

June 6, 1967

N. LAEGREID ETAL

3,324,019

METHOD OF SPUTTERING SEQUENTIALLY FROM A PLURALITY OF CATHODES

Filed Dec. 11, 1962

FIG. 1

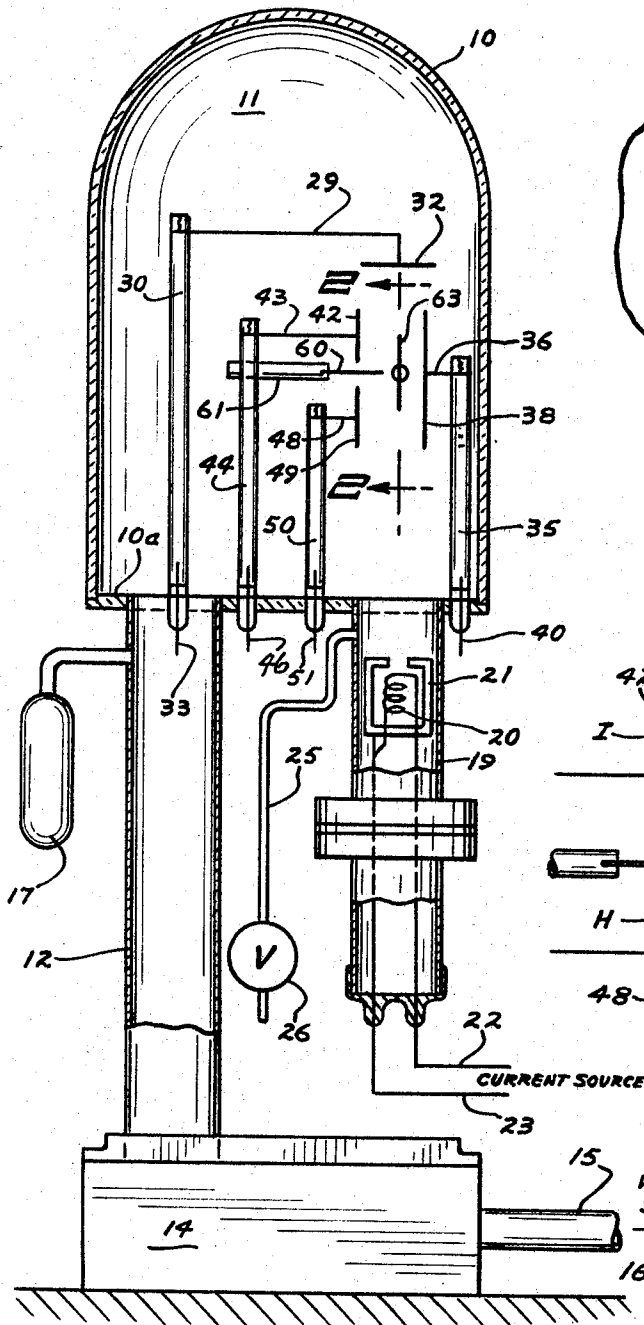


FIG. 2

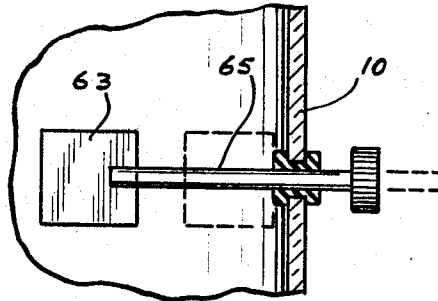
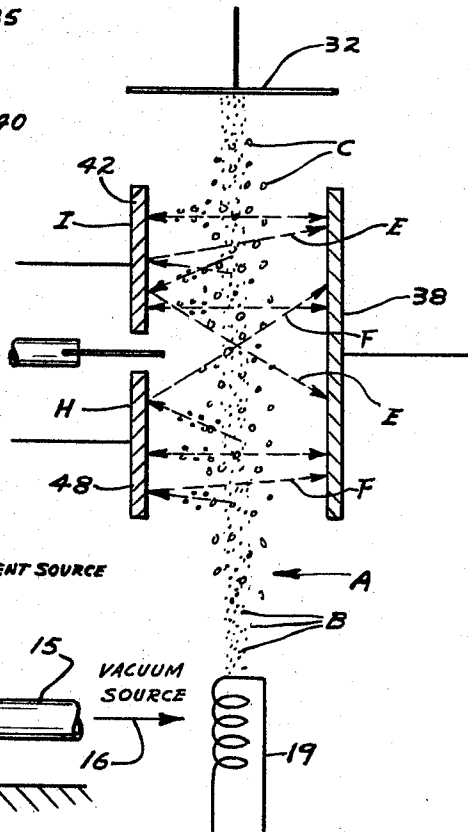


FIG. 3



INVENTORS
NILS LAEGREID
 BY **ROGER M. MOSES**
Reif and Gregory
 ATTORNEYS

1

3,324,019

METHOD OF SPUTTERING SEQUENTIALLY FROM A PLURALITY OF CATHODES

Nils Laegreid and Roger M. Moseson, Minneapolis, Minn., assignors, by mesne assignments, to G. T. Schjeldahl Company, Northfield, Minn., a corporation of Minnesota

Filed Dec. 11, 1962, Ser. No. 243,826

3 Claims. (Cl. 204—192)

This invention relates to an improvement in a method for the application of a thin film in coating a surface. More particularly this invention has to do with an improvement in the sputtering method of coating a surface and it represents a substantial improvement over the method of coating a surface directly as by cathode disintegration or by evaporation in having a more definite and specific control in the application of the coating materials. Applicants employ a cathode only for the purpose of ionizing atoms of an inert gas, which atoms are used for sputtering material to coat a given article.

It is an object of this invention to provide a plurality of source materials for sputtering with a certain and definite control being had over each such material.

It is another object of this invention in connection with an article to be coated to provide a plurality of electrodes for sputtering by immersing the electrodes in a low pressure inert gas, ionizing atoms of said gas and attracting the ionized atoms to the respective electrodes in whatever degree is desired to sputter said electrodes in releasing the surface atoms therefrom to coat said article.

More specifically it is an object of this invention to provide a plurality of electrodes immersed in a plasma comprising an inert gas including atoms ionized by electrons emitted by a cathode attracting said ionized atoms to said electrodes for sputtering the same to coat a collector or an article whereby there is specific control over the sputtering of each electrode by control of the voltage applied thereto in determining the intensity of attraction of ionized atoms thereto.

It is a further object of this invention relative to the above object to attract said ionized atoms to said collector or article for the purpose of cleaning the surface thereof prior to and in connection with the application of a coating surface thereto.

These and other objects and advantages of the invention will be fully set forth in the following description made in connection with the accompanying drawings in which like reference characters refer to similar parts throughout the several views and in which:

FIG. 1 is a diagrammatic view partially in elevation and partially in vertical section of apparatus for practicing the instant invention;

FIG. 2 is a fragmentary view in vertical section taken on line 2—2 of FIG. 1, as indicated by the arrows; and

FIG. 3 is a fragmentary schematic view in section illustrative of the operation of the apparatus.

This invention relates to the deposition by electrode sputtering of alloy and graded alloy films of metals and of semiconductors onto various surfaces. The sputtering is achieved in a low pressure high density plasma with definite control being had over the sputtering of the coating materials. This invention may also be used to obtain controlled doping of semiconductors even to the point of providing a concentration of dopant controllably graded. It is not uncommon to achieve a graded alloy junction between two dissimilar materials such as by a process of evaporation, but it is difficult by known methods to exercise specific independent control over the rate of deposition of any or all of the materials used. It is in this area that applicants' disclosure sets forth a specific advantage

2

in the exercise of a specific and accurate control in the sputtering of any coating material.

Sputtering as such may be carried out in various specific ways. Applicants disclose what they refer to as a plasma method.

In describing one specific embodiment of applicants' invention, reference is had to FIGS. 1 and 2 of the drawing wherein is shown a conventionally designed bell jar 10 having a chamber 11 formed therein. Said jar is supported by a cylindrical column 12 integral therewith and in communication therewith and is upstanding from a supporting base 14 and in communication with a tube 15 running to a conventional vacuum means 16, such as a pump, by means of which said jar 10 is evacuated. Integral with said column 12 is an ion gauge 17.

Depending from said jar is a vacuum tube 19 containing a cathode 20 having a heat shield 21 thereabout and having lines 22 and 23 running to a current source.

A tube 25 runs from adjacent the base plate 10a of said jar to a source of inert gas, which for purposes herein is indicated as being argon, and a valve 26 carried by said tube controls the flow of said gas into said jar.

Spaced within said jar 10 supported by an arm 29 carried on a bracket 30 upstanding from the base plate of said jar is an anode 32 in connection with said cathode and energized by a conductor 33. Said conductor and the conductors hereinafter referred to will be taken to represent suitable circuitry in connection with a source of current.

Within said chamber 11 is an upstanding bracket 35 having a right-angled arm 36 conventionally designed to hold or support a collector 38 to be energized by a conductor 40. Said collector will be taken to represent the work piece or article which is to be coated. The collector represents the surface of any given article which it is desired to coat. The collector will be positioned to have its surface to be coated facing the electrodes which will hereinafter be described.

Supported in said jar 10 suitably spaced away from said collector 38 with the path between said cathode and said anode being located therebetween are a pair of electrodes 42 and 48. Electrode 42 is suitably carried on an arm 43 supported by a vertical bracket 44 upstanding from the base plate of said jar 10.

The electrode 48 is here shown in vertical alignment with said electrode 42 and is carried on an arm 49 supported by a vertical bracket 50 upstanding from the base plate of said jar. Said electrodes 42 and 48 are respectively energized by conductors 46 and 51. Said electrodes may sometime hereinafter be referred to as targets for a reason which will hereinafter become apparent. Said electrodes although here shown as a pair, may be used singly or in greater number and may be variously positioned to have a suitable operative relationship with the collector 38.

A shield 60, preferably of inert material comprising a plate member, is disposed between said electrodes and is carried by a bracket 61 secured to said vertical bracket or post 44. A second shield 63 is provided carried on an arm 65 which extends outwardly of said jar 10 for removable placement of said shield between said collector 38 and the electrodes 42 and 48 at such times as will hereinafter be indicated.

Operation

With reference to FIG. 3, an inert gas A, such as argon, will be introduced into the jar 10 through the valve 26. A constant pressure of the gas introduced is maintained and a suitable pressure range has been found to be on the order of $\frac{1}{10,000}$ of an atmosphere pressure to $\frac{1}{1,000,000}$ of an atmosphere pressure.

3

The cathode will be energized to a temperature at which a sufficient number of electrons B are emitted therefrom. A positive potential is applied to the anode 32 with respect to the cathode and the electrons emitted from the cathode are accelerated toward the anode and the free electrons are collected there. A constant flow of said electrons will be maintained and the acceleration of said electrons in the direction of said anode will be directly controlled by the potential applied to said anode.

Some of the electrons emitted from the cathode in passing through the gas A will collide with gas atoms C in the area between the cathode and the anode, thus causing such gas atoms to become positively charged or ionized. The area between the cathode and the anode particularly and the chamber 11 of said jar 10 generally will thus contain charged gas atoms, free electrons and neutral gas atoms. Thus said gas, said neutral gas atoms, said charged gas atoms or ions and the free electrons make up what is here referred to as plasma. Thus the collector 38 and the electrodes 42 and 48 will be immersed within said plasma.

A negative potential is applied to the collector 38 with the shield 63 having first been positioned between the collector and the electrodes. Thus the collector will attract charged gas atoms which in impinging on or striking the surface thereof will provide an atomically clean surface. The electrodes in like manner with the application of a negative potential may respectively attract charged gas atoms to become atomically cleaned. The shield 63 will prevent any material thus sputtered from the collector from reaching the electrodes, or material sputtered from the electrodes from reaching the collector.

The negative potentials will next be removed from the collector and from the electrodes. The shield 63 will be removed to allow unobstructed passage between the collector and the electrodes.

A negative potential or voltage is next applied to the electrodes. The electrodes will be formed of whatever material it is desired to coat the collector. One electrode will be of the same material as the collector or will be of a compatible material for satisfactory adhesion therewith.

The other electrode will be formed of a material which it is desired to have for a final or surface coating of the collector. For purposes herein the electrode 42 will be considered to have a material compatible with that of the collector 38 and the electrode 48 will be considered to comprise a material dissimilar and incompatible with that of the collector relative to adhesion therewith but which is desired as a surface coating of the collector.

A negative potential or voltage is applied first to the electrode 42. This will attract positively charged gas atoms in the plasma as indicated by the character D, and these atoms will impinge on the surface of the electrode with an energy substantially proportional to the applied negative voltage. Thus the electrode is in effect a target. The negative voltage applied will be sufficient for the charged gas atoms or ions to remove surface atoms from the electrode, and the surface atoms thus removed by such bombardment will have such velocity in the flight away from the electrode as to carry them to the collector to the surface of which they will adhere and thus build up a base layer or coating.

When a sufficient base layer has been applied to the collector, such as may be determined by the judgment of the operator, a negative voltage will next be applied to the electrode 48. A low voltage for slight bombardment will first be applied, and the atoms F freed from the surface of the electrode 48 will mix with the atoms E freed from the surface of the electrode 42 in their flight to the collector 38, and a coating of a mixture of such atoms from both electrodes will build up on the base layer already applied to the collector 38. The negative voltage applied to the electrode 48 will be gradually increased and the negative voltage applied to

4

the electrode 42 will be gradually decreased to the point where it is discontinued. Thus there is a mixture of the material sputtered gradually increasing in quantity of the material sputtered from the electrode 48 until the material only from the electrode 48 finally forms the final or surface coating of the collector.

As described above, a negative voltage was initially applied to the collector 38 to clean the surface thereof. A relatively low negative voltage may be continued in application to the collector during the sputtering of the electrodes 42 and 48 or for any desired portion of the time thereof. There will thus be a continual cleaning of the collector surface with relatively less material being sputtered therefrom than is accumulating thereon so that there is a continued buildup of the material sputtered from said electrodes. This activity may be desirable in view of the difficulty involved in attempting to provide an atmosphere within the chamber 11 which is completely free of contaminants.

The shield 60 between the two electrodes prevents the sputtered material of one electrode from reaching the other.

Relative to the electrodes, materials commonly used by the applicants as a base coating are tantalum and titanium. These materials have been found to have a wide application for good adhesion. The surface coating may be of any desired material such as copper, gold, silver, aluminum and the like.

It is seen from the operation that definite control is had over sputtering of the electrodes by the control of the voltage applied to said electrodes. This control of the sputtering from the respective electrodes is completely independent of the action of the cathode in emitting electrons and providing the plasma with a supply of charged gas atoms. It is seen also that control is had over the emission of electrons from the cathode by a control of the voltage applied to the anode and this is completely free and independent of the control of the sputtering. Such specific control as this is believed to represent a substantial improvement in this art.

It will of course be understood that various changes may be made in the form, details, arrangement and proportions of the apparatus and in the steps and sequence of steps of the method without departing from the scope of applicants' invention which, generally stated, consists in a method and apparatus capable of carrying out the objects above set forth, such as disclosed and defined in the appended claims.

What is claimed is:

1. The method of applying a coating to an article disposed in a coating apparatus having a chamber with an atmosphere of an inert gas at low pressure contained within said chamber, electrodes comprising a cathode, an anode and at least two target electrodes immersed in said inert gas, and circuit means for applying a biasing potential to said article and to said electrodes, said method comprising the steps of

(a) energizing said cathode to provide a supply of free electrons,

(b) biasing said anode so as to accelerate said free electrons through said inert gas to ionize atoms thereof,

(c) variably biasing said target electrodes to attract ionized atoms of said inert gas so as to sputter therefrom atoms of said target electrodes, said biasing step being particularly carried out by initially biasing said target electrodes so that the sputtering rate from one of said target electrodes is substantially zero while the sputtering rate from another of said target electrodes is at a predetermined level greater than zero, changing the bias on said one target electrode to increase the sputtering rate therefrom while continuing to sputter atoms from said other target electrode, and simultaneously controllably changing the on bias on said other target electrode to reduce the

5

sputtering rate therefrom to substantially zero, and
(d) de-energizing the apparatus at a finite time after the sputtering rate from said other target electrode reaches substantially zero.

2. The method of applying a coating as defined in claim 1, being particularly characterized in that said target electrode is composed of a material which is incompatible with the material of said article and said other target electrode is composed of a material which is compatible with the material of said article.

3. The method of sputtering a coating onto an article retained within a coating chamber which consists in:

(a) mounting an article to be coated within said chamber;

(b) mounting a first target electrode in said chamber, the surface of said first target electrode consisting essentially of a material compatible with the surface of said article to be coated;

(c) mounting a second target electrode in said chamber, the surface of said second target electrode consisting essentially of a material which is substantially incompatible with the surface of said article to be coated;

(d) providing a low pressure inert gas atmosphere in said chamber;

(e) mounting a thermonic cathode and an anode in spaced relationship in said chamber and energizing said thermonic cathode to establish a substantially constant discharge plasma zone between said thermonic cathode and said anode;

6

(f) applying a negative potential to said first target electrode to attract positively charged particles from said plasma to dislodge surface atoms therefrom for deposition of a film on the surface of said article;

(g) applying a second negative potential of relatively lower magnitude to the second target electrode to attract positively charged particles from said plasma to dislodge surface atoms therefrom for coincident deposition of a film on the surface of said article; and

(h) gradually decreasing the magnitude of the negative potential applied to said first target electrode to the point of discontinuing the same, and gradually increasing the magnitude of the negative potential applied to said second target electrode for a certain finite time after said first negative potential is discontinued.

References Cited

UNITED STATES PATENTS

2,164,595	7/1939	Siebertz	204—192
2,189,580	2/1940	Hewlett	204—192
2,373,639	4/1945	Turner	204—182
2,886,502	5/1959	Holland	204—192
2,917,442	12/1959	Hanlet	204—192
3,021,271	2/1962	Wehner	204—191

JOHN H. MACK, *Primary Examiner*.

MURRAY TILLMAN, *Examiner*.

G. BATTIST, R. MIHALEK, *Assistant Examiners*.