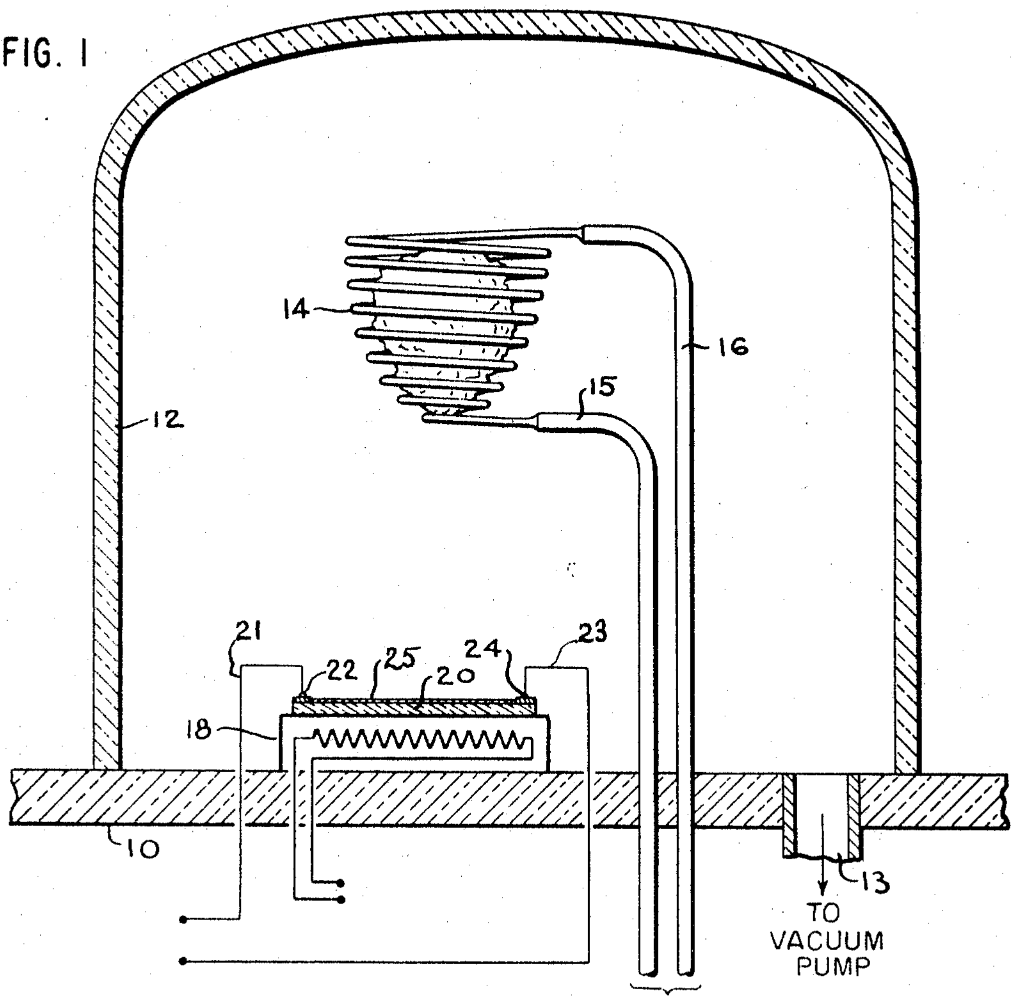
Aug. 26, 1969 K. L. CHOPRA **3,463,663**

DEPOSITION OF THIN FILMS

Filed May 7, 1965 7 Sheets-Sheet 1

FIG. 1



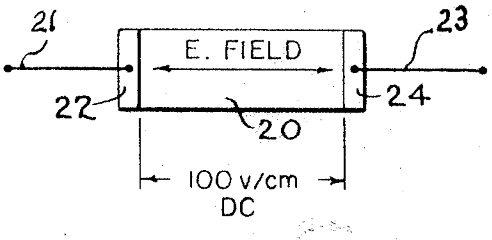


FIG. 2

INVENTOR.
KASTURI L. CHOPRA

BY Kenway Jenney & Hildreth

ATTORNEYS

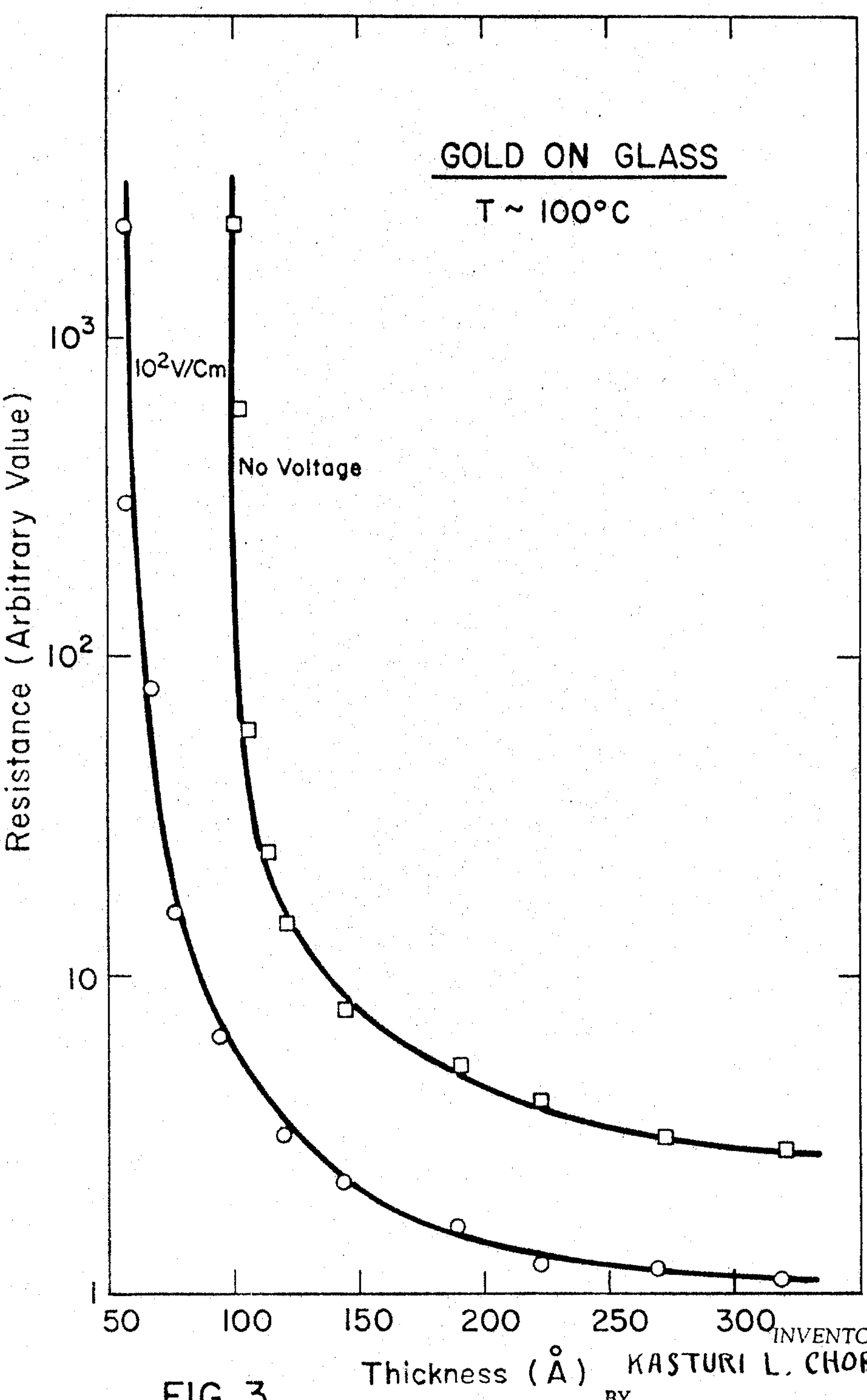


FIG. 3

INVENTOR.
KASTURI L. CHOPRA
BY
Kenway, Jenney & Hildreth
ATTORNEYS

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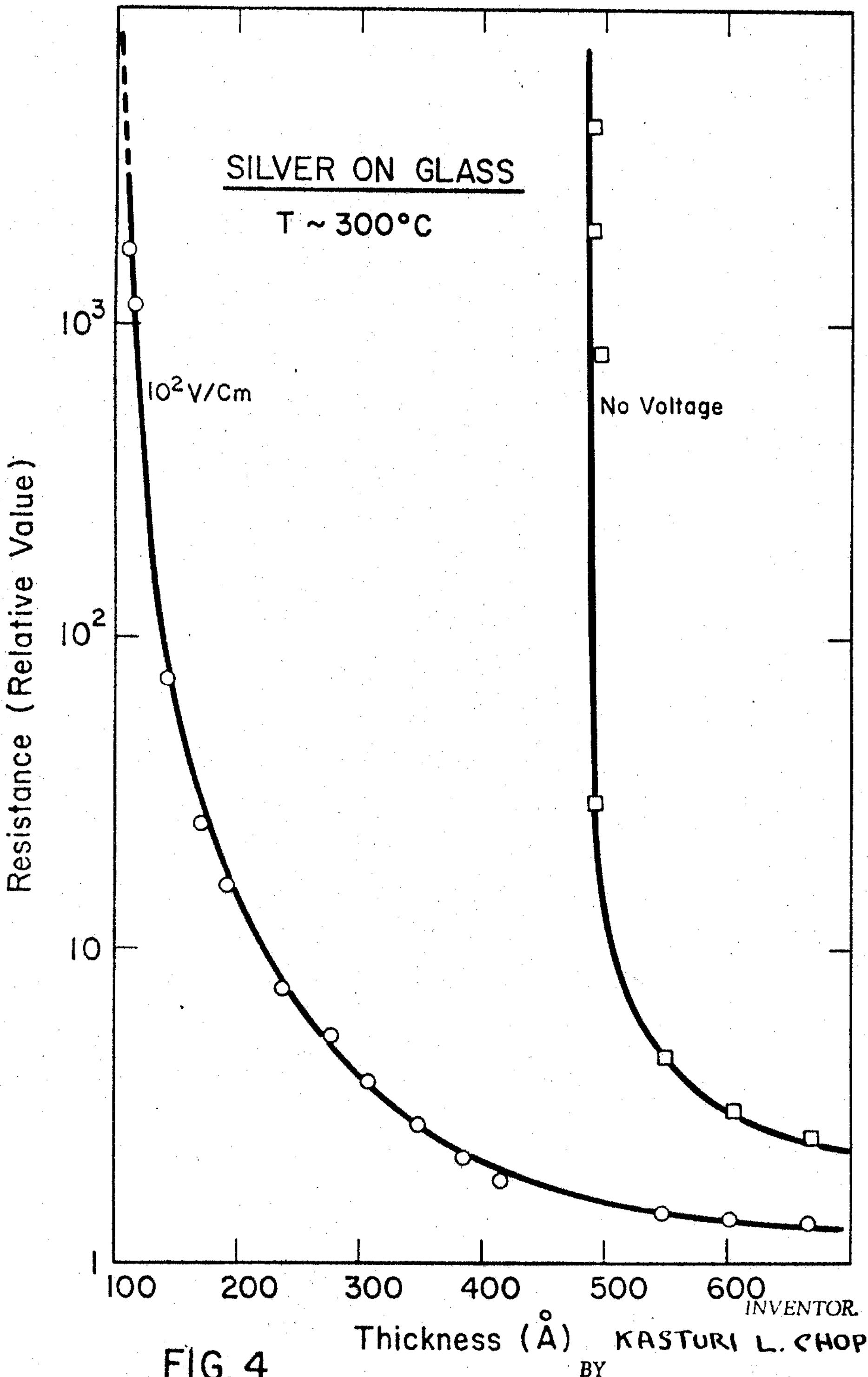
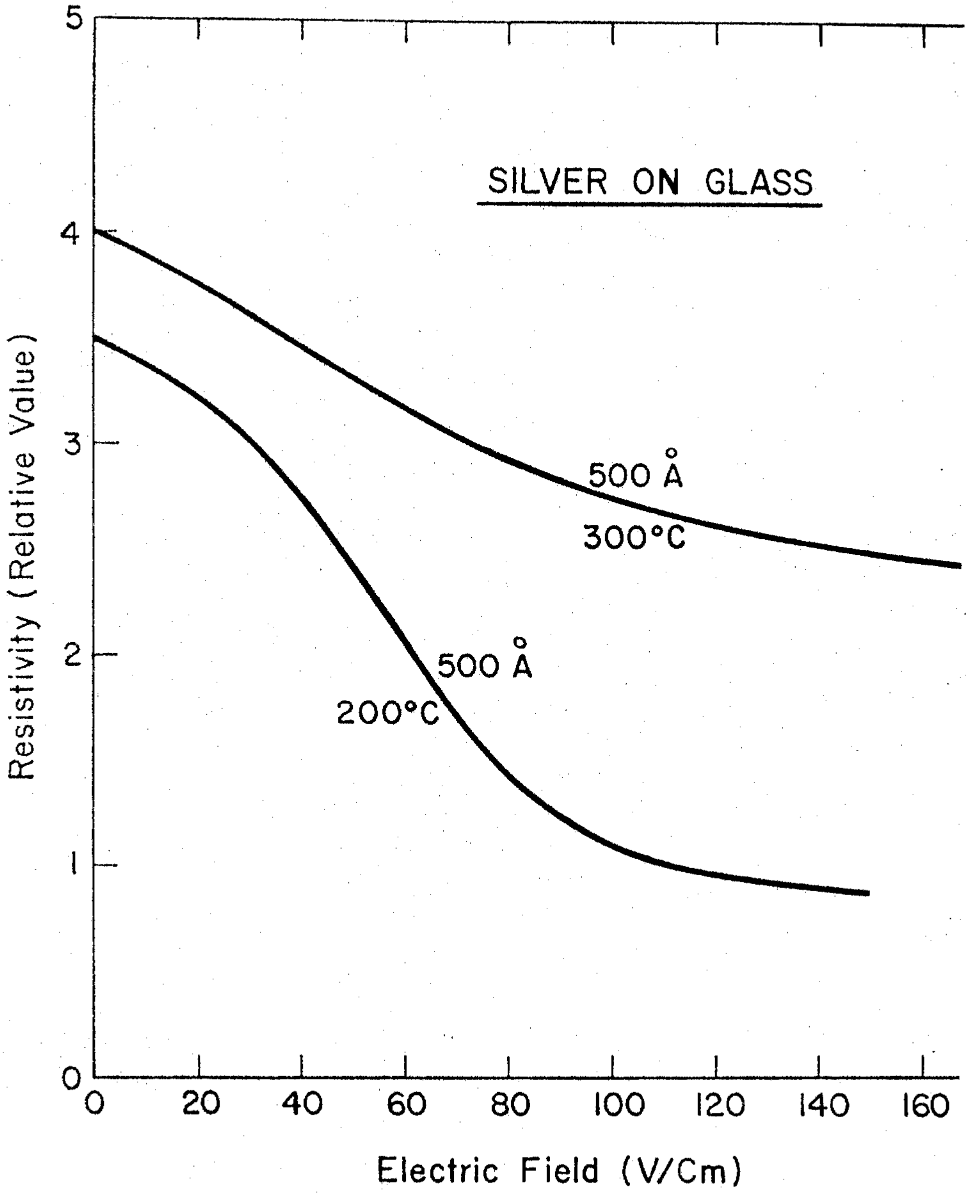


FIG. 4

INVENTOR.
KASTURI L. CHOPRA
BY
Kenway, Jenney & Hildreth
ATTORNEYS

FIG. 5



INVENTOR.
KASTURI L. CHOPRA
BY
Kenway, Jenney & Hildreth
ATTORNEYS

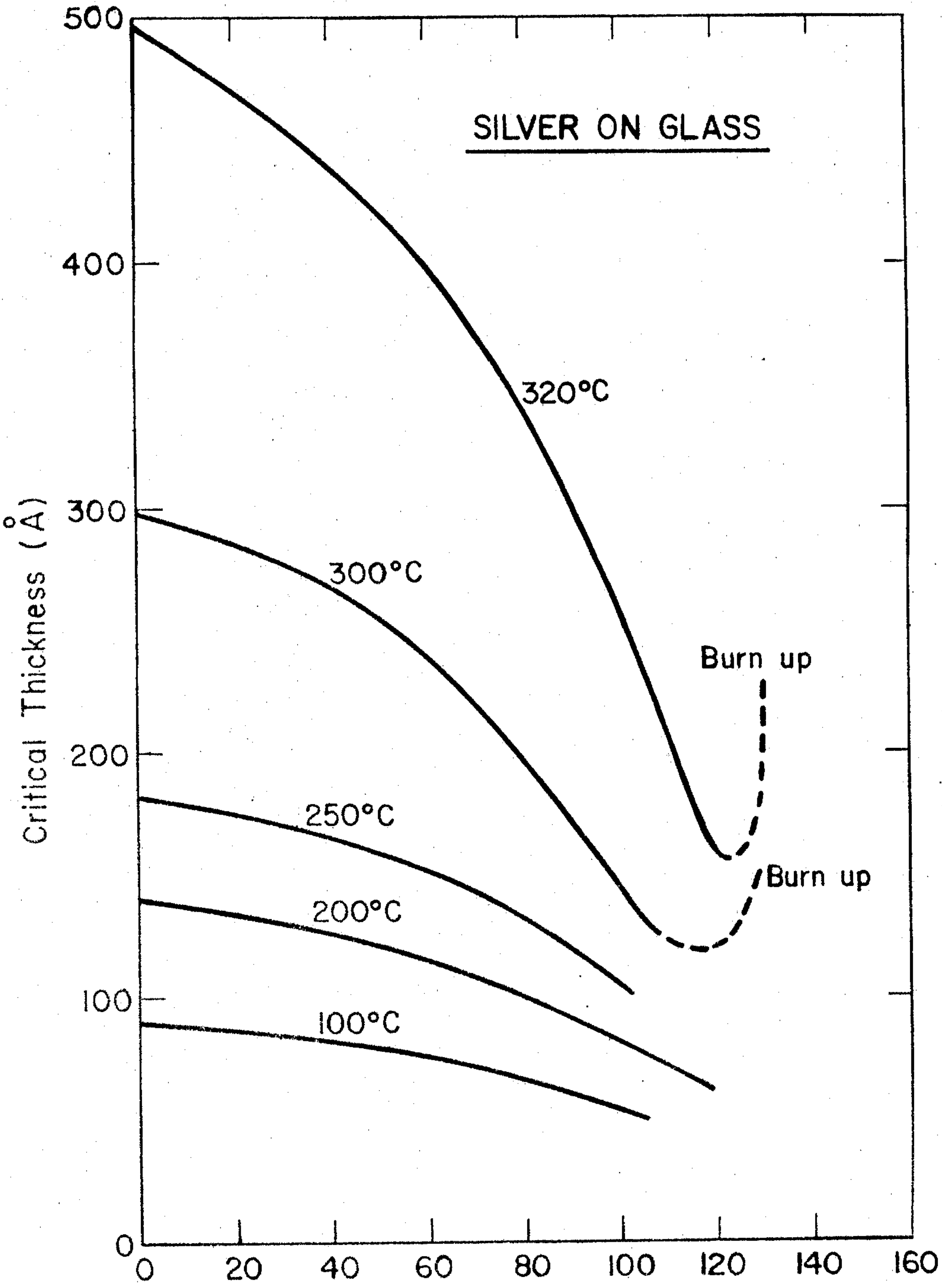


FIG. 6

INVENTOR
KASTURI L. CHOPRA
BY
Kenway, Jenney & Hildreth
ATTORNEYS

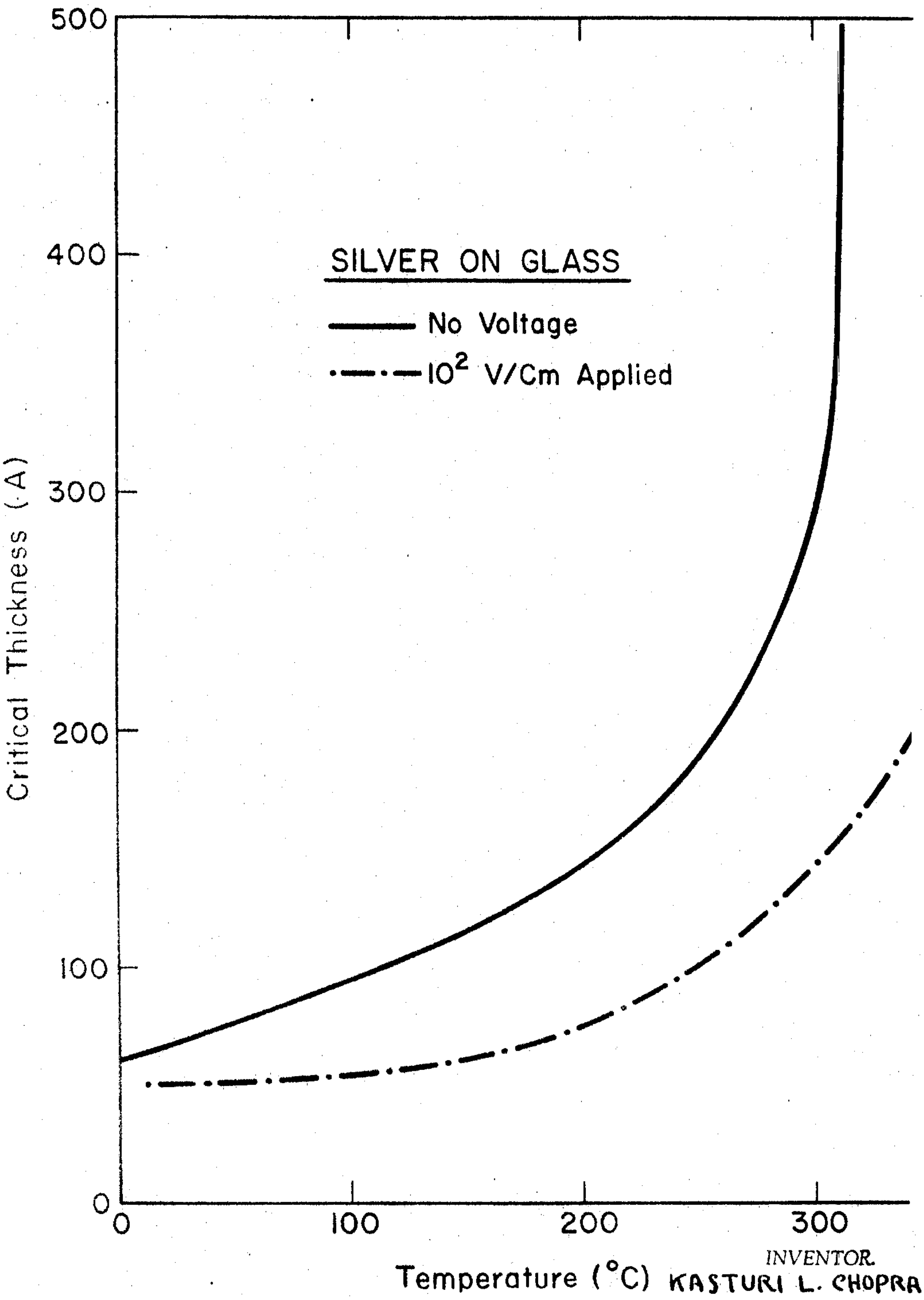


FIG. 7

INVENTOR.
KASTURI L. CHOPRA
BY
Kenway, Jenney & Hildreth
ATTORNEYS

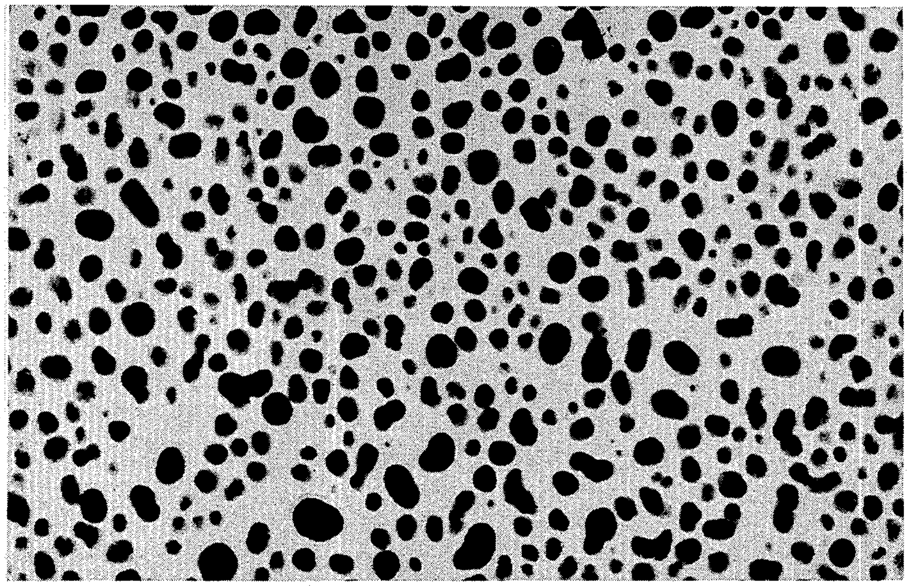


FIG. 8

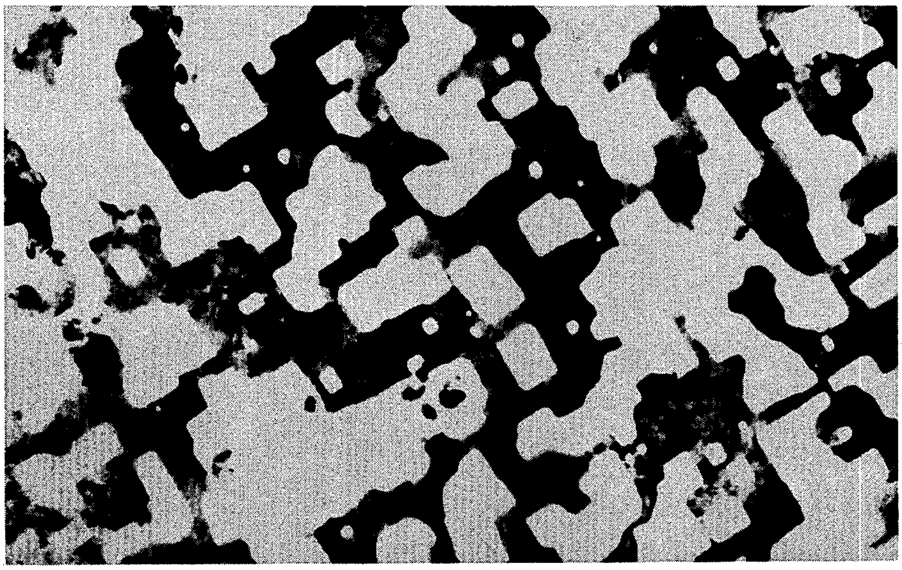


FIG. 9

INVENTOR.
KASTURI L. CHOPRA
BY
Kenway, Jenney & Hildreth
ATTORNEYS

United States Patent Office

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3,463,663

DEPOSITION OF THIN FILMS

Kasturi L. Chopra, Lexington, Mass., assignor to Kennecott Copper Corporation, New York, N.Y., a corporation of New York

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Int. Cl. C23c *13/02, 13/08*
U.S. Cl. 117—227 9 Claims

ABSTRACT OF THE DISCLOSURE

In the formation of thin metal films by vacuum deposition, the maintainence of an electric field in the plane of the substrate surface induces coalition of the particles and crystal orientation whereby improved conductivity at reduced thicknesses is realized.

This invention relates in general to the formation of thin metal films by vacuum deposition techniques, and utilizes novel means to control the deposition of the films to provide several improved characteristics.

Numerous processes are known for forming thin films on various types of substrates. Extremely thin films of metals may be formed on insulating substrates by such techniques as sputtering, pyrolysis of metal forming compounds, e.g. metal carbonyls, and by vacuum evaporation. Frequently it is desirable that the film be electrically conducting, and in all known processes it is necessary to deposit sufficient material that a continuous electrical path is formed. This requires that a certain threshold thickness of film be formed before electrical conductivity is established.

The present invention provides substrate-supported conducting films thinner than any heretofore obtained by comparable techniques. In addition, the process of this invention provides control over the crystal orientation of vacuum deposited metal films, whereby ultra thin films having oriented crystallinity may be produced. The thin film products provided by this invention may be used in such application as capacitors, wherein the films serve as condenser plates; provides coatings which are extremely thin, and continuous; electrodes or contacts for semiconductors and other electronic devices; printed circuits and similar microminaturized electronic applications; and reflective devices such as half mirrors, to name but a few.

The invention is based on the discovery that if an electrical field is applied in the plane of the substrate, the condensation of metal onto the substrate is modified in several respects. From electronphotomicrographs of vacuum deposited metal it can be seen that the deposit forms as a number of initially unconnected droplets which gradually build up to the point where they contact, and eventually cover the substrate surface entirely. Electrical conductivity of the film is established when the build up is sufficient to form a continuous path across the coalescing droplets. I have discovered that if a DC field is applied in the plane of the substrate the condensation process is modified so that the droplets are drawn out and merge when far less material has been applied. Moreover electron beam diffraction photographs of these films show a single crystal pattern, whereas films formed without the field give a pattern of random orientation.

In general, the thin films of this invention are formed by conventional vacuum evaporation methods and equipment, with the exception that a pair of spaced electrodes are applied to the substrate surface across which a DC voltage may be applied. In practice I prefer a voltage of about 100 volts per centimeter, but as will appear from the data herein presented, the effect of the applied voltage on the film is realized at much lower levels. I have also found that certain characteristics of the film may be controlled by varying the temperature of the substrate surface. For instance, at low temperatures, conductivity is established with films thinner than films formed at higher temperatures, but at higher temperatures, a higher degree of crystal orientation is established than at lower temperatures.

The thin films of this invention may be formed of any of the metals suitable for vacuum deposition processes, such as gold, silver and copper on insulating substrates, typically having a specific resistivity greater than 10^4 ohm-centimeters. Suitable substrates include glass, mica, quartz, metal oxides, metal halides, and conductive materials having an insulating layer of for instance zinc sulfide, bismuth oxide, silicon dioxide, or magnesium oxide.

In practice, the surface of the substrate material to be coated is provided with a pair of spaced electrodes, which may be vacuum deposited or painted on. After electrical connections have been made to the electrodes the substrate is placed in the vacuum chamber of conventional vacuum deposition apparatus, and a potential is applied between the electrodes so that a voltage gradient exists along the surface at the time the initial deposit is formed. It is preferable that the voltage source have a high internal resistance so that large currents sufficient to destroy the film will not flow as the conductivity of the film increases.

A description of this invention and the results of its practice are given below in greater detail, wherein reference is made to the drawings in which:

FIG. 1 is a schematic elevation in cross-section of one form of apparatus for carrying out this invention;

FIG. 2 is a plan view of a substrate surface arranged for the deposition of a film in accordance with this invention;

FIGS. 3 and 4 are graphs showing resistance as a function of thickness of gold and silver films formed at both no voltage and at 100 v./cm.;

FIG. 5 is a graph showing the resistivity of silver films as a function of electric field, when formed at 200° C. and 300° C;

FIG. 6 is a graph showing the critical thickness (at which conductivity is established) as a function of the electric field when formed at various temperatures between 100° C. and 320° C;

FIG. 7 is a graph showing the critical thickness of silver films as a function of temperature when formed at both no voltage and at 100 v./cm.;

FIG. 8 is an electronphotomicrograph at 25,000 times enlargement of a silver film 50 A. thick formed on sodium chloride at 300° C. and no voltage;

FIG. 9 is an electronphotomicrograph at 25,000 times enlargement of a silver film 50 A. thick formed on sodium chloride at 300° C. and 100 v./cm.

The practice of this invention utilizes conventional vacuum deposition apparatus such as that illustrated in FIG. 1. The material to be deposited is placed in a basket **14** of a coiled tungsten filament supported on power leads **15** and **16** which are mounted in the vacuum table **10**. The substrate material **20** is provided with a pair of spaced electrodes **22** and **24** on its surface, to which are attached electrical leads **21** and **23** which also pass through the vacuum table **10**, and is placed on a heating plate **18**, the leads to which extend through the vacuum table to a rheostat control or variable transformer (not shown). A bell jar **12** supported on the vacuum table **10** provides for the establishment of a vacuum, which is drawn through the vacuum connection **13**.

In a typical operation, a vacuum of about 10^{-6} millimeters of mercury is established within the chamber. The heating plate **18** is controlled to bring the substrate to the desired temperature, and the desired voltage to cross the substrate is applied to the leads **21** and **23**, from high impedance source, such as a bank of dry cells in series with a 100,000 ohm resistor. Power is then applied to the power leads **15** and **16** to cause the filament basket **14** to incandesce and evaporate the metal to be applied. Typically a movable mechanical shutter (not shown) is interposed between the basket and the substrate surface to control the deposition, and is swung to the side after evaporation of the material to be deposited has commenced.

As the material deposits, it first forms droplets at numerous nucleation centers and as the nuclei grow the electrostatic attraction appears to cause them to spread out and merge into each other at a much earlier stage in the process than when no field is applied to the substrate surface. If the voltage across the leads **21** and **23** is measured, it will be seen to be initially high, and then suddenly to drop as conductivity is established. The process is terminated when a film of desired thickness has been formed.

The effect of establishing a conductive film is illustrated in FIGS. 3 and 4 from which it will be seen that a film formed at 100 v./cm. is initially conducting at a much thinner stage than one formed under no voltage, and has a much lower resistivity at all thickness.

A shown in FIG. 5 a film formed at lower temperatures has lower resistivity than one formed at higher temperatures, and its relative improvement over a film formed at no voltage is greater. Films formed at higher temperatures, however, demonstrate a higher degree of uniform crystal orientation than those formed at lower temperatures, the latter giving electron defraction photographs in which the dots characteristic of a single crystal tend to merge into rings.

FIG. 6 similarly shows that as the tempearture is increased the film thickness at which conductivity is established (critical thickness) is greater. This may be explained on the basis of the tendency of the depositing material to accumulate into spheres or globules being greater at higher temperatures than at lower temperatures. At lower temperatures the depositing film appears to be more amenable to being spread out by the applied voltage.

FIG. 7 similarly demonstrates that as the temperature is increased the critical thickness increases, however, with an applied voltage of 100 v./cm. the critical thickness is less than when no voltage is applied. In addition it will be noted that when no voltage is applied a conducting film of silver can not be formed at a temperature above about 320° C., whereas with the application of 100 v./cm. the limiting temperature is much higher.

The effect of the applied surface voltage gradient is illustrated in FIGS. 8 and 9, the former showing an actual silver film 50 A. thick formed at 300° C. with no voltage. The silver has deposited in unconnected droplets, and the film is not conducting. FIG. 9 shows a similar film of silver 50 A. thick formed at 300° C. under an applied voltage of 100 v./cm. In this case it will be seen that the particles have merged into one another, and that a definite crystalline pattern appears. This film is conducting and an electron diffraction photograph substantiates its crystalline nature.

In practising this invention, it will be appreciated that the application of the electric field is primarily required only during the initial stage of film formation. After the film has become conductive the voltage gradient disappears as substantially the entire voltage appears across the current limiting resistor. The deposit which forms under the influence of the field appears to have something of a seeding effect on material subsequently deposited, whereby the initial orientation and crystallinity is reflected in the final film. The initial deposit thus appears to create a lattice which largely controls the crystal structure of the additional material subsequently deposited.

From the foregoing description it will be seen that this invention is essentially one in which metal atoms or molecules are released in a vacuum and collected on a substrate surface, and that it is primarily dependent on the conditions prevalent at the substrate surface at the time of initial deposition. Although the invention has been described with reference to the formation of films from evaporated metal vapors, it is conceived of as being applicable to the formation of films by other condensation processes in which the same physical and chemical factors are present at the time and place the film substance is formed on the substrate surface. It is accordingly contemplated that modifications of the preferred embodiment described herein will readily occur to those skilled in the art and familiar with the principles herein set forth, and that such may be made without departing from the scope of this invention. In particular, it is apparent that alternating fields may also be employed to achieve certain of the advantageous effects, particularly the films of increased conductivity. AC fields, however, do not ordinarily give completely oriented crystal structures. The invention is also useful in forming this insulating film, by oxidizing such metal films as silicon or aluminum.

Having thus described my invention, I claim and desire to secure by Letters Patent:

1. The method of forming a thin conductive metal film on an insulating substrate surface, comprising placing the substrate and the metal in a chamber, evacuating said chamber to a pressure of less than 10^{-4} mm. of Hg, applying an electric field of at least about 100 v./cm. to and in the plane of said substrate surface, heating said substrate to between 100° C. and 350° C., and heating said metal sufficiently to cause evaporation thereof, while maintaining said field at said surface, whereby metal is caused to condense on said surface in the presence of said field.

2. In the process of forming a metal film in which the metal is caused to deposit by a condensation process, on a substrate surface, the improvement which comprises, coalescing said deposited metal by applying an electric field to and in the plane of the substrate surface at the time the metal is initially deposited.

3. A process in accordance with claim **2** wherein the electric field is a direct current electric field and the field is mainained until a conducting film is formed.

4. The process of claim **2** including the further step of simultaneously heating the substrate surface and film.

5. A process in accordance with claim **2** wherein said electric field has a value greater than 20 volts per centimeter.

6. The process in accordance with claim **2** wherein said electric field has a value of substantially 100 volts per centimeter.

7. A metallized article produced by the process of claim **2** comprising,

a substrate having an electrically insulating surface and a continuous conductive metal film on said surface having a resistivity less than that of a like film vacuum deposited without a voltage gradient on the substrate surface.

8. The method of forming a thin metal film on a substrate surface which comprises,

placing the substrate and the metal to be deposited in a chamber,

evacuating the chamber to a pressure suitable for vacuum deposition, heating said metal sufficiently to cause the evaporation thereof into said vacuum, whereby metal is caused to condense on said substrate surface, and

coalescing said deposited metal by applying an electric field to and in the plane of said surface while said metal is condensing thereon.

9. The process of claim **8** wherein the substrate surface is heated at the time the metal is caused to condense thereon.

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WILLIAM L. JARVIS, Primary Examiner

U.S. Cl. X.R.

117—93, 107, 215, 217