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ANODIC SPUTTERING

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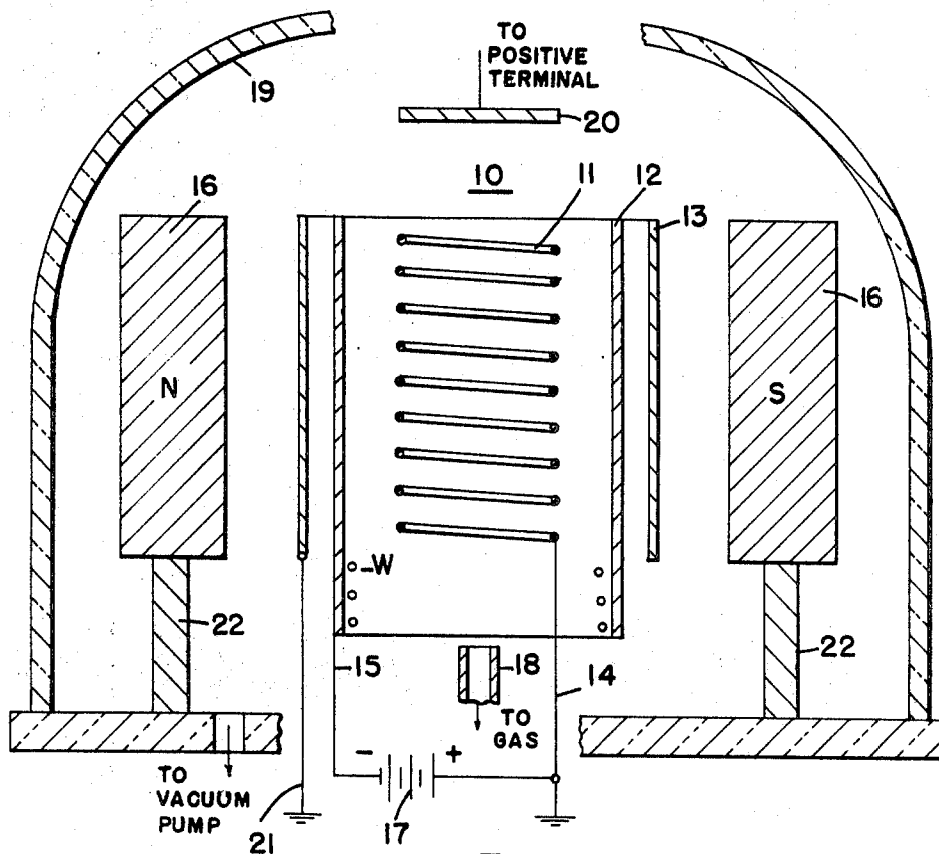


FIG. 1.

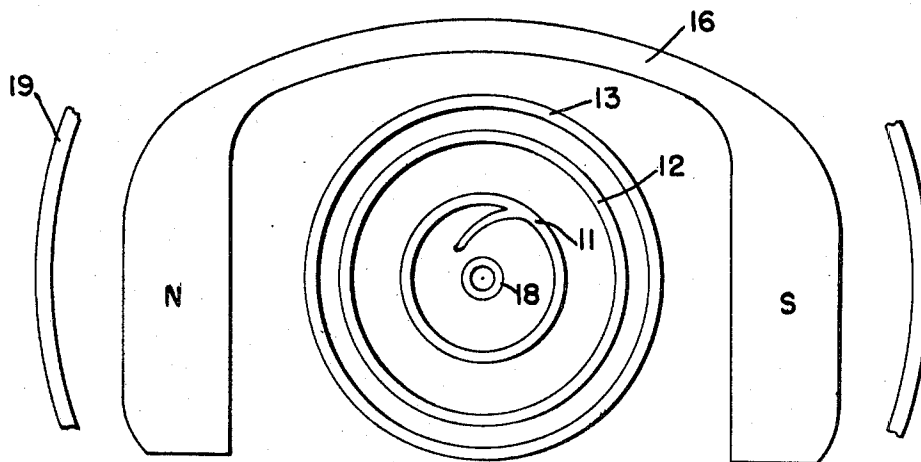


FIG. 2.

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## ANODIC SPUTTERING

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20 Claims

## ABSTRACT OF THE DISCLOSURE

Processes for anodizing or sputtering metal anodes, or for sputtering and anodizing valve metal anodes such as tantalum substantially simultaneously, by electrically connecting the anode in a vacuum vessel and controllably impacting the anode with negative ions. Anodization will occur when lower voltages are employed to propel the negative ions toward the anode whereas higher voltages will result in sputtering of the anode. Intermediate voltages will produce the phenomenon of sputtering and anodization of suitable surfaces.

Reference is hereby made to patent application Ser. No. 704,463, of Thomas A. Jennings et al., for "Negative Ion Generator," filed Feb. 9, 1968, abandoned in favor of streamlined application of Thomas A. Jennings et al., Ser. No. 37,360, filed May 5, 1970, for "Negative Ion Generator," and assigned to the same assignee of this patent application.

This invention relates to anodic phenomena and more particularly concerns the anodization and/or sputtering of suitable anode surfaces by impact with negative ions.

Cathodic sputtering, or impact evaporation, is now well known and has been used successfully in the vacuum deposition of materials and in thin film technology. This technique comprises the generation of positive ions, acceleration of these ions through an electrical potential gradient, and bombardment of a negatively charged, or cathodic surface of a material to be sputtered. Cathodic sputtering is thus a surface removal process which resembles evaporation but wherein particles of the surface are removed due to the impacting therewith of positive ions.

Cathodic sputtering techniques therefore are capable of sputtering cathodic surfaces. Cathodic sputtering cannot be used for anodizing surfaces. Anodic sputtering, however, will not only permit the anodization of suitable surfaces, if sufficiently low voltages are employed in propelling negative ions toward the surface to be anodized, but suitable surfaces may efficiently and readily be sputtered if higher voltages are employed. Similarly, both phenomena of sputtering and anodizing of suitable surfaces may result if intermediate voltages are judiciously employed.

It is therefore a broad object of this invention to provide methods for anodic sputtering.

Another object of the invention is to provide methods wherein suitable surfaces may be sputtered, or anodized, depending upon the voltages used to propel negative ions toward said surfaces.

Still another object of the invention is to provide methods wherein sputtering and anodization will occur substantially simultaneously.

The exact nature of the invention as well as other objects and advantages thereof will be readily apparent from consideration of the following specification relating to the annexed drawings wherein:

FIG. 1 illustrates a sectional view, partially diagrammatic, of the device used in practicing our invention; and

FIG. 2 is a plan view of the device of FIG. 1.

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Referring now to the drawing, there is shown a negative ion generator at 10 including a helix 11, suitably of tungsten wire, but not limited thereto. The helix illustrated is about 1.5 cm. in diameter, and is disposed within an open ended cylinder 12 of tantalum, for example, having a length of about 3.0 cm. and an inner diameter of about 1.9 cm., the cylinder wall having a thickness of about 0.002 inch to 0.020 inch. Proper cooling of the cylinder when operated at high currents will increase its lifetime, and may be accomplished conveniently by water cooled coils W, suitably of stainless steel, copper, platinum, etc., which are mounted at a lower interior portion of cylinder 12. Alternatively, fine tubing may be mounted along the outer surfaces of the cylinder. The cylinder and helix are generally concentric, but this is not a limitation, and will be spaced from each other as shown. The helix may be supported by attachment to a suitable grounded supporting structure, such, for example, as a projection from a base plate of a high vacuum chamber (not shown) or from a ground electrical conductor such as that designated at 14. A second concentric cylinder 13 surrounds cylinder 12, the distance therebetween being about  $\frac{1}{16}$  inch. Wall thickness and composition of cylinder 13 will be similar to that of 12, the latter cylinder being supported on the same grounded structure as that of the helix, or on another grounded conductor as indicated at 21, thus preventing generation of a plasma or discharge between magnet 16 and cylinder 12.

A power supply 17 shown herein as a battery, has its negative terminal connected to cylinder 12 through conductor 15 and its positive terminal connected to helix 11 through conductor 14, which, as aforementioned, is grounded. Cylinders 12 and 13 are disposed centrally in the gap of permanent magnet 16 which is capable of maintaining a magnetic field of approximately 1500 gauss. The battery 17 is capable of maintaining a potential on cylinder 12 of from 0 to -1500 volts D.C. with respect to ground. The outer wall of cylinder 12 should not be more than about  $\frac{1}{8}$  inch from the apparatus as aforesaid, and the outer wall of cylinder 13 will be approximately  $\frac{1}{16}$  inch from the magnet.

The gas which is fed into the cylinder 12 through helix 11 at inlet port 18 may be oxygen, for example, supplied by a commercially available compressed oxygen tank, or hydrogen sulfide, and the like, or alternatively, may be sulfur or arsenic vapor, and the like, which can be introduced from a heated reservoir. Our device will be contained within a bell jar 19, for example, in which one can maintain low pressures by means of a vacuum pump communicating with the bell jar. The pressure controlling equipment, sensing elements, electric and cooling means, will be connected to the bell jar chamber by techniques and components well known in the art. When toxic or unpleasant substances are used, such as sulfur, arsenic, and the like, a trap cooled by liquid nitrogen, for example, will be disposed between the bell jar and vacuum pump. The negative ions formed by our device will be attracted to an anode 20, suitably of gold, platinum, silver, copper, or a valve metal, which is maintained positive with respect to ground by means well known, or the ions, if generated in an ion propulsion system, will be ejected into free space. Magnet 16 is suitably supported on a plurality of supports 22.

In the formation of negative ions, it must be borne in mind that the electrostatic field through the center portions of the helix will be weaker than the field between the helix and the cylinder 12, and an electron population will be caused to build up in the center of the helix. The formation of negative ions by electron capture will be favored if electron energies are low, of the order of a few electron volts. As electron energies increase between

10 and 20 volts, the cross-section for dissociation of a polyatomic gas increased. The geometry of our device, in conjunction with our controlled electrostatic field, promotes this low field region, along the axis of cylinder 12, wherein large populations of low energy electrons may be sustained.

The inelastic collisions of the electrons and the oxygen gas flowing into the helix results in large quantities of negative oxygen ions being formed. As a result thereof, not only will electrons be present in the space defined by the helix, but negative oxygen ions, oxygen molecules, and even positive ions may also be present therein. Positive ions will tend to enter the space between the cylinder wall 12 and the helix 11 and will be de-ionized at this cylinder's surface. Electrons generated in this space between the cylinder 12 and helix will be accelerated into the space defined by the helix, and thus the center portion of the space defined by the helix will take on a negative space charge. This space charge and the direction of the flow of the oxygen gas toward the upper end of the cylinder, combined to cause the negative species and oxygen molecules and atoms to flow upward therewith to impact the anode.

The presence of the magnetic field aforedescribed will cause the charged species affected thereby to tend to acquire a radial motion. The radius of curvature imparted to these particles will be inversely proportional to the square root of the masses thereof. Therefore, the negative oxygen ions, being more massive than the electrons, will have a radius of curvature larger than that of the electrons, calculated to be approximately 100 fold greater thus restricting electrons from leaving the device.

As will be apparent to those skilled in this art, the composition and dimensions of our helix and cylinder may be other than those described, and that the structure of the electrostatic and magnetic fields will be altered in accordance therewith. Quite obviously, if the dimensions of the device are increased or decreased, a corresponding change in the applied potentials will be necessary. Similarly, the distance separating the cylinders from the magnet can be varied.

The rate of flow of the gas source is important. In the device illustrated, having the dimension aforediscussed, a rate of flow of oxygen between about 2500 l./sec. at 1.0 millitorr and 100 l./sec. at 100 millitorr was found satisfactory, the preferred rate being about 200 l./sec. at 70 millitorr. If the rate falls below 200 l./sec. at 1.0 millitorr, heavy oxidation of cylinder 12 will result.

Our device can be operated over a wide range of pressures which may extend from greater than 300 millitorr to as low as ultra high vacuum.

The current should not be less than 10 ma., for the dimensions described, and provisions for cooling cylinder 12 as aforedescribed should be made if the currents exceed about 100 ma.

Gas composition is limited only to the extent that the negative ion forming material must be maintained in a vapor state before and during passage through the device. It is apparent, of course, that selection of the composition of the cylinder 12 and the helix will depend on the nature of the gaseous species.

In the device illustrated, the magnetic field was 1500 gauss. However, magnetic fields as low as about 500 gauss or as high as 5000 gauss could be used advantageously.

In the actual sputtering, anodization, or where sputtering and anodization occur substantially simultaneously, on anode surfaces, the general procedure outlined below may be followed:

(1) The anode 20, of tantalum, for example, is connected to a positive terminal of a suitable electric source.

(2) The cell 19 is evacuated to a pressure substantially less than 1 millitorr.

(3) Oxygen, or other electronegative gas, is admitted to the cell through inlet port 18, at a flow rate which is controlled such that over-all cell pressure is maintained in

the range of about 10 to 100 millitorr, depending upon whether anodization, sputtering, or a combination of both is desired.

(4) The negative ion source voltage and current, and magnetic fields are adjusted to produce negative ions which are directed toward the anode.

(5) The source to anode voltage is adjusted to a value required to maintain a pre-selected anode current density.

(6) At a constant pressure, ion cathode current and voltage and anode voltage and current, the amount of material sputtered, anodized, or sputtered and anodized will depend on both the nature of the material and the period of time at which the anode is subjected to ion magnet.

The processes of our invention are further described and illustrated by the non-limiting examples hereinunder set forth:

#### EXAMPLE I

In selectively removing a gold film from an oxidized tantalum anode to obtain a required capacitance, which is a function of the surface area of the gold, the anode was placed within bell jar 19 which was evacuated to a pressure less than 1 millitorr. Oxygen was admitted into the bell jar and withdrawn by means of a vacuum pump such that a pressure therewithin of about 35 millitorr was maintained. The cathode current was maintained at about 25 ma. and the anode current density at about 5.0 ma./cm.<sup>2</sup> at 165 anode volts while the magnetic field was held constant at 1500 gauss. About 3 angstroms/minute/unit area of gold were removed using the above procedure. With this set-up, the cathode current may range from between about 10 to 80 ma.; the pressure, 10-50 millitorr; the anode current density, 0.25-10.0 ma./cm.<sup>2</sup>; and the anode voltage, 60-100 volts. The magnetic field may vary from between about 500-1500 gauss. If the magnetic field is made lower than about 500 gauss, a higher percentage of electrons would leave the ion source whereas fields in excess of about 1500 gauss would decrease the percentage.

#### EXAMPLE II

In anodizing the surface of tantalum anode, the procedure as set forth under Example I was substantially followed with the following exceptions:

The pressure was maintained at 85 millitorr, the cathode current at 80 ma., and the anode current density at 2.5 ma./cm.<sup>2</sup> at 100 volts. A layer of Ta<sub>2</sub>O<sub>5</sub> was formed at the rate of about 30 Å per minute. In anodizing, using this set-up, the pressure may effectively range between about 10-100 millitorr; cathode current, about 10-80 ma.; anode current density, 0.25-50.0 ma./cm.<sup>2</sup>; anode voltage, 60-100 volts; magnetic field, 500-1500 gauss.

#### EXAMPLE III

In removing gold from an oxidized tantalum anode and substantially anodizing the tantalum surface from where the gold was removed, the procedure as set forth under Example I was substantially followed except the anode current density was maintained at about 0.75 ma./cm.<sup>2</sup>.

The pressure may be varied from between about 10-50 millitorr; the cathode current, 25-80 ma.; the anode current density, 0.25-1.5 ma./cm.<sup>2</sup>; anode voltage, 60-100 volts; magnetic field, 500-1500° gauss.

We claim:

1. A process for impacting an anode surface with negative ions comprising the steps of  
 placing said anode within a vacuum chamber,  
 connecting said anode to a positive terminal of a suitable electric source,  
 evacuating said chamber to a low pressure by means of a vacuum pump,  
 admitting an electronegative gas into said chamber such that a higher pressure therewithin is obtained, said higher pressure being controllable by said vacuum pump and pressure control equipment,  
 providing a source of said negative ions, said source comprising a metal helix disposed within a metal

cylinder concentrically disposed within another metal cylinder located within a gap of a permanent magnet, regulating the voltages, currents, and magnetic fields present in said source to ionize said gas and to provide a negative ion output beam, and directing said negative ions toward said anode.

2. The process as described in claim 1 wherein said anode surface, said metal cylinder and said other metal cylinder are tantalum, and said metal helix is tungsten.

3. The process as described in claim 2 wherein impacting of said tantalum anode with negative ions results in sputtering of said anode.

4. The process as described in claim 3 wherein sputtering will occur on said anode when cathode current ranges between about 10 to 80 ma., when pressure within said vacuum chamber ranges from between about 10 to 50 millitorr, when anode current density ranges between about 0.25 to 10.0 ma./cm.<sup>2</sup>, and when anode voltage ranges between about 60 to 200 volts, and wherein said magnetic field ranges between about 500 to 1500 gauss, and wherein said helix has a diameter of about 1.5 cm., said tantalum cylinder has a length of about 3.0 cm., an inner diameter of about 1.9 cm., and a wall thickness of about 0.002 to 0.020 inch, and wherein said another tantalum cylinder is separated from said tantalum cylinder by about 1/16 inch and has a wall thickness of about .002 to .020 inch, and wherein said magnetic field is about 1500 gauss.

5. The process as described in claim 4 wherein cathode current is 25 ma., pressure within said vacuum chamber is 35 millitorr, and anode current density is 5.0 ma./cm.<sup>2</sup> at 165 anode volts.

6. The process as described in claim 3 wherein said anode is gold.

7. The process as described in claim 3 wherein said anode is platinum.

8. The process as described in claim 3 wherein said anode is silver.

9. The process as described in claim 3 wherein said anode is copper.

10. The process as described in claim 3 wherein a film of tantalum oxide is sputtered from an anode surface containing a film of tantalum oxide on a metal substrate.

11. The process as described in claim 3 wherein a film of cadmium sulfide is sputtered from an anode surface containing a film of cadmium sulfide on a metal substrate.

12. The process as described in claim 2 wherein impacting of said tantalum anode with negative ions results in anodization of said anode.

13. The process as described in claim 12 wherein anodization will occur on said anode when cathode current ranges from between about 10 to 80 ma., when pressure within said vacuum chamber ranges from between about 10 to 100 millitorr, when anode current density ranges from between about 0.25 to 50.0 ma./cm.<sup>2</sup>, and when anode voltage ranges between about 20 to 200 volts and wherein said magnetic field ranges between about 500 to

1500 gauss, and wherein said helix has a diameter of about 1.5 cm., said tantalum cylinder has a length of about 3.0 cm., and an inner diameter of about 1.9 cm., and a wall thickness of about 0.002 to 0.020 inch, and wherein said another tantalum cylinder is separated from said tantalum cylinder by about 1/16 inch and has a wall thickness of about .002 to .020 inch, and wherein said magnetic field is about 1500 gauss.

14. The process as described in claim 13 wherein cathode current is 80 ma., pressure within said vacuum chamber is 85 millitorr, and anode current density is 2.5 ma./cm.<sup>2</sup> at 100 anode volts.

15. The process as described in claim 2 wherein impacting of said tantalum anode with negative ions results in sputtering said anode and in the substantially simultaneous anodization of said sputtered anode.

16. The process as described in claim 15 wherein sputtering will occur on said anode, and substantially simultaneously therewith, anodization of said sputtered anode, when cathode current ranges from between about 25 to 80 ma., when pressure within said vacuum chamber ranges between about 10 to 50 millitorr, when anode current density ranges between about 0.25 to 1.5 ma./cm.<sup>2</sup>, and when anode voltage ranges between about 60 to 100 volts and wherein said magnetic field ranges between about 500 to 1500 gauss, and wherein said helix has a diameter of about 1.5 cm., said tantalum cylinder has a length of about 3.0 cm., an inner diameter of about 1.9 cm., and a wall thickness of about 0.002 to 0.020 inch, and wherein said another tantalum cylinder is separated from said tantalum cylinder by about 1/16 inch and has a wall thickness of about .002 to .020 inch, and wherein said magnetic field is about 1500 gauss.

17. The process as described in claim 16 wherein cathode current is 25 ma., pressure within said vacuum chamber is 35 millitorr, anode current density is 0.75 ma./cm.<sup>2</sup> at 65 volts.

18. The process as described in claim 2 wherein said electronegative gas is oxygen.

19. The process as described in claim 2 wherein said low pressure is substantially less than 1 millitorr.

20. The process as described in claim 2 wherein said higher pressure falls within a range of about 10 to 100 millitorr.

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