May 12, 1959 L. A. HOLLAND 2,886,502

CATHODIC SPUTTERING OF METAL AND DIELECTRIC FILMS

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FIG. 1.

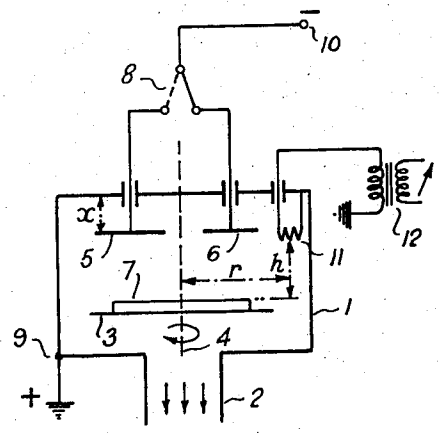


FIG. 2.

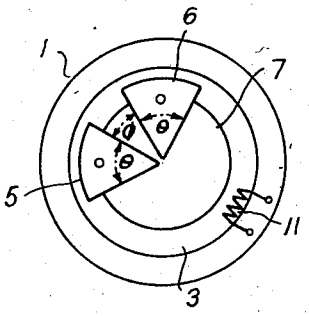


FIG. 3.

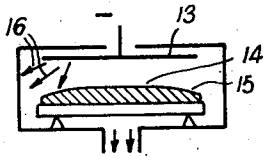


FIG. 4a.

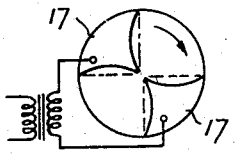


FIG. 4b

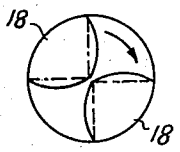


FIG. 5.

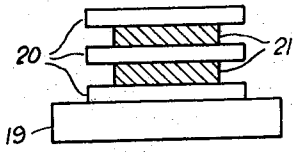
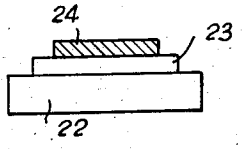


FIG. 6.



LESLIE A. HOLLAND,
INVENTOR

BY Hall & Houghton

ATTORNEY

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FIG. 7

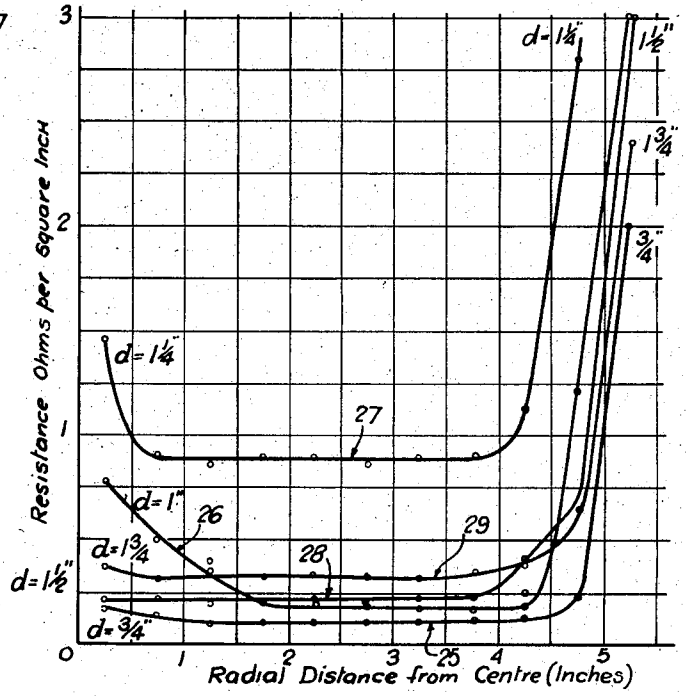
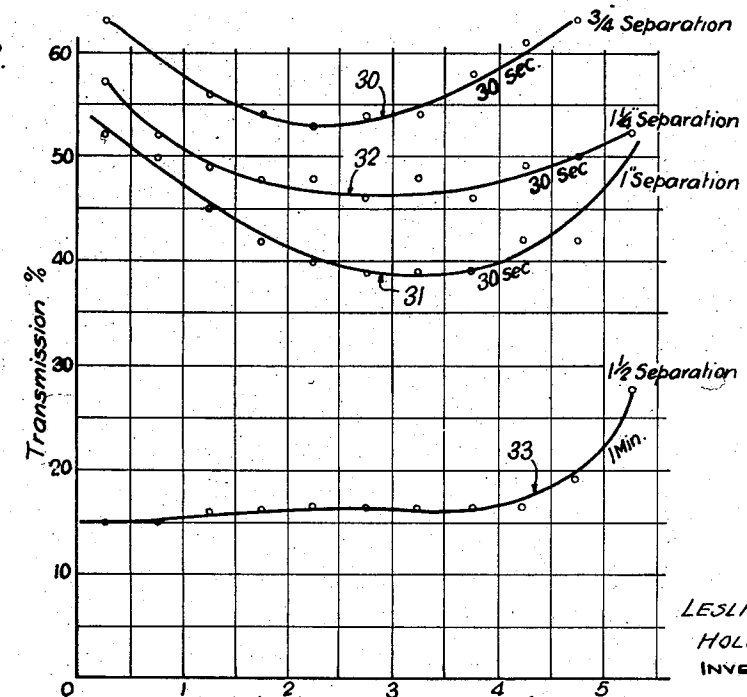


FIG. 8.



LESLIE A. HOLLAND, INVENTOR

BY Hall & Houghton

ATTORNEY

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FIG. 9.

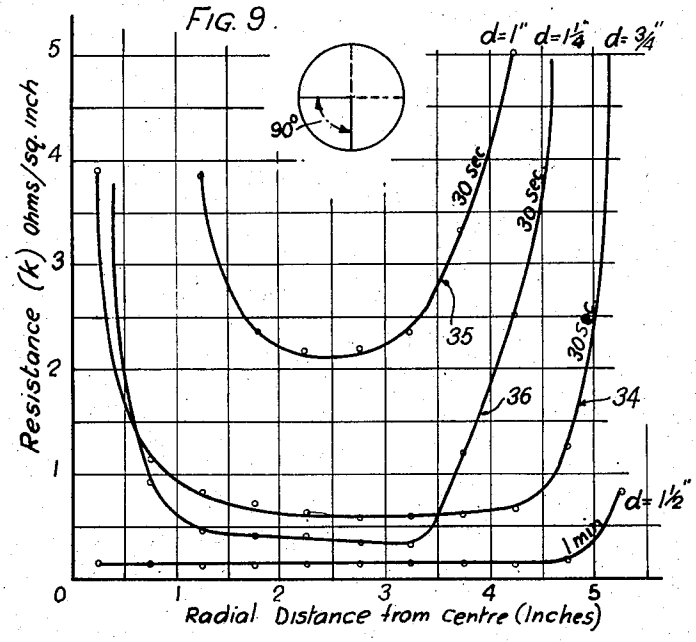
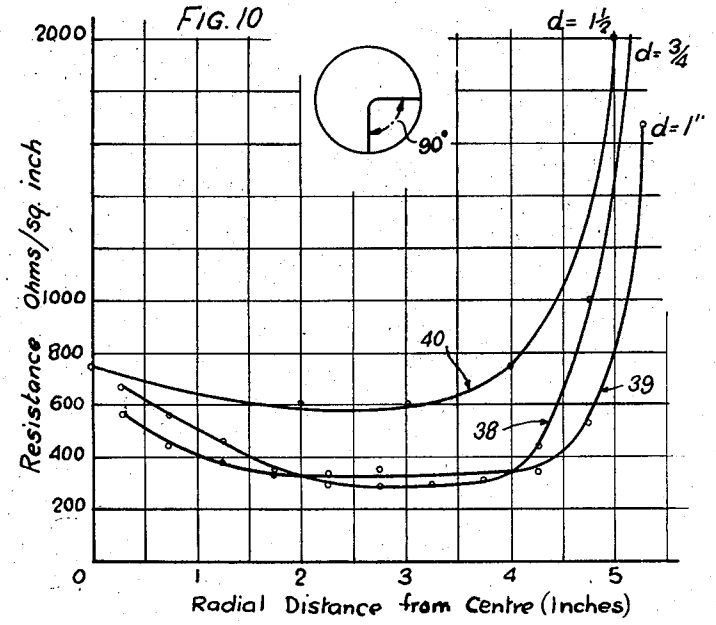


FIG. 10.



LESLIE A. HOLLAND,
INVENTOR

BY Hall & Houghton,

ATTORNEY

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FIG. 11.

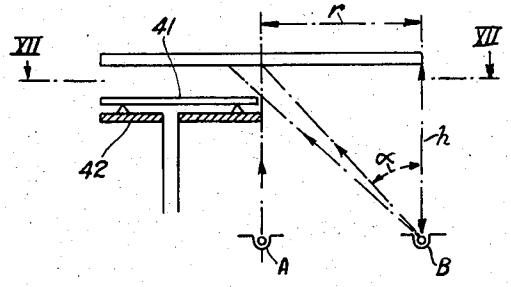
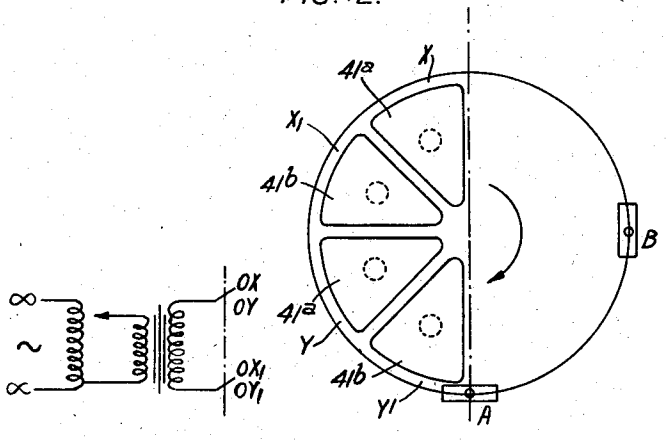


FIG. 12.



LESLIE A. HOLLAND,

INVENTOR

BY Hall & Houghton

ATTORNEY

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2,886,502

CATHODIC SPUTTERING OF METAL AND DIELECTRIC FILMS

Leslie Arthur Holland, Northgate, Crawley, England, assignor to Edwards High Vacuum Limited, Crawley, England, a British company

Application October 23, 1956, Serial No. 617,867

Claims priority, application Great Britain October 28, 1955

2 Claims. (Cl. 204—192)

The present invention relates to cathodic sputtering of metal and dielectric films, and has for an object to provide improved methods of, and apparatus for, the cathodic sputtering of metal and dielectric films.

Important applications of deposition by cathodic sputtering such as for example in the manufacture of optical interference filters, involve the deposition of multi-layer coatings of different substances. In the conventional cathode sputtering apparatus in which the work piece is supported upon a fixed support within a vacuum chamber and a fixed cathode of the substance to be sputtered is suspended above the work support, the said multi-layer coatings can only be produced by changing the cathode for each layer, for which purpose it is necessary to break the vacuum and build the vacuum up again to the desired value, each time the cathode is changed. The operation thus becomes a complicated and time-consuming process.

According to the present invention, a method of cathodic sputtering a film of a given substance or substances on to a work piece consists in positioning the work piece in a vacuum chamber provided with two or more cathodes or electrodes comprising the said substance or substances and depositing the film by sputtering the substance or substances from the cathodes or electrodes on to the work piece while effecting relative rotational movement of the cathodes or electrodes and the work piece respectively in planes spaced along the axis of said relative rotational movement.

Conveniently the work piece is supported upon a rotary work table and the cathodes or electrodes are spaced from the table in the direction of the axis of rotation of the table and in angularly spaced relation one with respect to another. Thus by connecting each cathode or electrode in turn to a source of high tension and rotating the table while each cathode or electrode is sputtered, a succession of films are sputtered on to the work piece thereby to form a composite layer thereon and in order to form a composite layer of films of different substances it is only necessary that the assembly of cathodes or electrodes shall include at least one cathode or electrode of each of the said different substances.

The cathodes or electrodes are preferably of sector shape the enclosed angle of which may vary over wide limits e.g. from 10° to 180° while the angular displacement of the electrodes i.e. the spacing of the electrodes one from another must be such that the equal distribution of the discharge is not impaired. The desired spacing can readily be determined for the required number of cathodes or electrodes by means of a few simple experimental operations.

The invention further contemplates the combination with cathodic sputtering of vapour deposition to enable composite layers to be formed of sputtered films and vapour-deposited films, and to this end a heated crucible for containing a substance to be vapourised may be provided within the chamber and positioned relative to the

said axis of rotation so as to cause the required film to be deposited on the work piece.

The invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic sectional elevation of a cathodic sputtering apparatus according to the invention,

Figure 2 is a plan of the apparatus of Figure 1,

Figure 3 is a diagrammatic sectional elevation of a known form of cathodic sputtering apparatus showing in exaggerated form the variation in the thickness of a film produced thereby,

Figures 4(*a*) and 4(*b*) show respectively two forms of shaped cathodes for use in apparatus according to the invention,

Figures 5 and 6 show respectively multi-layer deposits produced by apparatus of the present invention,

Figures 7 to 10 are graphs respectively illustrating the characteristics of films deposited according to the invention under varying conditions,

Figure 11 is a diagrammatic elevation of a further arrangement for combining cathodic sputtering with vapour deposition, and,

Figure 12 is a plan view taken along the line XII, XII of Figure 11.

In the form of cathodic sputtering apparatus shown in Figures 1 and 2, a cylindrical vacuum chamber **1** is provided in the base thereof with an outlet **2** for connection to a vacuum pump (not shown). A flat circular work table **3** is mounted near the lower end of the chamber for rotation about an axis **4** coinciding with that of the chamber, and a suitable driving means (not shown) is provided for rotating the table.

Supported from the top of the chamber, and electrically insulated therefrom are two cathodes **5** and **6** respectively of different materials required to be deposited in multi-layer form on a plane work piece **7** supported on the work table. The said cathodes are of sector shape each enclosing an angle θ, and are spaced one from the other by an angle ϕ. The cathodes are connected through a two-way switch **8** to the negative pole **10** of a D.C. high tension supply, the positive pole of which is connected as at **9** to the vacuum chamber **1** and to earth.

In order to suppress the discharge from the face of the cathodes remote from the work piece, to the top of the chamber, the cathodes are spaced from the top of the chamber a distance x less than the cathode dark space.

It will be apparent that by means of the two-way switch **8**, one or other of the cathodes can be energised so that the material tthereof is sputtered on to the work piece supported on the rotating work table, in the form of a film of substantially uniform thickness. After the film has reached the desired thickness, the other cathode is switched to the high tension supply and another film of the material of the other electrode is formed on the film already produced, thereby producing a multi-layer coating.

Means are also provided for positioning a vapour source diagrammatically indicated at **11** within the chamber for depositing layers by evaporation, the said means comprising a suitable container or crucible for containing the material to be evaporated, and having electrical heating means connected by suitable leads extending through the walls of the chamber to an alternating current source **12**.

By reason of the shape and spacing of the cathodes, it is possible to position the said crucible in the chamber in a position such that the ratio of the vertical distance h of the crucible above the table to the distance r of the crucible from the axis of rotation of the work table is that required for obtaining an optimum uniformity of coating.

Thus it is possible to alternate coatings deposited by

sputtering from the cathodes, with coatings deposited by vacuum evaporation.

Heretofore it has been usual when designing sputtering apparatus to rectify the H.T. supply to ensure that sputtering occurs only from the desired electrode and not from other metal fittings in the apparatus. It has been shown that to prevent positive ion bombardment of earthed fittings it is not necessary to rectify a high tension supply if both sides of an A.C. source are insulated from earth and connected respectively to two insulated electrodes in the vacuum chamber. These then operate as cathodes and anodes alternately. Such a system is difficult to operate with a large plane work piece because if the electrode is formed of two halves of substantially semi-circular shape a pattern of the sputtering is produced on the work piece due to variation in the thickness of the deposited layer along the plane of the work table. If the work piece is rotated this pattern is no longer localised and the deposit is uniform when measured along any circle concentric with the electrode and rotary table centres. The distribution of the film measured along any radial line from the centre of the holder can be made uniform by slightly shaping the electrodes and or altering the angle thereof.

Thus the apparatus according to the invention can be applied to the use of nonrectified high tension supply by providing two sector electrodes each connected to one side of an A.C. high tension source.

Obviously such a system can be extended for use on three phase supplies by employing three electrodes with a similar saving in the cost of power supply rectifiers.

For normal coating work, films of uniform thickness are required but occasionally it is necessary to produce films which vary in thickness following some specified law. With the apparatus according to the invention it follows that since it is possible, by suitably shaping the cathodes or electrodes, to produce a uniform coating, it is also possible to vary the film thickness along a radial line by shaping the cathodes or electrodes correspondingly. With the known sputtering apparatus (Fig. 3) using a large disc cathode **13** and a fixed table the deposited film **14** is uniform over a small central area of the deposit and then decreases towards the edges of the cathode, as shown at **15**. This is due to edge losses of the sputtered metal by side diffusion as shown at **16** and it is not possible to change the general nature of the film distribution, that it, make it completely uniform or even to vary the distribution of the film in apparatus using a disc cathode, because the deposit distribution is fixed by the geometry of the system.

With apparatus according to the invention using shaped cathodes or electrodes and a rotary work table, it is possible to vary the rate of change of the cathode area measured from the centre of the cathode to its outer extremity, as shown in Figures *4a* and *4b*. A deposit will then be produced whose thickness varies in the radial direction approximately in accordance with the radial rate of change of the cathode area.

Thus for certain optical purposes it is necessary to prepare a metallic coating on a circular glass plate whose optical density increases progressively along a radial line and which is uniform when measured on a circle concentric with the centre of the plate. This can be achieved by making the film thickness progressively increase towards the periphery of the plate by shaping the cathodes in the form shown at **17** in Figure *4a*. Conversely, by shaping the cathodes as shown at **18** in Figure *4b*, the film thickness will decrease progressively towards the periphery of the plate.

The apparatus described with reference to Figure 1 is of particular value for producing a film of uniform thickness upon a work piece covering for example, substantially the whole of the rotating table and such apparatus would be essential if the work piece or article to be coated are in the form of single large sheets. In the case of smaller articles for example, small discs, the articles may be arranged in an annulus on the rotating work table and in this case the inwardly directed ends of the cathodes may be abbreviated by removing a small portion of the pointed end of the electrode so as to provide a concave edge surface to the inner end of the electrode the axis of which surface coincides with the axis of rotation of the work table, the said discs may, for example, comprise sun-glasses upon which an iron oxide absorbing film is sputtered on to their surfaces by means of the apparatus described. In the production of sunglasses it is conventional to provide the glasses with a graduated coating which selectively absorbs light thereby to take into account the more intense light reaching the top of the glasses from the sky or from the sun. Such graduated coatings can be obtained by placing the glasses upon the work table in an annulus co-axial therewith and employing cathodes having the shape shown in Figure *4a* or *4b*. After sputtering of the iron oxide film the glasses would then be coated by vapour deposition with a film of magnesium fluoride or silicon mon-oxide to reduce their reflection.

As has been described with reference to Figure 1 the V-shaped cathodes can be used for producing sputtered films in combination with layers deposited by evaporation. When the cathodes are not present, the optimum position of the vapour source for obtaining maximum uniformity of thickness of the vapour deposit corresponds approximately to a distance spaced from the plane of rotation of the work piece a distance equal to the radius of the rotary work table, i.e. $r=h$ as indicated in Figure 11. The said optimum position is dependent upon a number of factors including the vapour emission characteristic of the vapour source. Three principle types of vapour emitting sources are known, viz, (*a*) a point source which gives uniform vapour emission in all directions, (*b*) a surface which emits vapour within a solid angle 2π, and (*c*) a directed source in which the sides of a crucible containing the substance to be evaporated confine to varying degrees the width or divergency of the vapour beam. For the purpose of producing uniform deposits all three types of vapour source referred to give reasonably uniform coatings when the source is positioned with respect to the work table as above described, providing that in the case of the type (*c*) source the vapour beam is not confined within a solid angle so small that the work plane is not completely exposed to the emitted vapour.

When a rotary work table and a vapour source are used in combination with V electrodes as shown in Figure 11, both the electrodes **41** and the earthed glow discharge shield **42** associated therewith will prevent a quantity of the vapour from reaching the work table and as will be apparent from Figure 11, if the vapour source is positioned as shown at B there will be a graduated edge to the vapour shadow produced by the electrode and its shield.

This graduated shadow will show a penumbra and umbra and when the work table is rotated a portion of the work enclosed within the penumbra will be constantly exposed to the beam of vapour whilst that portion of the work distant from the axis of rotation will be shielded during part of each revolution of the table. This will result in a variation in the deposited film thickness which will vary from a maximum at the centre of the work piece to approximately ½ the maximum at the edge of the work piece. However, if the vapour source be placed in the position A the size of the penumbra is limited by the dimension of the vapour source emitting region which is much less than when the source is in the position B and by carefully arranging the source in the position shown at A it is possible to produce a very uniform evaporated film.

However, in certain cases it may be desirable to place the vapour source at the position B or even at some posi-

tion intermediate the positions A and B. It is known for example that some substances form a granular structure when deposited by vapour deposition in which the vapour atoms impinge upon the surface of the receiver at a high angle of incidence, i.e. the angle with respect to the perpendicular from the receiver surface. This effect arises because the obliquely impinging atoms condense on the outer surfaces of previously deposited nuclei or surface prominences which then grow more rapidly in a direction inclined with respect to the receiver plane than they do in a direction parallel to the receiver plane. When the vapour source is in the position A and h is made equal to r the angle of incidence may vary from between 0° to about to 60° and at the higher value the vapour may form a film of granular structure and it may be found that the evaporated deposit is hard and dense at the centre of the work plane and soft and porous at the edges. By positioning the vapour source at position B or at a position intermediate positions A and B, the maximum value of the incidence angle is reduced and granulation thereby prevented or at least materially reduced. On the other hand, with such positioning of the vapour source it is more difficult to arrange the relative distances of the electrodes and the vapour source from the work table to ensure that the thickness of the vapour film is not greater at the centre than at the edges as previously described. However, if the work pieces are in the form of small articles arranged in an annulus around the work holder the increase of thickness of the deposit at the centre of the work holder is not so objectionable, and the thickness of the film on each small article will be substantially uniform.

Although the invention finds general application in the field of electronic deposition of metals and dielectrics, two specific examples of its application are as follows:

(*a*) *Preparation of multi-layer interference filters*

Interference filters are currently produced with different spectral characteristics by depositing dielectric materials of different optical thicknesses in sequence. For example, a mirror which has a high reflectivity in one range of wavelengths and a high transmission in another range of wavelengths can be made by depositing layers of high and low refractive index materials in sequence, each layer being of a constant optical thickness. It is difficult to produce by vacuum evaporation highly durable filters of this type because of the materials which are available. The invention makes it possible to utilise the most durable coatings that can be obtained by either vacuum evaporation or cathodic sputtering. Most of the high refractive index materials which can be vacuum evaporated either lack durability or are optically absorbent but high refractive index materials can be prepared by the well-known technique of sputtering a metal in an oxygen bearing atmosphere to form an oxide deposit. This technique is known as re-active sputtering, but is not however, suitable for preparing durable oxide coatings of low refractive index (—1.3) as these do not appear to occur in nature. However, an extremely durable low index material (magnesium fluoride) can be prapared in film form by vacuum evaporation.

Thus, in one application of the invention, the cathode is made of titanium and the vapour source is charged with magnesium fluoride. The apparatus is connected to a pumping system which will permit, first the operation of a gas discharge in an oxygen bearing atmosphere and at intermediate pressures for sputtering, and secondly the reduction of pressure to a value (—0.1 micron Hg) suitable for vacuum evaporation. This process can then be repeated several times so that a multi-layer coating can be prepared as shown in Figure 5 in which a glass base **19** is provided with a coating in which layers **20** of titanium oxide having a high refractive index and which are deposited by sputtering, alternate with layers **21** of magnesium fluoride which are deposited by vacuum evaporation and which have a low refractive index. With the known techniques it would be necessary to deposit the titanium oxide film by sputtering in one apparatus and then transfer the work piece to another apparatus for depositing the magnesium fluoride by evaporation, and so on until the required number of alternate layers are deposited, thereby resulting in a tedious and very time consuming operation.

Multi-layer filters formed of sputtered titanium dioxide and evaporated magnesium fluoride films are extremely durable and in order to be able to sputter the titanium dioxide within a reasonable time very high current densities must be used. A highly durable coating can be prepared more readily by employing the more readily sputtered bismuth oxide laminated with evaporated magnesium fluoride films. Such coatings find useful application as mirrors in optical systems used for combining or separating coloured images such as for example, optical systems used in colour television monitors and transmitters. Coatings formed by evaporated magnesium fluoride and sputtered bismuth oxide films are also used on the surfaces of imitation precious stones to produce interference sparkle and colour.

(*b*) *Preparation of conducting metal films*

It is known that the electrical conductivity and optical transparency of thin films of some metals is greater when the glass substrate is coated with a film of certain oxides prior to the deposition of the metal film. Further, it is known that the metal deposit may be prepared by either vacuum evaporation or sputtering. The metal oxide film must, however, usually be prepared by cathodic sputtering if reduction of the oxide is to be avoided.

With the apparatus according to the invention two cathodes can be used, one of metal from which the required oxide is to be formed, and the other of gold. (With an A.C. high tension supply each "cathode" would comprise two electrodes.) It is then possible to sputter on to a glass base **22** (Figure 6) first the metal oxide film **23** and then the gold film **24** and obtain uniform deposits without mechanically changing either of the cathodes or displacing the work support laterally with respect to the cathodes.

In Figures 7 to 10 are shown curves obtained experimentally in carrying out the invention and which illustrate the characteristics obtained in films deposited by sputtering. Thus in Figure 7 the curves indicate the relation between the electrical resistance in ohms per square (ordinate) of a nickel film and the radial distance in inches (abscissa) from the centre of a circular plate on which the film is deposited. By "ohms per square" is meant the resistance of a square sample of film when measured with electrodes extending fully along two opposed sides of the square. Such a measurement does not depend upon the dimension of the square since as the size of the square increases for example, the distance between the electrodes increases but the length of the electrodes also increase correspondingly so that the effective resistance measured between the electrodes remains constant. The cathode used is a single semi-circular cathode supported a distance d above a circular work-table rotated at 30 r.p.m The sputtering is effected in argon at a voltage of 3 kv. and a current of 0.5 amp. for a time of between 30 and 60 seconds. The curves **25**, **26**, **27**, **28** and **29** respectively indicate the characteristic of the nickel film obtained when the distance d is made ¾", 1", 1¼", 1½" and 1¾". In Figure 8 curves are shown giving the light transmission characteristics of nickel films sputtered under similar conditions to those described with reference to Figure 7, the ordinate representing the light transmission percent measured at λ=5460 A. Curves **30**, **31** and **32** represent respectively the light transmission characteristic of the nickel film obtained after 30 seconds sputtering with distances d of ¾, 1 and 1¼" while curve **33** indi-

cates the characteristic of the film obtained after 1 minute sputtering and with a distance *d* of 1½".

The curves of Figure 9 are curves obtained under similar conditions to those of Figure 7 but using a cathode in the form of a 90° sector of a circle. The curves **34** **35** and **36** are obtained with 30 seconds sputtering and distances *d* of ¾", 1" and 1¼" respectively while the curve **37** is obtained with 1 minute sputtering and a distance *d* of 1½".

Finally, the curves of Figure 10 show the electrical resistance at varying distances from the centre of a circular film of cadmium oxide deposited by reactive sputtering for two minutes in an argon and oxygen mixture, the cathode being similar to that used to obtain the curves of Figure 9, i.e. at 90° sector, but having the tip or point thereof rounded-off. The speed of rotation of the work table is 30 r.p.m., the voltage 3kv. and the current 0.5 amp. The curves **38**, **39** and **40** are obtained with distances *d* of ¾", 1" and 1½" respectively.

It will be apparent that there is provided according to the invention a cathode sputtering system by means of which it is possible to deposit either sputtered metal films or sputtered metal oxides, with or without interposed vacuum evaporated layers, in succession on to the surface of a work piece, the said sputtered films each being if desired of substantially uniform thickness throughout, or by suitably shaping the cathodes, of a predetermined variation in thickness. The geometrical shape of the cathode electrodes lends itself to the use of alternating current high tension supply thereby dispensing with the need for expensive rectifying apparatus.

It will be understood that the invention is not limited to the above described specific methods and forms of apparatus. For example, instead of employing a rotary work table and fixed electrodes, the table could be fixed and the electrodes mounted so as to rotate about an axis of the table.

I claim:

1. A method of cathodic sputtering a film of at least one given substance on to a workpiece which consists in supporting the workpiece in a vacuum chamber for rotation about an axis, positioning at least two fixed cathodes in the vacuum chamber angularly spaced with respect to said axis of rotation and spaced from the workpiece along the said axis, said cathodes being of the same substance to be sputtered, effecting rotation of the workpiece and connecting the cathodes to a source of potential to deposit a film on to the workpiece by cathodic sputtering from the cathodes during the rotation of the workpiece, the method further comprising forming a further film on to the workpiece by vapour deposition from a source of vapor positioned within the chamber.

2. Apparatus for cathodic sputtering a film of at least one given substance on to a workpiece comprising a vaccum chamber, a work-table supported in said chamber for continuous rotation about a vertical axis for rotating the workpiece about said axis, at least two sector-shaped fixed stationary cathodes of the same substance to be sputtered spaced from the said table along the axis of rotation thereof and relatively angularly spaced with respect to said axis, means for connecting the cathodes to a source of potential for effecting cathodic sputtering of the substance on to the workpiece, a vapor source positioned within the chamber for depositing a film on to the workpiece by evaporation, and means for continuously rotating the workpiece about said axis.

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