July 2, 1968 H. C. THEUERER 3,391,071

METHOD OF SPUTTERING HIGHLY PURE REFRACTORY METALS IN AN ANODICALLY BIASED CHAMBER

Original Filed July 22, 1963 2 Sheets-Sheet 1

FIG. 1

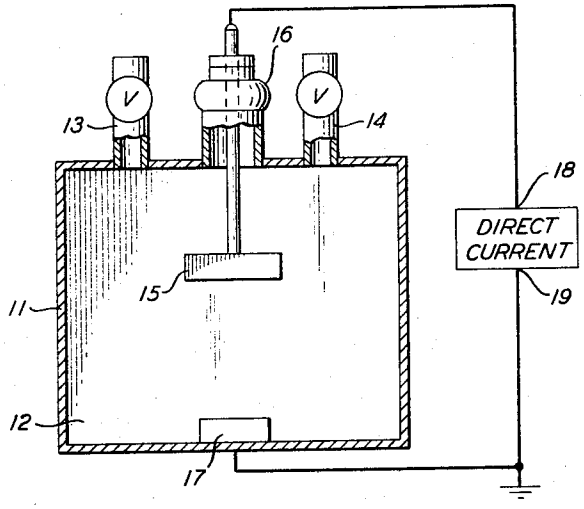

FIG. 2

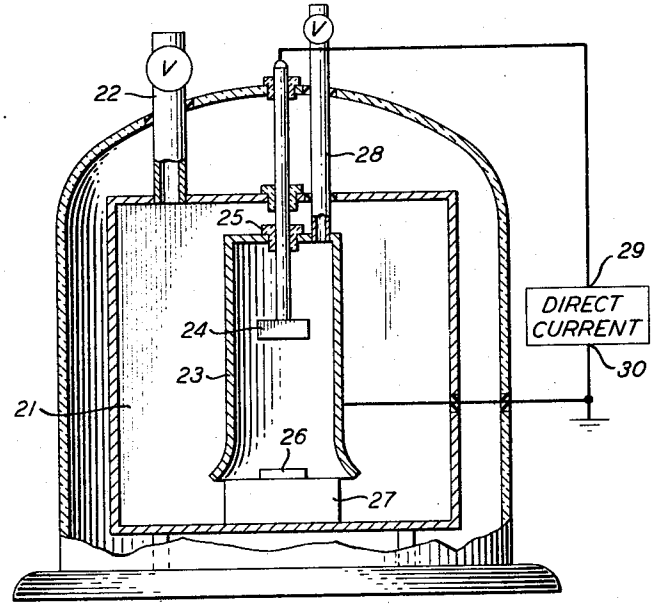

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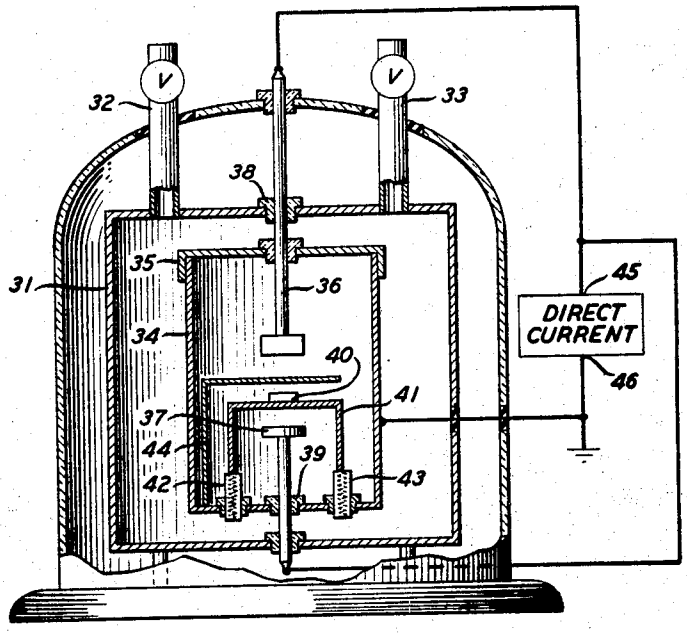
FIG. 3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DIRECT CURRENT
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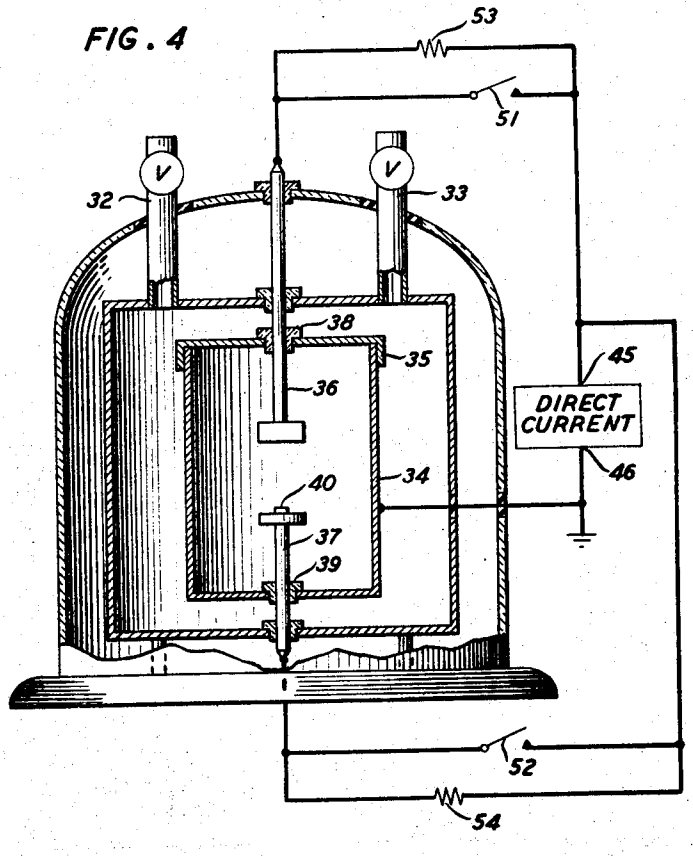
FIG. 4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DIRECT CURRENT
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United States Patent Office 3,391,071 Patented July 2, 1968

3,391,071

METHOD OF SPUTTERING HIGHLY PURE REFRACTORY METALS IN AN ANODICALLY BIASED CHAMBER

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Original application July 22, 1963, Ser. No. 296,550, now Patent No. 3,294,669, dated Dec. 27, 1966. Divided and this application Aug. 4, 1966, Ser. No. 570,351

1 Claim. (Cl. 204—192)

ABSTRACT OF THE DISCLOSURE

Active gases in a stream of an inert gas entering a sputtering chamber during the course of cathodic sputtering processes are reacted with sputtering material at their point of entry, so resulting in purification of the inert gas prior to its reaching the area of the system in which deposition occurs.

This application is a division of copending application Ser. No. 296,550, filed July 22, 1963, now U.S. Patent 3,294,669.

The present invention relates to a technique for cathodic sputtering of thin films.

In recent years, considerable interest has been generated in thin films and the preparation of such films by cathodic sputtering techniques. Unfortunately, considerable difficulty has been encountered in the preparation of certain of these films since the materials being sputtered, typically composed of one or more of the chemically active elements, evidence a strong affinity for active gases such as oxygen and nitrogen. Accordingly, satisfactory deposition can only be attained when the reactive gases in the sputtering ambient are maintained at partial pressures less than 10^{-9} torr, so necessitating the use of elaborate high vacuum techniques.

In accordance with the present invention, a cathodic sputtering technique suitable for the deposition of superconductive and other reactive materials is described wherein the partial pressure of active gases is maintained at 10^{-4} torr and higher. The inventive technique involves cathodic sputtering in an apparatus having a configuration such that active gases entering the sputtering chamber as contaminants in the inert gas react with sputtering material at their point of entry and are deposited upon the walls of an anode member substantially surrounding the cathode, so resulting in the purification of the inert gas prior to its reaching the area of the system in which coating of the substrate occurs.

FIG. 1 is a front elevational view of an apparatus suitable for the practice of the present invention;

FIG. 2 is a front elevational view of an alternative apparatus suitable for the practice of the present invention;

FIG. 3 is a front elevational view of an apparatus suitable for the practice of the present invention wherein two cathodes in combination with an enveloping anode are employed; and

FIG. 4 is a front elevational view of an apparatus suitable for the practice of the present invention wherein two cathodes are connected to a D-C power supply through a pair of switches and resistors.

With reference now more particularly to FIG. 1, there is shown anode member **11** which defines the limits of sputtering chamber **12**. Anode member **11** is provided with an outlet **13** for connection to a vacuum pump (not shown) and an inlet **14** for the introduction of an inert gas into chamber **12**. Shown disposed within sputtering

chamber **12** is a cathode member **15** which is supported by anode **11** and electrically insulated therefrom by Kovar-glass seal **16**. Cathode **15** is comprised of the material which is required to be deposited upon a plane workpiece or substrate **17**. Cathode **15** is connected to the negative pole **18** of a D-C high tension supply, the positive pole of which is connected, as at **19**, to anode **11** and to ground.

FIG. 2 shows an alternative apparatus for use in the practice of the present invention. Shown in the figure is vacuum chamber **21** provided with an outlet **22** for connection to a vacuum pump (not shown). Shown disposed within chamber **21** is an anode member **23** which defines a space gradient in an area substantially surrounding cathode **24** which is supported thereby and electrically insulated therefrom by insulator **25**. Cathode **24** is comprised of the material which is required to be deposited upon a plane workpiece or substrate **26** supported on work table **27**, workpiece **26** being situated at a point opposite cathode **24** wihtin the noted space gradient. Inlet **28** is provided for introducing an inert gas into the volume defined by the intercept of the plane of said cathode and said space gradient. Cathode **24** is connected to the negative pole **29** of D-C high tension supply, the positive pole of which is connected, as at **30**, to anode **23** and to ground.

FIG. 3 shows still another apparatus suitable for the practice of the present invention. Shown in this figure is vacuum chamber **31** provided with an outlet **32** for connection to a vacuum pump (not shown) and an inlet **33** for the introduction of an inert gas. Shown disposed within chamber **31** is an anode member **34** having affixed thereto tightly fitting lid **35**, anode **34** completely enveloping cathodes **36** and **37**, respectively, which are electrically insulated therefrom by means of insulators **38** and **39**. In practice, insulators **38** and **39** are so fitted as to provide sufficient clearance to permit inert gases introduced into vacuum chamber **31** to flow into the sputtering chamber, i.e., the interior of anode **34**.

Cathodes **36** and **37** are comprised of materials which are required to be deposited upon a plane workpiece or substrate **40** supported on work table **41** positioned between cathodes **36** and **37**. Work table **41** is an electrical resistance element which may be heated by means of electrodes **42** and **43**. A movable shutter **44** for controlling coating is shown disposed between cathode **36** and substrate **40**. Cathodes **36** and **37** are connected to the negative pole **45** of a D-C high tension supply, the positive pole of which is connected, as at **46**, to anode **34** and to ground.

Still another alternative apparatus is shown in FIG. 4 wherein the apparatus of FIG. 3 is modified by removing the substrate support **41** and electrodes **42** and **43** which are connected thereto, in addition to removing shutter **44** and connecting cathodes **36** and **37** to a D-C high tension supply through shorting switches **51** and **52**, respectively, and resistors **53** and **54**, respectively.

The present invention may conveniently be described in detail by reference to a first illustrative example in which tantalum is employed as the cathode in an apparatus similar to that shown in FIG. 1.

The conditions employed in cathodic sputtering are known (see "Vacuum Deposition of Thin Films," L. Holland, J. Wiley & Sons, Inc., New York, 1956). In this process, the vacuum chamber is first evacuated. A partial pressure of a nonreactive gas as, for example, hydrogen or any of the members of the rare gas family such as helium, argon or neon, is then introduced to the chamber. The system may be operated statically by maintaining a fixed pressure of gas in the system. It may also be operated dynamically such that a fixed gas pressure is maintained with a constant flow of gas through the system. The extent of the

vacuum used in either case is dependent on consideration of several factors.

Increasing the inert gas pressure and thereby reducing the vacuum within chamber **12** increases the rate at which the metal being sputtered is removed from the cathode, and, accordingly, increases the rate of deposition. The maximum pressure may not exceed the value at which a stable glow discharge may be obtained, but in practice is usually dictated by power supply limitations since increasing the pressure also increases the current flow between anode **11** and cathode **15**. A practical upper limit in this latter respect is 200 microns of Hg for a sputtering voltage of the other of 3000 volts. The ultimate maximum pressure is that at which the sputtering can be reasonably controlled within the prescribed tolerances. It follows, from the discussion above, that the minimum pressure is determined by the lowest deposition rate which can be economically tolerated.

After the requisite pressure is attained, cathode **15**, which may be composed of tantalum or alternatively may be covered with tantalum, for example, in the form of a foil, is made electrically negative with respect to anode **11**.

The minimum voltage necessary to produce sputtering is dependent upon the particular material employed as the cathode. For example, a D.-C. potential of about 1500 volts is required to produce a sputtered layer of tantalum suitable for the purposes of this invention. The minimum voltage for other metals, as well as compounds and alloys, is known in the art. Increasing the potential difference between anode **11** and cathode **15** has the same effect as increasing the pressure, that of increasing both the current flow and the rate of deposition. Accordingly, the maximum voltage is dictated by consideration of the same factors controlling the maximum pressure.

The spacing between anode and cathode is not critical. However, the minimum separation is that required to produce a glow discharge which must be present for sputtering to occur. Many dark striations occur in the glow discharge produced during sputtering. Some of these striations are well known and have been given names as, for example, Crooke's Dark Space. For the best efficiency during the sputtering step substrate **16** should be positioned immediately without Crooke's Dark Space. Location of substrate **16** closer to cathode **14** limits the rate of deposition. Locating substrate **16** further away from cathode **14** results in the impingement on the substrate by a smaller fraction of the total metal sputtered, thereby increasing the time necessary to produce a deposit of a given thickness. The anode should not penetrate the cathode dark space, and for this purpose the minimum distance from any point on the cathode surface and the anode should be one-half inch.

It must be noted that the location of Crooke's Dark Space changes with variations in the pressure, it moving closer to the cathode with increasing pressure. As the substrate is moved closer to the cathode it tends to act as an obstacle in the path of gas ions, which are bombarding the cathode.

Accordingly, the pressure should be maintained sufficiently low so that Crooke's Dark Space is located beyond the point at which a substrate would cause shielding of the cathode.

The balancing of these various factors of voltage, pressure, and relative positions of the cathode, anode and substrate to obtain a high quality deposit is well known in the sputtering art. In addition to the effect of the parameters noted above, it is to be appreciated that the actual sputtering rate is also dependent on the particular material being sputtered. For the purposes of this invention sputtering is allowed to proceed in all directions from the cathode. The sputtering rate must be sufficiently high to ensure capture of reactive gases before they can reach the coating area. Sputtering rates of the order of 50 A./Nm. are satisfactory for this purpose.

With reference now more particularly to the example under discussion, by employing a proper voltage, pressure and spacing of the various elements within the vacuum chamber, a layer of tantalum is deposited upon substrate **17**. The sputtering is conducted for a period of time calculated to produce the desired thickness.

During the course of the sputtering reaction, argon entering vacuum chamber **12** via conduit **14** is ionized in the region surrounding anode **11**, the resultant charged particles then bombarding cathode **15**, so causing cathode particles to dislodge from the crystal lattice in all directions toward anode **11**. Thus, a cloud of sputtering material is produced and as the argon, containing traces of reactive bases, enters vacuum chamber **11** via conduit **14**, the sputtering material reacts with or getters the reactive gases, so forming compounds which are deposited upon the interior surfaces of anode **11** and permitting the now-purified inert argon to reach that part of the system in which coating of the substrate occurs.

To obtain the best quality of deposit, it is preferred that the substrate be possessed of a smooth surface which is completely free from sharp changes in contour. The substrate should also be able to withstand temperatures within the range of 300–400° C. since it may be heated to temperatures in this range during the deposition. In the cathodic sputtering process the substrate surface is heated by bombardment with gas ions in addition to acting as a sink for the heat released by the deposition of the sputtered layer. However, in certain cases it has been found advantageous to heat the substrate surface to temperatures within the range of 650–1000° C. during the sputtering process. This technique has proven satisfactory for obtaining thin films of elemental, alloy and compound superconducting materials which manifest the properties of the bulk material.

All types of refractory materials such as glass, ceramics and high melting metals are suitable for use as substrate materials. In those cases wherein additional heating is required during sputtering, magnesium oxide has proven particularly satisfactory.

Several examples of the present invention are described in detail below. These examples are included merely to aid in the understanding of the invention and variations may be made by one skilled in the art without departing from the spirit and scope of the invention. It will be appreciated by those skilled in the art that the main impact of the present invention lies in the use of partial pressures of 10^{-4} torr and higher in order to obtain satisfactory deposition, conventional sputtering parameters otherwise being employed.

Example I

A cathodic sputtering apparatus similar to that shown in FIG. 3 was employed wherein two V_3Si rods one inch in diameter and ⅜ inch in length, prepared by alloying the constituents were used as cathodes. The anode consisted of a nickel can and lid made from 0.012 inch stock and was 4 inches high and had an inner diameter of 2⅜ inches. The substrate was a sheet of crystalline magnesium oxide. In the apparatus actually employed, the anode was grounded, the potential difference being obtained by making the cathodes negative with respect to ground.

The system was initially evacuated by pumping to a pressure of approximately 5×10^{-6} mm. of Hg. In order to condition the system, titanium purified argon maintained at a pressure of 150 microns was introduced into the system and sputtering initiated by applying 1500 volts at 4.3 milliamperes to each electrode, a temperature of 700° C. being maintained. Sputtering was conducted for 110 minutes to bring the target to steady state. This is required since sputtering rates for silicon and vanadium are different. Following, the substrate was introduced and the system evacuated to 5×10^{-6} mm. of Hg. Next, the substrate support was outgassed at 900° C. for 30 minutes after which argon was admitted at a pressure of 135 microns. Finally, the substrate support was heated to 700° C. and sputtering begun by applying 1800 volts at 5.0 milliamperes to each electrode.

Sputtering was conducted for 50 minutes yielding a layer of V_3Si approximately 3470 A. thick. Coating was terminated by replacing the tantalum shield, turning OFF the power used to heat the substrate surface, and after 50 minutes turning OFF the sputtering voltage. The resultant film was found to be superconducting in liquid helium at 13.9° K.

Example II

The procedure of Example I was repeated with the exception that the substrate was maintained at 900° C. during sputtering at a current of 4.0 milliamperes in an argon atmosphere maintained at 125 microns of Hg. Sputtering was continued for 50 minutes yielding a coating of 2300 A. The resultant film was superconducting in liquid helium at 13.6° K.

Example III

The procedure of Example I was repeated employing V_3Ge cathodes, a substrate temperature of 1000° C., a supporting voltage of 1900 volts D.-C. and an argon pressure of 100 microns. Sputtering was continued for one hour yielding a coating of 5690 A. The resultant film was superconducting in liquid helium at 6.8° K.

Example IV

The procedure of Example I was repeated employing V_3Ga cathodes, a sputtering voltage of 2250 volts D.-C. and an argon pressure of 100 microns, the substrate being heated to 1000° C. during sputtering. Sputtering was continued for 30 minutes yielding a film of 2560 A. The resultant film was superconducting in liquid helium at 12.35° K.

Example V

The procedure of Example I was repeated employing Ta cathodes, a sputtering voltage of 1500 volts D.-C. with the substrate heated to 300° C. and an argon pressure of 85 microns. Sputtering was conducted for 10 minutes yielding a coating of 2030 A. The resultant film was superconducting in liquid helium at 3.9° K.

Example VI

The procedure of Example I was employed with the exception that an apparatus similar to that shown in FIG. 3 was employed with niobium cathodes.

Stabilization of the system was attained by first biasing the upper cathode with 94,000 ohms with respect to the lower cathode and applying a potential of 1500 volts D.-C. for 15 minutes under an argon pressure of 100 microns, the substrate being positioned atop the lower cathode. Following the electrical bias was reversed and substrate coating initiated at a current of 5.5 milliamperes in an atmosphere of argon maintained at 100 microns of Hg. Sputtering was continued for 50 minutes yielding a coating of 7660 A. in thickness. The resultant film was superconducting in liquid helium at 9.6° K.

While the invention has been described in detail in the foregoing specification and the drawing similarly illustrates the same, the aforesaid is by way of illustration only and is not restrictive in character. It will be readily appreciated by those skilled in the art that although the invention is described in terms of superconducting materials, the described technique may suitably be employed in any sputtering technique wherein reactive gases are deleterious.

What is claimed is:

1. A method for cathodic sputtering of thin films of a tantalum or niobium based metallic film upon a substrate in an apparatus including an anode member defining a vacuum chamber, the said chamber having disposed thereing in succession (a) a substrate support having a substrate disposed thereon, (b) a pair of nonshielded cathode members consisting essentially of tantalum or niobium, (c) means for evacuating said chamber, and (d) means for admitting inert gas into said chamber, one of said cathode members being disposed significantly nearer to (d) than (a) which comprises the steps of evacuating said chamber, introducing an inert gas into said chamber and applying an electrical potential across the said anode and cathodes, thereby initiating sputtering and causing the disintegration of said cathode member, the resultant disintegrated material purifying said inert gas near its point of entry by reacting with active gases contained therein.

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