Oct. 8, 1968 SHIGERU HAYAKAWA ETAL 3,405,301

APPARATUS FOR PRODUCING QUIESCENT PLASMA

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FIG. 1a

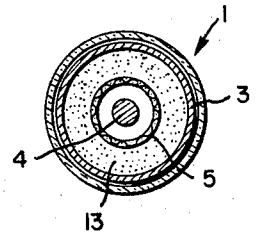

FIG. 1b

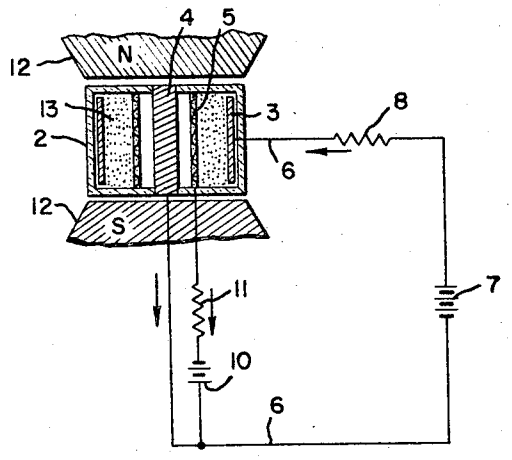

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FIG. 2

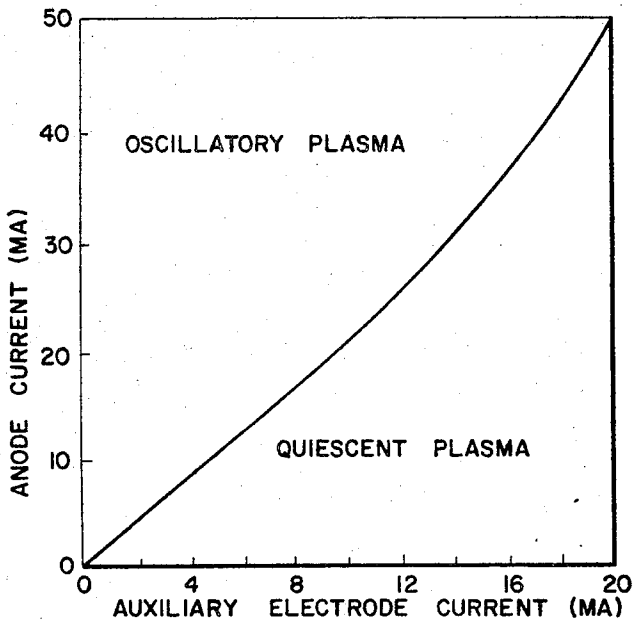
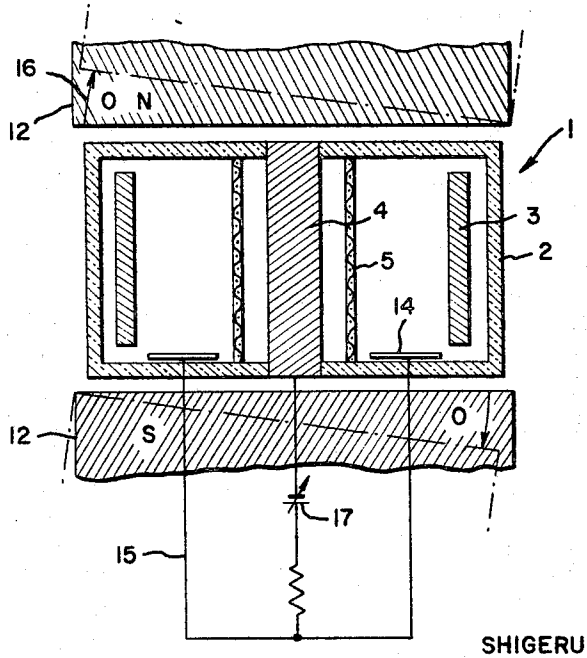


FIG. 3



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APPARATUS FOR PRODUCING QUIESCENT PLASMA

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3 Claims. (Cl. 313—162)

ABSTRACT OF THE DISCLOSURE

A discharge tube for producing a high density quiescent plasma. The tube has a sealed envelope and two cylindrical electrodes within said envelope and positioned with each other, one of said two cylindrical electrodes is a cold cathode and the other of said two cylindrical electrodes is an anode. Said discharge tube further has a negatively biased, cylindrical grid electrode positioned between said two cylindrical electrodes, said cylindrical grid electrode being coaxial with said two cylindrical electrodes and positioned near said cold cathode. Said sealed envelope is filled with an ionizable medium at a subatmospheric pressure and a magnet superposing an axial magnetic field is positioned adjacent the outside of said envelope.

This invention relates to an apparatus for production of quiescent plasma, and more particularly to an apparatus for the production of quiescent plasma for a plasma machining operation such as plasma anodization.

Among the discharge tubes for a plasma source which are in wide use are DC glow discharge tubes, DC arc discharge tubes, and high frequency discharge tubes. Usually these tubes are not suited for use as a plasma source because of the low efficiency of the plasma production and/or because of instability in the plasma produced. A higher efficiency of plasma production has been achieved with a Penning type discharge tube or a coaxial discharge tube having a magnetic field. However, the plasma produced therein is highly oscillatory and is not readily useful for a plasma machining operation requiring a quiescent plasma.

An object of the present invention is to provide a new and improved discharge tube which produces a quiescent plasma for effectively carrying out plasma reactive sputtering.

Other object of the present invention is to provide a new and improved discharge tube which produces a quiescent plasma suitable for plasma anodization.

A further object of the present invention is to provide a new and improved discharge tube for use as an ion source for plasma machining.

Further features and advantages of the invention will appear from the following description and drawings wherein;

FIGURE 1*a* is a diagrammatic longitudinal sectional view of the discharge tube in accordance with the present invention in an operating circuit;

FIGURE 1*b* is a cross sectional view of the discharge tube of FIGURE 1*a*;

FIGURE 2 is a graph illustrating operating characteristics of the discharge tube shown in FIGS. 1*a* and 1*b*; and

FIGURE 3 is a diagrammatic view showing a modified discharge tube in accordance with the present invention having a high efficiency.

For a better understanding of the invention, the features of a crossed field discharge tube for a plasma source will be described utilizing principles of gaseous discharge.

It is well known from the principles of gaseous discharge that, in a crossed field discharge tube comprising coaxial electrodes with an axial magnetic field, charged particles therein will move in a cycloidal path caused by a superposition of a cyclotron motion of charged particles and a uniform drift motion of its guiding center. Ionization will be caused by a collision between electrons and neutral gas atoms, and the efficiency of ionization will increase with an increase in the number of collisions therebetween. As predicted by many workers, such as von Engel, the number of collisions between electrons and neutral gas atoms increases with an increase in the strength of the magnetic field. Therefore, the efficiency of ionization in a magnetic field is higher than that of a discharge tube which is not in a magnetic field.

On the basis of the aforesaid consideration, a coaxial tube with an axial magnetic field can be used as a plasma source of high efficiency. The discharge, however, is very oscillatory and unstable as the discharge current increases. The plasma therein is not useful in applications where a stable plasma source is required. It would be desirable to eliminate this drawback.

Referring to FIGURE 1, the discharge tube **1** comprises a cylindrical envelope **2**, an inner cylindrical anode **3**, an outer cylindrical cathode **4** and a cylindrical grid **5** acting as an auxiliary electrode. These electrodes can be made from molybdenum, titanium, aluminum or copper etc. The envelope **2** contains an ionizable medium. This ionizable medium can be hydrogen, krypton, neon, argon, oxygen, nitrogen, sulfur or possible mixtures thereof, at a pressure ranging from 10^{-5} to 10 torrs. A high voltage source **7** is connected in series to a stabilizing resistor **8** and across the anode **3** and cathode **4**. An auxiliary circuit **9** comprises a bias current supply **10** and a stabilizing resistor **11**. A magnet **12** provides an axial magnetic field. The discharge tube **1** is essentially a crossed electric and magnetic field tube. When the tube operates, the envelope **2** contains a plasma in the space **13**.

Although the novel discharge tube is constructed in such a way that the inner electrode is the cathode as shown in FIGURE 1, the novel discharge tube can operate even when the inner electrode is used as an anode.

A quiescent plasma having only a small oscillation can be obtained by locating a negatively biased auxiliary electrode **5** near the cathode **4** as shown in FIGURE 1 in accordance with the invention.

It is known that an increase in the anode current results in a plasma of high density and in undesired oscillation which prevents practical application of the plasma. With the discharge tube according to the present invention the undesired oscillation occurs predominantly near the cathode when no auxiliary electrode is used, but disappears when an auxiliary electrode **5** as shown in FIGURE 1 is used. The highest anode current which can be used for producing the quiescent plasma is shown in FIGURE 2 as a function of auxiliary electrode circuit current. The highest anode current increases as the auxiliary circuit current increases. The oscillation is attributed to a high degree of an accumulation of ions of the discharge gas near the cathode. The accumulation of ions is prevented by the negative biasing of the auxiliary electrode **5**, and as a result the oscillation can be suppressed.

Therefore, according to the invention, the anode current for producing a quiescent plasma can be increased considerably by increasing the auxiliary electrode current. Since the density of the plasma in the space **13** increases with increasing anode current, the discharge tube can readily generate a high density quiescent plasma in ac-

cordance with the present invention. A conventional discharge tube without the auxiliary circuit produces a quiescent plasma density of only 10^{10} particles/cm.^{3}, whereas the discharge tube of the present invention produces a quiescent plasma density on the order of 10^{12} to 10^{13} particles/cm.^{3}. Another feature of the discharge tube of the present invention is that the plasma generated therein has a uniform density throughout the space **13**. According to the present invention, a lower magnetic field strength of the magnet **12** can be used for producing a quiescent plasma when the auxiliary electrode **5** is employed. A conventional tube without the auxiliary electrode requires a magnetic field strength higher than 5000 gauss for practical use. The discharge tube of the present invention, however, requires only 1000 gauss of magnetic field strength, which is easily achieved by a small permanent magnet commercially available.

The novel discharge tube can be used as an ion source in ion beam machining because it has a high efficiency of ion production and high stability of produced plasma. The novel tube of the invention also can be used for any kind of plasma device such as a plasma wave guide or a plasma source for a mass-spectrometer.

A novel discharge tube can be prepared using the skills of the prior art in vacuum tube techniques. A cylindrical envelope can be made of any kind of gas-tight material such as glass, ceramics, metal or alloy. Glass is preferable because of the ease of fabrication and the necessity for gas-tight sealing of lead wires. Cathode materials vary with the applications of discharge tube. For example, refractory material such as Mo and W is preferable when the discharge tube is used as an ion source. Use in a plasma sputtering operation requires a cathode material having the same composition as that to be sputtered. A thin film of titanium or titanium oxide, for example, can be formed by employing a titanium cathode and argon or oxygen at a low pressure. Anode cylinders can be formed of any metal or alloy such as copper, aluminum or brass having a very high melting point.

The auxiliary grid electrode is preferably made of the same material as the cathode material. A different material is liable to contaminate the resultant film formed by sputtering. It is preferable that the thickness of the wire of the grid be 0.1 mm. to 0.5 mm. and the openings of the grid be 0.01 to 10 mm.^{2}. The distance between the cathode and auxiliary electrode during operation depends upon the strength of the magnetic field and the pressure of ionizable medium, and it is preferably 1 mm. to 10 mm.

The electrodes are mounted in the envelope and connected to a power supply through lead wires sealed into the envelope in gas-tight relationship by any known method. Finally the envelope is sealed gas-tight after a given ionizable medium has been placed in it at a given pressure.

The operating voltage of the high voltage supply varies with the distance between the cathode and anode, the pressure of the ionizable medium and the strength of the magnetic field, and ranges from 500 to 5000 v. The operating voltage of the bias current supply is also governed by the said pressure, the said strength and the distance between the cathode and the auxiliary electrode, and ranges from 0 to —200 v. Currents flowing through the anode or the auxiliary electrode can be controlled by employing two variable resistors.

A plasma sputtering can be readily achieved by employing the novel discharge tube. Molecules of the gas are strongly ionized by electrons and attack the surface of the cathode to excite the atoms of the cathode material. The excited atoms jump out from the surface and rush around toward the wall of the envelope, reacting with ions or molecules of the gaseous medium. Consequently, the surface of a wall or substrate placed between the anode and cathode or on the anode is provided with a thin film of the resultant product.

The combination of the cathode material and ionizable medium forms a thin film consisting of the combination composition on a substrate placed between the anode and the auxiliary electrode. For example, the combination of a titanium cathode and oxygen as a gas forms a thin film of titanium oxide on a substrate for use in a capacitor, and the combination of a tantalum cathode and nitrogen as the gaseous medium forms a thin film of tantalum nitride for use in a thin film resistor. The thickness of the film can be easily controlled by controlling the operating time, anode current, pressure of the ionizable medium and the strength of the axial magnetic field.

A film of uniform thickness and composition can be obtained by employing a uniform plasma in accordance with the present invention.

Plasma anodization also can be carried out by employing the novel discharge tube having a suitable ionizable medium such as oxygen, nitrogen or sulfur.

Referring to FIGURE 3 wherein reference characters **1** to **12** designate the same parts as those of FIGS. 1*a* and 1*b*, reference character **14** designates sample stands which are connected to a bias voltage supply **17** through lead wires **15**. According to the present invention the bias voltage applied to sample stands clearly elevates the efficiency of plasma anodization. It has also been discovered according to the invention that the efficiency can be promoted by inclining the magnet by an angle θ as shown in FIGURE 3. The inclined magnet promotes the axial drift motion of the ionized gas atoms and consequently accelerates the formation of a thin film of the resultant compound on the surface of a substrate placed on the sample stands **14**. The angle θ shown in FIGURE 3 is preferably 5 to 30° for plasma sputtering equipment and 0.1 to 5° for plasma anodization equipment.

The following example sets forth a specific embodiment of this invention and should not be construed as limitative.

An envelope is formed in the shape of a glass cylinder 20 cm. in diameter and 5 cm. in length. A cathode is made from a tantalum cylinder 2 cm. in outside diameter and 4.5 cm. long. An anode is made from a copper cylinder 8 cm. in inside diameter, 8.5 cm. outside diameter and 4.5 cm. long. An auxiliary electrode is formed from a cylindrical grid composed of tantalum wire having 0.1 mm. diameter and openings of 0.05 mm.^{2}. The said cylindrical grid is 2.5 cm. in diameter and 4.5 cm. long. These electrodes are combined coaxially in the manner described in the foregoing specification. Nitrogen gas is placed in the envelope at a pressure of 10^{-3} torrs. A glass substrate is placed on a sample stand which is connected to a bias voltage. A magnet of Alnico 5 produces a magnetic field of approximate 1000 gauss. The magnet is inclined at an angle of 10°. A DC source of 2000 v. supplies 50 ma. of anode current and another DC source of 100 v. supplies a negative bias on the order of 20 ma. of auxiliary electrode current. A thin film is formed on the glass substrate which consists of tantalum nitride and has a 500$\mu\Omega$ cm. of specific resistivity after 30 minutes of plasma sputtering.

We claim:

1. A discharge tube for producing a high density quiescent plasma, comprising a sealed envelope, two cylindrical electrodes coaxial with each other within said envelope, one of said two cylindrical electrodes being a cold cathode and the other of said two cylindrical electrodes being an anode, a negatively biased cylindrical grid electrode positioned between said two cylindrical electrodes, said cylindrical grid electrode being coaxial with said two cylindrical electrodes and positioned near said cold cathode and said envelope being filled with an ionizable medium at a subatmospheric pressure, and a magnet means positioned adjacent the outside of said envelope superposing on said envelope an axial magnetic field.

2. A discharge tube as claimed in claim **1** in which said magnet means has means for varying the inclination

of the magnetic field up to 5° from a direction parallel to the axis of said cylindrical electrodes, whereby the discharge tube is particularly useful for plasma anodization.

3. A discharge tube as claimed in claim 1 in which said magnet means has means for varying the inclination of the magnetic field from 5° to 30° from a direction parallel to the axis of said cylindrical electrodes, whereby the discharge tube is particularly useful for plasma reactive sputtering.

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