

- [54] **LOW TEMPERATURE PLASMA ANODIZATION APPARATUS** 3,650,929 3/1972 Lertes 204/164
3,650,930 3/1972 Jones et al. 204/177
3,730,863 5/1973 Keller 204/164
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- [22] Filed: **Aug. 30, 1972**
- [21] Appl. No.: **284,824**
- [52] **U.S. Cl.**..... **250/542**, 204/164, 250/546
[51] **Int. Cl.**..... **C23b 11/00**, B01k 1/00
[58] **Field of Search** 204/164; 250/542, 546

- [56] **References Cited**
UNITED STATES PATENTS
3,394,066 7/1968 Miles 204/164

Primary Examiner—F. C. Edmundson
Attorney, Agent, or Firm—George Baron

[57] **ABSTRACT**

A method of forming a resistive barrier film on an electrically conducting body of an anodizable material through reaction of negative ions with positive ions in a plasma with the positive ions of the anodizable material. A grid of positively charged wires, in the plasma adjacent the anodizable material, absorbs the low energy or cold electrons, while trapping the hot electrons in a potential well of considerable spatial extent, so that the anodization process is speeded up.

5 Claims, 4 Drawing Figures

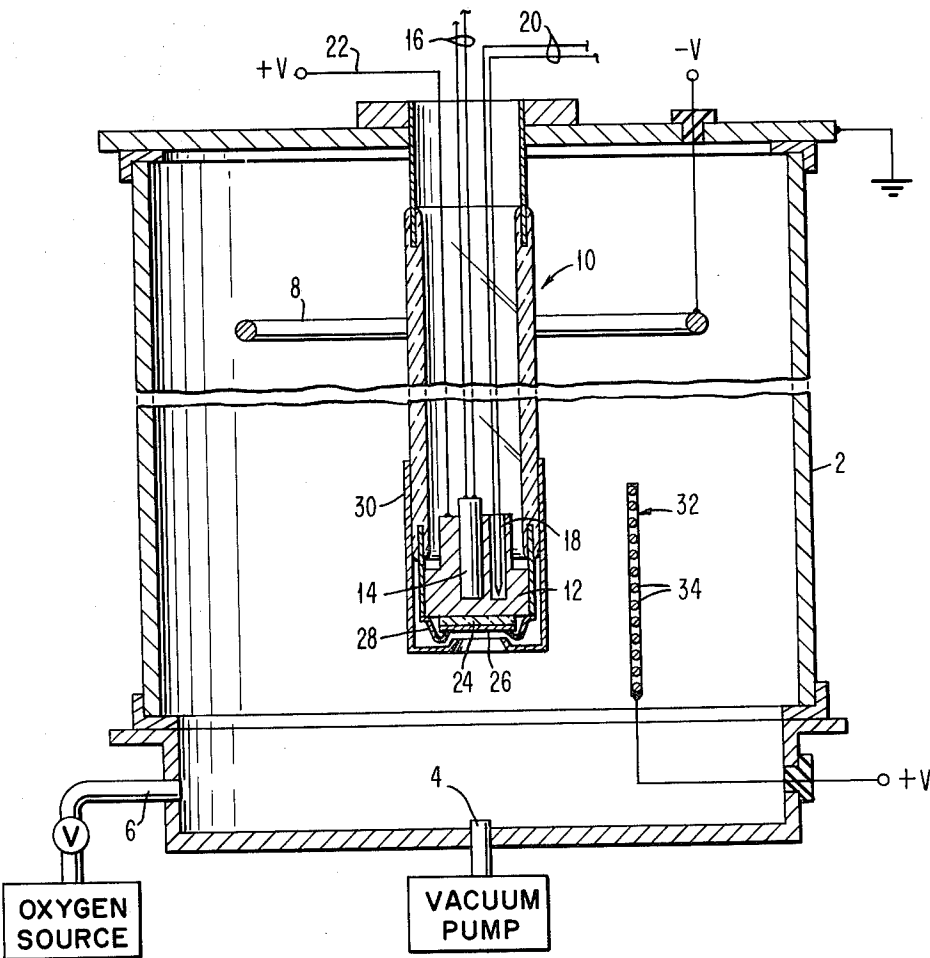


FIG. 1

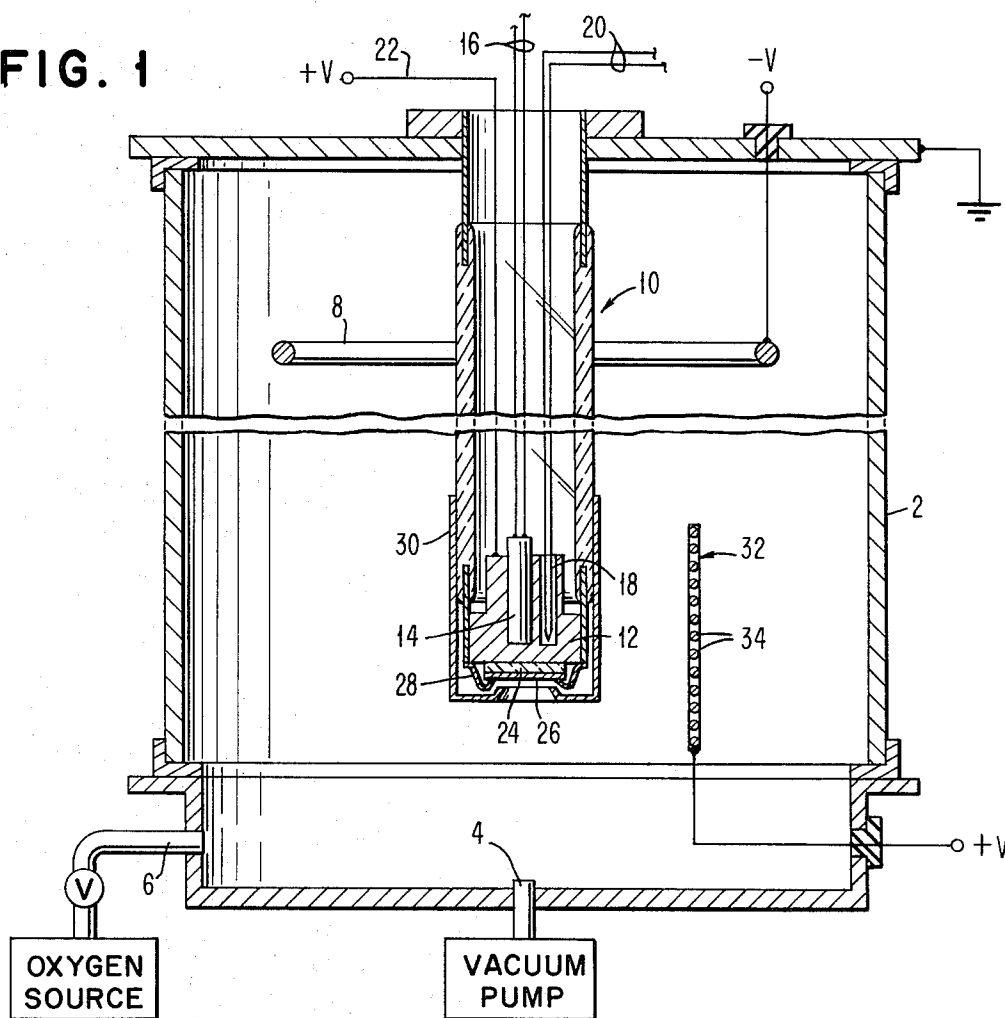


FIG. 2

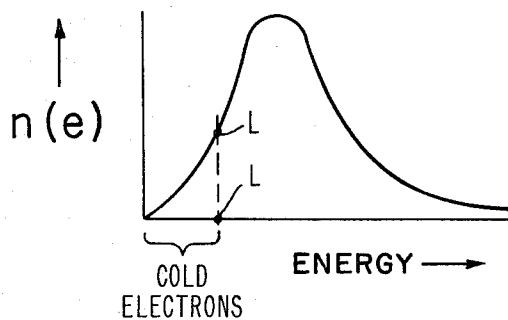


FIG. 3

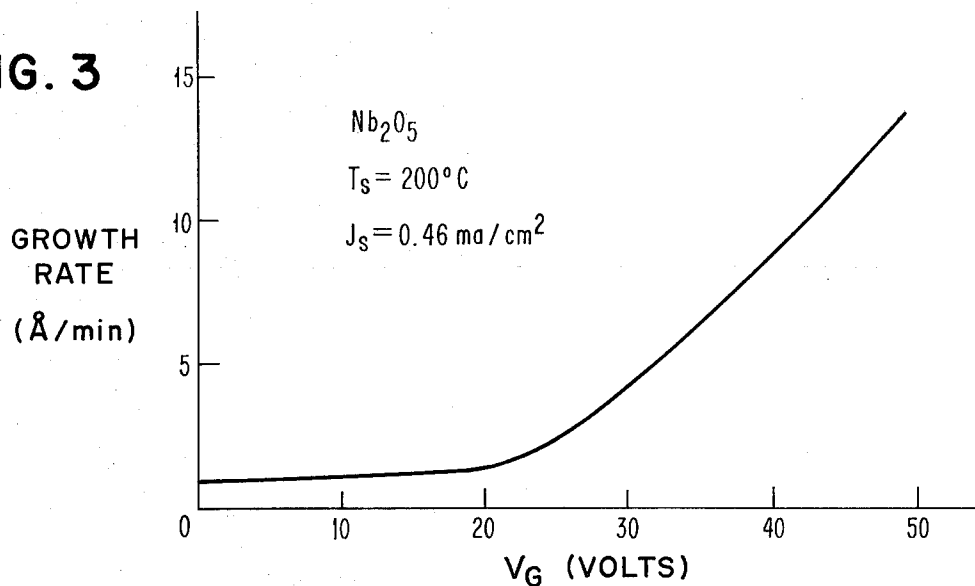
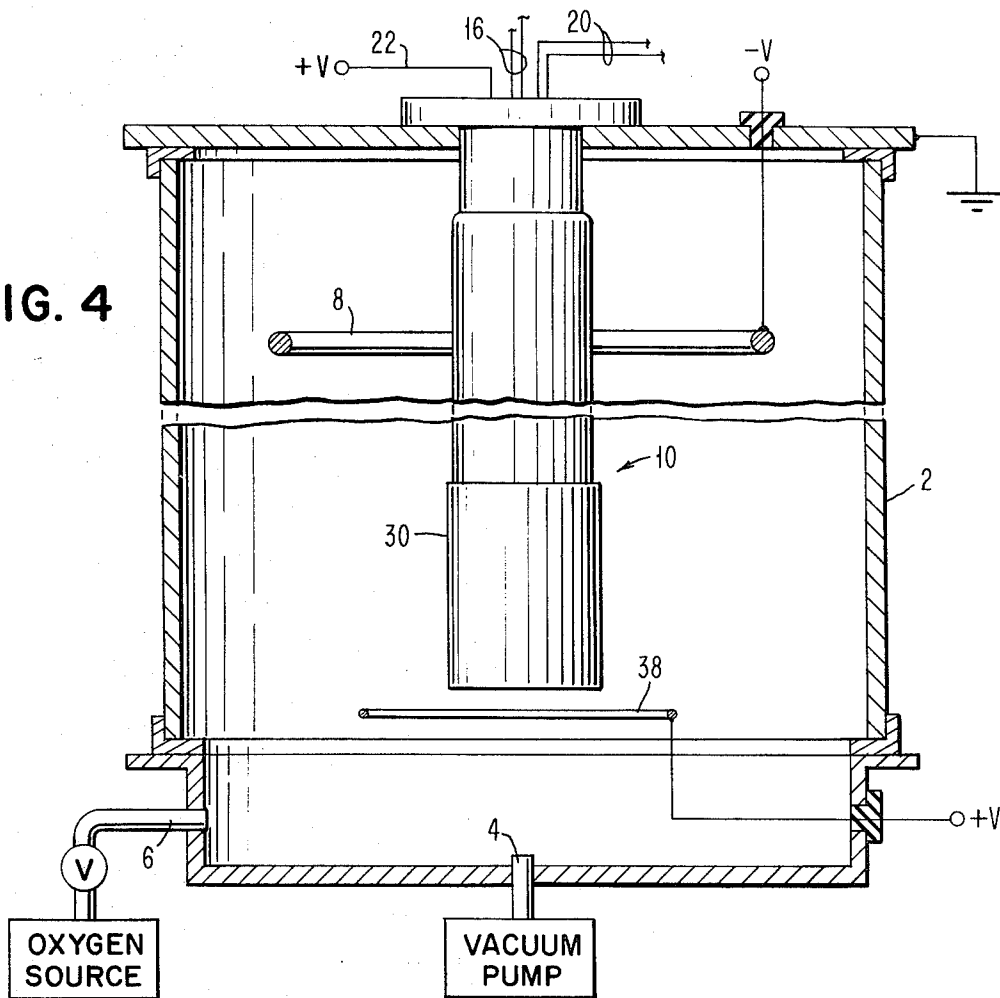


FIG. 4



LOW TEMPERATURE PLASMA ANODIZATION APPARATUS

BACKGROUND OF THE INVENTION

A known method of anodizing a thin film of metal so that the latter assumes a resistivity higher than it possesses in its unanodized state is taught in the U.S. Pat. No. 3,394,066 to J. L. Miles which issued on July 23, 1968. In such patent, a metal, such as aluminum, is anodized at room temperature without the use of a wet electrolyte. The method of anodizing relies on the steps of forming a priming barrier on the surface of the aluminum by reaction with a gaseous reactant, exposing the barrier to a plasma comprising negatively charged ions of the gaseous reactant, and impressing across the priming barrier an electrical potential to increase the thickness of the priming barrier and form the resistive barrier film which is characterized as being the reaction product of the negatively charged ions and the conducting material.

The plasma anodization shown and described in the above-noted patent to John L. Miles comprises a "sea" of ions and electrons, the latter being of different energies. The energetic electrons are referred to in the literature as "hot" and the substantially less energetic electrons are referred to as "cold." When the plasma anodization is carried out in accordance with the teaching of said Miles' patent, the presence of the cold electrons in the plasma tends to slow up the anodization process. What is desired is a simple means for removing said cold electrons without interfering with the anodization process so as to speed up the anodization step.

Such removal of the cold electrons is now achieved by the expedient of putting a grid of thin wires, of the order of 0.001 inch in diameter, in the vicinity of the metal being anodized and biasing such grid positively with respect to the plasma surrounding such metal. Such grid serves to increase the energy of the electron gas forming the plasma by absorbing the cold or low energy electrons, while trapping the hot electrons in a potential well in the anodizing chamber. Such use of a biased grid of wires has caused a tenfold increase in the rate of anodization and has also been effective in reducing sputter contamination of the metal being anodized.

Thus, it is a primary object of this invention to improve the efficiency of plasma anodization by effectively trapping the cold electrons in such plasma but preserving the hot electrons which are needed to create gaseous ions that anodize a metal in the vicinity of the plasma. Furthermore, a preferred means for trapping such cold electrons comprises a grid of thin wires that are positively biased with respect to the plasma.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of one embodiment of the invention.

FIG. 2 is the Maxwell-Boltzmann plot of electrons in a plasma.

FIG. 3 is a curve showing the rate of anodization in a chamber as the bias on the grid varies from 0 to 50 volts.

FIG. 4 is a modification of the invention shown in FIG. 1.

A typical dry anodization apparatus is shown in FIG. 1 and comprises a closed chamber 2 which is pumped down through opening 4 in said chamber 2 to a pres-

sure of 10^{-5} to 10^{-6} mm. of Hg prior to admitting through valved pipe 6 about 50–100 millitorrs of pure oxygen. Ring cathode 8 surrounds an insulated sample holder 10 which is composed of a compound structure of Kovar-glass-Kovar. Within holder 10, near its base, is a metal block 12 having two wells in which are located a heating element 14 whose leads 16 are connected to a source of current not shown and a thermocouple 18 whose leads 20 go to a monitoring system, not shown, for maintaining block 12 at a desired temperature. Wire 22 has a bias voltage applied to it from an appropriate source, not shown, for maintaining block 12 at any desired positive potential, with a range of a fraction of a volt to 50 volts being a practical range. A substrate wafer 24 is affixed to metal block 12 and supports the sample film 26 which is to be anodized, with metallic spring ohmic contacts 28 applying the positive bias of block 12 to sample 26. The thickness of the oxide grown is greater when such bias is large, and such bias is varied as the thickness of the anodization builds up. As the thickness of oxide is built up, such bias is increased in increments. Changes in bias voltage applied are determined by monitoring current flow through the anodized sample and when such current has diminished to a predetermined level, the voltage bias is increased accordingly. The ring cathode 8 is maintained at a negative voltage of 600 to 900 volts with respect to the inner walls of chamber 2, with -800 volts being typical, compatible with the vacuum system being used.

An electrostatic shield 30 surrounds the lower region of holder 10 and serves to protect the metal block 12 and its lower Kovar wall from attack by ionized particles in the plasma.

In a plasma anodizing system, of the type shown in the above-noted U.S. Pat. No. 3,394,066, the curve of FIG. 2 in this application is a plot of the number of electrons $N(e)$ as a function of energy. For the purpose of describing the operation of this invention, it will be assumed that electrons to the left of line L—L of the figure are cold electrons (low energy) and those to the right of the line L—L are hot electrons (high energy). The gas plasma consists of oxygen in the form of neutral molecules and atoms, positive ions, negative ions and electrons. The higher energy electrons in the plasma do one of two things, namely, ionize oxygen in the gas or (2) ionize the oxygen upon the surface of metal sample 26. The greater the ratio of hot electrons to cold electrons in the plasma, the more numerous will be the number of oxygen ions to combine with the metal sample 26, and the faster will the latter anodize.

In order to increase such ratio of hot electrons to cold electrons, a grid 32 of fine platinum wires 34, each about 0.001 inch in diameter, or finer, are placed about 5 to 10 cm. from electrostatic shield 30 in the vicinity of the substrate 24 and its associated metal film 26 to be anodized. This grid is biased positively with respect to the gas plasma in the chamber. The grid 32 performs the role of capturing the cold or low energy electrons in the plasma by transmitting the hot electrons. The region surrounding the positively biased grid serves as a potential well, capturing the cold electrons but allowing the more energetic electrons to escape and create the needed ions that perform the anodizing step. In general, without the use of grid 32, 97 to 98 percent or more of the current drawn by the anodizing sample will be composed of electrons and 2 to 3 percent or less of

negative oxygen ions. However, in the presence of the grid 32, the efficiency will be increased, resulting in an increased growth rate of the oxide.

For a grid consisting of fifteen 20 cm. long wires 34 in the array 32 that was 6 cm. high, a positive voltage of 50 volts on the grid showed an increase in the anodization rate of niobium, the metal 26 chosen to be anodized. The increase was from 1A/min. to 14A/min. An additional benefit accruing from the use of the array 32 lies in a decrease in contamination of film 26 from the sputtering of cathode ring 8, because of the shorter growth time of the oxide. For this sample, the shorter exposure time results in a reduction of sputter contamination from 2 to 0.14 percent.

Another effective modification of the grid 32 shown in FIG. 1, consists in employing a single turn of 0.001 inch diameter platinum wire shaped into a ring about 8 cm in diameter and located about 1 cm below and concentric with the sample 26. Such modification is shown in FIG. 4 where such single turn 38 is the positively biased grid. It should be obvious that as the configuration of the sample to be anodized changes, other geometries for the grid 32, 38 may be used to suit such configuration.

The improved deposition has been achieved with the anodization of niobium, using a d.c. oxygen discharge. A constant voltage bias or a constant current bias may be employed for biasing substrate 24, with the constant current bias being preferred in that it is easier to control. Although niobium and aluminum are good examples of metals that can be anodized more quickly by the invention shown and described herein, as is noted in the Miles' patent, any material capable of conducting an electrical current can be used. This includes nonme-

tallic materials such as doped silicon and doped germanium. Since oxides are now grown in a clean environment at a reasonable rate with high purity cathode materials, using controlled amounts of selected dopants, the positively biased screen of this invention is particularly useful.

What is claimed is:

1. In an anodizing system comprising a gaseous plasma composed of ions and electrons in a closed chamber system, the latter having a certain ratio of high energy electrons to low energy electrons.

means for supporting a metal film to be anodized in said plasma,

a first electrode supported in said chamber and maintained at a negative potential,

means for applying a positive potential with respect to said first electrode to said metal film so as to support anodization of said film, and

a grid supported in said chamber, and biased positively with respect to said plasma so as to increase said ratio of high energy electrons to low energy electrons in said plasma during the anodization of said metal film.

2. In the anodizing system of claim 1 wherein the positively biased electrode grid is between 5 to 10 cm from said metal to be anodized.

3. In the anodizing system of claim 1 wherein said positively biased grid consists of a plurality of fine wires.

4. In the anodizing system of claim 3 wherein said fine wires are of the order of 0.001 inch in diameter.

5. In the anodizing system of claim 3 wherein said fine wires are platinum.

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