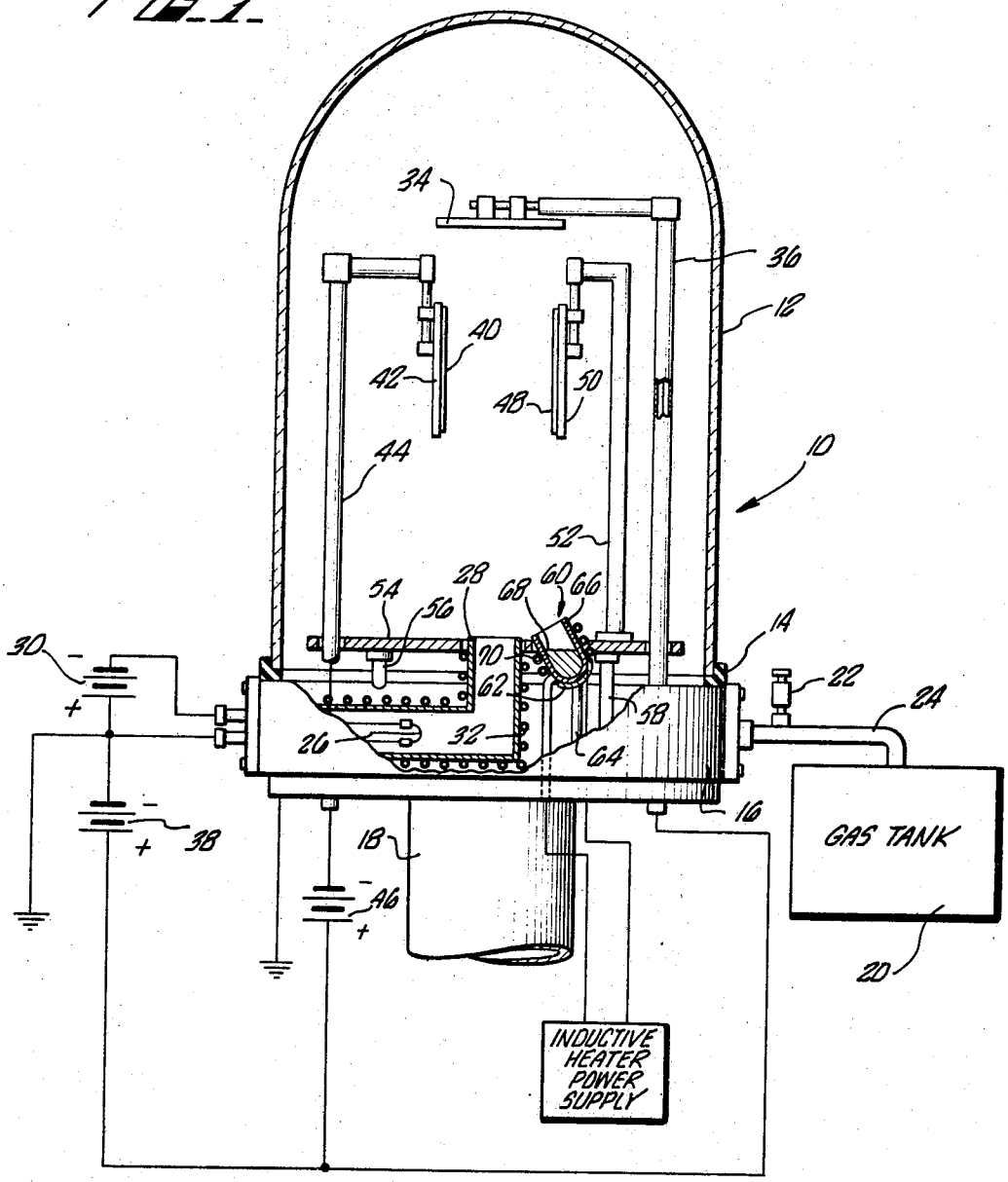
Jan. 27, 1970 L. A. CONANT 3,492,215

SPUTTERING OF MATERIAL SIMULTANEOUSLY EVAPORATED ONTO THE TARGET

Filed Feb. 27, 1967 3 Sheets-Sheet 1

FIG. 1



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Filed Feb. 27, 1967 3 Sheets-Sheet 2

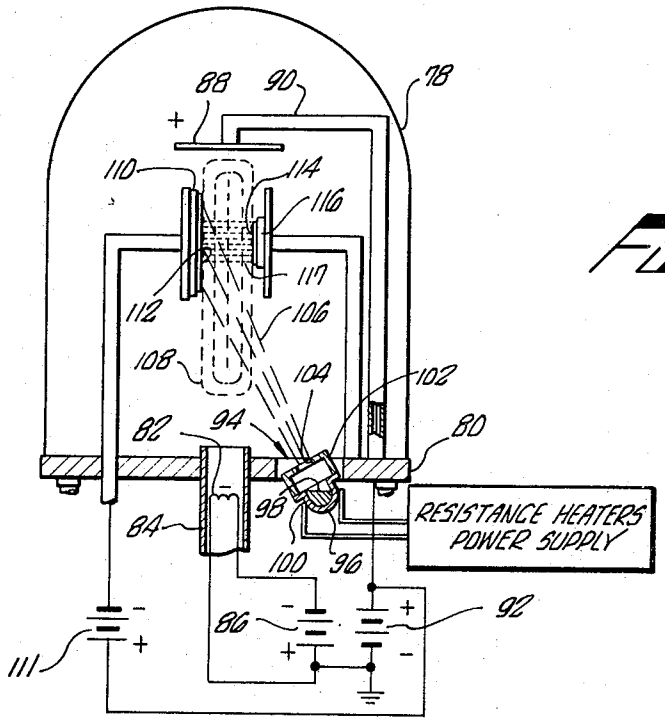

FIG. 2

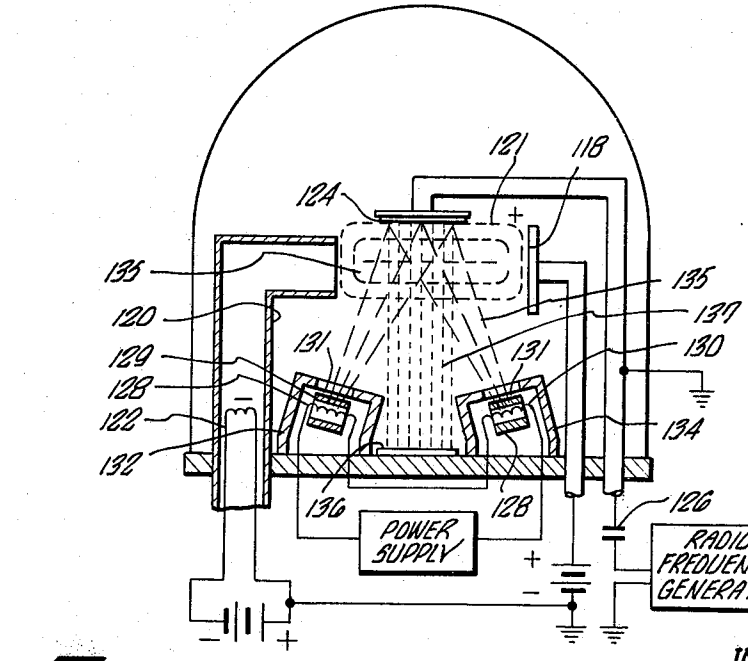

FIG. 3

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Filed Feb. 27, 1967 3 Sheets-Sheet 3

FIG. 4

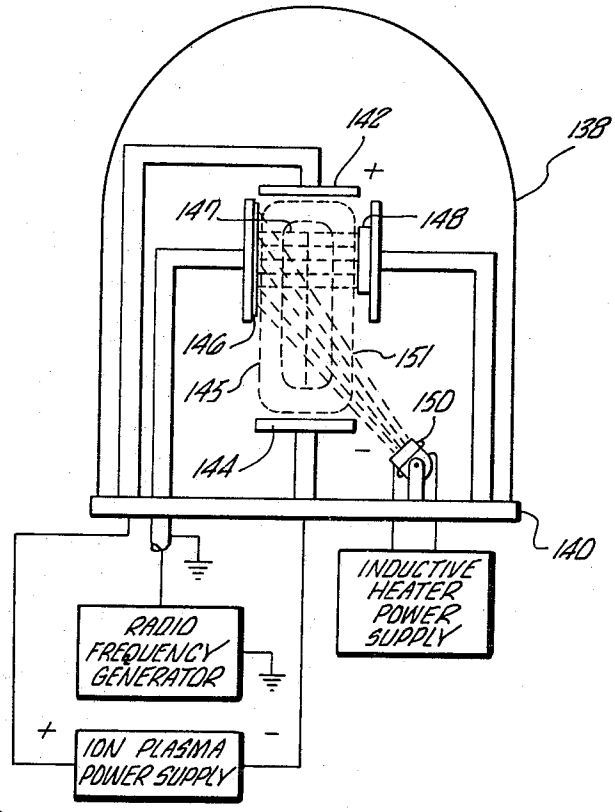
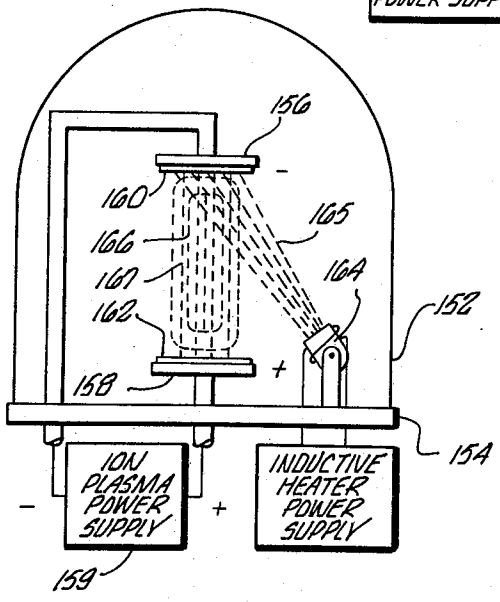


FIG. 5



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3,492,215

SPUTTERING OF MATERIAL SIMULTANEOUSLY EVAPORATED ONTO THE TARGET

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Filed Feb. 27, 1967, Ser. No. 618,873
Int. Cl. C23c 15/00
U.S. Cl. 204—192 5 Claims

ABSTRACT OF THE DISCLOSURE

A film method and apparatus which utilizes sputtering together with evaporation in the production of films on a substrate. Evaporant from a source is directed into and through an ion plasma to a target. The evaporant in the plasma increases in energy to form evaporant ions and energized atoms both of which augment the film production process.

Background of the invention

The subject invention relates to the art of sputtering and, more particularly, to an apparatus and method for depositing thin films of material on a surface of a substrate by sputtering.

Sputtering has been used in the deposition of thin films of material onto substrates. Typical sputtering apparatus includes an enclosure which is capable of being evacuated to relatively high vacuums. An anode and cathode are provided within the enclosure to generate an ion plasma. An ion target composed of the material desired as a film on a substrate is disposed within the enclosure for bombardment by ions from the plama. Typically, the substrate is mounted on a pedestal or the like to receive sputtered material from the ion target in the form of a dense coating or film. Ions from the plasma impinge the target's surface at extremely high energies to remove atoms or molecules from the surface; these atoms or molecules form the substrate's film.

Both diode and triode sputtering systems are presently being used. The ion target in a diode system is either mounted within the plasma or acts as the system's cathode. The substrate is generally in the plasma and is often mounted on the anode. Triode systems in general mount the ion target with its ion impinging surface parallel to the axis of the plasma. The target is negatively biased to attract ions from the plasma. The substrate is usually mounted proximate the ion target and parallel to the plasma's axis to receive sputtered material.

Sputtering systems may be further classified into "hot" cathode and "cold" cathode systems. A hot cathode system generates electrons at its cathode through thermionic emission while a cold cathode system relies upon a large voltage potential between its cathode and anode.

Targets of dielectric material are difficult to sputter because a field develops around the sputtering surface which acts to repel ions from the plasma. The imposition of a radio frequency field around the impinging surface of the target in both diode and triode systems, however, aids in overcoming this problem resulting in the successful sputtering of dielectric materials.

Presently known sputtering techniques have provided extremely dense and adherent films of sputtered material on a substrate. However, in any film deposition system it is highly desirable to have a fast rate of film accumulation on a substrate without affecting the quality of the film. For film formation of many materials, existing sputtering rates are too low to merit supplanting other film deposition techniques, such as evaporation, despite the recognized superiority of sputtered films. Sputtered

coatings produced at pressures below those dictated today would increase coating purity and definition. Film purity would be increased because contaminants in the atmosphere used to sustain an ion plasma will be reduced at low pressures. Definition is improved at low pressures because the mean free path of sputtered material is increased resulting in less scattering. The superiority of sputtered films makes it highly desirable for film fabrication of alloys and intermixtures of materials, but the technique is limited because of the apparatus presently employed. Moreover, existing sputtering techniques are not suitable for materials which do not lend themselves to formation into suitable ion targets or for highly sputter-resistant materials. Dielectric targets used with radio frequency sputtering have heretofore been in the form of sheets of material or relatively thick layers placed over a metal backing plate to which the radio frequency power is fed; the sputtering rates have been correspondingly low because of the thickness of the dielectric.

Summary of the invention

The present invention is directed to a sputtering method and apparatus which is marked in its flexibility for producing sputtered coating of a wide range of materials, improved sputtering and deposition rates and the ability to sputter at pressures below those presently employed. The invention permits vaporizing at least one material so that substantially all of the evaporant is initially deposited onto the target while simultaneously sputtering from the target onto a substrate.

The invention includes an evacuable enclosure, such as a bell jar or glass cross, with means for evacuating the enclosure to a pressure level consonant with the establishment of an ion plasma. Such prior art evacuating means as fore-pumps and getter-ion pumps may be used. In addition, means for creating and maintaining an ionizable atmosphere within the enclosure are provided such as an inert gas distribution system which is allowed to leak gas at a selected rate into the enclosure. Means are also employed to establish and sustain an ion plasma within the enclosure. For this purpose, known cathode and anode systems are suitable. Means are also employed for mounting an ion target within the enclosure in position to be sputtered by ions from the ion plasma. In addition, means are employed for mounting a substrate within the enclosure in position to receive sputtered material from the ion target. Means are included for evaporating a material to produce an evaporant which may be directed through the ion plasma to the ion target. The evaporant may also be directed to the ion target without feeling the effects of the ion plasma or may constitute the means for creating and maintaining the ion plasma. Suitable evaporating means include a crucible to contain evaporant material which may be evaporated by inductive or resistance heating as well as by an electron gun. If desired, a current heated filament coated with evaporant material may be used. Other methods of generating evaporant material include radiation heating from a heated filament or by conduction through a refractory support layer from a filament. The substrate and evaporant sources are disposed in such a way as to shield the substrate from impingement of evaporant material. Shielding may be accomplished by disposing the substrate out of the line-of-sight of the evaporant material. The film or coating produced on the substrate, therefore, consists of material sputtered from the ion target. The material sputtered from the ion target will include evaporant material because of its impingement on the ion target.

It is important to avoid the formation of an evaporant coating on the substrate because of the superiority of sputtered coatings. The high means free path of evaporant at the operating pressures employed is used to avoid

evaporant coatings. By placing the substrate out of the line-of-sight of evaporant the problem of evaporant contamination is avoided. To effect this result and to collimate the evaporant to form a stream, which may pass through the ion plasma on its way to the target, a number of direction schemes may be employed. Apertured covers over the crucible or other evaporant container, for example, serve to confine the evaporant into a well defined stream. Employing deep crucibles or confining walls also results in collomating the evaporant. In addition, parabolic crucibles or housings effect the desired collimation.

The sputtering system of the present invention is not limited to any particular sputtering apparatus. It may be employed in cold cathode diode systems, for example. Triode systems, with either a hot or cold cathode, are also adapted for use with the present invention. When it is desired to sputter dielectric materials, known methods for imposing a radio frequency field about the ion target may as well be used.

The present invention has many advantages over prior art sputtering deposition systems. The evaporant which passes through the ion plasma will become energized to such an extent that a significant proportion of evaporant atoms are converted to ions. Many of those atoms which are not converted to ions are raised to an elevated energy state. The disposition of the ion target with respect to the evaporant is such that the atoms which are energized in the ion plasma impinge the surface of the target. Ions from the ion plasma, including the normal gaseous ions as well as the evaporant ions, bombard the ion target. The combination of normal gaseous ions and evaporant ions increases the plasma density and increases the number of energetic ions bombarding the target and therefore increases the sputtering rate. A further increase in rate will normally be experienced as a result of the arrival at the target of evaporant which is free of oxides or other impurities normally present in undistilled solid material, thus producing a layer of pure material on the target which is more easily sputtered than a target formed of the solid material. It is thought that the molecules of evaporant arriving at the target also possess additional thermal energy or may be excited by the plasma discharge to higher energy levels so that they are more disposed to be sputtered than molecules embedded in the crystal lattice of a solid target at normal temperatures. Through adjustment of apparatus and operating parameters, a mixture of ion target material with a different evaporant material can be sputtered onto a substrate if so desired. This provides an easy and convenient method for alloying or mixing materials in film form, thus increasing the number of applications for sputtered coatings. One of the more significant aspects of the present invention is the generation of a plasma discharge by ionizing a beam of vapor directed toward the target or the enhancement of plasma density in a low pressure gas discharge by ionizing evaporant directed through the gas toward the target. The generation of plasma from the vapor beam allows sputtering at pressures considerably lower than those presently available. At low environmental pressures, contamination of the sputtered coating on the substrate is minimized and the adherence of the film to the substrate is increased. Cold cathode systems which have heretofore operated at relatively high pressures may be operated at pressures considerably lower because of the availability and protection of evaporant ions. Radio frequency sputtering techniques are also enhanced because it is possible to maintain a very thin layer of material, less than 50 angstroms, for example, on the target surface, the layer being constantly replenished by the evaporant. These atoms will sputter more readily than the target itself because of their freedom from interfering oxides or other impurities and because these atoms may possess additional thermal energy or be in an excited state so that they are more susceptible to sputtering than atoms or molecules embedded in the target. The constantly replenished layer increases sputtering rates for dielectric materials for sputtering rates of dielectrics are high when dielectric thickness is low. The use of an evaporant in a sputtering system also produces a relatively uniform sputtered coating on a substrate more readily than a coating produced by an evaporant. The uniform sputtered coating is produced because uniformity is more likely to result when the coating material emanates from a relatively large area, such as a target surface, than when it comes from a small area such as is typical with evaporant sources. Vapor fractionalization may also be performed in this sputtering environment by generating an evaporant of a volatile material while leaving less volatile impurities behind in the crucible and, if necessary, using an ion target that has a low sputtering rate. Evaporant is generated from a relatively impure source where the impurities have a low volatility rate. Volatile evaporant which accumulates on the target surface is sputtered by ions from the ion plasma to form a high purity film on the substrate.

Brief description of the drawings

The above and other features, aspects and advantages of the instant invention will become more apparent from the following description, appended claims and drawings, in which:

FIGURE 1 is an elevational view, partly in section, of one embodiment of the instant invention;

FIGURE 2 is a schematic depiction of the embodiment shown in FIGURE 1, with a modification;

FIGURE 3 is a schematic depiction of an alternate embodiment;

FIGURE 4 is a schematic view of another embodiment; and

FIGURE 5 is a schematic view of still a further embodiment.

Description of the preferred embodiments

FIGURE 1 depicts a preferred sputtering apparatus **10** of the instant invention. Enclosure **12**, in the form of a bell jar, is mounted through an annular gasket **14** to base **16**. Conduit **18** communicates the interior of enclosure **12** with a vacuum pump (not shown). The gas which forms the ionizable atmosphere within bell jar **12** is supplied through gas tank **20**. Valve **22** is connected in gas line **24** to meter the flow of gas from tank **20** to the interior of bell jar **12**. Cathode **26**, in the form of a filament, is disposed in cathode shield **28**. Direct current source **30** is connected in series with cathode **26** to energize the cathode and bias it negative with respect to its complementary anode. Cooling coils **32** are disposed about shield **28** to prevent its overheating. Anode **34** is mounted above the opening in shield **28** on mounting bracket **36**. The anode is biased positive with respect to the cathode through connection with the positive terminal of direct current power source **38**. Ion target **40** is secured to mounting plate **42**. The ion target and the mounting plate are held in position through bracket **44**. Direct current source **46** negatively biases mounting plate **42** and ion target **40**, if the latter is conductive, with respect to ions in an ion plasma developed between cathode **26** and anode **34**. A source of radio frequency energy (not shown) may be coupled to ion target **40** to establish a radio frequency field around its ion impinging surface. This field is required for proper sputtering of dielectric materials. Substrate **48** is secured to plate **50** and in turn to bracket **52** for receiving sputtered material from ion target **40**. In the disposition shown, the substrate and the ion target are both parallel to an ion plasma which is developed between anode **34** and cathode **26**. Baffle plate **54** is provided between the ion plasma and the interior of base **16** to shield apparatus within the

base from sputtering. Baffle plate **54** is supported from base **16** by stands **56** and **58**.

Evaporant source **60** is mounted on a socket **62** which is supported by stand **64** above the floor of base **16**. Evaporant source **60** includes a crucible **66** which contains evaporant material **68**. Coils **70** are disposed about the outer periphery of crucible **66**. These coils inductively heat evaporant material **68** to form an evaporant. The inductive heater power supply is coupled to these coils to effect the evaporation.

In order to form a film on substrate **48** an ion plasma is established between cathode **26** and anode **34** in a high vacuum with an inert gas such as argon. Ion target **40** is biased negative with respect to ions in the plasma through direct current power supply **46**. If desired, the film receiving surface of substrate **48** can be cleaned by the scrubbing action of a plasma glow discharge or by sputtering before film deposition begins. When a film is desired, evaporant material **68** is heated to create an evaporant. This evaporant, owing to the high mean free path within enclosure **12**, will pass through the ion plasma to impinge upon ion target **40**. Evaporant material within the ion plasma will increase in energy resulting in the generation of evaporant ions and energized atoms. The evaporant ions will, together with gaseous ions, impinge the surface of ion target **40** to sputter it of material. However, the sputtered material is not only the material of the target but includes energized atoms from the evaporant material **68**. These energized atoms are easily sputtered because of their high energy state. Control of the amount of evaporant material generated from evaporant source **68** affects the proportion of evaporant atoms and ion target material sputtered. This control can be used to effect alloying and mixing when the ion target is of a different material than the evaporant. The sputtered material will accumulate as a film on substrate **48**.

The effect of evaporant in a sputtering system is more clearly illustrated with reference to FIGURE 2. Bell jar **78** is mounted on a base **80** to define an enclosed space. The space is evacuable to pressures consonant with the establishment and maintenance of an ion plasma. Hot cathode **82** is mounted in cathode housing **84**. Direct current power supply **86** supplies the energy for generating electrons from cathode **82** and for biasing the cathode negative with respect to anode **88**. Anode **88** is disposed above cathode **82** on bracket **90**. Bracket **90** is connected to base **80**. The anode is positively biased by direct current power source **92**. Evaporant source **94** includes a crucible **96** in which is contained an evaporant material **98** to be melted and evaporated by resistance heating from leads **100** which are connected to the resistance heater power supply. Cover **102** is mounted on the crucible and has the central aperature **104**. This aperture allows for the passing of evaporant from the crucible to the interior of bell jar **78**. The aperture serves to direct and confine or collimate evaporant into a relatively coherent stream. This stream is shown by reference numeral **106**. The ion plasma developed between anode **88** and cathode **82** is shown by reference numeral **108**. Evaporant stream **106** passes into the ion plasma **108** and augments its ion content by the creation of evaporant ions. Ions of both gaseous atmosphere and evaporant material will be attracted to ion target **110** because the latter is biased negative with respect to the ions by connection with the negative terminal of potential source **111**. A thin film **112** of evaporant atoms will form on the surface of the ion target. This film will be sputtered by impinging positive ions from the plasma. Control of the thickness and density of this film is readily accomplished by adjusting the evaporation rate of evaporant from crucible **96**. Sputtered material **117** will accumulate as a film **114**, on substrate **116**. As in the previously described embodiment, substrate **116** is out of the line-of-sight of evaporant stream **106** to avoid the creation of an evaporant film.

FIGURE 3 depicts another embodiment of the instant invention. The embodiment shows the use of filaments to generate an evaporant material in a system which develops a horizontal, as opposed to a vertical, ion plasma. The evaporant material may be coated on the filament or the filament used as a heat source to produce evaporant material from a source proximate to the filament. In addition, the use of multiple evaporant sources and a typical use of a radio frequency field are illustrated. Vertically disposed anode **118** is mounted to face the opening in cathode shield **120** to establish a relatively horizontal ion plasma **121**. Shield **120** contains cathode **122**. Ion target **124** is mounted above the axis of and borders the ion plasma developed between anode **118** and cathode **122**. The target is coupled through capacitor **126** to a radio frequency generator to impose a radio frequency field around its ion impinging surface to facilitate sputtering of dielectrics. The radio frequency field can also be used to correctly bias the target. Filaments **128** and **130** are coupled to a power supply. Each of the filaments may be coated with evaporant material or may be separated therefrom by a refractory material. The refractory material is shown schematically by reference numeral **129** as a cylinder disposed on filament **128**. The evaporant material itself is shown by reference numeral **131** as a film on refractory **129**. Filament **128** is contained within housing **132** while filament **130** is contained in housing **134**. Each of the housings has an aperture for the confinement and direction of the streams of evaporant material **135** generated by the filaments. This confinement is to avoid evaporant material directly striking substrate **136**, that is, to be sure that the film on the substrate is entirely sputter deposited. In the embodiment illustrated, substrate **136** is disposed below the openings in the housings and thus will not exeperience the creation of an evaporant film on surface. Evaporant materials generated by filaments **128** and **130** will pass into the ion plasma where some of it will ionize while other atoms will be excited and pass directly for accumulation and sputtering from the surface of ion target **124**. Sputtered material **137** will accumulate as a tenacious and dense film on substrate **136**. The use of multiple evaporant sources may be used as a vehicle to effect an even distribution of energized atoms on the surface of the ion target. Intersecting beams of evaporant material striking the target where it is most remote from the evaporant source effect this distribution. In addition, the use of a rotating target which alternately presents remote and proximate surfaces to the evaporant stream will accomplish an even coating. However, it has been found that even with evaporant stream-target angles as severe as the embodiment shown in FIGURE 1, the sputtered coating on the substrate is relatively constant in thickness throughout. An even distribution of condensed evaporant on the target surface is not too essential as long as the layer of evaporant on the target is maintained at more than one or two monolayers thickness over the whole surface. Although the layer of evaporant may be thicker near the source end of the target (when not using multiple sources), the sputtering is from the surface. However, the arrival rate of ionized evaporant molecules which contribute to the sputtering rate may be higher on the source side of the target when only one source is used and hence multiple evaporant sources can accomplish a more uniform coating of sputtered material on the substrate.

The embodiment shown in FIGURE 4 is similar to the embodiments shown in FIGURES 1 and 2 except for the use of a cold cathode. Bell jar **138** is mounted on base **140**. Anode **142** is disposed within bell jar **138** as is cold cathode **144**. These electrodes are connected to a source of energy for the establishing and maintenance of ion plasma **145** within the bell jar. For this purpose, the bell jar can be evacuated and supplied with an inert gas atmosphere

as previously described. Ion target **146** as well as substrate **148** are cooperatively disposed within the bell jar for the production of a film on substrate **148**. Preferably the target and substrate border and parallel the ion plasma. Evaporant source **150** directs evaporant material **147** into the ion plasma and onto the surface of ion target **146**. Sputtered material **153** will form a film on substrate **148**.

FIGURE 5 shows the evaporant sputtering apparatus in a diode system. Bell jar **152** is mounted on base **154**. The interior of the bell jar can be evacuated and supplied with an inert gas atmosphere for the creation of an ion plasma as indicated in reference to FIGURE 1. Cathode **156** and anode **158** are coupled to a direct current power source **159**. Anode **158** is connected to the positive terminal of source **159** while cathode **156** is connected to the negative terminal. Ion target **160** is held in place on the surface of cathode **156**. Alternatively, the cathode itself can serve as the ion target. Substrate **162** is mounted on anode **158** for the accumulation of a film on its exposed surface. This substrate can, as well, be positioned elsewhere within bell jar **152** on a grounded substrate holder, for example, so long as it is out of the line-of-sight of evaporant emanating from evaporant source **164**. Evaporant is produced by inductive heating from the inductive heater power supply. Evaporant **165** from source **164** passes into and through ion plasma **166** which is developed between cathode **156** and anode **158**. The ion plasma is indicated by the long dashed lines in FIGURE 5. Within the ion plasma, evaporant material will ionize to form evaporant ions and energized atoms. The atoms will impinge the surface of ion target **160** because of the direction imparted by evaporant source **164** where they, as well as surface material, are sputtered by ions from the plasma. The sputtered material, indicated by the small dash lines of the figure, will form a film on substrate **162**.

EXAMPLES

The following examples illustrate the use of evaporant supplemented sputtering.

EXAMPLE 1

The apparatus used in this example is similar to that depicted in FIGURE 1 except that resistance heating was employed for generating an evaporant stream, a magnet was used to confine the ion plasma and the target was coupled to a radio frequency generator. A glass plate was used as a substrate. A cylindrical copper disc was used as the ion target. The ion target and substrate were diametrically mounted on opposite sides of the ion plasma. Approximately 70 milligrams of copper were used as the evaporant source. The evaporant source copper was contained in a molybdenum crucible or boat. The boat was arranged to direct evaporant copper to the ion target as illustrated in FIGURE 1. A hot cathode in a cathode shield with an opening coaxial with an anode was used.

The glass substrate was scrubbed for one minute from a direct current discharge glow between the cathode and anode. The cleaning of the glass substrate eliminated contaminants from its surface. After the scrubbing, the radio frequency source was energized and operated at a frequency of 13 megacycles per second. The copper ion target was energized by the radio frequency source and triode sputtered for two and one-half minutes without an evaporant stream. The evaporation source was energized, after the two and one-half minutes of triode sputtering, to cause the copper to volatilize. The starting pressure within the bell jar was 2×10^{-5} torr while the actual operating pressure for radio frequency triode sputtering and radio frequency triode sputtering with an evaporant was 0.8 micron in an atmosphere of argon. The cathode drew 45 amperes. The voltage drop across the ion plasma was 40 volts at 3.5 amperes. The duration of actual evaporation was 20 seconds but the heating source was energized for 30 seconds. The 10 second difference was required to heat the copper evaporant source to generate the evaporant. The total time of normal radio frequency triode sputtering and such sputtering with the evaporant was three minutes.

The interaction of evaporant copper with the radio frequency and direct current plasmas caused the evaporant beam to glow a bright emerald green. The evaporant beam or plasma contained excited copper atoms, copper ions and neutral atoms at lower energy states.

The film produced on the glass substrate was compared with a sputtered deposited film produced under the same conditions with a total sputtering time of three minutes without the benefit of the evaporant. By known optical methods, the film on the substrate which was produced utilizing the evaporant was at least two times as optically dense as the film which was merely sputtered.

To determine whether evaporant material reached the substrate to form an evaporant as opposed to a sputtered coating, a glass slide was mounted in the same position on the substrate as the slide sputter-coated with the copper evaporant. In this configuration, the glass slide was out of the direct line of evaporating copper atoms. The copper in the crucible was allowed to evaporate without energizing the sputtering system. There was no evidence of a coating on the glass slide. It is apparent, therefore, that coatings produced by the instant invention are entirely sputtered.

EXAMPLE 2

An experiment was conducted to determine the comparative results between a film produced by normal sputtering with a film produced with the aid of evaporant. The experimental conditions were maintained to produce the best coating with both systems.

A glass substrate was mounted in an apparatus similar to that depicted in FIGURE 1 and discussed in Example 1. The substrate was ion or glow discharge scrubbed to cleanse its surface. The starting pressure within the bell jar was 5×10^{-5} torr. The operating pressure in the bell jar was 6×10^{-4} torr. The atmosphere within the bell jar was argon. The hot cathode drew 45 amperes and the ion plasma had a voltage drop of 75 volts at 4.5 amperes. An aluminum target was mounted parallel to the ion plasma and opposite the similarly disposed glass substrate. The aluminum target was triode sputtered for three minutes with the radio frequency source energized at a frequency of 13 megacycles per second. The film or coating produced on the glass substrate was adherent and of good quality.

A new glass substrate was mounted and ionically cleaned. The starting pressure was 5×10^{-6} torr in an atmosphere of argon. The operating pressure was 6×10^{-4} torr. The cathode drew 45 amperes. The ion plasma had a voltage drop of 70 volts while drawing a current of 4.5 amperes. The radio frequency source was energized for three minutes at 13 megacycles per second. The total sputtering time was three minutes. The evaporant material was aluminum contained in a molybdenum boat having a tantalum cover with an aperture. The boat and its cover were arranged relative to the ion target of aluminum to direct evaporant toward the target. The evaporation time was from one to one and one-half minutes and took place during the radio frequency sputtering. The film produced on the glass substrate was two to three times as dense as the film produced without use of the evaporant. Density was determined by known optical methods.

EXAMPLE 3

As in the previous examples, the following experiment was conducted with an apparatus similar to that depicted in FIGURE 1 and discussed in EXAMPLE 1. The evaporant was copper resistively melted in a tantalum crucible. The ion target was silica (SiO_2). The starting pressure was 5×10^{-6} torr, the atmosphere argon, and the operating pressure 6.2×10^{-4} torr. The cathodic filament drew 45 amperes and the ion plasma had a voltage drop of 50 volts at a current of 4 amperes. A glass substrate was employed which was ionically cleaned. The

radio frequency source was used at 13 megacycles per second. The total evaporation time was two minutes. The total radio frequency triode sputtering time was three minutes.

The result of this experiment yielded an opaque bright copper-silica film having extremely good adherence to the glass substrate. The coating on the substrate was entirely sputtered because of the position of the substrate with respect to the evaporant beam as previously discussed.

The significance of this experiment is that it demonstrated the sputtering of a metal film, evaporant copper atoms, from a non-metallic target. The experiment also illustrated improved adherence of copper, hence other metals, to glass which resulted from the mixing of copper atoms sputtered from the target with silica molecules of the target. Most metals are poor adherents to glass while silica is a strong adherent. It is evident that the amount of silica in a film of silica and copper can be varied from virtually zero percent to virtually 100 percent by merely varying the rate of evaporation of evaporant to the silica target. An extremely fast evaporation rate would give a practically pure copper film while a slow evaporation rate would result in a mixture of copper silica.

The properties of the film can be modified by varying its constituent amounts of silica and copper. An example of varying properties is resistivity. The sheet resistivity of a copper silicon dioxide film was increased from less than about 0.2 ohm per square to 1 to 2 ohms per square. (The terminology "per square" is used in thin film technology when referring to resistivity since what is meant is "sheet resistivity" or resistivity per unit film thickness, and therefore the actual linear dimensions cancel out.)

It is apparent that coatings or films produced by the use of an evaporant in a sputtering system has broad applicability in such areas as: corrosion protection, abrasion resistance, thermal expansion control, fatigue resistance, thermal shock improvement of ceramic and other non-metallic materials and the variance of electrical and physical properties. In short, results obtainable by atomic and molecular intermixtures are readily attained by the system of the present invention. The use of an evaporant in a sputtering system provides extremely fine control of these mixtures. One particularly significant application of the present technique is in the application of ceramic or glass coatings on a metal substrate. Vapor deposited or sputtered coatings without the use of an evaporant are generally very thin and, therefore, of little value where abrasion is a factor. Films on the order of 10,000 angstroms to several mils are generally required. Films of this thickness range are too brittle and fracture because of thermal expansion mismatch during their application. However, the rapid deposition of metal oxide plus metal molecules in a controlled ratio by sputtering with an evaporant can produce a transition layer for adapting the thermal expansion of the substrate to that of the final coating, thus allowing the use of thick wear-resistant films on otherwise incompatible substrates.

EXAMPLE 4

This example demonstrates the utility of sputtering using an evaporant in a low pressure diode system with a cold cathode.

This experiment was conducted with an apparatus similar to that depicted in FIGURE 1 and discussed in the foregoing examples but, as will become apparent, the actual evaporation-sputtering apparatus had a tungsten filament cathode and an anode disposed coaxially with the electron in a cathode shield. A target was mounted to one side of the axis between the anode and the shield's opening while a glass substrate was disposed on the opposite side of the axis facing the target. An evaporant source in the form of a molybdenum crucible or boat with heating means was placed to direct evaporant to the target. The substrate was out of the line-of-sight of the crucible's opening. The target was coupled to a radio frequency generator.

Initially, an attempt was made to establish a direct current discharge between the system's anode and cathode at a low pressure. The anode was biased with respect to the cathode 200 volts and the cathodic filament drew 45 amperes. The starting pressure was 1.6×10^{-5} torr. During the experiment, no current was observed between the anode and the cathode and, therefore, this portion of the circuit was not functioning to produce a direct current discharge with residual gases as the sustaining atmosphere. The evaporation boat was biased 200 volts with respect to the anode. The copper contained in the boat was heated to a temperature of between 1200 and 1400 degrees centigrade to generate a copper vapor. The boat did not act as an electron emitting source because the pressure, during the vaporization of the copper, varied between 1.6×10^{-5} torr and 2×10^{-4} torr. At these pressures, gaseous molecules of residual atmospheric gases are not numerous enough to sustain a gaseous, ionized dicharged. A second reason for concluding that the boat was not functioning to ionize the copper vapor was shown by evaporating copper from the boat without the radio frequency generator in the system. Without the imposition of a high voltage radio frequency field at the target, no green glow or direct current across the system's anode and cathode was observed at the low voltage difference of 200 volts.

However, when the radio frequency power source was used to energize the target at a voltage of between 2000 and 2500 volts, ionization of the copper vapor occurred. Thus, the target was a cold cathode and the molybdenum boat an anode in a diode system. The fact that the boat was biased with respect to the normal anode did not contribute to the ionization of the vapor, at least during the formation of the ion plasma.

Actual film deposition on the substrate occurred during the operation of this effectively cold cathode, diode system when an evaporant source was used together with the radio frequency source. The total evaporation time was one and one-half minutes. However, the period of the green glow, the period of the ion plasma between the target and the boat, was 30 seconds. When the glow started, the pressure was 2×10^{-4} torr where it remained for the glow's duration. The glass substrate was coated with copper having good electrical conductivity with a thickness of about 500 angstroms.

To determine whether the coating on the substrate was in fact the product of evaporation sputtering, the following test was conducted. A clean glass slide was used as a substrate and disposed in the same position as the previous slide (see the relative positions of the substrate, target and crucible in FIGURE 1). The molybdenum boat was recharged with copper and evaporated at an initial pressure of 8×10^{-6} torr which raised to 6×10^{-5} torr as evaporation continued. The molybdenum boat was biased to the anode at 200 volts. The total evaporation time was two minutes. There was no glow despite the bias of the boat. The radio radio frequency source was not used. The glass slide did not have a copper film which indicates that the slide described previously in this example was coated by a sputtering process which relied on an evaporant to produce the film in a pressure of from 1.6×10^{-5} to 2×10^{-4} torr.

Low pressure sputtering, which is possible when using an evaporant, is conducted in high purity sputtering atmosphere which results in high purity sputtered films. The atmosphere is cleaner because it is more rarified. In addition, the higher mean free path for evaporant and sputtered atoms and molecules resulting from the lower pressure produces coatings having better definition with less scattering.

The subject invention has been described with reference to certain preferred embodiments. It is not intended, however, that the spirit and scope of the appended claims necessarily be limited to the foregoing description.

What is claimed is:

1. In a method of depositing films of sputtered material onto a substrate from a target having an ion impinging surface wherein the improvement comprises vaporizing at least one material onto said target and shielding said substrate from said evaporant while sputtering said material from said target onto said substrate.

2. A method as recited in claim 1 wherein the improvement comprises the additional step of impressing a radio frequency field proximate the ion impinging surface of said target while sputtering.

3. A method of sputtering a film of at least one given substance from a target onto a substrate which comprises:

supporting said substrate in a vacuum chamber;

positioning a means for vaporizing said substance in line of sight of said target and out of line of sight of said substrate so as to shield said substrate from direct impingement of the evaporant produced; and

vaporizing said substance so that substantially all of said evaporant is directed to said target to produce a coating thereon while sputtering from said target onto said substrate.

4. A method for depositing, within a vacuum chamber, films of sputtered material from an ion target onto a substrate having a film receiving surface comprising:

mounting said target having an ion impinging surface within said chamber;

mounting said substrate within said chamber with its film receiving surface substantially parallel to, spaced apart from, and facing the ion impinging surface of said target;

evacuating said chamber and establishing an ionizable atmosphere therein;

establishing an ion plasma within said chamber between and generally parallel to the ion impinging surface of said target and the film receiving surface of said substrate;

applying an ion attracting potential to said target; and,

evaporating at least one material so that substantially all of said evaporant is directed to said target through said plasma to produce a coating thereon while sputtering from said target onto said substrate.

5. An apparatus for depositing films of sputtered material from an ion impinging surface of an ion target onto a film receiving surface of a substrate, comprising:

(a) an enclosure;

(b) means for evacuating the enclosure and for establishing an ionizable atmosphere therein;

(c) means for mounting an ion target having an ion impinging surface within the enclosure;

(d) means for mounting the substrate within the enclosure with its film receiving surface substantially parallel to, spaced apart from and facing the ion impinging surface of the ion target;

(e) means for establishing an ion plasma within the enclosure between and generally parallel to the ion impinging surface of the target and the film receiving surface of the substrate, such means including an anode and a thermionic cathode which are independent from the substrate and ion target;

(f) means for applying to the anode a positive electric potential with respect to the cathode;

(g) means for applying a negative potential to the ion target to attract ions from the ion plasma;

(h) means for supplying electrical energy to the cathode to generate electrons; and

(i) means for evaporating a material to produce an evaporant, such means being disposed to direct substantially all of said evaporant onto the ion target through the ion plasma and out of the line-of-sight of the film receiving surface of the substrate to produce evaporant ions and energized evaporant atoms.

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