired mechanical and electrical characteristics of the target electrode and is controlled to provide a finished target membrane of the above-discussed desired thickness.

Thereafter, the assembly is placed in an oven and heated in an oxidizing atmosphere, which can be air, at a temperature of approximately 480° C. up to approximately 520° C. for a period of approximately 3 hours. This baking step serves to decompose and vaporize the nitrocellulose film, to convert the magnesium to a fine-grained homogeneous polycrystalline magnesium oxide and to convert the boron oxide borne by the nitrocellulose to a glassy substantially clear translucent medium or binder which appears between the interstices of the oxide granules and extends in a very thin amount over the grains. This gives the membrane a substantially glassy appearance. Additionally, as discussed above, the binder can serve to tighten the membrane up to approximately 10 times greater than obtainable some membranes composed of essentially only magnesium oxide. Still further, while the binder is a glassy substance and extends to some degree over the surfaces of the individual oxide granules, it does not subtract from the above-described desired electric characteristics of the membrane, including the substantially straight through grain boundary electron conduction.

Method #2

Another method of manufacturing a storage tube membrane according to my invention also involves dissolving a compound of material from the above-noted preferred group in a solvent thereof. Then a vaporizable nitrocellulose support film is provided on an annular support and the film is coated, either before or after the deposition of a magnesium layer thereon, with the compound-bearing solution either by spraying or dipping. The solvent in that solution is preferably a poor solvent for nitrocellulose to avoid adverse effects when applied to the nitrocellulose support film. Following this operation the assembly is baked in an oxidizing atmosphere for

the same duration and the same temperature described above in respect to Method #1.

According to the present method, a plain nitrocellulose solvent, or in other words one to which no oxide compound has been added, is used for forming the thin plastic support film on the surface of a pan of water. Then the film is picked up on the support ring in the manner described above.

After the film has dried on the ring it can, for example, be coated with a solution of boron or boron hydroxide and water or alcohol. Preferably, this coating step is accomplished by spraying the solution in a fine mist or haze on the support film. This method avoids undesirable spot formation or relatively large marks which can result due to uneven drying.

Alternatively, the coating of the support film with the oxide-carrying solution can be effected by dipping. When dipping is employed, and if alcohol is utilized as the compound solvent, the dipping operation is preferably carried out in successive steps. Specifically, the film can be first dipped into a five percent concentration of alcohol in pure water, then into a ten percent alcohol-water solution, then twenty percent, thirty percent, forty percent and fifty percent and up to sixty percent solution of alcohol and water, with all such solutions bearing some of the oxide compound from the preferred group of materials noted above and preferably in amounts up to saturation.

Subsequently, a layer of magnesium is evaporated on the vaporizable support film and the assembly is baked in an oxidizing atmosphere for preferably the same time duration and at preferably the same temperatures described above in connection with Method #1. This thermal treatment results in the formation of a target electrode identical in structure and purpose to that described above and illustrated in FIGURES 1 and 2.

As indicated above, the spraying or dipping operation whereby the oxide compound for the binder is deposited on the support film can take place after the metallic magnesium layer is deposited on the vaporizable film. Following such a step a thermal treatment of the assembly identical to that described above is carried out. This procedure is also effective for affording the presence of the glassy phase binder in the finished article for tightening the polycrystalline oxide membrane and for cooperating in providing reduced graininess of the membrane. Additionally, the finished article obtained with this method is also identical in structure and purpose to that shown in FIGURES 1 and 2.

Method #3

Another method according to my invention involves depositing a dry oxide or hydroxide, instead of an oxide solution, on the vaporizable support film before or after the evaporation thereon of the metallic magnesium.

Specifically, this method of my invention involves first forming a plain nitrocellulose thin plastic film on a support ring in the same manner as described above. After the film is dry on the ring it can, for example, be coated by evaporation with a deposit of boron oxide or hydroxide. Due to the extreme thinness of the deposition employed it is extremely difficult to determine the optimum thickness of the oxide or hydroxide thus deposited. However, by weighting the deposition and measuring the time and temperature of the evaporation process it has been estimated that the thicknesses of these materials attributing best results are on the order of approximately 1000 angstroms. The temperature of the evaporating vessel is of the order of approximately 800° centigrade to approximately 1200° centigrade when satisfactory deposition is obtained. Also, the time duration of evaporation is preferably of the order of approximately 10 seconds to approximately 300 seconds.

Additionally, the desired oxide or hydroxide deposition can be obtained by evaporating in a vacuum either the elemental metal, the oxides or the hydroxides of boron. The choice of whether a metal, oxide or an hydroxide will be used in forming the desired oxide deposition depends essentially on the ease of evaporation thereof. It is to be noted, however, that when the elemental metal is evaporated it converts in transit to the film and deposits as an oxide if oxygen is present or as an hydroxide if water is present. If oxygen is not present it will convert to provide the desired oxidized deposition upon subjection to an oxidizing atmosphere.

Following evaporation of the oxide on the support film, the magnesium is evaporated on the oxide coating. It is not essential to follow this sequence of deposition of materials inasmuch as the invention is also effective in providing tightened films when the magnesium is deposited on the support film before the oxide. However, the deposition of the oxide or hydroxide coating before the magnesium is preferred in that the resultant graininess and the overall yield are more satisfactory when this procedure is followed.

In the just-described method the atmosphere surrounding the assembly can be let down to air or, in other words, normal atmosphere can be admitted into the evaporating equipment after deposition of the oxide. However, if desired, the oxide or hydroxide deposition can be conducted in vacuum and can be followed immediately by evaporation of magnesium on the coating without letting any air or any other atmosphere into the evaporation equipment. This simplifies the procedure and has a further beneficial effect of preventing formation of a surface film on the oxide. Additionally, this procedure leads to taut targets as well as desirably finer grain structure.

The thermal treatment of the thus formed assembly is somewhat higher than that described above. Specifically, the thermal treatment of this form of the invention preferably involves baking the assembly in an oxidizing atmosphere for approximately 2 to 3 hours at approximately 480° C. to approximately 520° C. The resultant finished article is the same in structure and purpose to that shown in FIGURES 1 and 2 and described above.

It will be understood from the foregoing that the oxides and hydroxides of the other materials from the mentioned preferred group can also be deposited on the vaporizable support film before or after the deposition of the metallic magnesium. Where necessary, the evaporating temperatures and time durations will be selected according to the material.

Method #4

Still another method according to my invention involves the addition of a glassy phase forming oxide to the target structure after the magnesium has been converted to an oxide.

This form of my invention involves first forming a target electrode by the method disclosed in the above-noted Hannam patent. Briefly, this involves providing a vaporizable film on a support ring, subsequently depositing metallic magnesium on the vaporizable film and heating the assembly in an oxidizing atmosphere starting at a temperature of about 170° C. and terminating at about 400° C. for a period in the order of approximately five hours for vaporizing the support film and converting the magnesium to a homogeneous polycrystalline magnesium oxide membrane.

According to the present form of my invention I introduce the glassy phase forming material to the assembly after the formation of a magnesium oxide membrane. Specifically, I accomplished this by placing the target constructed according to the patented Hannam invention in a vacuum chamber and therein evaporating on the magnesium oxide membrane a coating of a material selected from the above-noted preferred group of materials. The

thusly coated target is then given a thermal treatment involving baking in an oxidizing atmosphere for a period of from approximately 10 minutes to approximately 2 hours at approximately 400° C. to approximately 500° C. This procedure results in tightening the magnesium oxide membrane and the provision of a finished article having substantially all of the structural features and operational capabilities of the device of FIGURES 1 and 2.

A modified form of this method involves baking in an atmosphere other than vacuum, such as air, the already converted magnesium oxide membrane target supported above a surface on which is provided a layer of material selected from the mentioned preferred group of materials. More specifically and by way of example, a layer of the oxide material can be provided on a tray and a magnesium oxide membrane supported thereabove in closely spaced relation and thus heated in an oxidizing atmosphere for approximately 10 minutes to approximately 2 hours at approximately 400° C. to approximately 500° C. In this manner, the glassy phase binder ingredient is added to the membrane and the layer is modified to constitute a structure such as that shown in FIGURES 1 and 2 and having the same mechanical and electrical characteristics.

The target assembly including the tightened membrane described above and illustrated in FIGURES 1 and 2 is subject to thermal expansion and contraction during both processing and operation of a tube including the assembly. In order to avoid fracture of the membrane it is desirable that the support ring 3 be formed of a material having compatible expansion and contraction characteristics, such for example as molybdenum.

However, I have found that most of the materials, including molybdenum, which are desirable from expansion and contraction standpoints are subject to oxidation and when heated cause the sublimation of undesirable materials on the oxide membrane. The sublimated material appears most often as a whitish edge about the marginal portions of the membrane which limits and reduces the useful area of the target. Thus, the sublimated material is detrimental to the target and impairs performance of a tube including the target.

According to another feature of my invention, sublimation of membrane-affecting materials from the membrane support ring is minimized to a point where it has no adverse effects on the target or operation of a tube incorporating the target. More specifically, my invention involves the use of an improved membrane support ring shown in FIGURES 1 and 2. As disclosed above, the ring 3 includes a core 4. The material of the core 4 is selected for predetermined thermal expansion and contraction characteristics which are compatible with those of the membrane target. Provided on the surface of the core 4 is a coating 5 of a material which is not readily oxidized and is characterized by a very low vapor pressure. The coating material can advantageously comprise silver, platinum, gold, chromium, nickel, molybdenum silicide or any like material which will afford a surface on the membrane support ring which is highly refractory and substantially impervious to gaseous ingredients tending to evolve from the ring core material and which can result in the mentioned undesirable sublimation. Nickel plating has been found convenient and reliable with a molybdenum core.

While a nickel-plated molybdenum ring has been found highly satisfactory in overcoming the mentioned difficulty it is to be understood from the foregoing that my invention is not limited to such structure but is essentially directed to structure including a thin homogeneous polycrystalline magnesium oxide target membrane and a support ring therefor adapted for having thermal expansion and contraction characteristics compatible with those of the membrane, by having at least an outer surface of an oxidation resistant, low vapor pressure material, and further adapted for avoiding deposition of an undesirable

material on the target membrane as a result of sublimation of ingredients, such as oxide, from the material of the support. The compatibility of the support and membrane materials is such that the membrane will be to some extent maintained taut by the support but without fracturing the membrane.

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. A storage electrode comprising an annular support member, a taut membrane supported solely by said member and having a thickness of approximately 500 to approximately 1000 angstroms, said membrane consisting of a layer of interconnected granules of an homogeneous polycrystalline semi-conductive oxide characterized by substantially straight through electrical conductivity along the grain boundaries of said membrane, and a glassy phase of a material selected from the group consisting of the oxides and hydroxides of boron, silicon, calcium, strontium, barium, sodium, lithium, potassium, germanium and combinations thereof disposed in the interstices between said oxide granules, said glassy phase contributing to the tautness of said membrane and having no appreciable adverse effect on the electrical characteristics of said membrane.
2. A storage electrode comprising a taut storage membrane consisting of a layer of interconnected granules of an homogeneous polycrystalline magnesium oxide and a glassy phase of a material selected from the group consisting of the oxides and hydroxides of boron, silicon, calcium, strontium, barium, sodium, lithium, potassium, germanium and combinations thereof disposed in the interstices between said oxide granules, said glassy phase contributing to the tautness of said membrane and having no appreciable adverse effect on the electrical characteristics of said membrane.
3. A storage electrode comprising a taut storage membrane consisting of a layer of interconnected granules of an homogeneous polycrystalline magnesium oxide having a grain size up to approximately only 10 microns, a glassy phase of a material selected from the group consisting of the oxides and hydroxides of boron, silicon, calcium, strontium, barium, sodium, lithium, potassium, germanium and combinations thereof disposed in the interstices between said oxide granules, said glassy phase contributing to the tautness of said membrane and having no appreciable adverse effect on the electrical characteristics of said membrane and said membrane having an overall thickness of approximately 500 to approximately 1000 angstroms.
4. A storage electrode comprising a support member, a taut polycrystalline semi-conductive oxide membrane supported by said member, said support member having thermal expansion and contraction characteristics compatible with those of said membrane, and at least the surface portion of said support member constituting a metal characterized by high oxidation resistance and low vapor pressure.
5. A storage electrode comprising an annular support member, a taut polycrystalline semi-conductive oxide membrane extending across and supported at the periphery thereof by said support member, said support member comprising a core of a metal having substantially the same thermal expansion and contraction characteristics as said membrane, and said support member having a coating of a highly refractory material characterized by high oxidation resistance and low vapor pressure.
6. A storage electrode comprising an annular support member, a taut polycrystalline semi-conductive oxide membrane extending across and supported at the periphery thereof by said support member, said support member

comprising a core of molybdenum and a surface portion formed of a material selected from the group consisting of silver, platinum, gold, chromium, nickel, molybdenum silicide and combinations thereof.

7. A storage electrode comprising an annular support member including a molybdenum core and a coating of a highly refractory material characterized by high oxidation resistance and low vapor pressure, a taut homogeneous polycrystalline magnesium oxide membrane extend-

ing across and solely supported at the periphery thereof by said support member.

References Cited in the file of this patent

UNITED STATES PATENTS

2,743,150	Rudy	Apr. 24, 1956
2,922,907	Hannam	Jan. 26, 1960
2,926,419	Harris	Mar. 1, 1960